IIT CHEMISTRY

PHYSICAL CHEMISTRY

LIQUID SOLUTION

LIQUID SOLUTION

Types of Solution :

	Solvent	Solute	Examples
1.	Gas	Gas	Mixture of gases, eg. air.
2.	Gas	Liquid	Water vapour in air, mist. $CHCl_3(\ell) + N_2(g)$
3.	Gas	Solid	Smoke, 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.

Vapour pressure :

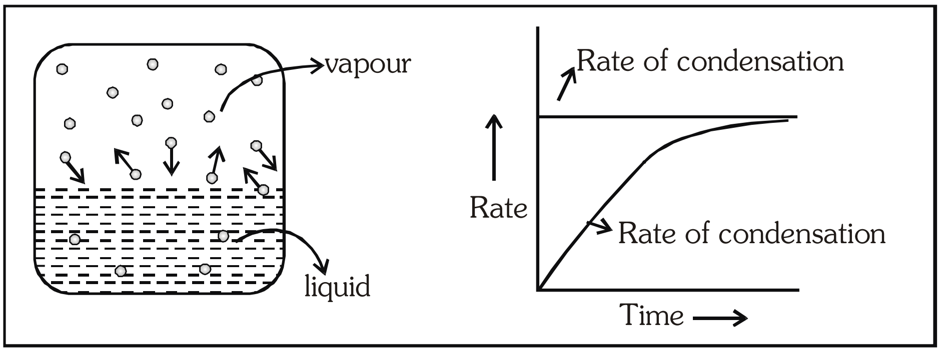
The Evaporation of a Liquid in a Closed Container

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.



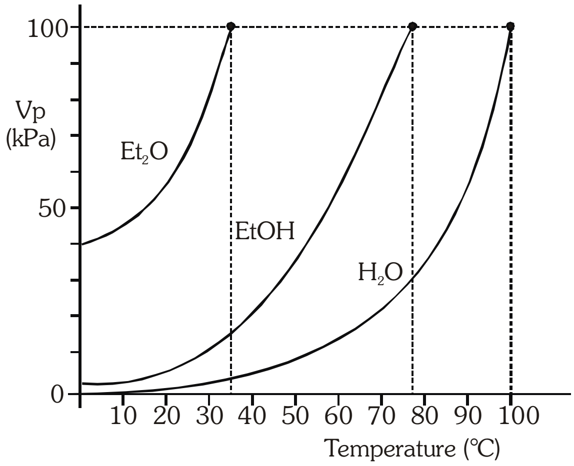
This pressure at equilibrium is called the **saturated vapour pressure** (also known as **saturation vapour pressure).**

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 saturated vapour pressure.



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

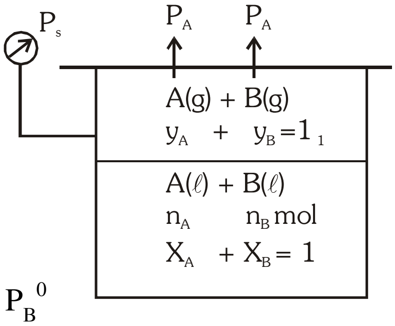
$n\text{–}C_6H_{14} > n\text{– }C_7H_{16} > C_8H_{18}$

◆ **Raoult's law :**

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

(i) For liquid – liquid solution :

Let a mixture (solution) be prepared by mixing n_A moles of liquid A and n_B moles of liquid B. Let P_A and P_B be the partial pressures of two constituents A and B in solution and P_A^0 and P_B^0 the vapour pressures in pure state respectivity.



Thus, according Raoult's law

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

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

If total pressure be P_S, then

$$P_S = P_A + P_B = \frac{n_A}{n_A+n_B}P_A^0 + \frac{n_B}{n_A+n_B}P_B^0 = X_AP_A^0 + X_BP_B^0$$

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

$$P_S = X_AP_A^0 - X_AP_B^0 + P_B^0$$

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

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. Let p_A and p_B be the partial pressure of vapours A and B respectively and total pressure P.

$p_A = Y_AP_S$ ....(1)

$p_B = Y_BP_S$ ....(2)

$p_A = X_AP_A^0$ ....(3)

$p_B = X_BP_B^0$ ....(4)

Equating eqs. (i) and (iii),

$$Y_AP_S = X_AP_A^{\,0}$$

or $Y_A = \dfrac{X_AP_A^0}{P_S} = \dfrac{p_A}{P_S}$

Similarly, equating eqs. (ii) and (iv),

$$Y_B = \dfrac{X_BP_B^0}{P_S} = \dfrac{p_B}{P_S}$$

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

(ii) For Solid – liquid solution :

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

According to Raoult's law –

$\because \quad P_s = X_AP_A^{\,0} + X_BP_B^{\,0}$

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

$\therefore \quad P_s = X_BP_B^{\,0}$ ....(5)

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

here X_B is mole fraction of solvent

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

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

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

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

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

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

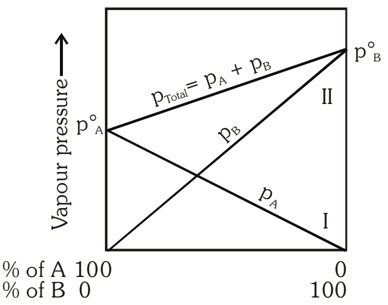
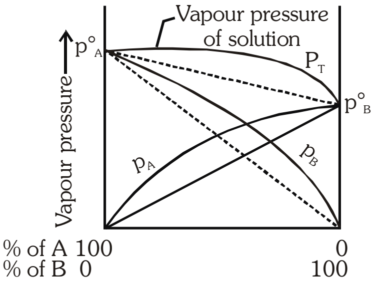
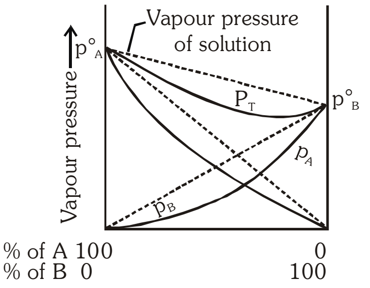
or $\dfrac{P^0}{P^0 - P_S} = \dfrac{n_A + n_B}{n_A}$ or $\dfrac{P^0}{P^0 - P_S} = 1 + \dfrac{n_B}{n_A}$ or $\dfrac{P^0}{P^0 - P_S} - 1 = \dfrac{n_B}{n_A}$

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

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

IDEAL AND NON IDEAL SOLUTIONS

Table : Comparison between Ideal and Non-ideal solutions

Ideal solutions	Non-ideal solutions	
	+ve deviation from Raoult's law	**– deviation from Raoult's law**
1. Obeys Raoult's law at every concentrations.	Do not obey Raoult's law.	Do not obey Raoult's law.
2. $\Delta H_{mix} = 0$; 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 : dilute solutions ; benzene + toluene ; n-hexane + n-heptane ; chlorobenzene + bromobenzene ; ethyl bromide + ethyl iodide ; n-butyl chloride + n-butyl bromide CCl_4 + $SiCl_4$; $C_2H_4Br_2 + C_2H_4Cl_2$ $C_2H_5Br + C_2H_5Cl$	**Example :** acetone + ethanol ; acetone + CS_2 ; water + methanol ; water + ethanol ; CCl_4 + $CHCl_3$; CCl_4 + toluene ; acetone + benzene CCl_4 + CH_3OH ; cyclohexane + ethanol	**Example :** acetone + aniline ; acetone + chloroform ; CH_3OH + CH_3COOH ; $H_2O + HNO_3$; chloroform + diethyl ether ; water + HCl ; acetic acid + pyridine ; chloroform + benzene $HNO_3 + CHCl_3$
		

Colligative properties :

Those properties of a dilute solution which depends upon the relative number of solute particles in a given volume of the solution or the mole fraction of the solute are called colligative properties.

The following four properties are colligative properties of solution :

(i) Relative lowering of vapour pressure.

(ii) Elevation in boiling point.

(iii) Depression in freezing point.

(iv) Osmotic pressure.

Coll. prop. α No. of particles/molecules/ions α No. of moles of solute α Mole fraction of solute α 1/mol. wt. of solute

(i) Lowering of vapour pressure :

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

If at a certain temperature P° is the vapour pressure of pure solvent, and P_s is the vapour pressure of solution then

Lowering of vapour pressure = $P° - P_s$

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

from equation (8)

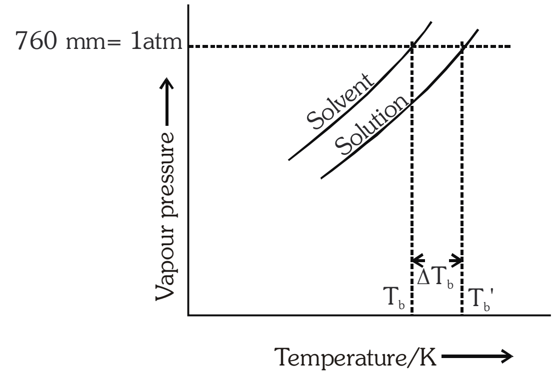
$$\boxed{\frac{\mathbf{P^0 - P_S}}{\mathbf{P^0}} = \frac{\mathbf{\Delta P}}{\mathbf{P^0}} = \frac{\mathbf{n_A}}{\mathbf{n_A + n_B}} = \mathbf{X_A}}$$

for a more dilute solution $n_A <<< n_B$

so $\boxed{\frac{\mathbf{P^0 - P_S}}{\mathbf{P^0}} = \frac{\mathbf{n_A}}{\mathbf{n_B}} = \frac{\mathbf{w_A}}{\mathbf{m_A}} \times \frac{\mathbf{m_B}}{\mathbf{w_B}}}$ [Only for v.dilution solutions]

(ii) Elevation in boiling point (Ebullioscopy) :

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



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

ΔT_b denotes the elevation of boiling point of a solution.

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

∴ $\boxed{\mathbf{\Delta T_b = molality \times K_b}}$

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

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

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

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

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

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

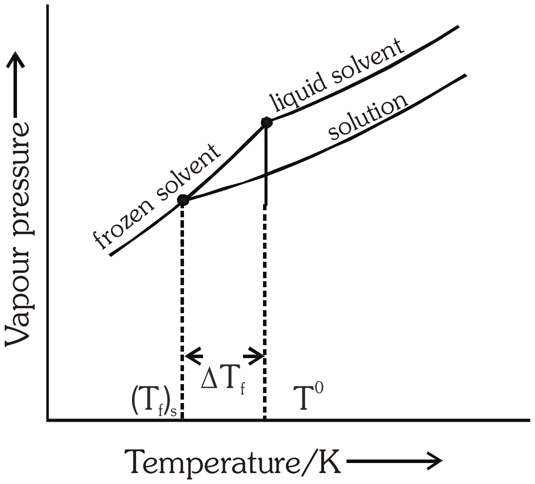
The molal elevation constant for some common solvents are given in the following table

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

(iii) Depression in freezing point (Cryoscopy) :

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

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



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

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

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

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

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

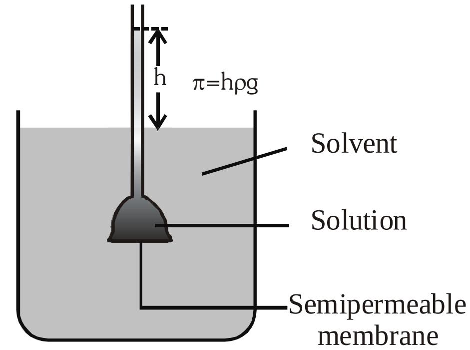
$$K_f = \frac{0.002 \times (273)^2}{80} = 1.86 \text{ K-kg/mol}$$

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

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

(iv) Osmosis and osmotic pressure :

- **Osmosis :**



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

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

- **Osmotic presssure** (π) **:**

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

or

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

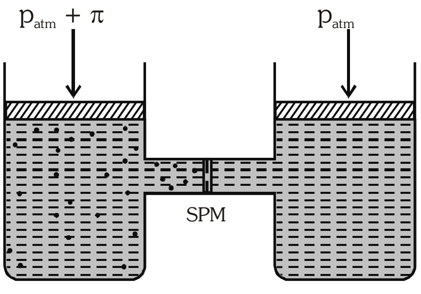
osmotic pressure = hydrostatic pressure

π = hdg

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

d = density of solution,

g = acceleration due to gravity



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

Van't Hoff law for dilute solution :

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

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

or $P \propto \frac{1}{V}$

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

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

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

  $$\pi_1 = \pi_2$$

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

  $$C_1 = C_2$$

- **Hypertonic solution**

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

- **Hypotonic solution**

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

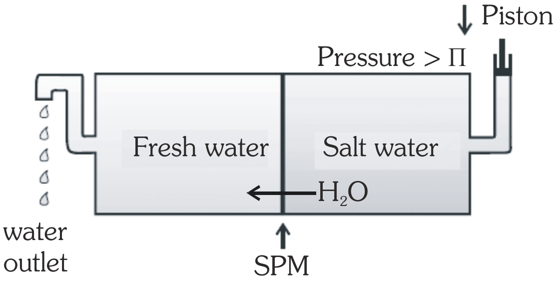
  When isotonic solutions are separated by semipermeable membrane no osmosis occurs between them. For example, the osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/volume) sodium chloride solution, called normal saline solution and it is safe to inject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

- **Semipermeable Membrane**

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

- **Reverse Osmosis :**

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



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

Abnormal colligative properties :

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

Association of solute particles :

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

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

$$\underset{\text{(n single molecules)}}{nX} \longrightarrow \underset{\text{(one bigger molecule)}}{(X)_n} \quad [n > 1]$$

As a result, the total number of particles in solution becomes less than the number of molecules initially dissolved in the solution and hence the colligative properties will have lower value.

