LIQUID SOLUTION

1. SOLUTION

It is the homogeneous mixture of two or more components.

The substance which dissolve other substance is **solvent** & the substance which is dissolved is **solute**, independent of their quantity. If both are soluble in each other then the substance present in larger amount by mole is solvent.

* A solution may exist in any physical state.

Types of Solution :

	Solvent	Solute	Examples
1.	Gas	Gas	Mixture of gases, eg. air.
2.	Gas	Liquid	$CHCl_3(\ell) + N_2(g)$
3.	Gas	Solid	Camphor (s) + N_2(g).
4.	Liquid	Gas	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.

2. SOLUBILITY

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

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

3. 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.

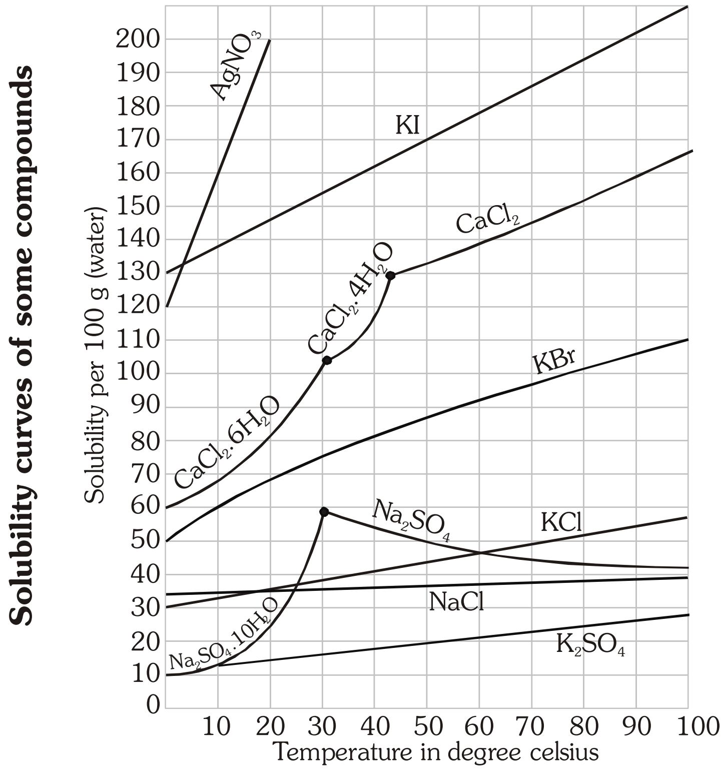
When solid solutes are dissolved in solvent, then following equilibrium exits.

$$\text{Solute} + \text{Solvent} \underset{\text{Crystallization}}{\overset{\text{Dissolution}}{\rightleftharpoons}} \text{Solution.} \; ; \Delta H \text{ may be positive or negative}$$

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.

3.1 Effect of temperature :

The solubility of a solid in a liquid is significantly affected by temperature changes, obeying ***Le Chateliers Principle***. In general, if in a nearly saturated solution, the dissolution process is endothermic ($\Delta_{sol}H > 0$), the solubility should increase with rise in temperature and if it is exothermic ($\Delta_{sol}H < 0$) the solubility should decrease. These trends are also observed experimentally.



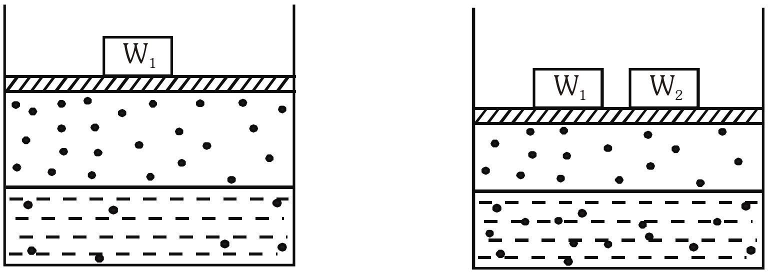
3.2 Effect of pressure :

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.

4. SOLUBILITY OF GASES IN LIQUID

Certain gases are highly soluble in water like NH_3, HCl, etc, and certain gases are less soluble in water like O_2, N_2, He, etc. Solubility of gases is greatly effected by pressure and temperature. Increasing pressure increases solubility and increase in temperature decreases solubility since dissolution of any gas in any liquid is exothermic in nature.

4.1 Henry' Law :



(a) Low pressure

(b) High pressure

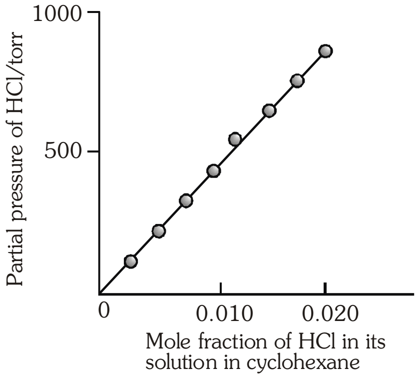
Effect of pressure on the solubility of a gas. The concentration of dissolved gas is proportional to the pressure on the gas above the solution.

The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution, at constant temperature

$$\mathbf{P = K_H X}$$

K_H = Henry's Law Constant

- * Henry's Law Constant depends on nature of gas and liquid as well as temperature.
- * K_H increases with increases in temperature.
- * Greater K_H means low solubility.



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

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

Gas	**Temperature/K**	**K_H /kbar**
He	293	144.97
H_2	293	69.16
N_2	293	76.48
N_2	303	88.84
O_2	293	34.86
O_2	303	46.82
Argon	298	40.3
CO_2	298	1.67
Formaldehyde	298	1.83×10^{-5}
Methane	298	0.413
Vinyl chloride	298	0.611

4.2 Limitations of Henry' Law :

(1) It is valid only for ideal behaviour of gas. As none of the gas is ideal, this law may be applied at low pressure and high temperature.

(2) It gives better result when the solubility of gas in the liquid is low.

(3) The gas should neither dissociate nor associate in the liquid.

4.3 Henry' Law application :

(1) To increase the solubility of 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.

4.4 Effect of Temperature :

Solubility of any gas in any liquid decreases with rise in temperature as dissolution is an exothermic process.

At constant pressure, $$\ell n\frac{C_2}{C_1}=\frac{\Delta H_{sol}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

where C = molar concentration of gas in solution

Ex.1. ***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? Assume that 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.***

Sol: *x (Nitrogen) =* $\frac{\text{p(nitrogen)}}{K_H}=\frac{0.98\text{ bar}}{76{,}480\text{ bar}}=1.29\times10^{-5}$

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

x (Nitrogen) = $\frac{n\,\text{mol}}{n\,\text{mol}+55.5\,\text{mol}}=\frac{n}{55.5}=1.29\times10^{-5}$

(n in denominator is neglected as it is < < 55.5)

Thus $n = 1.29\times10^{-5}\times 55.5\text{ mol} = 7.16\times10^{-4}\text{ mol} = 0.716\text{ m mol}$

Ex.2 ***The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% is to 79% by volume at 298 K. The water is in equilibrium with air at a pressure of 10 atm. At 298 K, if the Henry's law constants for oxygen and nitrogen are 3.30×10^7 mm and 6.51×10^7 mm respectively, calculate the composition of these gases in water.***

Sol: *Percentage of oxygen (O_2) in air = 20%*

Percentage of nitrogen (N_2) in air = 79%

Also, it is given that water is in equilibrium with air at a total pressure of 10 atm, that is, (10 × 760) mm Hg = 7600 mm Hg

Partial pressure of oxygen, $p_{O_2}=\frac{20}{100}\times7600\,\text{mm Hg}=1520\text{ mm Hg}$

Partial pressure of nitrogen, $p_{N2} = \frac{79}{100} \times 7600\,\text{mm Hg}$ *= 6004 mm of Hg*

Now, according to Henry's law :

$p = K_H x$

For oxygen :

$$p_{O_2} = K_H . x_{O_2}$$

$$\Rightarrow x_{O_2} = \frac{p_{O_2}}{K_H} = \frac{1520 \text{ mm of Hg}}{3.30 \times 10^7 \text{mm of Hg}}$$ *(Given* $K_H = 3.30 \times 10^7$ *mm of Hg* $= 4.61 \times 10^{-5}$

For nitrogen,

$$p_{N_2} = K_H . x_{N_2}$$

$$\Rightarrow x_{N_2} = \frac{P_{N_1}}{K_H} = \frac{6004 \text{ mm Hg}}{6.51 \times 10^7 \text{ mm Hg}} = 9.22 \times 10^{-5}$$

Hence, the mole fractions of oxygen and nitrogen in water are 4.61×10^{-5} *and* 9.22×10^{-5} *respectively.*

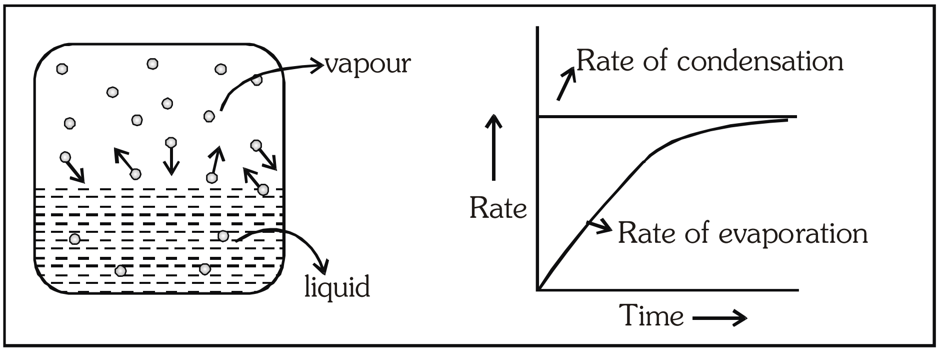
5. *Vapour pressure :*

The Evaporation of a Liquid in a Closed Container

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 rapidaly be an equilibrium set up in which the number of particles leaving the surface is exactly balanced by the number rejoining it.



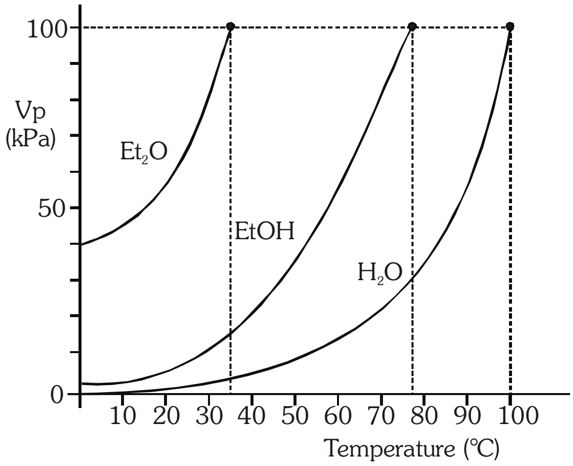
This pressure at equilibrium is called the **vapour pressure** (also known as **saturation vapour pressure**) **of the liquid at that temperature.**

5.1 Effect of Temperature on vapour pressure

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

$$\text{liquid} \rightleftharpoons \text{vapour}, \quad \Delta H > 0$$

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 vapour pressure.



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

$$\textbf{n–C}_6\textbf{H}_{14} > \textbf{n– C}_7\textbf{H}_{16} > \textbf{C}_8\textbf{H}_{18}$$

The dependence of vapour pressure of a liquid on temperature is given by clausius-clapeyron equation : $\ln\dfrac{P_2}{P_1} = \dfrac{\Delta H_{vap.}}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

5.2 Nature of liquid : Weaker the intermolecular attraction , higher will be the vapour pressure.

6. VAPOUR PRESSURE OF LIQUID SOLUTION

6.1 Raoult's 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, at equilibrium.

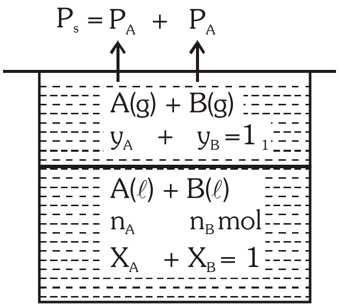
6.2 Vapour pressure of liquid – liquid solution :

Let P_A and P_B be the partial vapour pressures of two constituents A and B in solution and P_A^0 and P_B^0 the vapour pressures in pure state respectivity.

Thus, according Raoult's law

$$\mathbf{P_A = \frac{n_A}{n_A + n_B} P_A^0 = X_A P_A^0} \qquad \text{....(1)}$$

and $$\mathbf{P_B = \frac{n_B}{n_A + n_B} P_B^0 = X_B P_B^0} \qquad \text{....(2)}$$



If total pressure be P_S, then

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

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

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

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

6.2.1 Relation between Dalton's Law and Raoult's Law :

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

$$p_A = Y_A P_S = X_A P_A^0 \qquad ....(1)$$

$$p_B = Y_B P_S = X_B P_B^0 \qquad ....(2)$$

Now, $X_A = \dfrac{Y_A \cdot P_S}{P_A^0}$ and $X_B = \dfrac{Y_B \cdot P_S}{P_B^0}$

As, $X_A + X_B = 1, \ \dfrac{Y_A \cdot P_S}{P_A^0} + \dfrac{Y_B \cdot P_S}{P_B^0} = 1$

$$\therefore \quad \frac{1}{P_S} = \frac{Y_A}{P_A^0} = \frac{Y_B}{P_B^0}$$

Hence, the total vapour pressure of solution may be calculated from liquid composition at equilibrium as

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

and from vapour composition at equilibrium at

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

6.2.2 Comparision between liquid and vapour composition :

$$\frac{Y_A}{Y_B} = \frac{P_A / P_S}{P_B / P_S} = \frac{P_A}{P_B} = \frac{X_A \cdot P_A^0}{X_B \cdot P_B^0}$$

If A is more volatile than B $\left(P_A^0 > P_B^0\right)$, then $\dfrac{Y_A}{Y_B} > \dfrac{X_A}{X_B}$

It means that the mole-fraction of A is vapour form is relatively greater than that in liquid form, relative to B. Hence, in any ideal solution, vapour is always more richer in the more volatile component.

6.2.3 Raoult's law as a special case of Henry's law :

From Raoult's law, the vapour pressure of volatile component in the solution is $P = P^0.X$.

In the solution of gas in liquid, one component is so volatile that it exist as gas and its pressure is given by Henry's law as $P = K_H.X$

In both laws, the partial pressure of volatile component is directly proportional to its mole-fraction is solution. Only the proportionality constant K_H differs from P^0. Hence, Raoult's law becomes a special case of Henry's law in which K_H becomes P^0.

