SOLUTION & COLLIGATIVE PROPERTIES

CONTENTS

JEE (Advanced) Syllabus

Concentration in terms of mole fraction, molarity, molality and normality.
Raoult's law; Molecular weight determination from lowering of vapour pressure, elevation of boiling point and depression of freezing point.

JEE (MAIN) Syllabus

Different methods for expressing concentration of solution- molality, molarity, mole fraction, percentage (by volume and mass both), vapour pressure of solutions and Raoult's Law-Ideal and non-ideal solutions, vapour pressure-composition, plots for ideal and non-ideal solutions; Colligative properties of dilute solutions-relative lowering of vapour pressure, depression of freezing point, elevation of boiling point and osmotic pressure; Determination of molecular mass using colligative properties; Abnormal value of molar mass, van.t Hoff factor and its significance.

SOLUTION & COLIGATIVE PROPERTIES

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. Concentration Terms :

3.1 % Concentration

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

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

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

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

% wt/vol. (w/v)

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

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

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

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

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

3.2 Strength of solution in g/L

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

Ex. 10% (w/v) sucrose solution, then specify its concentration in g/L

100 mL .... 10 g

$\therefore$ 1000 mL .... $\frac{10}{100}\times 1000 = 100$ g/L

SOLVED EXAMPLE

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

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

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

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

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

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

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

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

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

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

If V_1 mL of C_1 molarity solution is mixed with V_2 mL of C_2 molarity solution (same substance or solute)

$\therefore$ $C_f\,(V_1+V_2) = C_1V_1 + C_2V_2$

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

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

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

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

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

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

Molality not depends on temperature.

SOLVED EXAMPLE

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

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

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

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

10 m. moles H_2SO_4

20 m. moles H^+ ; $[H^+] = \frac{20}{100} = 0.2$ M

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

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

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

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

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

mass of 1 lit solution = (1000 d) g

moles of solute = (molarity)

mass of solute = (molarity) x m

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

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

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

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

For binary mixture.

- $X_{\text{solute}} = \frac{\text{moles of solute}}{\text{total moles in solutions}} = \frac{n}{n+N}$
- $X_{\text{Solvent}} = \frac{\text{moles of solvent}}{\text{Total moles in solutions}} = \frac{N}{n+N}$
- $X_{\text{solute}} + X_{\text{Solvent}} = 1$

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

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

Table : 1

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

Note : All volume related concentration terms are temperature dependent.

SOLVED EXAMPLE

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

Solution : 10 moles urea in 1000 g of water

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

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

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

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

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

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

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

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

4. 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.

Solute + Solvent $\underset{\text{Crystallization}}{\overset{\text{Dissolution}}{\rightleftharpoons}}$ Solution. ; ΔH 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.

4.1 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.

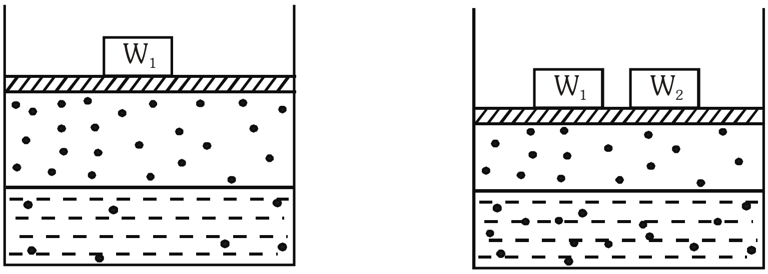
4.2 Effect of pressure :

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.

5. 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.

5.1 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

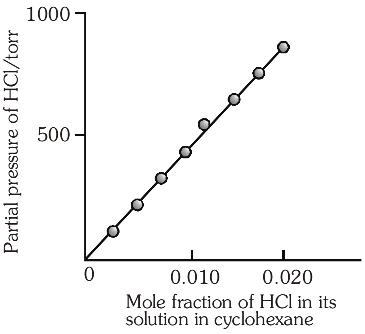
$$\mathbf{P = K_H X}$$

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

5.2 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.

5.3 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.

5.4 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

SOLVED EXAMPLE

Ex.5. ***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) =* $\frac{p(\text{nitrogen})}{K_H} = \frac{0.98\text{ bar}}{76{,}480\,\text{bar}} = 1.29 \times 10^{-5}$

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

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

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

Thus n = $1.29 \times 10^{-5} \times$ 55.5 mol = 7.16×10^{-4} mol = 0.716 m mol

Ex.6 ***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, $p_{O_2} = \frac{20}{100} \times 7600\,\text{mm Hg}$ *= 1520 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 × 10^7 mm of Hg = 4.61 × 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 × 10^{-5}*

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

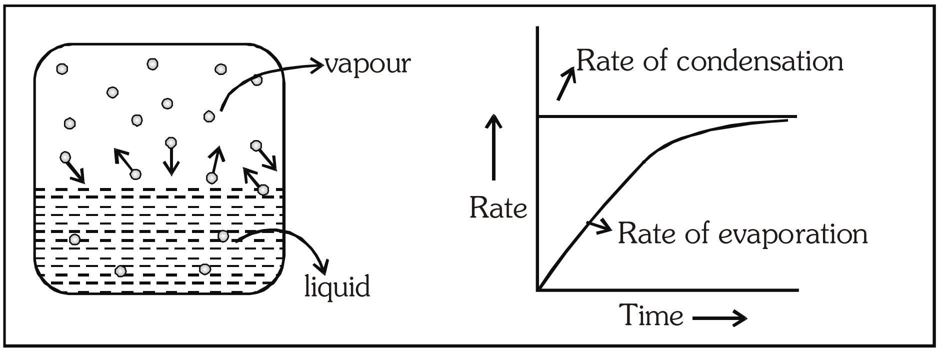
6. *Vapour pressure :*

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.



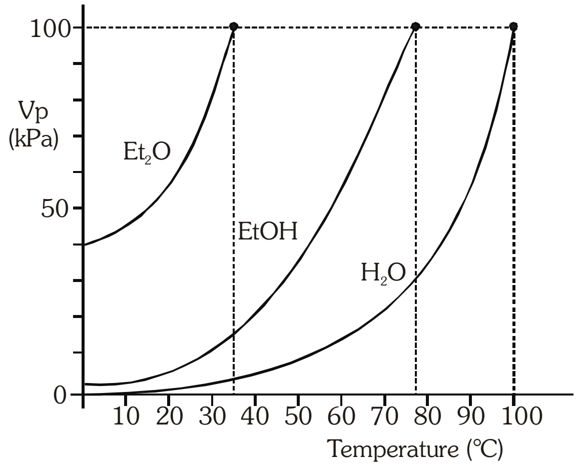
This pressure at equilibrium is called the **vapour pressure** (also known as **saturation vapour pressure**) **of the liquid at that temperature.**

6.1 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 : V.pr α $\dfrac{1}{\text{Inter molecular attraction force(I.M.A.F.)}}$

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

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

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

7. VAPOUR PRESSURE OF LIQUID SOLUTION

7.1 Completely Immiscible Liquids and Steam Distillation

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

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

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

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

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

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

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

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

But boiling point = H_2O (pure) C_6H_6 (pure)
100°C   80.2°C

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

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

7.2 Completely miscible liquids : 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.

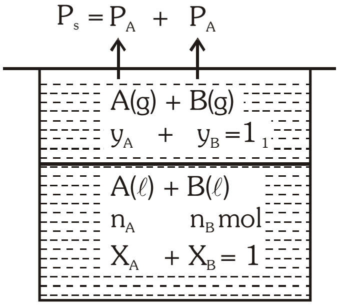
7.3 Vapour pressure of liquid – liquid solution :

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

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

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



If total pressure be P_S, then

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

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

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

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

7.3.1 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.

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

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

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

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

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

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

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

7.3.2 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 $\frac{Y_A}{Y_B}>\frac{X_A}{X_B}$

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.

7.3.3 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.

7.4 Vapour pressure of solution of solids in liquid :

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

According to Raoult's law –

$\because\ P_s = X_AP_A^0 + X_BP_B^0$

for A, $P_A^0 = 0$

$\therefore\ P_s = X_BP_B^0$ ....(5)

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

here X_B is mole fraction of solvent

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

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

$\Rightarrow\ P_S = X_BP_B^0 \Rightarrow P_S = (1 - X_A)\,P_B^0$

$\Rightarrow\ P_S = P_B^0 - X_A\,P_B^0$

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

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

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

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

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

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

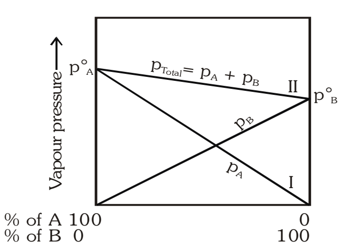
$$\boxed{\frac{\mathbf{P^0-P_S}}{\mathbf{P_S}}=\frac{\mathbf{n_A}}{\mathbf{n_B}}=\frac{\mathbf{w_A.m_B}}{\mathbf{m_A.w_B}}} \quad ....(9)$$

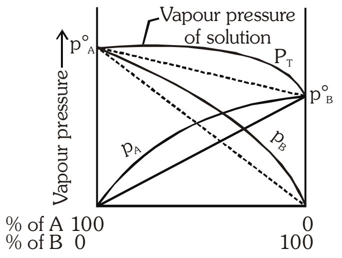
7.5 Ideal and Non ideal solutions :

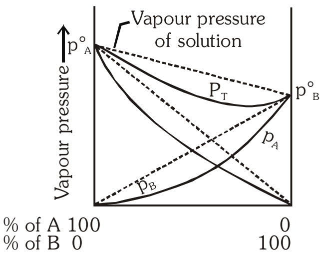
The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions.

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 + $CHCl_3$







SOLVED EXAMPLE

Ex.7. 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

$P_S = X_AP_A{}^0 + X_BP_B{}^0 = \frac{1}{5}\times 92 + \frac{4}{5}\times 31 =$ 43.2 mm of Hg.

Ex.8. 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 = 900 x + 360 (1 –x)

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

Ex.9. 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. $\frac{P^0 - P_S}{P_S} = \frac{w\times M}{m\times W} \Rightarrow \frac{1020-990}{990} = \frac{5\times 78}{m\times 58.5} \Rightarrow$ m = 220

Ex.10. 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]

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

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

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

$2800 = p_A^0 + p_B^0$ ....(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.11. 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.12. 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.13. 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 $B = \frac{4}{5} = 0.8$

Note : For multi-step condensation at constant temperature,

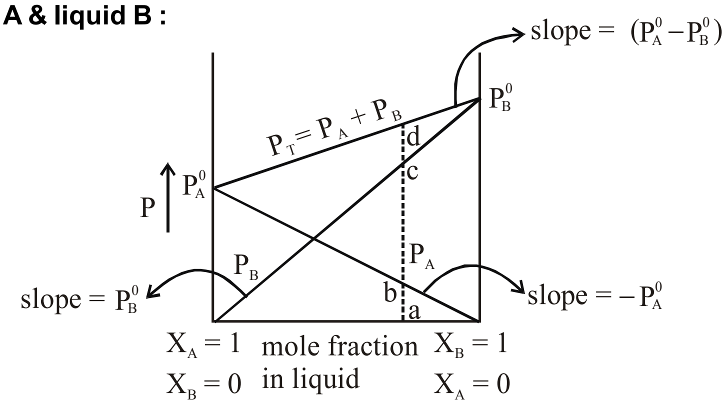
$$\boxed{\frac{n_B^f}{n_A^f} = \frac{n_B^i}{n_B^i} \cdot \left(\frac{P_B^0}{P_A^0}\right)^n}$$

n : number of steps

7.6 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

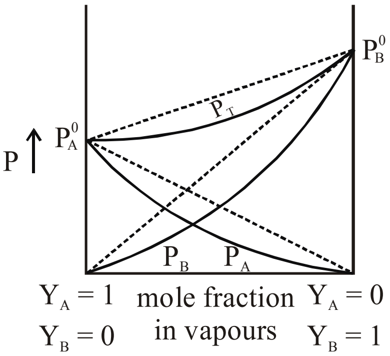
II. Vapour pressure V/s vapour composition

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

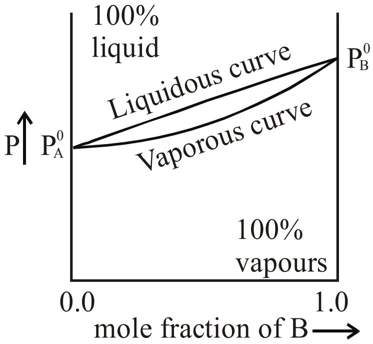
$$\frac{1}{P_T}=\frac{1}{P_A^0}+Y_B\left(\frac{1}{P_B^0}-\frac{1}{P_A^0}\right)$$

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

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.

7.7 Boiling point :

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

SOLVED EXAMPLE

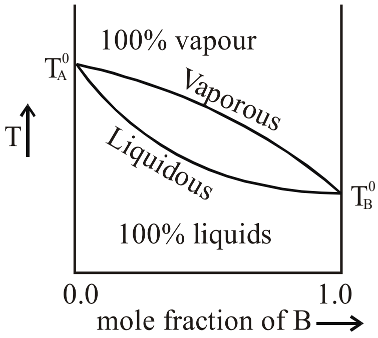
Ex.14 Liquid 'A' and 'B' form an ideal solution. At 27°C, the vapour pressure of pure liquids 'A' and 'B' are 0.6 atm and

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

7.8 Boiling point curves for ideal binary solution :



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

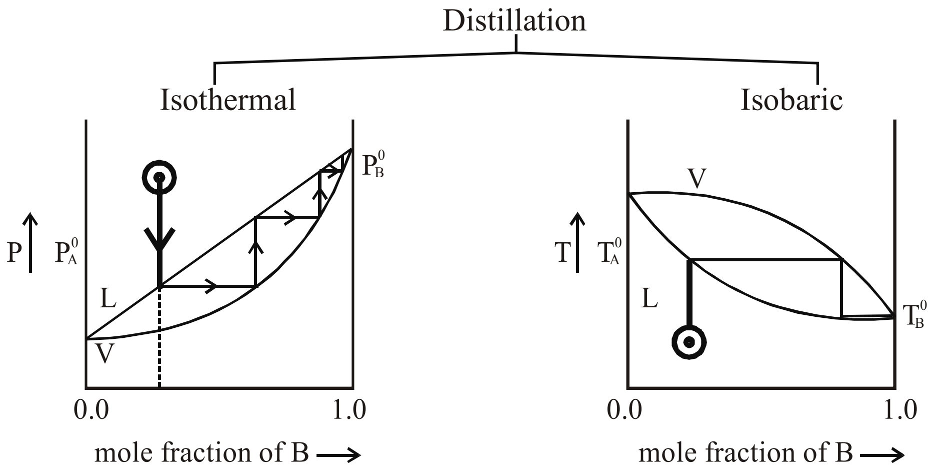
(ii) Below liquidus curve, the system in 100% liquid and above vapourus curve, the systm is 100% vapour. Both the physical states exists only in between the curves.

(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.

7.9 Distillation

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

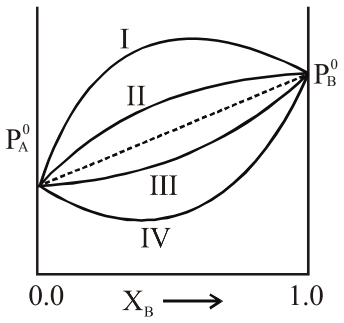


(i) The seperation of liquid by distillation occurs because at any T or P, the composition of distillate or condensate is different than the composition of original liquid.

(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.

7.10 Graphs for Non-ideal solutions and azeotropic mixture



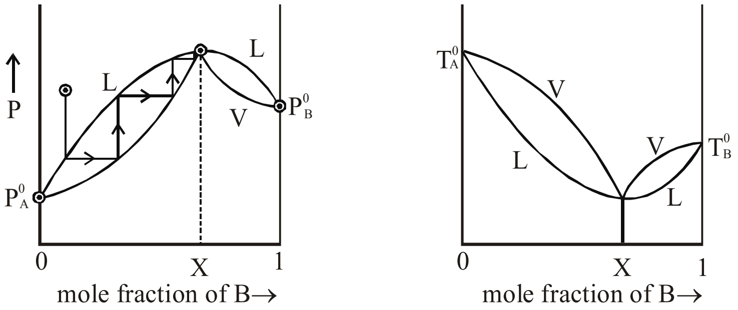
(I) Large positive deviation : $(\text{V.P.})_{\text{solution}} > P_B^0$ at some composition

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

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

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

7.10.1 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.

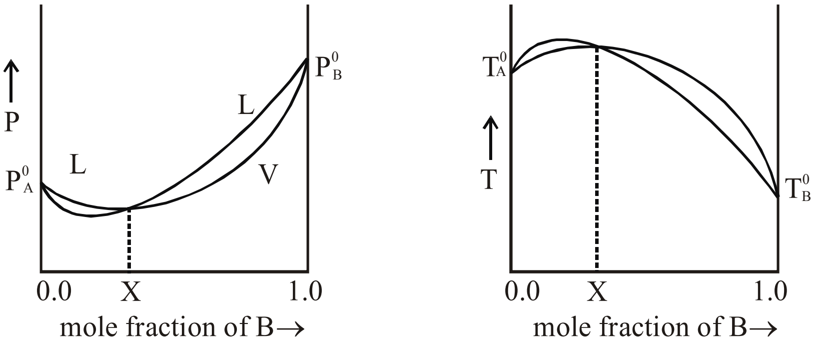
Such solution which can not be saperated by distillation are called **azeotropic mixture or constant boiling solution.**

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

7.10.2 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.

8. Colligative properties & constitutional properties :

- **Constitutional Properties :**

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

- **Colligative properties :**

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

There are 4 colligative properties of solution.

1. Relative lowering in vapour pressere $\left(\frac{\Delta P}{P}\right)$ 2. Elevation in boiling point (ΔT_b)

3. Depression in freezing pt. (ΔT_f) 4. Osmotic pressure (π)

8.1 Abnormal Colligative Properties :

Vant–Hoff correction :

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

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

- If solute gets associated or dissociated in solution then experimental / observed / actual value of colligative property will be different from theoretically predicted value so it is also known as **abnormal colligative property.**
- This abnormality can be calculated in terms of Vant-Hoff factor.

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

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

$i > 1$ dissociation

$i < 1$ association

Case - I : Electrolyte dissociates

Relation between i & α (degree of dissociation) :

Let the electrolyte be A_xB_y

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

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

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

$n = x + y$

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

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

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

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

Case - II : Electrolyte associates

Relation between degree of association β & i.

$$\begin{array}{lll} & nA & \longrightarrow A_n. \\ t = 0 & C & 0 \\ t_{eq} & C(1-\beta) & \dfrac{C\beta}{n} \end{array}$$

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

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

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

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

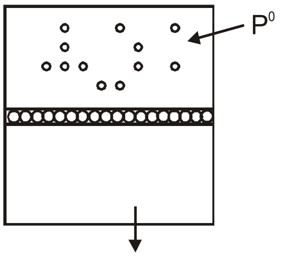
e.g. CH_3COOH 100% dimerise in benzene, i = $\frac{1}{2}$; C_6H_5COOH 100% dimerise in benzene, i = $\frac{1}{2}$

8.2 Relative lowering in vapour pressure (RLVP) :

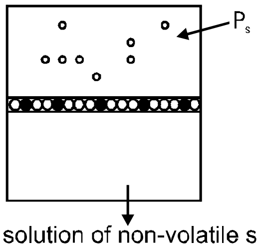
Vapour Pressure of a solution of non-volatile solute in a volatile solvent

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

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



Pure solvent



solution of non-volatile solute in volatile solvent

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

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

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

OR Relative Lowering in Vapour Pressure = mole fraction of the non volatile solute in solution.

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

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

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

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

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

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

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

$$\frac{P^0\text{-}P_s}{P_s} = \textbf{(molality)} \times \frac{M}{1000}$$

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

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

SOLVED EXAMPLE

Example-15 : Calculate weight of urea which must be dissolved in 400 g of water so final solutions has vapour pressure 2% less than vapour pressure of pure water :

Solution : Let vapour pressure be P^o of water

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

$P_s = 0.98\ V$

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

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

Example-16 : 10 g of a solute is dissolved in 80 g of acetone. Vapour pressure of this sol = 271 mm of Hg. If vapour pressure of pure acetone is 283 mm of Hg, calculate molar mass of solute.

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

m = 163 g/mol.

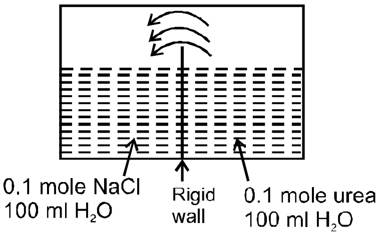
Example-17 : Vapour pressure of solute containing 6 g of non volatile solute in 180 g of water is 20 Torr. If 1 mole of water is further added into it, vapour pressure increases by 0.02 torr.Calculate vapour pressure of pure water and molecular weight of non-volatile solute.

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

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

m = 54 g/mol.

Example-18 :



What is the final volume of both container.

Solution : $i_1C_1 = i_2C_2$

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

$200 - 2x = 100 + x.$

$x = 33.3$ ml.