As the molar mass of solute is inversely proportional to the colligative properties, so the molar mass of solute will be greater than theoretical value.

Dissociation of solute molecules :

Molecules of electrolytes undergo ionization or dissociation in ionizing solvents to give more particles in solution.

For example, one AB molecule ionizes in solution to give two particles.

$$AB \longrightarrow A^+ + B^-$$

This dissociation results in an increase in the total number of particles, and therefore the value of colligative properties of such solutions will be higher.

As the colligative properties are inversely related to molecular weight, so the molecular weight of ionizable solute will be less than the theoretical value.

Van't Hoff factor (i) :

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

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

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

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

Van't Hoff factor and degree of dissociation :

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

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

Calculation of 'i' :

Let, solute be A_xB_y

	A_xB_y	$\longrightarrow$ $x\,A^{y+}$ +	yB^{x-}
Initial mol	1	0	0
after dissociation	$1-\alpha$	$x\alpha$	$y\alpha$

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

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

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

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

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

for complex compound

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

S.no.	Solute type	Example	Ionisation	No. of particles in the solution from 1 mole solute (n)	van't Hoff factor ('i')	Abnormal molecular mass
1.	Non-electrolyte	Urea, sucrose, glucose, fructose	—	1	1	m_{normal}
2.	Binary electrolyte AB type	NaCl, KCl, HCl CH_3COOH NH_4OH, NaOH etc.	$\underset{1-\alpha}{AB} \rightleftharpoons \underset{\alpha}{A^+} + \underset{\alpha}{B^-}$	2	$1+\alpha$	$\frac{m_{normal}}{1+\alpha}$
3.	Ternary electrolyte AB_2 type or A_2B type	$CaCl_2$, $BaCl_2$ H_2SO_4, $K_2[PtCl_6]$	$\underset{1-\alpha}{AB_2} \rightleftharpoons \underset{\alpha}{A^{2+}} + \underset{2\alpha}{2B^-}$ $\underset{1-\alpha}{A_2B} \rightleftharpoons \underset{2\alpha}{2A^+} + \underset{\alpha}{B^-}$	3 3	$1+2\alpha$ $1+2\alpha$	$\frac{m_{normal}}{1+2\alpha}$ $\frac{m_{normal}}{1+2\alpha}$
4.	Quanternary electrolyte AB_3 or A_3B type	$AlCl_3$, $K_3[Fe(CN)_6]$	$\underset{1-\alpha}{AB_3} \rightleftharpoons \underset{\alpha}{A^{3+}} + \underset{3\alpha}{3B^-}$ $\underset{1-\alpha}{A_3B} \rightleftharpoons \underset{3\alpha}{3A^+} + \underset{\alpha}{B^{3-}}$	4 4	$1+3\alpha$ $1+3\alpha$	$\frac{m_{normal}}{1+3\alpha}$ $\frac{m_{normal}}{1+3\alpha}$
5.	General electrolyte AB_{n-1}	One mole of solute giving 'n' ions in the solution	$\underset{1-\alpha}{AB_{n-1}} \rightleftharpoons \underset{\alpha}{A^{+(n-1)}} + \underset{(n-1)\alpha}{(n-1)B^-}$	n	$1+(n-1)\alpha$	$\frac{m_{normal}}{[1+(n-1)\alpha]}$

Van't Hoff factor and degree of association :

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

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

Calculation of 'i' :

Let, solute be A

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

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

$$\mathbf{i = 1 - \alpha + \alpha/n}$$

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

AZEOTROPIC MIXTURES

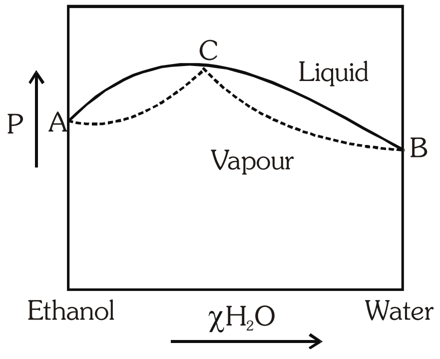
Binary mixtures that have same compostion in liquid and vapour phase and boil at a constant temperature and can be distilled unchanged in composition are known as azeotropic mixture or simply azeotropes. Thus aceotropes behave as pure liquid.

There are two types of azeotropes called as minimum boiling azeotropes and maximum boiling azeotropes respectively.

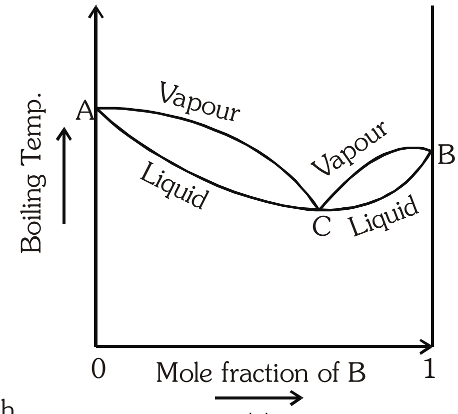
Types of Azeotropic mixtures

(i) Minimum boiling Azeotropic mixtures

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



Vapour pressure-composition graph



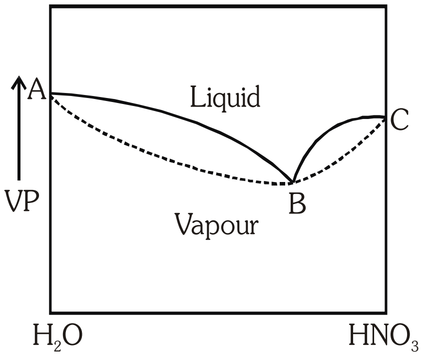
(a)

Minimum boiling point Azeotropic

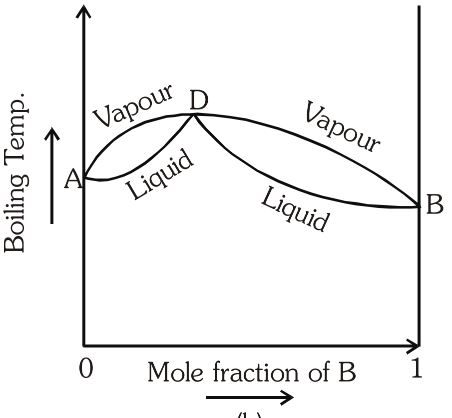
Mixture	% Composition of azeotrope	Boiling point (pressure = 1atm)
1. Water-Ethanol	96 Ethanol	78.15°C
2. Pyridine-Water	57.00 Pyridine	92.60°C
3. Ethanol-Benzene	32.4 Ethanol	67.80°C
4. Acetic acid-Toluene	28.0 Acetic acid	105.40°C

(ii) Maximum boiling Azeotropic mixtures

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



Vapour pressure-composition diagram



(b)

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

Solubility :

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

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

Solubility of Solid in a Liquid : Polar solutes are soluble in polar solvent and non polar solutes are solubile in non polar solvent due to similar intermolecular forces.

When solid solutes are dissolved in solvent than following equilibrium exits.

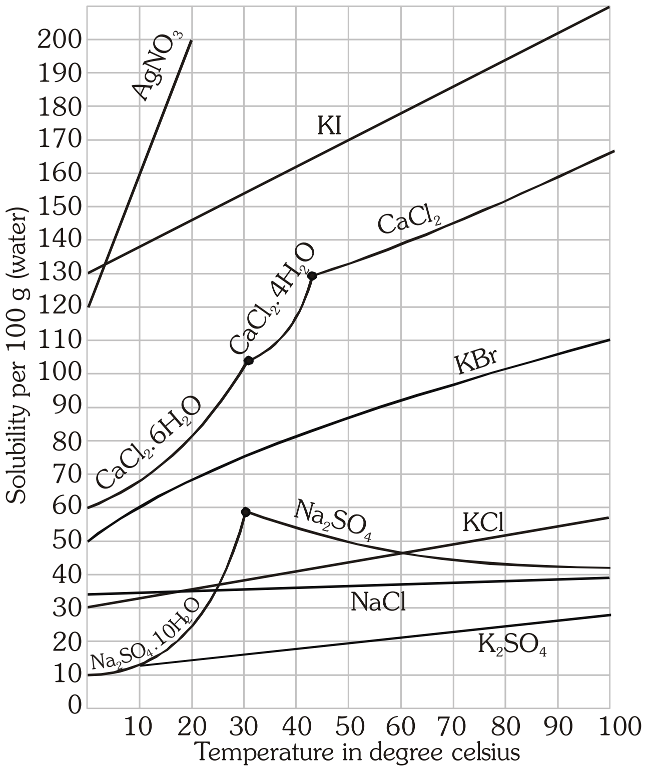
Solute + Solvent $\underset{\text{Crystallization}}{\overset{\text{Dissolutioni}}{\rightleftharpoons}}$ Solution. ; ΔH may be positive or negative

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.

Effect of temperature :

The solubility of a solid in a liquid is significantly affected by temperature changes. Consider the equilibrium represented by equation 2.10. This, being dynamic equilibrium, must follow ***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.

Solubility curves of some compounds



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.

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 highly effected by pressure and temperature. Increasing pressure increases solubility increase in temperature decreases solubility since dissolution of any gas in any liquid is exothermic in nature.

Henry' Law :

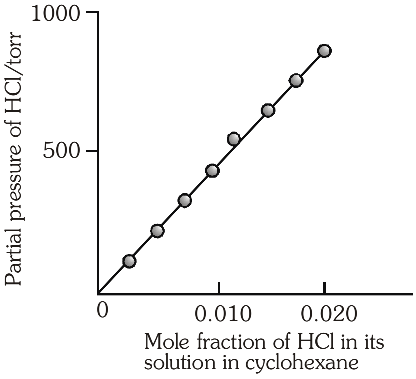
Mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution.

or

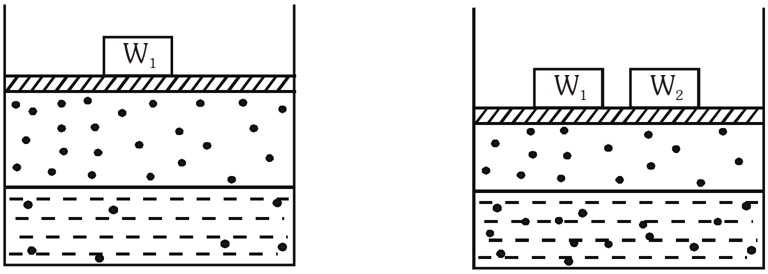
The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.

$\mathbf{P = K_HX}$ K_H = Henry's Constant

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



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



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

Effect of Temperature

Solubility of gases in liquids decreases with rise in temperature. When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved in this process. Dissolution process involves dynamic equilibrium and thus must follow Le Chatelier's Principle. As dissolution is an exothermic process, the solubility should decrease with increase of temperature

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.

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

EXERCISE # (S-I)

Raoult's law

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?

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

3. What weight of the non-volatile solute, urea needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution?

4. The vapour pressure of pure benzene at 25° C is 639.7 mm of Hg and the vapour pressure of a solution of a solute in C_6H_6 at the same temperature is 631.7 mm of Hg. Calculate molality of solution.

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

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

7. At 25°C, the vapour pressure of methyl alcohol is 96.0 torr. What is the mole fraction of CH_3OH in a solution in which the (partial) vapor pressure of CH_3OH is 23.0 torr at 25°C?

8. The vapour pressure of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is prepared at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate total vapour pressure of the solution.

9. Benzene and toluene form two ideal solution A and B at 313 K. Solution A (total pressure P_A) contains equal mole of toluene and benzene. Solution B contains equal masses of both (total pressure P_B). The vapour pressure of benzene and toluene are 160 and 60 mm Hg respectively at 313 K. Calculate the value of P_A/P_B.

Boiling point elevation and freezing point depression

10. When 10.6 g of a nonvolatile substance is dissolved in 740 g of ether, its boiling point is raised 0.284°C. What is the molecular weight of the substance? Molal boiling point constant for ether is 2.11°C·kg/mol.

11. The molecular weight of an organic compound is 58.0 g/mol. Compute the boiling point of a solution containing 24.0 g of the solute and 600 g of water, when the barometric pressure is such that pure water boils at 99.725°C.

12. Pure benzene freeze at 5.45°C. A solution containing 7.24 g of $C_2H_2C_{l4}$ in 115.3 g of benzene was observed to freeze at 3.55°C. What is the molal freezing point constant of benzene?

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

14. Calculate the molal elevation constant, K_b for water and the boiling of 0.1 molal urea solution. Latent heat of vaporisation of water is 9.72 kcal mol^{-1} at 373.15 K.

15. A solution of 0.643 g of an organic compound in 50ml of benzene (density ; 0.879 g/ml) lowers its freezing point from 5.51°C to 5.03°C. If K_f for benzene is 5.12 K, calculate the molecular weight of the compound.