6.3 Vapour pressure of solution of solids in liquid :

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

According to Raoult's law –

$\because \quad P_s = X_A P_A{}^0 + X_B P_B{}^0$

for A, $P_A{}^0 = 0$

$\therefore \quad P_s = X_B P_B{}^0$ ....(5)

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

here X_B is mole fraction of solvent

$$P_S = \frac{n_B}{n_A + n_B} P^0 \qquad \text{....(6)}$$

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

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

$\Rightarrow \quad P_S = P_B{}^0 - X_A\, P_B{}^0$

$$\Rightarrow \quad \frac{P_B^0 - P_S}{P_B^0} = X_A$$

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

$$\boxed{\mathbf{\frac{P^0 - P_S}{P^0} = \frac{n_A}{n_A + n_B}}} \qquad \text{....(8)}$$

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

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

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

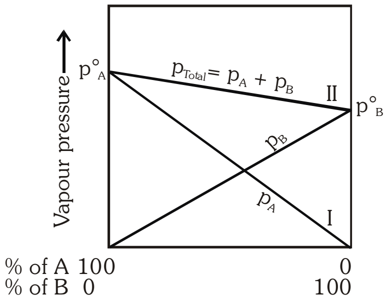
$$\boxed{\mathbf{\frac{P^0 - P_S}{P_S} = \frac{n_A}{n_B} = \frac{w_A . m_B}{m_A . w_B}}} \quad \text{....(9)}$$

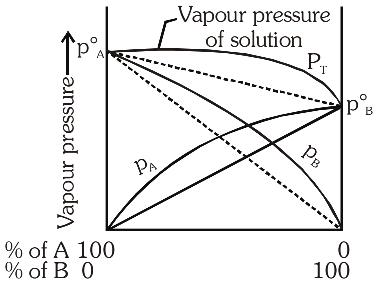
6.4 Ideal and Non ideal solutions :

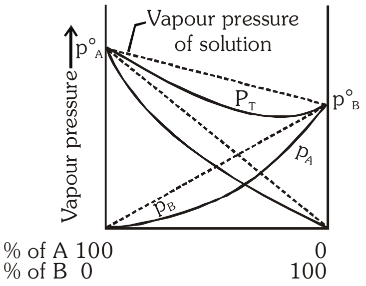
The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions.

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. $\Delta H_{mix} = 0$; Neither heat is evolved nor absorbed during dissolution.	$\Delta H_{mix} > 0$. Endothermic dissolution; heat is absorbed.	$\Delta H_{mix} < 0$; exothermic dissolution heat is evolved.
3. $\Delta V_{mix} = 0$; total volume of solution is equal to sum of volumes of the components.	$\Delta V_{mix} > 0$. Volume is increased after dissolution.	$\Delta V_{mix} < 0$; 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 identical in shape, size and character.	A — B, attraction force should be weaker than A — A and B — B attractive forces. 'A' and 'B' have different shape, size and character.	A — B, attraction force should be greater than A — A and B — B attractive forces. 'A' and 'B' have different shape, size and charater.
6. Escaping tendency of 'A' and 'B' should be same in pure liquids and in the solution.	'A' and 'B' escape easily showing high vapour pressure than the expected value.	Escaping tendency of both components A and B is lowered showing lower vapour pressure than expected ideally.
Example :	**Example :**	**Example :**
dilute solutions ;	acetone + ethanol ;	acetone + aniline ;
benzene + toluene ;	acetone + CS_2 ;	acetone + chloroform ;
n-hexane + n-heptane ;	water + methanol ;	$CH_3OH + CH_3COOH$;
chlorobenzene + bromobenzene ;	water + ethanol ;	$H_2O + HNO_3$;
ethyl bromide + ethyl iodide ;	$CCl_4 + CHCl_3$;	
n-butyl chloride + n-butyl bromide	CCl_4 + toluene ;	water + HCl ;
$CCl_4 + SiCl_4$;	acetone + benzene	acetic acid + pyridine ;
$C_2H_4Br_2 + C_2H_4Cl_2$	$CCl_4 + CH_3OH$;	
$C_2H_5Br + C_2H_5Cl$	cyclohexane + ethanol	$HNO_3 + CHCl_3$







Ex.3. ***1 mole heptane (V.P. = 92 mm of Hg) is mixed with 4 mole Octane (V.P. = 31 mm of Hg), form an ideal solution. Find out the vapour pressure of solution.***

Sol. *Total mole = 1 + 4 = 5*

Mole fraction of heptane $= X_A = 1/5$

Mole fraction of octane $= X_B = 4/5$

$$P_S = X_A P_A^{\,0} + X_B P_B^{\,0} = \frac{1}{5}\times 92 + \frac{4}{5}\times 31 = 43.2 \text{ mm of Hg.}$$

Ex.4. ***At 88°C, benzene has a vapour pressure of 900 torr and toluene has a vapour pressure of 360 torr. What is the mole fraction of benzene in the mixture with toluene that will be boil at 88°C at 1 atm pressure, benzene – toluene form an ideal solution.***

Sol. P_S *= 760 torr, because solution boils at 88°C*

$\therefore\ 760 = 900x + 360(1-x)$

$x = 0.74$ *where 'x' is mole fraction* C_6H_6.

Ex.5. ***The vapour pressure of benzene at 90°C is 1020 torr. A solution of 5 g of a solute in 58.5 g benzene has vapour pressure 990 torr. What is the molecular weight of solute ?***

Sol. $\dfrac{P^0 - P_S}{P_S} = \dfrac{w \times M}{m \times W} \Rightarrow \dfrac{1020-990}{990} = \dfrac{5\times 78}{m \times 58.5} \Rightarrow m = 220$

Ex.6. ***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 mole of B is 550 mm of Hg. At the same temperature, if one more 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.***

Sol. *Let the vapour pressure of pure A be =* p_A^0 *; and the vapour pressure of pure B be =* p_B^0.

Total vapour pressure of solution (1 mole A + 3 mole B)

$= X_A.p_A^0 + X_B.p_B^0$ *[*X_A *is mole fraction of A and* X_B *is mole fraction of B]*

$$550 = \frac{1}{4}p_A^0 + \frac{3}{4}p_B^0 \quad \textit{or} \quad 2200 = p_A^0 + 3p_B^0 \qquad ....(i)$$

Total vapour pressure of solution (1 mole A + 4 mole B) = $\dfrac{1}{5}p_A^0 + \dfrac{4}{5}p_B^0$

$$560 = \frac{1}{5}p_A^0 + \frac{4}{5}p_B^0$$

$2800 = p_A^0 + p_B^0$ ....*(ii)*

Solving eqs. (i) and (ii)

p_B^0 = *600 mm of Hg = vapour pressure of pure B*

p_A^0 = *400 mm of Hg = vapour pressure of pure A*

Ex.7. ***Liquids 'A' and 'B' form an ideal solution. Calculate the vapour pressure of solution having 40 mole-percent of A in the vapour at equilibrium.*** $\left(P_A^0 = 80\text{cm Hg},\ P_B^0 = 30\text{cm Hg}\right)$

Sol.

$$\frac{1}{P_{total}} = \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0} = \frac{0.4}{80} + \frac{0.6}{30} = \frac{1}{40}$$

P_{total} = *40 cm Hg*

Ex.8. ***Liquids 'A' and 'B' form an ideal solution. Calculate the molar-fraction of 'A' in vapour form above the liquid solution containing 25 mole-percent of 'A' at equilibrium*** $\left(P_A^0 = 0.2\text{atm},\ P_B^0 = 0.5\text{atm}\right)$

Sol.

$$Y_A = \frac{P_A}{P_{total}} = \frac{X_A \cdot P_A^0}{X_A \cdot P_A^0 + X_B \cdot P_B^0} = \frac{0.25 \times 0.2}{0.25 \times 0.2 + 0.75 \times 0.5} = \frac{2}{17}$$

Ex.9. ***Liquids 'A' and 'B' form an ideal solution. At 80°C,*** $P_A^0 = 0.4\text{bar}$ ***and*** $P_B^0 = 0.8\text{bar}$. ***All the vapour above the liquid solution containing equal moles of both the liquids at equilibrium is collected in another empty vessel and condensed. Now, the condesate is heated to 80°C and all the vapours above the liquid solution at equilibrium is again collected in another empty vessel and condensed. What is the mole-fraction of 'B' is new condensate ?***

Sol. *For the first condensate,*

$$\frac{n_B'}{n_A'} = \frac{X_B'}{X_A'} = \frac{Y_B}{Y_A} = \frac{X_B}{X_A} \cdot \frac{P_A^0}{P_B^0} = \frac{n_B}{n_A} \times \frac{P_B^0}{P_A^0}$$

For second condensate,

$$\frac{n_B''}{n_A''} = \frac{X_B''}{X_A''} = \frac{Y_B'}{Y_A'} = \frac{X_B' \cdot P_B^0}{X_A' \cdot P_A^0} = \frac{n_B}{n_A} \times \left(\frac{P_B^0}{P_A^0}\right)^2 = \frac{x}{x} \times \left(\frac{0.8}{0.4}\right) = \frac{4}{1}$$

$\therefore$ *Mole fraction of* $\text{B} = \frac{4}{5} = 0.8$

Note : For multi-step condensation at constant temperature,

$$\boxed{\frac{n_B^f}{n_A^f} = \frac{n_B^i}{n_B^i} \cdot \left(\frac{P_B^0}{P_A^0}\right)^n}$$

n : number of steps

Ex.10. ***Liquid A & B form an ideal solution. In a cylinder piston arrangement, 2 moles of vapours of liquid A & 3 moles of vapours of liquid B are taken at 0.3 atm.*** $P_A^0 = 0.4\,\text{atm}$, $P_B^0 = 0.6\,\text{atm}$.

(i) Predict whether vapours will condense or not ?

(ii) If the vapours are compressed slowly & isothermly, at what pressure I^{st} drop of liquid will form

(iii) If the initial volume of vapours was 10L, at what volume I^{st} drop of liquid will form ?

(iv) What is the composition of I^{st} drop of liquid formed ?

(v) If the vapours are further compressed slowly & isothermally, at what P almost complete condensation will occur ?

(vi) What is the composition of last traces of vapours remained ?

(vii) What is the composition of system at 0.58 atm ?

(viii) What is the composition of system at 0.51 atm ? Also calculate moles of A & B in liquid & vapour form.

(ix) At what P, half of the total amount of vapours will condense ?

Sol. *(i)* $\frac{1}{P_T} = \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0} = \frac{2/5}{0.4} + \frac{3/5}{0.6}$ $\Rightarrow$ $P_{total} = 0.5\ atm > 0.3\ atm$

$\therefore$ *100% gas, no condensation*

(ii) 0.5 atm.

(iii) $P_iV_i = P_fV_f$

$$V_f = \frac{0.3\times10}{0.5} = 6L$$

(iv) $P_{total} = X_A \cdot P_A^0 + X_B \cdot P_B^0$

or $0.5 = X_A \times 0.4 + (1 - X_A) \times 0.6 \quad \Rightarrow \quad X_A = 0.5$

(v) $P_T = 0.4 \times 0.4 + 0.6 \times 0.6 = 0.52\ atm$

Note: *For a pure liquid, there is a fixed P(V.P.) below & above which, the system will be 100% gas & 100% liquid, respectively but for a solution, a pressure range exist in which both physical states will be present.*

(vi) $Y_A = \frac{X_A \cdot P_A^0}{P_{total}} = \frac{0.4\times0.4}{0.52} = \frac{4}{13}$

(vii) *100% liquid, A = 2mole and B = 3 mole*

(viii) $P_{total} = X_AP_A^0 + X_BP_B^0$

$0.51 = X_A \times (0.4) + (1 - X_A) \times 0.6$ & $Y_A = \frac{X_AP_A^0}{P_{total}} = \frac{0.45\times0.4}{0.51} = 0.35$

$X_A = 0.45$

A = 2mol
B = 3 mol

Liquid
A = x mol
B = y mol

Vapour
A = (2 – x)
B = (3 – y)

$$X_A = \frac{9}{20} = \frac{x}{x+y} \qquad \textit{and} \qquad Y_A = \frac{18}{51} = \frac{2-x}{(2-x)+(3-y)}$$

$\therefore$ *x = 1.09 ; y = 1.33*

(ix)

A = 2mole
B = 3 mole

Liquid = 2.5 mole
A = z mole
B = (2.5 – z) mole

Vapour = 2.5 mole
A = (2 – z) mole
B = (0.5 – z) mole

$$P_T = \frac{z}{2.5} \times 0.4 + \frac{2.5-z}{2.5} \times 0.6$$

$$\frac{2-z}{2.5} = \frac{z \times 0.4}{2.5 \times P_T}$$

On solving, z = 1.12, P_T = 0.5104 atm

6.5 Graphs for ideal Binary solution of liquid A & liquid B :

(Assume $P_A^0 < P_B^0$)

I. Vapour pressure V/s liquid composition

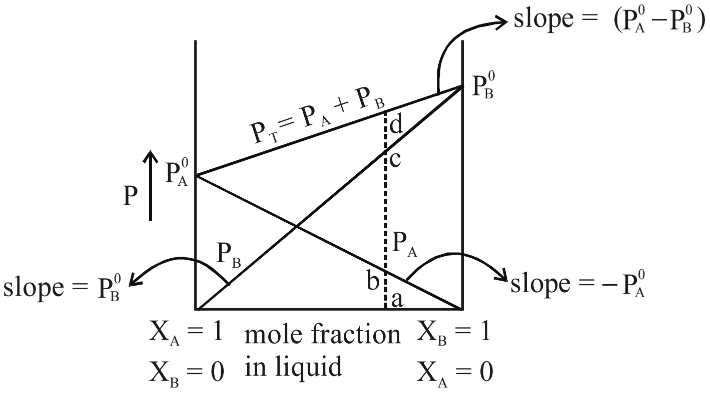
$$P_A = X_A P_A^0 = (1 - X_B) P_A^0$$

$$P_A = P_A^0 - X_B P_A^0$$

$$P_B = X_B P_B^0$$

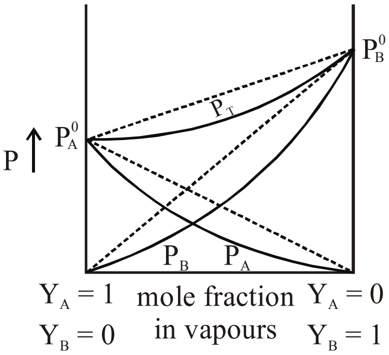
$$P_T = X_A P_A^0 - X_B P_B^0 = (1 - X_B) P_A^0 + X_B P_B^0$$

$$\therefore \quad P_T = P_A^0 + X_B \left(P_B^0 - P_A^0\right)$$



As $P_T = P_A + P_B$, ad = ab + ac

II. Vapour pressure V/s vapour composition



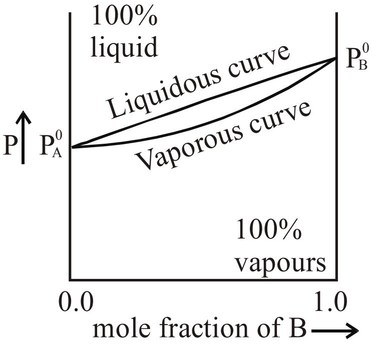
$$\frac{1}{P_T} = \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0}$$

$$\frac{1}{P_T} = \frac{1}{P_A^0} + Y_B\left(\frac{1}{P_B^0} - \frac{1}{P_A^0}\right)$$

$$\frac{1}{y} = c + mx$$

So curve will be rectangular hyperbola.

