SOLUTIONS

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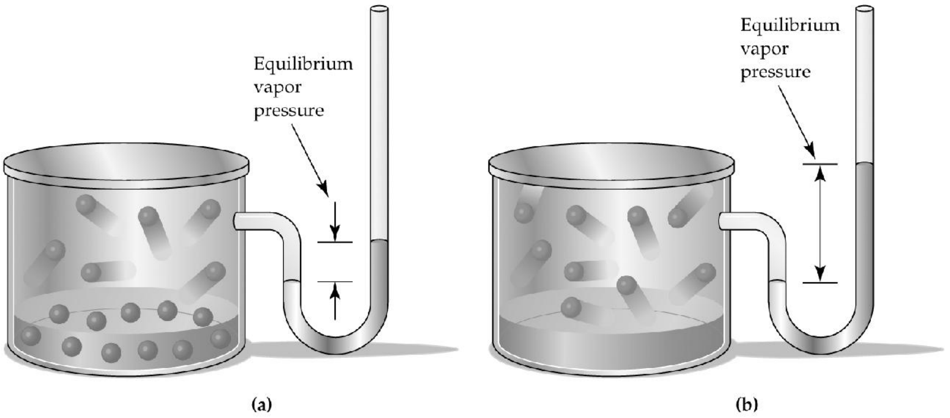


Vapour pressure of a solution with (a) a non-volatile solute is always lower than that of (b) the pure solvent by an amount that depends on mole fraction of solvent in solution.

THEORY

INTRODUCTION

In normal life we rarely come across pure substances. Most of these are mixtures containing two or more pure substances. Their utility or importance in life depends on their composition. The air around us is a mixture of gases primarily oxygen and nitrogen; the water we drink contains very small amounts of various salts dissolved in it. Our blood is a mixture of different components. Alloys such as brass, bronze, stainless steel, etc. are also mixtures. In this Unit, we will consider mostly liquid solutions and their properties.

1. SOLUTIONS

1.1 Definition

A solution is a homogeneous mixture of two or more than two components.

For example, common salt in water.

1.2 Classification

Solutions which contain two components in it are called **Binary Solutions.**

Substances which are used to prepare a solution are called as **Components**.

The component that is present in the largest quantity is known as **Solvent**. Solvent determines the physical state in which solution exists.

The other component present in lesser quantity in the solution is termed as **Solute**.

Each component may be solid, liquid or in gaseous state.

Type of Solution	Solute	Solvent	Common Examples
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid Solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

1.3 Strength of Solutions

The amount of solute dissolved per unit solution or solvent is called Strength of solution. There are various methods of measuring strength of a solution. :

1. **Mass Percentage (%w/w):**

   "It represents mass of a component present in 100 g of solution"

$$\text{Mass \% of a component} = \frac{\text{Mass of component in the sol.}}{\text{Total Mass of sol.}} \times 100$$

2. **Volume percentage (%v/v):**

   "It represents volume of a component in 100 mL of solution"

$$\text{Vol. \% of a component} = \frac{\text{Vol. of component}}{\text{Total vol. of solution}} \times 100$$

3. Mass by volume percentage (%w/v):

"It represents mass of solute in grams present in 100 mL of solution"

$$\text{Mass by vol. percent} = \frac{\text{Mass of solute in g}}{\text{Vol. of sol. in mL}} \times 100$$

4. Parts per Million (ppm)

$$\text{Parts per Million} = \frac{\text{No. of parts of the component}}{\text{Total no. of all the componens of sol.}} \times 10^6$$

Concentration in parts per million can be expressed as mass to mass, volume to volume and mass to volume.

5. Mole Fraction (x)

"It represents the moles of a solute present in one mole of solution"

$$\text{Mole fraction} = \frac{\text{No. of moles of the component}}{\text{Total no. of moles all the components}}$$

For example, in a binary mixture, if the number of moles of A and B are n_A and n_B respectively, the mole fraction of A will be

$$x_A = \frac{n_A}{n_A + n_B}$$

6. Molarity, M

"It represents moles of solute present in 1 L of solution"

$$\text{Molarity, M} = \frac{\text{Moles of solute}}{\text{Vol. of sol. in L}}$$

Units of Molarity are mol/L also represented by 'M' or 'Molar'.

"Density of a solution is mass of the solution per unit volume"

$$\text{Density, d} = \frac{\text{Mass of sol.}}{\text{Vol. of sol.}} = m/V$$

7. Molality, m

"It represents moles of solute present per kg of solvent"

$$\text{Molality, m} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$$

Units of molality are mol/kg which is also represented by 'm' or 'molal'.

8. Normality, N

It represents no. of equivalents of solute present in 1 L of solution.

$$\text{Normality, N} = \frac{\text{No. of Equivalents of solute}}{\text{Vol. of sol. in L}}$$

$$\text{No. of equivalents, eq} = \frac{\text{Weight}}{\text{Equivalent weight (W/E)}}$$

$$E = \frac{M}{z} \text{ (z is the valency factor)}$$

SOME IMPORTANT RELATIONSHIPS

Dilution Law

If a solution is diluted by adding solvent to it, then the amount of solute remains constant and we can write:

$M_1V_1 = M_2V_2$ and $N_1V_1 = N_2V_2$

Molarity and Normality

Normality = z × Molarity

IMPORTANT :

Mass %, ppm, mole fraction and molality are independent of temperature, whereas molarity & normality are a function of temperature. This is because volume depends on temperature and the mass does not.

2. VAPOUR PRESSURE

2.1 Definition

Vapour pressure of a liquid/solution is the pressure exerted by the vapours in equilibrium with the liquid/solution at a particular temperature.

Vapour pressure $\propto$ escaping tendency

2.2 Vapour pressure of liquid solutions and Raoult's Law :

(Raoult's law for volatile solutes)

Raoult's law states that **for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction**.

Consider a solution containing two volatile components 1and 2 with mole fractions x_1 and x_2 respectively. Suppose at a particular temperature, their partial vapour pressures are p_1 and p_2 and the vapour pressure in pure state are p_1^0 and p_2^0.

Thus, according to Raoult's Law, for component 1

$$p_1 \propto x_1$$

and $p_1 = p_1^0 x_1$

Similarly, for component 2

$$p_2 = p_2^0 x_2$$

According to **Dalton's law of partial pressure,** the total pressure (p_{total}) over the solution phase in the container will be the sum of the partial pressures of the components of the solution and is given as :

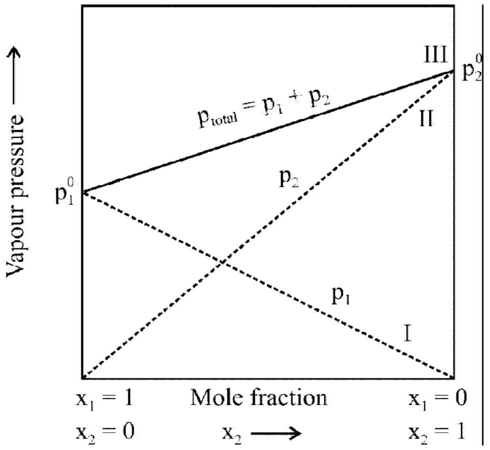
$$p_{total} = p_1 + p_2$$

Substituting the values of p_1 and p_2, we get

$$p_{total} = x_1 p_1^0 + x_2 p_2^0$$

$$= (1 - x_2) p_1^0 + x_2 p_2^0$$

$$= p_1^0 + (p_2^0 - p_1^0) x_2$$



The plot of vapour pressure and mole fraction of an ideal solution at constant temperature. The dashed line I and II represent the partial pressure of the components. It can be seen from the plot that p_1 and p_2 are directly proportional to x_1 and x_2, respectively. The total vapour pressure is given by line marked III in the figure.

Mole fraction in vapour phase

If y_1 and y_2 are the mole fractions of the components 1 and 2 respectively in the vapour phase then, using Dalton's law of partial pressures:

$$p_1 = y_1 p_{total}$$

$$p_2 = y_2 p_{total}$$

In general

$$p_i = y_i p_{total}$$

2.3 Vapour pressures of solutions of solids in liquids and Raoult's Law

(Raoult's law for non volatile solutes)

If a non-volatile solute is added to a solvent to give a solution, the number of solvent molecules escaping from the surface is correspondingly reduced, thus, the vapour pressure is also reduced.

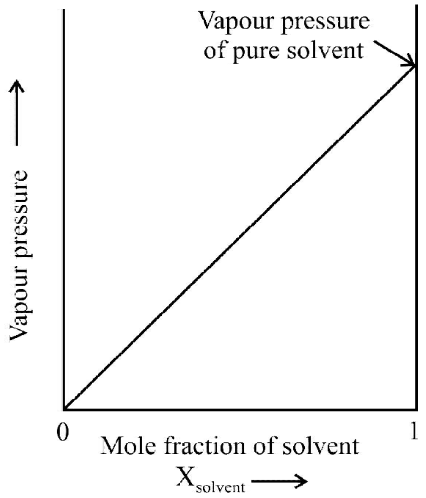
The decrease in the vapour pressure of solvent depends on the quantity of non-volatile solute present in the solution, irrespective of its nature.

Raoult's law in its general form can be stated as, **for any solution the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction**.

In a binary solution, let us denote the solvent by 1 and solute by 2. When the solute is non-volatile, only the solvent molecules are present in vapour phase and contribute to vapour pressure. Let p_1 be the vapour pressure of the solvent, x_1 be its mole fraction, p_1^0 be its vapour pressure in the pure state. Then according to Raoult's law

$$p_1 \propto x_1$$

and $p_1 = x_1 p_1^0 = p_{total}$



If a solution obeys Raoult's law for all concentrations, its vapour pressure would vary linearly from zero to the vapour pressure of the pure solvent.

2.4 Ideal and Non-ideal solutions

Ideal solutions :

An ideal solution is the solution in which each component obeys Raoult's law under all conditions of temperatures and concentrations.

Properties of Ideal solutions :

- $\Delta H_{MIXING} = 0$
- $\Delta V_{MIXING} = 0$
- Intermolecular attractive forces between the A-A and B-B are nearly equal to those between A-B.

Eg. solution of benzene and toluene,

solution of n-hexane and n-heptane

Non – ideal solutions :

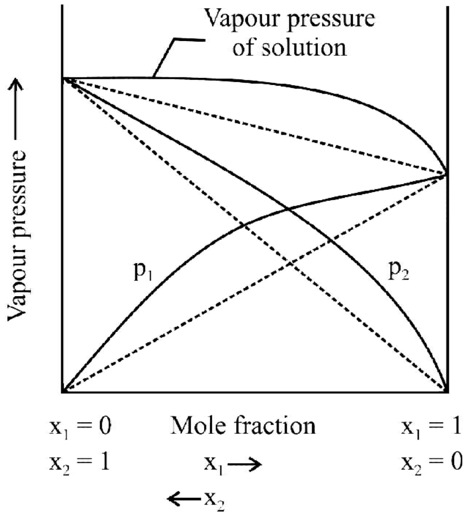
When a solution does not obey Raoult's law over the entire range of concentration, then it is called *non-ideal solution*.

Solutions showing positive deviation from Raoult's Law :

- Solvent-Solute(A-B) type of force is weaker than Solute-Solute(B-B) & Solvent-Solvent(A-A) forces.
- The vapour pressure is higher than predicted by the law.
- $\Delta H_{MIXING} > 0$
- $\Delta V_{MIXING} > 0$

Eg. ethanol and acetone, carbon disulphide and acetone

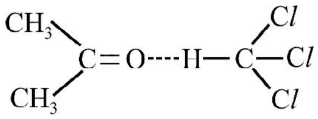
Pressure composition curve for solution showing positive deviation



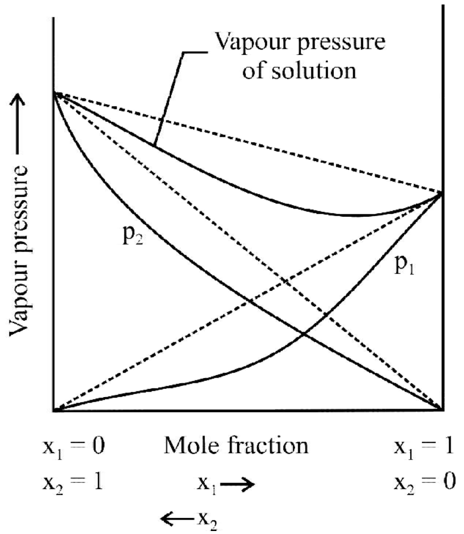
Solutions showing negative deviations from Raoult's law :

- Solvent-Solute(A-B) type of force is stronger than the other two.
- The vapour pressure is lower than predicted by the law
- $\Delta H_{MIXING} < 0$
- $\Delta V_{MIXING} < 0$

For example,phenol and aniline, chloroform and acetone etc



Pressure composition curves for solution showing negative deviation



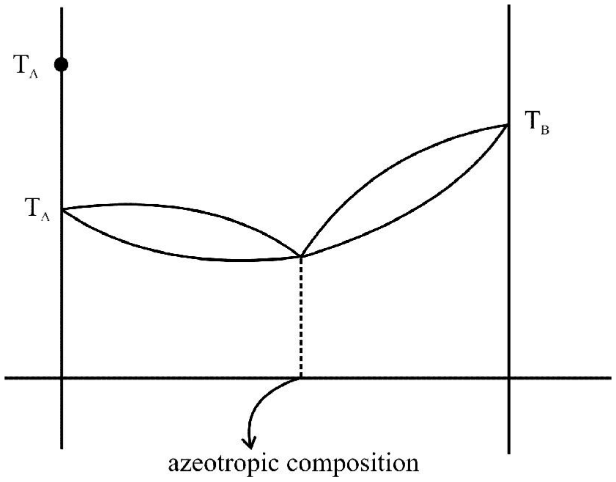
2.5 Azeotropes

Azeotropes are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature.

Minimum boiling azeotrope

The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition.

For example, ethanol-water mixture containing approximately 95% of ethanol forms an azeotrope with boiling point 351.15 K.

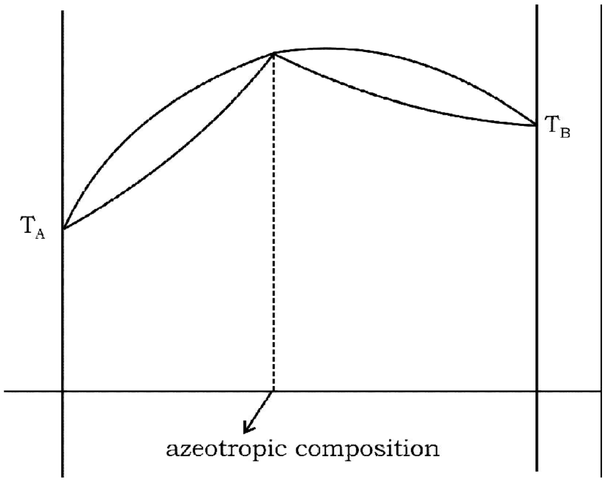


Boiling temperature - composition Diagram for solutions showing large positive deviations.

(Minimum boiling azeotrope)

Maximum boiling azeotrope :

The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition. Nitric acid and water mixture containing 68% nitric acid forms an azeotrope with a boiling point of 393.5 K.



Boiling temperature - composition Diagram for solutions showing large negative deviations.

(Maximum boiling azeotrope)

3. SOLUBILITY

3.1 Solubility of a solid in liquid

Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent.

Factors affecting the solubility of a solid in liquid :

1. **Nature of solute and solvent :**

   Like dissolves like. For example, While sodium chloride and sugar dissolve readily in water, naphthalene and anthracene do not. On the other hand, naphthalene and anthracene dissolve readily in benzene but sodium chloride and sugar do not.

2. **Temperature :**

   In a *nearly saturated solution,*

   If ($\Delta_{sol}H > 0$), the solubility increases with rise in temperature and

   If ($\Delta_{sol}H < 0$) the solubility decreases with rise in temperature.

Effect of pressure :

Does not have any significant effect as solids and liquids are highly incompressible.

3.2 Henry's law

Henry's law states that at a constant temperature, **the solubility of a gas in a liquid is directly proportional to the pressure of the gas.**

The most commonly used form of Henry's law states that **"the partial pressure of the gas in vapour phase (*p*) is proportional to the mole fraction of the gas (*x*) in the solution". This** is expressed as:

$$p = K_H x$$

Here K_H is the Henry's law constant.

Characteristics of K_H :

- K_H is a function of the nature of the gas.
- Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.
- K_H values increase with increase of temperature indicating that the solubility of gases increases with decrease of temperature.

Applications of Henry's law

1. In the production of carbonated beverages.
2. In the deep sea diving.
3. For climbers or people at high altitudes.

Raoult's Law as a special case of Henry's Law

According to Raoult's law,

$$p_i = x_i\ p_i^0$$

In the solution of a gas in a liquid, one of the components is so volatile that it exists as a gas. Its solubility according to Henry's law,

$$p = K_H\, x.$$

Thus, Raoult's law becomes a special case of Henry's law in which K_H becomes equal to p_i^0.

4. COLLIGATIVE PROPERTIES

The properties that depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution are called colligative properties.

There are four colligative properties:

1. Relative Lowering of vapour Pressure
2. Elevation in Boiling Point
3. Depression in freezing point
4. Osmotic pressure

4.1 Relative Lowering of vapour Pressure

When a non-volatile solute is added to a solvent, the vapour pressure decreases.