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

17. Find the freezing point of a glucose solution whose osmotic pressure at 25oC is found to be 30 atm. K_f(water) = 1.86kg. mol^{-1}.K.

Osmotic pressure

18. A 5% solution (w/v) of cane-sugar (Mol. weight = 342) is isotonic with 0.877%(w/v) of urea solution. Find molecular weight of urea.

19. A storage battery contains a solution of H_2SO_4 38% by weight. What will be the Van't Hoff factor if the $\Delta T_{f(\text{experiment})}$ in 29.08. [Given K_f = 1.86 mol^{-1} Kg]

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

21. 2.0 g of benzoic acid dissolved in 25.0g of benzene shows a depression in freezing point equal to 1.62K. Molal depression constant (K_f) of benzene is 4.9 K.kg.mol^{-1}. What is the percentage association of the acid?

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

23. The freezing point of a solution containing 0.2 g of acetic acid in 20.0g of benzene is lowered by 0.45°C. Calculate the degree of association of acetic acid in benzene.
(K_f for benzene = 5.12 K mol^{-1} kg)

24. 0.85 % aqueous solution of $NaNO_3$ is apparently 90% dissociated at 27°C. Calculate its osmotic pressure. (R= 0.082 l atm K^{-1} mol^{-1})

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

EXERCISE # (S-II)

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

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

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

4. A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.750 g in 125 cm^3 of an aqueous medium. At 4°C an osmotic pressure rise of 2.6 mm of the solution was observed. The solution had a density of 1.00 g/cm^3. Determine the molecular weight of the protein.

5. 0.1 mol K_4 $Fe(CN)_6$ is added to 1 llitre of 0.2M $CuCl_2$ solution at 31ºC, osmotic pressure (in atm) of the resulting solution.

6. 30 ml of CH_3OH (d = 0.7980 gm cm^{-3}) and 70 ml of H_2O (d=0.9984 gm cm^{-3}) are mixed at 25°C to form a solution of density 0.9575 gm cm^{-3}. Calculate the freezing point of the solution. K_f (H_2O) is 1.86 kg mol^{-1} K. Also calculate its molarity.

7. An aqueous solution containing 288 gm of a non-volatile compound having the stoichiometric composition $C_xH_{2x}O_x$ in 90 gm water boils at 101.24°C at 1.00 atmospheric pressure. What is the molecular formula?

$K_b(H_2O)$ = 0.512 K mol–1 kg

$T_b(H_2O)$ = 100°C

8. A complex is represented as $CoCl_3\cdot$ x NH_3. It's 0.1 molal solution in a solution shows ΔT_f = 0.558°C. K_f for H_2O is 1.86 K mol^{-1} kg . Assuming 100% ionisation of complex and coordination no. of Co is six, calculate formula of complex.

9. Phenol associates in benzene to a certain extent to form a dimer. A solution containing 20×10^{-3} kg phenol in 1 kg of benzene has its freezing point depressed by 0.69 K. Calculate the fraction of phenol that has dimerised. K_f for benzene = 5.12 kg mol^{-1}K.

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

EXERCISE # (O-I)

Single correct :

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

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

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

[Given : $P_A^o = 100$ mm Hg and $B°_P = 200$ mm Hg]

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

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

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

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

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

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

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

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

(A) Mole fraction of the solvent (B) Mole fraction of the solute

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

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

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

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

($P_A° = 100$mm, $P_B° = 200$mm)

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

8. The vapour pressure of a pure liquid 'A' is 70 torr at 270C. 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 270C. The vapour pressure of pure liquid B at 270C is

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

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

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

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

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

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

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

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

(A) Directly proportional to mole fraction of the solvent

(B) Inversely proportional to mole fraction of the solvent

(C) Directly proportional to mole fraction of the solute

(D) Inversely propartional to mole fraction of the solute

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

(A) $\frac{2}{3}$ (B) $\frac{1}{3}$ (C) $\frac{1}{2}$ (D) $\frac{3}{2}$

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

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

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

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

16. Vapour pressure of CCl_4 at 250C is 143 mm Hg. 0.5 gm of a non-volatile solute (mol. wt. 65) is dissolved in 100 ml of CCl_4. Fine the vapour perssure of the solution. (Density of CCl_4 = 1.58 gm/cm^3)

(A) 141.93 mm (B) 94.39 mm (C) 199.34 mm (D) 143.99 mm

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

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

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

18. Colligative properties of the solution depend upon

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

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

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

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

20. When common salt is dissolved in water

(A) Melting point of the solution increases

(B) Boiling point of the solution increases

(C) Boiling point of the solution decreases

(D) Both Melting point and Boiling point is decreases

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

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

22. The boiling point of an aqueous solution of a non volatile solute is 100.15 °C. What is the freezing point of an aqueous solution obtained by diluting the above solution with an equal volume of water ? The values of K_b and K_f for water are 0.512 and 1.86 K $molality^{-1}$:

(A) –0.544 °C (B) –0.512 °C (C) –0.272 °C (D) –1.86 °C

23. A 5% solution (by mass) of cane sugar in water has freezing point of 271 K and freezing point of pure water is 273·15K. The freezing point of a 5% solution (by mass) of glucose in water is–

(A) 271 K (B) 273·15 K (C) 269·07 K (D) 277·23 K

24. As a result of osmosis, the volume of the concentrated solution

(A) Gradually decreases (B) Gradually increases

(C) Suddenly increases (D) None

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

(A) Vapour pressure of solution increases (B) B. P. decreases

(C) Osmotic pressure increases (D) All are correct

26. 5% solution of sucrose is isotonic with 1% solution of a compound 'A' then the molecular weight of compound 'A' is -

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

27. Osmotic pressure of a sugar solution at 240C 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

28. A solution containing 4 g of a non volatile organic solute per 100 ml was found to have an osmotic pressure equal to 500 cm of mercury at 270C. The molecular weight of solute is :

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

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

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

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

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

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

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

32. 1.0 molal aqueous solution of an electrolyte A_2B_3 is 60% ionised. The boiling point of the solution at 1 atm is (= 0.52 K kg mol^{-1})

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

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

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

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

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

34. 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

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

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

36. The lowerring of vapour pressure of 0.1M aqueous solutions of NaCl, $CuSO_4$ and K_2SO_4 are:

(A) All equal (B) In the ratio of 1 : 1 : 1.5
(C) In the ratio of 3 : 2 : 1 (D) In the ratio of 1.5 : 1 : 2.5

37. 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%

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

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

39. The molal elevation constant of water is 0.51. The boiling point of 0.1 molal aqueous NaCl solution is nearly :

(A) 100.05 °C (B) 100.1 °C (C) 100.2° C (D) 101.0° C

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

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

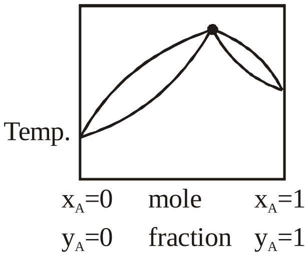
41. If a ground water contains H_2S at concentration of 2 mg/l, determine the pressure of H_2S in head space of a closed tank containing the ground water at 20ºC. Given that for H_2S, Henry's constant is equal to 6.8×10^3 bar at 20ºC.

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

EXERCISE # (O-II)

More than one may be correct

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



Which of the following statement is correct about the process

(A) The composition of distillate differs from the mixture

(B) The boiling point goes on changing

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

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

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

(A) ΔH_{mix} = –ve

(B) ΔV_{mix} = –ve

(C) ΔS_{mix} = +ve

(D) ΔG_{mix} = –ve

3. Acetone and carbon disulphide form binary liquid solution showing positive deviation from Raoult law. The normal boiling point (T_b) of pure acetone is less than that of pure CS_2. Pick out the incorrect statements among the following.

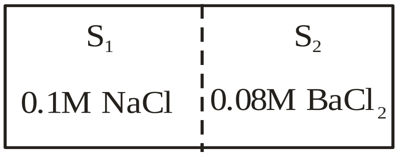
(A) Boiling temperature of mixture is always less than boiling temperature of acetone.

(B) Boiling temperature of Azeotropic mixture is always less than boiling temperature of pure CS_2.

(C) When a small amount of CS_2 (less volatile component) is added to excess of acetone boiling point of resulting mixture increases.

(D) A mixture of CS_2 and CH_3COCH_3 can be completely separated by simple fractional distillation.

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



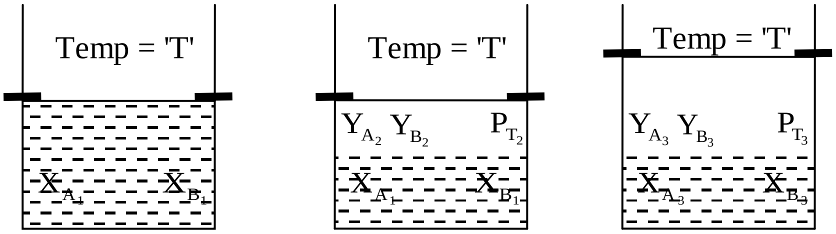
(A) S_1 and S_2 are isotonic

(B) S_1 is hypertonic and S_2 is hypotonic

(C) S_1 is hypotonic and S_2 is hypertonic

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

5. Using given information :



X_A , X_B = mol fraction of 'A' & 'B' in liquid, Y_A , Y_B = mol fraction of 'A' & 'B' in vapour

P_A^0, P_B^0 = vapour pressure of pure liquid A and pure liquid B respectively,

P_T = vapour pressure of solution, Given : $X_{A_1} = X_{B_1}$, $P_A^0 > P_B^0$,

Select the correct set/ sets of relation

(A) $Y_{A_2} > Y_{B_2}, P_{T_2} = P_{T_3}$

(B) $Y_{A_2} > Y_{A_2}, Y_{B_2}, X_{B_2}$

(C) $Y_{A_2} > Y_{A_3}, P_{T_2} > P_{T_3}$

(D) $X_{A_2} < X_{B_2}, P_{T_2} < P_{T_3}$

6. For an ideal binary liquid solution with $P_A^0 > P_B^0$, which relation between X_A (mole fraction of A in liquid phase) and Y_A(mole fraction of A in vapour phase) is correct?

(A) $Y_A < Y_B$

(B) $X_A > X_B$

(C) $\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$

(D) $\frac{Y_A}{Y_B} < \frac{X_A}{X_B}$

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

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

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

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

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

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

(A) 0.635 MeOH, 0.365 EtOH (B) 0.365 MeOH, 0.635 EtOH

(C) 0.574 MeOH, 0.326 EtOH (D) 0.173 MeOH, 0.827 EtOH

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

(Molar mass of A = 80g/mol)

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

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

(A) Decimolar $Al_2(SO_4)_3$

(B) Decimolar $BaCl_2$

(C) Decimolar Na_2SO_4

(D) A solution obtained by mixing equal volumes of (B) and (C)

11. A mixture contains 1 mole of volatile liquid A (P_A^0 =100 mm Hg) and 3 moles of volatille liquid B (P_B^0= 80 mm Hg). If solution behaves ideally, the total vapour pressure of the distillate is

(A) 85 mm Hg (B) 85.88 mm Hg

(C) 90 mm Hg (D) 92 mm Hg

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

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

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

(A) 0.200 (B) 0.478

(C) 0.549 (D) 0.786

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

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

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

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

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

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

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

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

Match the column :

16.