III. Vapour pressure V/s composition



(i) The V.P. of ideal solution always lie in between the V.P. of pure components.

(ii) Below vapourous curve, the system will by 100% vapour & above liquidous and curve, 100% liquid. Both the physical states exists only in between the curves.

(iii) At any composition, the physical state of system may be changed by changing the pressure.

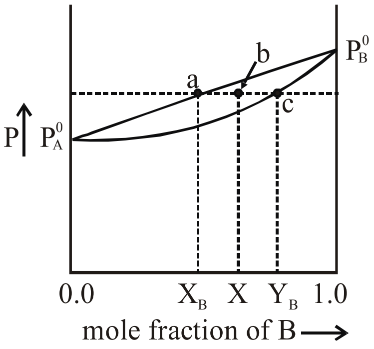
(iv) At any pressure in between P_A^0 and P_B^0, the physical state of system may be changed by changing the composition.

(v) Length ab ∝ total moles of vapour

Length cb ∝ total moles of liquid

$$\frac{ab}{cb} = \frac{\text{total moles of vapour}}{\text{total moles of liquid}}$$

or $$\frac{X - X_B}{Y_B - X} = \frac{n_{A(g)} + n_{B(g)}}{n_{A(\ell)} + n_{B(\ell)}}$$ (Lever's rule)



6.6 Boiling point :

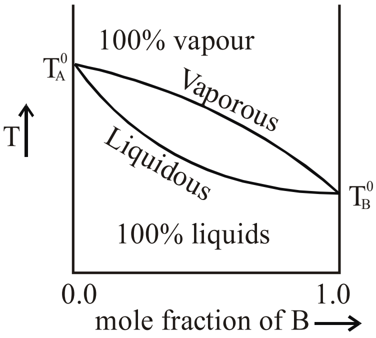
Boiling point of a liquid is the temperature at which the vapour pressure of the liquid become equal to the atmospheric pressure.

Ex.11 Liquid 'A' and 'B' form an ideal solution. At 27°C, the vapour pressure of pure liquids 'A' and 'B' are 0.6 atm and 1.2 atm, respectively. What the coposition of liquid solution boiling at 27°C?

Sol. $P_T = X_A \cdot P_A^0 + X_B \cdot P_B^0$

or 1 $= X_A \times 0.6 + (1 - X_A) \times 1.2 \;\Rightarrow X_A = \frac{1}{3}$

6.7 Boiling point curves for ideal binary solution :



(i) The boiling point of ideal solutioin always lie in between the boiling points of pure liquids.

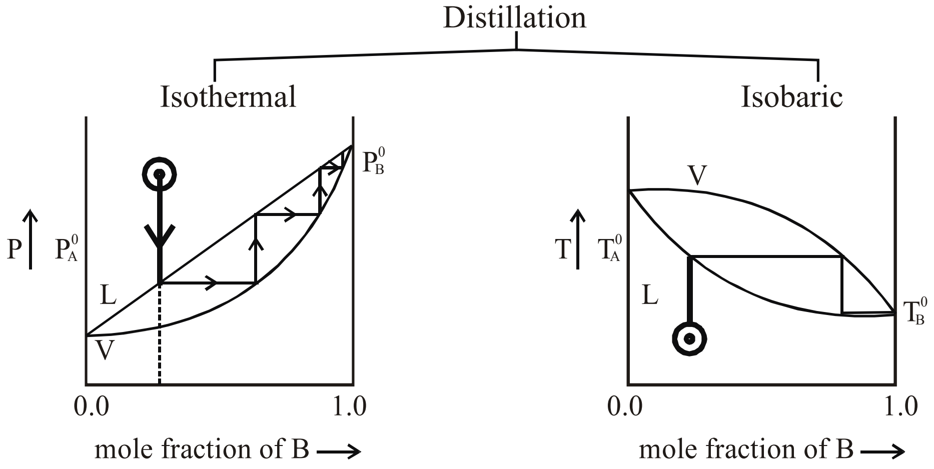
(ii) Below liquidus curve, the system in 100% liquid and above vapourus curve, the systm is 100% vapour. Both the physical states exists only in between the curves.

(iii) At any composition, the physical state of system may be changed by changing the temperature.

(iv) At any temperature in between T_A^0 and T_B^0, the physical state of system may be changed by changing the composition.

6.8 Distillation

It is the method of seperation of liquids by converting them into vapours (boiling).

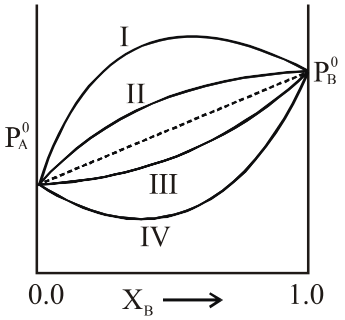


(i) The seperation of liquid by distillation occurs because at any T or P, the composition of distillate or condensate is different than the composition of original liquid.

(ii) With the elemination of vapour above the liquid, the boiling point of residual liquid increases.

(iii) The boiling point of distillate is less than that of original liquid.

6.9 Graphs for Non-ideal solutions and azeotropic mixture



(I) Large positive deviation : $(V.P.)_{solution} > P_B^0$ at some composition

(II) Small positive deviation : $P_A^0 < (V.P.)_{solution} < P_B^0$

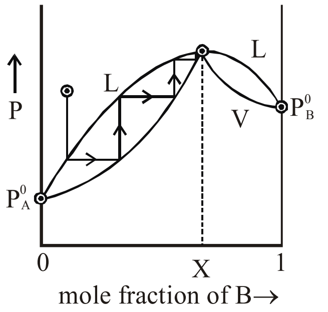
(III) Small negative deviation : $P_A^0 < (V.P.)_{solution} < P_B^0$

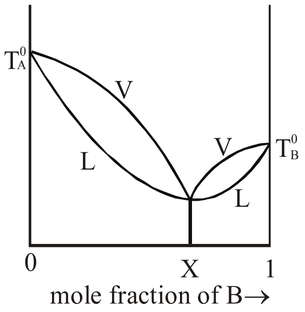
(IV) Large negative deviation : $(V.P.)_{solution} < P_A^0$ at some composition

6.9.1 Konowaloff's rule :

In ideal or non-idal solution the vapour is always more rich in the component, addition of which in liquid, increase the vapour pressure of solution.

6.9.2 Large (+)ve derivation (Minimum boiling azeotrope)





The solution of large positive deviation can not be seperated by distillation becasue at composition 'x', the liquid & vapour composition becomes identical.

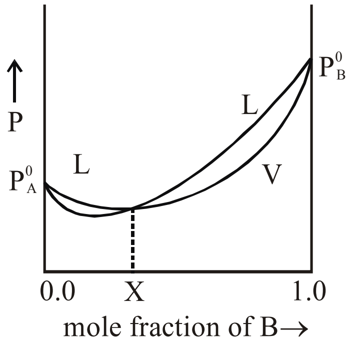
Such solution which can not be saperated by distillation are called **azeotropic mixture or constant boiling solution.**

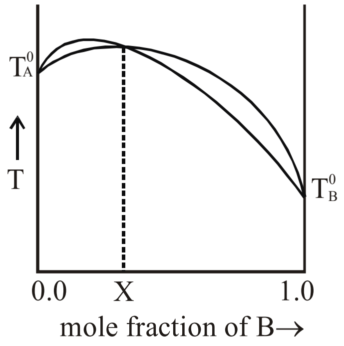
At any composition less than X, traces of pure A may be obtained but not pure B. Similarly at composition greater than X, traces of pure B may be obtained but not pure A.

Minimum boiling point Azeotropic

Mixture	% Composition of azeotrope	Boiling point (pressure = 1atm)
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

5.9.3 Large (–)ve derivation (Maximum boiling azeotrope)





Maximum boiling point Azeotropic

Mixture	% Composition of azeotrope	Boiling point (pressure = 1atm)
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

Note : Azeotrope is not formed in ideal solution or solution of small deviations.

7. COLLIGATIVE PROPERTIES

Properties of a solution which depends on the number of solute particles irrespective of their nature, relative to the total number of particles present in solution are called colligative properties.

The following properties are colligative properties of solution :

(i) Relative lowering of vapour pressure.

(ii) Elevation in boiling point.

(iii) Depression in freezing point.

(iv) Osmotic pressure.

7.1 Lowering of 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° is the vapour pressure of pure solvent, and P_s is the vapour pressure of solution then

Lowering of vapour pressure = $P° - P_s$

Relative lowering of vapour pressure $= \dfrac{P^0 - P_s}{P^0}$

from equation (8)

$$\mathbf{\frac{P^0 - P_S}{P^0} = \frac{\Delta P}{P^0} = \frac{n_A}{n_A + n_B} = X_A}$$

For a very dilute solution $n_A <<< n_B$

so $$\frac{\mathbf{P^0 - P_S}}{\mathbf{P^0}} = \frac{\mathbf{n_A}}{\mathbf{n_B}} = \frac{\mathbf{w_A}}{\mathbf{m_A}} \times \frac{\mathbf{m_B}}{\mathbf{w_B}}$$

Ex.12. Calculate the vapour pressure lowering caused by addition of 50 g of sucrose (molecular mass = 342) to 500 g of water if the vapour pressure of pure water at 25°C is 23.8 mm Hg.

Sol. According to Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{n}{n+N} \quad \text{or} \quad \Delta p = \frac{n}{n+N} . p_0$$

Given : $n = \frac{50}{342} = 0.146$; $N = \frac{500}{18} = 27.78$ and $p_0 = 23.8$ mmHg

Substituting the values in the above equation,

$$\Delta p = \frac{0.146}{0.146 + 27.78} \times 23.8 = 0.124 \text{ mm Hg}$$

7.1.1 Measurement of Lowering in Vapour Pressure by Dynamic Method (Ostwald and Walker Method)

The apparatus used is shown in Fig. It consists of two sets of bulbs. The first set of three bulbs is filled with solution to half of their capcity and second set of another three bulbs is filled with the pure solvent.

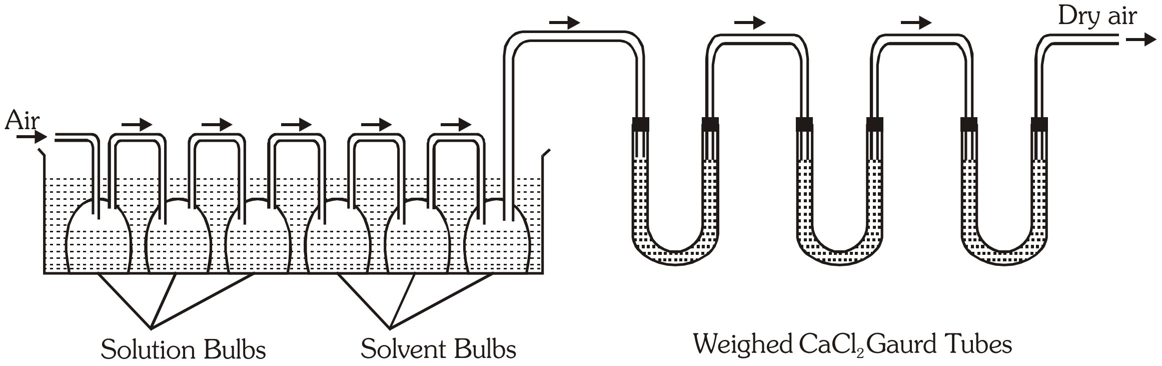


Fig. Ostwald and Walker method

Each set is separately weighed accurately. Both sets are connected to each other and then with the accurately weighed set of guard tubes filled with anhydrous calcium chloride or some other dehydrating agents like P_2O_5, conc. H_2SO_4 etc. The bulbs of solution and pure solvent are kept in a thermostat maintained at a constant temperature.

A current of pure dry air is bubbled through the series of bulbs as shown in fig. The air gets saturated with the vapour in each set of bulbs. The air takes up an amount of vapours proportional to the vapour pressure of the solution first and then it takes up more amount of vapours from the solvent which is proportional to the difference in the vapour pressure of the solvent and the vapour pressure of solution, i.e., $p_0 - p_s$.

The two sets of bulbs are weighed again. The guard tubes are also weighed.

Loss in mass in the solution bulbs $\propto p_s$

Loss in mass in the solvent bulbs $\propto (p_0 - p_s)$

Total loss in both sets of bulbs $\propto [p_s + (p_0 - p_s)] \propto p_0$

Total loss in mass of both sets of bulbs is equal to gain in mass of guard tubes.