The lowering of vapour pressure w.r.t. the vapour pressure of the pure solvent is called "Relative lowering in vapour pressure".

According to Raoult's Law :

$$p_1 = x_1\ p_1^0$$

The reduction in the vapour pressure of solvent (Δp_1) is given as:

$$\Delta p_1 = p_1^0 - p_1 = p_1^0 - p_1^0\ x_1$$

$$= p_1^0\ (1 - x_1)$$

Knowing that $x_2 = 1 - x_1$, equation reduces to

$$\Delta p_1 = x_2\ p_1^0$$

Equation can be wirtten as

$$\frac{\Delta p_1}{p_1^0} = \frac{p_1^0 - p_1}{p_1^0} = x_2$$

The expression on the left hand side of the equation as mentioned earlier is called relative lowring of vapour pressure and is equal to the mole fraction of the solute. The above equation can be written as :

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2}\ \left(\text{since } x_2 = \frac{n_2}{n_1 + n_2}\right)$$

Here n_1 and n_2 are the number of moles of solvent and solute respectively present in the solution. For dilute solutions $n_2 << n_1$, hence neglecting n_2 in the denominator we have

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1}$$

or $$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

Here w_1 and w_2 are the masses and M_1 and M_2 are the molar masses of the solvent and solute respectively.

4.2 Elevation in Boiling Point

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

On addition of non-volatile solute the vapour pressure of the solvent decreases and therefore, to boil the solution the required temperature will be higher. So, there will be a rise in the boiling point of the solution.

The increase in boiling point $\Delta T_b = T_b - T_b^0$ where T_b^0 is the boiling point of pure solvent and T_b is the boiling point of solution is known as **elevation of boiling point**.

Expression :

$$\Delta T_b = K_b\, m$$

K_b is called **Boiling Point Elevation Constant or Molal Elevation Constant (Ebullioscopic Constant).**

Calculation of molar mass of solute :

$$m = \frac{w_2 / M_2}{w_1 / 1000} = \frac{1000 \times w_2}{M_2 \times w_1}$$

Substituting the value of molality in equation we get

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$$

$$M_2 = \frac{1000 \times w_2 \times K_b}{\Delta T_b \times w_1}$$

K_b :

It is defined as the elevation in boiling point when the molality of the solution is unity.

The unit of K_b is K kg mol^{-1}

Determination of K_b :

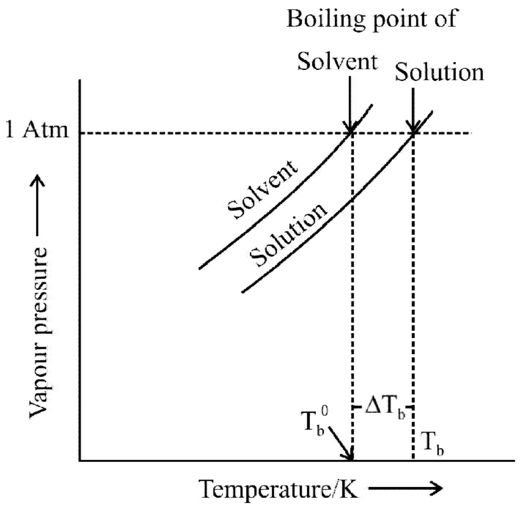
$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{vap} H}$$

where: R = gas constant (8.314 JK/mol),

T_f = freezing temperature in K,

M_1 = Molar mass of solvent in Kg/mol,

$\Delta_{vap}H$ = enthalpy of vapourisation of solvent in J/mol.



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

4.3 Depression in freezing point

The freezing point of a substance may be defined as the temperature at which the vapour pressure of the substance in its liquid phase is equal to its vapour pressure in the solid phase.

When a non-volatile solid is added to the solvent its vapour pressure decreases and now it would become equal to that of solid solvent at lower temperature. Thus, the freezing point of the solvent decreases.

$\mathbf{\Delta T_f} = T_f^0 - \mathbf{T_f}$ where T_f^0 is the freezing point of pure solvent and T_f is its freezing point when non-volatile solute is dissolved is known as **depression in freezing point.**

Expression :

$\Delta T_f = K_f m$

K_f is known as **Freezing Point Depression Constant or Molal Depression Constant or Cryoscopic Constant.**

Calculation of molar mass of solute :

$$m = \frac{w_2 / M_2}{w_1 / 1000}$$

Substituting this value of molality in equation we get :

$$\Delta T_f = \frac{K_f \times w_2 / M_2}{w_1 / 1000}$$

$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1}$$

$$M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1}$$

K_f :

It is defined as the depression in freezing point when the molality of the solution is unity. The unit of K_f is K kg mol^{-1}.

Determination of K_f :

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{fus} H}$$

where : R = gas constant (8.314 JK/mol),

T_f = freezing temperature in K,

M_1 = Molar mass of solvent in Kg/mol,

$\Delta_{fus}H$ = enthalpy of fusion of solvent in J/kg

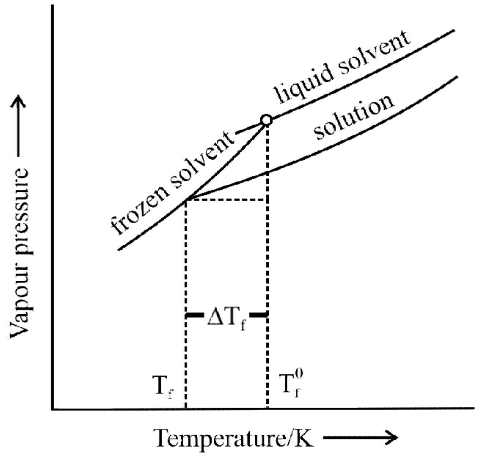
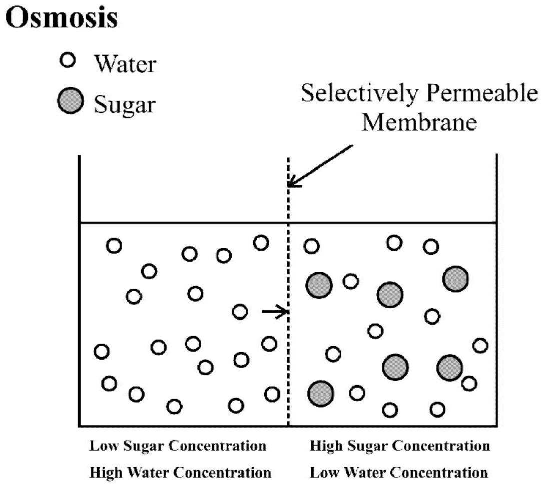


Diagram showing ΔT_f, depression of the freezing point of a solvent in a solution.

4.4 Osmosis

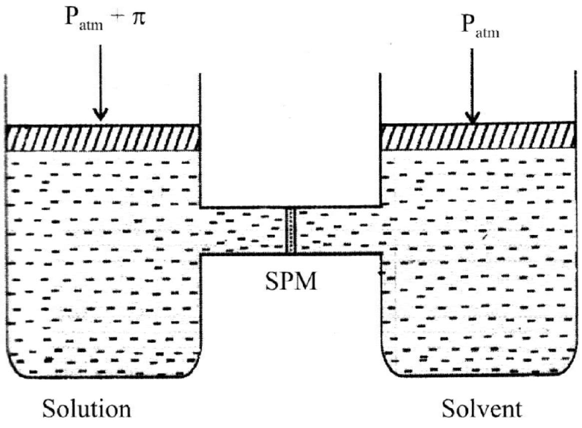
When a pure solvent and solution are kept with a semi-permeable membrane between them then the solvent particles pass through the membrane from the solvent side to the solution side. This phenomenon is called "Osmosis".

The semi-permeable membrane is a membrane that allows only small molecules to pass through and blocks the larger solute molecules.



Osmotic pressure :

The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis, i.e., to stop the passage of solvent molecules through a semipermeable membrane into the solution.



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

Expression :

For dilute solutions, **osmotic pressure is proportional to the molarity, *C* of the solution at a given temperature *T*.** Thus:

$\pi = CRT$

Here π is the osmotic pressure and R is the gas constant.

Calculation of molar mass :

$$\pi = (n_2 / V)\, RT$$

Here V is volume of a solution in litres containing n_2 moles of solute. If w_2 grams of solute, of molar mass, M_2 is present in the solution, then $n_2 = w_2 / M_2$ and we can write,

$$\pi V = \frac{w_2 RT}{M_2}$$

or $$M_2 = \frac{w_2 RT}{\pi V}$$

Isotonic solutions :

Two solutions having same osmotic pressure at a given temperature are called isotonic solutions.

The solution with lower concentration or lower osmotic pressure is known as **"Hypotonic"** with respect to more concentrated solution.

The solution with higher concentration or higher osmotic pressure is known as **"Hypertonic"** with respect to dilute solution.

Reverse osmosis :

If a pressure larger than the osmotic pressure is applied to the solution side, the solvent will flow from the solution into the pure solvent through the semi permeable membrane. This phenomenon is called **reverse osmosis.**

Application :

Desalination of sea water :

When pressure more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane.

4.5 Abnormal Molar Masses

When the molecular mass of a substance determined by studying any of the colligative properties comes out to be different than the theoretically expected value, the substance is said to show abnormal molar mass.

Abnormal Molar Masses are observed:

1. When the solute undergoes association in the solution.
2. When the solute undergoes dissociation in the solution.

van't Hoff Factor :

To calculate extent of association or dissociation, van't Hoff introduced a factor *i*, known as the van't Hoff Factor.

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$$i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

$$= \frac{\text{Total no. of moles of particles after association (dissociation)}}{\text{No. of moles of particles before association (dissociation)}}$$

Association :

Number of particles will always decrease due to association therefore $i < 1$.

$nA \rightarrow A_n$

Let initial particles $(n_i) = 1$

Final number$(n_f) = 1 - \alpha + \alpha/n$

van't Hoff factor, $i = n_f/n_i = 1 - \alpha + \alpha/n$

Dissociation :

The number of particles will always increase due to dissociation and hence $i > 1$.

$A_n \rightarrow nA$

Initial particle = 1

Final particles $= 1 - \alpha + n\alpha$

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

Modified Expressions :

Relative lowering of vapour pressure of solvent,

$$\frac{p_1^0 - p_1}{p_1^0} = i.\frac{n_2}{n_1}$$

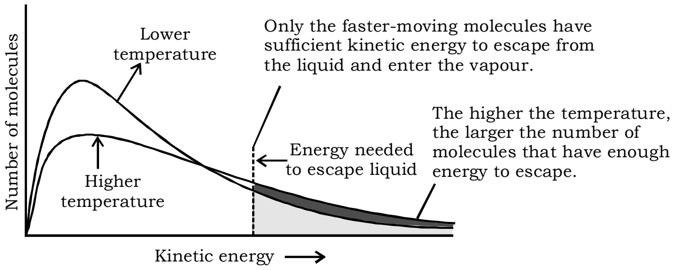
Elevation of Boiling point $\Delta T_b = i\,K_b\,m$

Depression of Freezing point, $\Delta T_f = i\,K_f m$

Osmotic pressure of solution, $\pi = i\,n_2\,RT/V$

5. VAPOUR PRESSURE

On increasing the temperature of the liquid the escaping tendency of the molecules increases and the vapour pressure increases.



The distribution of molecular kinetic energies in a liquid

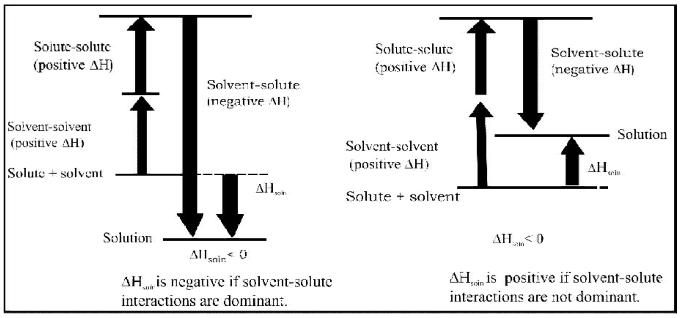
Claussius-Clapeyron Equation

In $p_2/p_1 = (\Delta H_{VAP}/R)\,(1/T_1 - 1/T_2)$

where ΔH_{VAP} represents the enthalpy of vaporisation of the liquid.

6. THERMODYNAMICS OF DISSOLUTION

If the interactions grow stronger the process is exothermic and if they go weaker during the formation of solution the process becomes endothermic. In general ΔS is positive in dissolution process. If the mixing process is spontaneous/natural then ΔG has to be negative.

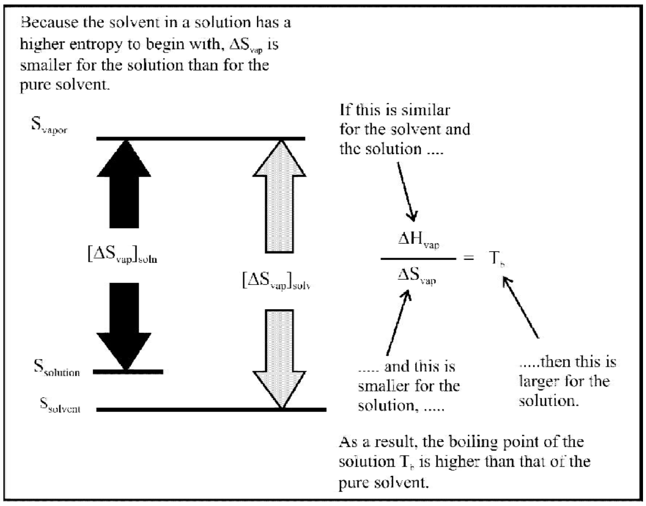


6.1 Boiling Point Elevation

$\Delta G_{VAP} = 0$

$T_b = \Delta H_{VAP}/\Delta S_{VAP}$

The non-volatile solute increases the randomness of the solution phase and the entropy of the vapours remains the same. Due to this, ΔS_{VAP} decreases thus giving rise to the boiling point.



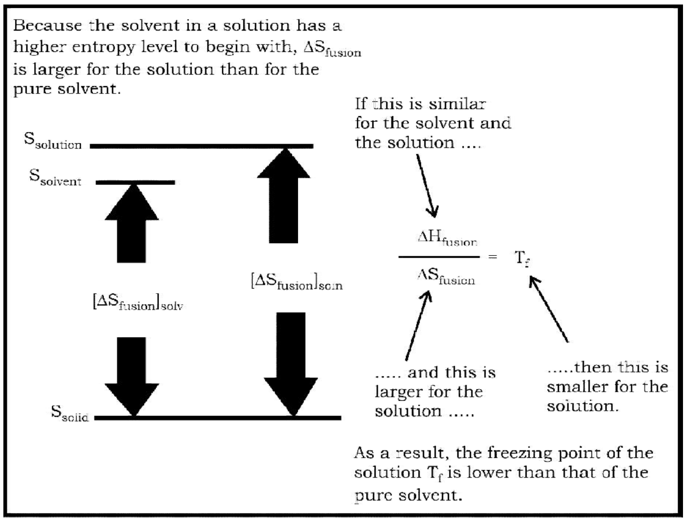
The higher boiling point of a solution relative to that of a pure solvent is due to a difference in their entropies of vapourization, ΔS_{vap}.

6.2 Freezing Point Depression

$\Delta G_{FUS} = 0$

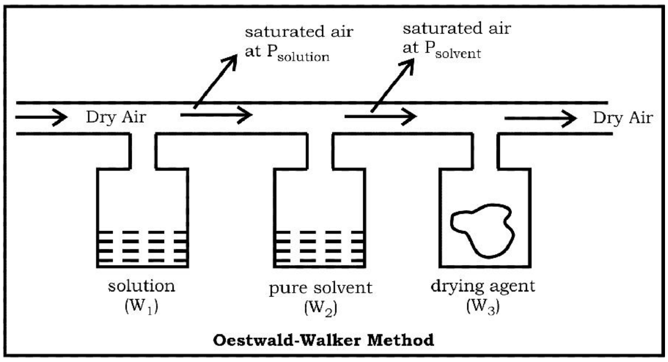
$T_f = \Delta H_{FUS}/\Delta S_{FUS}$

The entropy difference will increase in this case due to the increase in the entropy of solution. This increase in entropy will result in decrease of the freezing point according to the above relation.



The lower freezing point of a solution relative to that of a pure solvent is due to a difference in their entropies of fusion, ΔS_{fusion}.

7. OSTWALD WALKER METHOD



Oestwald-Walker Method

This is a typical method to measure the relative lowering in vapour pressure of a solution. Dry air is passed successively through three systems: solution, pure solvent and then a drying agent.

w_1 and w_2 represent the decrease in weight of the vessels and w_3 represents the increase in weight of the third vessel due to absorption.

$w_1 \propto P_{SOLUTION}$ $w_2 \propto P_{SOLVENT} - P_{SOLUTION}$

(as the air was already saturated)

$w_3 \propto P_{SOLVENT}$

Using the above relations the relative lowering in vapour pressure can be calculated.

IMPORTANT FORMULAE

In the formulae given below A represents solvent and B represents solute, also

M_A = Molar mass of solvent	M_B = Molar mass of solute
W_A = Mass of solvent	V_B = volume of solute
V = Volume of solution	d = density of solution.