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

Example-19 : If 0.1 M solutions of $K_4[Fe(CN)_6]$ is prepared at 300 K then its density = 1.2 g/mL. If solute is 50% dissociated calculate ΔP of solution if P of pure water = 25 mm of Hg. (K = 39, Fe = 56)

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

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

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

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

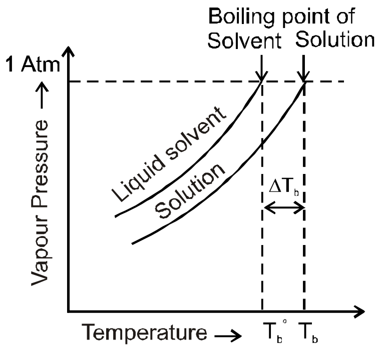
$P_s = 24.82$ mm of Hg

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

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

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

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



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

Elevation of Boiling point of any solution :

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

$\Delta T_b = T_b - T_b^o$
$\Delta T_b \propto m$
m = Molality
$\Delta T_b = K_b m$

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

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

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

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

$$K_b = \frac{RT_b^2 M}{1000 \times \Delta H_{vap}} = \frac{RT_b^2}{1000 \times L_{vap}}$$

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

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

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

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

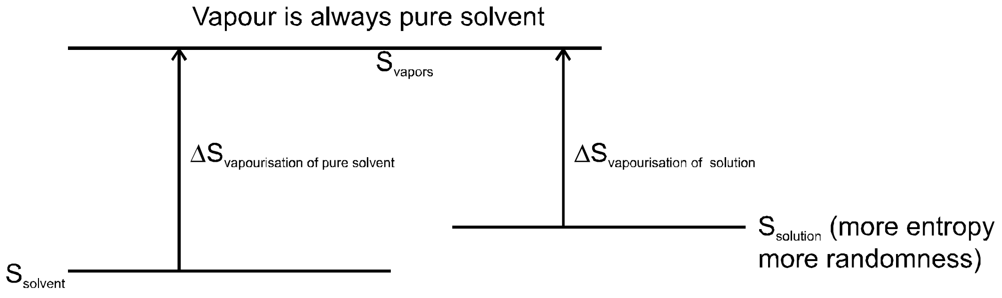
$$\Rightarrow \quad K_b = \frac{2 \times 373 \times 373}{1000 \times 540} = \text{K kg mol}^{-1} = 0.52 \text{ K k/g}$$

Extra Information (Not for Boards)

As only solvent particles are going into vapours,

we have: $\Delta H_{\text{vapourisation of solvent}} = \Delta H_{\text{vapourisation of solution}}$

S means "entropy".



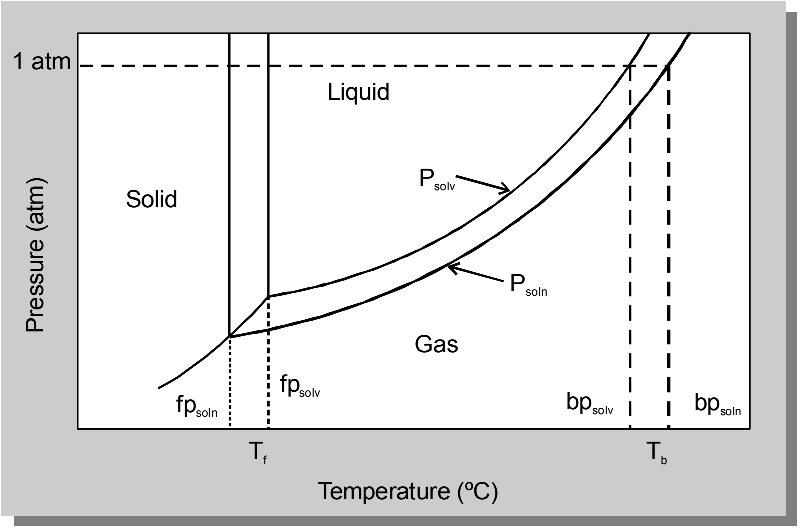
$$\Delta S_{\text{vapourisation}} = \frac{\Delta H_{\text{vapourisation}}}{T_{\text{b,solvent}}}$$

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

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

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

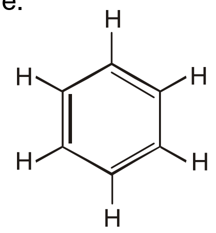
Due to presence of solute, it is difficult to vapourise the solution, i.e it is difficult to boil the solution. So, there is elevation in boiling point with respect to pure solvent.



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

SOLVED EXAMPLE

Example-20 : A solution of 122 g of benzoic acid in 1000 g of benzene shows a boiling point elevation of 1.4º. Assuming that solute is dimerized to the extent of 80 percent, calculate normal boiling point of benzene. Given molar enthalpy of vapourization of benzene = 7.8 Kcal/mole.



Solution :

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

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

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

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

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

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

Example-21 : 1 Lit. of aq. solution of urea having density = 1.060 g/mL is found to have $\Delta T_b = 0.5^\circ C$. If temperature of this solution increase to 101.5ºC, then calculate amount of water which must have gone in vapour state upto this pt. given $K_b = 0.5$ K kg mol^{-1} for water

Solution : mass of solution = $1.060 \times 10^3 = 1060$ g

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

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

mass of water = 1060 – 60 = 1000 g

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

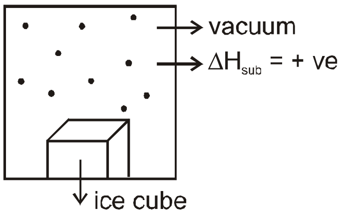
$$(\text{Molality})_f = 3 \quad \Rightarrow \quad 3 = 1 \times \frac{1000}{W_{water}}$$

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

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

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

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



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

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

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

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

= vapour pressure of solid

Reason for Depression In Freezing Point :

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

Depression In Freezing Point :

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

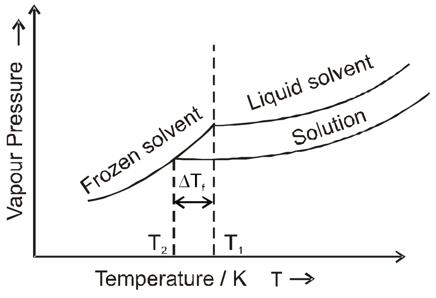


Diagram showing ΔT_f depression of the freezing point of a solvent in a solution.

$\Delta T_f = T_f^o - T_f$
$\Delta T_f \propto m$
m = Molality

$\Delta T_f = K_f m$

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

where, ΔH_{fusion} is molar enthalpy of fusion (cal/mol ; J/mol)
L_{fusion} is Latent Heat of fusion in cal/g or J/g
M is molar mass of the solvent in gram
T_f = freezing point of solvent

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

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

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

Note: (i) Depression in freezing point is proportional to the lowering of vapoure pressure i.e. $\Delta T_f \propto \Delta P$
(ii) If solute gets associated/dissociated then $\Delta T_f = i \times K_f \times$ molality

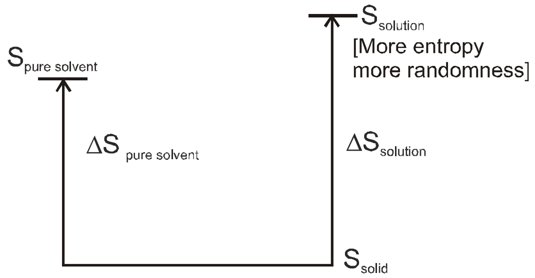
(iii) **Units of** K_f **:** $\dfrac{\Delta T_f}{\text{molality}} = \dfrac{K}{\text{mol/kg}}$. Thus units of K_f = K kg mol^{-1}

(iv) At freezing point or below it, only solvent molecules will freeze not solute molecules (solid will be of pure solvent)
(v) K_f = depression in freezing point of 1 molal solution.

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

ΔH_{Fusion} for solvent and solution is same.

But for entropy, we can see following diagram.



Only pure solvent.

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

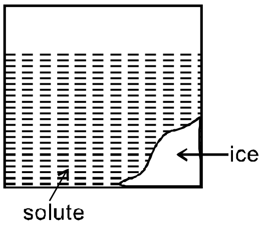
SOLVED EXAMPLE

Example-22 : Van't Hoff factors of aqueous solutions of X, Y, Z are 1.8, 0.8 and 2.5. Hence, their (assume equal concentrations in all three cases)

(A) b.p. : $X < Y < Z$ (B) f. p. $Z < X < Y$
(C) osmotic pressure : $X = Y = Z$ (D) v. p. : $Y < X < Z$

Solution : As van't Hoff factor increases RLVP increases i.e., V.P. decreases $y > x > z$
Elevation in b.p. increases i.e., b.p. increases $y < x < z$
Depresion in f.p increases i.e., f.p decreases $y > x > z$
Osmotic pressure increases so $y < x < z$. **Ans. (B)**

Example-23 : 1000 g H_2O have 0.1 mole urea and its freezing point is – 0.2ºC and now it is freezed upto – 2ºC then how much amount of ice will form.



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

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

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

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

Example-24 : If boiling point of an aqueous solution is 100.1ºC. What is its freezing point? Given latent heat of fusion and vaporization of water are 80 cal g^{-1} and 540 cal g^{-1} respectively.

Solution : For a given aqueous solution

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

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

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

$T_b = 100 + 273 = 373$ K.
$T_f = 0 + 273 = 273$ K.
$l_f = 80$ cal g^{-1}.
$l_v = 540$ cal g^{-1}.

$$\therefore \quad \frac{0.1}{\Delta T_f} = \frac{373 \times 373 \times 80}{273 \times 273 \times 540}. \qquad \therefore \quad \Delta T_f = 0.362.$$

$$\therefore \quad T_f = 0.0 - 0.362. = \mathbf{-\,0.362^\circ C.}$$

Example-25 : A 0.001 molal solution of a complex reprsented as $Pt(NH_3)_4Cl_4$ in water had a freezing point depression of 0.0054ºC. Given K_f for H_2O = 1.86 molality^{-1}. Assuming 100% ionisation of the complex, write the ionisation nature and formula of complex.

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

$$[Pt(NH_3)_4Cl_n]Cl_{(4-n)} \longrightarrow [Pt(NH_3)_4Cl_n]^{+(4-n)} + (4-n)\,Cl^-$$

1	0	0
0	1	(4 – n)

Thus particles after dissocation = 4 – n + 1 = 5 – n
and therefore, van't Hoff factor (i) = 5 – n
Now $\Delta T_f = K'_f \times$ molality × van't Hoff factor
$0.0054 = 1.86 \times 0.001 \times (5 - n)$
$\therefore$ $n = 2.1 \approx 2$ (integer value)
Thus complex and its ionisation is :

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

Example-26 : Depression of freezing point of 0.01 molal aq. CH_3COOH solution is 0.02046°. 1 molal urea solution freezes at – 1.86°C. Assuming molality equal to molarity, pH of CH_3COOH solution is :

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

Solution : For urea

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

Now for CH_3COOH

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

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

Now $i = 1 + \alpha$

so $\alpha = 1.1 - 1 = 0.1$

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

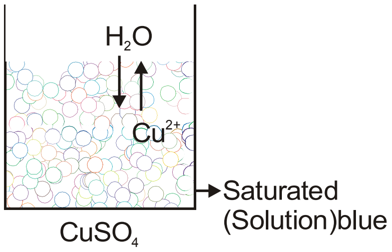
$[H^+] = C\alpha = 0.01 \times 0.1 = 0.001$

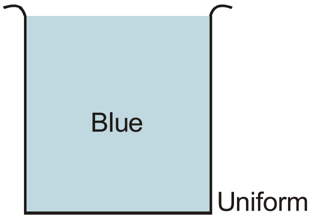
so pH = 3. **Ans. (B)**

8.5 Osmosis & Osmotic pressure :

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

Ex.





Osmosis :

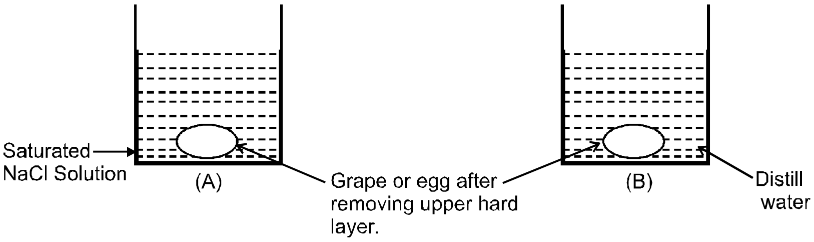
The spontaneous flow of solvent particles from solvent side to solution side or from solution of low concentration side to solution of high concentration side through a semipermeable membrane (SPM) is known as osmosis.

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

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

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

Ex.



Figure

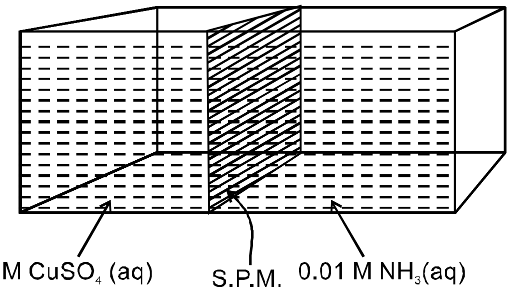
Conclusion : After some time in (A) grape or egg will shrink and in (B) grape or egg will swell.

e.g. (i) A raw mango placed in concentrated salt solution loses water & shrivel into pickle.

(ii) People taking lot of salt, experience water retention in tissue cells. This results in puffiness or swelling called edema.

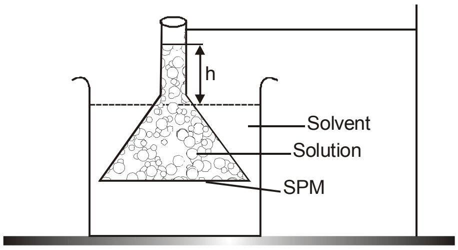
SOLVED EXAMPLE

Example-27 : In which soluton side complex $[Cu(NH_3)_4]^{2+}$ will form and deep blue colour will obtain.



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

Osmotic Pressure :



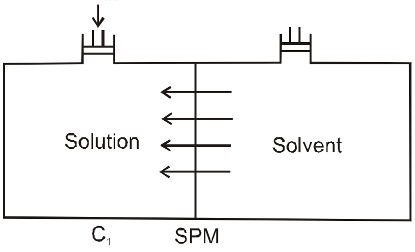
Figure

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

$\pi = \rho gh$; ρ = density of solution

g = acceleration due to gravity ; h = eq. height

1 atm = 1.013×10^5 N/m^2



Figure

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

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

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

Reverse Osmosis :

If the pressure applied on the solution side is more than osmotic pressure of the solution then the solvent particles will move from solution to solvent side. This process is known as reverse osmosis.
Berkely : Hartely device/method uses the above pressure to measure osmotic pressure.
e.g. used in desalination of sea-water.

Vant – Hoff Formula (For calculation of osmotic pressure)

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

π = atm. $\begin{cases} C - \text{mol/lit.} \\ R - 0.082 \text{ lit.atm. } mol^{-1} K^{-1} \\ T - \text{kelvin} \end{cases}$

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

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

$\therefore$ C = total concentration of all types of particles.
$= C_1 + C_2 + C_3 +$ s.................
$= \frac{(n_1 + n_2 + n_3 + ...)}{V}$

SOLVED EXAMPLE

Example-28 : If V_1 mL of C_1 solution + V_2 mL of C_2 solution are mixed together then calculate final concentration of solution and final osmotic pressure. If initial osmotic pressure of two solutions are π_1 and π_2 respectively ?

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

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

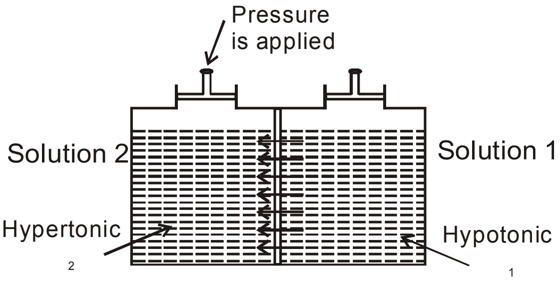
$$\pi = \left(\frac{C_1V_1 + C_2V_2}{V_1 + V_2}\right)RT$$

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

Type of solutions :

(a) Isotonic solution : Two solutions having same osmotic pressure are consider as isotonic solution.
$\pi_1 = \pi_2$ (at same temperature)

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



Figure

Conclusion :

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

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

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

SOLVED EXAMPLE

Example-29 : Calculate osmotic pressure of 0.1 M urea aqueous solution at 300 K ,

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

π = CRT

π = 0.1 x 0.082 x 300

π = 2.46 atm.

Example-30 : If 10 g of an unknown substance (non-electrolytic) is dissolved to make 500 mL of solution, then osmotic pressure at 300 K is observed to be 1.23 atm find molecular weight ?

Solution :

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

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

Example-31 : If 6 g of urea, 18 g glucose & 34.2 g sucrose is dissolved to make 500 mL of a solution at 300 K calculate osmotic pressure ?

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

π = C x 0.082 x 300

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

Example-32 : If 200 mL of 0.1 M urea solution is mixed with 300 mL of 0.2 M glucose solution at 300 K. Calculate osmotic pressure ?

Solution : 0.02 moles urea

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

Example-33 : If urea (aq) solution at 500K has O.P. = 2.05 atm. & glucose solution at 300 K has OP = 1.23 atm. If 200 ml of Ist solution & 400 ml of 2nd solution are mixed at 400 K then calculate O.P. of resulting solution at 400 K (assume molarity is not dependent on temp.)

Solution :

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

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

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

π = CRT = 0.05 × 0.082 × 400

π = 1.64 atm

Example-34 : $\frac{0.1\text{M urea}}{(A)}$, $\frac{0.1\text{M NaCl}}{(B)}$, $\frac{0.1\text{M BaCl}_2}{(C)}$

Solution :

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

(Calculating osmotic pressure when reaction is not taking place)

Example-35 : Calculate osmotic pressure of a solutions having 0.1 M NaCl & 0.2 M Na_2SO_4 and 0.5 MHA. (Given : Weak acid is 20% dissociated at 300 K).

Soluiton : $\pi = \pi_{NaCl} + \pi_{Na_2SO_4} + \pi_{HA}$

$= 0.1\ RT \times 2 + 0.2\ RT \times 3 + 0.5\ RT \times 1.2\ \ = 0.0821 \times 300\ (0.2 + 0.6 + 0.6) = 34.482$ atm.

Example-36 : If 0.04 M Na_2SO_4 solutions at 300 K is found to be isotonic with 0.05 M NaCl (100 % disscociation) solutions. Calculate degree of disscociation of sodium sulphate ?

Soluiton : $i_1\ C_1\ RT = i_2\ C_2\ RT$

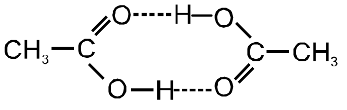
$i_1\ C_1 = i_2\ C_2$

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

$\alpha = 0.75 = 75\%$.

Example-37 : If 6 g of CH_3 COOH is dissolved in benzene to make 1 litre at 300 K. Osmotic pressure of solution is found to be 1.64 atm. If it is known that CH_3COOH in benzene forms a dimer. Calculate degree of association of acetic acid in benzene ?

Soluiton :



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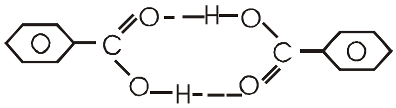


$$i = 1 + \left(\frac{1}{n} - 1\right)\beta.$$

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

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

$$\frac{1.64}{0.0821 \times 30} = \frac{2 - \beta}{2} \quad ; \quad \frac{1.64}{2.46} = \frac{2 - \beta}{2} \qquad 4 = 6 - 3\beta$$

$3\beta = 2$

$\beta = 2/3$

(Calculating osmotic pressure when reaction is taking place)

Example-38 : If 200 ml of 0.2 M $BaCl_2$ solution is mixed with 500 ml of 0.1 M Na_2SO_4 solution. Calculate osmotic pressure of resulting solutions ?

Solution :

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

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

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

Example-39 : If 200 ml of 0.2 M $HgCl_2$ solution is added to 800 ml of 0.5 M KI (100% dissociated) solution. Assuming that the following complex formation taken place to 100% extent.

$$\begin{array}{ll} Hg^{2+} + 4I^- \longrightarrow [HgI_4]^{2-} \\ 0.04 \quad 0.4 \end{array}$$

Calculate osmotic pressure of resulting initially solution at 300K ?

Solution :

$$\begin{array}{ccccccc} HgCl_2 & + & 4KI & \longrightarrow & K_2[HgI_4] & + & 2KCl. \\ 40 & & 400 & & 0 & & 0 \\ 0 & & 400-160 & & 40 & & 80 \\ & & \frac{240}{1000} & & \frac{40}{1000} & & \frac{80}{1000} \end{array}$$

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

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

Example-40 : (**Note:** Attempt this problem after you have studied co-ordination compounds) Ba^{2+} ions, CN^- & Co^{2+} ions form a water soluble complex with Ba^{2+} ions as free cations. For a 0.01 M solution of this complex, osmotic pressure = 0.984 atm & degree of dissociation = 75%. Then find coordination number of Co^{2+} ion in this complex (T = 300 K, R = 0.082 L atm. mol^{-1} k^{-1})

Solution : Say C.N. = x

0.984 = i CRT

0.984 = i 0.01 × 0.082 × 300 = i × 0.246

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

$\Rightarrow$ n = 5

Charge on co-ordination sphere = charge on Cobalt ion - charge on x cyanide ions = - (x-2)

i.e. co-ordination sphere is $[Co(CN)_x]^{-(x-2)}$

Charge on Barium ion is +2

THus, formula of the complex will be $Ba_{(x-2)}[Co(CN)_x]_2$ by charge balance.