Thus, $\frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Total loss in mass in both sets of bulbs}} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}}$

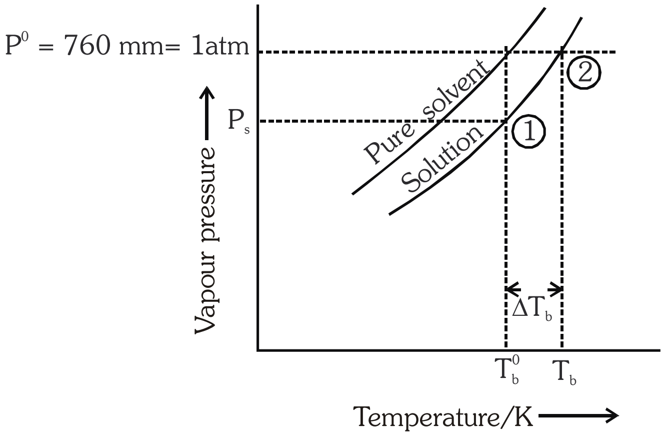
Further, we know from Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{w_A / m_A}{w_A / m_A + w_B / m_B}$$

$$\therefore \quad \frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of gaurd tubes}} = \frac{w_A / m_A}{w_A / m_A + w_B / m_B}$$

6.2 Elevation in boiling point (Ebullioscopy) :

$\text{solvent}(\ell) \rightleftharpoons \text{solvent}(g)$



The vapour pressure curve for solution lies below the curve for pure solvent .

ΔT_b denotes the elevation of boiling point of a solution.

When a non-volatile solute A is dissolved in a pure solvent B, its vapour pressure decreases and hence the boiling point increases. The difference ΔT_b of boiling points of the solution and pure solvent is called elevation in boiling point.

If T_b^0 is the boiling point of pure solvent and T_b is the boiling point of the solution then, $T_b > T_b^0$

and the elevation in boiling point $\quad \Delta T_b = T_b - T_b^0$

Experiments have shown that for dilute solutions, the elevation of boiling point (ΔT_b) is directly proportional to the molal concentration of the solute in a solution. Thus

$$\Delta T_b \propto m$$

or $$\Delta T_b = K_b.m$$

where K_b = boiling point elevation constant or molal elevation constant or ebulioscopic constant.

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

$$\mathbf{K_b = \frac{RT_b^2 . M}{1000\ \Delta H_{vap}}}$$

where, R is molar gas constant = 2 cal/mol–K , M = molar mass of solvent

T_b is the boiling point of the pure solvent (in K)

and ΔH_{vap} is the latent heat of vaporisation of pure solvent

For water $K_b = \frac{2 \times (373)^2}{1000 \times 540} = 0.515$ 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 tetrachloride	76.8	5.03
Benzene	80.0	2.53
Ethyl alcohol	78.4	1.20

Ex.13. ***0.15 g of a substance dissolved in 15 g of solvent boiled at a temperature higher by 0.216°C than that of the pure solvent. What is the molecular weight of the substance. [K_b for solvent = 2.16 K-kg/mol]***

Sol. ***Given : K_b = 2.16°C, w = 0.15 g, ΔT_b = 0.216°C, W = 15 g***

ΔT_b = molality × K_b

$$\Delta T_b = \frac{w}{m \times W} \times 1000 \times K_b$$

$$0.216 = \frac{0.15}{m \times 15} \times 1000 \times 2.16$$

$$m = \frac{0.15 \times 1000 \times 2.16}{0.216 \times 15} = \mathbf{100}$$

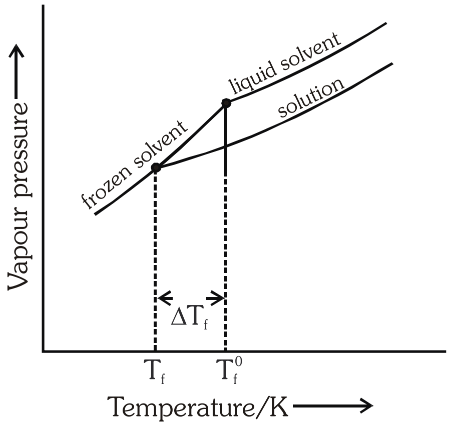
Ex.14 ***The rise in boiling point of a solution containing 1.8 g glucose in 100 g of a solvent is 0.1°C. The molal elevation constant of the liquid is –***

Sol. *ΔT_b= 0.1°C, m = 180, W = 100, w = 1.8*

$$K_b = \frac{\Delta T_b \times m \times W}{1000 \times w} = \frac{180 \times 0.1 \times 100}{1000 \times 1.8} = 1.0$$

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



When a non-volatile non-electrolyte is dissolved in a pure solvent, the vapour pressure of the solvent is lowered and it become equal to that of solid solvent at lower temperature.

If T_f^0 is the freezing point of pure solvent and (T_f) is the freezing point of its solution then,

$$T_f < T_f^0$$

The difference in the freezing point of pure solvent and solution is the depression of freezing point (ΔT_f) Thus,

$$T_f^0 - T_f = \Delta T_f$$

Similar to elevation in boiling point, depression in freezing point for dilute solution is directly proportional to its molality,

$$\Delta T_f \propto m$$

or $$\Delta T_f = K_f . m$$

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

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

$$K_f = \frac{R \cdot T_f^{0^2} \cdot M}{1000 \cdot \Delta H_{fus}}$$

where, T_f^0 is the freezing point of pure solvent in (Kelvin) and ΔH_{fus} is the latent heat of fusion pure solvent.

For water,

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

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 tetrachloride	– 22.8	31.8
Benzene	5.5	5.12
Camphor	179.0	39.70

Ex.15. If freezing point of a solution prepared from 1.25 g of a non electrolyte and 20 g of water is 271.9 K, the molar mas of the solute will be – (K_f of water = 1.86 K-kg/mol)

Solution : Given $T_f = 271.9$ K

$w = 1.25$ g $\quad W = 20$ g $\quad K_f = 1.86$

$\Delta T_f = T_f^0 - T_f = 273 - 271.9 = 1.1$ K

$\Delta T_f =$ molality × K_f

$$\Rightarrow \quad \Delta T_f = \frac{w}{m \times W} \times 1000 \times K_f$$

$$\text{or} \quad m = \frac{w \times 1000 \times K_f}{\Delta T_f \times W} = \frac{1.25 \times 1000 \times 1.86}{1.1 \times 20} = 105.68 \text{ mol/kg}$$

Ex.16. Molal depression constant for water is 1.86. What is freezing point of a 0.05 molal solution of a non electrolyte in water ? (K_f of water = 1.86 K-kg/mol)

Solution : $\Delta T_f =$ molality × K_f

$= 0.05 \times 1.86 = 0.093°C$

$T_f = T_f^0 - 0.093 = 0 - 0.093$

$T_f = -0.093°C$

Ex.17. 2m aqueous urea solution is cooled to –7.44°C. Calculate the mass percent of water present in solution, which will separate as ice, (K_f of water = 1.86 K-kg/mol)

Sol. Let the initial mass of water in the solution = 1kg

$\therefore$ Moles of solute = 2

$$\text{Now, } \Delta T_f = K_f m = K_f \cdot \frac{n_{\text{solute}}}{Kg_{\text{solvent}}} \quad \text{or } 7.44 = 1.86 \times \frac{2}{Kg_{\text{solvent}}}$$

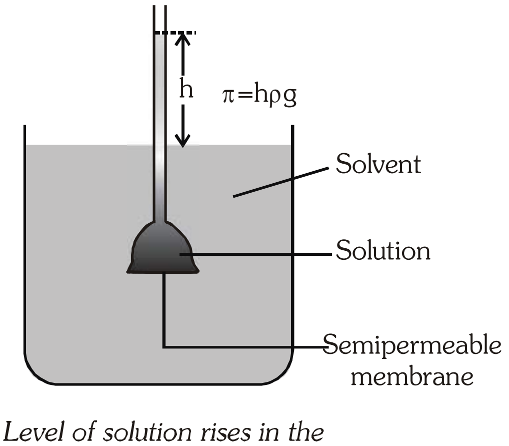
$\therefore$ $Kg_{solvent}$ left in the solution = 0.5

$$\therefore \quad \text{Mass percent of water separated as ice} = \frac{0.5}{1} \times 100 = 50\%$$

7.4 Osmosis and osmotic pressure :

7.4.1 Osmosis :

Osmosis is defined as the spontaneous flow of solvent molecules through semipermeable membrane from a pure solvent to solution.



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

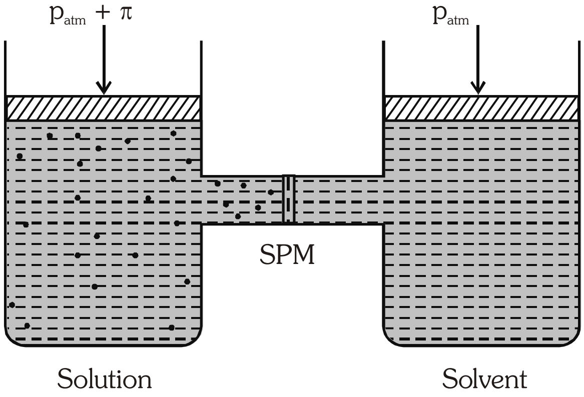
7.4.2 Semi-permeable membrane (SPM) :

There are the membranes (substances) which allow selective movement of particles across them. For a solution of solid solute in a liquid solvent, ideal SPM allow free movement of solvent particles across it, but not solute particles. These membranes contain a network of submicroscopic holes or pores through which small solvent molecules may pass but not the bigger solute particle.

7.4.3 Osmotic presssure (π) : It is the pressure which should be applied on the solution to just prevent osmostis or The hydrostatic pressure built up on the solution which just stops the osmosis.

osmotic pressure = hydrostatic pressure

$\pi = \rho g h$



The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis

7.4.4 Van't Hoff laws :

(i) The osmotic pressure (π) of a solution is directly proportional to its molar concentration(C), when the temperature is kept constant. (Van't Hoff-Boyle's law)

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

(ii) Concentration remaining same, the osmotic pressure of a dilute solution is directly proportional to its absolute temperature (T). (Van't Hoff-Charle's law)

$\pi \propto T$ (when C is constant)

Combining the two laws, i.e., when concentration and temperature both are changing, the osmotic pressure will be given by :

$\pi \propto C.T$ or $\pi = CRT$

Where R = Universal gas constant.

7.4.5 Isotonic or iso-osmotic solution :

Solutions which have the same osmotic pressures at a given temperature are called isotonic or iso-osmotic solutions

When isotonic solutions 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 we 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.

Ex.18. A cane sugar solution has an osmotic pressure of 2.46 atm at 300 K. What is the strength of the solution.

Sol. $\pi = CRT$

$$\text{or } C = \frac{\pi}{RT} = \frac{2.46}{300 \times 0.0821} = 0.1\,M$$

Ex.19 A solution containing 8.6 g urea in one litre was found to be isotonic with 0.5% (wt./vol.) solution of an organic, non-volatile solution. The molecular weight of latter is

Sol. *Solutions are isotonic*

so $\pi_1 = \pi_2$

$$\frac{n_1}{V_1}RT = \frac{n_2}{V_2}RT \qquad \{R \,\&\, T \text{ are constant}\}$$

$$\text{so, } \frac{n_1}{V_1} = \frac{n_2}{V_2}$$

$$\text{or } \left(\frac{w_1}{m_1 \times v_1}\right)_{\text{urea}} = \left(\frac{w_2}{m_2 \times v_2}\right)_{\text{organic}}$$

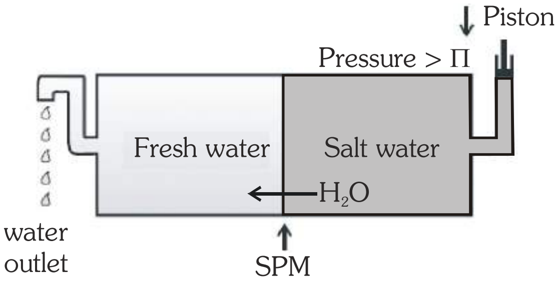
$$\text{or } \frac{8.6}{60 \times 1000} = \frac{0.5}{m_2 \times 100}$$

m_2 = 34.89 gm/mol

7.5 Reverse Osmosis and water purification :

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 water.



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

8 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.

Van't Hoff in 1880, introduced a factor, called Van't Hoff factor (i). The factor 'i' is defined as

$$\mathbf{i} = \frac{\textbf{observed colligative property}}{\textbf{Calculated colligative property}} = \frac{\textbf{ormal molecular mass}}{\textbf{observed molecular mass}}.$$

$$= \frac{\text{total number of particles after dissociation / association}}{\text{Number of particles initially taken}}$$

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.

8.1 Calculation of 'i' in case of dissociation

$$A_xB_y \longrightarrow x\,A^{y+} + yB^{x-}$$

Initial mol $\quad 1 \quad 0 \quad 0$

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

Total no. of solute particles $= 1 - \alpha + x\alpha + y\alpha = 1 - \alpha + \alpha(x + y)$

or $\quad i = 1 - \alpha + n\alpha \quad$ [where $x + y = n$ (total ions.)]

or $\quad \mathbf{i = 1 + \alpha (n - 1)}$

For strong electrolytes : $\alpha = 1$ or 100%, so $i = n$ (total no. of ions)

$NaCl \rightarrow Na^+ + Cl^-$ $\quad (i = 2)$

$K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$ $\quad (i = 3)$

For complex compound

$K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-} \Rightarrow \quad n = 5$

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_{normal}
2.	Binary electrolyte AB type	NaCl, KCl, HCl CH_3COOH NH_4OH, NaOH etc.	$\underset{1-\alpha}{AB} \rightleftharpoons \underset{\alpha}{A^+} + \underset{\alpha}{B^-}$	2	$1+\alpha$	$\frac{m_{normal}}{1+\alpha}$
3.	Ternary electrolyte AB_2 type or A_2B type	$CaCl_2$, $BaCl_2$ H_2SO_4, $K_2[PtCl_6]$	$\underset{1-\alpha}{AB_2} \rightleftharpoons \underset{\alpha}{A^{2+}} + \underset{2\alpha}{2B^-}$ $\underset{1-\alpha}{A_2B} \rightleftharpoons \underset{2\alpha}{2A^+} + \underset{\alpha}{B^-}$	3 3	$1+2\alpha$ $1+2\alpha$	$\frac{m_{normal}}{1+2\alpha}$ $\frac{m_{normal}}{1+2\alpha}$
4.	Quanternary electrolyte AB_3 or A_3B type	$AlCl_3$, $K_3[Fe(CN)_6]$	$\underset{1-\alpha}{AB_3} \rightleftharpoons \underset{\alpha}{A^{3+}} + \underset{3\alpha}{3B^-}$ $\underset{1-\alpha}{A_3B} \rightleftharpoons \underset{3\alpha}{3A^+} + \underset{\alpha}{B^{3-}}$	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	$\underset{1-\alpha}{AB_{n-1}} \rightleftharpoons \underset{\alpha}{A^{+(n-1)}} + \underset{(n-1)\alpha}{(n-1)B^-}$	n	$1+(n-1)\alpha$	$\frac{m_{normal}}{[1+(n-1)\alpha]}$

8.2 Calculation of 'i' in case of assocation

	$nA \longrightarrow$	$(A)_n$
Initial mol	1	0
after dissociation	$1-\alpha$	α/n

$$i = \frac{1-\alpha+\frac{\alpha}{n}}{n}\ , \quad \alpha = \text{degree of assocation}$$

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

Ex.20. ***Determine the amount of $CaCl_2$ (i = 2.47) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27°C.***

Sol. *We know that,*

$$\pi = i\frac{n}{V}RT \Rightarrow \pi = i\frac{w}{MV}RT$$

$$\Rightarrow w = \frac{\pi MV}{iRT} = \frac{0.75\times 111\times 2.5}{2.47\times 0.0821\times 300} = 3.42\ g$$

Hence, the required amount of $CaCl_2$ is 3.42 g.