1. **Mass of percentage (w/w) =** $\dfrac{W_B}{W_A + W_B} \times 100$

Volume percentage (v/v) = $\dfrac{V_B}{V_A + V_B} \times 100$

Mass by volume percentage $\left(\dfrac{w}{v}\right) = \dfrac{W_B \times 100}{V\ (\text{mL})}$

Parts per million (ppm) = $\dfrac{W_B}{W_A + W_B} \times 10^6$

2. Mole fraction of A, $x_A = \dfrac{n_A}{n_A + n_B}$

mole fraction of B, $x_B = \dfrac{n_B}{n_A + n_B}$

$x_A + x_B = 1$

3. Molarity (M) = $\dfrac{\text{Moles of solute}}{\text{Volume of solution in litre}} = \dfrac{n_B}{V_{(L)}} = \dfrac{W_B}{M_B \times V_{(L)}}$

4. Molality (m) = $\dfrac{\text{Moles of solute}}{\text{Mass of solvent in kg}} = \dfrac{n_B}{W_A} \times 1000 = \dfrac{W_B \times 1000}{M_B \times W_A}$

5. Normality (N) = $\dfrac{\text{Gram Equivalents of solute}}{\text{Volume of solution in litre}} = \dfrac{W_B}{\text{GEM of solute} \times V_{(L)}}$

GEM = Gram Equivalent Mass

6. **Relationship between Molarity and Normality**

The normality (N) and molarity (M) of a solution are related as follows :

Normality × Equivalent. mass (solute) = Molarity × Molar mass (solute)

7. **Relationship between Molarity and Mass percentage (p)**

If p is the mass percentage and d is the density of the solution then

$$\text{Molarity} = \frac{p \times d \times 10}{\text{Mol. mass (solute)}}$$

$$\text{Normality} = \frac{p \times d \times 10}{\text{Eq. mass (solute)}}$$

8. **Dilution formula :** If the solution of some substance is diluted by adding solvent from volume V_1 to volume V_2, then

$M_1V_1 = M_2V_2$ Similarly, $N_1V_1 = N_2V_2$

9. **Molarity of a mixture :** If V_1 mL of a solution of molarity M_1 is mixed with another solution of same substance with volume V_2 and molarity M_2, then molarity of the resulting mixture of solution (M) can be obtained as :

$$M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$

10. **Raoult's law for volatile solute.** $p_A = p_A^0 x_A$ and $p_B = p_B^0 x_B$

where p_A and p_B are partial vapour pressures of component 'A' and component 'B' in the solution. p_A^0 and p_B^0 are vapour pressures of pure components 'A' and 'B' respectively.

Total vapour pressure = $p = p_A + p_B = p_A^0 x_A + p_B^0 x_B$.

11. **Raoult's law for non-volatile solute.**

$$\frac{p_A^0 - p}{p_A^0} = x_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n_A} = \frac{W_B}{M_B} \times \frac{M_A}{W_A} \qquad \text{(For a dilute solution } n_B << n_A\text{)}$$

where x_B is mole-fraction of solute and $\frac{p_A^0 - p_A}{p_A^0}$ is relative lowering of vapour pressure.

12. **Elevation in boiling point.** $\Delta T_b = K_b \times m$

$$M_B = \frac{K_b \times W_B \times 1000}{\Delta T_b \times W_A}$$

where, $\Delta T_b = T_b - T_b^0$

13. **Depression in freezing point.** $\Delta T_f = K_f \times m$

$$M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$$

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

14. Osmotic pressure (π).

π = cRT where 'c' is molarity.

15. Van't Hoff factor.

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

or $$i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

or, $$i = \frac{\text{Total number of moles of particles after association / dissociation}}{\text{Number of moles of particles before association / dissociation}}$$

Modified forms of colligative properties :

(a) $\frac{p_A^0 - p_A}{p_A^0} = ix_B$ (b) $\Delta T_b = i\,K_b m$

(c) $\Delta T_f = iK_f m$ (d) $\pi V = in_B RT$

16. $\alpha = \frac{i-1}{n-1}$ wher α is degree of dissociation, 'i' is van't Hoff factor, 'n' is number of ions produced per formula of the compound.

17. $$\alpha = \frac{1-i}{1-\frac{1}{n}}$$

where α is degree of association, $\frac{1}{n}, n$ is the number of molecules of solute associate to form an associated molecule, $\frac{1}{n} < 1.$

18. If i > 1, solute undergoes dissociation.

i < 1, solute undergoes association.

i = 1, neither association nor dissociation.

$i = \frac{1}{2}$, solute is dimer.

SOLVED EXAMPLES

Example - 1

Give an example of a solution containing a liquid solute in a solid solvent.

Sol. An example of a solution containing a liquid solute in a solid solvent is amalgam of mercury (Hg) with sodium (Na). In this solution, sodium is solid solvent and mercury is liquid solute.

Example - 2

Differentiate between molality and molarity of solution. What is the effect of change in temperature of a solution on its molality and molarity ?

Sol. Molarity is defined as number of moles of solute dissolved in 1 L of the solution. Molality is defined as number of moles of solute dissolved per kg of the solvent. Molarity is a function of temperature as volume depends on temperature. With increase in temperature, volume of solution increases, hence molarity decreases. Molality is not dependent on temperature because mass does not change with temperature.

Example - 3

Calculate the mole fraction of methanol in a solution containing 100 g of water and 50 g of methanol.

Sol. Mole fraction of solute,

$$x_B = \frac{\text{Moles of solute}}{\text{Moles of solute} + \text{Moles of solvent}}$$

Mole fraction of methanol,

$$x_{CH_3OH} = \frac{\text{Moles of } CH_3OH}{\text{Moles of } CH_3OH + \text{Moles of } H_2O}$$

$$\text{Moles of } CH_3OH = \frac{\text{Mass of } CH_3OH}{\text{Molar mass of } CH_3OH}$$

Molar mass of $CH_3OH = 12 + 1 \times 3 + 16 + 1 = 32 \text{ g mol}^{-1}$

$$\text{Moles of } CH_3OH = \frac{50}{32} = 1.56 \text{ mol}$$

Now, moles of H_2O

$$= \frac{\text{Mass of } H_2O}{\text{Molar mass of } H_2O} = \frac{100}{18} = 5.56 \text{ mol}$$

So, the mole fraction of methanol,

$$x_{CH_3OH} = \frac{1.56}{1.56 + 5.56} = \frac{1.56}{7.12} = \mathbf{0.219}$$

Example - 4

Consider 18 g of glucose (molar mass 180 g mol^{-1}) to be present in 500 cm^3 of its aqueous solution. What is the molarity of the solution ?

Sol.
$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume in mL}} \times 1000$$

Here, solute is glucose whose mass = 18 g and molar mass = 180 g mol^{-1}. Therefore,

Number of moles of glucose =

$$\frac{\text{Given mass}}{\text{Molar mass}} = \left(\frac{18}{180}\right) \text{moles}$$

Also, the volume of solution = 500 cm^3. Therefore,

$$\text{Molarity} = \frac{18}{180 \times 500} \times 1000 = \mathbf{0.2\ M}$$

Example - 5

A solution is 25% water, 25% ethanol and 50% acetic acid by mass. Calculate the mole fraction of each component.

Sol. Let the total mass of solution = 100 g

Mass of water = 25 g

Mass of ethanol = 25 g

Mass of acetic acid = 50 g

$$\text{Moles of water} = \frac{25}{18} = 1.388$$

$(\because$ Molar mass of $H_2O = 18)$

Moles of ethanol $= \frac{25}{46} = 0.543$

$(\because$ Molar mass of $C_2H_2OH = 46)$

Moles of acetic acid $= \frac{50}{60} = 0.833$

$(\because$ Molar mass of $CH_3COOH = 60)$

Total number of moles $= 1.388 + 0.543 + 0.833 = 2.764$

Mole fraction of water $= \frac{1.388}{2.764}$ **= 0.502**

Mole fraction of ethanol $= \frac{0.543}{2.764}$ **= 0.196**

Mole fraction of acetic acid $= \frac{0.833}{2.764}$ **= 0.302**

Example - 6

A sugar syrup of weight 214.2 g contains 34.2 g of sugar ($C_{12}H_{22}O_{11}$). Calculate :

(i) molal concentration, and

(ii) mole fraction of sugar in the syrup.

Sol. **(i)** Weight of sugar syrup = 214.2 g

Weight of sugar in syrup = 34.2 g

Weight of water in syrup = 214.2 – 34.2 = 180.0 g

Moles of sugar $= \frac{34.2}{342} = 0.1$ (Molar mass = 342)

Molality $= \frac{0.1}{180} \times 1000$ **= 0.56 m.**

(ii) Moles of sugar $= \frac{34.2}{342} = 0.1$

Moles of water $= \frac{180}{18} = 10$

Moles fraction of sugar $= \frac{0.1}{10 + 0.1}$ **= 0.0099.**

Example - 7

What is the mole fraction of the solute in 2.5 m aqueous solution ?

Sol. 2.5 m aqueous solution means that 2.5 moles of solute are present in 1000 g of water. Thus,

Moles of solute = 2.5

Moles of water $= \frac{1000}{18} = 55.6$

Mole fraction of solute $= \frac{2.5}{2.5 + 55.6}$ **= 0.043.**

Example - 8

A 6.90 M solution of KOH in water contains 30% by mass of KOH. Calculate the density of the KOH solution. (Molar mass of KOH = 56 g mol^{-1}).

Sol. 6.90 M solution of KOH contains 6.90 moles of KOH in 1000 mL of solution.

Wt. of KOH in solution = 6.90 × 56 = 386.4 g

Wt. of KOH in 1000 mL solution = 386.4 g

Since the solution is 30% by weight, it means that 30 g of KOH are present in 100 g of solution.

$\therefore$ 386.4 g of KOH is present in $= \frac{100}{30} \times 386.4$

= 1288 g of solution

Density $= \frac{\text{Weight}}{\text{Volume}}$

$= \frac{1288}{1000}$ **= 1.288 g mL^{-1}**

Example - 9

Calculate the moles of methanol in 5 litres of its 2 m solution, if the density of the solution is 0.981 kg L^{-1} (Molar mass of methanol = 32.0 g mol^{-1}).

Sol. Mass of 5L solution = 5L × 0.981 kg L^{-1} = 4.905 kg

= 4905 g

Mass of 2 m solution = 1000 g + 2 moles of methanol

= 1000 + 2 × 32

= 1000 + 64 = 1064 g

Now 1064 g of solution contains methanol = 2 mol

4905 g of solution contains methanol $= \frac{2}{1064} \times 4905$

= 9.22 mol.

Example - 10

State Raoult's law for solutions of volatile liquids. Taking suitable examples explain the meaning of positive and negative deviations from Raoult's law.

Sol. **Raoult's law :** It states that for a solution of volatile liquids the partial pressure of each component is directly proportional to its mole fraction.

Mathematically,

$p_A \propto x_A \qquad p_B \propto x_B$

$p_A = p_A^o x_A \qquad p_B = p_B^o x_B$

Positive deviation from Raoults law : In this type of deviation the partial pressure of each component of solution is greater than that calculated from Raoults's law, i.e., $p_A > p_A^o x_A$ & $p_B > p_B^o x_B$.

Example : A solution of water and ethanol.

Negative deviation from Raoult's : In this type of deviation the partial pressure of each component of solution is less than that expected from Raoult's law, i.e., $p_A < p_A^o x_A$ & $p_B < p_B^o x_B$.

Example : A solution of acetone and chloroform.

Example - 11

Why does a solution of ethanol and cyclohexane show positive deviation from Raoult's law ?

Sol. On adding cyclohexane, its molecules get in between the molecules of ethanol thus breaking the hydrogen bonds and reducing ethanol-ethanol interactions. This will increase the vapour pressure of the solution and result in positive deviation from Raoult's law.

Example - 12

Why is an increase in temperature observed on mixing chloroform with acetone ?

Sol. The bonds between chloroform molecules and molecules of acetone are dipole-dipole interactions but on mixing, the chloroform and acetone molecules start forming hydrogen bonds which are stronger bonds resulting in the release of energy. This gives rise to an increase in temperature.

Example - 13

Heptane and octane form an ideal solution at 373 K, The vapour pressures of the pure liquids at this temperature are 105.2 kPa and 46.8 kPa respectively. If the solution contains 25g of heptane and 28.5g of octane, calculate

(i) vapour pressure exerted by heptane

(ii) vapour pressure exerted by solution

(iii) mole fraction of octane in the vapour phase.

Sol. $p^o_{C_7H_{16}} = 105.2\text{ kPa},\ p^o_{C_8H_{18}} = 46.8\text{ Kpa}$

$M_{C_7H_{16}} = 100\text{g mol}^{-1},\ M_{C_8H_{18}} = 114\text{ g mol}^{-1}$

$$n_{C_7H_{16}} = \frac{25}{100} = 0.25$$

$$n_{C_8H_{18}} = \frac{28.5}{114} = 0.25$$

$$x_{C_7H_{16}} = \frac{n_{C_7H_{16}}}{n_{C_7H_{16}} + n_{C_8H_{18}}} = \frac{0.25}{0.25+0.25} = 0.5$$

$$x_{C_8H_{18}} = 1 - x_{C_7H_{16}} = 1 - 0.5 = 0.5$$

(i) $p_{C_7H_{16}} = p^o_{C_7H_{16}}\ x_{C_7H_{16}} = 105.2 \times 0.5 = \mathbf{52.60\ kPa}$

(ii) $p_{C_8H_{18}} = p^o_{C_8H_{18}}\ x_{C_8H_{18}} = 46.8 \times 0.5$

$p_{C_8H_{18}} = 23.4\text{ kPa}$

$p = p_{C_7H_{16}} + p_{C_8H_{18}} = 52.6 + 23.4 = \mathbf{76.0\ kPa}$

(iii) Mole fraction of octane $(y_{C_8H_{18}})$ in the vapour phase.

$p_{C_8H_{18}} = y_{C_8H_{18}}\ p_{\text{total}}$

$23.4 = y_{C_8H_{18}} \times 76.0$

$$y_{C_8H_{18}} = \frac{23.4}{76.0} = \mathbf{0.308}$$

Example - 14

Define the following terms :-

(i) Dissolution (ii) Crystallisation

(iii) Saturated solution

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

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

(iii) A solution in which no more solute can be dissolved at the same temperature and pressure is called a saturated solution.

Example - 15

What is the effect of temperature on the solubility of a solid solute in a liquid solvent ?

Sol. Solubility of solid in liquid is significantly affected by temperature changes. This is because of dynamic equilibrium which follow Le Chatelier's principle. For saturated solution such as $NaNO_3$,KNO_3, etc. the solubility increases with increase of temperature because in these substances, the process of dissolution is endothermic.

$$\text{Solute} + \text{Solvent} + \text{Heat} \rightarrow \text{Solution}$$

There are few substances such as cerium sulphate, lithium carbonate, etc. whose solubility decreases with increase of temperature. This is because the process of dissolution is exothermic ($\Delta_{sol.} H < 0$).

Example - 16

CCl_4 and water are immiscible whereas ethanol and water are miscible in all proportions. Correlate this behaviour with molecular structure of these compounds.

Sol. CCl_4 is non-polar covalent compound, whereas water is a polar compound. CCl_4 can neither form H-bonds with water molecules nor can it break H-bonds between water molecule, therefore, it is insoluble in water.

Ethanol is a polar compound and can form H-bonds with water, which is a polar solvent, therefore it is miscible with water in all proportions.

Example - 17

State Henry's Law. What is the significance of K_H ?

Sol. **Henry's law :** It state that "the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution" and is expressed as

$$p = K_H x$$

where, k_H is the Henry's law constant.

Significance of K_H. As $p_A = K_H x_A$. Thus at constant temperature for the same partial pressure of different gases, $x_A \propto 1/K_H$. In other words solubility is inversely proportional to Henry's constant of the gas. Higher the value of k_H, lower is the solubility of the gas. As H_2 is more soluble than helium, H_2 will have lower value K_H than that of helium.

Example - 18

What is the effect of pressure on the solubility of (a) gases in liquids and (b) solids in liquids ?

Sol. (a) Solubility of gases in liquid increases with the increase of pressure at a particular temperature. If the system is in dynamic equilibrium, then the rate of dissolution is equal to the rate of evaporation. If the pressure increases over the system, the number of gaseous particles per unit volume increases. As a result, more particles strike the surface of the solution and enter it. Thus, a new equilibrium is established. Hence, on increasing the pressure, the solubility of gases in liquid also increases.

(b) Pressure has very little effect on the solubility of a solid in a liquid because solids have definite shape and volume; whereas liquids have definite volume but not shape. Hence, solids and liquids cannot be compressed much by increase in pressure.

Example - 19

Why are the aquatic species more comfortable in cold water rather than warm water ?

Sol. The aquatic species are more comfortable in cold water rather than warm water because the solubility of gas in liquid decreases with increase in temperature, and increases with decrease in temperature. Therefore, the percentage of oxygen present in cold water will be more because in cold water, solubility of oxygen gas in water will be more than in hot water. Now, we know that oxygen is essential for respiration or breathing. Hence, the aquatic species are comfortable in cold water; whereas in hot water, the concentration of oxygen is less which makes the breathing process difficult for the aquatic species.

Example - 20

Why oxygen mixed with helium is used by deep sea divers ?

Sol. Deep sea divers must cope with high concentration of dissolved gases while breathing air at high pressure under water as according to Henry's law, solubility of gases increases with pressure. However, when the divers come towards the 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. To avoid bends and also the toxic effect of high concentration of nitrogen in the blood, the tanks used by divers are filled with air diluted with helium. Value of K_H for He is 144.97 kbar and N_2 is 76.08 kbar, therefore He has a lower solubility.