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

EXERCISE # (JEE-MAIN)

1. Which one of the following aqueous solutions will exhibit highest boiling point ? **[AIEEE-2004]**

(1) 0.01M Na_2SO_4 (2) 0.01M KNO_3 (3) 0.015M urea (4) 0.015M glucose

2. Which of the following liquid pairs shows a positive deviation from Raoult's law ? **[AIEEE-2004]**

(1) Water-hydrochloric acid (2) Benzene-methanol

(3) Water-nitric acid (4) Acetone-chloroform

3. Which one of the following statement is False ? **[AIEEE-2004]**

(1) Raoult's law states that the vapour pressure of a component over a solution is proportional to its mole fraction

(2) The osmotic pressure (π) of a solution is given by the equation π = MRT where M is the molarity of the solution

(3) The correct order of osmotic pressure for 0.01M aqueous solution of each compound is $BaCl_2 > KCl > CH_3COOH >$ Sucrose

(4) Two sucrose solutions of same molality prepared in different solvent will have the same freezing point depression

4. If a is the degree of dissociation of Na_2SO_4, the vant of Hoff's factor (i) used for calculating the molecular mass is **[AIEEE-2005]**

(1) $1 - \alpha$ (2) $1 + \alpha$ (3) $1 - 2\alpha$ (4) $1+2\alpha$

5. Benzene and toluene form nearly ideal solutions. At 20°C, the vapour pressure of benzene is 75 torr and that of toluene is 22 torr. The partial vapour pressure of benzene at 20°C for a solution containing 78 g of benzene and 46 g of toluene in torr is - **[AIEEE-2005]**

(1) 25 (2) 50 (3) 53.5 (4) 37.5

6. Two solutions of a substance (non electrolyte) are mixed in the following manner. 480 ml of 1.5 M first solution + 520 mL of 1.2 M second solution. What is the molarity of the final mixture ? **[AIEEE-2005]**

(1) 1.50 M (2) 1.20 M (3) 2.70 M (4) 1.344 M

7. Equimolar solutions in the same solvent have **[AIEEE-2006]**

(1) Same freezing point but different boiling point

(2) Same boiling point but different freezing point

(3) Different boiling and different freezing point

(4) Same boiling and same freezing points

8. 18 g of glucose (C6H12O6) is added to 178.2g of water. The vapour pressure of water for this aqueous solution at 100° C is **[AIEEE-2006]**

(1) 7.60 Torr (2) 76.00 Torr (3) 752.40 Torr (4) 759.00 Torr

9. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be **[AIEEE-2007]**

(1) 350 (2) 300 (3) 700 (4) 360

10. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass=60g mol^{-1}) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 gcm^{-3}, molar mass of the substance will be **[AIEEE-2007]**

(1) 90.0 g mol^{-1} (2) 115.0 g mol^{-1} (3) 105.0 g mol^{-1} (4) 210.0 g mol^{-1}

11. At 80°C, the vapoure pressure of pure liquid 'A' is 520 mm Hg and that of pure liquid 'B' is 1000 mm Hg. If a mixture solution of 'A' and 'B' boils at 80°C and 1 atm pressure, the amount of 'A' in the mixture is (1 atm = 760 mm Hg) **[AIEEE-2008]**

(1) 52 mol % (2) 34 mol % (3) 48 mol % (4) 50 mol %

12. The vapour pressure of water at 20°C is 17.5 mm Hg. If 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water at 20°C, the vapour pressure of the resulting solution will be **[AIEEE-2008]**

(1) 17.675 mm Hg (2) 15.750 mm Hg (3) 16.500 mm Hg (4) 17.325 mm Hg

13. Two liquids X and Y form an ideal solution. At 300K, vapour pressure of the solution containing 1 mol of X and 3 mol of Y is 550 mm Hg. At the same temperature, if 1 mol of Y is further added to this solution, vapour pressure of the solution increases by 10 mm Hg. Vapour pressure (in mmHg) of X and Y in their pure states will be, respectively : **[AIEEE-2009]**

(1) 400 and 600 (2) 500 and 600 (3) 200 and 300 (4) 300 and 400

14. A binary liquid solution is prepared by mixing n-heptane and ethanol. Which one of the folloowing statements is correct regarding the behaviour of the solution ? **[AIEEE-2009]**

(1) The solution is non-ideal, showing –ve deviation from Raoult's law

(2) n-heptane shows +ve deviation while ethanol shows –ve deviation from Raoult's law

(3) The solution formed is an ideal solution.

(4) The solutionis non-ideal, showing +ve deviation from Raoult's law

15. 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 mol of sodium sulphate is dissolved in 1 kg of water, is (K_f = 1.86 K kg mol^{-1}) : **[AIEEE-2010]**

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

16. 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 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]**

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

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

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

18. Ethylene glycol is used as an antifreeze in a cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at – 6°C will be : **[AIEEE-2011]**

(K_f for water = 1.86 K $kgmol^{-1}$, and molar mass of ethylene glycol = 62 $gmol^{-1}$)

(1) 400.00 g (2) 304.60 g (3) 804.32 g (4) 204.30 g

19. A 5% solution of cane sugar (molar mass 342) is isotonic with 1% of a solution of an unknown solute. The molar mass of unknown solute in g/mol is : **[AIEEE-2011]**

(1) 136.2 (2) 171.2 (3) 68.4 (4) 34.2

20. The molality of a urea solution in which 0.0100g of urea, $[(NH_2)_2CO]$ is added to 0.3000 dm3 of water at STP is : **[AIEEE-2011]**

(1) 0.555 m (2) 5.55×10^{-4} m (3) 33.3 m (4) 3.33×10^{-2} m

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

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

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

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

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

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

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

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

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

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25. 12g of a nonvolatile solute dissolved in 108g of water produces the relative lowering of vapour pressure of 0.1. The molecular mass of the solute is : **[JEE (MAIN)-2013 ONLINE]**

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

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

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

27. Vapour pressure of pure benzene is 119 torr and that of toluene is 37.0 torr at the same temperature. Mole fraction of toluene in vapour phase which is in equilibrium with a solution of benzene and toluene having a mole fraction of toluene 0.50, will be :

[JEE (MAIN)-2013 ONLINE]

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

28. How many grams of methyl alcohol should be added to 10 litre tank of water to prevent its freezing at 268 K ?

(K_f for water is 1.86 K kg mol^{-1}) **[JEE (MAIN)-2013 ONLINE]**

(1) 899.04 g (2) 886.02 g (3) 868.06 g (4) 880.07 g

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

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

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

(3) They all have the same osmotic pressure.

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

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

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

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

(3) They all have the same osmotic pressure.

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

31. For an ideal Solution of two components A and B, which of the following is true ?

(1) $\Delta H_{mixing} < 0$ (zero) **[JEE(MAIN)-2014 ONLINE]**

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

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

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

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

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

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

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

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

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

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

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

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

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

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

37. 18 g glucose ($C_6H_{12}O_6$) is added to 178.2 g 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

38. 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

39. 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

40. 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: **[JEE (MAIN)- 2017]**

(K_f for benzene = 5.12 K kg mol^{-1})

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

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

(1) $[Co(H_2O)_3Cl_3]$. $3H_2O$ (2) $[Co(H_2O)_6]Cl_3$

(3) $[Co(H_2O)_5Cl]Cl_2.H_2O$ (4) $[Co(H_2O)_4Cl_2]Cl._2H_2O$

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

(1) The value of K_H increases with function of the nature of the gas **[JEE MAIN-2019(Jan.)]**

(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.

43. Liquids A and B form an ideal solution in the entire composition range. At 350 K, the vapor pressures of pure A and pure B are 7×10^3 Pa and 12×10^3 Pa, respectively. The composition of the vapor in equilibrium with a solution containing 40 mole percent of A at this temperature is : **[JEE MAIN-2019(Jan.)]**

(1) $x_A = 0.76$; $x_B = 0.24$
(2) $x_A = 0.28$; $x_B = 0.72$
(3) $x_A = 0.37$; $x_B = 0.36$
(4) $x_A = 0.4$; $x_B = 0.6$

44. Elevation in the boiling point for 1 molal solution of glucose is 2 K. The depression in the freezing point for 2 molal solution of glucose in the same solvent is 2 K. The relation between K_b and K_f is: **[JEE MAIN-2019(Jan.)]**

(1) $K_b = 1.5\ K_f$
(2) $K_b = K_f$
(3) $K_b = 0.5\ K_f$
(4) $K_b = 2\ K_f$

45. The freezing point of a diluted milk sample is found to be –0.2°C, while it should have been –0.5°C for pure milk. How much water has been added to pure milk to make the diluted sample ? **[JEE MAIN-2019(Jan.)]**

(1) 2 cups of water to 3 cups of pure milk
(2) 1 cup of water to 3 cups of pure milk
(3) 3 cups of water to 2 cups of pure milk
(4) 1 cup of water to 2 cups of pure milk

46. Molecules of benzoic acid (C_6H_5COOH) dimerise in benzene. 'w' g of the acid dissolved in 30 g of benzene shows a depression in freezing point equal to 2K. If the percentage association of the acid to form dimer in the solution is 80, then w is : **[JEE MAIN-2019(Jan.)]**

(Given that $K_f = 5$ K kg mol^{-1}, Molar mass of benzoic acid = 122 g mol^{-1})

(1) 1.5 g
(2) 1.0 g
(3) 2.4 g
(4) 1.8 g

47. K_2HgI_4 is 40% ionised in aqueous solution. The value of its van't Hoff factor (i) is :-

(1) 1.6
(2) 2.0 **[JEE MAIN-2019(Jan.)]**
(3) 2.2
(4) 1.8

48. Freezing point of a 4% aqueous solution of X is equal to freezing point of 12% aqueous solution of Y. If molecular weight of X is A, then molecular weight of Y is :

(1) 2A
(2) A **[JEE MAIN-2019(Jan.)]**
(3) 3A
(4) 4A

EXERCISE # (JEE-ADVANCED)

1. A 0.004 M solution of Na_2SO_4 is isotonic with a 0.010 M solution of glucose at same temperature. The apparent degree of dissociation of Na_2SO_4 is **[JEE 2004]**

(A) 25% (B) 50% (C) 75% (D) 85%

2. 1.22 g of benzoic acid is dissolved in (i) 100 g acetone (K_b for acetone = 1.7) and (ii)100 g benzene (K_b for benzene = 2.6). The elevation in boiling points Tb is 0.17°C and 0.13°C respectively. **[JEE 2004]**

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

(b) What do you deduce out of it in terms of structure of benzoic acid?

3. The elevation in boiling point, when 13.44 g of freshly prepared $CuCl_2$ are added to one kilogram of water, is [Some useful data, K_b (H_2O) = 0.52 kg K mol^{-1}, mol. wt. of $CuCl_2$ = 134.4 gm] **[JEE 2005]**

(A) 0.05 (B) 0.1 (C) 0.16 (D) 0.21

4. 72.5 g of phenol is dissolved in 1 kg of a solvent (k_f = 14) which leads to dimerization of phenol and freezing point is lowered by 7 kelvin. What percent of total phenol is present in dimeric form? **[JEE 2006]**

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

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

Paragraph for Question No. Q.6 to Q.8

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

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

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

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

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

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

Standard freezing point of water = 273 K

Standard freezing point of ethanol = 155.7 K

Standard boiling point of water = 373 K

Standard boiling point of ethanol = 351.5 K

Vapour pressure of pure water = 32.8 mm Hg

Vapour pressure of pure ethanol = 40 mm Hg

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

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

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

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

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

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

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

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

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

9. The Henry's law constant for the solubility of N2 gas in water at 298 K is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water at 298 K and 5 atm pressure is– **[JEE 2009]**

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

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

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

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

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

12. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take K_b=0.76 K kg mol^{-1}) **[JEE 2012]**

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

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

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

14. A compound H_2X with molar weight of 80 g is dissolved in a solvent having density of 0.4 g mol^{-1}, Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is **[JEE-Adv. 2014]**

15. If the freezing point of a 0.01 molal aqueous solution of a cobalt (III) chloride-ammonia complex (which behaves as a strong eletrolyte) is – 0.0558°C, the number of chloride (s) in the coordination sphere of the complex is **[JEE-Adv. 2015]**

[K_f of water = 1.86 K kg mol^{-1}]

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

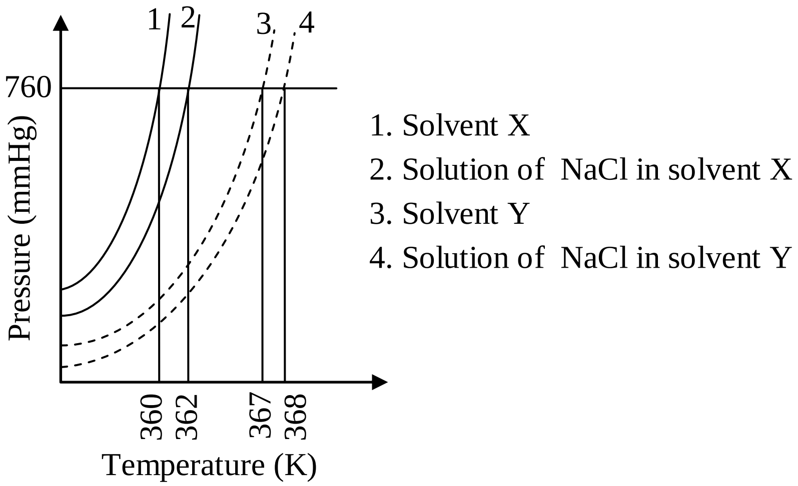
(A) carbon tetrachloride + methanol (B) carbon disulphide + acetone

(C) benzene + toluene (D) phenol + aniline

17. 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 xA and xB respectively, has vapour pressure of 22.5 Torr. The value of xA/xB in the new solution is ____.

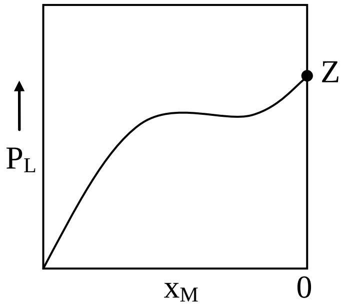
(given that the vapour pressure of pure liquid A is 20 Torr at temperature T) **[JEE Adv. 2018]**

18. 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 of 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]**



On addition of equal number of moles of 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 ____.

19. 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 xL and xM represent mole fractions of L and M, respectively, in the solutions. The correct statement(s) applicable to this system is(are) **[JEE Adv. 2017]**



(A) Attractive intermolecular 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.