Ex.21 ***19.5 g of CH_2FCOOH is dissolved in 500 g of water. The depression in the freezing point of water observed is 1.0°C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.***

Sol. *It is given that :*

$w_1 = 500\ g$

$w_2 = 19.5\ g$

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

$\Delta T_f = 1\ K$

We know that :

$$M_2 = \frac{K_f\times w_2\times 1000}{\Delta T_f\times w_1} = \frac{1.86\,K\,kg\,mol^{-1}\times 19.5g\times 1000g\,kg^{-1}}{500g\times 1K} = 72.54\ mol^{-1}$$

Therefore, observed molar mass of CH_2FCOOH, $(M_2)_{obs} = 72.54\ mol$

The calculated molar mass of CH_2FCOOH is :

$(M_2)_{cal} = 14+19+12+16+16+1 = 78\ g\ mol^{-1}$

Therefore, van't Hoff factor, $i = \frac{(M_2)_{cal}}{(M_2)_{obs}} = \frac{78\,g\,mol^{-1}}{72.54\,g\,mol^{-1}} = 1.0753$

Let α be the degree of dissociation of CH_2FCOOH

	CH_2FCOOH	$\rightleftharpoons$ CH_2FCOO^-	+ H^+	
Initial conc.	$C\ mol\ L^{-1}$	0	0	
At equilibrium	$C\,(1-\alpha)$	$C\alpha$	$C\alpha$	Total = $C\,(1+\alpha)$

$$\therefore\ i=\frac{C(1+\alpha)}{C}$$

$\Rightarrow i = 1 + \alpha \Rightarrow \alpha = i - 1$

$= 1.0753 - 1 = 0.0753$

Now, the value of K_a is given as :

$$K_a=\frac{[CH_2FCOO^-][H^-]}{[CH_2FCOOH]}=\frac{C\alpha.C\alpha}{C(1-\alpha)}=\frac{C\alpha^2}{1-\alpha}$$

Taking the volume of the solution as 500 mL. We have the concentration : 19.5 M

$$C=\frac{78}{500}\times 1000\,M = 0.5\ M$$

Therefore, $K_a=\dfrac{C\alpha^2}{1-\alpha}$

$$=\frac{0.5\times(0.0753)^2}{1-0.0753}=\frac{0.5\times 0.00567}{0.9247}=0.00307\ \text{(approximately)} = 3.07\times 10^{-3}$$

EXERCISE # S-I

(Raoult's law)

1. At 25°C, the vapour pressure of methyl alcohol is 96.0 torr. What is the mole fraction of CH_3OH in a solution in which the (partial) vapor pressure of CH_3OH is 24.0 torr at 25°C?

2. The vapour pressure of ethanol and methanol are 44.0 mm and 88.0 mm Hg respectively. An ideal solution is prepared at the same temperature by mixing 69 g of ethanol with 40 g of methanol. Calculate total vapour pressure of the solution.

3. Liquide 'A' and 'B' form an ideal solution. The vapour pressure of solution containing equal moles of both liquids is 80 cm Hg. At the same temperature, the vapour pressure of solution containing 25 mole percent of liquid 'A' is 70 cm Hg. Calculate P_A^0 and P_B^0.

4. Liquids 'A" and 'B' form an ideal solution. Calculate the mole-fraction of 'A' in the vapours above the liquid solution containing the liquids 'A' and 'B' in 2 : 3 mole ratio, at equilibrium.

[Given : $P_A^0 = 0.4$ atm, $P_B^0 = 0.8$ atm]

5. Liquids 'P' and 'Q' form an ideal solution. At equilibrium, the vapours contain 40% molecules of 'P'. Calculate the vapour presure of solution.

[Given : $P_P^0 = 0.4$ bar, $P_Q^0 = 0.6$ bar]

6. Liquids 'X' and 'Y' form an ideal solution. The vapour pressure of solution may be expressed as : **P[/cmHg] = (80 – 25x)**, where 'x' is the mole-fraction of liquid 'X' in the liquid solution at equilibrium. Calculate the vapour pressures of pure liquids 'X' and 'Y'.

7. Liquid 'R' and 'S" form an ideal solution. The mole-fraction of 'R' in liquid and vapour phases at equilibrium are 0.25 and 0.40, respectively. If the vapour pressure of solution is 0.50 bar, calculate P_R^0 and P_S^0

Colligative properties

8. The vapour pressure of pure liquid solvent A is 0.80 atm. When a nonvolatile substance B is added to the solvent its vapour pressure drops to 0.60 atm. What is the mole fraction of component B in the solution?

9. Calculate the relative lowering in vapour pressure if 100 g of a nonvolatile solute (mol.wt.100) are dissolved in 432 g water.

10. The vapour pressure of pure benzene at 30° C is 640 mm of Hg and the vapour pressure of a solution of a solute in C_6H_6 at the same temperature is 624 mm of Hg. Calculate molality of solution.

11. The vapour pressure of pure benzene at a certain temperature is 640 mm of Hg. A nonvolatile nonelectrolyte solid weighing 2.175 g is added to 39.0 of benzene. The vapour pressure of the solution is 600 mm of Hg. What is molecular weight of solid substance?

12. The vapour pressure of water is 17.54 mm Hg at 293 K. Calculate vapour pressure of 0.5 molal solution of a solute in it.

13. When 10.5 g of a nonvolatile substance is dissolved in 742 g of ether, its boiling point is raised 0.25°C. What is the molecular weight of the substance? Molal boiling point constant for ether is 2.12°C·kg/mol.

14. Calculate the molal elevation constant, K_b for water and the boiling point of 0.1 molal urea solution. Latent heat of vaporisation of water is 9.72 kcal mol^{-1} at 373.15 K. $[(373.15)^2 = 258 \times 540]$

15. Pure benzene freeze at 5.45°C. A solution containing 6.72 g of $C_2H_2Cl_4$ in 120 g of benzene was observed to freeze at 3.75°C. What is the molal freezing point constant of benzene?

16. The freezing point of a solution containing 2.40 g of a compound in 60.0 g of benzene is 0.10°C lower than that of pure benzene. What is the molecular weight of the compound? (K_f is 5.12°C/m for benzene)

17. Normal boiling point of diethyl ether is 327° and at 190 mmHg boiling points in 27°C. What is the value of $\Delta H^{\circ}_{vap.}$ in kJ/mole.

(Use : R = 8.3 J/K-mole, ln2 = 0.7)

18. A 6.84% solution (w/v) of cane-sugar (Mol. weight = 342) is isotonic with 0.8%(w/v) solution of non-volatile solute. Find molecular weight of solute.

19. Calculate the osmotic pressure of 12% (w/v) aq. urea solution at 27°C.

20. Calculate the osmotic pressure of a solution containing 18 gm glucose and 17.1 gm canesugar ($C_{12}H_{22}O_{11}$) per litre, at 27°C.

21. A storage battery contains a solution of H_2SO_4 38% by weight. What will be the Van't Hoff factor if the $\Delta T_{f(experiment)}$ is 22.8K. [Given $K_f = 1.86\ mol^{-1}\ Kg$]

22. A certain mass of a substance, when dissolved in 100 g C_6H_6, lowers the freezing point by 1.28°C. The same mass of solute dissolved in 100g water lowers the freezing point by 1.40°C. If the substance has normal molecular weight in benzene and is completely ionized in water, into how many ions does it dissociate in water? K_f for H_2O and C_6H_6 are 1.86 and 5.12K kg mol^{-1}.

23. 2.0 g of benzoic acid dissolved in 25.0g of benzene shows a depression in freezing point equal to 1.96K. Molal depression constant (K_f) of benzene is 4.9 K.kg.mol^{-1}. What is the percentage association of the acid?

24. A decimolar solution of potassium ferrocyanide is 50% (w/v) dissociated at 300K. Calculate the osmotic pressure of the solution. (R=8.314 $JK^{-1}\ mol^{-1}$)

25. A 1.2% solution (w/v) of NaCl is isotonic with 7.2% solution (w/v) of glucose. Calculate degree of ionization and Van't Hoff factor of NaCl.

Henry's law

26. How many gm O_2 gas will disolve in 100 gm water at 9 bar and 27°C? (K_H = 40 Kbar)

27. The Henry law constant for dissolution of a gas in aqueous medium is 3×10^2 atm. At what partial pressure of the gas (in atm), the molality of gas in aqueous solution will be $\frac{5}{9}$m.

EXERCISE # S-II

1. At 90°C, the vapour pressure of toluene is 400 torr and that of σ-xylene is 150 torr. What is the composition of the liquid mixture that boils at 90°C, when the pressure is 0.50 atm? What is the composition of vapour produced?

2. The vapour pressure of an aqueous solution of glucose is 750 mm Hg at 373 K. Calculate molality and mole fraction of solute.

3. Calculate the amount of ice that will separate out of cooling a solution containing 50g of ethylene glycol in 200 g water to –9.3°C. (K_f for water = 1.86 K mol^{-1} kg)

4. A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.750 g in 125 cm^3 of an aqueous medium. At 4°C an osmotic pressure rise of 2.77 mm of the solution was observed. The solution had a density of 1.013 g/cm^3. Determine the molecular weight of the protein. (g = 10 m/s^2)

5. The vapour pressure of an aqueous solution is found to be 750 torr at certain temperature 'T'. If 'T' is the temperature at which pure water boils under atmospheric pressure, calculate the atmospheric pressure. The boiling point of solution is 101.04ºC. (K_b = 0.52 K kg mol^{-1}).

6. How many grams of sucrose (mol.wt. = 342) should be dissolved in 100 gm water in order to produce a solution with 105°C difference between the freezing point & boiling point temperature at 1 atm? **(Unit: K_f = 2 K.kg mol^{-1} ; k_b = 0.5 K.kg mol^{-1})**

7. An aqueous solution containing 288 gm of a non-volatile compound having the stoichiometric composition $C_xH_{2x}O_x$ in 90 gm water boils at 101.36°C at 1.00 atmospheric pressure. What is the molecular formula? $K_b(H_2O)$ = 0.52 K mol^{-1} kg

8. A complex is represented as $CoCl_3 \cdot xNH_3$. It's 0.1 molal solution in a solution shows ΔT_f = 0.558°C. K_f for H_2O is 1.86 K mol^{-1} kg . Assuming 100% ionisation of complex and coordination no. of Co is six, calculate formula of complex.

9. Phenol associates in benzene to a certain extent to form a dimer. A solution containing 18.8 × 10^{-3} kg phenol in 1 kg of benzene has its freezing point depressed by 0.768 K. Calculate the fraction of phenol that has dimerised. K_f for benzene = 5.12 kg mol^{-1}K.

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

11. A solution of 0.1 M CH_3COOH is placed between parallel electrodes of cross-section area 4cm^2, separated by 2cm. For this solution resistance measured is 100Ω. If the elevation in boiling point of the 0.1 M CH_3COOH solution is 'x'K, then the value of (160x) is.

K_b = 0.5 K kg/mol; $\Lambda_m^{\infty}(H^+)$ = 300 Scm^2 mole^{-1}; $\Lambda_m^{\infty}(CH_3COO^-)$ = 100 Scm^2 mole^{-1}

12. Cane sugar underoges the inversion as follow

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

If solution of 0.025 moles of sugar in 200 gm of water show depresion in freezing point 0.372ºC, then what % sucrose has inverted. ($K_f(H_2O)$ = 1.86 K kg mol^{-1})

13. When 0.1 M $Pb(NO_3)_2$ solution is titrated with 0.1 M KI solution then what will be the osmotic pressure (in atm) of solution when equivalence point is reached at 300 K .

(Take : R = 0.08 atm L/mol-k)

14. Using the following information determine the boiling point of a mixture contains 1560 gm benzene and 1125 gm chlorobenzene, when the external pressure is 1000 torr. Assume the solution is ideal.

Temperature (0°C)	**Vapour pressure of benzene(torr)**	**Vapour pressure of chlorobenzene(torr)**
80	750	120
90	1000	200
100	1350	300
110	1800	400
120	2200	540

15. The cryoscopic constant for acetic acid is 3.6 K kg/mol. A solution of 1 g of a hydrocarbon in 100 g of acetic acid freezes at 16.14°C instead of the usual 16.60°C. The hydrocarbon contains 92.3% carbon. What is the molecular formula?