Example - 21

The solubility of $Ba(OH)_2.8H_2O$ in water at 288 K is 5.6 g per 100 g of water. What is the molality of hydroxide ion in saturated solution of $Ba(OH)_2.8H_2O$ at 288 K.

Sol. The molar mass of $Ba(OH)_2.8H_2O$ is

$$= 137 + 2 \times 17 + 8 \times 18$$

$$= 137 + 34 + 144 = 315$$

$Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^-$

Suppose x is molality of Ba^{2+} ions, molality of $(OH)^-$ is 2x.

100 g water has 5.6 g of $Ba(OH)_2.8H_2O$

$\therefore$ 1000 g water will have $\frac{5.6}{100} \times 1000 = 56$

Moles of $Ba(OH)_2.8H_2O = \frac{56}{315} = 0.178$ mol

$\therefore$ Molality of hydroxyl ion $= 0.178 \times 2 =$ **0.356 m**

Example - 22

What is meant by colligative properties ? Give expressions for any two.

Sol. Colligative properties are the properties of solutions which depend only on the relative numbers of solute and solvent particles, but not on the nature of the solute. The four important colligative properties are as follows :

(a) Relative lowering of vapor pressure.

(b) Elevation in boiling point.

(c) Depression in freezing point.

(d) Osmotic pressure.

Relative lowering of vapor pressure : In the presence of a non-volatile solute, the vapor pressure of the solution becomes lower than the vapor pressure of pure solvent. The relative lowering of vapor pressure is

$$\Delta p = (p_A^o - p_A)/p_A^o$$

where p_A^o is the vapor pressure of pure solvent. The relative lowering depends only on the concentration of the solute and not in nature of solute

$$\Delta p = p_A^o x_B$$

where x_B is the mole fraction of the solute.

Osmotic pressure : When two solutions of different concentration are separated by a semiperimeable membrane, the solvent shows a tendency to move from dilute to concentrated solution. This property is known as osmosis. This uneven passage of the solvent creates pressure called osmotic pressure. It can be measured by determining the amount of counter pressure needed to prevent osmosis. It is proportional to concentration and temperature of the solution and is given by

$$\Pi = CRT$$

Expressing concentration in terms of moles per liter, we have

$$\Pi = \frac{n_B}{V} RT$$

where n_B is the number of moles of the solute.

Example - 23

Why does vapour pressure of a liquid decrease when a non-volatile solute is added into it ?

Sol. It is because some liquid molecules at the surface are replaced by the molecules of the solute which are non-volatile.

Example - 24

Derive an equation to express that relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute in it when the solvent alone is volatile.

Sol. For a solution of volatile liquids Raoult's law, is given as

$$p = p_A + p_B$$

If solute (component B) is nonvolatile then

$$p = p_A = p_A^o x_A$$

$$p = p_A^o (1 - x_B)$$

$$p = p_A^o - p_A^o x_B$$

$$p_A^o x_B = p_A^o - p$$

$$\frac{p_A^o - p}{p_A^o} = x_B$$

Thus, relative lowering of vapour pressure is equal to the mole fraction of non-volatile solute.

Example - 25

A solution is made by dissolving 30 g of a non-volatile solute in 90 g of water. It has a vapour pressure of 2.8 kPa at 298 K. At 298 K, the vapour pressure of pure water is 3.64 kPa. Calculate the molar mass of solute.

Sol. Let the molar mass of non-volatile solute be M_B

Moles of water $= \frac{90}{18} = 5$, Moles of solute $= \frac{30}{M_B}$

Applying Raoult's law,

$$\frac{p_0 - p_s}{p} = \frac{w_B}{M_B} \times \frac{M_A}{w_A}$$

$$\frac{3.64 - 2.8}{3.64} = \frac{30}{M_B} \times \frac{18}{90}$$

$$\frac{0.84}{3.64} = \frac{6}{M_B}$$

$$M_B = \frac{6 \times 3.64}{0.84}$$

M_B = **26 g mol^{-1}**

Example - 26

The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, non-electrolyte solid weighing 0.5 g when added to 39.0 g of benzene (molar mass 78 g mol^{-1}), then vapour pressure of the solution is 0.845 bar. What is the molar mass of the solid substance ?

Sol. The various quantities known to us are as follows :

$P_A^o = 0.850$ bar; p = 0.845 bar; $M_A = 78$ g mol^{-1};

w_B 0.5 g; $w_A = 39$ g

Substituting these values in equation

$$\frac{p_A^o - p}{p_1^o} = \frac{w_B \times M_A}{M_B \times w_A}, \text{ we have}$$

$$\frac{0.850 \text{ bar} - 0.845 \text{ bar}}{0.850 \text{ bar}} = \frac{0.5 \text{ g} \times 78 \text{ g mol}^{-1}}{M_B \times 39 \text{ g}}$$

Thus, M_B = **170 g mol^{-1}.**

Example - 27

What weight of the non-volatile urea ($NH_2 - CO - NH_2$) needs to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 25% ? What will be molality of the solution ?

Sol. Here, $\frac{p^o - p_s}{p^o} = \frac{25}{100}$ or $\frac{p^o - p_s}{p_s} = \frac{25}{75}$

$w_A = 100$ g, W_B = ?

For urea, $M_B = 60$ g mol^{-1}

For water, $M_A = 18$ g mol^{-1}

$$\frac{p^o - p_s}{p_s} = \frac{n_B}{n_A} = \frac{w_B / M_B}{w_A / M_A}$$

$$\therefore \qquad \frac{25}{75} = \frac{w_B / 60}{100/18}$$

or $\qquad w_B = \mathbf{111\ g}$

$$\text{Molality of the solution} = \frac{111\text{g}}{60\ \text{g mol}^{-1}} \times \frac{1}{100\ \text{g}} \times 1000\text{g kg}^{-1}$$

$$\mathbf{= 18.5\ mol\ kg^{-1}\ or\ 18.5\ m}$$

Example - 28

Explain why the freezing point of a solution is lower than the freezing point of the pure solvent.

Sol. Freezing point of a substance may be defined as the temperature at which the vapor pressure of the substance in its liquid phase is equal to its vapor pressure in the solid phase. the freezing point of a solution is lower than that of the pure solvent because the vapor pressure of solution is less than that of pure solvent. So according to Raoult's law, when a non-volatile solid is added to the solvent, its vapor pressure decreases and it becomes equal to that of solid solvent at a lower temperature. The decrease in the freezing point is known as depression of freezing point, and it is denoted by ΔT_f.

Example - 29

Define molal boiling point elevation constant and molal freezing point depression constant. Explain the cause for elevation in boiling point and depression in freezing point when non-volatile solute is added to a solvent.

Sol. **Molal boiling point elevation constant :** It may be defined as the elevation in boiling point when the molality of solution is unity, that is, 1 mol of solute is dissolved in 1 kg (1000 g) of the solvent. The units of molal elevation constant is degree molality^{-1}, that is, K molal^{-1} or °C molal^{-1} or K kg mol^{-1}. It is denoted by K_b.

Molal freezing point elevation constant : It may be defined as the depression in freezing point when the molality of the solutions is unity, that is, 1 mol of the solute is dissolved in 1000 g (1 kg) of the solvent. It is denoted by K_f. The unit of K_f is degree molality^{-1}, that is, K molal^{-1} or K kg mol^{-1}.

Cause of elevation in boiling point : Vapor pressure of the solution is lower than that of pure solvent. Hence, when the non-volatile solute is added to pure solvent, the solution has to be heated more to make vapor pressure equal to the atmosphric pressure.

Cause of depression in freezing point : Vapor pressure of the solution is less than that of pure solvent. Freezing point of a substance is the temperature at which the solid and the liquid forms of the substance are in equilibrium, that is, the solid and the liquid forms of substance have the same vapor pressure. Therefore, for the solution, this will occur at a lower temperature.

Example - 30

Ethylene glycol (molar mass = 62 g mol^{-1}) is a common automobile antifreeze. Calculate the freezing point of a solution containing 12.4 g of this substance in 100 g of water. Would it be advisable to keep this substance in the car radiator during summer ?

Given : $\quad$ **K_f for water = 1.86K kg/mol**

K_b for water = 0.512K kg/mol

Sol. $$\Delta T_f = K_f \times \frac{w_B}{m_B} \times \frac{1000}{w_A}$$

$$= 1.86 \times \frac{12.4}{62} \times \frac{1000}{100} = 3.76\ \text{K}$$

since water freezes at 0°C, so freezing point of the solution containing ethylene glycol will be – 3.76° C.

$$\Delta T_b = K_b \times \frac{w_B}{M_B} \times \frac{1000}{w_A}$$

$$= 0.512 \times \frac{12.4}{62} \times \frac{1000}{100} = 1.024\ \text{K}$$

$$T_b = T_b^o + \Delta T_b = 100 + 1.024 \ \mathbf{= 101.024\ °C}$$

since water boils at 100°C, so a solution containing ethylene glycol will boil at 101.024°C, so it is advisable to keep this substance in car radiator during summer.

Example - 31

Ethylene glycol ($C_2H_6O_2$) is used as an antifreeze. What mass of ethylene glycol should be added to 5.00 kg of water to lower the freezing point to –5.0 °C ? Given that K_f = 1.86 °C molal^{-1}. Consider ethylene glycol to be a non-electrolyte.

Sol. Given that $\Delta T_f = 5.0$ °C and $K_f = 1.86$ °C molal^{-1}. Therefore, molality is

$$\text{Molality} = \frac{\Delta T}{K_f} = \frac{5.0}{1.86} = 2.7 \text{ molal}$$

Therefore, the number of moles of ethylene glycol is found from the relation

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent}}$$

$$\frac{n}{5.00} = 2.7 \Rightarrow n = 13.5 \text{ mol}$$

Molar mass of ethylene glycol is = 2 × 12 + 4 × 1 + 2 × 16 = 62 g mol^{-1}. Hence, the mass of ethylene glycol to be added to water is

$$13.5 \text{ mol} \times \frac{62 \text{ g}}{\text{mol}} = \mathbf{837 \text{ g}}$$

Example - 32

A 0.1539 molal aqeuous solution of cane sugar (molar mass = 342 g mol^{-1}) has a freezing point of 271 K, whereas the freezing point of pure water is 273.15 K. What will be the freezing point of an aqueous solution containing 5 g of glucose (molar mass = 180 g mol^{-1}) per 100 g of solution ?

Sol. Molality of cane sugar solution = 0.1539 molal and the depression of freezing point, ΔT_f = 273.15 – 271 = 2.15 K. from $\Delta T_f = K_f m$, we have

$$K_f = \frac{\Delta T_f}{m} = \frac{2.15\text{K}}{0.1539 \text{ mol kg}^{-1}} = 13.97 \text{ molal}^{-1}$$

Amount of glucose in 100 g of solution = 5 g and amount of water in 100 g of solution = 100 g – 5 g = 0.095 kg. Number of moles of glucose = 5/180 mol = 0.0278 mol and the molality of solution m = 0.0278 mol/0.095 kg = 0.2926 mol kg^{-1}. So,

$$\Delta T_f = K_f \times m = 13.97 \text{K kg mol}^{-1} \times (0.2926) = 4.08 \text{ K}$$

Therefore, freezing point of glucose solution

$$= 273.15 - 4.08 = \mathbf{269.07K.}$$

Example - 33

Calculte the temperature at which a solution containing 54 g glucose, ($C_6H_{12}O_6$) in 250 g of water will freeze. (K_f for water = 1.86 K molal^{-1})

Sol. Molar mass of glucose M_B = 12 × 6 + 12 × 1 + 6 × 16 = 180 g mol^{-1}. According to depression in freezing point,

$$\Delta T_f = \frac{K_f \times w_B \times 1000}{M_B \times w_A}$$

where K_f is the molal depression constant, w_B is the given mass of solute, M_B is the molar mass of solute, w_A is the given mass of solvent (water). Substituting given values, we get

$$\Delta T_f = \frac{1.86 \times 54 \times 1000}{180 \times 250} = \frac{100440}{45000} = 2.23\text{K}$$

Therefore, the freezing point of the solution

$$= 0 - 2.23 = \mathbf{-2.23 \text{ K.}}$$

Example - 34

A solution prepared by dissolving 1.25 g of oil of winter green (methyl salicylate) in 99.0 g of benzene has a boiling point of 80.31°C. Determine the molar mass of this compound. (Boiling point of pure benzene = 80.10 °C and K_b for benzne = 2.53 °C molal^{-1}.)

Sol. The molar mass M_B of solute can be calculated from the relation,

$$M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A}$$

Mass of solute, w_B = 1.25 g, mass of solvent, w_A = 99 g, elevation in boiling point, (ΔT_b) = 80.31 – 80.10 = 0.21 °C. K_b for benzene = 2.53 °C molal^{-1}.

$$M_B = \frac{2.53 \times 1.25 \times 1000}{0.21 \times 99} = \mathbf{152.11 \text{ g mol}^{-1}}$$

Example - 35

Calculate the molal elevation constant of water, it being given that 0.1 molal aqueous solution of a substance boiling at 100.052 °C.

Sol. Molality of solution, m = 0.1 molal; the boiling point of solution T_b = 100.052 °C. Therefore, $\Delta T_b = T_b - T_b^o$ is the elevation in the boiling point, ΔT_b = 100.052 – 100 = 0.052 °C. By applying the relationship $\Delta T_b = K_b\, m$ we get

$$K_b = \frac{\Delta T_b}{m} = \frac{0.052\,^oC}{0.1\,\text{molal}} = 0.52\ ^oC\ \text{molal}^{-1}$$

Molal elevation constant K_b = **0.52 °C molal^{-1}.**

Example - 36

Define osmotic pressure and explain its origin. What is the effect of temperature on osmotic pressure ?

Sol. Osmosis is the phenomenon of the flow of solvent through a semipermeable membrane from pure solvent to the solution. Osmotic pressure is the pressure applied on the solution side to just stop the flow of the solvent from its side to the solution side across a semipermeable membrane. The increase in temperature will increase the osmotic pressure as $\Pi \propto T$.

Example - 37

Consider 100 mg of a protein to be dissolved in just enough water to make 10.0 mL of solution. If this solution hs an osmotic pressure of 13.3 mm Hg at 25 °C, what is the molar mass of the protein ? (Given that R = 0.0821 L atm mol^{-1} K^{-1} and 760 mm Hg = 1 atm.)

Sol. We know that osmotic pressure (Π) is given by

$$\pi = \frac{nRT}{V}$$

and

$$M_B = \frac{w_B RT}{\Pi V} \qquad (1)$$

where M_B is the molar mass of protein; Π = 13.3 mm Hg = 13.3/760 = 0.0175 atm; V = 10 mL = 10/1000 = 0.01 L; R = 0.0821 L atm mol^{-1}K^{-1}; T = 25 °C = (273 + 25) K = 298 K; w_B = 100 mg = 100/1000 g = 0.1 g. Substituting all the values in Eq. (1), we get

$$M_B = \frac{0.1\times 0.0821\times 298}{0.0175\times 0.01} = \mathbf{13980\ g\ mol^{-1}}$$

Example - 38

State the condition resulting in reverse osmosis.

Sol. Reverse osmosis will occur if a pressure higher than the osmotic pressure is applied on the solution.

Example - 39

How is it that measurement of osmotic pressures is more widely used for determining molar masses of macromolecules than the rise in boiling point or fall in freezing point of their solutions ?

Sol. The osmotic pressure method has the advantage over rise in boiling point or fall in freezing point for determining molar masses of macromolecules because

(i) Pressure measurement around the temperature and the molarity of solution is used instead of molality.

(ii) Compared to other colligative properties, its magnitude is large even for very dilute solutions.

Example - 40

What is van't Hoff factor and how is it related to the molar mass of the solute.

Sol. van't Hoff factor is defined as the ratio of the observed value of colligative property to the calculated value colligative property. It is denoted by i.

$$i = \frac{\text{Observed value of the colligative property}}{\text{Calculated value of the colligative property}}$$

van't Hoff factor is inversely proportional to the molecular mass of the solute. Therefore,

$$i = \frac{\text{Normal molecular mass}}{\text{Abnormal molecular mass}} = \frac{M_{\text{Calculated}}}{M_{\text{Observed}}}$$

Example - 41

Expalin why in case of sodium chloride, the observed values of colligative properties are greater than the calculated values.

Sol. In case of NaCl, the observed values of colligative properties are greater than the calculated values because in a dilute solution NaCl is expected to dissociate completely. Therefore, NaCl has observed values twice the calculated values of colligative properties.

$$NaCl \rightarrow Na^+ + Cl^-$$

Example - 42

A 0.118 molal solution of LiCl has a freezing point of –0.415 °C. What is the van't Hoff factor for this solute at this concentration ?

Sol. Molality of solution m = 0.118 molal. For LiCl, K_f = 1.86°C $molal^{-1}$ and ΔT_f(measured) = 0.415°C. Now, the depression in freezing point is found as

$$\Delta T_f \text{ (not ionized)} = K_f \times m$$

$$= (1.86\ °C\ molal^{-1}) \times 0.118\ molal = 0.219\ °C$$

The van't Hoff factor can be calculated using relation

$$i = \frac{\Delta T_f \text{ (measured)}}{\Delta T_f \text{ (not ionized)}} = \frac{+0.415\ °C}{+0.219\ °C} = \mathbf{1.89}$$

Example - 43

What mass of NaCl (molar mass = 58.5 mol^{-1}) must be dissolved in 65 g of water to lower the freezing point by 7.5 °C ? The freezing point depression constant K_f for water is 1.86 °C $molal^{-1}$. Assume van't Hoff factor for NaCl to be 1.87.