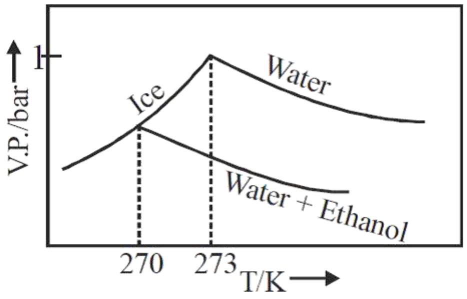
(B) The point Z represnts vapour pressure of pure liquid M and Raoult's law is obeyed when $x_L \rightarrow 0$

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

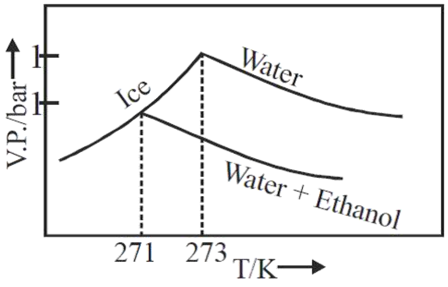
(D) The point Z represnts vapour pressure of pure liquid M and Raoult's law is obeyed when $x_L = 0$ $x_L = 1$

20. 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 represent plots of vapour pressure (V.P.) Among the following, the option representing change in the freezing point is

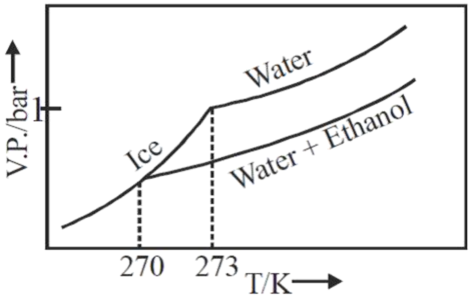
(A)



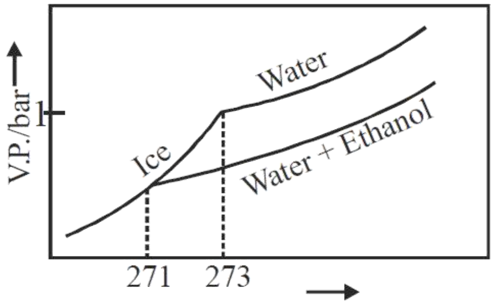
(B)



(C)



(D)



ANSWER KEY

EXERCISE # (S-I)

1.	0.25	**2.**	0.04	**3.**	111.1g, 18.52 molal	**4.**	0.162 m
5.	65.25	**6.**	17.38	**7.**	0.24	**8.**	66.13 mm Hg
9.	0.964	**10.**	106 g/mol	**11.**	100.079°C	**12.**	5.08°C/m
13.	2048 g/mol	**14.**	$K_b = 0.512$ kg mol K^{-1}, $T_b = 373.20$ K			**15.**	156.06
16.	C_6H_6	**17.**	$T_f = -2.28^{o}C$	**18.**	59.99	**19.**	i = 2.5
20.	3 ions	**21.**	$\alpha = 99.2\%$	**22.**	7.482×10^5 Nm^{-2}	**23.**	94.5 %
24.	4.64 atm	**25.**	0.95; 1.95				

EXERCISE # (S-II)

1.	92 mol% toluene; 96.8 mol % toluene			**2.**	0.741 m, 0.013	**3.**	38.71 g
4.	5.4×10^5 g/mol	**5.**	20	**6.**	–19.91°C, 7.64 M	**7.**	$C_{44}H_{88}O_{44}$
8.	$[Co(NH_3)_5Cl]Cl_2$	**9.**	a = 0.7333	**10.**	0.73		

EXERCISE # (O-I)

1.	(B)	**2.**	(C)	**3.**	(C)	**4.**	(D)	**5.**	(A)
6.	(C)	**7.**	(C)	**8.**	(C)	**9.**	(D)	**10.**	(C)
11.	(C)	**12.**	(A)	**13.**	(A)	**14.**	(B)	**15.**	(B)
16.	(A)	**17.**	(B)	**18.**	(C)	**19.**	(D)	**20.**	(B)
21.	(A)	**22.**	(C)	**23.**	(C)	**24.**	(B)	**25.**	(C)
26.	(B)	**27.**	(D)	**28.**	(B)	**29.**	(B)	**30.**	(D)
31.	(B)	**32.**	(D)	**33.**	(B)	**34.**	(B)	**35.**	(D)
36.	(B)	**37.**	(B)	**38.**	(B)	**39.**	(B)	**40.**	(B)
41.	(A)								

EXERCISE # (O-II)

1.	(C, D)	**2.**	(A, B, C, D)	**3.**	(A, C, D)	**4.**	(C, D)	**5.**	(B, C)
6.	(C)	**7.**	(C)	**8.**	(B)	**9.**	(D)	**10.**	(A)
11.	(B)	**12.**	(A)	**13.**	(B)	**14.**	(D)	**15.**	(C)

16. (A) → P ; (B) → Q, R, S ; (C) → T ; (D) → P, Q, R, S, T

EXERCISE # (JEE-MAIN)

1.	(1)	**2.**	(2)	**3.**	(4)	**4.**	(4)	**5.**	(2)
6.	(4)	**7.**	(4)	**8.**	(3)	**9.**	(1)	**10.**	(4)
11.	(4)	**12.**	(4)	**13.**	(1)	**14.**	(4)	**15.**	(3)
16.	(2)	**17.**	(3)	**18.**	(3)	**19.**	(3)	**20.**	(2)
21.	(1)	**22.**	(1)	**23.**	(3)	**24.**	(3)	**25.**	(4)
26.	(1)	**27.**	(3)	**28.**	(3)	**29.**	(3)	**30.**	(3)
31.	(2)	**32.**	(4)	**33.**	(1)	**34.**	(4)	**35.**	(1)
36.	(1)	**37.**	(4)	**38.**	(3)	**39.**	(1)	**40.**	(4)
41.	(1)	**42.**	(2)	**43.**	(2)	**44.**	(4)	**45.**	(3)
46.	(3)	**47.**	(4)	**48.**	(3)				

EXERCISE # (JEE-ADVANCED)

1. (C)

2. (a)122, (b) It means that benzoic acid remains as it is in acetone while it dimerises in benzene

3. (C)

4. 35% (degree of asso = 70%)

5.	(A)	**6.**	(D)	**7.**	(B)	**8.**	(B)	**9.**	(A)
10.	(A)	**11.**	(A)	**12.**	(A)	**13.**	(B,C,D)	**14.**	(8)
15.	(1)	**16.**	(A, B)	**17.**	(19)	**18.**	(0.05)	**19.**	(A,C)
20.	(C)								

EXERCISE # (S-I)

1. (0.25)

$$\frac{P^0 - P_S}{P^0} = \text{X solute}$$

$$X_B = \frac{0.8 - 0.6}{0.8} = \frac{1}{4} = 0.25$$

2. (0.04)

$$\frac{P^0 - P_S}{P^0} = \frac{n}{N + A}$$

$$\frac{P^0 - P_S}{P^0} = \frac{1}{1 + \alpha 4} = \frac{1}{\alpha 5} = 0.04$$

3. (18.52)

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

$$\frac{100 - 75}{75} = \frac{\text{n area}}{\frac{100}{18}}$$

$$\text{n area} = \frac{1}{3} \times \frac{100}{18} = \frac{100}{54}$$

mass of area = 111.1 g

$$m = \frac{100/54}{100} \times 1000 = 18.52$$

4. (0.162)

$$\frac{P^0 - P_S}{P_S} = \frac{m \times M_{\text{solvent}}}{1000}$$

$$\frac{639.7 - 631.7}{631.7} = \frac{M \times 18}{1000}$$

$$\frac{8}{631.7} = \frac{M \times 78}{1000}$$

$$M = \frac{8}{631.7} \times \frac{1000}{78} = 0.162$$

5. (62.25)

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

$$\frac{640 - 600}{600} = \frac{2.175/M}{0.5}$$

M = 65.25

6. (17.38)

$$\frac{P^0 - P_S}{P_S} = \frac{M \times M_{solvent}}{1000}$$

$$\frac{17.54 - P_S}{P_S} = \frac{0.5 \times 18}{1000}$$

$$\frac{17.54 - P_S}{P_S} = 1 + \frac{9}{1000} = 1.009$$

$$Ps = \frac{17.54}{1.009} = 17.38$$

7. $P_A = P^0{}_A X_A$

$23 = 96 \times X_{CH_3OH}$

$$X_{CH_3OH} = \frac{1}{4} = 0.25$$

8. $n_{C_2H_5OH} = \frac{60}{46}$ $\qquad$ $n_{CH_3OH} = \frac{40}{32}$

$= 1.3$ $\qquad$ $= 1.25$

$$P_T = 44.5 \times \frac{1.3}{2.55} + 88.7 \times \frac{1.25}{2.55}$$

= 66.16 M M of Hg

9. (0.964)

For solution A

$P_A = 0.5 \times P_B^0 + 0.5\ P_T^0 = (160 + 60) \times 0.5 = 110$

$$P_B = P_B^0 \times \frac{92}{170} + P_T^0 \times \frac{78}{170} = 160 \times \frac{92}{170} + 60 \times \frac{78}{170} = 114.11]$$

$$\frac{P_A}{P_B} = \frac{110}{114.11} = 0.964$$

10. (106.42 g/mol)

$\Delta T_b = K_b\ M$

$$0.284 = 2.11 \times \frac{10.6/M}{740} \times 1000$$

$$M = \frac{2.11 \times 10.6 \times 1000}{740 \times 0.284} = 106.42 \text{ g/mol}$$

11. (100.08°C)

$$\Delta T_b = K_b\ m \quad = 0.52 \times \frac{24/58}{600} \times 1000 = 0.358$$

$T_b = 99.725 + 0.358 \quad = 100.08°C$

12. (5.08° c/m)

$\Delta T_f = K_f\, m$

$$1.9 = K_f \times \frac{7.24/168}{115.3} \times 1000$$

$$K_f = \frac{1.9 \times 115.3 \times 168}{7.24 \times 1000} = 5.08°\ \text{c/m}$$

13. (2048 g/mol)

$\Delta T_f = K_f\, m$

$$0.1 = 5.12 \times \frac{2.4/M}{60} \times 1000$$

$$M = \frac{5.12 \times 2.4 \times 1000}{6} = 2048\ \text{g / mol}$$

14. (0.512)

$$K_b = \frac{RTb^2}{1000Lv} = \frac{2 \times (373.15)^2 \times 18}{1000 \times 9.72 \times 1000} = 0.512\ \text{kg K mol}^{-1}$$

15. (156 g/mol)

$\Delta T_f = K_f\, m$

$$0.48 = 5.12 \times \frac{0.643/M}{50 \times 0.879} \times 1000$$

$$M = \frac{5.12 \times 0.643 \times 1000}{50 \times 0.879 \times 0.48} = 156\ \text{g/mol}$$

16. ($C_6\,H_6$)

$\Delta T_f = K_f\, m$

$$0.46 = 3.6 \times \frac{1/M}{100} \times 1000$$

$$M = \frac{3.6 \times 1000}{0.46 \times 100} = 78.26$$

C	H
92.3 %	7.7 % (by mass)
$\frac{92.3}{12} = 7.7$	$\frac{7.7}{1} = 7.7$
1	1
EF = CH	$n = \frac{78.26}{13} = 6$

MF = $C_6\,H_6$

17. (2.27° C)

$\pi = CRT$

$30 = C \times 0.0821 \times 298$

$C = 1.22$ M

Consider $M = m$

$\Delta T_f = K_f m$

$= 1.86 \times 1.22 = 2.27$

$T_f = -2.27°C$

18. (60 g/mol)

If to solution are isotonic then

$\pi_1 = \pi_2$

$c_1 = c_2$

$$\frac{5}{342} = \frac{0.877}{M}$$

$$M = \frac{0.877}{5} \times 342$$

= 60 g/mol

19. (2.5)

$\Delta T_f = iK_f m$

$$29.08 = I \times 1.86 \times \frac{38/98}{62} \times 1000$$

$$i = \frac{29.08 \times 62 \times 98}{1.86 \times 38 \times 1000}$$

$i = 2.5$

20. (3)

$1.28 = 5.12 \times m$ (i)

$1.4 = i \times 1.86 \times m$ (ii)

(ii) / (i)

$$\frac{1.4}{1.28} = \frac{i \times 1.80}{5.12}$$

$i = 3$

21. (99.16 %)

$\Delta T_f = iK_f m$

$$1.62 = i \times 4.9 \times \frac{2/122}{25} \times 1000$$

i = $\frac{1.62 \times 122}{40 \times 2 \times 4.9}$ = 0.5042

i = 1 + $\left(\frac{1}{2} - 1\right)\alpha$

α = 2 × (1 – 0.5042)

= 99.16 %

22. (7.4826 × 10^5 Nm^{-2})

i = 1 + (5 – 1) × $\frac{1}{2}$ = 3

π = 3 × $\frac{0.1}{10^{-3}}$ × 8.314 × 300

= 7.4826 × 10^5 Nm^{-2}

23. (94.53%)

ΔT_f = i K_f m

0.45 = i × 5.12 × $\frac{0.2/60}{20} \times 1000$

i = 5.5273

i = 1 + $\left(\frac{1}{2} - 1\right)\alpha$

α = 2 × (1 – 0.5273)

= 94.53 %

24. (4.68 atm)

π = I c RT

i = 1 + 1 × 0.9 = 1.9

π = 1.9 × $\frac{0.85 \times 10}{85}$ =0.0821 × 300 = 4.68 atm

25. (0.95)

$\frac{7.2}{180}$ = i × $\frac{1.2}{58.5}$

i = $\frac{7.2 \times 58.5}{180 \times 1.2}$ = 1.95

1 + α = 1.95

α = 0.95

EXERCISE # (S-II)