EXERCISE # O-I

Single correct :

1. The boiling point of C_6H_6, CH_3OH, $C_6H_5NH_2$ and $C_6H_5NO_2$ are 80^0C, 65^0C, 184^0C and 212^0C respectively which will show highest vapour pressure at room temperature :

(A) C_6H_6 (B) CH_3OH (C) $C_6H_5NH_2$ (D) $C_6H_5NO_2$

2. Mole fraction of A vapours above the solution in mixture of A and B ($X_A = 0.4$) will be

[Given : P_A° = 100 mm Hg and P_B° = 200 mm Hg]

(A) 0.4 (B) 0.8 (C) 0.25 (D) none of these

3. At a given temperature, total vapour pressure in Torr of a mixture of volatile components A and B is given by

$$P_{Total} = 120 - 75\ X_B$$

hence, vapour pressure of pure A and B respectively (in Torr) are

(A) 120, 75 (B) 120, 195 (C) 120, 45 (D) 75, 45

4. Two liquids A & B form an ideal solution. What is the vapour pressure of solution containing 2 moles of A and 3 moles of B at 300 K? [Given : At 300 K, Vapour pr. of pure liquid A (P_A^o) = 100 torr, Vapour pr. of pure liquid B (P_B^o) = 300 torr]

(A) 200 torr (B) 140 torr (C) 180 torr (D) None of these

5. If Raoult's law is obeyed, the vapour pressure of the solvent in a solution is directly proportional to

(A) Mole fraction of the solvent
(B) Mole fraction of the solute
(C) Mole fraction of the solvent and solute
(D) The volume of the solution

6. 1 mole of heptane (V. P. = 92 mm of Hg) was mixed with 4 moles of octane (V. P. = 31mm of Hg). The vapour pressure of resulting ideal solution is :

(A) 46.2 mm of Hg (B) 40.0 mm of Hg
(C) 43.2 mm of Hg (D) 38.4 mm of Hg

7. Mole fraction of A vapours above solution in mixture of A and B ($X_A = 0.4$) will be :-
(P_A° = 100mm, P_B° = 200mm)

(A) 0.4 (B) 0.8 (C) 0.25 (D) None

8. The vapour pressure of a pure liquid 'A' is 70 torr at 27^0C. It forms an ideal solution with another liquid B. The mole fraction of B is 0.2 and total vapour pressure of the solution is 84 torr at 27^0C. The vapour pressure of pure liquid B at 27^0C is

(A) 14 (B) 56 (C) 140 (D) 70

9. At 88 °C benzene has a vapour pressure of 900 torr and toluene has a vapour pressure of 360 torr. What is the mole fraction of benzene in the mixture with toluene that will boil at 88 °C at 1 atm. pressure, benzene - toluence form an ideal solution:

(A) 0.416 (B) 0.588 (C) 0.688 (D) 0.740

10. The exact mathematical expression of Raoult's law is (n = moles of solute ; N = moles of solvent)

(A) $\frac{P^0 - P_s}{P^0} = \frac{n}{N}$ (B) $\frac{P^0 - P_s}{P^0} = \frac{N}{n}$ (C) $\frac{P^0 - P_s}{P_s} = \frac{n}{N}$ (D) $\frac{P^0 - P_s}{P^0} = n \times N$

11. The vapour pressure of a solvent decreased by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be mole fraction of the solvent if decrease in vapour pressure is 20 mm of Hg

(A) 0.2 (B) 0.4 (C) 0.6 (D) 0.8

12. The vapour pressure of a solution having solid as solute and liquid as solvent is :

(A) Directly proportional to mole fraction of the solvent

(B) Inversely proportional to mole fraction of the solvent

(C) Directly proportional to mole fraction of the solute

(D) Inversely propartional to mole fraction of the solute

13. One mole of non volatile solute is dissolved in two moles of water. The vapour pressure of the solution relative to that of water is

(A) $\frac{D}{i}$ (B) $\frac{s}{i}$ (C) $\frac{s}{D}$ (D) $\frac{i}{D}$

14. The vapour pressure of pure A is 10 torr and at the same temperature when 1 g of B is dissolved in 20 gm of A, its vapour pressure is reduced to 9.0 torr. If the molecular mass of A is 200 amu, then the molecular mass of B is :

(A) 100 amu (B) 90 amu (C) 75 amu (D) 120 amu

15. The vapour pressure of a pure liquid solvent (X) is decreased to 0.60 atm. from 0.80 atm on addition of a non volatile substance (Y). The mole fraction of (Y) in the solution is:-

(A) 0.20 (B) 0.25 (C) 0.5 (D) 0.75

16. Among the following, that does not form an ideal solution is :

(A) C_6H_6 and $C_6H_5CH_3$ (B) C_2H_5Cl and C_6H_5OH

(C) C_6H_5Cl and C_6H_5Br (D) C_2H_5Br and C_2H_5I

17. Colligative properties of the solution depend upon

(A) Nature of the solution (B) Nature of the solvent

(C) Number of solute particles (D) Number of moles of solvent

18. Elevation of boiling point of 1 molar aqueous glucose solution (density = 1.2 g/ml) is

(A) K_b (B) 1.20 K_b (C) 1.02 K_b (D) 0.98 K_b

19. When common salt is dissolved in water

(A) Melting point of the solution increases

(B) Boiling point of the solution increases

(C) Boiling point of the solution decreases

(D) Both Melting point and Boiling point is decreases

20. What should be the freezing point of aqueous solution containing 17 gm of C_2H_5OH in 1000 gm of water (water K_f = 1.86 deg – kg mol^{-1})

(A) – 0.69°C (B) – 0.34°C (C) 0.0°C (D) 0.34°C

21. If mole fraction of the solvent in solution decreases then :

(A) Vapour pressure of solution increases

(B) B. P. decreases

(C) Osmotic pressure increases

(D) All are correct

22. 5% (w/v) solution of sucrose is isotonic with 1% (w/v) solution of a compound 'A' then the molecular weight of compound 'A' is -

(A) 32.4 (B) 68.4 (C) 121.6 (D) 34.2

23. Osmotic pressure of a sugar solution at 24^0C is 2.5 atmosphere. The concentration of the solution in mole per litre is :

(A) 10.25 (B) 1.025 (C) 1025 (D) 0.1025

24. A solution containing 4 g of a non volatile organic solute per 100 ml was found to have an osmotic pressure equal to 500 cm of mercury at 27^0C. The molecular weight of solute is :

(A) 14.97 (B) 149.7 (C) 1697 (D) 1.497

25. If a 6.84% (wt. / vol.) solution of cane-sugar (mol. wt. 342) is isotonic with 1.52% (wt./vol.) solution of thiocarbamide, then the molecular wight of thiocarbamide is :

(A) 152 (B) 76 (C) 60 (D) 180

26. Which of the following aqueous solution will show maximum vapour pressure at 300 K?

(A) 1 M NaCl (B) 1 M $CaCl_2$ (C) 1 M $AlCl_3$ (D) 1 M $C_{12}H_{22}O_{11}$

27. The correct relationship between the boiling points of very dilute solution of $AlCl_3$ (T_1K) and $CaCl_2$ (T_2K) having the same molar concentration is

(A) $T_1 = T_2$ (B) $T_1 > T_2$ (C) $T_2 > T_1$ (D) $T_2 \leq T_1$

28. 1.0 molal aqueous solution of an electrolyte A_2B_3 is 60% ionised. The boiling point of the solution at 1 atm is ($K_{b(H_2O)} = 0.52 \text{ K kg mol}^{-1}$)

(A) 274.76 K (B) 377 K (C) 376.4 K (D) 374.76 K

29. The freezing point depression of a 0.1 M a solution of weak acid (HX) is –0.20°C.
What is the value of equilibrium constant for the reaction?

$$HX\ (aq) \rightleftharpoons H^+(aq) + X^-\ (aq)$$

[Given : K_f for water = 1.8 kg mol^{-1} K. & Molality = Molarity]

(A) 1.46×10^{-4} (B) 1.35×10^{-3} (C) 1.21×10^{-2} (D) 1.35×10^{-4}

30. The Vant Hoff factor (i) for a dilute solution of $K_3[Fe(CN)_6]$ is (Asuming 100% ionsation) :

(A) 10 (B) 4 (C) 5 (D) 0.25

31. The substance A when dissolved in solvent B shows the molecular mass corresponding to A_3. The vant Hoff's factor will be -

(A) 1 (B) 2 (C) 3 (D) 1/3

32. The value of observed and calcutated molecular wieght of silver nitrate are 92.64 and 170 respectively. The degree of dissociation of silver nitrate is :

(A) 60% (B) 83.5 % (C) 46.7% (D) 60.23%

33. The freezing point of 1 molal NaCl solution assuming NaCl to be 100% dissociated in water is : (K_f = 1.86 K Molality^{-1})

(A) –1.86 °C (B) –3.72 °C (C) +1.86 °C (D) + 3.72 °C

34. What is the freezing point of a solution containing 8.1 gm. of HBr in 100gm. water assuming the acid to be 90% ionised (K_f for water=1.86 K molality^{-1}) :-

(A) 0.85°C (B) –3.53°C (C) 0°C (D) –0.35°C

35. If a ground water contains H_2S at concentration of 2 mg/l, determine the pressure of H_2S in head space of a closed tank containing the ground water at 20ºC. Given that for H_2S, Henry's constant is equal to 6.8×10^3 bar at 20ºC.

(A) 720 Pa (B) 77×10^2 Pa (C) 553 Pa (D) 55×10^2 Pa

36. A pressure cooker reduces cooking time for food because -

(A) The higher pressure inside the cooker crushes the food material

(B) Cooking involves chemical changes helped by a rise in temperature

(C) Heat is more evenly distributed in the cooking space

(D) Boiling point of water involved in cooking is increased

EXERCISE # O-II

Single correct :

1. An ideal solution was obtained by mixing (MeOH) methanol and (EtOH) ethanol. If the partial vapour pressure of methanol and ethanol are 2.619 K Pa and 4.556 K Pa respectively, the composition of vapour (in terms of mole fraction) will be -

(A) 0.635 MeOH, 0.365 EtOH
(B) 0.365 MeOH, 0.635 EtOH
(C) 0.574 MeOH, 0.326 EtOH
(D) 0.173 MeOH, 0.827 EtOH

2. Molar volume of liquid A(d = 0.8gm/ml) increase by factor of 2000 when it vapourises at 200K. Vapour pressure of liquid A at 200K is [R = 0.08 L-atm/mol-K]

(Molar mass of A = 80g/mol)

(A) 0.4 atm
(B) 8 atm
(C) 0.8 atm
(D) 0.08 atm

3. Assuming each salt to be 90 % dissociated, which of the following will have highest boiling point?

(A) Decimolar $Al_2(SO_4)_3$
(B) Decimolar $BaCl_2$
(C) Decimolar Na_2SO_4
(D) A solution obtained by mixing equal volumes of (B) and (C)

4. The vapour pressure of a saturated solution of sparingly soluble salt (XCl_3) was 17.20 mm Hg at 27°C. If the vapour pressure of pure H_2O is 17.25 mm Hg at 300 K, what is the solubility of sparingly soluble salt XCl_3 in mole/Litre.

(A) 4.04×10^{-2}
(B) 8.08×10^{-2}
(C) 2.02×10^{-2}
(D) 4.04×10^{-3}

5. A solution has a 1 : 4 mole ratio of pentane to hexane. The vapour pressures of the pure hydrocarbons at 20°C are 440 mmHg for pentane and 120 mmHg for hexane. The mole fraction of pentane in the vapour phase would be :-

(A) 0.200
(B) 0.478
(C) 0.549
(D) 0.786

6. For which of the following vant' Hoff's factor is not correctly matched -

	Salt	**Degree of dissociation** (α)	***i***
(A)	Na_2SO_4	50 %	2
(B)	$K_3[Fe(CN)_6]$	75%	3.25
(C)	$[Ag(NH_3)_2]Cl$	80 %	1.8
(D)	$[Cr(NH_3)_5Cl]SO_4$	90 %	2.8

7. In the depression of freezing point experiment, it is found that

(I) The vapour pressure of the solution is less than that of pure solvent.

(II) The vapour pressure of the solution is more than that of pure solvent.

(III) Only solute molecules solidify at the freezing point.

(IV) Only solvent molecules solidify at the freezing point.

(A) I, II
(B) II, III
(C) I, IV
(D) I, II, III

8. **Statement-1** :Additon of ethylene glycol (non-volatile) to water lowers the freezing point of water hence used as antifreeze.

Statement-2 : Addition of any substance to water lowers its freezings point of water.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

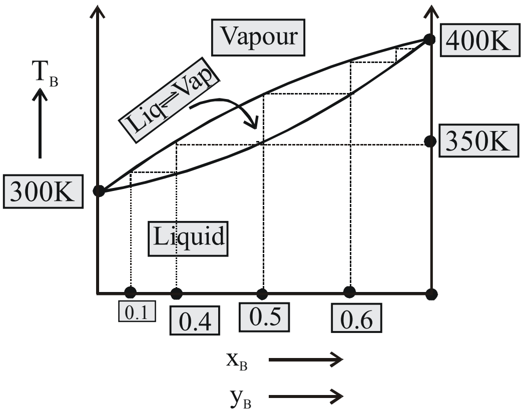
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

More than one may be correct

9. For an ideal solution having two liquid A(P_A^0 and liquid B(P_B^0) boiling point versus composition graph is given below, then select incorrect statement (s) :



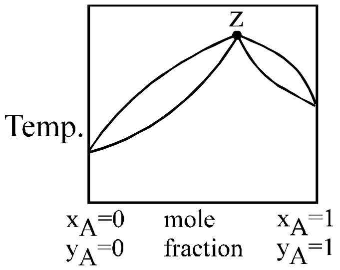
(A) B is less volatile than A

(B) If mole percent of A in liquid phase is 40% then mole percent of A in vapour phase is 50%

(C) If mole percent of B in liquid phase is 10% then mole percent of B in vapour phase is 40%

(D) If the mole percent of A in solution is 50% then its boiling point is 350K

10 A liquid mixture having composition corresponding to point z in the figure shown is subjected to distillation at constant pressure.



Which of the following statement is correct about the process

(A) The composition of distillate differs from the mixture

(B) The boiling point goes on changing

(C) The mixture has lowest vapour pressure than for any other composition.

(D) Composition of an azeotrope alters on changing the external pressure.

11. Which of the following is correct for a non-ideal solution of liquids A and B, showing negative deviation?

(A) $\Delta H_{mix} = -ve$ (B) $\Delta V_{mix} = -ve$

(C) $\Delta S_{mix} = +ve$ (D) $\Delta G_{mix} = -ve$

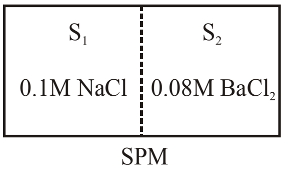
12. Two solutions S_1 and S_2 containing 0.1M NaCl(aq.) and 0.08M $BaCl_2$(aq.) are separated by semipermeable membrane. Which among the following statement(s) is/are correct -

(A) S_1 and S_2 are isotonic

(B) S_1 is hypertonic and S_2 is hypotonic

(C) S_1 is hypotonic and S_2 is hypertonic

(D) Osmosis will take place to from S_1 to S_2



13. For an ideal binary liquid solution with $P_A^\circ > P_B^\circ$, which relation between X_A (mole fraction of A in liquid phase) and Y_A(mole fraction of A in vapour phase) is correct?