Sol. Given that molar mass, M = 58.5 g mol^{-1}; van't Hoff factor for NaCl, i = 1.87; freezing point depression constant, K_f for water = 1.86 °C $molal^{-1}$ and $\Delta T_f = 0 - (-7.5) = 7.5$ °C. Now, applying the relation and substituting values, we get

$$\Delta T = i \times K_f \times m \Rightarrow 7.5 = 1.87 \times 1.86 \times m \Rightarrow m = 2.15 \text{ molal}$$

Grams of NaCl = 2.15 × 58.5 = 125.775 g per kg.

If 125.775 g of NaCl is added to 1000 g of water, then for 1g of water, the amount of NaCl to be added is $\frac{125.775}{1000}$ and for 65g of water, it is $\frac{(125.775 \times 65)}{1000} = 8.175g$

Hence, mass of NaCl to be added = **8.175 g** in 65 g of water.

Example - 44

(a) Urea forms an ideal solution in water. Determine the vapour pressure of an aqueous solution containing 10% by mass of urea at 40°C.

(Vapour pressure of water at 40°C = 55.3 mm of Hg)

(b) Why is freezing point depression of 0.1 M sodium chloride solution nearly twice that of 0.1 M glucose solution ?

Sol. (a) $\frac{p^o - p}{p^o} = x_{urea}$

Let the mass of solution be 100 g

∴ Mass of Urea = 10 g

$$n_{urea} = \frac{10}{60} = \frac{1}{6}$$

$$n_{H_2O} = \frac{90}{18}$$

$$n_{H_2O} = 5.$$

$$x_{urea} = \frac{n_{urea}}{n_{urea} + n_{H_2O}} = \frac{1/6}{1/6 + 5} = \frac{1/6}{31/6}$$

$$x_{urea} = \frac{1}{31}$$

$$\frac{55.3 - p}{55.3} = \frac{1}{31}$$

$$55.3 - p = \frac{55.3}{31}$$

$$\Rightarrow \quad 55.3 - \frac{55.3}{31} = p$$

$$\Rightarrow \quad 55.3\left(1 - \frac{1}{31}\right) = p$$

$$p = 55.3 \times \frac{30}{31}$$

p = **53.52 mm Hg.**

(b) NaCl being an electrolyte, dissociates almost completely to give Na^+ and Cl^- ions in solution whereas glucose being non-electrolyte, does not dissociate. Therefore, the number of particles in 0.1 M NaCl solution is nearly double than that in 0.1 M glucose solution. Freezing point depression, being a colligative property, is therefore, nearly twice for NaCl solution than for glucose solution of same molarity.

Example - 45

(i) Benzoic acid completely dimerises in benzene. What will be the vapour pressure of a solution containing 61g of benzoic acid per 500g benzene when the vapour pressure of pure benzene at the temperature of experiment is 66.6 torr ?

(ii) What would have been the vapour pressure in the absence of dimerisation ?

(iii) Derive a relationship between mole fraction and vapour pressure of a component of an ideal solution in the liquid phase and vapour phase.

Sol. (i) $$\frac{\Delta p}{p^o} = iX_B$$

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

$$X_B = \frac{n_B}{n_A + n_B} = \frac{61/122}{61/122 + \frac{500}{78}}$$

$$= \frac{0.5}{0.5 + 6.41} = \frac{0.5}{6.91}$$

$$\frac{\Delta p}{66.6} = \frac{1}{2} \times \frac{50}{691}$$

$$\Delta p = \frac{50 \times 66.6}{691 \times 2} = 2.41$$

$$p^o - p = 2.41$$

$$p = 66.6 - 2.40$$

$$\mathbf{= 64.20\ torr}$$

(ii) In the absence of dimerisation.

$$i = 1$$

$$\frac{\Delta p}{p^o} = X_B$$

$$\Delta p = \frac{50}{691} \times 66.6 = 4.82$$

$P = 66.6 - 4.82 = \mathbf{61.78\ torr}$

(iii) From Raoult's law, $p_A = x_A p_A^o$ and

$$p_B = x_B p_B^o$$

where, x_A = mole fraction of liquid A

$$p_A = x_A p_A^o$$

x_B = mole fraction of liquid B

$$p_B = x_B p_B^o$$

y_A = Mole fraction of component – 1 in vapour phase.

y_B = Mole fraction of component – 2 in vapour phase.

$$y_A = \frac{p_A}{p_{total}} = \frac{p_A}{p_A + p_B}$$

$$y_B = \frac{p_B}{p_{total}} = \frac{p_B}{p_A + p_B}$$

$$y_A = \frac{x_A p_A^o}{x_A p_A^o + x_B p_B^o} = \frac{x_A p_A^o}{x_A p_A^o + (1 - x_A)\, p_B^o}$$

$$y_B = \frac{x_B p_B^o}{x_A p_A^o + x_B p_B^o}$$

Example - 46

In an aqueous solution, KCl undergoes complete dissociation into K^+ and Cl^- ions. What is the value of osmotic pressure of a 0.525M solution of KCl at 300 K ? (Use R = 0.0821 L atm K^{-1})

Sol. As KCl dissociates K^+ and Cl^- ions,

$\therefore$ i = 2.

Osmotic pressure (Π) can be determined using the formula

$$\Pi = iCRT = 2 \times 0.525 \times 0.0821 \times 300 = \mathbf{25.86\ atm}$$

Example - 47

When 0.5 g KCl was dissolved in 100 g water, the solution originally at 20 °C, froze at – 0.24 °C. Calculate the percentage ionization of salt. K_f per 1000 g of water = 1.86 °C $molal^{-1}$.

Sol. Mass of solute KCl, w_2 = 0.5 g; mass of solute H_2O, w_1 = 100g. Molar mass of H_2O, $M_1 = 1 \times 2 + 16 = 18\ g\ mol^{-1}$ and $\Delta T_f = 0 - (-0.24) = 0.24$ °C. According to the equation,

$$M_2 = \frac{1000 \times K_f \times w_2}{\Delta T_f \times w_1} = \frac{1000 \times 1.86\,^\circ C\ \text{molal}^{-1} \times 0.5 g}{0.24\,^\circ C \times 100 g}$$

$$= \frac{930}{24} = 38.75 g\ \text{mol}^{-1}$$

Molar mass of KCl = 39 + 35.5 = 74.5 g mol^{-1}.

Therefore, van't Hoff factor is

$$i = \frac{\text{Calculate molecular mass}}{\text{Observed molecular mass}} = \frac{74.5}{38.75} = 1.92$$

Now, KCl dissociates as

	$KCl \rightleftharpoons$	K^+ +	Cl^-
Initial moles	1 mol	0	0
Moles after dissolution	$1 - \alpha$	α	α

Total number of moles after dissociation = $1 - \alpha + \alpha + \alpha = 1 + \alpha$. Therefore,

$$i = \frac{1 + \alpha}{1} \Rightarrow \alpha = i - 1 = 1.92 - 1 = 0.92$$

Therefore, percentage ionization = 0.92 × 100 = **92%.**

Example - 48

Phenol associates in benzene to a certain extent to form dimers. A solution containing 2.0 × 10^{-2} kg of phenol in 1.0 kg of benzene has its freezing point decreased by 0.69 K. Calculate the degree of association of phenol (K_f for benzene = 5.12 K molal^{-1})

Sol. Mass of phenol, $w_2 = 2.0 \times 10^{-2}$ kg; $K_f = 5.12$ K molal^{-1}; mass of benzene, $w_1 = 1.0$ kg; $\Delta T_f = 0.69$ K. Therefore, according to the equation

$$M_2\ (\text{observed}) = \frac{1000\ K_f w_2}{w_1 \Delta T_f}$$

$$= \frac{1000 g \times 5.12 K\ \text{kg mol}^{-1} \times 2.0 \times 10^{-2} \text{kg}}{1.0\ \text{kg} \times 0.69\ K} = \frac{10.240 \times 10^{-2}}{0.69}$$

$$= 14840.58 \times 10^{-2} = 148.4\ g\ \text{mol}^{-1}$$

Also, M_2 (calculated) for C_6H_5OH

= 12 × 6 + 1 × 5 + 16 + 1 = 94 g mol^{-1}. Therefore,

$$i = \frac{M_2\ (\text{calculated})}{M_2\ (\text{observed})} = \frac{94}{148.4} = 0.633$$

	$2C_6H_5OH \rightleftharpoons$	$(C_6H_5OH)_2$
Initial moles	1 mol	
Moles after dissociation	$1 - \alpha$	$\alpha/2$

Total moles after dissociation = $1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$. Therefore,

$$i = \frac{1 - (\alpha/2)}{1}$$

or $\alpha = 2(1 - i) = 2(1 - 0.633) = \mathbf{0.734}$

Example - 49

Calculate normality and molarity of the following :

(a) 0.74g of Ca $(OH)_2$ in 5 mL of solution.

(b) 3.65g of HCl in 200 mL of solution.

(c) 1/10 mole of H_2SO_4 in 500 mL of solution.

Sol. (a) $\because$ Eq. of $Ca(OH)_2 = \frac{0.74}{74/2} \left(\text{Eq.} \frac{w}{E}\right)$

Volume of solution = 5 / 1000 litre

$$\therefore N = \frac{0.74 \times 1000 \times 2}{74 \times 5}$$

$$N = 4 \ \therefore\ M = \frac{N}{\text{Valency}} = \frac{4}{2} = 2$$

(b) $\because$ Eq. of HCl $= \frac{3.65}{36.5}$

and Volume of solution = 200/1000 litre

$$\therefore N = \frac{3.65 \times 1000}{36.5 \times 200} = 0.5$$

and $M = \frac{N}{\text{Valency}} = \frac{0.5}{1} = 0.5$

(c) Eq. of $H_2SO_4 = \frac{1}{10} \times 2$ ($\therefore$ Eq. = mole × valency)

Volume of solution = 500/1000 litre

$$\therefore \quad N = \frac{2 \times 1000}{10 \times 500} = 0.4 \text{ and } M = \frac{0.4}{2} = 0.2$$

Example - 50

Calculate the normality of the resulting solution made by adding 2 drops (0.1 mL) of 0.1N H_2SO_4 in 1 litre of distilled water.

Sol. $\because$ Meq. of solute does not change on dilution

$$\text{Meq. of } H_2SO_4\ (\text{conc.}) = \text{Meq. of } H_2SO_4\ (\text{dil.})$$

$$0.1 \times 0.1 = N \times 1000\ (\because \text{Meq.} = N \times V \text{ in mL})$$

$$N = 10^{-5}$$

Example - 51

At 300 K, the vapour pressure of an ideal solution containing one mole of A and 3 mole of B, is 550 mm of Hg. At the same temperature, if one mole of B is added to this solution, the vapour pressure of solution increases by 10 mm of Hg. Calculate the V.P. of A and B in their pure state.

Sol. Initially, $P_M = P_A^0 . X_A + P_B^0 . X_B$

$$550 = P_A^0 . \frac{1}{1+3} + P_B^0 . \frac{3}{1+3}$$

or $\quad P_A^0 + 3P_B^0 = 2200$ ....(1)

When, one mole of B is further added to it

$$P_M = P_A^0 . X_A + P_B^0 . X_B$$

$$560 = P_A^0 . \frac{1}{1+4} + P_B^0 . \frac{4}{1+4}$$

$\therefore\ P_A^0 + 4P_B^0 = 2800$ .... (2)

Solving Eqs. (1) and (2), we get

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

Example - 52

Benzene and toluene form two ideal solutions A and B at 313K. Solution A contains 4 mole of the toluene and one mole of C_6H_6. Solution B contains equal masses of toluene and benzene. Calculate total pressure in each case. The vapour pressure of C_6H_6 and toluene are 160 and 60 mm respectively at 313 K.

Sol. **A:** $P_M = P'_B + P'_T = P_B^0 . X_B + P_T^0 . X_T$

$$\Rightarrow X_B = \frac{1}{1+4} \text{ and } X_T = \frac{4}{1+4}$$

$$P_M = 160 \times \frac{1}{1+4} + 60 \times \frac{4}{1+4};$$

$$= 32 + 48 = 80 \text{ mm}$$

B : $P_M = 160 \times \dfrac{w/78}{\dfrac{w}{78} + \dfrac{w}{92}} + 60 \times \dfrac{w/92}{\dfrac{w}{78} + \dfrac{w}{92}}$

(Given, equal weights are mixed)

$$= 160 \times \frac{92}{170} + 60 \times \frac{78}{170}$$

$$= 86.588 + 27.529 = 114.117 \text{ mm}$$

Example - 53

The vapour pressure of water at 293 K is 2338 Pa and the vapour pressure of an aqueous solution is 2295.8 Pa. If density of solution is 1010 Kg/m^3 at 313 K, calculate the osmotic pressure at 313 K. Molecular weight of solute = 60.

Sol. At 293 K ; $\dfrac{P^0 - P_s}{P_s} = \dfrac{n}{N} = \dfrac{n \times 18}{W}$

$$\therefore \frac{2338 - 2295.8}{2295.8} = \frac{n \times 18}{W}$$

$$\therefore \frac{n}{W} = \frac{42.2}{2295.8} \times \frac{1}{18}$$

or $W = 979.25 \times ng$

$\therefore$ Weight of solution $= 979.25n +$ wt. of solute

$= 979.25n + 60n = 1039.25\ ng = 1.0393n$ kg

$$\therefore \underset{(\text{at } 313\text{ K})}{\text{Volume of solution}} = \frac{\text{Weight}}{\text{density}} = \frac{1.0393n}{1010} m^3$$

Now, $PV = nST$

$$P \times \frac{1.0393n}{1010} = n \times 8.314 \times 313$$

$$\therefore P = 2.53 \times 10^6 \text{ Pa}$$

Example - 54

At 298 K, the vapour pressure of pure ethyl alcohol is 44 torr and that of pure benzene is 100 torr. Assuming ideal behaviour, calculate the vapour pressure at 298 K of a solution which contains 10.0g of each substance (At. wt., C = 12, H = 1, O = 16)

Sol. Wt. of benzene, C_6H_6 = 10.0g; g. mol. wt. of C_6H_6 = (6 × 12) (6 × 1) = 78 g; wt. of ethyl alcohol, C_2H_5OH = 10.0g; g. mol. wt. of $C_2H_5OH = (2 \times 12) + (5 \times 1) + 16 + 1 = 46.0g$.

Thus : No. of moles of $C_6H_6 = \frac{10}{78} = 0.128;$

No. of moles of $C_2H_5OH = \frac{10}{46} = 0.217$

$$X_{C_6H_6} = \frac{0.128}{0.128 + 0.217} = 0.371;$$

$$X_{C_2H_5OH} = 1 - 0.371 = 0.629$$

$$P_{C_6H_6} = P^0_{C_6H_6} X_{C_6H_6} = (0.371)\ (100) = 37.1 \text{ torr.};$$

$$P_{C_2H_5OH} = P^0_{C_2H_5OH} X_{C_2H_5OH} = (0.629)(44) = 28 \text{ torr.}$$

Total pressure = 37.1 + 28 = 65.1 torr.

Example - 55

The boiling point of chloroform was raised by 0.325°C when 0.5141 g of anthracene was dissolved in 35g of chloroform. Calculate the molecular weight of anthracene. (K_b = 39.0 per 100 g of chloroform)

Sol. wt. of solute, $W_2 = 0.5141g$; wt. of solvent,

$$W_1 = \frac{35}{1000} \text{kg} = 0.035 \text{ kg};$$

$\Delta T_b = 0.325°C$; $K_b = 39°C\ (100 \text{ g mol}^{-})$

$$= 39°C \times \frac{100}{1000} \text{kg mol}^{-}$$

$= 3.9°C \text{ kg mol}^{-}$; mol. wt. of anthracene, M_2 = ?

We know that $\Delta T_b = \frac{K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}};$

$$M_2 = \frac{K_b \times W_2 \text{ in g}}{\Delta T_b \times W_1 \text{ in kg}}$$

Or $M_2 = \frac{3.9°C \text{ kg mol}^{-1} \times 0.5141g}{0.325°C \times 0.035 \text{ kg}} = 176.26 \text{g mol}^{-1}$

Example - 56

A sample of naphthalene has freezing point, 80.6°C. When 0.512g of a solute is dissolved in 7.03g of naphthalene, the solution has a freezing point of 75.2°C. Calculate the molecular mass of the solute. (K_f for naphthalene = 6.8°C kg/mol)

Sol. $\Delta T_f = (80.6 - 75.2)°C = 5.4°C$; wt. of solute,

W_2 = 0.512 g; wt. of solvent,

W_1 = 7.03 g ; mol. wt. of solute,

M_2 = ?, $K_f = 6.8°C \text{ kg mol}^{-1}$. We know that:

$$\Delta T_f = \frac{K_f \ (\text{in}°C \text{ kg mol}^{-1}) \times W_2 \ (\text{in g})}{M_2 \ (\text{in g mol}^{-1}) \times \left(\frac{W_1 \text{ in g}}{1000}\right) \text{kg}};$$

$$5.4°C = \frac{6.8°C \text{ kg mol}^{-1} \times 0.512g}{M_2 \times \frac{7.03}{1000} \text{Kg}}$$

$$\therefore M_2 = \frac{6.8°C \text{ kg mol}^{-1} \times 0.512g}{5.4°C \times 00703 \text{ kg}} = 91.7 \text{ g mol}^{-1}$$

Example - 57

The osmotic pressure of a non-volatile solute in C_6H_6 at 25°C is 20.66 Nm^{-2}. If the solution had a concentration of $2g/dm^3$, what is mol. wt. of solute ?