$x - 2 + 2 = 5$

$x = 5$

$\therefore$ CN = 5

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

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

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

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

wt of solute = 6.9 × 56 gm

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

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

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

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

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

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

V = **147.2**

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

Sol. Let V = 1lt = 1000 ml

So mass of solution = 1800 gm

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

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

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

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

Ans. (a) 37.92 (b) 0.065

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

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

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

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

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

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

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

Ans. 3.94 atm

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

Now $\pi = C_{net} RT$

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

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

Ans. P_2 = 6.66 atm.

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

Exercise # 1

✍ **Marked Questions may have for Revision Questions.**

PART - I : SUBJECTIVE QUESTIONS

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

Commit to memory :

$$\text{Molarity} = \frac{\text{no. of moles of solute}}{\text{volume of solution (in L)}} \quad ; \quad \text{Molality} = \frac{\text{no. of moles of solute}}{\text{W(g) of solvent}} \times 1000$$

$$\text{Molality} = \frac{\text{molarity} \times 1000}{1000d - \text{molarity} \times \text{m.wt.of solute}}$$ (where d is density of solution in g/ml)

$$\%\frac{w}{w} = \frac{m_{solute}(g)}{m_{solution}(g)} \times 100 \quad ; \quad x_{solute} = \frac{n}{n+N}$$ (where, n is moles of solute, N is moles of solvent)

$$x_{solute} + x_{solvent} = 1$$

A-1. Calculate the concentration of NaOH solution in g/ml which has the same molarity as that of a solution of HCl of concentration 0.0365 g/ml.

A-2.✍ The density of 2M solution of sodium sulphate (Na_2SO_4) is 1.284 g/ml. Calculate
(i) amount of Na_2SO_4 in % w/w
(ii) mole fraction of Na_2SO_4
(iii) molality of Na^+ and SO_4^{2-} ions.

A-3.✍ Calculate the molality and molarity of a solution made by mixing equal volumes of 30% by weight of H_2SO_4 (density = 1.20 g/mL) and 70% by weight of H_2SO_4 (density = 1.60 g/mL).

Section (B) : General Introduction & types of solution

B-1.✍ What are the characteristics of the supersaturated solution.

B-2. Why are some solution processes exothermic whereas others are endothermic ?

Section (C) : Vapour Pressure

Commit to memory :

* The partial pressure of vapours of X in equilibrium with X at a given temperature is called as its vapour pressure. (X is given pure solid or pure liquid)

* A gas is said to be saturated with vapours of a liquid if the partial pressure of liquid vapours is equal to its (saturated) vapour pressure.

* Partial pressure of vapours of X (pure solid or liquid) will remain equal to its vapour pressure till the vapours of X are in equilibrium with X.

C-1._ Write the order of vapour pressure for the following
(i) n-C_6H_{14}
(ii) n-C_7H_{16}
(iii) n-C_8H_{18}

C-2.✍ The vapour pressure of water at 80ºC is 355 torr. A 100 ml vessel contained water–saturated oxygen at 80º C, the total gas pressure being 760 torr. The contents of the vessel were pumped into a 50.0 ml, vessel at the same temperature. What were the partial pressures of oxygen and of water vapour and the total pressure in the final equilibrium state ? Neglect the volume of any water which might condense.

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

Commit to memory :

* **Henry's law :** The solubility of gas in a liquid at a given temperature is directly proportional to its partial pressure above liquid in which it is dissolved.
$P = K_H x$ (where x is mole fraction of unreacted, dissolved gas and P is its partial pressure above liquid.)

D-1. How many gm O_2 gas will disolve in 100 gm water at 9 bar and 27°C? (K_H = 40 Kbar)

D-2.✍ If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 litre of water, if N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 kbar.

Section (E) : Immiscible Liquids

Commit to memory :

If A and B are volatile immiscible liquids, then above their mixture.

* $P_T = P^o_A + P^o_B$ (P_T = Total pressure above mixture of A and B, P^o_A = vapour pressure of A, P^o_B = vapour pressure of B)

$\frac{P_A^o}{P_B^o} = \frac{n_A}{n_B}$ (n_A and n_B are moles of A and B in distillate)

$\frac{w_A}{w_B} = \frac{P_A^{\circ} M_A}{P_B^{\circ} M_B}$ (w_A and w_B are masses of A and B in distillate, M_A and M_B are molar masses of A and B)

E-1.✍ A mixture of an organic liquid A and water distilled under one atmospheric pressure at 99.2ºC. How many grams of steam will be condensed to obtain 1.0 g of liquid A in the distillate ? (Vapour pressure of water at

E-2. Boiling point of a mixture of water and nitrobenzene is 99°C, the vapour pressure of water is 733 mm of Hg and the atmospheric pressure is 760 mm of Hg. The molecular weight of nitrobenzene is 123. Find the ratio of weights of the components of the distillate.

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

Commit to memory :

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

$p_A \propto x_A$

$\mathbf{p_A = x_A P_A^o}$ .... (1)

where p_A = Partial vapour pressure of component A, x_A = Mole fraction of component 'A' in solution, P_A^o = Vapour pressure of pure component 'A' at given temperature

Hence $\mathbf{P_T = x_A P_A^o + x_B P_B^o}$ .... (2)

(P_T = Total pressure of vapour above solution, P_B^o = vapour pressure of pure component 'B' at given temperature.)

Thus, $\frac{1}{P_T} = \frac{y_A}{P_A^o} + \frac{y_B}{P_B^o}$ (for complete derivation, refer page no. 12 of sheet)

(y_A = mole fraction of A in vapour phase above the solution and y_B = mole fraction of B in vapour phase above the solution)

F-1.✍ Two liquids, A and B, form an ideal solution. At the specified temperature, the vapour pressure of pure A is 200 mm Hg while that of pure B is 75 mm Hg. If the vapour over the mixture consists of 50 mol percent A, what is the mole percent A in the liquid ?

F-2._ 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'.

F-3. At 80°C, the vapour pressure of pure benzene is 753 mm Hg and of pure toluene 290 mm Hg. Calculate the composition of a liquid in mole per cent which at 80°C is in equilibrium with the vapour containing 30 mole per cent of benzene.

F-4._ 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

F-5.✍ Two liquids A and B form an ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of A and 3 moles of B is 550 mm of Hg. At the same temperature, if one mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of A and B in their pure states.

Section (G) : Non-ideal Solutions

Commit to memory :

*

+ve deviation	**–ve deviation**
$P_{T.exp} > (x_A P^o_A + x_B P^o_B)$	$P_{T.exp} < (x_A P^o_A + x_B P^o_B)$

(where $P_{T.exp}$ is experimental total pressure above mixture of volatile liquids A and B).

ΔH_{mix} = +ve	ΔH_{mix} = –ve
ΔV_{mix} = +ve	ΔV_{mix} = –ve
ΔS_{mix} = +ve	ΔS_{mix} = +ve
ΔG_{mix} = –ve	ΔG_{mix} = –ve

G-1. A non ideal solution was prepared by mixing 30 ml chloroform and 50 ml acetone. Comment on volume of mixture.

G-2.✍ Total vapour pressure of mixture of 1 mole of volatile component A (P^o_A = 100 mm Hg) and 3 mole of volatile component B (P^o_B = 80 mm Hg) is 90 mm Hg. Find out nature of solution and sign of entropy of solution.

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

Commit to memory :

*

For dissociation / association $i = 1 + (n - 1)\ \alpha$

(where n is total number of particles produced per solute particle after association / dissociation, i = vant Hoff factor, α = degree of dissociation / association.

$$i = \frac{\text{Moles of solute particles after association/dissociation of X}}{\text{Moles of X without association / dissociation}} = \frac{\text{Observed value of colligative property}}{\text{Theoretical value of that colligative property}}$$

$$i = \frac{\text{Theoretical molar mass of solute}}{\text{Observed molar mass of solute}}$$

H-1.✍ Complete the following table. (Use : $i = 1 + (n - 1)\alpha$)

Solute	Dissociation / association reaction	Degree of dissociation / association	n	i
NaCl		1		
H_2SO_4		1		
CH_3COOH (in water)		0.2		
CH_3COOH (in benzene)		0.5		
Glucose				
KBr		0.8		
A	$3A \rightarrow A_3$	1		

H-2.✍ Calculate the percentage degree of dissociation of an electrolyte XY_2 (Normal molar mass = 164) in water if the observed molar mass by measuring elevation in boiling point is 65.6.

Section (I) : Relative lowering of vapour pressure

Commit to memory :

* $$\text{RLVP} = \frac{P^o - P_S}{P^o} = x_{solute}\ ; \qquad \frac{P^o - P_S}{P_S} = \frac{n}{N}$$

(where P^o = vapour pressure of pure solvent, P_s = partial pressure of vapour above solution, n = dissolved moles of solute, N = moles of solvent.)

$$\frac{P^o - P_S}{P_s} = \frac{m_{solute(g)}}{M_{solute}} \times \frac{M_{solvent}}{m_{solvent(g)}}$$ (where m = given mass in solution, M = molar mass.)

$$\frac{P^o - P_S}{P_s} = (\text{ molality }) \times \frac{M_{solvent}}{1000}$$

If solution is of single solute and it gets associated or dissociated;

$$\frac{P^o - P_S}{P_s} = \frac{i.n}{N}\ ;\ \text{that is}\ \frac{P^o - P_S}{P_s} = i \times (\text{molality}) \times \frac{M_{solvent}}{1000}$$

I-1._ 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?

I-2.✍ The degree of dissociation of $Ca(NO_3)_2$ in a dilute aqueous solution containing 7 g salt per 100 g of water at 100ºC is 70%. If the vapour pressure of water at 100ºC is 760 mm of Hg, calculate the vapour pressure of the solution.

I-3._ 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.

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

Commit to memory :

* $\Delta T_b = i \times K_b \times m$ (where ΔT_b = elevation in boiling point of solution, K_b = ebullioscopic constant, m = molality of single solute, T_b = boiling point of solvent (in K).

$$K_b = \frac{RT_b^2 M}{1000 \times \Delta H_{vap}} = \frac{RT_b^2}{1000 \times L_{vap}} \qquad \text{(M = Molar mass of solvent)}$$

$\Delta T_f = i \times K_f \times m$ (where ΔT_f = depression in freezing point of solution, K_f = cryoscopic constant, T_f = freezing point of solvent (in K).

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

J-1.✍ (a) A solution containing 0.5 g of naphthalene in 50 g CCl_4 yield a boiling point elevation of 0.4 K, while a solution of 0.6 g of an unknown solute in the same mass of the solvent gives a boiling point elevation of 0.65 K. Find the molar mass of the unknown solute.

(b) The boiling point of a solution of 0.1 g of a substance in 16 g of ether was found to be 0.100ºC higher that of pure ether. What is the molecular mass of the substance. K_b(ether) = 2.16 K kg mol^{-1}.

J-2.✍ The amount of benzene that will separate out (in grams) if a solution containing 7.32 g of triphenylmethane in 1000 g of benzene is cooled to a temperature which is 0.2°C below the freezing point of benzene?
(K_f = 5.12 K-Kg/mol)

J-3.✍ The boiling point of a solution of 5 g of sulphur in 100 g of carbon disulphide is 0.474ºC above that of pure solvent. Determine the molecular formula of sulphur in this solvent. The boiling point of pure carbon disulphide is 47ºC and its heat of vaporisation is 84 calories per gram.

J-4.✍ Calculate the freezing point of a solution of a non-volatile solute in a unknown solvent of molar mass 30 g/ mole having mole fraction of solvent equal to 0.8. Given that latent heat of fusion of solid solvent = 2.7 kcal mol^{-1}, freezing point of solvent = 27°C and R = 2 cal mol^{-1} k^{-1}.

Section (K) : Osmotic Pressure

Commit to memory :

* $\pi = CRT = \frac{n}{V}RT$ (n = Total moles of solute particles in solution, V = Total volume of solution in L)

K-1.✍ **(a)** Predict the osmotic pressure order for the following(assume salts are 100% dissociated).

I	0.1 M urea	II	0.1 M NaCl
III	0.1 M Na_2SO_4	IV	0.1 M Na_3PO_4

(b) If equal volumes of all these solutions are mixed then calculate the osmotic pressure of the net resultant solution obtained at 300K.

K-2.✍ A solution containing 3.00 g of calcium nitrate in 100 c.c. of solution had an osmotic pressure of 11.2 atmosphere at 12° C. Calculate the degree of ionisation of calcium nitrate at this dilution and temperature.

K-3._ 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.

K-4.✍ At 2ºC the osmotic pressure of a urea solution is found to be 500 mm of Hg. The solution is diluted and the temperature is raised to 27ºC, when the osmotic pressure is found to be 109.09 mm of Hg. Determine the extent of dilution.

PART - II : ONLY ONE OPTION CORRECT TYPE

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

A-1.✍ Persons are medically considered to have lead poisoning if they have a concentration greater than 10 micrograms of lead per decilitre of blood. Concentration in parts per billion is : (Given : Density of Blood = 1g/ml)

(A) 1000 (B) 100 (C) 10 (D) 1

Section (B) : General Introduction & types of solution

B-1. Which statement best explains the meaning of the phrase “like dissolves like “ ?

(A) A Solute will easily dissolve a solute of similar mass
(B) A solvent and solute with similar intermolecular forces will readily form a solution
(C) The only true solutions are formed when water dissolves a non-polar solute
(D) The only true solutions are formed when water dissolves a polar solute

B-2.✍ An ionic compound that attracts atmospheric water so strongly that a hydrate is formed is said to be :

(A) Dilute (B) Hygroscopic (C) Immiscible (D) Miscible

Section (C) : Vapour Pressure

C-1.✍ A liquid is kept in a closed vessel. If a glass plate (negligible mass) with a small hole is kept on top of the liquid surface, then the vapour pressure of the liquid in the vessel is :

(A) More than what would be if the glass plate were removed
(B) Same as what would be if the glass plate were removed
(C) Less than what would be if the glass plate were removed
(D) Cannot be predicted

C-2.✍ The vapour pressure of water depends upon :

(A) Surface area of container (B) Volume of container
(C) Temperature (D) All

C-3. Among the following substances, the lowest vapour pressure is exerted by :

(A) Water (B) Mercury
(C) Acetone (D) Ethanol

C-4.✍ At higher altitudes, water boils at temperature < 100°C because

(A) temperature of higher altitudes is low (B) atmospheric pressure is low
(C) the proportion of heavy water increases (D) atmospheric pressure becomes more.

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

D-1.✍ The solubility of gases in liquids :

(A) increases with increase in pressure and temperature
(B) decreases with increase in pressure and temperature
(C) Increases with increase in pressure and decrease in temperature
(D) decreases with increase in pressure and increase in temperature

D-2.✍ According to Henry’s law, the solubility of a gas in a given volume of liquid increases with increase in :

(A) Temperature (B) Pressure (C) Both (A) and (B) (D) None of these

D-3.✍ Some of the following gases are soluble in water due to formation of their ions :

I : CO_2 ; II : NH_3 ; III : HCl ; IV : CH_4 ; V : H_2

Water insoluble gases can be :

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

D-4.✍ The solubility of $N_2(g)$ in water exposed to the atmosphere, when its partial pressure is 593 mm is 5.3×10^{-4} M. Its solubility at 760 mm and at the same temperature is :

(A) 4.1×10^{-4} M (B) 6.8×10^{-4} M (C) 1500 M (D) 2400 M

Section (E) : Immiscible Liquids

E-1. When a liquid that is immiscible with water was steam distilled at 95.2°C at a total pressure of 748 torr, the distillate contained 1.25 g of the liquid per gram of water. The vapour pressure of water is 648 torr at 95.2°C, what is the molar mass of liquid?
(A) 7.975 g/mol (B) 166 g/mol (C) 145.8 g/mol (D) None of these

E-2.. If two liquids A (P^o_A =100 torr) and B (P^o_B = 200 torr) are completely immiscible with each other, each one will behave independently of the other, are present in a closed vessel. The total vapour pressure of the system will be:
(A) less than 100 torr (B) less than 200 torr
(C) between 100 to 200 torr (D) 300 torr

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

F-1. For a binary ideal liquid solution, the total pressure of the solution is given as :
(A) $P_{total} = P^o_A + (P^o_A - P^o_B)\, X_B$ (B) $P_{total} = P^o_B + (P^o_A - P^o_B)\, X_A$
(C) $P_{total} = P^o_B + (P^o_B - P^o_A)\, X_A$ (D) $P_{total} = P^o_B + (P^o_B - P^o_A)\, X_B$

F-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

F-3. At 323 K, the vapour pressure in millimeters of mercury of a methanol-ethanol solution is represented by the equation p = 120 X_A + 140, where X_A is the mole fraction of methanol. Then the value of $\lim\limits_{x_A \to 1} \frac{p_A}{X_A}$ is

(A) 250 mm (B) 140 mm (C) 260 mm (D) 20 mm

F-4. Given at 350 K p_A° = 300 torr and p_B° = 800 torr, the composition of the mixture having a normal boiling point of 350 K is :
(A) X_A = 0.08 (B) X_A = 0.06 (C) X_A = 0.04 (D) X_A = 0.02

F-5. Two liquids A and B have P^o_A and P^o_B in the ratio of 1 : 3 and the ratio of number of moles of A and B in liquid phase are 1 : 3 then mole fraction of 'A' in vapour phase in equilibrium with the solution is equal to :
(A) 0.1 (B) 0.2 (C) 0.5 (D) 1.0

F-6. The vapour pressure of a pure liquid 'A' is 70 torr at 27°C. 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°C. The vapour pressure of pure liquid B at 27°C is
(A) 14 (B) 56 (C) 140 (D) 70

Section (G) : Non-ideal Solutions

G-1. The vapour pressure of the solution of two liquids A(p^o = 80 mm) and B(p^o = 120 mm) is found to be 100 mm when x_A = 0.4. The result shows that
(A) solution exhibits ideal behaviour
(B) solution shows positive deviations
(C) solution shows negative deviations
(D) solution will show positive deviations for lower concentration and negative deviations for higher concentrations.

G-2. Consider a binary mixture of volatile liquids. If at X_A = 0.4 the vapour pressure of solution is 580 torr then the mixture could be (p_A° = 300 torr, p_B° = 800 torr) :
(A) $CHCl_3 - CH_3COCH_3$ (B) $C_6H_5Cl - C_6H_5Br$
(C) $C_6H_6 - C_6H_5CH_3$ (D) $nC_6H_{14} - nC_7H_{16}$

G-3.✍ A solution of sulphuric acid in water exhibits :
(A) Negative deviations from Raoult's law
(B) Positive deviations from Raoult's law
(C) Ideal properties
(D) The applicability of Henry's law

G-4. When KCl dissolves in water (assume endothermic dissolution), then :
(A) $\Delta H = +$ ve, $\Delta S = +$ ve, $\Delta G = +$ ve
(B) $\Delta H = +$ ve, $\Delta S = -$ ve, $\Delta G = -$ ve
(C) $\Delta H = +$ ve, $\Delta S = +$ ve, $\Delta G = -$ ve
(D) $\Delta H = -$ ve, $\Delta S = -$ ve, $\Delta G = +$ ve

G-5. The dissolving process is exothermic when :
(A) The energy released in solvation exceeds the energy used in breaking up solute-solute and solvent-solvent interactions.
(B) The energy used in solvation exceeds the energy released in breaking up solute-solute and solvent-solvent interactions.
(C) The energy released in solvation is about the same as the energy used in breaking up solute-solute and solvent-solvent interactions.
(D) The energy used in solvation is about the same as the energy used in breaking up solute-solute and solvent-solvent interactions.

G-6.✍ Which of the following is less than zero for ideal solutions ?
(A) ΔH_{mix} (B) ΔV_{mix} (C) ΔG_{mix} (D) ΔS_{mix}

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

H-1.✍ One mole of a solute A is dissolved in a given volume of solvent. The association of the solute take place as follows: $nA \rightleftharpoons A_n$
If α is the degree of association of A, the van't Hoff factor i is expressed as:
(A) $i = 1 - \alpha$ (B) $i = 1 + \frac{\alpha}{n}$ (C) $i = \frac{1 - \alpha + \frac{\alpha}{n}}{1}$ (D) i = 1

H-2._ 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

H-3._ 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%

H-4.✍ A complex containing K^+, Pt(IV) and Cl^- is 100% ionised giving i = 3. Thus, complex is :
(A) $K_2[PtCl_4]$ (B) $K_2[PtCl_6]$ (C) $K_3[PtCl_5]$ (D) $K[PtCl_3]$

Section (I) : Relative lowering of vapour pressure

I-1. 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) $\frac{2}{3}$ (B) $\frac{1}{3}$ (C) $\frac{1}{2}$ (D) $\frac{3}{2}$

I-2. 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

I-3.✍ The vapour pressure of pure benzene, C_6H_6 at 50°C is 268 Torr. How many moles of non-volatile solute per mol of benzene is required to prepare a solution of benzene having a vapour pressure of 167 Torr at 50°C?
(A) 0.377 (B) 0.605 (C) 0.623 (D) 0.395

I-4. If relative decrease in vapour pressure is 0.4 for a solution containing 1 mol NaCl in 3 mol H_2O, NaCl is .... % ionised.