(A) $Y_A < Y_B$ (B) $X_A > X_B$ (C) $\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$ (D) $\frac{Y_A}{Y_B} < \frac{X_A}{X_B}$

14. Which of the following plots represents an ideal binary mixture?

(A) Plot of P_{total} v/s $1/X_B$ is linear (X_B = mole fraction of 'B' in liquid phase).

(B) Plot of P_{total} v/s Y_A is linear (Y_B = mole fraction of 'A' in vapour phase)

(C) Plot of $\frac{1}{P_{total}}$ v/s Y_A is linear

(D) Plot of $\frac{1}{P_{total}}$ v/s Y_B is non linear

Paragraph for Q.15 to Q.17

An ideal solution is obtained by mixing a non-volatile solute B with a volatile solvent A (molar mass = 60). If the mass ratio of A : B in solution is 10 : 1 and vapour pressure of pure A is 400 mm and vapour pressure decreases by 4% on forming the above solution at 300K.

15. The mole fraction of solute in the solution is -

(A) 0.96 (B) 0.04 (C) 0.16 (D) 0.84

16. The molality the solution is -

(A) 1 (B) $\frac{36}{25}$ (C) $\frac{25}{36}$ (D) $\frac{36}{25}$

17. The molar mass of B in the solution is -

(A) 1440 (B) 14400 (C) 4 (D) 144

Table type question :

	Column-I		Column-II		Column-III
(1)	$C_6H_6 + C_6H_5-CH_3$	(a)	$\Delta H = 0$	(P)	$\Delta G = -ve$
(2)	$CHCl_3 + CH_3COCH_3$	(b)	$\Delta H = +ve$	(Q)	Form minimum boiling azerotrope
(3)	$CCl_4 + CH_3COCH_3$	(c)	$\Delta H = -ve$	(R)	Form maximum boiling azerotrope
(4)	$C_2H_5OH + H_2O$	(d)	$\Delta S = +ve$	(S)	No azeotrope

18. Select the correct match -

(A) 1 , a, R (B) 2, b, P (C) 3, b, Q (D) 4, d, R

19. Select the correct match -

(A) 1 , d, S (B) 3, b, S (C) 2, b, S (D) 4, c, P

20. Select the incorrect match -

(A) 1 , d, P (B) 2, c, R (C) 3, d, S (D) 3, b, P

Match the column :

21.

	Column–I (Colligative properties)		Column–II (Aqueous solution) (Assume m = M)
(A)	$\Delta T_f = 0.3 \times K_f$	(P)	0.1 m – $Ca(NO_3)_2$
(B)	$\Delta T_b = 0.28 \times K_b$	(Q)	0.14 m – NaBr
(C)	$\pi = 0.19 \times RT$	(R)	0.1 m – $MgCl_2(\alpha = 0.9)$
(D)	$\dfrac{P^0 - P}{P^0} = \dfrac{\left(\dfrac{\Delta T_f}{K_f}\right)}{\left(\dfrac{1000}{18}\right) + \left(\dfrac{\Delta T_f}{K_f}\right)}$	(S)	0.28 m – Urea
		(T)	0.1 m – HA (monobasic acid, $K_a = 0.81$)

EXERCISE # (J-MAIN)

1. The degree of dissociation (1) of a weak electrolyte, A_xB_y is related to van't Hoff factor (i) by the expression :- **[AIEEE-2011]**

(1) $\alpha = \frac{x+y-1}{i-1}$ (2) $\alpha = \frac{x+y+1}{i-1}$ (3) $\alpha = \frac{i-1}{(x+y-1)}$ (4) $\alpha = \frac{i-1}{x+y+1}$

2. K_f for water is 1.86 K kg mol^{-1}. If your automobile radiator holds 1.0 kg of water, how many grams of ethylene glycol ($C_2H_6O_2$) must you add to get the freezing point of the solution lowered to –2.8°C ? **[AIEEE-2012]**

(1) 27 g (2) 72 g (3) 93 g (4) 39 g

3. A solution containing 0.85 g of $ZnCl_2$ in 125.0 g of water freezes at –0.23ºC. The apparent degree of dissociation of the salt is : **[JEE (MAIN)-2012 ONLINE]**

(k_f for water = 1.86 K kg mol^{-1}, atomic mass ; Zn = 65.3 and Cl = 35.5)

(1) 1.36% (2) 2.47% (3) 73.5% (4) 7.35%

4. Liquids A and B form an ideal solution. At 30ºC, the total vapour pressure of a solution containing 1 mol of A and 2 moles of B is 250 mm Hg. The total vapour pressure becomes 300 mm Hg when 1 more mol of A is added to the first solution. The vapour pressures of pure A and B at the same temperature are **[JEE (MAIN)-2012 ONLINE]**

(1) 450, 150 mm Hg (2) 250, 300 mm Hg (3) 125, 150 mm Hg (4) 150, 450 mm Hg

5. The freezing point of a 1.00 m aqueous solution of HF is found to be –1.91°C. The freezing point constant of water, K_f, is 1.86 K kg mol^{-1}. The percentage dissociation of HF at this concentration is **[JEE (MAIN)-2012 ONLINE]**

(1) 2.7% (2) 30% (3) 10% (4) 5.2%

6. How many grams of methyl alcohol should be added to 10 litre tank of water to prevent its freezing at 268 K ? **[JEE (MAIN)-2013 ONLINE]**

(K_f for water is 1.86 K kg mol^{-1})

(1) 899.04 g (2) 786 g (3) 860 g (4) 880.07 g

7. Vapour pressure of pure benzene is 119 torr and that of toluene is 37.0 torr at the same temperature. Mole fraction of toluene in vapour phase which is in equilibrium with a solution of benzene and toluene having a mole fraction of toluene 0.50, will be : **[JEE (MAIN)-2013 ONLINE]**

(1) 0.137 (2) 0.205 (3) 0.237 (4) 0.435

8. A molecule M associates in a given solvent according to the equation $M \rightleftharpoons (M)_n$. For a certain concentration of M, the van’t Hoff factor was found to be 0.9 and the fraction of associated molecules was 0.2. The value of n is : **[JEE (MAIN)-2013 ONLINE]**

(1) 2 (2) 4 (3) 5 (4) 3

9. 12g of a nonvolatile solute dissolved in 108g of water produces the relative lowering of vapour pressure of 0.1. The molecular mass of the solute is : **[JEE (MAIN)-2013 ONLINE]**

(1) 60 (2) 80 (3) 40 (4) 20

10. The molarity of a solution obtained by mixing 750 mL of 0.5(M)HCl with 250 mL of 2(M)HCl will be :- **[JEE (MAIN)-2013]**

(1) 0.875 M (2) 1.00 M (3) 1.75 M (4) 0.975 M

11. The observed osmotic pressure for a 0.10 M solution of $Fe(NH_4)_2(SO_4)_2$ at 25°C is 10.8 atm. The expected and experimental (observed) values of Van't Hoff factor (i) will be respectively : ($R = 0.082$ L atm k^{-} mol^{-1}) **[JEE (MAIN)-2014 ONLINE]**

(1) 3 and 5.42 (2) 5 and 3.42 (3) 4 and 4.00 (4) 5 and 4.42

12. For an ideal Solution of two components A and B, which of the following is true ? **[JEE(MAIN)-2014 ONLINE]**

(1) $\Delta H_{mixing} < 0$ (zero)

(2) A – A, B – B and A – B interactions are identical

(3) A – B interaction is stronger than A – A and B – B interactions

(4) $\Delta H_{mixing} > 0$ (zero)

13. Consider separate solution of 0.500 M $C_2H_5OH(aq)$, 0.100 M $Mg_3(PO_4)_2(aq)$, 0.250 M KBr(aq) and 0.125 M $Na_3PO_4(aq)$ at 25°C. Which statement is true about these solutions, assuming all salts to be strong electrolytes ? **[JEE (MAIN)-2014]**

(1) 0.125 M Na_3PO_4 (aq) has the highest osmotic pressure.

(2) 0.500 M C_2H_5OH (aq) has the highest osmotic pressure.

(3) They all have the same osmotic pressure.

(4) 0.100 M $Mg_3(PO_4)_2$ (aq) has the highest osmotic pressure.

14. Determination of the molar mass of acetic acid in benzene using freezing point depression is affected by : **[JEE (MAIN)-2015 ONLINE]**

(1) association (2) dissociation (3) complex formation (4) partial ionization

15. A solution at 20°C is composed of 1.5 mol of benzene and 3.5 mol of toluene. If the vapour pressure of pure benzene and pure toluene at this temperature are 74.7 torr and 22.3 torr, respectively, then the total vapour pressure of the solution and the benzene mole fraction in equilibrium with it will be, respectively : **[JEE (MAIN)-2015 ONLINE]**

(1) 38.0 torr and 0.589 (2) 30.5 torr and 0.389

(3) 35.8 torr and 0.280 (4) 35.0 torr and 0.480

16. The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 torr. The molar mass (g mol^{-1}) of the substance is : **[JEE (MAIN)-2015]**

(1) 128 (2) 488 (3) 32 (4) 64

17. An aqueous solution of a salt MX_2 at certain temperature has a van't Hoff factor of 2. The degree of dissociation for this solution of the salt is : **[JEE (MAIN-2016-ONLINE]**

(1) 0.50 (2) 0.80 (3) 0.67 (4) 0.33

18. The solubility of N_2 in water at 300 K and 500 torr partial pressure is 0.01 g L^{-1}. The solubility (in g L^{-1}) at 750 torr partial pressure is : **[JEE (MAIN-2016-ONLINE]**

(1) 0.02 (2) 0.005 (3) 0.015 (4) 0.0075

19. 18 g glucose ($C_6H_{12}O_6$) is added to 178.2g at 100ºC water. The vapour pressure of water (in torr) for this aqueous solution is : **[JEE (MAIN)-2016]**

(1) 759.0 (2) 7.6 (3) 76.0 (4) 752.4

20. The freezing point of benzene decreases by 0.45°C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be :- **(K_f for benzene = 5.12 K kg mol^{-1})** **[JEE (MAIN)-2017]**

(1) 64.6% (2) 80.4% (3)74.6% (4) 94.6%

21. 5 g of Na_2SO_4 was dissolved in x g of H_2O. The change in freezing point was found to be 3.82°C. If Na_2SO_4 is 81.5% ionised, the value of x **[JEE (MAIN-2017-ONLINE]**

(K_f for water = 1.86°C kg mol^{-1}) is approximately.

(Molar mass of S = 32 g mol^{-1} and that of Na = 23 g mol^{-1})

(1) 45 g (2) 65 g (3) 15 g (4) 25 g

22. A solution is prepared by mixing 8.5 g of CH_2Cl_2 and 11.95 g of $CHCl_3$. If vapour pressure of CH_2Cl_2 and $CHCl_3$ at 298 K are 415 and 200 mmHg respectively, the mole fraction of $CHCl_3$ in vapour form is: (Molar mass of Cl = 35.5 g mol^{-1}) **[JEE (MAIN-2017-ONLINE]**

(1) 0.486 (2) 0.325 (3) 0.162 (4) 0.675

23. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point ?

(1) $[Co(H_2O)_5Cl]Cl_2.H_2O$ **[JEE (MAIN)-2018]**

(2) $[Co(H_2O)_4Cl_2]Cl.2H_2O$

(3) $[Co(H_2O)_3Cl_3].3H_2O$

(4) $[Co(H_2O)_6]Cl_3$

24. Two 5 molal solutions are prepared by dissolving a non-electrolyte non-volatile solute separately in the solvents X and Y. The molecular weights of the solvents are M_X and M_Y, respectively where $M_X = \frac{3}{4} M_Y$. The relative lowering of vapour pressure of the solution in X is "m" times that of the solution in Y. Given that the number of moles of solute is very small in comparison to that of solvent, the value of "m" is - **[JEE (MAIN-2018-ONLINE]**

(1) $\frac{3}{4}$ (2) $\frac{4}{3}$ (3) $\frac{1}{2}$ (4) $\frac{1}{4}$

25. The mass of a non-volatile, non-electrolyte solute (molar mass = 50 g mol^{-1}) needed to be dissolved in 114 g octane to reduce its vapour pressure by 75%, is :- **[JEE (MAIN-2018-ONLINE]**

(1) 50 g (2) 37.5 g (3) 75 g (4) 150 g

EXERCISE # (J-ADVANCED)

1. To 500 cm^3 of water, 3×10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point ? K_f and density of water are 1.86 K kg^{-1} mol^{-1} and 0.997 g cm^{-3} respectively. **[JEE 2000]**

2. The vapour pressure of two miscible liquids (A) and (B) are 300 and 500 mm of Hg respectively. In a flask 10 mole of (A) is mixed with 12 mole of (B). However, as soon as (B) is added, (A) starts polymerising into a completely insoluble solid. The polymerisation follows first-order kinetics. After 100 minute, 0.525 mole of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation and ideal behaviour for the final solution. **[JEE 2001]**

3. Match the boiling point with K_b for x, y and z, if molecular weight of x, y and z are same. **[JEE 2003]**

	b.pt.	**K_b**
x	100	0.68
y	27	0.53
z	253	0.98

4. During depression of freezing point in a solution, the following are in equilibrium **[JEE 2003]**

(A) liquid solvent-solid solvent (B) liquid solvent-solid solute

(C) liquid solute-solid solute (D) liquid solute-solid solvent

5. 1.22 g of benzoic acid is dissolved in (i) 100 g acetone (K_b for acetone = 1.7) and (ii)100 g benzene (K_b for benzene = 2.6). The elevation in boiling points T_b is 0.17°C and 0.13°C respectively.

(a) What are the molecular weights of benzoic acid in both the solutions?

(b) What do you deduce out of it in terms of structure of benzoic acid? **[JEE 2004]**

6. A 0.004 M solution of Na_2SO_4 is isotonic with a 0.010 M solution of glucose at same temperature. The apparent degree of dissociation of Na_2SO_4 is

(A) 25% (B) 50% (C) 75% (D) 85% **[JEE 2004]**

7. The elevation in boiling point, when 13.44 g of freshly prepared $CuCl_2$ are added to one kilogram of water, is [Some useful data, K_b (H_2O) = 0.52 kg K mol^{-1}, mol. wt. of $CuCl_2$ = 134.4 gm]

(A) 0.05 (B) 0.1 (C) 0.16 (D) 0.21 **[JEE 2005]**

8. 72.5 g of phenol is dissolved in 1 kg of a solvent (k_f = 14) which leads to dimerization of phenol and freezing point is lowered by 7 kelvin. What percent of total phenol is present in dimeric form? **[JEE 2006]**

9. When 20 g of naphtholic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene (K_f = 1.72 K kg mol^{-1}), a freezing point depression of 2 K is observed. The van't Hoff factor (*i*) is **[JEE 2007]**

(A) 0.5 (B) 1 (C) 2 (D) 3

Paragraph for Question No. Q.10 to Q.12

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution **M** is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9.