1. For boiling $P = P_{ext} = 0.5 \times 760 = 380$ torr

$P_T = P^0_A + P^0_B X_B$

$380 = 400\, X_T + 150\,(1 - X_T)$

$250\, X_T = 230$

$X_T = \frac{23}{25}$

Mole % of toluene = $\frac{23}{25} \times 100 = 92\%$

Mole % of σ – xylene = $\frac{2}{25} \times 100 = 8\%$

2. $P^0 = 760$ mm $\quad P_S = 750$

$\frac{P^0 - P_S}{P^0} = X_{solute}$

$\frac{10}{760} = X_{solute} \Rightarrow \quad X_{solute} = \frac{1}{76}$

$\frac{P^0 - P_S}{P_S} = \frac{m \times M_{solvent}}{1000}$

$\frac{10}{750} = \frac{M \times 18}{1000} \quad \Rightarrow m = 0.74$

3. $\Delta T_f = K_f\, m$

$9.3 = 1.86 \times \frac{50/62}{W_{solvent}(kg)}$

W solvent (kg) = 0.161 $\quad$ = 161.3

ice separated = 200 – 161.3 = 38.7 gram

4. $P_1 h_1 = P_2 h_2$

$2.6 \times 1 = 13.6 \times h_2$

$h_2 = \frac{2.6}{13.6}$

$P = \frac{2.6}{13.6} \times \frac{1}{760}$ atm

$\pi = CRT$

$\frac{2.6}{13.6} \times \frac{1}{760} = \frac{0.750/M}{0.125} \times 0.0821 \times 277$

$M = 5.42 \times 10^5$ g/mol

5. $K_4[Fe(CN)_6] + 2CuCl_2 \longrightarrow Cl_2[Fe(CN)_6]\downarrow + 4KCl$

0.1 mol $\quad$ 0.2 mol

0 $\quad$ 0 $\quad$ - $\quad$ 0.4 mol

$\pi = i\,C\,R\,T = 2 \times 0.4 \times 0.0821 \times 304 = 20$ atm

6. $\Delta T_f = K_f m$

$$m = \frac{30\times0.798/32}{70\times0.9984}\times1000 = 10.7$$

$\Delta T_f = 1.86 \times 10.7 = 19.9$

$T_f = 0 - 19.9 = -19.9° C$

$$m = \frac{30\times0.798/32}{98}\times1000 = 7.63$$

7. $\Delta T_b = K_b m$

$$1.24 = 0.512 \times \frac{288/30x}{90}\times1000$$

$x = 44$

EF $\Rightarrow C_{44} H_{88} O_{44}$

8. $\Delta T_f = iK_f m$

$0.558 = i \times 1.86 \times 0.1$

$$i = \frac{5.58}{1.86} = 3$$

$[Co(NH_3)_5Cl] Cl_2 \qquad x = 5$

9. $\Delta T_f = iK_f m$

$$0.69 = i \times 5.12 \times \frac{20/94}{1}$$

$i = 0.633$

$$i = 1-\frac{\alpha}{2} = 0.633$$

$\alpha = 0.7332$

10. $$V_m, \text{Benzene} = \frac{78}{0.877}\times2750 = 244.58L$$

$$V_m, \text{toluene} = \frac{92}{0.867}\times7720 = 819.2\ L$$

By, $P_v = nRT \qquad P^0{}_B = 74.748$ torr

$P^0{}_T = 22.31$ torr

$46 = 74.748\ X_B + 22.31\ (1 - X_B)$

$X_B = 0.45$

$$y_B = \frac{P^0{}_B X_B}{P_T} = \frac{74.748\times0.45}{46} = 0.731$$

EXERCISE # (O-I)

1. Vapour pressure $\propto \frac{1}{\text{Boiling point}}$ (at same T)

2. $y_A = \frac{P^0_A X_A}{P_T}$

$P_T = P^0_A\ X_A + P^0_B\ X_B$

$= 100 \times 0.4 + 200 \times 0.6 = 160$

$y_A = \frac{40}{160} = 0.25$

3. $P_T = P^0_A\ X_A + P^0_B\ X_B$

$= P^0_A + (P^0_B - P^0_A)\ X_B$

$= P^0_A = 120 \qquad P^0_B - P^0_A = 75$

$P^0_B = 195$

4. $P_T = P^0_A\ X_A + P^0_B\ X_B$

$= 100 \times \frac{2}{5} + 300 \times \frac{3}{5}$

= 220 torr

5. $P_{solvent} = P^0_{solvent}\ X_{solvent}$

$P_{solvent} \propto X_{solvent}$

6. $P_T = P^0_A\ X_A + P^0_B\ X_B$

$= 92 \times \frac{1}{5} + 31 \times \frac{4}{5}$

= 43.2 mm of Hg

8. $P_T = P^0_A\ X_A + P^0_B\ X_B$

$84 = 70 \times 0.8 + P^0_B \times 0.2$

$P^0_B = 140$ torr

9. If a solution boils at 88°C at 1 atm, then v.p. = P_{ext} = 1 atm = 760 torr

$P_T = P^0_A\ X_A + P^0_B\ X_B$

$760 = 900 \times X_B + 360\ (1 - X_B)$

$X_B = \frac{20}{27} = 0.740$

10. $\frac{P^0 - P_S}{P^0} = \frac{n}{n + N}$ or $\frac{P^0 - P_S}{P^0} = \frac{n}{N}$

11. $\frac{10}{P^0} = 0.2$ (i)

$\frac{20}{P^0} = X_{solute}$ (ii)

$X_{solute} = 0.4$, $X_{solvent} = 0.6$

12. $\frac{P^0 - P_S}{P^0} = X_{solute}$

$P^0 - P_S = P^0 X_{solute}$

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

$= P^0 X_{solvent}$

$P_S \propto X_{solvent}$

13. $\frac{P^0 - P_S}{P^0} = \frac{n}{n + N}$ $\Rightarrow$ $\frac{P^0 - P_S}{P^0} = \frac{1}{1+2} = \frac{1}{3}$

14. $\frac{P^0 - P_S}{P_S} = \frac{n}{N}$ $\Rightarrow$ $\frac{10-9}{9} = \frac{1/M_B}{0.1}$

$M_B = 90$ amu

15. $\frac{P^0 - P_S}{P^0} = X_{solute}$ $\Rightarrow$ $\frac{0.8-0.6}{0.8} = X_{solute}$

$X_{solute} = 0.25$

16. $\frac{P^0 - P_S}{P_S} = \frac{n}{N} \Rightarrow \frac{143 - P_S}{P_S} = \frac{0.5/65}{158/154}$

$P_S = \frac{143}{1.00745} = 141.93$ mm

19. $\Delta T_b = K_b \times m$

$m = \frac{1 \times 1000}{1200 - 180} = \frac{1000}{1020} = 0.98$

$\Delta T_b = 0.98\ K_b$

20. When non volatitile solute is added

B. P $\uparrow$, F. P. $\downarrow$

21. $\Delta T_f = K_f\, m$

$= 1.86 \times \frac{17/46}{1}$

$\Delta T_f = 0.69$

$T_f = 0 - 0.69 = -0.69°C$

22. $\Delta T_b = K_b \times m$

$0.15 = 0.512 \times m$ (i)

$\Delta T_f = K_f \times m$

$\Delta T_f = 1.86 \times \frac{m}{2}$ (ii)

$$\frac{0.15}{\Delta T_f} = \frac{0.512}{1.86} \times 2$$

$\Delta T_f = 0.272$

$T_f = 0 - 0.272 = -0.272°C$

23. $\Delta T_f = K_f\, m$

$2.15 = K_f \times \frac{5/342}{95/1000}$

$\Delta T_f = K_f \times \frac{5/180}{95/1000}$

$$\frac{2.15}{\Delta T_f} = \frac{180}{342}$$

$\Delta T_f = 4.085$

$T_f = 273.15 - 4.085 = 269.07\ K$

24. due osmosis, solvent particles flow from lower con. Sode to higher conc. side.

25. $X_{solvent} \downarrow$, $X_{solute} \uparrow$

Number of solute particles $\uparrow$, V. P. $\downarrow$

B. P. $\uparrow$

F. P. $\downarrow$

$\pi \uparrow$

26. $\pi_1 = \pi_2$

$C_1 = C_2$

$$\frac{5}{342} = \frac{1}{M_A}$$

$$\Rightarrow M_A = \frac{342}{5} = 68.4$$

27. $\pi = CRT$

$2.5 = C \times 0.0821 \times 297$

$C = 0.1025$ M

28. $\pi = CRT$

$$\frac{500}{76} = \frac{40}{M} \times 0.0821 \times 300$$

$M = 149.75$

29. $\pi_1 = \pi_2$

$C_1 = C_2$

$$\frac{6.84}{342} = \frac{1.52}{M}$$

$M = 76$

30. 1 M NaCl $i = 2$

1 M $CaCl_2$ $i = 3$

1 M $AlCl_3$ $i = 4$

1 M $C_{12}H_{22}O_{11}$ $i = 1$

Number of solute particle ↑, V.P. ↓

31. $AlCl_3$ $i = 4$ $CaCl_2$ $i = 3$

$\Delta T_b \propto i$ $\Delta T_b \uparrow$, B.P. ↑

$T_1 > T_2$

32. $i = 1 + (n - 1)\alpha$

$= 1 + 4 \times 0.6 = 3.4$

$\Delta T_b = 3.4 \times 0.52 \times 1 = 1.768$

$T_b = 373 + 1.768 = 374.76$ K

33. $\Delta T_f = iK_f m$

$0.2 = i \times 1.8 \times 0.1$

$$i = \frac{2}{1.8} = 1.11$$

$i = 1 + \alpha = 1.11$

$\alpha = 0.11$

$$HX \rightleftharpoons H^+ + X^-$$

$$C(1-\alpha) \qquad C\alpha \qquad C\alpha$$

$$K = \frac{C\alpha^2}{1-\alpha} = \frac{0.1 \times (0.11)^2}{1 - 0.11}$$

$= 1.35 \times 10^{-3}$

34. $i = 1 + (n - 1)\,\alpha = \frac{1}{3}$

35.

	NaCl	$CuSO_4$	K_2SO_4
i	2	2	3

$$\frac{P^0 - P_S}{P^0} = \frac{i\,n}{i\,n + N}$$

37. $i = \frac{170}{92.64} = 1.835$

$i = 1 + \alpha = 1.835$

$\alpha = 0.835$

$\%\ \alpha = 83.5$

38. $i = 2$

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

$= 2 \times 1.86 \times 1 = 3.72$

$T_f = 0 - 3.72 = -3.72°C$

39. $\Delta T_b = K_b\,M = 0.51 \times 0.1 \quad = 0.051$

$T_b = 100 + 0.051 = 100.051°C$

40. $i = 1 + \alpha = 1.9$

$\Delta T_f = 1.9 \times 1.86 \times \frac{0.1}{91.9} \times 1000 \quad = 3.84$

$T_f = -3.84°\ C$

41. $Pgas = K_H\,X_{gas}$

$= KH \times \frac{m \times M_{solvent}}{1000}$

$P_{gas} = 6.8 \times 10^8 \times \frac{2 \times 10^{-3}}{34 \times 10^{-3}} \times \frac{18 \times 10^{-3}}{1000}$

$= 720$ Pa

EXERCISE # (O-II)

1. (A) Composition of azeotrope does not alter on distillation. $y_A = x_A$

(B) B.P. of azeotrope remains constant because composition of solution does not change.

(C) For maximum boiling azeotrope vapour pressure of mixture will be lower than v.p. of any component.

(D) On changing P_{ext}. Boling point of solution of also changes hance composition is changed.

2. For –ve deviation.

$\Delta H_{mix} < 0$ $\quad \Delta V_{mix} < 0$

$\Delta S_{mix} > 0$ $\quad \Delta G_{mix} < 0$

3. (A) If a solution show + ve deviation then $P > P_{theo.}$, boiling point of solution is less than BP of CH_3COCH_3 at particular ratio

(B) When azeotropes is formed by a solution showing +ve deviation. It will be min. boiling azeotrope. BP of solution will be less than BP of any component.

4. For solution S_1

$n_1 = 2 \times 0.1 \times RT = 0.2\ RT$

For solution S_2

$n_2 = 3 \times 0.02 \times RT = 0.06\ RT$

$\pi_1 > \pi_2$

S_1 is hypertonic and S_2 is hypotonic osmosis take place from higher conc. to lower conc. solution side.

6. If $P^0_A > P^0_B$

Then $Y_A = \dfrac{P^0_A X_A}{P_T}$

$$P^0_A = \frac{Y_A P_T}{X_A}$$

$$P^0_A = \frac{Y_B P_T}{X_B}$$

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

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

7. $P_{total} = P^0_A X_A + P^0_B X_B$

$= P^0_A (1 - X_B) + P^0_B X_B$

$P_{total} = P^0_A + (P^0_B - P^0_A) X_B$

Plot of P_{total} VS X_B or X_A is linear.