(A) 60% (B) 50% (C) 100% (D) 40%

I-5.✍ The vapour pressure of a solution of a non-volatile solute B in a solvent A is 95% of the vapour pressure of the solvent at the same temperature. If the molecular weight of the solvent is 0.3 times the molecular weight of the solute, what is the ratio of weight of solvent to solute.

(A) 0.15 (B) 5.7 (C) 0.2 (D) none of these

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

J-1.✍ At a constant temperature, ΔS will be maximum for which of the following processes :

(A) Vaporisation of a pure solvent
(B) Vaporisation of solvent from a solution containing nonvolatile and nonelectrolytic solute in it
(C) Vaporisation of solvent from a solution containing nonvolatile but electrolytic solute in it
(D) Entropy change will be same in all the above cases

J-2. 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}) (Assumption : consider solute to be non volatile)

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

J-3.✍ A solute'S' undergoes a reversible trimerization when dissolved in a certain solvent. The boiling point elevation of its 0.1 molal solution was found to be identical to the boiling point elevation in case of a 0.08 molal solution of a solute which neither undergoes association nor dissociation. To what percent had the solute 'S' undergone trimerization?

(A) 30% (B) 40% (C) 50% (D) 60%

J-4.✍ A complex of iron and cyanide ions is 100% ionised at 1m (molal). If its elevation in b.p. is 2.08. Then the complex is (K_b = 0.52° mol^{-1} kg) :

(A) $K_3[Fe(CN)_6]$ (B) $Fe(CN)_2$ (C) $K_4[Fe(CN)_6]$ (D) $Fe(CN)_4$

J-5.✍ $PtCl_4.6H_2O$ can exist as a hydrated complex 1 molal aq. solution has depression in freezing point of 3.72°. Assume 100% ionisation and $K_f(H_2O)$ = 1.86° mol^{-1} kg, then complex is -

(A) $[Pt(H_2O)_6]Cl_4$ (B) $[Pt(H_2O)_4Cl_2]Cl_2 . 2H_2O$
(C) $[Pt(H_2O)_3Cl_3]Cl . 3H_2O$ (D) $[Pt(H_2O)_2Cl_4] . 4H_2O$

J-6. How many moles of sucrose should be dissolved in 500 g of water so as to get a solution which has a difference of 104°C between boiling point and freezing point. (K_f = 1.86 K Kg mol^{-1}, K_b = 0.52 K Kg mol^{-1})

(A) 1.68 (B) 3.36 (C) 8.40 (D) 0.840

J-7.✍ Which of the following has been arranged in order of decreasing freezing point?

(A) 0.05 M KNO_3 > 0.04 M $CaCl_2$ > 0.140 M sugar > 0.075 M $CuSO_4$
(B) 0.04 M $BaCl_2$ > 0.140 M sucrose > 0.075 M $CuSO_4$ > 0.05 M KNO_3
(C) 0.075 M $CuSO_4$ > 0.140 M sucrose > 0.04 M $BaCl_2$ > 0.05 M KNO_3
(D) 0.075 M $CuSO_4$ > 0.05 M $NaNO_3$ > 0.140 M sucrose > 0.04 M $BaCl_2$

J-8. A solution of x moles of sucrose in 100 grams of water freezes at –0.2ºC. As ice separates the freezing point goes down to – 0.25ºC. How many grams of ice would have separated?

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

Section (K) : Osmotic Pressure

K-1.✍ Select correct statement :

(A) Osmosis produced by semipermeable membrane.
(B) Desalination of sea-water is done by reverse osmosis
(C) Both are correct statements
(D) None is correct statement

K-2. The relationship between osmotic pressure at 273 K when 10 g glucose (P_1) ,10 g urea (P_2) and 10 g sucrose (P_3) are dissolved in 250 mL of water is :

(A) $P_1 > P_2 > P_3$ (B) $P_3 > P_1 > P_2$ (C) $P_2 > P_1 > P_3$ (D) $P_2 > P_3 > P_1$

K-3. Osmotic pressure of blood is 7.40 atm at 27°C. Number of moles of glucose to be used per litre for an intravenous injection that is to have the same osmotic pressure as blood is :
(A) 0.3 (B) 0.2 (C) 0.1 (D) 0.4

K-4._ 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

K-5.✍ Osmotic pressure of a solution of glucose is 1.20 atm and that of a solution of cane sugar is 2.5 atm. The osmotic pressure of the mixture containing equal volumes of the two solutions will be
(A) 2.5 atm (B) 3.7 atm (C) 1.85 atm (D) 1.3 atm.

K-6.✍ Consider following cases :
I : 2M CH_3COOH solution in benzene at 27°C where there is dimer formation to the extent of 100%
II : 0.5 M KCl aq. solution at 27°C, which ionises 100%
Which is/are true statements(s) :
(A) both are isotonic (B) I is hypertonic (C) II is hypotonic (D) none is correct

PART - III : MATCH THE COLUMN

1.

If at a particular temperature, the density of 18 M H_2SO_4 is 1.8 g cm^{-3}. Then :

Column – I	**Column – II**
(A) Molality	(p) 0.1
(B) % concentration by wt. of solute	(q) 0.9
(C) mole fraction of H_2SO_4	(r) 500
(D) mole fraction of H_2O	(s) 98

2.✍

Column – I	**Column – II**
(A) Ethyl methyl ketone + $CHCl_3$	(p) $\Delta S_{mix.} > 0$
(B) Ethanol + hexane	(q) $\Delta V_{mix.} > 0$
(C) $C_2H_5Br + C_2H_5I$	(r) $\Delta H_{mix.} < 0$
(D) Acetone + Benzene	(s) Maximum boiling azeotropes
	(t) Minimum boiling azeotropes

3.✍

Assuming all the solutes are non volatile and all solutions are ideal and neglect the hydrolysis of cation and anion.

Column – I	**Column – II**
(A) 10 ml 0.1 M KOH aqueous solution is added to 10 ml 0.1 M HCl aqueous solution	(p) Osmotic pressure of solution increases
(B) 10 ml 0.1 M KOH aqueous solution is added to 10 ml 0.1 M CH_3COOH aqueous solution	(q) Vapour pressure of solution increases
(C) 10 ml 0.1 M HNO_3 aqueous solution is added to 10 ml 0.1 M NH_3 aqueous solution	(r) Boiling point of solution increases
(D) 10 ml 0.1 M HNO_3 aqueous solution is added to 10 ml 0.1 M KOH aqueous solution	(s) Freezing point of solution increases

Exercise # 2

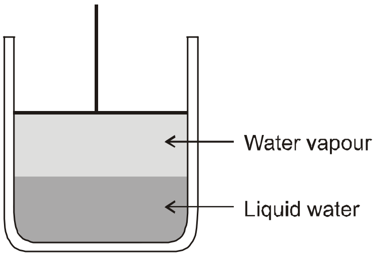
✍ **Marked Questions may have for Revision Questions.**

PART - I : ONLY ONE OPTION CORRECT TYPE

1. All of the water in a 0.20 M solution of NaCl was evaporated and a 0.150 mol of NaCl was obtained. What was the original volume of the sample ?

(A) 30 mL (B) 333 mL (C) 750 mL (D) 1000 mL

2.✍ The vapour pressure of water at 20°C is 17.54 mmHg. What will be the vapour pressure of the water in the apparatus shown after the piston is lowered, decreasing the volume of the gas above the liquid to one half of its initial volume (assume temperature constant).



(A) 8.77 mmHg
(B) 17.54 mmHg
(C) 35.08 mmHg
(D) between 8.77 and 17.54 mmHg

3.✍ A sample of air is saturated with benzene (vapor pressure = 100 mm Hg at 298 K) at 298K, 750mm Hg pressure. If it is isothermally compressed to one third of its initial volume, the final pressure of the system is

(A) 2250 torr (B) 2150 torr (C) 2050 torr (D) 1950 torr

4.✍ Consider two liquids A & B having pure vapour pressures P_A° & P_B° forming an ideal solution. The plot of $\frac{1}{X_A}$ v/s $\frac{1}{Y_A}$ (where X_A and Y_A are the mole fraction of liquid A in liquid and vapour phase respectively) is linear with slope and Y intercepts respectively :

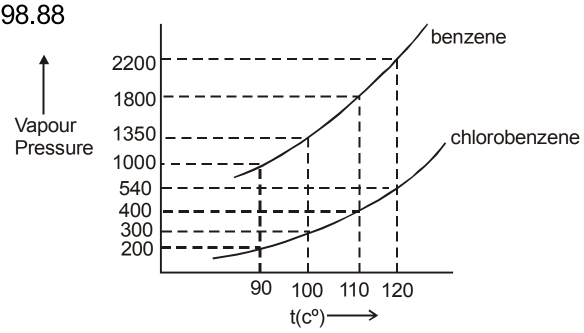
(A) $\frac{P_A^\circ}{P_B^\circ}$ and $\frac{(P_A^\circ - P_B^\circ)}{P_B^\circ}$ (B) $\frac{P_A^\circ}{P_B^\circ}$ and $\frac{(P_B^\circ - P_A^\circ)}{P_B^\circ}$

(C) $\frac{P_B^\circ}{P_A^\circ}$ and $\frac{(P_A^\circ - P_B^\circ)}{P_B^\circ}$ (D) $\frac{P_B^\circ}{P_A^\circ}$ and $\frac{(P_B^\circ - P_A^\circ)}{P_B^\circ}$

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

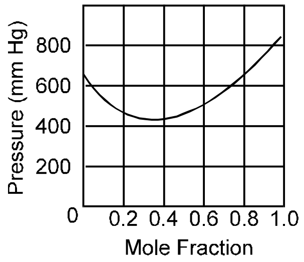
(A) 150 (B) 180
(C) 188.88 (D) 198.88

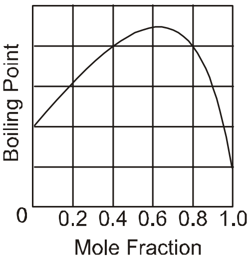
6.✍ Assuming the formation of an ideal solution, determine the boiling point of a mixture containing 1560 g benzene (molar mass = 78) and 1125 g chlorobenzene (molar mass = 112.5) using the following against an external pressure of 1000 Torr.

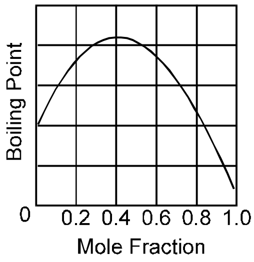


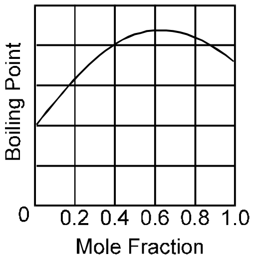
(A) 90°C (B) 100°C
(C) 110° (D) 120°C

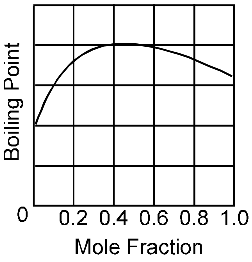
7.✍ Given P-x curve for a non-ideal liquid mixture (Fig.). Identify the correct T-x curve for the same mixture.



(A)


(B)


(C)


(D)


8.✍ If vapour pressures of pure liquids ‘A’ & ‘B’ are 300 and 800 torr respectively at 25°C. When these two liquids are mixed at this temperature to form a solution in which mole percentage of ‘B’ is 92, then the total vapour pressure is observed to be 0.95 atm. Which of the following is true for this solution.

(A) $\Delta V_{mix} > 0$ (B) $\Delta H_{mix} < 0$ (C) $\Delta V_{mix} = 0$ (D) $\Delta H_{mix} = 0$

9.✍ The vapour pressure of two pure liquids A and B, that form an ideal solution are 100 and 900 torr respectively at temperature T. This liquid solution of A and B is composed of 1 mole of A and 1 mole of B. What will be the pressure, when 1 mole of mixture has been vapourized ?

(A) 800 torr (B) 500 torr (C) 300 torr (D) 400 torr

10. In the following aqueous solutions.

(A) 1 m sucrose (B) 1 m potassium ferricyanide and (C) 1 m potassium sulphate

maximum value of vapour pressure of solution is that of :

(A) A (B) B (C) C (D) equal

11.✍ When only a little quantity of $HgCl_2(s)$ is added to excess KI(aq) to obtain a clear solution, which of the following is true for this solution? (no volume change on mixing).

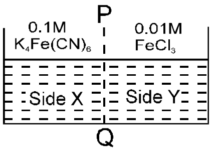
The reaction is $4KI(aq.) + HgCl_2(s) \longrightarrow K_2[HgI_4]\,(aq.) + 2KCl\,(aq.)$

(A) Its boiling and freezing points remain same (B) Its boiling point is lowered

(C) Its vapour pressure become lower (D) Its boiling point is raised

(E) Its freezing point is lowered.

12.✍ $FeCl_3$ on reaction with $K_4[Fe(CN)_6]$ in aq. solution gives blue colour. These are separated by a semipermeable membrane PQ as shown. Due to osmosis there is-



(A) blue colour formation in side X

(B) blue colour formation in side Y

(C) blue colour formation in both of the sides X and Y

(D) no blue colour formation

13.✍ Two beakers, one containing 20 ml of a 0.05 M aqueous solution of a non volatile, non electrolyte and the other, the same volume of 0.03 M aqueous solution of NaCl, are placed side by side in a closed enclosure. What are the volumes in the two beakers when equilibrium is attained ? Volume of the solution in the first and second beaker are respectively.

(A) 21.8 ml and 18.2 mL (B) 18.2 mL and 21.8 mL

(C) 20 mL and 20 mL (D) 17.1 mL and 22.9 mL

PART - II : NUMERICAL TYPE QUESTIONS

1.✍ What volume of 98% sulphuric acid (in ml) should be mixed with water to obtain 200 mL of 15% solution of sulphuric acid by weight ? Given density of H_2O = 1.00 g cm^{-3}, sulphuric acid (98%) = 1.88 g cm^{-3} and sulphuric acid (15%) = 1.12 g cm^{-3}.

2.✍ Calculate the concentration of CO_2 in a soft drink that is bottled with a partial pressure of CO_2 of 4 atm over the liquid at 25ºC. The Henry's law constant for CO_2 in water at 25^{0}C is 3.1 × 10^{-2} mol/litre–atm. Write answer after multiplying by 100.

3.✍ An ideal aqueous solution containing liquid A(M.Wt. = 128) 64% by weight has a vapour pressure of 145 mm Hg. If the vapour pressure of A is x mm of Hg and that of water is 155 mm Hg at the same temperature. Then find x/5. The solutions is ideal.

4. A and B form ideal solutions; at 50ºC, P_A^o is half P_B^o. A solution containing 0.2 mole of A and 0.8 mole of B has a normal bolling point of 50ºC. Find 18 × P_B^o. (P_B^o is in atm)

5.✍ Two liquids A and B are miscible over the whole range of composition and may be treated as ideal (obeying Raoult's law.) At 350 K the vapour pressure of pure A is 24.0 kPa and of pure B is 12.0 kPa. A mixture of 60% A and 40% B is distilled at this temperature. A small amount of the distillate is collected and and redistilled at 350 K; what is the mole percent of B in the second distillate ?

6. How many facts related to $CHCl_3$ + ethylmethylketone solution are correct ?

(a) It shows negative derivation.
(b) It forms maximum boiling azeotropic mixture
(c) $\Delta S > 0$
(d) $\Delta G < 0$
(e) Components can be separated by fractional distillation.

7.✍ How many of the following solutions show negative deviation from Raoult's Law ?

	Liquid A	+	Liquid B
(i)	$(CH_3)_2CO$	+	CS_2
(ii)	CCl_4	+	C_6H_6
(iii)	CCl_4	+	$CHCl_3$
(iv)	H_2O	+	C_2H_5OH
(v)	$(C_2H_5)_2O$	+	$(CH_3)_2CO$
(vi)	CH_3COOH	+	C_5H_5N (pyridine)
(vii)	$C_6H_5NH_2$	+	$(CH_3)_2CO$
(viii)	C_6H_5Cl	+	C_6H_5Br
(ix)	Cyclohexane	+	Ethanol

8.✍ Determine i (vant-Hoff factor) for a tribasic acid H_3A. Assuming first dissociation to be 100%, second dissociation 50%, third dissociation 20%. (Round off your answer to nearest integer).

9.✍ 0.1 mole XY_2 is dissolved in 2L water, where it ionizes to give X^{2+} and Y_2^{2-}. Observed osmotic pressure is 3 atm. Molar mass of X is 24 and Y is 32. Find $M_{observed}$ + 2i (where $M_{observed}$ is observed molar mass of XY_2) (Use R = 1/12 L-atm/mol.K and temperature is 87°C)

10.✍ How many grams of sucrose ($C_{12}H_{22}O_{11}$) must be dissolved in 90 g of water to produce a solution over which the relative humidity is 80%? Assume the solution is ideal. Give your answer after dividing by 10.

11.✍ 1.22 g of a monobasic acid is dissolved in 100 g of benzene. Boiling point of solution increases by 0.13ºC with respect to pure benzene. Find the molecular mass of acid in benzene solvent (in u). Report your answer after dividing it by 100 and Round it off to nearest integer. (K_b of benzene = 2.6 K kg mol^{-1}).

12._ At 27ºC, a 1.2% solution (wt./vol.) of glucose is isotonic with 4.0 g/litre of solution of solute X. Find the molar mass of X, if the molar mass of glucose is 180. (R = 0.082 L atm mol^{-1} K^{-1}, Molar mass of glucose = 180 g/ mole)

13. 10 g of solute A and 20 g of solute B both are dissolved in 500 ml. of water. The solution has the same osmotic pressure as 6.67 g of A and 30 g of B are dissolved in the same volume of water at the same temperature. If the ratio of molar masses of A and B is x/y, find x + y.

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1.✍ We have 100 mL of 0.1 M KCl solution. To make it 0.2 M,
(A) evaporate 50 mL water
(B) evaporate 50 mL solution
(C) add 0.1 mol KCl
(D) add 0.01 mol KCl

2.✍ The vapour pressure of a dilute solution of a solute is influenced by :
(A) Temperature of solution
(B) Mole fraction of solute
(C) M.pt. of solute
(D) Degree of dissociation of solute

3.✍ According to Henry's law, the partial pressure of gas (P'_g) is directly proportional to mole fraction of gas in dissolved state , i.e., $P_{gas}' = K_H . X_{gas}$ where K_H is Henry's constant. Which are correct ?
(A) K_H is characteristic constant for a given gas–solvent system
(B) Higher is the value of K_H , lower is solubility of gas for a given partial pressure of gas
(C) K_H has temperature dependence
(D) K_H increases with temperature

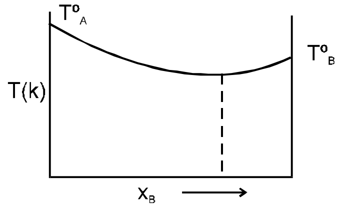
4.✍ Select correct statements :
(A) Gases which have high value of van der Waals constant 'a' are easily liquefied
(B) Easily liquefiable gases are water soluble
(C) Gases which forms ions in a solvent are soluble in that solvent
(D) Under same conditions, NH_3 has low solubility in water than that of CO_2.

5.✍ Two liquids X and Y are perfectly immiscible. If X and Y have molecular masses in ratio 1 : 2, the total vapour pressure of a mixture of X and Y prepared in weight ratio 2 : 3 should be (P_x^0 = 400 torr, P_y^0 = 200 torr)
(A) 600 torr
(B) 400 torr
(C) 800 torr
(D) 1000 torr

6.✍ Which of the following is/are correct for an ideal binary solution of two volatile liquids (eg. benzene & toluene)?
(A) Its vapor is always richer in the more volatile component (compared to the liquid).
(B) The liquid will gradually become richer in the less volatile component if such a mixture is boiled (distilled).
(C) The P_T (ie. the total pressure) above the solution will be the sum of the vapor pressures of the two pure components.
(D) The boiling point of the solution will be less than the boiling points of the two components.

7.✍ Which is/are true about ideal solutions ?
(A) The volume change on mixing is zero
(B) The enthalpy of mixing is zero
(C) The entropy of mixing is zero
(D) The enthalpy of mixing is negative

8.✍ The diagram given below represents boiling point composition diagram of solution of components A and B, which is/are incorrect among the following?



(A) The solution shows negative deviation
(B) A-B-interactions are stronger than A-A and B-B
(C) The solution is ideal solution
(D) The solution shows positive deviation.

9. Which is/are correct statement(s) ?

(A) When mixture is more volatile than both pure components, there is positive deviation from Raoult's law

(B) When mixture is less volatile than both pure components, there is negative deviation from Raoult's law

(C) Ethanol and water form ideal solution

(D) $CHCl_3$ and water form ideal solution

10.✍ At 35°C, the vapour pressure of CS_2 is 512 mmHg, and of acetone is 344 mmHg. A solution of CS_2 and acetone in which the mole fraction of CS_2 is 0.25, has a total vapour pressure of 600mmHg. Which of the following statements is/are correct ?