Sol. Given that,

$\pi = 20.66\,Nm^{-2}$,

$$\frac{w}{V} = 2g/dm^3 = \frac{2\times10^{-3}}{10^{-3}}\,kg/m^3$$

$S = 8.314\,JK^{-1}\,mol^{-1}$, $T = 273 + 25 = 298\,K$

$$\pi V = \frac{w}{m}ST \qquad \therefore \quad m = \frac{w}{V}\frac{ST}{\pi}$$

$$m = \frac{2\times10^{-3}\times8.314\times298}{10^{-3}\times20.66} = 239.84\,kg\,mol^{-1}$$

Example - 58

The freezing point of a solution of 4.0g CdI_2 in 95g of water was – 0.25°C. Calculate the degree of dissociation of salt. (K_f for water = 1.85°C kg/mol (At. wt. Cd = 112; I = 127).

Sol. Wt. of solute, $W_2 = 4.0g$; wt. of solvent,

$W_1 = 0.095$ kg;

$$\Delta T_f = 0.25\,°C;\; M_2 = \frac{K_f \times W_2 \text{ in g}}{\Delta T_f \times W_1 \text{ in g}}$$

$$\Rightarrow \; M_2 = \frac{1.85°C\,kg\,mol^{-1}\times 4g}{0.25°C\times0.095\,kg} = 311.6\,mol^{-1}$$

Theoretical molar mass (M_{Th}) of CdI_2

$= 112 + (2\times127) = 366\,g\,mol^{-1}$

For	CdI_2	$\rightleftharpoons$	Cd^{2+}	+	$2I^-$
Initial conc.	1		0		0
At equilibrium	$1-\alpha$		α		2α

$\therefore \; i = 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$ ...... (1)

$$\text{But } i = \frac{M_{Th}}{M_{obs}} = \frac{366g\,mol^{-1}}{311.6g\,mol^{-1}} \quad ....(2)$$

Substituting the value of i from (2) in (1), we get

$$\frac{366}{311.6} = 1 + 2\alpha \quad \text{or} \quad \alpha = \frac{1}{2}\left(\frac{366}{311.6} - 1\right)$$

or $\alpha = 0.087$ or $0.087 \times 100 = 8.7\,\%$ dissociated

EXERCISE - 1 : BASIC OBJECTIVE QUESTIONS

Strength of Solutions

1. What is the mass percentage of carbon tetrachloride if 22g of benzene is dissolved in 122g of carbon tetrachloride ?

(a) 84.72%
(b) 15.28 %
(c) 50%
(d) 44%

2. What is the molarity of a solution containing 10g of NaOH in 500 mL of solution ?

(a) 0.25 mol L^{-1}
(b) 0.75 mol L^{-1}
(c) 0.5 mol L^{-1}
(d) 1.25 mol L^{-1}

3. What will be the molarity of 30 mL of 0.5 M H_2SO_4 solution diluted to 500 mL ?

(a) 0.3 M
(b) 0.03 M
(c) 3 M
(d) 0.103 M

4. What will be the molality of a solution of glucose in water which is 10% w/W ?

(a) 0.01 m
(b) 0.617 m
(c) 0.668 m
(d) 1.623 m

5. What is the mole fraction of glucose in 10% w/w glucose solution ?

(a) 0.01
(b) 0.02
(c) 0.03
(d) 0.04

6. A solution is obtained by mixing 200 g of 30% and 300 g of 20% solution by weight. What is the percentage of solute in the final solution ?

(a) 50%
(b) 28%
(c) 64%
(d) 24%

7. An aqueous solution of urea containing 18g urea in 1500 cm^3 of the solution has a density equal to 1.052 g/cm^3. If the molecular weight of urea is 60, then the molality of the solution is

(a) 0.200
(b) 0.192
(c) 0.100
(d) 1.200

8. To a 4L of 0.2M solution of NaOH, 2L of 0.5 M NaOH are added. The molarity of resulting solution is :

(a) 0.9 M
(b) 0.3 M
(c) 1.8 M
(d) 0.18 M

9. Rectified spirit contains 95% ethanol by weight. The mole fraction of ethanol will be

(a) 0.881
(b) 0.99
(c) 0.118
(d) 0.81

10. 150 mL of C_2H_5OH (density = 0.78g mL^{-1}) is diluted to one litre by adding water ; molarity of the solution is

(a) 2.54
(b) 11.7
(c) 2.99
(d) 29.9

11. How many grams of a dibasic acid (Mol. wt. = 200) should be present in 100 mL of its aqueous solution to give decinormal strength ?

(a) 1g
(b) 2g
(c) 10g
(d) 20g.

12. The normality of 10% H_2SO_4 solution (d = 1.1g/cm^3) is

(a) 2.04
(b) 1.02
(c) 1.85
(d) 2.25

13. The mole fraction of C_2H_5OH (Mol. wt. = 46) in 5 molal aqueous ethyl alcohol solution is

(a) 0.082
(b) 0.82
(c) 5
(d) $\frac{5}{55.55}$

Raoult's Law

14. The vapour pressure of pure benzene and toluene are 160 and 60 torr respectively. The mole fraction of toluene in vapour phase in contact with equimolar solution of benzene and toluene is

(a) 0.50
(b) 0.6
(c) 0.27
(d) 0.73

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

(a) 14 (b) 56

(c) 140 (d) 70.

16. The vapour pressure of water at room temperature is 23.8 mm Hg. The vapour pressure of an aqueous solution of sucrose with mole fraction 0.1 is equal to

(a) 23.9 mm Hg (b) 24.2 Hg

(c) 21.42 mm Hg (d) 21.44 mm Hg.

17. Liquid A and B form an ideal solution. If vapour pressure of pure A and B are 500 Nm^{-2} and 200 Nm^{-2} respectively, the vapour pressure of a solution of A in B containing 0.2 mole fraction of A would be

(a) 700 $N\,m^{-2}$ (b) 300 $N\,m^{-2}$

(c) 260 $N\,m^{-2}$ (d) 140 $N\,m^{-2}$

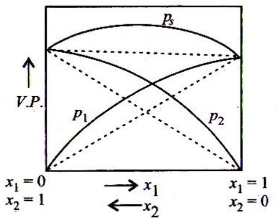
18. 3 moles of P and 2 moles of Q are mixed, what will be their total vapour pressure in the solution if their partial vapour pressures are 80 and 60 torr respectively ?

(a) 80 torr (b) 140 torr

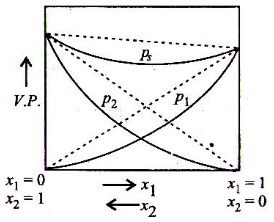
(c) 72 torr (d) 70 torr

Ideal & Non-Ideal Solutions

19. Study the figures given below and mark the correct statement.



(i)



(ii)

(a) (i) Nitric acid + Water, (ii) Acetone + Ethyl alcohol

(b) (i) Water + Ethyl alcohol, (ii) Acetone + Benzene

(c) (i) Acetone + Ethyl alcohol (ii) Acetone + Chloroform

(d) (i) Benzene + Chloroform (ii) Acetone + Chloroform

20. Two liquids HNO_3 (A) and water (B) form a maximum boiling azeotrope when mixed in the ratio of 68% and 32% respectively. It means

(a) A – B interactions are stronger than A – A and B – B interactions

(b) A – B interactions are weaker than A – A and B – B interactions

(c) vapour pressure of solution is more than the pure components

(d) vapour pressure of solution is less since only one component vaporises.

21. When acetone and chloroform are mixed together, hydrogen bonds are formed between them. Which of the following statements is correct about the solution made by mixing acetone and chloroform ?

(a) On mixing acetone and chloroform will form an ideal solution

(b) On mixing acetone and chloroform positive deviation is shown since the vapour pressure increases.

(c) On mixing acetone and chloroform negative deviation is shown since there is decrease in vapour pressure.

(d) At a specific composition acetone and chloroform will form minimum boiling azeotrope.

22. Intermolecular forces between n-hexane and n-heptane are nearly same as between hexane and heptane individually. When these two are mixed, which of the following is not true about the solution formed ?

(a) It obeys Raoult's law, i.e. $p_A = x_A p_A^o$ and $p_B = x_B p_B^o$

(b) ΔH_{mixing} is zero.

(c) ΔV_{mixing} is zero.

(d) It forms minimum boiling azeotrope.

23. Given below are few mixtures formed by mixing two components. Which of the following binary mixtures will have same composition in liquid and vapour phase ?

(i) Ethanol + Chloroform (ii) Nitric acid + Water

(iii) Benzene + Toluene

(iv) Ethyl chloride + Ethyl bromide

(a) (i) and (iii) (b) (i) and (ii)

(c) (i), (ii) and (iii) (d) (iii) and (iv)

Colligative Properties

Relative lowering in V.P.

24. 2g of sugar is added to one litre of water to give sugar solution. What is the effect of addition of sugar on the boiling point and freezing point of water ?

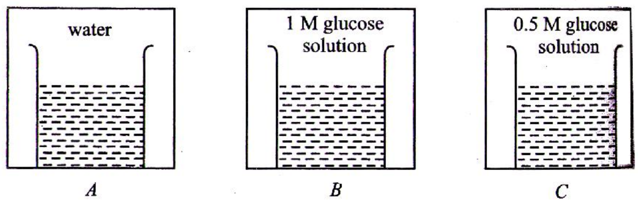
(a) Both boiling point and freezing point increase.

(b) Both boiling point and freezing point decrease.

(c) Boiling point increases and freezing point decreases.

(d) Boiling point decreases and freezing point increases.

25. In three beakers labelled as (A), (B) and (C), 100 mL of water, 100 mL of 1M solution of glucose in water and 100 mL of 0.5 M solution of glucose in water are taken respectively and kept at same temperature.



Which of the following statements is correct ?

(a) Vapour pressure in all the three beakers is same.

(b) Vapour pressure of beaker B is highest.

(c) Vapour pressure of beaker C is highest.

(d) Vapour pressure of beaker B is lower than that of C and vapour pressure of beaker C is lower than that of A.

26. Vapour pressure of a pure liquid X is 2 atm at 300 K. It is lowered to 1 atm on dissolving 1g of Y in 20g of liquid X. If molar mass of X is 200, what is the molar mass of Y ?

(a) 20 (b) 10

(c) 100 (d) 30

27. The vapour pressure of benzene at a certain temp. is 640 mm Hg . A non-volatile-non-electrolyte solid weighing 2.175g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular weight of the solid substance ?

(a) 6.96 (b) 60

(c) 63.8 (d) none of the above

28. The vapour pressure of solution of 5g of non-electrolyte in 100g of water at a particular temperature is 2985 Nm^{-2}. The vapour pressure of pure water at that temperature is 3000 Nm^{-2}. The molecular weight of the solute is

(a) 180 (b) 90

(c) 270 (d) 200.

29. Vapour pessure of CCl_4 at 25°C is 143 mm Hg. 0.5g of a non-volatile solute (mol. wt. 65) is dissolved in 100 cm^3 of CCl_4. Find the vapour pressure of the solution. (Density of CCl_4 = 1.58 g/cm^3).

(a) 141.93 mm (b) 94.39 mm

(c) 199.34 mm (d) 143.99 mm

Elevation in Boiling Point

30. A solution containing 12.5g of non-electrolyte substance in 185g of water shows boiling point elevation of 0.80 K. Calculate the molar mass of the substance.

(K_b = 0.52 K kg mol^{-1})

(a) 53.06g mol^{-1} (b) 25.3 g mol^{-1}

(c) 16.08g mol^{-1} (d) 43.92g mol^{-1}

31. If 1g of solute (molar mass = 50g mol^{-1}) is dissolved in 50g of solvent and the elevation in boiling point is 1K. The molar boiling constant of the solvent is

(a) 2 (b) 3

(c) 2.5 (d) 5

32. The molal elevation constant for water is 0.56°C per kg of water. The boiling point of solution made by dissolving 6.0g of water (NH_2CONH_2) in 200g of water is

(a) 10.028°C (b) 100.28°C

(c) 50.14°C (d) none of these

33. The boiling point of 0.1 molal aqueous solution of urea is 100.18°C at 1 atm. The molal elevation constant of water is

(a) 1.8 (b) 0.18

(c) 18 (d) 18.6

34. At certain hill-station, pure water boils at 99.725°C. If K_b for water is 0.513°C kg mol^{-1}, the boiling point of 0.69m solution of urea will be

(a) 100.079°C (b) 103°C

(c) 100.359°C (d) unpredictable

35. The molal b.p. constant for water is 0.513°C kg mol^{-1}. When 0.1 mole of sugar is dissolved in 200g of water, the solution boils under a pressure of 1 atm at

(a) 100.513°C (b) 100.0513°C

(c) 100.256°C (d) 101.025°C

36. An aqueous solution containing 1g of urea boils at 100.25°C. The aqueous solution containing 3g of glucose in the same volume will boil at

(a) 100.75°C (b) 100.5°C

(c) 100°C (d) 100.25°C

37. If the elevation in boiling point of a solution of 10gm of solute (mol. wt. = 100) in 100 gm of water is ΔT_b, the ebullioscopic constant of water is

(a) 10 (b) $10\Delta T_b$

(c) ΔT_b (d) $\Delta T_b/10$

Depression in Freezing Point

38. What weight of glycerol should be added to 600 g of water in order to lower its freezing point by 10°C ? (K_f = 1.86°C m^{-1}). (Molecular mass of glycerol is 92)

(a) 496 g (b) 297 g

(c) 310 g (d) 426 g

39. Sprinkling of salt helps in clearing the snow covered roads in hills. The phenomenon involved in the process is

(a) lowering in vapour pressure of snow

(b) depression in freezing point of snow

(c) increase in freezing point of snow

(d) melting of ice due to increase in temperature by putting salt.

40. A solution of 1.25g of non-electrolyte in 20g of water freezes at 271.94 K. If K_f = 1.86 K Kg mol^{-1}, then the molecular weight of the solute will be $(T_f^o = 0^\circ C)$

(a) 179.79g mol^{-1} (b) 207.8g mol^{-1}

(c) 209.6g mol^{-1} (d) 109.6g mol^{-1}

41. The amount of urea to be dissolved in 500 cc of water (K = 1.86) to produce a depression of 0.186°C in the freezing point is

(a) 0.3 gm (b) 3 gm

(c) 6 gm (d) 9 gm.

42. The molar freezing point constant for water is 1.86° C/m. If 342g of cane sugar ($C_{12}H_{22}O_{11}$) is dissolved in 1000 g of water, the solution will freeze at

(a) –1.86° (b) 1.86°C

(c) –3.92°C (d) 2.42°C

43. Pure benzene freezes at 5.45°C at a certain place but a 0.374m solution of tetrachloroethane in benzene freezes at 3.55°C. The K_f for benzene is

(a) 5.08 K kg mol^{-1} (b) 508 K kg mol^{-1}

(c) 0.508K kg mol^{-1} (d) 50.8°C kg mol^{-1}

44. If 15 gm of a solute in 100 gm of water makes a solution that freezes at –1.0°C, then 30 gm of the same solute in 100 gm of water will make a solution that freezes at

(a) –0.5°C (b) –2.0°C

(c) 0°C (d) 2.0°C

Osmotic Pressure

45. An aqueous solution of a non-electrolyte solute boils at 100.52°C. The freezing point of the solution will be (K_f = 1.86K Kg mol^{-1}, K_b = 0.52 K kg mol^{-1})

(a) 0°C (b) –1.86°C

(c) 1.86°C (d) None of the above.

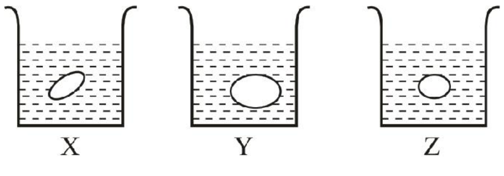
46. A solution is made by dissolving 20g of a substance in 500 mL of water. Its osmotic pressure was found to be 600mm of Hg at 15°C. Find the molecular weight of the substance.

(a) 1198 (b) 500

(c) 1200 (d) 1000

47. Grapes placed in three beakers X, Y and Z containing different type of solutions are shown in figures.

If beaker X contains water, Y and Z contain



(a) Y-hypotonic solution, Z-hypertonic solution

(b) Y-hypertonic solution, Z-hypotonic solution

(c) Y and Z-isotonic solution

(d) Y and Z-hypotonic solutions

48. Osmotic pressure of a solution containing 2g dissolved protein per 300 cm^3 of solution in 20 mm of Hg at 27ºC. The molecular mass of protein is

(a) 6239.6g mol^{-1}
(b) 12315.5 g mol^{-1}
(c) 3692.1 g mol^{-1}
(d) 7368.4 g mol^{-1}

49. The osmotic pressure of a solution can be increased by

(a) increasing the volume
(b) increasing the number of solute molecules
(c) decreasing the temperature
(d) removing semipermeable membrane.

50. Sea water is desalinated to get fresh water by which of the following methods ?

(a) When pressure more than osmotic pressure is applied pure water is squeezed out of sea water by reverse osmosis.
(b) When excess pressure is applied on sea water pure water moves in by osmosis.
(c) Water moves out from sea water due to osmosis.
(d) Salt is precipitated from sea water when kept undisturbed for sometime.