Given : Freezing point depression constant of water $\left(K_f^{water}\right) = 1.86\ K\ kg\ mol^{-1}$

Freezing point depression constant of ethanol $\left(K_f^{ethanol}\right) = 2.0\ K\ kg\ mol^{-1}$

Boiling point elevation constant of water $\left(K_b^{water}\right) = 0.52\ K\ kg\ mol^{-1}$

Boiling point elevation constant of ethanol $\left(K_b^{ethanol}\right) = 1.2\ K\ kg\ mol^{-1}$

Standard freezing point of water = 273 K

Standard freezing point of ethanol = 155.7 K

Standard boiling point of water = 373 K

Standard boiling point of ethanol = 351.5 K

Vapour pressure of pure water = 32.8 mm Hg

Vapour pressure of pure ethanol = 40 mm Hg

Molecular weight of water = 18 g mol^{-1}

Molecular weight of ethanol = 46 g mol^{-1}

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

10. The freezing point of the solution **M** is **[JEE 2008]**

(A) 268.7 K (B) 268.5 K (C) 234.2 K (D) 150.9 K

11. The vapour pressure of the solution **M** is **[JEE 2008]**

(A) 39.3 mm Hg (B) 36.0 mm Hg (C) 29.5 mm Hg (D) 28.8 mm Hg

12. Water is added to the solution **M** such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is **[JEE 2008]**

(A) 380.4 K (B) 376.2 K (C) 375.5 K (D) 354.7 K

13. The Henry's law constant for the solubility of N_2 gas in water at 298 K is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water at 298 K and 5 atm pressure is- **[JEE 2009]**

(A) 4.0×10^{-4} (B) 4.0×10^{-5} (C) 5.0×10^{-4} (D) 4.0×10^{-5}

14. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is-(take K_b=0.76 K kg mol^{-1}) **[JEE 2011]**

(A) 724 (B) 740 (C) 736 (D) 718

15. The freezing point (in °C) of a solution containing 0.1 g of $K_3[Fe(CN)_6]$ (Mol. Wt. 329) in 100 g of water ($K_f = 1.86$ K kg mol^{-1}) is - **[JEE 2011]**

(A) -2.3×10^{-2} (B) -5.7×10^{-2} (C) -5.7×10^{-3} (D) -1.2×10^{-2}

16. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is

(take K_b=0.76 K kg mol^{-1}) **[JEE 2012]**

(A) 724 (B) 740 (C) 736 (D) 718

17. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is(are) **[J-Adv. 2013]**

(A) ΔG is positive (B) ΔS_{system} is positive (C) $\Delta S_{surroundings} = 0$. (D) $\Delta H = 0$

18. If the freezing point of a 0.01 molal aqueous solution of a cobalt (III) chloride-ammonia complex (which behaves as a strong eletrolyte) is -0.0558°C, the number of chloride (s) in the coordination sphere of the complex is- [K_f of water = 1.86 K kg mol^{-1}] **[JEE-Adv. 2015]**

19. Mixture(s) showing positive deviation from Raoult's law at 35°C is (are) **[JEE-Adv. 2016]**

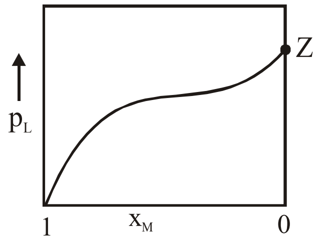
(A) carbon tetrachloride + methanol

(B) carbon disulphide + acetone

(C) benzene + toluene

(D) phenol + aniline

20. For a solution formed by mixing liquids L and M, the vapour pressure of L plotted against the mole fraction of M in solution is shown in the following figure, Here x_L and x_M represent mole fractions of L and M, respectively, in the solution. the correct statement(s) applicable to this system is(are)



(A) Attractive intramolecular interactions between L–L in pure liquid L and M–M in pure liquid M are stronger than those between L–M when mixed in solution **[JEE-Adv. 2017]**

(B) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when $x_L \to 0$

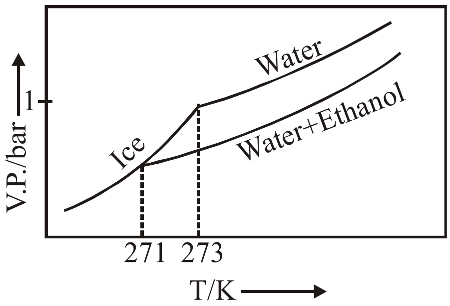
(C) The point Z represents vapour pressure of pure liquid L and Raoult's law is obeyed when $x_L \to 1$

(D) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed from $x_L = 0$ to $x_L = 1$

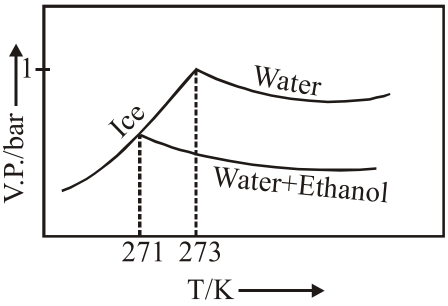
21. Pure water freezes at 273 K and 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as 2 K kg mol^{-1}. The figures shown below represents plots of vapour pressure (V.P.) versus temperature (T). [Molecular weight of ethanol is 46 g mol^{-1}]

Among the following, the option representing change in the freezing point is - **[JEE-Adv. 2017]**

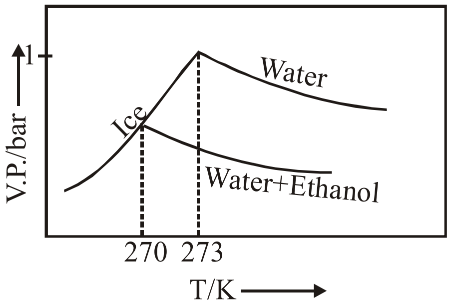
(A)



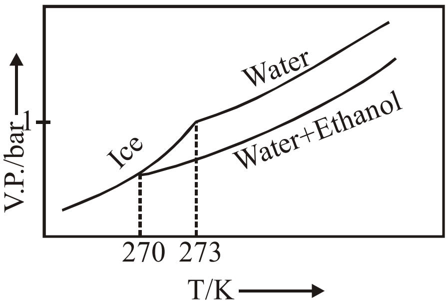
(B)



(C)



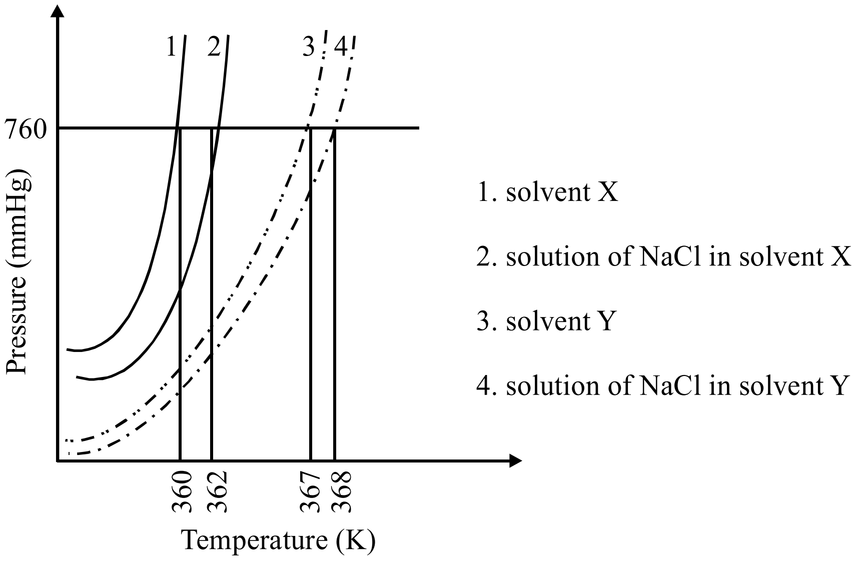
(D)



22. Liquids A and B form ideal solution over the entire range of composition. At temperature T, equimolar binary solution of liquids A and B has vapour pressure 45 Torr. At the same temperature, a new solution of A and B having mole fractions x_A and x_B, respectively, has vapour pressure of 22.5 Torr. The value of x_A/x_B in the new solution is____. **[JEE-Adv. 2018]**

(Given that the vapour pressure of pure liquid A is 20 Torr at temperature T)

23. The plot given below shows P–T curves (where P is the pressure and T is the temperature) for two solvents X and Y and isomolal solutions of NaCl in these solvents. NaCl completely dissociates in both the solvents.



On addition of equal number of moles a non-volatile solute S in equal amount (in kg) of these solvents, the elevation of boiling point of solvent X is three times that of solvent Y. Solute S is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent Y, the degree of dimerization in solvent X is ___. **[JEE-Adv. 2018]**

ANSWER-KEY

EXERCISE # S-I

1.	Ans. 0.25	2.	Ans. 64.0 mm Hg
3.	Ans. P_A^0 = 100 cmHg, P_B^0 = 60 cmHg.	4.	Ans. 0.25
5.	Ans. 0.5 bar	6.	Ans. P_X^0 = 55 cmHg, P_Y^0 = 80 cmHg
7.	Ans. P_R^0 = 0.8 bar, P_S^0 = 0.4 bar	8.	Ans. 0.25
9.	Ans. 0.04	10.	Ans. 0.32 m
11.	Ans. 65.25	12.	Ans. 17.38 mm Hg
13.	Ans. 120 g/mol	14.	Ans. K_b= 0.516kg mol K^{-1}, T_b = 373.20 K
15.	Ans. 5.1 K-kg/mol	16.	Ans. 2048 g/mol
17.	Ans. (6.972)	18.	Ans. 40 g/mol
19.	Ans. 49.26 atm	20.	Ans. 3.69 atm
21.	Ans. 1.96	22.	Ans. 3 ions
23.	Ans. 78 %	24.	Ans. 7.482 ×105 Nm^{-2}
25.	Ans. 0.95; 1.95	26.	Ans. 0.04
27.	Ans. (3)		

EXERCISE # S-II

1.	Ans. 92 mol% toluene;96.8 mol % toluene	2.	Ans. 0.741 m, 0.0136
3.	Ans. 38.71 g	4.	Ans. 4.8 × 10^4 g/mol
5.	Ans. (777)	6.	Ans. (68.4)
7.	Ans. $C_{40}H_{80}O_{40}$	8.	Ans. $[Co(NH_3)_5Cl]Cl_2$
9.	Ans. a = 0.50	10.	Ans. 0.73
11.	Ans. (9)	12.	Ans (60%)
13.	Ans. (3.2)	14.	Ans. (100°C)
15.	Ans. C_6H_6		

EXERCISE # O-I

1.	Ans. (B)	2.	Ans. (C)	3.	Ans. (C)	4.	Ans. (D)
5.	Ans. (A)	6.	Ans. (C)	7.	Ans. (C)	8.	Ans. (C)
9.	Ans. (D)	10.	Ans. (C)	11.	Ans. (C)	12.	Ans. (A)
13.	Ans. (A)	14.	Ans. (B)	15.	Ans. (B)	16.	Ans. (B)
17.	Ans. (C)	18.	Ans. (D)	19.	Ans. (B)	20.	Ans. (A)
21.	Ans. (C)	22.	Ans. (B)	23.	Ans. (D)	24.	Ans. (B)
25.	Ans. (B)	26.	Ans. (D)	27.	Ans. (B)	28.	Ans. (D)
29.	Ans. (B)	30.	Ans. (B)	31.	Ans. (D)	32.	Ans. (B)
33.	Ans. (B)	34.	Ans. (B)	35.	Ans. (A)	36.	Ans. (D)

EXERCISE # O-II

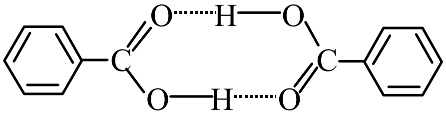
1. Ans. (B)
2. Ans. (D)
3. Ans. (A)
4. Ans. (A)
5. Ans. (B)
6. Ans. (D)
7. Ans. (C)
8. Ans. (C)
9. Ans. (C)
10. Ans. (C, D)
11. Ans. (A,B,C,D)
12. Ans. (C,D)
13 Ans. (C)
14. Ans. (C)
15. Ans. (B)
16. Ans. (C)
17. Ans. (D)
18. Ans. (C)
19. Ans. (A)
20. Ans. (C)
21. Ans. (A) → P ; (B) → Q, R, S ; (C) → T ; (D) → P, Q, R, S, T

EXERCISE # (J-MAIN)

1. Ans. (3)
2. Ans. (3)
3. Ans. (3)
4. Ans. (1)
5. Ans. (1)
6. Ans. (3)
7. Ans. (3)
8. Ans. (1)
9. Ans. (4)
10. Ans. (1)
11. Ans. (4)
12. Ans. (2)
13. Ans. (3)
14. Ans. (1)
15. Ans. (1)
16. Ans. (4)
17. Ans. (1)
18. Ans. (3)
19. Ans. (4)
20. Ans. (4)
21. Ans. (1)
22. Ans. (2)
23. Ans. (3)
24. Ans. (1)
25. Ans. (4)

EXERCISE # (J-ADVANCED)

1. Ans. 0.23 K
2. Ans. $(1.0 \times 10^{-4})\text{min}^{-1}$
3. Ans. $K_b(x) = 0.68$, $K_b(y) = 0.53$, $K_b(z) = 0.98$
4. Ans. (A)
5. Ans. (a)122, (b) It means that benzoic acid remains as it is in acetone while it dimerises in benzene as



6. Ans. (C)
7. Ans. (C)
8. Ans. 35% (degree of asso = 70%)
9. Ans. (A)
10. Ans. (D)
11. Ans. (B)
12. Ans. (B)
13. Ans. (A)
14 Ans. (A)
15. Ans. (A)
16. Ans. (A)
17. Ans. (B,C,D)
18. Ans. (1)
19. Ans. (A,B)
20. Ans. (A,C)
21. Ans. (D)
22. Ans. (19)
23. Ans. (0.05)