(A) A mixture of 100 mL of acetone and 100 mL of CS_2 has a volume of 200 mL

(B) When acetone and CS_2 are mixed at 35°C, heat must be absorbed in order to produce a solution at 35°C.

(C) Process of mixing is exothermic

(D) Entropy of mixing is zero

11.✍ In which of the following pairs of solutions will the values of the vant Hoff factor be the same?

(A) 0.05 M $K_4[Fe(CN)_6]$ and 0.10 M $FeSO_4$

(B) 0.10 M $K_4[Fe(CN)_6]$ and 0.05 M $FeSO_4(NH_4)_2SO_4 . 6H_2O$

(C) 0.20 M NaCl and 0.10 M $BaCl_2$

(D) 0.05 M $FeSO_4(NH_4)_2SO_4 . 6H_2O$ and 0.02 M $KCl . MgCl_2 . 6H_2O$

12. 2 g of non-volatile hydrocarbon solute dissolved in 100 g of hypothetical organic solvent (molar mass = 50) was found to lower vapour pressure from 75.50 to 75 mm of Hg at 20°C. Given that hydrocarbon contains 96% of C. Then which of the following are true ?

(A) molecular wt of solute = 150
(B) molecular formula = $C_{12}H_6$
(C) molecular wt. of solute = 132
(D) molecular formula = $C_{10}H_{12}$

13.✍ In the depression of freezing point experiment , it is found that the :

(A) Vapour pressure of the solution is less than that of pure solvent

(B) Vapour pressure of the solution is more than that of pure solvent

(C) Only solute molecules solidify at the freezing point

(D) Only solvent molecules solidify at the freezing point

14.✍ Consider following solutions :

I : 1 M aqueous glucose solution
II : 1M aqueous sodium chloride solution
III : 1M aqueous ammonium phosphate solution
IV : 1M benzoic acid in benzene

Select correct statements for the above solutions :

(A) All are isotonic solutions
(B) III is hypertonic of I, II and IV
(C) IV is hypotonic of I, II and III
(D) II is hypotonic of III but hypertonic of I and IV

15.✍ Which facts are true when we use van't Hoff equation PV = nST for osmotic pressure P of dilute solutions?

(A) The equation is identical to that of ideal gas equation

(B) The solute particles in solution are analogous to the gas molecules and the solvent is analagous to the empty space between the gas molecules

(C) Solute molecules are dispersed in the solvent the way the gas molecules are dispersed in empty space

(D) The equation is not identical to that of ideal gas equation

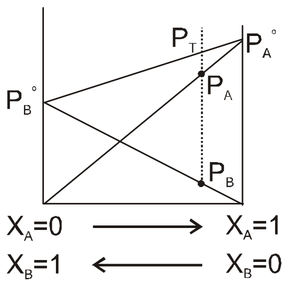
PART - IV : COMPREHENSIONS

Read the following passage carefully and answer the questions.

Comprehension # 1

$P_A = x_A P_A^\circ$ & $P_B = x_B P_B^\circ$

$P_T = x_A P_A^\circ + x_B P_B^\circ$ (Note : $P_A^\circ > P_B^\circ$; A is more volatile than B)



Vapour pressure of mixtures of Benzene (C_6H_6) & toluene (C_7H_8) at 50ºC are given by $P_M = 179\ X_B + 92$, where X_B is mole fraction of C_6H_6.

1.✍ What is vapour pressure of pure liquids ?

(A) $P_B^\circ = 92$ mm, $P_T^\circ = 179$ mm (B) $P_B^\circ = 271$ mm, $P_T^\circ = 92$ mm

(C) $P_B^\circ = 180$ mm, $P_T^\circ = 91$ mm (D) none of these

2.✍ Vapour pressure of liquid mixture obtained by mixing 936 g C_6H_6 & 736 g tolene is :

(A) 300 mm Hg (B) 250 mm Hg

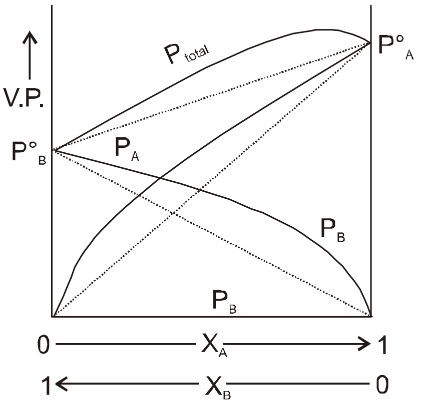
(C) 199.4 mm Hg (D) 180.6 mm Hg

Comprehension # 2

Answer the questions (given below) which are based on the following diagram.

Consider some facts about the above phase diagram :

Vapour pressure diagram for real solutions of two liquids A and B that exhibit a positive deviation from Raoult's law. The vapour pressure of both A and B are greater than predicted by Raoult's law. The dashed lines represented the plots for ideal solutions.



3.✍ A : This is observed when A...B attractions are greater than average of A...A and B...B attraction:

B : ΔH_{mix} = +ve, ΔV_{mix} = +ve

C : Boiling point is smaller than expected such that vaporisation is increased

D : Mixture can form azeotropic mixture

Select correct facts

(A) A, B, C (B) B, C, D (C) A, C, D (D) A, B, C, D

4.✍ Total vapour pressure of mixture of 1 mol of volatile component A (p°_A = 100 mm Hg) and 3 mol of volatile component B (p°_B = 60 mm Hg) is 75 mm. For such case :

(A) There is positive deviation from Raoult's law

(B) Boiling point has been lowered

(C) Force of attraction between A and B is smaller than that between A and A or between B and B.

(D) All the above statements are correct.

Comprehension # 3

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.

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

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

6. The molality the solution is -

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

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

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

;

Exercise # 3

*** Marked Questions may have more than one correct option.**

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. 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 of 298 K and 5 atm pressure is : **[JEE 2009, 3/160]**
(A) 4×10^{-4} (B) 4.0×10^{-5} (C) 5.0×10^{-4} (D) 4.0×10^{-6}

2. The freezing point (in ºC) 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, 3/180]**
(A) -2.3×10^{-2} (B) -5.7×10^{-2} (C) -5.7×10^{-3} (D) -1.2×10^{-2}

3. 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 2ºC. 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})**[IIT 2012, 3/136]**
(A) 724 (B) 740 (C) 736 (D)718

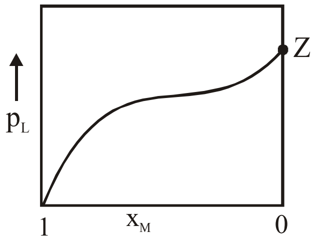
4.* Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is (are) : **[JEE(Advanced) 2013, 4/120]**
(A) ΔG is positive (B) ΔS_{system} is positive (C) $\Delta S_{surroundings} = 0$ (D) $\Delta H = 0$

5. **MX_2** dissociates into **M^{2+}** and **X^-** ions in an aqueous solution, with a degree of dissociation (α) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is **[JEE(Advanced) 2014, 3/120]**

6. If the freezing point of a 0.01 molal aqueous solution of a cobalt(III) chloride-ammonia complex (which behaves as a strong electrolyte) is –0.0558ºC, the number of chloride(s) in the coordination sphere of the complex is [K_f of water = 1.86 K kg mol^{-1}] **[JEE(Advanced) 2015 4/168]**

7. 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

8. 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

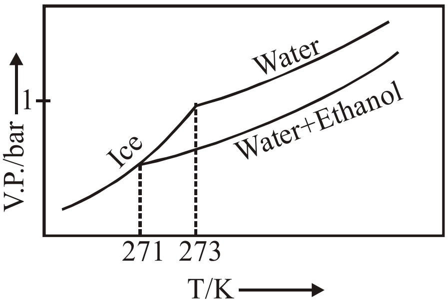
(B) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when $x_L \to 0$

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

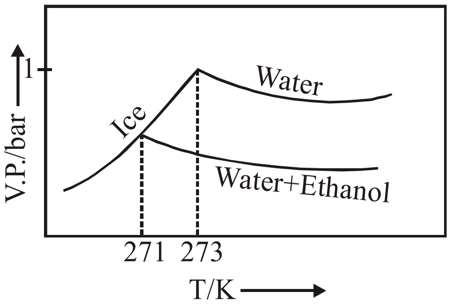
(D) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed from $x_L = 0$ to $x_L = 1$

9. 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]**

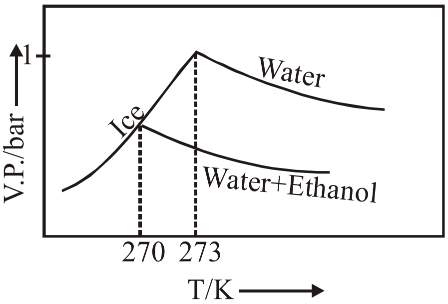
(A)



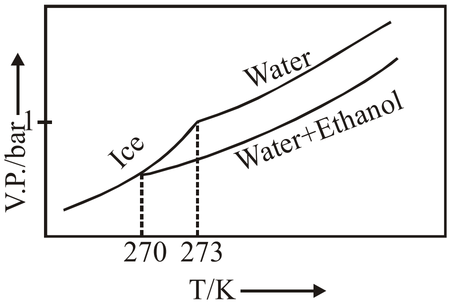
(B)



(C)



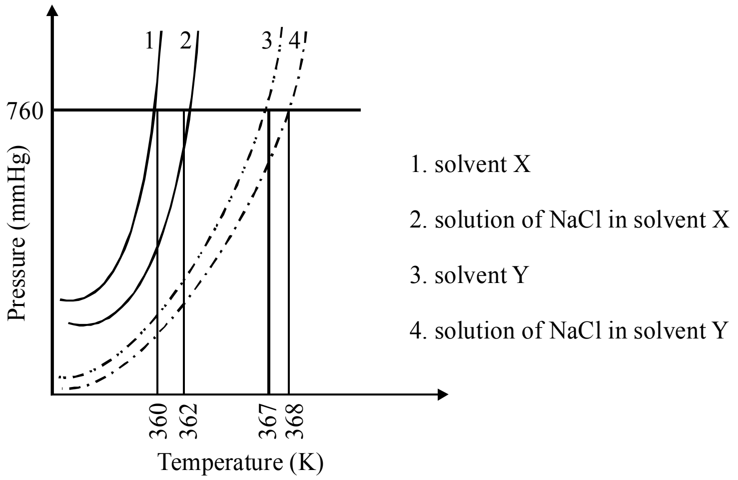
(D)



10. 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)

11. 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]**

12. On dissolving 0.5 g of a non-volatile non-ionic solute to 39 g of benzene, its vapor pressure decreases from 650 mm Hg to 640 mm Hg. The depression of freezing point of benzene (in K) upon addition of the solute is ______ **[JEE-Adv. 2019]**

(Given data : Molar mass and the molal freezing point depression constant of benzene are 78 g mol^{-1} and 5.12 K kg mol^{-1}, respectively)

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

1. If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (ΔT_f), when 0.01 mole of sodium sulphate is dissolved in 1 kg of water, is (K_f = 1.86 K kg mol^{-1}) **[AIEEE-2010, 4/144]**

(1) 0.0372 K (2) 0.0558 K
(3) 0.0744 K (4) 0.0186 K

2. On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively. Vapour pressure of the solution obtained by mixing 25.0 g of heptane and 35 g of octane will be (molar mass of heptane = 100 g mol^{-1} and of octane = 114 g mol^{-1}) **[AIEEE-2010, 4/144]**

(1) 72.0 kPa (2) 36.1 kPa
(3) 96.2 kPa (4) 144.5 kPa

3. K_f for water is 1.86 K kg mol^{-1}. If your automobile radiator holds 1.0 kg of water, how may grams of ethylene glycol ($C_2H_6O_2$) must you add to get the freezing point of the solution lowered to –2.8ºC ?

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

4. 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 solution, assuming all salts to be strong electrolytes ? **[AIEEE 2014, 4/120]**

(1) They all have the same osmotic pressure.
(2) 0.100 M $Mg_3(PO_4)_2$(aq) has the highest osmotic pressure.
(3) 0.125 M Na_3PO_4(aq) has the highest osmotic pressure.
(4) 0.500 M C_2H_5OH(aq) has the highest osmotic pressure.

5. The vapour pressure of acetone at 20ºC is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20ºC, its vapour pressure was 183 torr. The molar mass (g mol^{-1}) of the substance is: **[JEE(Main) 2015, 4/120]**

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

6. 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

7. 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

8. 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

9. 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%

10. 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

11. 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

12. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point ? **[JEE (MAIN)-2018]**

(1) $[Co(H_2O)_5Cl]Cl_2.H_2O$ (2) $[Co(H_2O)_4Cl_2]Cl.2H_2O$

(3) $[Co(H_2O)_3Cl_3].3H_2O$ (4) $[Co(H_2O)_6]Cl_3$

13. 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) $\frac{1}{4}$

14. 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

15. Which one of the following statements regarding Henry's law is not correct ?

[JEE (MAIN-2019_JAN-ONLINE]

(1) The value of K_H increases with increase of temperatrue and K_H is function of the nature of the gas

(2) Higher the value of K_H at a given pressure, higher is the solubility of the gas in the liquids.

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

(4) Different gases have different K_H (Henry's law constant) values at the same temperature.

16. A solution containing 62 g ethylene glycol in 250 g water is cooled to –10°C. If K_f for water is 1.86 K kg mol^{-1}, the amount of water (in g) separated as ice is : **[JEE (MAIN-2019_JAN-ONLINE]**

(1) 32 (2) 48 (3) 16 (4) 64

17. The vapour pressures of pure liquids A and B are 400 and 600 mmHg, respectively at 298K. On mixing the two liquids, the sum of their initial volumes is equal to the volume of the final mixture. The mole fraction of liquid B is 0.5 in the mixture. The vapour pressure of the final solution, the mole fraction of components A and B in vapour phase, respectively are- **[JEE (MAIN-2019_April-ONLINE]**

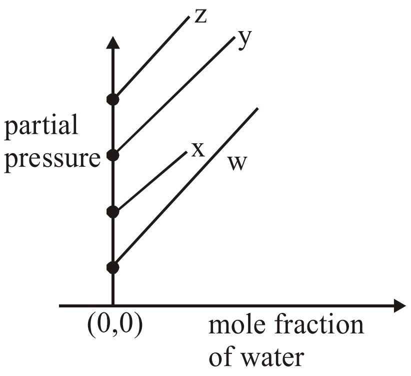
(1) 500 mmHg, 0.5, 0.5 (2) 450 mmHg, 0.4, 0.6

(3) 450 mmHg, 0.5, 0.5 (4) 500 mmHg, 0.4, 0.6

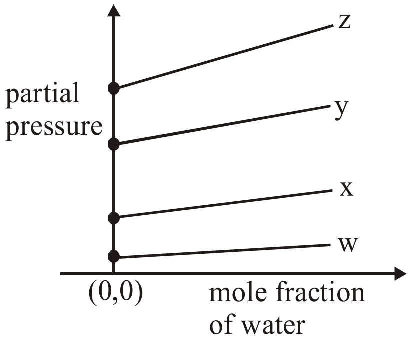
18. For the solution of the gases w, x, y and z in water at 298K, the Henrys law constants (K_H) are 0.5, 2, 35 and 40 kbar, respectively. The correct plot for the given data is :-

[JEE (MAIN-2019_April-ONLINE]

(1)



(2)



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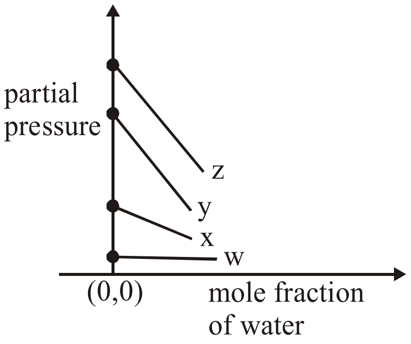

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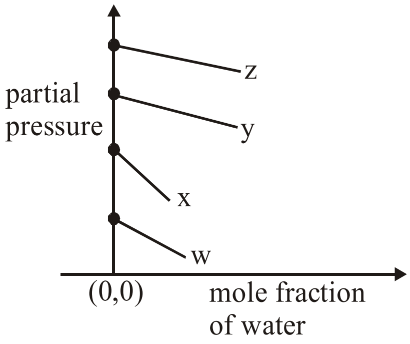


19. At 35° C, the vapour pressure of CS_2 is 512 mm Hg and that of acetone is 344 mm Hg. A solution of CS_2 in acetone has a total vapour pressure of 600 mm Hg. The false statement amongst the following is :

[JEE (MAIN-2020_Jan-ONLINE]

(1) Heat must be absorbed in order to produce the solution at 35°C
(2) Raoult's law is not obeyed by this system
(3) A mixture of 100 mL CS_2 and 100 mL acetone has a volume < 200 mL
(4) CS_2 and acetone are less attracted to each other than to themselves.

20. Two open beakers one containing a solvent and the other containing a mixture of that solvent with a non volatile solute are together sealed in a container. Over time : [JEE (MAIN-2020_Jan-ONLINE]

(1) the volume of the solution decreases and the volume of the solvent increases
(2) the volume of the solution and the solvent does not change
(3) the volume of the solution increases and the volume of the solvent decreases
(4) the volume of the solution does not change and the voluem of the solvent decreases

ANSWER KEY

EXERCISE # 1

PART - I

A-1. 0.04 g/mL

A-2. (i) 22.12%, (ii) 0.035 (iii) $Na^+ = 4$ m, $SO_4^{2-} = 2$ m

A-3. Molality = 11.44 m, Molarity = 7.55 M

B-1. Some of the characteristics of supersaturated solution are given below
(i) If a crystal of solute is added to supersaturated solution, crystallisation occurs rapidly.
(ii) Supersaturated solutions contain more solute than they should have at a particular temperature.

B-2. The overall energy change associated with dissolution depends on the relative magnitude of the solute–solute , solvent–solvent and solute–solvent interactions. The process is exothermic if the new interaction release more energy than disrupting the old interactions requires, it is endothermic if opposite is true.

C-1. (i) > (ii) > (iii)

C-2. $P_{O_2} = 810$ mm Hg, $P_{H_2O} = 355$ mm Hg , $P_{total} = 1165$ mm Hg

D-1. **0.04** **D-2.** 0.716 mmol. **E-1.** 5.15 g

E-2. $\frac{W_W}{W_N} = 3.973$ **F-1.** 27.3 mole %

F-**2.**_ $P_X^0 = 55$ cmHg, $P_Y^0 = 80$ cmHg F-**3.** 14.16 mole percent benzene

F-**4.**_ $P_R^0 = 0.8$ bar, $P_S^0 = 0.4$ bar **F-5.** $p_A{}^0 = 400$ mm of Hg, $p_B{}^0 = 600$ mm of Hg

G-1. V < 80ml.

G-2.✍ There is positive deviation from Raoult's law, $\Delta S > 0$.

H-1.✍

Solute	Dissociation / association reaction	Degree of dissociation / association	n	i
NaCl	$NaCl \rightarrow Na^+ + Cl^-$	1	2	2
H_2SO_4	$H_2SO_4 \rightarrow 2H^+ + SO_4{}^{2-}$	1	3	3
CH_3COOH (in water)	$CH_3COOH \rightarrow H^+ + CH_3COO^-$	0.2	2	1.2
CH_3COOH (in benzene)	$2CH_3COOH \rightarrow (CH_3COOH)_2$	0.5	0.5	0.75
Glucose	No association or dissociation	No association or dissociation	Not defined	1
KBr	$KBr \rightarrow K^+ + Br^-$	0.8	2	1.8
A	$3A \rightarrow A_3$	1	0.33	0.33

H-2. 75% **I-1.**_ **0.25** **I-2.** 746.2 mm of Hg **I-3.**_ **0.32 m**

J-1. **(a)** M = 94.52, **(b)** m = 135 **J-2.** 232 **J-3.** S_8

J-4. 10.33°C **K-1.** (a) Urea < NaCl < Na_2SO_4 < Na_3PO_4 (b) 6.15 atm **K-2.** $\alpha = 0.81$

K-3. 3.69 atm **K-4.** Volume must have been made 5 times

PART - II

A-1.	(B)	**B-1.**	(B)	**B-2.**	(B)	**C-1.**	(B)	**C-2.**	(C)	**C-3.**	(B)	**C-4.**	(B)
D-1.	(C)	**D-2.**	(B)	**D-3.**	(D)	**D-4.**	(B)	**E-1.**	(C)	**E-2.**	(D)	**F-1.**	(B)
F-2.	(C)	**F-3.**	(C)	**F-4.**	(A)	**F-5.**	(A)	**F-6.**	(c)	**G-1.**	(C)	**G-2.**	(A)
G-3.	(A)	**G-4.**	(C)	**G-5.**	(A)	**G-6.**	(C)	**H-1.**	(C)	**H-2.**	(B)	**H-3.**	(B)
H-4.	(B)	**I-1.**	(A)	**I-2.**	(B)	**I-3.**	(B)	**I-4.**	(C)	**I-5.**	(B)	**J-1.**	(A)
J-2.	(A)	**J-3.**	(A)	**J-4.**	(A)	**J-5.**	(C)	**J-6.**	(D)	**J-7.**	(A)	**J-8.**	(B)
K-1.	(C)	**K-2.**	(C)	**K-3.**	(A)	**K-4.**	(D)	**K-5.**	(C)	**K-6.**	(A)		

PART - III

1. (A) → (r) ; (B) → (s) ; (C) → (q) ; (D) → (p)

2. (A) – (p, s, r); (B) – (p, q, t); (C) – (p); (D) – (p, q, t)

3. (A) – q, s ; (B) – q, s ; (C) – q, s ; (D) – q, s

EXERCISE # 2

PART - I

1.	(C)	**2.**	(B)	**3.**	(C)	**4.**	(B)	**5.**	(C)	**6.**	(B)	**7.**	(B)
8.	(B)	**9.**	(C)	**10.**	(A)	**11.**	(B)	**12.**	(D)	**13.**	(B)		

PART - II

1.	18	**2.**	12 mol/litre.	**3.**	21	**4.**	20	**5.**	14	**6.**	4 (A,B,C,D)
7.	2	**8.**	3	**9.**	48	**10.**	43	**11.**	2	**12.**	60
13.	4										

PART - III

1.	(ABD)	**2.**	(ABD)	**3.**	(ABCD)	**4.**	(AC)	**5.**	(A)	**6.**	(AB)
7.	(AB)	**8.**	(ABC)	**9.**	(AB)	**10.**	(B)	**11.**	(BD)	**12.**	(AB)
13.	(AD)	**14.**	(BCD)	**15.**	(ABC)						

PART - IV

1.	(B)	**2.**	(C)	**3.**	(B)	**4.**	(D)	**5.**	(B)	**6.**	(C)
7.	(D)										

EXERCISE # 3

PART - I

1.	(A)	**2.**	(A)	**3.**	(A)	**4.**	(BCD)	**5.**	2	**6.**	1	**7.**	(AB)
8.	(AC)	**9.**	(D)	**10.**	19	**11.**	0.05	**12.**	0.97 to 1.06				

PART - II

1.	(2)	**2.**	(1)	**3.**	(2)	**4.**	(1)	**5.**	(2)	**6.**	(1)	**7.**	(3)
8.	(4)	**9.**	(4)	**10.**	(1)	**11.**	(2)	**12.**	(3)	**13.**	(1)	**14.**	(4)
15.	(2)	**16.**	(4)	**17.**	(4)	**18.**	(3)	**19.**	(3)	**20.**	(3)		

✍ **Marked Questions may have for Revision Questions.**

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Reliable students.