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

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

$$\frac{1}{P_{total}} = \left(\frac{1}{P^0{}_A} - \frac{1}{P^0{}_B}\right)Y_A + \frac{1}{P^0{}_B}$$

Plot of $\frac{1}{P_{total}}$ V_S Y_A is linear

Plot of $\frac{1}{P_{total}}$ V_S Y_B is also linear

9. $V_m = \frac{80}{0.8} = 0.1$ L

Pv = nRT

$P \times 0.1 = 1 \times 0.08 \times 200 \times 2000$

$P = 0.08$ atm

10. (A) $\Delta Tb = 4.6 \times 0.1 \times RT$

(B) $\Delta Tb = 2.8 \times 0.1 \times RT$

(C) $\Delta Tb = 2.8 \times 0.1 \times RT$

(D) $\Delta Tb = \left(\frac{2.8\times0.1+2.8\times0.1}{2}\right)\times RT = 2.8 \times 0.1 \times RT$

If $\Delta T_b \uparrow$, B.P. $\uparrow$, So

For 0.1 M $Al_2(SO_4)_3$ B. P is hignest

11. $P_T = P^0{}_A X_A + P^0{}_B X_B$ $= 1000 \times \frac{1}{4} + 80 \times \frac{3}{4}$ $= 85$ m m

$Y_A = \frac{25}{85}$ $Y_B = \frac{60}{85}$

$X'_A = Y_A = \frac{25}{85}$

$X'_B = Y_B = \frac{60}{85}$

For distillate

$P_T = P^0{}_A X'_A + P^0{}_B X'_B$ $= 100 \times \frac{25}{85} + 80 \times \frac{60}{85}$ $= 85.88$ mm Hg

12. $\frac{P^0 - P_S}{P_S} = \frac{i \times m \times M_{solvent}}{1000}$

$\frac{0.05}{17.2} = \frac{4 \times m \times 18}{1000}$

$M = 4.04 \times 10^{-2}$

$M \simeq m = 4.04 \times 10^{-2}$

13. $P_T = \frac{1}{5} + 440 + \frac{4}{5} \times 120$

$= 184$ m m of Hg

$Y_P = \frac{88}{184} = 0.478$

14. (A) $i = 1 + 2 \times 0.5 = 2$

(B) $i = 1 + 3 \times 0.75 = 3.25$

(C) $i = 1 + 1 \times 0.8 = 1.8$

(D) $i = 1 + 1 \times 0.9 = 2.9$

15. When a non volatile solution is added is to a liquid, it lowers it's freezing point.

16. (A) $\Delta T_f = i\, K_f\, m$

$i\, m = 0.3$

for $Ca(NO_3)_2 \Rightarrow i = 3$

$A \rightarrow P$

(B) $\Delta T_b = 0.28\, K_b$

$i\, m = 0.28$

for NaBr $\Rightarrow i = 2$ $\quad i\, m = 2 \times 0.14 = 0.28$

For urea $\Rightarrow i = 1$

$B \rightarrow Q, R, S$

(C) $\pi = i\, C \times RT$ $\quad i\, 6 = 0.19$

For HA $\Rightarrow$ $i = 1 + 0.9 = 1.9$

$K_a = \frac{C\alpha^2}{1-\alpha}$ $\quad 0.81 = \frac{0.1\alpha^2}{1-\alpha}$

$C \rightarrow T$ $\quad \alpha = 0.9$

(D)
$$\frac{P^0 - P_S}{P^0} = \frac{n}{n+N} = \frac{\frac{n}{N}}{\frac{n}{N}+1}$$

$$= \frac{\frac{n}{18N} \times 1000}{\frac{n}{18N} \times 1000 + \frac{1000}{18}} = \frac{\frac{\Delta T_f}{K_f}}{\frac{\Delta T_f}{K_f} + \frac{1000}{18}}$$

$D \rightarrow P, Q, R, S, T$

$P_{total} = 2.619 + 4.556$

$= 7.175$ KPa

$Y_{MeOH} = \frac{2.619}{7.175} = 0.365$

$Y_{EtoH} = \frac{4.556}{7.175} = 0.635$

EXERCISE # (J-MAIN)

1. Elevation in boiling point is a colligative property which depends upon the number of solute particles. Greater the number of solute particles in a solution, higher the extent of elevation in boiling point.

$$Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-}$$

2. Benzene-methanol shows a positive deviation from Raoult's law

3. $\Delta T_f = iK_f m$; K_f depends on nature of solvent.

4.

$$\begin{array}{llll} Na_2SO_4 & \rightarrow & 2Na^+ & + \ SO_4^{2-} \\ 1 & & 0 & \ \ 0 \\ 1-\alpha & & 2\alpha & \ \ \alpha \end{array}$$

Vant Hoff factor (i) = $\frac{1-\alpha+2\alpha+\alpha}{1} = 1+2\alpha.$

5. $P_B = P^o_B\, XB \quad P^o_B = 75$ torr

$X_B = \frac{78/78}{(78/78)+(46/92)} = \frac{1}{1+0.5} = \frac{1}{1.5}$ $P_B = 75 \times \frac{1}{1.5}$ = 50 torr.

6. Total millimoles of solute = 480 × 1.5 + 520 × 1.2 = 720 + 624 = 1344.

Total volume = 480 + 520 = 1000.

Molarity of the final mixture = $\frac{1344}{1000}$ = 1.344 M.

7. Equimolar solutions in the same solvent have same boiling and same freezing points because colligative properties depends on concentration of solution and does depend on nature of solute.

8. $\frac{P^0 - P_s}{P^0} = \frac{n}{n+N}$; $\qquad \frac{760 - P_s}{760} = \frac{0.1}{9.9+0.1}$

$\therefore P_s$ = 752.4 torr

9. According to Raoult's law

$P = P_A + P_B = P^o_A x + P^o_B x_B$ or $290 = P^o_A \times (0.6) + 200 \times (1 - 0.6)$

or $290 = 0.6 \times P^o_A + 0.4 \times 200$ or $P^o_A = 350$ mm.

10. Isotonic solutions have same osmotic pressure.

$\pi_1 = C_1 RT$, $\pi_2 = C_2 RT$

For isotonic solution, $\pi_1 = \pi_2$

$\therefore \quad C_1 = C_2$.

or $\quad \frac{1.5/60}{V} = \frac{5.25/M}{V}$ [where M = molecular weight of the substance]

or $\quad \frac{1.5}{60} = \frac{5.25}{M}$ or M = 210.

11. $P_{total} = P^o_A X_A + P^o_B (1 - X_A) = 520 \times X_A + 1000 \times (1 - X_A) = 760$

$520X_A + 1000 - 1000X_A = 760$; $\quad 480X_{A = 240}$

$\therefore X_A = 0.5$ So, mixture contains 50% moles of A

12. $P_A = P^0_A \ x_A = 17.5 \times \frac{178.2/18}{\frac{178.2}{18} + \frac{18}{180}} = 17.325$

13. $P_{total} = P^o_A X_A + P^o_B X_B = P^o_A \times \frac{1}{4} + P^o_B \times \frac{3}{4} = 550 \Rightarrow P^o_A + 3P^o_B = 550 \times 4$ .....(i)

Similary, $\quad 560 = P^o_A \times \frac{1}{5} + P^o_B \times \frac{4}{5} \Rightarrow P^o_A + 4P^o_B = 560 \times 5$ .....(ii)

eq. (ii) – eq.(i)

$P^o_B = 560 \times 5 - 550 \times 4 = 600$

so, $\quad P^o_A = 400$.

14. The solution is non-ideal, showing +ve deviation from Raoult's Law.

15. $Na_2SO_4 \text{ (s)} \xrightarrow{H_2O} 2Na^+ \text{ (aq.)} + SO_4^{2-} \text{ (aq.)}$

$\Delta T_f = i K_f m = 3 \times 1.86 \times 0.01 = 0.0558$ K.

16. $P_T = X_{Heptane} P^o_{Heptane} + X_{Octane} P^o_{Octane}$

$= \frac{0.25}{0.557} \times 105 + \frac{0.307}{0.557} \times 45$

$47.127 + 24.80 = 71.92 \approx 72$ kPa

17. $A_xB_y \xrightarrow{\quad} xA^{y+} + yB^{x-}$

$1 - \alpha \qquad x\alpha \qquad y\alpha$

$i = 1 - \alpha + x\alpha + y\alpha = 1 + \alpha(x + y - 1)$

So, $\alpha = \dfrac{i-1}{(x+y-1)}$

18. $\Delta T_f = i \times K_f \times m$; $\quad 6 = 1 \times 1.86 \times \dfrac{w}{62 \times 4}$

$w = 800$ g

19. $\pi_1 = \pi_2$

$i_1C_1 = i_2C_2$

$1 \times \dfrac{5 \times 1000}{342 \times 100} = 1 \times \dfrac{1 \times 1000}{M \times 100}$

$M = 68.4$ g/ mol

20. **m =** $\dfrac{0.01}{60 \times 0.3} = 5.55 \times 10^{-4}$ m

21. $\Delta T_f = i \times K_f \times m$; $\quad 1.91 = i \times 1.86 \times 1$

$i = \dfrac{1.91}{1.86} = 1.027 \qquad \because\ i = 1 + \alpha = 1.027$

$\therefore\ \alpha = 0.027, \qquad$ % dissociation = 2.7 %

22. Since $\mathbf{P_s} = X_A\ P_A^0 + X_B\ P_B^0$

$\Rightarrow \quad 250 = \dfrac{1}{3} \times P_A^0 + \dfrac{2}{3} \times P_B^0$ ……. (1) $\qquad \Rightarrow \quad 300 = 0.5 \times P_A^0 + 0.5 \times P_B^0$ ……..(2)

On solving eq. (1) and (2) we get $\quad P_A^0 = 450$ mm Hg $\qquad P_B^0 = 150$ mm Hg

23. $\Delta T_f = i \times K_f \times m$; $\quad 0.23 = i \times 1.86 \times \dfrac{0.85 \times 1000}{136.3 \times 125}$

$i = 2.47 \qquad \because\ i = 1 + 2\alpha = 2.47$

$\therefore\ \alpha = 0.735, \qquad$ % dissociation = 73.5 %

24. $\Delta T_f = i \times K_f \times m$; $2.8 = 1 \times 1.86 \times \frac{w}{62 \times 1}$

w = 93.3 g

25. $\frac{P^0 - P_s}{P^0} = \frac{n}{n + N}$; $0.1 = \frac{\frac{12}{M}}{\frac{12}{M} + \frac{108}{18}}$

M ≈ 20

26. $nM \longrightarrow (M)_n$

$1 - \alpha$ $\frac{\alpha}{n}$ $\Rightarrow i = 1 - \alpha + \frac{\alpha}{n} = 0.9$

Given ; $\frac{\frac{\alpha}{n}}{0.9} = 0.2$ $\therefore \alpha = 0.18\ n$

$\Rightarrow i = 1 - 0.18\ n + \frac{0.18\ n}{n} = 0.9$: n = 1.55

27. $P_s = X_b\ P_B^0 + X_t\ P_t^0 = 0.5 \times 119 + 0.5 \times 37 = 78$

$P_t = X_t\ P_t^0 = Y_t\ P_s$

$\Rightarrow$ $18.5 = Y_t \times 78 \Rightarrow$ $Y_t = 0.237$

28. $\Delta T_f = 273 - 268 = 5$ K

$\Delta T_f = i \times K_f \times m$; $\Rightarrow$ $5 = 1 \times 1.86 \times \frac{w}{32 \times 10}$

w = 860.2 g

29. Effective concentration of particles = iC

$C_2H_5OH(aq)$ = 1× 0.5 = 0.5 M

$Mg_3(PO_4)_2(aq)$ = 5 × 0.1 = 0.5 M

KBr(aq) = 2 × 0.25 = 0.5 M

KBr(aq) = 4 × 0.125 = 0.5 M

30. $\Delta H_{mixing} = 0$ (zero)

A – A, B – B and A – B interactions are identical

31. $\pi_1 = iCRT$; $\Rightarrow 10.8 = i \times 0.1 \times 0.082 \times 298$

$\Rightarrow i = 4.42$ (experimental)

$\Rightarrow i = 5$ (expected)

$Fe(NH_4)_2(SO_4)_2 \longrightarrow Fe^{2+} + NH_4^{+} + 2SO_4^{2-}$

32. $M_1V_1 + M_2V_2 = M_3V_3$

$0.5 \times 750 + 2 \times 250 = M_3 \times 1000$

$M_3 = 0.875$ M

33. $\dfrac{P^0 - P_S}{P_S} = \dfrac{n}{N} \qquad \Rightarrow \qquad \dfrac{185-183}{183} = \dfrac{1.2/M}{100/58}$

$M = 64 \text{ g mol}^{-1}$

34. $P_s = X_b\ P_B^0 + X_t\ P_t^0 = \dfrac{1.5}{5} \times 74.7 + \dfrac{3.5}{5} \times 22.3 = 22.41 + 15.687 = 38.097$

$P_b = X_b\ P_b^0 = Y_b\ P_s$

$\Rightarrow \quad 22.41 = Y_b \times 38$

$\Rightarrow \quad Y_b = 0.589$

35. Acetic acid is associated in benzene due to intermolecular H – bonding.

36. $\dfrac{P^0 - P_s}{P^0} = \dfrac{n}{n+N}; \qquad \dfrac{760 - P_s}{760} = \dfrac{0.1}{9.9 + 0.1}$

$\therefore P_s = 752.4$ torr

37. Solubility α Partial pressure of gas

$\dfrac{0.01}{S} = \dfrac{500}{750}$; $\qquad S = 0.015 \text{ g L}^{-1}$

38. $MX_2 \longrightarrow M + 2X$

$1 - \alpha \qquad \alpha \qquad 2\alpha$

$i = 1 + 2\alpha = 2$

$\alpha = 0.5$

39. $\Delta T_f = i \times K_f \times m$

$0.45 = i \times 5.12 \times \frac{0.2 \times 1000}{60 \times 20}$

$i = 0.527 = 1 - \frac{\alpha}{2}$; $\alpha = 0.945$

40. $[Co(H_2O)_3Cl_3]$. $3H_2O$ produces least number of particles in solution so, dression in freezing will also be least and freezing point will be maximum.