51. Osmotic pressure is generally preferred for determining the molecular masses of protein because

(a) it is difficult to find out mole fraction of protein for calculations by other methods
(b) at elevated temperature the proteins are likely to decompose and osmotic pressure is measured around room temperature
(c) the apparatus involved in finding out osmotic pressure is simpler than other methods
(d) it is easy to boil or freeze a solution containing proteins.

52. What will be the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0g of polymer of molar mass 150,000 in 500 mL of water at 37ºC ?

(a) 30.96 Pa
(b) 34.36 Pa
(c) 68.72 Pa
(d) 48.25 Pa

Deviation In Colligative Properties

53. Which of the following will have same value of van't Hoff factor as that of K_4 [Fe $(CN)_6$] ?

(a) $Al_2(SO_4)_3$
(b) $AlCl_3$
(c) $Al(NO_3)_3$
(d) $Al(OH)_3$

54. What will be the degree of dissociation of 0.1 M $Mg(NO_3)_2$ solution if van't Hoff factor is 2.74 ?

(a) 75%
(b) 87%
(c) 100%
(d) 92%

55. A solute X when dissolved in a solvent associated to form a pentamer. The value of van't Hoff factor (i) for the solute will be

(a) 0.5
(b) 5
(c) 0.2
(d) 0.1

56. The van't Hoff factor of 0.005 M aqueous solution of KCl is 1.95. The degree of ionisation of KCl is

(a) 0.95
(b) 0.97
(c) 0.94
(d) 0.96

57. For which of the following solutes the van't Hoff factor is not greater than one ?

(a) $NaNO_3$
(b) $BaCl_2$
(c) $K_4[Fe(CN)_6]$
(d) NH_2CONH_2

58. Why is the molecular mass determined by measuring colligative property in case of some solutes is abnormal ?

(a) Due to association or dissociation of solute molecules.
(b) Due to insolubility of solute molecules.
(c) Due to decomposition of solute molecules.
(d) Due to large size of solute molecules.

59. The elevation in boiling point of a solution of 9.43g of $MgCl_2$ in 1 kg of water is (K_b = 0.52 K kg mol^{-1}, Molar mass of $MgCl_2$=94.3g mol^{-1})

(a) 0.156
(b) 0.52
(c) 0.17
(d) 0.94

60. Which of the following has the highest freezing point ?

(a) 1m NaCl solution (b) 1m KCl solution

(c) 1m $AlCl_3$ solution (d) 1m $C_6H_{12}O_6$ solution

61. What amount of $CaCl_2$ (i = 2.47) is dissolved in 2 litres of water so that its osmotic pressure is 0.5 atm at 27ºC ?

(a) 3.42 g (b) 9.24 g

(c) 2.834 g (d) 1.825 g

62. Which of the following statements is not correct ?

(a) Osmotic pressure (π) of a solution is given by the relation $\pi = MRT$ where M is the molarity of the solution.

(b) The correct order of osmotic pressure for 0.2 M aqueous solution of each solute is $CaCl_2 > NaCl > CH_3COOH >$ glucose.

(c) Two solutions of sucrose of same molality prepared in different solvents will have same elevation boiling point.

(d) Relative lowering in vapour pressure of a solution containing non-volatile solute is directly proportional to mole fraction of solute is Raoult's law.

EXERCISE - 2 : PREVIOUS YEAR JEE MAINS QUESTION

1. An aqueous solution freezes at – 0.186ºC (k_f = 1.86; k_b = 0.512). What is the elevation in boiling point **(2002)**

(a) 0.186 ºC (b) 0.512 ºC

(c) 0.86 ºC (d) 0.0512 ºC

2. In a mixture A and B components show negative deviation as **(2002)**

(a) $\Delta V_{mix} > 0$ (b) $\Delta V_{mix} < 0$

(c) A–B interactions are weaker then A–A and B–B interactions

(d) None of the above reasons is correct

3. If liquid A and B from ideal solutions **(2003)**

(a) The enthalpy of mixing is zero

(b) The entropy of mixing is zero

(c) The free energy of mixing is zero

(d) The free energy as well as entropy of mixing are each zero

4. A pressure cooker reduces cooking time for food because **(2003)**

(a) heat is more evenly distributed in cooking space

(b) boiling point of water involved in cooking is increased

(c) higher pressure inside the cooker crushed food material

(d) cooking involves chemical changes helped by rise in temperature

5. The elevation in boiling point of a solution of 13.44 g of $CuCl_2$ (molecular weight = 134.4, Kb = 0.52 K molarity^{-1}) in 1 kg water using the following information will be **(2003)**

(a) 0.16 (b) 0.05

(c) 0.1 (d) 0.2

6. In 0.2m aqueous solution of weak acid HX, the degree of ionization is 0.3. Taking K_f for water as 1.85, the freezing point of solution will be nearest to **(2003)**

(a) + 0.480 ºC (b) – 0.360 ºC

(b) – 0.260 ºC (d) – 0.480 ºC

7. Which one of the following statements is false ? **(2004)**

(a) Two sucrose solutions of same molality prepared in different solvents will have same value of ΔT_f

(b) Osmotic pressure of a solution is given by equation π = MRT where M is molarity of solution

(c) The correct order of osmotic pressure for 0.01 M aqueous solution of each compound is

$BaCl_2 > KCl > CH_3COOH >$ Sucrose.

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

8. To neutralize completely 20 mL of 0.1 M aqueous solution of phosphrous acid (H_3PO_3), the volume of 0.1 M aqueous solution of KOH required is **(2004)**

(a) 60 mL (b) 20 mL

(c) 40 mL (d) 10 mL

9. Which of the following pairs show positive deviation from Raoult's law ? **(2004)**

(a) Acetone–chloroform (b) Benzene-methanol

(c) Water-Nitric acid (d) Water hydrochloric acid

10. Which one of the following aqueous solutions will exhibit highest boiling point **(2004)**

(a) 0.015 m glucose (b) 0.01 m KNO_3

(c) 0.015 m urea (d) 0.01 m Na_2SO_4

11. 6.02×10^{20} molecules of urea are present in 100 mL of its solution. The concentration of urea is **(2004)**

(a) 0.1 M (b) 0.01 M

(c) 0.02 M (d) 0.001 M

12. If α is degree of dissociation of Na_2So_4, the van't Hoff's factor, i, used for calculating the molar mass is **(2005)**

(a) $1 - 2\alpha$ (b) $1 + 2\alpha$

(c) $1 - \alpha$ (d) $1 + \alpha$

13. Benzene and toluene form nearly ideal solutions. At 20ºC, the vapour pressure of benzene is 75 Torr and that of toluene is 22 Torr. The partial vapour pressure of benzene at 20ºC for a solution containing 78 g of benzene and 46 g of toluene in Torr is **(2005)**

(a) 53.5 (b) 37.5

(c) 25 (d) 50

14. Two solutions of a substance (non-electrolyte) are mixed in the following manner.

480 mL of 1.5M first solution + 520 mL of 1.2M second solution.

What is the molarity of the final mixture ? **(2005)**

(a) 2.70 M (b) 1.34 M

(c) 1.50 M (d) 1.20 M

15. 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2g of water. The vapour pressure of water for this aqueous solution at 100°C is (p^o_{water} = 760 mm Hg) **(2006)**

(a) 759.00 Torr (b) 7.60 Torr

(c) 76.00 Torr (d) 752.40 Torr

16. Density of a 2.05 M solution of acetic acid in water is 1.02g/mL. The molality of the solution is **(2006)**

(a) 1.14 mol kg^{-1} (b) 3.28 mol kg^{-1}

(c) 2.28 mol kg^{-1} (d) 0.44 mol kg^{-1}

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

(a) 90.0g mol^{-1} (b) 115.0g mol^{-1}

(c) 105.0g mol^{-1} (d) 210.0g mol^{-1}

18. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is **(2007)**

(a) $\frac{2}{3}$ (b) $\frac{1}{3}\times\frac{273}{298}$

(c) $\frac{1}{3}$ (d) $\frac{1}{2}$

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

(a) 350 (b) 300

(c) 700 (d) 360

20. The density in g/ml of a 3.60 M sulphuric acid solution which is 29% H_2SO_4 (molar mass = 98 g/mol) by mass will be **(2007)**

(a) 1.45 (b) 1.64

(c) 1.88 (d) 1.22

21. The vapour pressure of water at 20ºC is 17.5 mmHg. If 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water at 20ºC, the vapour pressure of the resulting solution will be **(2008)**

(a) 17.675 mmHg (b) 15.750 mmHg

(c) 16.500 mmHg (d) 17.325 mmHg

22. At 80ºC, the vapour 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 80ºC and 1 atm pressure the amount of 'A' in the mixture is (1 atm = 760 mmHg) **(2008)**

(a) 52 mole percent (b) 34 mole percent

(c) 48 mole percent (d) 50 mole percent

23. A binary liquid solution is prepared by mixing n-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution ? **(2008)**

(a) The solution formed is an ideal solution

(b) The solution is non-ideal, showing positive deviation from Raoult's law.

(c) The solution is non-ideal, showing negative deviation from Raoult's law

(d) n-heptane shows positive deviation while ethanol show negative deviation from Raoult's law

24. Two liquids X and Y form an ideal solution at 300 K, 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 mm Hg) of X and Y in their pure states will be, respectively **(2009)**

(a) 200 and 300 (b) 300 and 400

(c) 400 and 600 (d) 500 and 600

25. 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 25g of heptane and 35g octane will be (molar mass of heptane = 100 g mol^{-1} and of octane = 114 g mol^{-1}) **(2010)**

(a) 72.0 kPa (b) 36.1 kPa

(c) 96.2 kPa (d) 144.5 kPa

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

(a) 0.0372 K (b) 0.0558 K

(c) 0.0744 K (d) 0.0186 K

27. A solution containing 2.675 g of $CoCl_3 . 6NH_3$ (molar mass = 267.5g mol^{-1}) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 4.78 g of AgCl (molar mass = 143.5g mol^{-1}). The formula of the complex is (Atomic mass of Ag = 108 u)

(a) $[Co(NH_3)_6]Cl_3$
(b) $[CoCl_2(NH_3)_4]Cl$
(c) $[CoCl_3(NH_3)_3]$
(d) $[CoCl(NH_3)_5]Cl_2$

28. The molality of a urea solution in which 0.0100g of urea, $[(NH_2)_2CO]$ is added to 0.3000 dm^3 of water at STP is **(2011)**

(a) 0.555 m
(b) 5.55×10^{-4} m
(c) 33.3 m
(d) 3.33×10^{-2} m

29. 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 **(2011)**

(a) 136.2
(b) 171.2
(c) 68.4
(d) 34.2

30. The degree of dissociation (α) of a weak electrolyte, A_xB_y is related to van't Hoff factor (i) by the expression **(2011)**

(a) $\alpha = \frac{i-1}{(x+y-1)}$
(b) $\alpha = \frac{i-1}{x+y+1}$
(c) $\alpha = \frac{x+y-1}{i-1}$
(d) $\alpha = \frac{x+y+1}{i-1}$

31. 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 (K_f for water = 1.86 K kg mol^{-1}. and molar mass of ethylene glycol = 62 g mol^{-1}) **(2011)**

(a) 804.32 g
(b) 204.30 g
(c) 400.00 g
(d) 304.60 g

32. A 5.2 molal aqueous solution of methyl alcohol, CH_3OH, is supplied. What is the mole fraction of methyl alcohol in the solution ? **(2011)**

(a) 0.100
(b) 0.190
(c) 0.086
(d) 0.050

33. 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 ? **(2012)**

(a) 72 g
(b) 93 g
(c) 39
(d) 27 g

34. The density of a solution prepared by dissolving 120g of urea (mol. mass = 60 u) in 1000 g of water is 1.15g/mL. The molarity of this solution is **(2012)**

(a) 0.50 M
(b) 1.78 M
(c) 1.02 M
(d) 2.05 M

35. Consider separate solutions 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 ? **(2014)**

(a) 0.100 M $Mg_3(PO_4)_2(aq)$ has the highest osmotic pressure.
(b) 0.125 M $Na_3PO_4(aq)$ has the highest osmotic pressure.
(c) 0.500 M $C_2H_5OH(aq)$ has the highest osmotic pressure.
(d) They all have the same osmotic pressure.

36. The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a 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: **(2015)**

(a) 128
(b) 488
(c) 32
(d) 64

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: **(2016)**

(a) 76.0
(b) 752.4
(c) 759.0
(d) 7.6

38. The freezing point of benzene decreases by 0.45°C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be :

(K_f for benzene = 5.12 K kg mol^{-1}) **(2017)**

(a) 80.4%
(b) 74.6%
(c) 94.6%
(d) 64.6%

39. What quantity (in mL) of a 45% acid solution of a mono-protic strong acid must be mixed with a 20% solution of the same acid to produce 800 mL of a 29.875% acid solution ? **(2017)**

(a) 320 (b) 325

(c) 316 (d) 330

40. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point? **(2018)**

(a) $[Co(H_2O)_4Cl_2]Cl.2H_2O$ (b) $[Co(H_2O)_3Cl_3].3H_2O$

(c) $[Co(H_2O)_6]Cl_3$ (d) $[Co(H_2O)_5Cl]Cl_2.H_2O$

JEE MAINS ONLINE QUESTION

1. Choose the correct statement with respect to the vapour pressure of a liquid among the following :

Online 2014 SET (1)

(a) Decreases linearly with increasing temperature

(b) Increases linearly with increasing temperature

(c) Increases non-linearly with increasing temperature

(d) Decreases non-linearly with increasing temperature.

2. For an ideal solution of two components A and B, which of the following is true ? **Online 2014 SET (4)**

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

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

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

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

3. 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}) **Online 2014 SET (4)**

(a) 5 and 4.42 (b) 5 and 3.42

(c) 3 and 5.42 (d) 4 and 4.00

4. Determination of the molar mass of acetic acid in benzene using freezing point depression is affected by :

Online 2015 SET (1)

(a) partial ionization (b) dissociation

(c) complex formation (d) association

5. 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 : **Online 2016 SET (1)**

(a) 0.0075 (b) 0.015

(c) 0.02 (d) 0.005

6. An aqueous solution of a salt MX_2 at certain temperature has a van't Hoff factor of 2. The degree of dissociation for this solution of the salt is **Online 2016 SET (2)**

(a) 0.33 (b) 0.50

(c) 0.67 (d) 0.80

7. 5g of Na_2SO_4 was dissolved in x g of H_2O. The change in freezing point was found to be 3.82°C. If Na_2SO_4 is 81.5% ionized, the value of x **Online 2017 SET (1)**

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

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

(a) 15 g (b) 25 g

(c) 45 g (d) 65 g

8. A solution is prepared by mixing 8.5 g of CH_2Cl_2 and 11.95 g of $CHCl_3$. If vapour pressure of CH_2Cl_2 and $CHCl_3$ at 298 K are 415 and 200 mm Hg respectively, the mole fraction of $CHCl_3$ in vapour form is : **Online 2017 SET (2)**

(Molar mass of Cl = 35.5 g mol^{-1})

(a) 0.162 (b) 0.675

(c) 0.325 (d) 0.486

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

Online 2018 SET (2)

(a) $\frac{4}{3}$	(b) $\frac{3}{4}$
(c) $\frac{1}{2}$	(d) $\frac{1}{4}$

10. The mass of a non-volatile, non-electrolyte solute (molar mass =50 g mol^{-1}) needed to be dissolved in 114 g octane to reduce its vapour pressure to 75 percent is :

Online 2018 SET (3)

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

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

1. All questions marked **"S"** are single choice questions
2. All questions marked **"M"** are multiple choice questions
3. All questions marked **"C"** are comprehension based questions
4. All questions marked **"A"** are assertion–reason type questions
   (A) If both assertion and reason are correct and reason is the correct explanation of assertion.
   (B) If both assertion and reason are true but reason is not the correct explanation of assertion.
   (C) If assertion is true but reason is false.
   (D) If reason is true but assertion is false.
5. All questions marked **"X"** are matrix–match type questions
6. All questions marked **"I"** are integer type questions

Strength of Solutions

1. (S) In which mode of expression, the concentration of solution remains independent of temperature ?

(a) Molarity (b) Normality
(c) Formality (d) Molality

2. (S) If 0.50 mole of $BaCl_2$ is mixed with 0.20 mole of Na_3PO_4, the maximum number of moles of $Ba_3(PO_4)_2$ that can be formed is

(a) 0.1 (b) 0.2
(c) 0.5 (d) 0.7

3. (S) The normality of 10% (weight/volume) acetic acid is

(a) 1 N (b) 10 N
(c) 1.7 N (d) 0.83 N

4. (S) 30 ml of solution is neutralised by 15 ml of 0.2 N base. The strength of the acid solution is

(a) 0.1 N (b) 0.15 N
(c) 0.3 N (d) 0.4 N

5. (S) The formula weight of H_2SO_4 is 98. The weight of the acid in 400 ml of 0.1 M solution is

a) 2.45 g (b) 3.92 g
(c) 4.90 g (d) 9.8 g

6. (S) 10 ml of 3N-HCl, 20 ml of N/2 H_2SO_4 and 30 ml of N/3 HNO_3 are mixed together and volume made to one litre. The normality of the resulting solution is

(a) N/2 (b) N/10
(c) N/20 (d) N/40

7. (S) To 5.85 g of NaCl, one kg of water is added to prepare a solution. What is the strength of NaCl in this solution ? (Molecular weight of NaCl = 58.5)

(a) 0.1 Normal (b) 0.1 Molal
(c) 0.1 Molar (d) 0.1 Formal

8. (S) What is the normality of a 1 M solution of H_3PO_4 ?