Self Assessment Test

PART- 1 : PAPER JEE (MAIN) PATTERN

SECTION–I : (Maximum Marks : 80)

- This section contains **TWENTY** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :
  Full Marks : +4 If only the bubble corresponding to the correct option is darkened.
  Zero Marks : 0 If none of the bubbles is darkened.
  Negative Marks : –1 In all other cases

1.✍ Colligative properties have many practical uses, some of them may be :
I : Melting of snow by salt
II : Desalination of sea water
III : Determination of molar mass
IV : Determination of melting point and boiling point of solvent
Actual practical uses are :
(A) I, II (B) III, IV (C) I, II, III (D) II, III, IV

2.✍ If $pK_a = -\log K_a = 4$, and $K_a = Cx^2$ then Van't Hoff factor for weak monobasic acid when C = 0.01 M is :
(A) 1.01 (B) 1.02 (C) 1.10 (D) 1.20

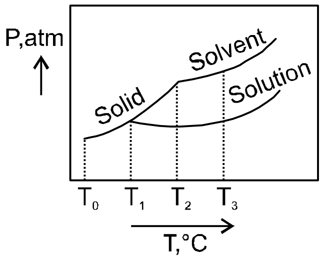
3. Elevation in b.p. of an aqueous urea solution is 0.52°. (K_b = 0.52° mol^{-1} kg) Hence, mole-fraction of urea in this solution is :
(A) 0.982 (B) 0.567 (C) 0.943 (D) 0.018

4.✍ Sea water is found to contain 5.85 % NaCl and 9.50% $MgCl_2$ by weight of solution. Calculate its normal boiling point assuming 80% ionisation for NaCl and 50% ionisation of $MgCl_2$ ($K_b(H_2O)$ = 0.51 kgmol^{-1} K).
(A) T_b = 101.9°C (B) T_b = 102.3°C
(C) T_b = 108.5°C (D) T_b = 110.3°C

5.✍ An aqueous solution of a solute AB has b.p. of 101.08°C (AB is 100% ionised at boiling point of the solution) and freezes at – 1.80°C. Hence, AB ($K_b / K_f = 0.3$)
(A) is 100% ionised at the f.p. of the solution (B) behaves as non-electrolyte at the f.p. of the solution
(C) forms dimer (D) none of the above

6.✍ Density of 1M solution of a non-electrolyte $C_6H_{12}O_6$ is 1.18 g/mL. If K_f (H_2O) is 1.86° mol^{-1} kg, solution freezes at :
(A) – 1.58°C (B) – 1.86°C
(C) – 3.16°C (D) 1.86°C

7.✍ What is the normal freezing point of the solution represented by the phase diagram ?



(A) T_1 (B) T_2 (C) T_3 (D) T_0

8. Total vapour pressure of mixture of 1 mol of volatile component A ($p_A°$ = 100 mmHg) and 3 mol of volatile component B ($p_B°$ = 60 mmHg) is 75 mm. For such case :
(A) there is positive devitation from Raoult's low
(B) boiling point has been lowered
(C) force of attraction between A and B is smaller than that between A and A or between B and B
(D) all the above statements are correct

9. Select correct statements :
(A) The fundamental cause of all colligative properties is the higher entropy of the solution relative to that of the pure solvent
(B) The freezing point of hydrofluoride solution is larger than that of equimolal hydrogen chloride solution
(C) 1M glucose solution and 0.5 M NaCl solution are isotonic at a given temperature
(D) All are correct statements

10. An azeotropic solution of two liquids has a boiling point lower than either of them when it :
(A) shows negative deviation from Raoult's law (B) shows positive deviation from Raoult's low
(C) shows ideal behaviour (D) is saturated

11.✍ Depression of freezing point of 0.01 molal aq. CH_3COOH solution is 0.02046°. 1 molal urea solution freezes at – 1.86°C. Assuming molality equal to molarity, pH of CH_3COOH solution is :
(A) 2 (B) 3 (C) 3.2 (D) 4.2

12. Which of the following azeotropic solutions has the boiling point more than boiling point of the constituents A and B ?
(A) CH_3CH_2OH and CH_3COCH_3 (B) CS_2 and CH_3COCH_3
(C) $CHCl_3$ and CH_3COCH_3 (D) CH_3CHO and CS_2

13.✍ The depression of freezing points of 0.05 molal aqueous solution of the following compounds are measured.
1. NaCl 2. K_2SO_4 3. $C_6H_{12}O_6$ 4. $Al_2(SO_4)_3$
Which one of the above compounds will exhibit the maximum depression of freezing point ?
(A) 3 (B) 2 (C) 4 (D) 1

14. On mixing 10 mL of acetone with 40 mL of chloroform , the total volume of the solution is :
(A) < 50 mL (B) > 50 mL (C) = 50 mL (D) Cannot be predicted

15.✍ Select correct statement ?
(A) Heats of vaporisation for a pure solvent and for a solution are similar because similar intermolecular forces between solvent molecules must be overcome in both cases
(B) Entropy change between solution and vapour is smaller than the entropy change between pure solvent and vapour
(C) Boiling point of the solution is larger than that of the pure solvent
(D) All are correct statements

16.✍ What will be the molecular weight of NaCl determined experimentally from elevation in the boiling point or depression in freezing point method ?
(A) < 58.5 (B) > 58.5 (C) = 58.5 (D) None of these.

17. Which characterises the weak intermolecular forces of attraction in a liquid ?
(A) High boiling point (B) High vapour pressure
(C) High critical temperature (D) High heat of vaporization

18.✍ On the basis of intermolecular forces predict the correct order of decreasing boiling points of the compounds:
(A) $CH_3OH > H_2 > CH_4$ (B) $CH_3OH > CH_4 > H_2$
(C) $CH_4 > CH_3OH > H_2$ (D) $H_2 > CH_4 > CH_3OH$

19.✍ During depression of freezing point in a solution the following are in equilibrium :
(A) Liquid solvent, solid solvent (B) Liquid solvent, solid solute
(C) Liquid solute, solid solute (D) Liquid solute, solid solvent

20. Which of the following liquid pairs shows a positive deviation from Raoult's law ?
(A) Acetone – chloroform (B) Benzene – methanol
(C) Water – nitric acid (D) Water – hydrochloric acid

SECTION-II : (Maximum Marks: 20)

- This section contains **FIVE** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:

  Full Marks : +4 If ONLY the correct numerical value is entered as answer.

21. Calculate mole fraction of $C_3H_5(OH)_3$ in a solution of 36 g of water and 46 g of glycerine.

22.✍ Mole fraction of a non-electrolyte in aqueous solution is 0.07. If K_f is 1.86° mol^{-1} kg. Calculate depression in freezing point (ΔT_f in °C)

23.✍ The vapour pressure of a pure liquid A is 40 mmHg at 310 K. The vapour pressure of this liquid in a solution with liquid B is 32 mmHg. Calculate mole fraction of A in the solution, if it obeys Raoult's law.

24. Calculate mole fraction of the toluene in the vapour phase which is in equilibrium with a solution of benzene (p° = 120 Torr) and toluene (p° = 80 Torr) having 2.0 mol of each.

25.✍ A 0.50 molal solution of ethylene glycol in water is used as coolant in a car. If the freezing point constant of water is 1.86° per molal, at which temperature (in °C) will the mixture freeze ?

PART 2 : PAPER JEE (ADVANCED) PATTERN

SECTION-I : (Maximum Marks : 12)

- This section contains **FOUR** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :

  Full Marks : +3 If only the bubble corresponding to the correct option is darkened.
  Zero Marks : 0 If none of the bubbles is darkened.
  Negative Marks : –1 In all other cases

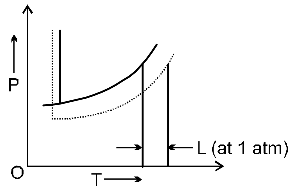
1. Assuming each salt to be 90% dissociated which of the following will have highest osmotic pressure ?
(A) Decimolar $Al_2(SO_4)_3$
(B) Decimolar $BaCl_2$
(C) Decimolar Na_2SO_4
(D) A solution obtained by mixing equal volumes of (A), (B) and (C) and filtering.

2.✍ The melting points of most of the solid substances increases with an increase of pressure acting on them. However, ice melts at a temperature lower than its usual melting point , when the pressure increases. This is because :

(A) Ice is less dense than water
(B) Pressure generates heat
(C) The bonds break under pressure
(D) Ice is not a true solid

3. The phase diagrams for the pure solvent (solid lines) and the solution (non-volatile solute, dashed line) are recorded below :

The quantity indicated by L in the figure is :



(A) Δp
(B) ΔT_f
(C) $K_b m$
(D) $K_f m$

4.✍ Available are 1L of 0.1 M NaCl and 2L of 0.2 M $CaCl_2$ solutions. Using **<u>only these two solutions</u>** what maximum volume of a solution can be prepared having $[Cl^-] = 0.34$ M exactly. Both electrolytes are strong

(A) 2.5 L
(B) 2.4 L
(C) 2.3 L
(D) None of these

SECTION-II : (Maximum Marks: 32)

- This section contains **EIGHT** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:

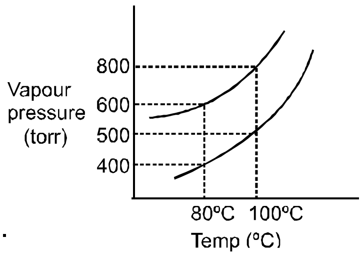
Full Marks : +4 If only (all) the correct option(s) is (are) chosen.
Partial Marks : +3 If all the four options are correct but ONLY three options are chosen.
Partial Marks : +2 If three or more options are correct but ONLY two options are chosen, both of which are correct options.
Partial Marks : +1 If two or more options are correct but ONLY one option is chosen and it is a correct option.
Zero Marks : 0 If none of the options is chosen (i.e. the question is unanswered).
Negative Marks : –1 In all other cases.

- **For Example :** If first, third and fourth are the **ONLY** three correct options for a question with second option being an incorrect option; selecting only all the three correct options will result in +4 marks. Selecting only two of the three correct options (e.g. the first and fourth options), without selecting any incorrect option (second option in this case), will result in +2 marks. Selecting only one of the three correct options (either first or third or fourth option), without selecting any incorrect option (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), with or without selection of any correct option(s) will result in –1 marks.

5.✍ For K_H, Henry's constant, which are correct ?

(A) K_H is characteristic constant for a given gas–solvent system.
(B) Higher is the value of K_H, lower is solubility of gas for a given partial pressure of gas.
(C) K_H has temperature dependence.
(D) K_H increases with temperature.

6.✍ The vapour pressure of ideal solution of benzene and toluene is 550 torr at 80°C then what would be correct statement about same solution at 100°C.



(A) Vapour pressure of solution = 725 torr
(B) at 725 torr pressure at 90°C, no vapour form
(C) Composition of vapour is $\frac{2}{11}$ and $\frac{9}{11}$
(D) Composition of liquid remain same at equilibrium condition at any temp.

7. Select incorrect statement :

(A) Na^+ and K^+ ions are responsible for maintaining isotonic property inside and outside of the cell of organism.

(B) Aquatic species are more comfortable in lakes present at sea level in comparison to lakes present at high altitude.

(C) Solubility of N_2 decreases, in presence of He when oxygen cylinder is utilised by Scuba divers.

(D) The K_H value of CO_2 is higher than K_H of N_2.

8.✍ Following is false when in a volatile solvent A and a non volatile solute B is mixed (where symbols have their usual meaning):

(A) $\frac{P_A^0 - P_B^0}{P_A} = \frac{n_B}{n_A}$ (B) $\frac{P_A^0 - P_B^0}{P_A} = \frac{n_B}{n_A + n_B}$

(C) $P_A^0 = \frac{P_A}{1 - X_B}$ (D) $\frac{P_A^0 - P_A}{P_A} = \frac{n_B}{n_A}$

9. 0.2 moles of A and 0.3 moles of B are taken in separate beakers and enclosed in chamber I. Another 0.2 moles of A and 0.3 moles of B are mixed in a beaker and enclosed in chamber II. At equilibrium. Which of the following are not true. (A and B are volatile liquids and they form ideal solution on mixing)

(A) The vapour pressure in chamber I is greater than vapour pressure in chamber II.

(B) The vapour pressure in chamber I is less than vapour pressure in chamber II.

(C) The vapour pressure in both chambers are equal.

(D) The vapour pressure in chamber II can not be determined.

10.✍ For a dilute solution having molality m of a given solute in a solvent of mol.wt. M , b.pt. T_b and heat of vaporisation per mole ΔH ; $\left[\frac{\partial T_b}{\partial m}\right]_{m \to 0}$ is equal to :

(A) Molal elevation constant of solvent

(B) $\frac{RT_b^2 M}{\Delta_{vap} H}$; where M in kg Δ_{vap} H and R in J mol^{-1}

(C) $\frac{RT_b^2 M}{\Delta_{vap} S}$; where M in kg ; Δ_{vap}S and R in J mol^{-1}

(D) $\frac{RT_b^2 M}{1000\,\Delta_{vap} H}$; where M in g ; R and Δ_{vap}H expressed in same unit of heat.

11. At 40°C, vapour pressure in Torr of methanol and ethanol solution is P = 119x + 135 where x is the mole fraction of methanol. Hence

(A) vapour pressure of pure methanol is 119 Torr

(B) vapour pressure of pure ethanol is 135 Torr

(C) vapour pressure of equimolar mixture of each is 127 Torr

(D) mixture is completely immiscible

12. For the given electrolyte A_xB_y, the degree of dissociation 'α' can be given as

(A) $\alpha = \frac{i - 1}{x + y - 1}$ (B) $i = (1 - \alpha) + x\alpha + y\alpha$ (C) $\alpha = \frac{1 - i}{1 - x - y}$ (D) None

SECTION-III : (Maximum Marks: 18)

- This section contains **SIX** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the **second decimal place**; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.
  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks	: +3	If ONLY the correct numerical value is entered as answer.
Zero Marks	: 0	In all other cases.

13. A very small amount of a non-volatile solute (non-associative, non-dissociative) is dissolved in 100 cm^3 of a solvent. At room temperature, vapour pressure of this solution is 98.7 mm of Hg while that of pure solvent is 100 mm of Hg. If the freezing temperature of this solution is 0.72 K lower than that of pure solvent, what is the value of cryoscopic constant of solvent (in K Kg/mol) ? Round off your answer to the nearest whole number. Report your answer as 0 (zero) if you find data insufficient.
Given : Molar mass of solvent = 78 g/mol.

14. At 10ºC the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25ºC, when the osmotic pressure is found to be 105.3 mm. Determine extent of dilution.

15.✍ In aqueous solution of 1×10^{-3} molal $K_x[Fe(CN)_6]$ depression in freezing point is 7.2×10^{-3} K. Determine sum of primary and secondary valency of complex (K_f of H_2O = 1.8 K Kg/mole). (Assume that % ionisation of complex is 100%)

16.✍ Calculate molarity of final solution obtained by mixing I and II HNO_3 solution.

	I	II
$\%\frac{w}{w}$	12.6	6.3
d (in g/mL)	1.5	1
Volume (in L)	5	5

17.✍ 8×10^{-x} moles of gas A is dissolved in 36 mL of water when pressure of gaseous mixture above water is 4 atm. Mole percentage of gas A in mixture is 25. Henry constant for gas A in water is 2.5×10^3 atm. Find x.

18.✍ A solution containing 0.1 g of a non volatile organic substance P(Molecular mass 100) in 100 g of benzene raises the boiling point of benzene by 0.2ºC while a solution containing 0.1 g of another non volatile substance Q in same amount of benzene raises the boiling point of benzene by 0.4ºC. If ratio of molecular masses of P and Q is $\frac{x}{y}$ then. Find minimum value of x + y.

PART - 3 : OLYMPIAD (PREVIOUS YEARS)

1. Solutions having the same osmotic pressure are called **[NSEC-2000]**
(A) isotonic solutions (B) molar solutions
(C) hypotonic solutions (D) ideal solutions

2. A colligative property of a solution depends on the **[NSEC-2000]**
(A) arrangement of atoms in solute molecule. (B) total number of molecules of solute and solvent
(C) number of molecules of solute in solution. (D) mass of the solute molecules.

3. When 0.6 gm of urea dissolved in 100g of water, the water will boil at (K_b for water = 0.52 kJ. mol^{-1} and normal boiling point of water = 100ºC) : **[NSEC-2001]**
(A) 373.052 K (B) 273.52 K (C) 372.48 K (D) 273.052 K

4. The osmotic pressure of a solution is given by the equation : **[NSEC-2001]**
(A) $p = \frac{CR}{T}$ (B) $\frac{\pi}{C} = RT$ (C) $p = \frac{CT}{R}$ (D) $p = \sqrt{C} \cdot \frac{R}{T}$

5. The relative lowering of vapour pressure is equal to the mole fraction of the solute. This is the statement of: **[NSEC-2001]**
(A) Raoult's law (B) Boyle's law
(C) Osmotic pressure law (D) Graham's law

6. Azeotropes are : **[NSEC-2002]**
(A) liquid mixtures which distil unchanged in composition
(B) liquids which can mix with each other in all proportions
(C) solids which form solid solutions of definite compositions
(D) gases which can be separated.

7. Swimming for a long time in salt water makes the skin of one's finger tips wrinkled. Which one of the following properties is responsible for this observation ? **[NSEC-2002]**
(A) osmosis (B) dialysis (C) electrodialysis (D) coagulation.

8. A 2% solution of glucose has the same elevation in the boiling point as that of a 5% solution of a non-volatile solute. The molar mass of the solute is : **[NSEC-2003]**
(A) 180 (B) 450 (C) 72 (D) 18

9. A 1.0 molal solution with the lowest freezing point is that of : **[NSEC-2004]**
(A) $FeCl_3$ (B) HCl (C) KCl (D) $MgCl_2$.

10. From among the following, the aqueous solution which has the highest freezing point depression is : **[NSEC-2005]**
(A) 0.1 M $Sr(NO_3)_2$ (B) 0.1 M KCl
(C) 0.1 M HNO_3 (D) 0.1 M glucose.

11. In chemical industries, the preferred method of purification of liquids is : **[NSEC-2006]**
(A) differential extraction (B) fractional distillation
(C) chromatography (D) leaching.

12. The solubility of a gas in a liquid is driectly proportional to the partial pressure of the gas over the solution. This statement is known as: **[NSEC-2007]**
(A) Raoult's law (B) Henry's law
(C) Boyle's law (D) Charles' and Gay Lussac's Law

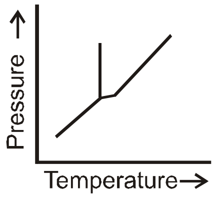
13. Which of the following is not a colligative property ? **[NSEC-2007]**
(A) solubility. (B) vapor pressure lowering.
(C) boiling point elevation. (D) osmotic pressure.