41. $P_{gas} = K_H X_{gas}$

$K_H \uparrow$ Solubility $\downarrow$

$T \uparrow, K_H \uparrow$

42. $X_A = 0.4$

$P_A = X_A P_A^O = Y_A P_s$	$P_A^O = 7 \times 10^3$ Pa
$0.4 \times 7 \times 10^3 = Y_A \times 10^4$	$P_B^O = 12 \times 10^3$ Pa
$Y_A = 0.28$	$P_s = X_A P_A^O + X_B P_B^O$
$Y_B = 0.72$	$= 0.4 \times 7 \times 10^3 + 0.6 \times 12 \times 10^3 = 2.8 \times 10^3 + 7.2 \times 10^3 = 10^4$

43. $\because$ $\Delta Tb = K_b \times m$

$K_b = \frac{2}{1} = 2$

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

$K_f = \frac{2}{2} = 1$

$\therefore$ $K_b = 2K_f$

44. ΔT_f for diluted milk = 0.2

ΔT_f for pure milk = 0.5

$$\frac{(\Delta T_f)_{diluted}}{(\Delta T_f)_{pure}} = \frac{(iK_f m)_{diluted}}{(iK_f m)_{pure}}$$

$$\frac{0.2}{0.5} = \frac{m_1}{m_2}; \ \frac{m_1}{m_2} = \frac{2}{5}$$

Assume that Solution is dilute so molality = molarity

$$\frac{M_1}{M_2} = \frac{2m}{5m}$$

So 3 cups of water are added to 2 cups of pure milk.

45. For dimerisation

$$i = 1 + \alpha \left(\frac{1}{n} - 1\right) = 1 + 0.8 \left(\frac{1}{2} - 1\right) = 0.6$$

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

$2 = 0.6 \times 5 \times \frac{W/122}{30} \times 1000$

$W = 2.44$

46. $K_2[HgI_4] \rightarrow 2K^+ + [HgI_4]^{\Theta 2}$

$i = 1 + (n - 1)\,\alpha = 1 + (3-1) \times 0.4 = 1 + 2 \times 0.4$

i.e.: $i = 1.8$

47. $(\Delta T_f)_X = (\Delta T_f)_Y$

$K_f M_X = K_f M_Y$

$\frac{4}{A} = \frac{12}{M_Y}$

$M_Y = 3\,A$

48. Let amount of water (ing) separated as ice is x

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

$\Rightarrow \quad 10 = 1 \times 1.86 \times \frac{62 \times 1000}{62 \times (250 - x)} \quad \Rightarrow \quad x = 64$

49. Since on mixing two liquids A and B change in volume after mixing is zero, therefore binary solution is an ideal solution.

$\because \quad P_T = P_A^0 X_A + P_B^0 X_B = (400 \times 0.5) + (600 \times 0.5) = 500$ Torr

$\therefore$ Mole fraction of A is vapour phase $= \frac{P_A^0 X_A}{P_T} = \frac{400 \times 0.5}{500} = 0.4$

50. $P_{gas} = K_H \times$ mole fraction of gas.

i.e. $P_{gas} = K_H \cdot X_{gas} \quad \Rightarrow P_{gas} = K_H \left(1 - X_{H_2O}\right)$

$$P_{gas} = K_H - K_H . X_{H_2O}$$

$$\Rightarrow \underset{y}{\downarrow} \quad \underset{c}{\downarrow} \quad \underset{m}{\downarrow} \; \underset{x}{\downarrow}$$

For Z, K_H is maximum

51. $P_M^O = 450$ mm of Hg $\quad P_N^O = 700$ mm of Hg

That is 'N' is more volatile liquid as compare to 'M' so,

$$\frac{x_N}{x_M} > \frac{y_N}{y_M}$$

or $\dfrac{x_M}{x_N} > \dfrac{y_M}{y_N}$

52. $\pi_1 = \pi_2 \times 4$

$i_1C_1RT = i_2C_2RT \times 4$

$2 \times C_1 = 3 \times 0.01 \times 4$

$C_1 = 6 \times 10^{-2}M$

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

$= 3 \times 4 \times 0.03 = 0.36$ K

54. $\dfrac{\Delta P}{P^0} = \dfrac{n}{n+N}$

$$\frac{\Delta P}{35} = \frac{0.01}{0.01+20}$$

$$\Delta P = \frac{0.01}{20.01} \times 35 = 0.017 \text{ mm}$$

55. $\Delta T_b = K_b \times m$

$$\frac{(\Delta T_b)_A}{(\Delta T_b)_B} = \frac{(K_b)_A \times m}{(K_b)_B \times m} = \frac{1}{5}$$

56. $\pi = CRT$

$$= \frac{\left(\frac{0.6}{60} + \frac{1.5}{180}\right)}{0.1} \times 0.08206 \times 300$$

$\Rightarrow \pi = 4.92$ atm.

EXERCISE # (J-ADVANCED)

1. $(\pi_{obs})_{Na_2SO_4} = \pi_{glucose}$

or $\frac{10}{4} = \frac{1+2\alpha}{1}$ or $10 = 4 + 8\alpha$

$\alpha = \frac{10-4}{8} = 0.75$ % of $\alpha = 75\%$

2. (i) In first case,

$$\Delta T_b = K_b \times m = K_b \times \frac{\text{Wt. of solute}}{\text{Mol. wt. of solute}} \times \frac{1000}{\text{wt. of solvent}}$$

or $0.17 = 1.7 \times \frac{1.22}{M \times 100 \times 10^{-3}}$

or **M = 122 g/mole**

Thus the benzoic acid exists as a monomer in acetone

(ii) In second case,

$$\Delta T_b = K_b \times \frac{\text{Wt.of solute}}{\text{Mol.wt.of solute}} \times \frac{1000}{\text{wt. of solvent}}$$

or $0.13 = 2.6 \times \frac{1.22}{M` \times 100 \times 10^{-3}}$ or **M` = 224**

Double molecular weight of benzoic acid (244) in acetone solution indicates that benzoic acid exists as a dimer in acetone.

3. $\Delta T_b = i\, K_b\, m$ i (vant Haff factor) of $CuCI_2$ = 3

$\Delta T_b = 3 \times 0.52 \times \frac{13.44}{134.4 \times 1} = 0.156 = 0.16.$

4. $\Delta T_f = i \times K_f \times$ molality

$7 = i \times 14 \times \frac{72.5}{94 \times 1}$; $i = 0.648$

$i = 0.648 = 1 - \frac{\alpha}{2}$; $\alpha = 0.704$

5. $\Delta T_f = i \times K_f \times$ molality $\Rightarrow$ $2 = i \times 1.72 \times \frac{20}{172} \times \frac{1000}{50}$

$\Rightarrow$ $2 = 4i$

$\Rightarrow$ $i = 1/2 = 0.5$

6. $\Delta T_f = K_f \,.\, m \quad = 2 \times \dfrac{0.1}{0.9 \times 46} \times 1000 \quad = \dfrac{2000}{414} = \dfrac{1000}{207} = 4.83$

$\Delta T'_f = T_f - 4.83$

$\Delta T'_f = 155.7 - 4.83$

$\Delta T'_f = 150.9$ K

7. Total vapour pressure

$P = P^o_A X_A$ (considering solute to be non-volatile as given in the question)

$P = 40 \times 0.9 = 36$ mm Hg

8. $\Delta T_b = K_b \,.\, m \quad = 0.52 \times \dfrac{0.1}{0.9 \times 18} \times 1000 = \dfrac{520}{9 \times 18} = 3.20$

$T_b = 373 + 3.20 \qquad\qquad T_b = 376.2$ K

9. $P_{N2} = K_H \times x_{N_2}$

$x_{N_2} = \dfrac{1}{10^5} \times 0.8 \times 5 = 4 \times 10^{-5}$ per mole

In 10 mole solubility is 4×10^{-4} .

10. $\Delta T_f = i \times K_f \times m \quad = 4 \times 1.86 \times \dfrac{0.1}{329 \times 0.1} = 2.3 \times 10^{-2}$

$\Rightarrow \quad T_f = 0 - 2.3 \times 10^{-2} = -2.3 \times 10^{-2}$ °C.

11. $\Delta T_b = 2^oC$; $\quad m_a = 2.5$ g

$m_{solvent} = 100$ g

$K_b = 0.76$ K. kg. mol^{-1}

$P_{solution} = ?$

$\Delta T_b = K_b \times m$

$2 = 0.76 \times m \qquad \therefore \qquad m = \dfrac{2}{0.76}$

$\dfrac{P^0 - P}{P} = m \times MM \times 10^{-3} \qquad \therefore \qquad \dfrac{760 - P}{P} = \dfrac{2}{0.76} \times 18 \times 10^{-3}$

$760 - P = \dfrac{36}{760} P \qquad \therefore \qquad 760 = \dfrac{796}{760} P$

$\therefore \qquad P = 760\left(\dfrac{796}{760}\right)$ torr = 725.6 torr ≈ 724 torr

12. $\Delta G = -$ ve, $\quad \Delta S_{system} = +$ ve Always for solution formation.

$\Delta S_{surr.} = 0$	No heat exchange between solution and surrounding.
$\Delta H = 0$	For ideal solution.

13. 3.2 M = 3.2 moles of solute present in 1L of solution.

Volume of solute = volume of solution = 1L = 1000 mL

Mass of solute = Volume × density = 1000 mL × 0.4 g/ mL = 400 g =0.4 kg

$$\text{Molality} = \frac{3.2}{0.4} = 8\,\text{m}$$

14. $\Delta T_f = K_f \times i \times m$

$0.0558 = 1.86 \times i \times 0.01$

$i = 3$

Given complex behaves as a strong electrolyte

$\alpha = 100\ \%$

n = 3 (number of particles given by complex)

∴ complex is $[Co(NH_3)_5Cl]Cl_2$

number of Cl^- ions in the co-ordination sphere of the complex = 1

15. (carbon tetrachloride + methanol) and (carbon disulphide + acetone) do not having any attraction forces.

16. From the graph it is clear that there is +ve deviation from Raoult law with respect to L, therefore option A is correct. When $X_L \longrightarrow 1$, then Z will have value equal to P_L^0 (Vapour pressure of pure L) so, option C is also correct.

17. $$\Delta T_f = K_f \times m = 2 \times \frac{34.5 \times 2}{46} = 2 \times 1.5 = 3$$

So, freezing point of ethanol + water solution = 273 – 3 = 270 K

18. $X_A = X_B = \frac{1}{2}$; $P_T = \frac{1}{2} \times P_A^0 + \frac{1}{2} \times P_B^0$ (Given $P_A^0 = 20$ Torr)

90 = 45 × 2 = $P_A^0 + P_B^0$ ……….(1) ; $P_B^0 = 70$

22.5 = $\mathbf{X_A} P_A^0 + (1 - \mathbf{X_A})\ P_B^0$ ……….(1)

22.5 = $\mathbf{X_A} \times 20 + (1 - \mathbf{X_A})\ 70 = 70 - 50\ X_A$

$\mathbf{X_A} = \frac{47.5}{50} = \frac{19}{20}$; $X_B = \frac{1}{20}$; $\frac{X_A}{X_B} = 19$

19. $2 = 2 \times K_{b(x)} \times m$; $1 = 2 \times K_{b(y)} \times m$; $\frac{K_{b(x)}}{K_{b(y)}} = 2$

$$\Delta T_{b(x)} = \left(1 - \frac{\alpha_1}{2}\right) K_{b(x)} m \quad ; \quad \Delta T_{b(y)} = \left(1 - \frac{\alpha_2}{2}\right) K_{b(y)} m$$

$$2S \longrightarrow S_2$$

$$1 - \alpha \qquad \alpha/2 \quad ; \quad i = 1 - \alpha + \alpha/2 = 1 - \alpha/2$$

$$3 = \frac{\Delta T_{b(x)}}{\Delta T_{b(y)}} = \frac{\left(1 - \frac{\alpha_1}{2}\right) K_{b(x)}}{\left(1 - \frac{0.7}{2}\right) K_{b(y)}} \quad ; \quad \left(1 - \frac{\alpha_1}{2}\right) = \frac{3 \times 0.65}{2}$$

$\alpha = 0.05$

20. $$\frac{P^\circ - Ps}{Ps} = \frac{n}{N} = \frac{0.5}{M_{solute} \times 0.5} = \frac{650 - 640}{640}$$

$M_{solute} = 64$

$\Delta T_f = iK_f m = 1 \times 5.12 \times \frac{0.5 \times 1000}{64 \times 39} = 1.025$