14. Which of the following has the lowest freezing point and the highest boiling point? **[NSEC-2007]**
(A) 1.5 m magnesium phosphate (B) 1.0 m sodium chloride
(C) 1.5 m aluminum nitrate (D) 1.5 m calcium chloride

15. A solution of urea was found to be isotonic with a solution of salt XY of molecular weight 74.6. If 0.15 moles of urea are dissolved in a certain volume V mL of the isotonic solution, the amount of salt in the solution will be : **[NSEC-2008]**
(A) 22.4g (B) 5.6 g (C) 11.2 g (D) 7.46 g

16. The desalination of sea water involves the phenomenon of : **[NSEC-2008]**
(A) Sedimentation (B) Distillation (C) Precipitation (D) Reverse osmosis

17. According to this phase diagram, which phases can exist at pressures lower than the triple point pressure ? **[NSEC-2008]**



(A) gas only
(B) solid and gas only
(C) liquid only
(D) solid and liquid only

18. For a dilute solution, Raoult's law states that : **[NSEC-2009]**
(A) the lowering of vapour pressure is equal to the mole fraction of the solute.
(B) the relative lowering of vapour pressure is equal to the mole fraction of the solute
(C) the vapour pressure of solution is equal to the mole fraction of solution.
(D) the relative lowering of vapour pressure is proportional to the amount of solute in the solution.

19. A mixture of two liquids which boils without change in composition is called **[NSEC-2010]**
(A) Stable mix ture (B) Binary liquid mixture
(C) Azeotropic mixture (D) Zerotropic mixture

20. The aqueous solution having osmotic pressure nearest to that of an equimolar solution of $K_4[Fe(CN)_6]$ is **[NSEC-2010]**
(A) K_2SO_4 (B) Na_3PO_4 (C) $Al_2(SO_4)_3$ (D) $C_6H_{12}O_6$

21. The elevation in boling point of a solution containing 13.44 g of $CuCl_2$ in 1 kg of water is : ($K_b = 0.52$ K kg mol^{-1}) **[NSEC-2011]**
(A) 0.05 (B) 0.10 (C) 0.16 (D) 0.21

22. The freezing point of a solution containing 8.1 g of HBr in 100 g of water, assuming the acid to be 90% ionized is [H = 1, Br = 80, K_f for water = 1.86 K kg mol^{-1}] **[NSEC-2011]**
(A) 0.85ºC (B) –3.53ºC (C) 0ºC (D) –0.35ºC

23. Which of the following observation indicates colligative properties ? **[NSEC-2012]**
I. A 0.5 M NaBr solution has a higher vapour pressure than 0.5 M $BaCl_2$.
II. A 0.5 M NaOH solution freezes at a lower temperature than pure water.
III. Pure water freezes at a higher temperature than pure ethanol.
(A) Only I (B) Only II (C) Only III (D) I and II

24. Osmotic pressure of a 2 % w/v solution of glucose is same as 5% w/v solution of a nonvolatile non-electrolyte solute. The molar mass of the solute is : **[NSEC-2014]**
(A) 180 (B) 450 (C) 72 (D) 45

25. The colligative property used in the determination of molar mass of a polymer is : **[NSEC-2014]**
(A) lowering of the vapour pressure
(B) elevation in the boiling point
(C) depression in the freezing point
(D) osmotic pressure.

26. The vapor pressure of benzene is 53.3 kPa at 60.3ºC, but it fall to 51.5 kPa when 19 g of a nonvolatile organic compound is dissolved in 500g benzene. The molar mass of the nonvolatile compound is **[NSEC-2015]**
(A) 82 (B) 85 (C) 88 (D) 92

27. The vapor pressure of two pure isomeric liquids X and Y are 200 torr and 100 torr respectively at a given temperature. Assuming a solution of these components to obey Raoult's law, the mole fraction of component X in vapor phase in equilibrium with the solution containing equal amounts of X and Y, at the same temperature, is **[NSEC-2015]**
(A) 0.33 (B) 0.50 (C) 0.66 (D) 0.80

28. In cold climate, the water in a radiator of car gets frozen causing damage to the radiator. Ethylene glycol is used as an antifreezing agent. The amount of ethylene glycol that should be added to 5 kg of water to prevent it from freezing at –7ºC is : **[NSEC-2016]**
(Given : K_f for water = 1.86 K mol^{-1} kg ; Molar mass of ethylene gycol = 62 g mol^{-1})
(A) 1165 g (B) 46.7 g (C) 116.7 g (D) 93.4 g

29. Which of the following is correct ? **[NSEC-2017]**
A liquid with
(A) low vapour pressure will have a low surface tension and high boiling point
(B) high vapour pressure will have high intermolecular forces and high boiling point
(C) low vapour pressure will have high surface tension and high boiling point
(D) low vapour pressure will have low surface tension and low boiling point

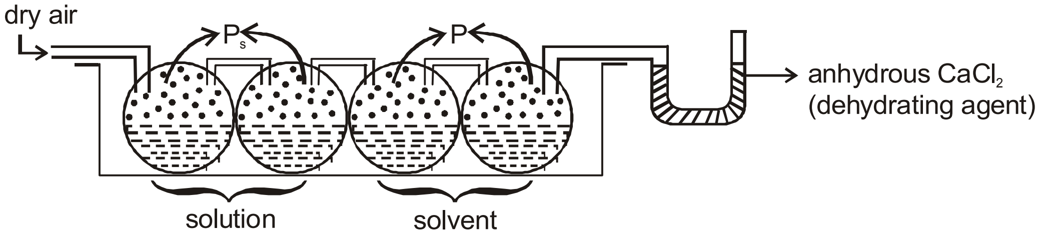
30. About sea water, which of the following statement/s is/are correct? **[NSEC-2019]**
I. Frozen sea water melts at a lower temperature than pure ice
II. Boiling point of sea water increases as it evaporates
III. Sea water boils at a lower temperature than fresh water
IV. Density of sea water at STP is same as that of fresh water
(A) I only (B) I and II (C) I, II and III (D) III only

PART - 4 : ADDITIONAL PROBLEMS

Theory

Ostwald–Walker Method :

Experimental or lab determination of relative lowering of vapoure pressure i.e. $\frac{\Delta P}{P^0}$ or $\frac{\Delta P}{P_s}$.



(i) Initially note down the weights of the solution set, solvent set containers & of dehydrating agent before start of experiment.
(ii) Note down the same weights after the experiment is complete.
Loss of weight of solution containers $\propto P_s$.
Loss of in weight of solvent containers $\propto (P^o - P_s)$
gain in weight of dehydriating agent $\propto P^o$.

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

$$\frac{P^o - P_s}{P_s} = \frac{\text{loss is weight of solvent}}{\text{gain is weight of dehydrating agent}} = \frac{w}{m} \times \frac{M}{W} = (\text{molality}) \times \frac{M}{1000}$$

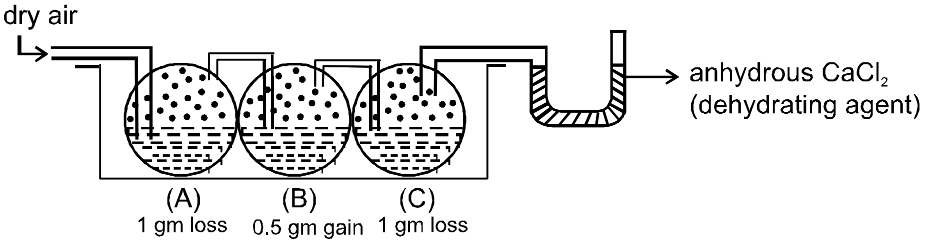
Suppose, dry air was passed through a solution of 5 g of a solute in 80 g of water & then it is passed through pure water. Loss in weight of solution was 2.50 g & loss in weight of pure water was 0.04 g. Then, to find molecular weight of the solute, we have

$$\frac{P^o - P_s}{P_s} = \frac{\text{loss in wt.of solvent}}{\text{loss in wt.of solution}}$$

$$\frac{P^o - P_s}{P_s} = \frac{0.04}{2.50} = \frac{w}{m} \times \frac{M}{W} = \frac{5}{m} \times \frac{18}{80}.$$ Thus. m = molecular weight of the solute = 70 g/mol.

SOLVED EXAMPLE

Example :



If same volume solution of different solute is used then what is order of (a) vapour pressure (b) moles of solute (c) molar mass of solute.

Solution : $P_A \propto 1$ g. ; $P_A - P_B \propto 0.5$ g, $P_B \propto 0.5$ g.

$P_C - P_B \propto 1$ g ; $P_C \propto 1.5$ g.

$P_C > P_A > P_B$; $n_C < n_A < n_B$. ; $M_C > M_A > M_B$.

NUMERICAL TYPE QUESTION

1. Two solutions of A and B are available. The first is known to contain 1 mole of A and 3 moles of B and its total vapour pressure is 1.0 atm. The second is known to contain 2 moles of A and 2 moles of B; its vapour pressure is greater than 1 atm, but it is found that this total vapour pressure may be reduced to 1 atm by the addition of 6 moles of C. The vapour pressure of pure C is 0.80 atm. Assuming ideal solutions and that all these data refer to 25°C, calculate the vapour pressure of pure A and of pure B.

2.✍ Vapour pressure of C_6H_6 and C_7H_8 mixture at 50ºC is given P (mm Hg) = $180X_B + 90$, where X_B is the mole fraction of C_6H_6. A solution is prepared by mixing 936 g benzene and 736 g toluene and if vapours over this solution are removed and condensed into liquid and again brought to the temperature 50ºC, what would be mole fraction of C_6H_6 in the vapour state. (At. wt. of C = 12, H = 1)

3.✍ Twenty grams of a solute are added to 100 g of water at 25ºC. The vapour pressure of pure water is 23.76 mmHg; the vapour pressure of the solution is 22.41 Torr.

(a) Calculate the molar mass of the solute.

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

4✍ Dry air was passed through bulbs containing a solution of 40 grams of non-volatile electrolytic solute in 360 grams of water, then through bulbs containing pure water at the same temperature and finally through a tube in which pumice moistened with strong H_2SO_4 was kept. The water bulbs lost 0.0870 grams and the sulphuric acid tube gained 2.175 grams. Calculate the molecular weight of solute.

5.✍ A 0.01 molal solution of ammonia freezes at – 0.02ºC. Calculate the van't Hoff factor, i and the percentage dissociation of ammonia in water. $(K_{f(H_2O)}) = 1.86$ deg molal^{-1}.

6.✍ 17.4% (w/v) K_2SO_4 solution at 27ºC is isotonic with 5.85% (w/v) NaCl solution at 27ºC. If NaCl is 100% ionised, what is % ionisation of K_2SO_4 in aq. solution ?

7.✍ At 300 K, 40 mL of O_3 (g) dissolves in 100 g of water at 1.0 atm. What mass of ozone (in gram) dissolved in 1600 g of water at a pressure of 4.0 atm at 300 K ?

8. The vapour pressure of pure liquid A at 300 K is 577 Torr and that of pure liquid B is 390 Torr. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.35. Find the mole % of A in liquid.

9.✍ Dry air was successively passed through a solution of 5g solute in 80 g water and then through pure water. The loss in weight of solution was 2.5 g and that of pure water was 0.04 g. What is mol. wt of solute ?

10.✍ 1 g of a monobasic acid dissolved in 200 g of water lowers the freezing point by 0.186ºC. On the other hand when 1 g of the same acid is dissolved in water so as to make the solution 200 mL, this solution requires 125 mL of 0.1 M NaOH for complete neutralization. Calculate % dissociation of acid ? ($K_f = 1.86\ \frac{K-kg}{mol}$)

11.✍ The vapour pressure of fluorobenzene at t°C is given by the equation

$$\log p\ (\text{mm Hg}) = 7.0 - \frac{1250}{t+220}$$

Calculate the boiling point of the liquid in ºC if the external (applied) pressure is 5.26% more than required for normal boiling point. (log 2 = 0.3)

ONLY ONE OPTION CORRECT TYPE

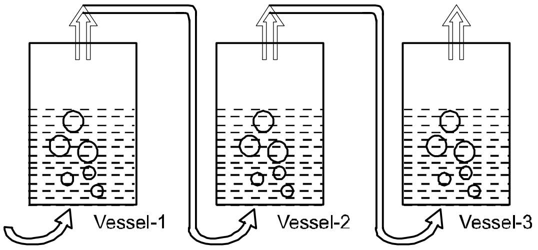
12.✍ Insulin $(C_2H_{10}O_5)_n$ is dissolved in a suitable solvent and the osmotic pressure π of the solution of various concentration (in kg/m^3) is measured at 20ºC. The slope of a plot of π against c is found to be 8.134×10^{-3} (SI units) The molecular weight of the insulin (in kg/mol) is :
(A) 4.8×10^5 (B) 9×10^5 (C) 293×10^3 (D) 8.314×10^5

13. The total concentration of dissolved particles inside red blood cells is approximately 0.30 M and the membrane surrounding the cells is semipermeable. What would the osmotic pressure (in atmosphere) inside the cells become if the cells were removed from the blood plasma and placed in pure water at 298 K ?
(A) 7.34 atm (B) 1.78 atm (C) 2.34 atm (D) 0.74 atm

14.✍ A 20.0 mL sample of $CuSO_4$ solution was evaporated to dryness, leaving 0.967 g of residue. What was the molarity of the original solution ? (Cu = 63.5)
(A) 48.4 M (B) 0.0207 M (C) 0.0484 M (D) 0.303 M

15.✍ Barium ions, CN^- and Co^{2+} form an ionic complex. If that complex is supposed to be 75% ionised in water with vant Hoff factor ' i ' equal to four, then the coordination number of Co^{2+} in the complex can be :
(A) Six (B) Five (C) Four (D) Six and Four both

16.✍ Dry air is slowly passed through three solutions of different concentrations, c_1, c_2 and c_3 ; each containing (non volatile) NaCl as solute and water as solvent, as shown in the Fig. If the vessel 2 gains weight and the vessel 3 loses weight, then



(A) $c_2 > c_3$ (B) $c_1 < c_2$
(C) $c_1 < c_3$ (D) Both (A) and (B)

17.✍ x mole of KCl and y mole of $BaCl_2$ are both dissolved in 1 kg of water. Given that x + y = 0.1 and K_f for water is 1.85 K/molal, what is the observed range of ΔT_f, if the ratio of x to y is varied ?
(A) 0.37º to 0.555º (B) 0.185º to 0.93º (C) 0.56º to 0.93º (D) 0.37º to 0.93º

18.✍ For a solution of 0.849 g of mercurous chloride in 50 g of $HgCl_2(\ell)$ the freezing point depression is 1.24ºC. K_f for $HgCl_2$ is 34.3. What is the state of mercurous chloride in $HgCl_2$? (Hg – 200, Cl – 35.5)
(A) as Hg_2Cl_2 molecules (B) as HgCl molecules
(C) as Hg^+ and Cl^- ions (D) as Hg_2^{2+} and Cl^- ions

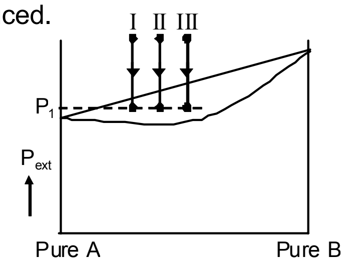
19.✍ The vapor pressures of chlorobenzene and water at different temperatures are

t/ºC	90	100	110
Pº(ϕCl)/mm Hg	204	289	402
Pº(H_2O)/mm Hg	526	760	1075

At what temperature will ϕCl steam-distillation under a total pressure of 800 mmHg?
(A) ≈ 95ºC (B) ≈ 92ºC
(C) ≈ 94ºC (D) ≈ 89ºC

20. A teacher one day pointed out to his students the peculiar fact that water is unique liquid which freezes exactly at 0^0 C and boils exactly at 100^0 C. He asked the students to find the correct statement based on this fact :
(A) Water dissolves anything however sparingly the dissolution may be
(B) Water is a polar molecule
(C) Boiling and freezing temperatures of water were used to define a temperature scale
(D) Liquid water is denser than ice

21.✍ Three different ideal solutions (I, II, III) each containing total 10 moles of A & B in different composition are taken as shown in figure and pressure over the solutions is gradually reduced.
Initially external pressure is same for all three solutions.
At a particular external pressure (P_1), II solution is found to have
$X_A = 0.4$ & $Y_A = 0.8$
(liq composition)(Vap. composition)
Then select correct statement :



(A) At the same external pressure, for solution I, $X_A < 0.4$, $Y_A < 0.8$.
(B) At the same external pressure, for solution III, $X_A > 0.4$, $Y_A > 0.8$.
(C) For all three solutions at same external pressure (P_1) liquid & vapour composition will be same
(D) None of these.

22.✍ For an ideal binary solution with P^o_A / P^o_B which relation between X_A (mole fraction of A in liquid phase) and Y_A (mole fraction of A in vapour phase) is correct , X_B and Y_B are mole fraction of B in liquid and vapour phase respectively : (Given : $P^o_A > P^o_B$)

(A) $X_A = Y_A$ (B) $X_A > Y_A$

(C) $\frac{X_A}{X_B} < \frac{Y_A}{Y_B}$ (D) X_A, Y_A, X_B and Y_B cannot be correlated

23.✍ Relative decrease in vapour pressure of an aqueous solution containing 2 moles $[Cu(NH_3)_3Cl]Cl$ in 3 moles H_2O is 0.50. On reaction with $AgNO_3$, this solution will form(assuming no change in degree of ionisation of substance on adding $AgNO_3$)

(A) 1 mol AgCl (B) 0.25 mol AgCl

(C) 0.5 mol AgCl (D) 0.40 mol AgCl

24. The freezing point of aqueous solution that contains 3% urea, 7.45% KCl and 9% of glucose is (given K_f of water = 1.86 and asume molarity = molality).

(A) 290 K (B) 285.5 K

(C) 267.42 K (D) 250 K

Comprehension # 25 & 26

A solution is made by mixing 1 mole benzene (P_B° = 100 mm Hg) & 1 mole toluene (P_T° = 40 mm Hg).Suppose, initially the pressure over the solution is very high so that no vapour exist above the liquid. As we gradually decrease the pressure, a point (bubble point) comes when we aross the bubble point curve & first bubble of vapour starts forming (hence called bubble point curve). Now we have entered the vapour-liquid equilibrium region. On further decreasing the pressure, a point (dew point) comes when we cross the dew point curve then almost all the liquid has evaporated into vapour i.e. only the last drop of liquid (dew) remains. Beyond this point no liquid exist in the system. Then answer the following questions :

25. If the pressure over the mixture at 300 K is reduced, at what pressure does the first bubble form :

(A) 140 mm Hg (B) 90 mm Hg

(C) 65 mm Hg (D) 70 mm Hg

26. What is the composition of first bubble formed ?

(A) $Y_A = 2/7, Y_B = 5/7$ (B) $Y_A = 3/7 , Y_B = 4/7$

(C) $Y_A = 1/7 , Y_B = 6/7$ (D) none of these

27. What will be the pressure when 1 mole of mixture has been vapourised ?

(A) 70 mm Hg (B) 63.25 mm Hg

(C) 100 mm Hg (D) 40 mm Hg

MATCH THE COLUMM

28. Match each List-I with an appropriate pair of characteristics from List-II and select the correct answer using the code given below the lists.

0.1 mol of each solute in the list-I are dissolved in 10 mole water separately.

List-I	**List-II**
P. $AlCl_3$ if $\alpha = 0.8$	1. i = 3.4
Q. $BaCl_2$ if $\alpha = 0.9$	2. has minimum osmotic pressure among the given solutions.
R. Na_3PO_4 if $\alpha = 0.9$	3. has minimum freezing point among the given solutions.
S. $K_4[Fe(CN)_6]$ if $\alpha = 0.7$	4. has RLVP = 37/1037.

Code :

	P	Q	R	S
(A)	4	2	3	1
(B)	1	2	4	3
(C)	2	1	3	4
(D)	1	2	3	4

RRP ANSWER KEY

PART- 1

1.	(C)	**2.**	(C)	**3.**	(D)	**4.**	(B)	**5.**	(B)	**6.**	(B)	**7.**	(A)
8.	(D)	**9.**	(D)	**10.**	(B)	**11.**	(B)	**12.**	(C)	**13.**	(C)	**14.**	(A)
15.	(D)	**16.**	(A)	**17.**	(B)	**18.**	(B)	**19.**	(A)	**20.**	(B)		
21.	0.20	**22.**	7.78	**23.**	0.8	**24.**	0.40	**25.**	– 0.93				

PART - 2

1.	(A)	**2.**	(A)	**3.**	(C)	**4.**	(A)	**5.**	(ABCD)		**6.**	(AB)	
7.	(CD)	**8.**	(AB)	**9.**	(ABD)	**10.**	(ABD)	**11.**	(B)		**12.**	(ABC)	
13.	4	**14.**	5	**15.**	9	**16.**	2	**17.**	4		**18.**	$\frac{x}{y}=\frac{2}{1}$	

PART - 3

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

PART - 4

1.	P_B^0 = 0.7 atm P_A^0 = 1.9 atm			**2.**	Y'_B = 0.932.	**3.**	(a) 60 g/mol ,	(b) 333.3 g	
4.	M = 48			**5.**	1.075, 7.5.	**6.**	50% K_2SO_4	**7.**	5
8.	27	**9.**	70	**10.**	60	**11.**	85	**12.**	(C)
13.	(A)	**14.**	(D)	**15.**	(B)	**16.**	(D)	**17.**	(A)
18.	(A)	**19.**	(B)	**20.**	(C)	**21.**	(C)	**22.**	(C)
23.	(A)	**24.**	(C)	**25.**	(D)	**26.**	(A)	**27.**	(B)
28.	(B)								

RRP SOLUTIONS

PART- 1

1. I. Melting of snow by salt : Depression in freezing point

II. Desalination of sea water : Reverse osmosis

III. Osmosis is used to determine the molar mass.

2. $HA \rightleftharpoons H^+ + A^-$

$i = [1 + (y - 1)\,x] = 1 + x$

$pK_a = 4 = -\log K_a$ $\quad\therefore\quad$ $K_a = 10^{-4} = Cx^2$

$1 \times 10^{-4} = 0.01 \times x^2 \Rightarrow x = 0.1$ $\quad\therefore\quad$ $i = 1 + x = 1.1$

3. As $\Delta T_b = \text{molality} \times K_b$

$0.52 = m \times 0.52$

molality = 1 mol kg^{-1} $\quad\therefore\quad$ urea = 1 mol

moles of water = $\frac{1000}{18} = 55.55$

mole fraction of urea = $\frac{1}{56.55}$ = **0.018**

4. $\Delta T_b = K_b.m.i$

In 100 g of solution

moles of NaCl = 0.1 $(\alpha = 0.8)$

moles of $MgCl_2$ = 0.1 $(\alpha = 0.5)$

$NaCl \longrightarrow Na^+ + Cl^-$

$i_{NaCl} = 1 + (2 - 1)\,0.8 = 1.8$

Effective no. of moles of NaCl = 0.1 × 1.8 = 0.18

$i_{MgCl_2} = 1 + (3-1)\,0.5 = 2$

Effective no. of moles of $MgCl_2$ = 0.1 ×2 = 0.2

Total no.of mole = 0.18 + 0.2 = 0.38

$$\Delta T_b = \frac{0.38}{84.65} \times 1000 \times 0.51 = 3.8 \times 0.51 = 2.28$$

So, $T_b = 100 + 2.28 = 102.28 \approx 102.3$

5. Given $\Delta T_b = 1.08^0C$, $\quad i = 2$ at boiling pt. of solution.

and $\Delta T_f = 1.80^0C$, and $\frac{k_b}{k_f} = 0.3$

so $$\frac{\Delta T_b}{\Delta T_f} = \frac{i_b k_b m}{i_f k_f m}$$

so $i_f = 1$

i.e., AB behaves as non–electrolyte at the f.p of the solution.

6.✍ 1M $C_6H_{12}O_6$ (molar mass = 180 g mol^{-1})
1000 mL solution has = 180 g solute
1180 g solution has = 180 g solute
1000 g solvent has = 180 g solute
Thus, molality = 1 molal
$\therefore$ $\Delta T_f = K_f$ molality
$= 1.86 \times 1 = 1.86°$
$\therefore$ F.P. = – 1.86°C

7.✍ From given graph , we can say T_1 is that temp at which solid state and liquid (solution) are in equilibrium.

8. $P = P_A°X_A + P_B°X_B$

$$\frac{100}{4} + \frac{60 \times 3}{4}$$

= 70 mm < 75 mm (experimental)
Thus, there is positive deviation (1) is true, mixture is more volatile due to decrease in b.p. Thus, (2) is true also force of attraction is decreased thus (3) is true.

9. In HF hydrogen bonding is present so there is association of molecules due to this van't hoff factor is less , so depression in f.p decreases therefore f.p. value is larger than HCl. Similarly value of i = 2 for NaCl and i = 1 for Glucose.

10. Boiling point get lowered when vapour pr. increases and it happens when there is a positive deviation from Raoult's law.

11.✍ For urea, $\Delta T_f = k_f \times m$ or $k_f = \frac{\Delta T_f}{m} = \frac{1.86}{1} = 1.86$

Now for CH_3COOH
$\Delta T_f = i\, k_f\, m$

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

Now $i = 1 + \alpha$
so $\alpha = 1.1 - 1 = 0.1$

Now $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
$C \quad 0 \quad 0$
$C - C\alpha \quad C\alpha \quad C\alpha$
$[H^+] = C\alpha = 0.01 \times 0.1 = 0.001$
so pH = 3.

12. Mixtures of $CHCl_3$ and CH_3COCH_3 shows negative deviation from Raoult's law, so vapour pressure decreases and boiling point increases.

13.✍ More the value of van't hoff factor , more will be the depression in freezing point.

14. Acetone and chloroform forms hydrogen bonding so volume decreases.

15.✍ All are facts.
We should remember that , Entropy of solution is more than entropy of pure solvent. So the difference in entropy change will be less in case of solution.

16.✍ $M_{\text{observed (प्रेक्षित)}} = \frac{58.5}{i}$; $i > 1$.

17. Due to weak force of attraction more vapour will be forrmed so vapour pressure will be high.

18.✍ The order of force attraction and boiling point is $CH_3OH > CH_4 > H_2$.

19.✍ At freezing point liquid solvent and solid solvent are in equilibrium.

20. There is very weak attraction between benzene and methanol as compare to attraction between molecules of methanol.

21. Mole of $H_2O = \frac{36}{18} = 2$

Mole of glycerine = $\frac{46}{92} = 0.5$
total mole = 2 + 0.5 = 2.5

Mole fractions of glycerine = $\frac{n_1}{n_1+n_2} = \frac{0.5}{2.5}$
$X_0 = 0.2$ Ans.

22.✍ Firstly we have to convert mole fraction into molality .

$$\text{Molality} = \frac{x_{\text{solute}}}{x_{\text{solvent}}\, M_{\text{solvent}}/1000} = \frac{0.07\times1000}{0.93\times18} = 4.18$$

Now , $\Delta T_f = k_f m$
$= 1.86 \times 4.18 = 7.78^0$.

23.✍ $p_A = X_A p°_A$
$32 = X_A 40$

$\therefore$ $X_A = \frac{32}{40} = 0.8$

24. $P_T = X_A p°_A + X_B p°_B$ $= \left(\frac{2}{4}\right) \times 80 + \left(\frac{2}{4}\right) \times 120 = 100$ Torr

Now mole fraction in vapour phase $= \frac{X_A P_A^0}{P_T} = \frac{40}{100} = 0.4$.

25.✍ $\Delta T_f = k_f m$.
$\Delta T_f = 1.86 \times 0.5 = 0.93$.
so $T_f = -0.93^0C$.

PART 2

1. $\pi = MRT\, i$: $y\uparrow, i\uparrow, \pi\uparrow$

2.✍ This is due to cage like structure ice.

3. L indicates elevation in boiling pt. i.e., $k_b m$.

4.✍ Let volumes taken by 'x' & 'y' litres, so $\frac{0.1x+0.4y}{x+y}$ = 0.34& $V_g = (x + y)$ (to be maximised)

so y = 4x so for maximum volume ; $y = 2L$ & $x = \frac{1}{2}L$

5.✍ A,B,C,D

6.✍ $P = P_A^o X_A + P_B^o X_B$ (X_B = mole fraction of benzene)

$550 = 400 \times (1 \times X_B) + 600(X_B)$

$150 = (600 - 400)\, X_B$; $\frac{150}{200} = \frac{3}{4} = X_B$

$X_A = \frac{1}{4}$

At 100°C mole fraction will be same initially but get change at equilibrium.

8.✍ $\frac{P_A^0}{P_A^0 - P_A} = \frac{n_A}{n_B} + 1$ or $\frac{P_A^0 - P_A}{P_A} = \frac{n_B}{n_A}$

9. In both chamber vapour compositions are same so vapour pressure are equal.

10.✍ $\Delta T_b = mK_b\, i$; $K_b = \frac{RT^2}{1000\Delta H_{vapour}}$

11. $P = 119\,x + 135$

x = 1 for pure methanol.

so $P^o_{methanol} = 119 + 135 = 254$ Torr

But for pure ethanol x = 0

so $P^o_{ethanol} = 135$ Torr

12. $A_xB_y \rightleftharpoons xA^{y+} + yB^{x+}$

Initial moles n o o

At eq b. $n(1–\alpha)$ $nx\alpha$ $ny\alpha$

$$i = \frac{\text{Total mol at equilirium}}{\text{Initial mol}} = \frac{n[(1-\alpha)+x\alpha+y\alpha]}{n}$$

$i = (1 - \alpha) + x\alpha + y\alpha$

It can also seen that all other expressions imply the same thing.

(A) $\alpha = \frac{i-1}{x+y-1}$ (B) $i = (1 - \alpha) + x\alpha + y\alpha$. (C) $\frac{1-i}{1-x-y}$

13. $\frac{P_o - P_s}{P_o} = X_{solute}$ $\therefore$ $\frac{100-98.7}{100} = X_{solute} = 0.013$

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

$0.72 = K_f \times \frac{0.013 \times 1000}{0.978 \times 78}$ $\therefore$ $K_f \approx 4.2$ K Kg/mol

$\therefore$ Reported answer = 4

14. Initially $P = \frac{500}{760}$ atm, T = 283 K

Let $V = V_1$ $\quad \therefore \quad$ $pV = nRT$

Or $\left(\frac{500}{760}\right) \times V_1 = R \times 5 \times 283$ ...(1)

Let on dilution the volume becomes V_2 and temp is raised to 25ºC i.e. 298 K

$$\pi = \left(\frac{105.3}{760}\right)\text{atm}$$

$\therefore \quad \left(\frac{105.3}{760}\right) \times V_2 = n \times R \times 298$ ...(2)

(1)/(2) $\quad \frac{V_1}{V_2} = \frac{283}{298} \times \frac{105.3}{500}$; Or $V_2 = 5V_1$

15.✍ $\Delta T_f = iK_f m$

$7.2 \times 10^{-3} = i \times 1 \times 10^{-3} \times 1.8$

$i = \frac{7.2}{1.8} = 4$

now , $i = 1 + (x + 1 - 1)\alpha$

$= 1 + x$

$4 - 1 = x$

$x = 3$

So oxidation number of Fe $\quad 3 + y - 6 = 0,\ y = +3$

Sum of primary and sec valency $= 3 + 6 = 9$

16.✍ Molarity of I solution $= \frac{12.6 \times 1.5 \times 10}{63} = 3$

Molarity of II solution $= \frac{6.3 \times 10 \times 10}{63} = 10$

$$M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2} = \frac{3 \times 5 + 1 \times 5}{5 + 5} = \frac{4}{2} = 2$$

17.✍ $P_A = K_H X_A$

$4 \times \frac{25}{100} = 2.5 \times 10^3\ X_A \quad \Rightarrow \quad X_A = \frac{2}{5000}$

Number of moles of water $= \frac{36}{18} = 2$

Number of moles of gas A dissolved $\approx \frac{2}{5000} \times 2 = 0.8 \times 10^{-3} = 8 \times 10^{-4}$

18.✍ $\frac{x}{y} = \frac{2}{1}$

Hence $x + y = 3$

PART - 3

20. (C) it will produce 5 ions.

21. $\Delta T_b = iK_b\, m = 3\times 0.52 \times \frac{13.44/134.5}{1} = 0.3\times 0.52 = 0.16$

22. $\Delta T_f = (1-\alpha+2\alpha)\ 1.86 \times \frac{\frac{8.1}{81}}{0.1}$

$= 1.9 \times 1.86 = 3.53$

T_f of water = – 3.53ºC

23. I ⟶ Relative lowering of vapour pressure
II ⟶ Depression in freezing point.
III ⟶ Comparision of melting point of two different compounds.
∴ I & II are indicating colligative properties.

24. $\pi_{\text{gaseous}} = \pi_{\text{He}}$

$\frac{2}{180}\times\frac{1000}{100} = \frac{5}{M}\times\frac{1000}{100}$; $M = \frac{180\times 5}{2} = 450\,\text{g}$

30. I and II are correct.

PART - 4

1. The data provide the following two expressions for total pressure

$1 = \frac{1}{4}P_A^0 + \frac{3}{4}P_B^0$

or $4 = P_A^0 + 3P_B^0$ and $1 = \frac{1}{5}P_A^0 + \frac{1}{5}P_B^0 + \frac{3}{5}P_C^0$

or $4 = P_A^0 + P_B^0 + 2.4$
on solving these two equations simultaneously, one obtains $P_B^0 = 0.7$ atm and $P_A^0 = 1.9$ atm.

2.✍ P(mm Hg) = $180X_B + 90$

P_B° (Benzene) = 180 + 90 ($X_B = 1$) = 270 mm Hg

P_T° (Toluene) = 90 mm Hg ($X_B = 0$)

moles of C_6H_6 = 12, $X_B = 0.6$
moles of $C_6H_5CH_3$ = 8 $X_T = 0.4$

Vapour Pressure of solution $P_S = X_BP_B^{\circ} + X_TP_T^{\circ}$

$P_S = 198$ mm Hg

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

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

Mole fraction of Toluene in vapour state

$Y_T = 0.18$

Now this vapour when condensed

$$P_S = Y_T P_T^{\circ} + Y_B P_B^{\circ}$$

$$= 0.18 \times 90 + 0.82 \times 270 = 237.6 \text{ mm Hg.}$$

Now mole fraction of benzene in vapour state is

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

3. ✍ (a) Relative lowering of vapour pressure = mole fraction of solute

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

so $M = 60$ g/mol

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

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

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

$\therefore$ $w = 333.3$ g

4 ✍ $$\frac{P - P_S}{P} = \frac{0.087}{2.175} = \frac{\frac{40}{M}}{\frac{40}{M} + \frac{360}{18}}$$

$$\Rightarrow \quad \frac{2.175}{0.087} = 1 + \frac{360}{18} \times \frac{M}{40} \qquad \Rightarrow \qquad 25 = 1 + \frac{M}{2}$$

Ans. $M = 48$

5. ✍ Experimental $\Delta T = 0.02^{o}$

Theoretical $\Delta T = 1.86 \times 0.01 = 0.0186^{o}$

$$i = \text{van't Hoff factor} = \frac{0.02}{0.0186} = 1.075$$

Degree of dissociation , $\alpha = \frac{i-1}{v-1}$ (v = no. of species formed on dissociation)

$$= \frac{0.075}{2-1} = 0.075$$

% dissociation = 7.5.

6. ✍ For isotonic solutions, $i_1 C_1 = i_2 C_2$

for K_2SO_4 and NaCl, $i_1 \times \frac{17.4 \times 1000}{174 \times 100} = \frac{2 \times 5.85 \times 1000}{58.5 \times 100}$

so $i_1 = 2$

Now $K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$

At equilibrium $1 - x$ $\quad 2x \quad x$

or $1 + 2x = 2$

or $x = ½ = 0.5$

$\therefore$ 50% ionisation.

7. 40 mL O_3 dissolve in 100 g water at 300 K and 1 atm

40 × 4 mL O_3 dissolve in 400 g water at 300 K and 1 atm

$\because$ $m \propto P$ so (40 × 4) × 4 mL O_3 dissolve in 400 g water at 300 K and 4 atm

$$n_{O_3} \text{ dissolve} = \frac{4 \times 640 \times 10^{-3}}{0.0821 \times 300} = 0.1 \qquad \text{or} \qquad \text{mass of } O_3 = 4.8 \text{ g.}$$

8. A and B are volatile liquids, given $P_A^0 = 575$ Torr , $P_B^0 = 390$ Torr

let mole fraction of A in solution = X_A

hence, $P_{total} = P_A^0 X_A + P_B^0 (1 - X_A)$

also $X_A' =$ mole fraction of A in the vapour = 0.35

$$X_A' = \frac{P_A^0 X_A}{P_A^0 X_A + P_B^0 (1 - X_A)} = 0.35 \qquad = \frac{575 X_A}{575 X_A + 390 (1 - X_A)}$$

this gives $X_A = 0.27$

Composition of liquid mixture, A = 27 mol % , B = 73 mol %.

9. Loss in weight of solution $\propto P_S$

Loss in weight of solution $\propto P^0 - P_S$

Also, $\dfrac{P^0 - P_s}{P_s} = \dfrac{w \times M}{m \times W}$

By. eq (1) and (2) we get $\dfrac{0.04}{2.5} \times \dfrac{5 \times 18}{80 \times m} \Rightarrow m = 70.31$

10. $\dfrac{1}{M_{acid}} = \dfrac{125}{1000} \times 0.1 \qquad \Rightarrow \qquad M_{acid} = 80 \text{ g mol}^{-1}$

$0.186 = (1 + \alpha) \times 1.86 \times \left[\dfrac{\frac{1}{80}}{0.2}\right] \qquad \Rightarrow \qquad \alpha = 0.6 \Rightarrow 60$ percent

11. $1.0526 \times 760 = p_{ext}$

$p_{ext} = 799.976 \simeq 800$ Torr

$\therefore \quad \log 800 = 7 - \dfrac{1250}{t + 220}$

$\Rightarrow \quad 2.9 = 7 - \dfrac{1250}{t + 220} \qquad \Rightarrow \qquad t = 84.878$ °**C** **Ans. 85**

12. $\pi = CRT$

$\pi = \dfrac{c}{M} RT \qquad$ C = moles/liter, c = kg/m^3

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

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

[T = 293 k]

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

13. Osmotic pressure = CRT

$= 0.30 \times 0.082 \times 298 = 7.34$ atm

14.✍ Molarity = $\dfrac{0.967/159.5}{20/1000}$ $\left\{\begin{matrix}\text{Mol.wt.of } CuSO_4 \\ 159.5\end{matrix}\right\}$

$= 0.303$ M

15.✍ $i = 1 + \alpha (n - 1)$ or $4 = 1 + 0.75 (n - 1)$

$\therefore$ n = 5 , so complex will be $Ba_3[Co(CN)_5]_2$.

16.✍ Wt gain means weight loss means

$V.P_{incoming} > V.P_{outgoing}$ $V.P_{incoming} < V.P_{outgoing}$

So $p_1 > p_2 < p_3$ and $c_1 < c_2 > c_3$

17.✍ $x + y = 0.1$

$\Delta T_f = \dfrac{x + x + y + 2y}{1000} \times 1000 \times 1.85$

if only KCl is used then

$\Delta T_f = \dfrac{0.2}{1000} \times 1000 \times 1.85 = 0.37$

if only $BaCl_2$ is used then

$\Delta T_f = 0.3 \times 1.85 = 0.555$

18.✍ $1.24 = 34.3 \left[\dfrac{0.849/M}{0.05}\right] \Rightarrow M = 469.68$

$\therefore$ as Hg_2Cl_2 molecules.

19.✍ At 90ºC, Total $P_T = 730$ mm Hg

At 100ºC total $P_T = 289 + 760 = 1049$ mm Hg

so for 800 mm Hg, temperature will lie in between 90º –100ºC

Using extrapolation method, Temperature = $90 + \dfrac{(800 - 730)}{(1049 - 730)} \times (100 - 90) = 92.19$ºC.

20. Freezing point and boiling point are used in temperature scale.

21.✍ On the same tie line liquid & vapour composition will be same.

22.✍ Mole fraction of more volatile substance is greater in vapour phase.

23.✍ $\frac{\Delta P}{P} = \frac{ni}{ni+N}$

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

$i + 1.5 = 2\,i$

$i = 1.5$

$i = 1 + (y - 1)\,\alpha$

$1.5 = 1 + (2 - 1)\,\alpha$

$\alpha = 0.5$

mole of Cl^- = 1.0

mole of AgCl ppt. = 1.0 **Ans. (A)**

24. $\Delta T_f = i.m.\,K_f$

$\Delta T_f = i_1m_1K_f + i_2\,m_2\,K_f + i_3\,m_3\,K_f = (m_1 + 2m_2 + m_3)\,K_f$

$$\Delta T_f = \frac{\frac{3}{60}+\frac{7.45\times2}{74.5}+\frac{9}{180}}{100} \times 1000 \times 1.86$$

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

T_f of solution = 273 – 5.58 = 267.42 K Ans.

25.✍ $P = X_AP_A^0 + X_BP_B^0 = 0.5 \times 40 + 0.5 \times 100 = 70$

26.✍ $Y_A = \frac{0.5 \times 40}{70} = \frac{2}{7}\ ;\ Y_B = \frac{5}{7}$

27.✍

1 - x	x
B = x	T = 1 - x

$P = 40\,(1 - x) + 100\,x$

$$\frac{1}{P} = \frac{Y_A}{P_A^0} + \frac{Y_A}{P_B} \Rightarrow \frac{1}{P} = \frac{x}{40} + \frac{1-x}{100} = \frac{100x+(1-x)40}{40 \times 100}$$

So $p^2 = 40 \times 100$

$p = 20\sqrt{10} = 63.25$

28.✍ P. $AlCl_3 \rightarrow i = 1 + (4 - 1) \times 0.8 = 1 + 2.4 = 3.4$

Q. $BaCl_2 \rightarrow i = 1 + (3 - 1) \times 0.9 = 1 + 1.8 = 2.8$

R. $Na_3PO_4 \rightarrow i = 1 + (4 - 1) \times 0.9 = 1 + 2.7 = 3.7$

S. $K_4[Fe(CN)_6] \rightarrow i = 1 + (5 - 1) \times 0.7 = 1 + 2.8 = 3.8$

so, $K_4[Fe(CN)_6]$ has highest colligative property and hence minimum freezing point and $BaCl_2$ has lowest colligative property, so lowest osmotic pressure.