(a) 0.5 N (b) 1.0 N
(c) 2.0 N (d) 3.0 N

9. (S) The normality of a 2.3 M sulphuric acid solution is

(a) 0.46 N (b) 0.23 N
(c) 2.3 N (d) 4.6 N

10. (S) 50 ml of 0.2 N HCl, 50 ml of 0.1 N H_2SO_4 and 100 ml 0.2 N HNO_3 are mixed. The normality of resulting solution is

(a) 0.10 N (b) 0.15 N
(c) 0.175 N (d) 0.20 N

11. (S) In a solution of 7.8 g of benzene (C_6H_6) and 46 g of toluene ($C_6H_5CH_3$), the mole fraction of benzene is

(a) 1/6 (b) 1/5
(c) 1/2 (d) 1/3

12. (S) The molarity of a solution of Na_2CO_3 having 10.6 g/500 ml of solution is

(a) 0.2 M (b) 2 M
(c) 20 M (d) 0.02 M

13. (S) Molarity of a solution containing 1g NaOH in 250 ml of solution is

(a) 0.1 M (b) 1 M

(c) 0.01 M (d) 0.001 M

14. (S) Which one of the following solutions of sulphuric acid will exactly neutralise 25 ml of 0.2 M sodium hydroxide solution ?

(a) 12.5 ml of 0.1 M solution (b) 25 ml of 0.1 M solution

(c) 25 ml of 0.2 M solution (d) 50 ml of 0.2 M solution

Raoult's Law

15. (A) **Assertion (A) :** The sum of mole fractions of al components of a solution is unity.

Reason : Mole fraction is independent of temperature.

(a) A (b) B

(c) C (d) D

16. (S) A solution is prepared containing a 2 : 1 mol ratio of dibromo ethane ($C_2H_4Br_2$) and dibromo propane ($C_3H_6Br_2$) what is the total vapour pressure over the solution assuming ideal behaviour ?

Vapour pressure	**(mm Hg)**
$C_2H_4Br_2$	173
$C_3H_6Br_2$	127

(a) 300 mm Hg (b) 158 mm Hg

(c) 150 mm Hg (d) 142 mm Hg

17. (S) Which of the following graphs represent the behaviour of ideal binary liquid mixture ?

(a) Plot of $1/P_{Total}$ against y_A is linear

(b) Plot of $1/P_{Total}$ against y_B is non-linear

(c) Plot of P_{Total} against y_A is linear

(d) Plot of P_{Total} against y_B is linear

18. (S) Mixture of volatile components A and B has total vapour pressure (in torr) :

$$P = 254 - 119X_A$$

where, X_A is mole fraction of A in mixture. Hence p_A^0 and p_B^0 are (in torr) :

(a) 254, 119 (b) 119, 254

(c) 135, 254 (d) 154, 119

19. (S) The plot of $\frac{1}{y_A}$ against $\frac{1}{x_A}$ is linear with slope and intercept respectively :

(a) $\frac{P_A^0}{P_B^0}$ and $\frac{P_A^0 - P_B^0}{P_B^0}$ (b) $\frac{P_A^0}{P_B^0}$ and $\frac{P_B^0 - P_A^0}{P_B^0}$

(c) $\frac{P_B^0}{P_A^0}$ and $\frac{P_A^0 - P_B^0}{P_A^0}$ (d) $\frac{P_B^0}{P_A^0}$ and $\frac{P_B^0 - P_A^0}{P_B^0}$

20. (S) If P_A is the vapour pressure of a pure liquid A and the mole fraction of A in the mixture of two liquids A and B is x, the partial vapour pressure of A is :

(a) $(1-x)P_A$ (b) xP_A

(c) $\frac{x}{(1-x)}P_A$ (d) $\frac{1-x}{x}P_A$

21. (S) Which statement about the composition of vapour over an ideal 1 : 1 molar mixture of benzene and toluene is correct ? Assume the temperature is constant at 25°C.

Vapour pressure data (25°C) :

Benzene	75 mm Hg
Toluene	22 mm Hg

(a) The vapour will contain higher percentage of benzene

(b) The vapour will contain higher percentage of toluene

(c) The vapour will contain equal amount of benzene and toluene

(d) Not enough information is given to make a prediction

Ideal and Non-ideal Solutions

22. (S) 100 ml of a liquid A was mixed with 25 ml of a liquid B to give a non-ideal solution of A-B mixture. The volume of this mixture would be

(a) 75 ml (b) 125 ml

(c) close to 125 ml (d) just more than 125 ml

23. (S) A mixture of benzene and toluene forms

(a) an ideal solution (b) non-ideal solution

(c) suspension (d) emulsion

24. (S) Which of the following liquid pairs shows a positive deviation from Raoult's law ?

(a) Water–hydrochloric acid

(b) Water–nitric acid

(c) Acetone–chloroform

(d) Benzene–methanol

25. (S) Which of the following pairs shows a negative deviation from Raoult's law ?

(a) Acetone–benzene (b) Acetone–ethanol

(c) Acetone–chloroform (d) Benzene–methanol

26. (S) An azeotropic solution of two liquids has boiling point lower than either of them when it

(a) Shows a negative deviation from Raoult's Law

(b) Shows no deviation from Raoult's Law

(c) Shows positive deviation from Raoult's Law

(d) Is saturated

27. (S) Which of the following statements is correct for a binary solution ?

(a) A solution in which heat is evolved exhibits positive deviations from Raoult's law.

(b) A solution in which heat is absorbed shows negative deviations from Raoult's law.

(c) When one component in solution shows negative deviation from Raoult's law, the other exhibits positive deviation.

(d) When one component in solution shows positive deviation from Raoult's law, so does the other.

28. (S) Which one of the following pairs will not form an ideal solution ?

(a) Benzene and toluene

(b) Chloroform and acetone

(c) 2-Methyl propanol and 2-propanol

(d) Ethylene bromide and propylene bromide

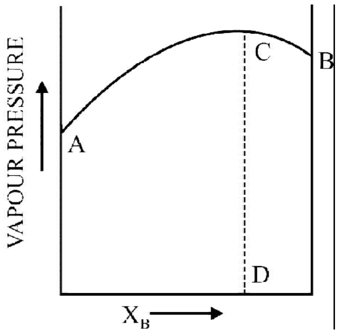
29. (S) The diagram given below is a vapour pressure-composition diagram for a binary solution of A and B. In the solution, A–B interactions are

(a) similar to A–A and B–B interactions

(b) greater than A–A and B–B interactions

(c) smaller than A–A and B–B interactions

(d) unpredictable.



30. (M) A binary liquids mixture of two liquid A and B showing the departure from the ideal behaviour :

(a) behaves as an ideal solution of B into A when $X_B \to 0$

(b) behaves as an ideal solution of A into B when $X_A \to 0$

(c) ΔH_{Soln} is always positive

(d) $T\Delta S_{Soln}$ is always positive

31. (M) Which pair (s) of liquids on mixing are expected to show no net volume change and no heat effect

(a) acetone and ethanol

(b) chlorobenzene and bromobenzene

(c) chloroform and benzene

(d) n-butyl chloride and n-butyl bromide.

32. (M) Composition of an azeotrope

(a) is independent of external pressure because it is a compound

(b) alters on changing the external pressure

(c) remains unchanged during distillation at a constant external pressure

(d) fluctuates even at constant pressure

33. (M) In binary liquid mixture of components, A and B, the former has greater tendency to escape into the vapour state than demanded by Raoult's law. Indicate the correct statement(s)

(a) Component A shows positive deviation and the component B negative deviation

(b) Both components show positive deviations

(c) Component A shows negative deviation and the component B positive deviation

(d) The component B has also greater tendency to escape into the vapour state than demanded by Raoult's law

34. (M) The solution showing positive deviation

(a) have ΔV (mixing) = + ve

(b) have ΔH (mixing) = – ve

(c) form minimum boiling azeotropes.

(d) have lower vapour pressure of each component in the solution than their pure vapour pressure.

35. (A) **Assertion (A) :** ΔH_{mix} and ΔV_{mix} are zero for the ideal solution.

Reason : The interactions between the particle of the components of a solution are almost identical as between particles in the liquids.

(a) A (b) B

(c) C (d) D

Henry's Law

36. (S) The millimoles of N_2 gas that will dissolve in 1 L of water at 298 K. when it is bubbled through water and has a partial pressure of 0.96 bar will be

(Given that at 298 K K_H = 76.8 k bar)

(a) 0.59 (b) 0.69

(c) 0.79 (d) 0.89

37. (S) Air contains O_2 and N_2 in the ratio of 1 : 4. The ratio of their solubilities in terms of mole fractions at atmospheric pressure and room temperature will be (Given Henry's constant for $O_2 = 3.30 \times 10^7$ torr, for $N_2 = 6.60 \times 10^7$ torr)

(a) 1 : 2 (b) 2 : 1

(c) 4 : 1 (d) 1 : 4

Colligative Properties

38. (M) Colligative properties of the solution depend on

(a) Nature of solute

(b) Nature of solvent

(c) Number of solute particles present in the solution

(d) Number of moles of solvent only

39. (S) Which one is a colligative property ?

(a) Boiling point (b) Vapour pressure

(c) Osmotic pressure (d) Freezing point

40. (S) The relative lowering of the vapour pressure is equal to the ratio between the number of

(a) solute molecules to the solvent molecules

(b) solute molecules to the total molecules in the solution

(c) solvent molecules to the total molecules in the solution

(d) solvent molecules to the total number of ions of the solute

41. (S) Vapour pressure of a solution of non-volatile solute is

(a) directly proportional to the mole fraction of the solvent

(b) Independent of mole fraction of the solute

(c) inversely proportional to the mole fraction of the solvent

(d) directly proportional to the mole fraction of the solute

42. (S) Vapour pressure of a solution of 5 g of non-electrolyte is 100 g of water at a particular temperature is 2985 N/m^2. The vapour pressure of pure water is 3000 N/m^2, the molecular weight of the solute is

(a) 60 (b) 120

(c) 178.2 (d) 380

43. (S) The vapour pressure of benzene at a certain temperature is 640 mm of Hg. A nonvolatile electrolyte solute weighing 2.175 g is added to 30.08 g of benzene. If the vapour pressure of the solution is 600 mm of Hg, what is the molecular weight of the solid substance ?

(a) 79.82 (b) 84.46

(c) 59.60 (d) 49.50

44. (M) Which of the following is/are correct statements (s) about the Raoult's law applied to a solution of non-volatile solute ?

(a) Vapour pressure of solution is proportional to mole fraction of solute

(b) V.P. of solution is proportional to the mole fraction of solvent

(c) Relative lowering of V.P. = mole fraction of solute

(d) Relative lowering of vapour pressure is proportional to the mole fraction of solute.

45. (A) **Assertion (A) :** The vapour pressure of a liquid decreases if some nonvolatile solute is dissolved in it.

Reason (R) : The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution.

(a) A (b) B

(c) C (d) D

46. (S) Elevation in boiling point was 0.52^0C when 6 gm of a compound X was dissolved in 100 gm of water. Molecular weight of X is (K_b of water is 0.52 K-kg/mol)

(a) 120 (b) 60

(c) 600 (d) 180

47. (S) The molal b.p. constant for water is 0.513^0C kg mol^{-1}. When 0.1 mole of sugar is dissolved in 200 g of water, the solution boils under a pressure of 1 atom at

(a) 100.513^0C kg/mol (b) 100.0513^0C kg/mol

(c) 100.256^0C kg/mol (d) 101.025^0C kg/mol

48. (S) The latent heat of vaporisation of water is 9700 cal/mole and if the b.p. is 100^0C, the ebullioscopic constant of water is

(a) 0.513^0C kg/mol (b) 1.026^0C kg/mol

(c) 10.26^0C kg/mol (d) 1.832^0C kg/mol

49. (S) The normal boiling point of toluene is 110.7^0C, and its boiling point elevation constant is 3.32 K kg mol^{-1}. The enthalpy of vapourization of toluene is nearly

(a) 17.0 kJ mol^{-1} (b) 34.0 kJ mol^{-1}

(c) 51.0 kJ mol^{-1} (d) 68.0 kJ mol^{-1}

50. (S) The freezing point of a 0.05 molal solution of a non-electrolyte in water is

(a) -1.86^0C (b) -0.93^0C

(c) -0.093^0C (d) 0.93^0C

51. (S) During depression of freezing point in a solution the following are in equilibrium

(a) liquid solution, solid solvent

(b) liquid solvent, solid solute

(c) liquid solute, solid solute

(d) liquid solute, solid solvent

52. (S) Calculate the molecular weight of a substance if the freezing point of a solution containing 100 g of benzene and 0.2g of the substance is 0.17 K below that of benzene. The cryoscopic constant of benzene is 5.16 K kg mol^{-1}.

(a) 70.46 (b) 85.66

(c) 60.23 (d) 178.25

53. (S) On freezing an aqueous solution sugar, the solid that starts separating out is

(a) sugar (b) ice

(c) solution with the same composition

(d) solution with a different composition.

54. (M) In the depression in freezing point experiment, it is observed that

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

(b) the vapour pressure of the solution is more than that of pure solvent

(c) only solute molecules solidify at the freezing point

(d) only solvent molecules solidify at the freezing point.

55. (A) **Assertion (A) :** If more and more non-volatile solute is added to a solvent, the freezing point of the solution keeps on reducing.

Reason (R) : Presence of large amount of the solid solute does not allow the solution to freeze.

(a) A (b) B

(c) C (d) D

56. (I) When 1.0 of urea is dissolved in 200 g of an unknown solvent X, the X freezing point is lowered by 0.25ºC. When 1.5g of an unknown, non-electrolytic solute Y is dissolved in 125 g of same solvent X, freezing point is lowered by 0.2 ºC and vapour pressure is lowered by 1%. If freezing point of X, is 12ºC, determine molar enthalpy of fusion of X in kJ.

57. (S) 10 g of glucose (π_1), 10 g of urea (π_2) and 10 g of sucrose (π_3) are dissolved in 250 mL of water at 300 K (π = osmotic pressure of solution). The relationship between the osmotic pressure of the solutions is

(a) $\pi_1 > \pi_2 > \pi_3$ (b) $\pi_3 > \pi_1 > \pi_2$

(c) $\pi_2 > \pi_1 > \pi_3$ (d) $\pi_2 > \pi_3 > \pi_1$

58. (S) A semipermeable membrane

(a) allows both the solute and solvent molecules to pass through

(b) does not allow the solute and solvent molecules to pass through

(c) allows only the solute molecules to pass through

(d) allows the solvent molecules to pass through but blocks the passage of the solute molecules

59. (S) Which statement is incorrect about osmotic pressure (π), volume (V) and temperature (T) ?

(a) $\pi \propto 1/v$ when T is constant.

(b) $\pi \propto T$ when V is constant.

(c) $\pi \propto V$ when T is constant.

(d) πV is constant when T is constant.

60. (S) The osmotic pressure of a solution increases if the

(a) number of solute molecules is increased

(b) temperature is decreased

(c) volume is increased

(d) value of R is increased

61. (S) Which of the following pairs of solutions is isotonic ?

(a) 6% urea and 6% glucose (w/v)

(b) 18% urea and 18% glucose (w/v)

(c) 6% urea and 18% fructose (w/v)

(d) 34.2% sucrose and 60% glucose (w/v)

62. (S) Two solutions A and B are separated by a semi-permeable membrane. As a result of osmosis, the level of solution A is found to rise. It implies that

(a) Solution A is more concentrated than solution B

(b) Solution B is more concentrated than solution A

(c) The solute molecules of A are smaller than those of B

(d) The solute molecules of B are smaller than those of A.

63. (S) Two aqueous solutions S_1 and S_2 are separated by a semi-permeable membrane. S_2 has lower vapour pressure than S_1. Then

(a) More solvent will flow from S_1 to S_2

(b) More solvent will flow from S_2 to S_1

(c) Solvent from S_1 and S_2 will flow at equal rates

(d) No flow will take place.

64. (S) What would happen if a thin slice of sugar beet is placed in a concentrated solution of NaCl ?

(a) Sugar beet will lose water from its cells

(b) Sugar beet will absorb water from solution

(c) Sugar beet will neither absorb nor lose water

(d) Sugar beet will dissolve in solution

65. (S) A plant cell shrinks when it is kept in

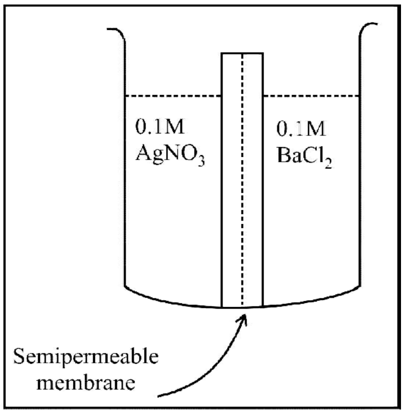
(a) Hypotonic solution

(b) A hypertonic solution

(c) A solution isotonic with cell sap

(d) Water.

66. (M) Study the figure given aside and pick out the correct option(s) of the following :



(a) A white precipitate of AgCl is formed on $AgNO_3$ side

(b) A white precipitate of AgCl is formed on $BaCl_2$ side

(c) No precipitate is formed on either side

(d) Meniscus of $BaCl_2$ solution rises and that of $AgNO_3$ solution falls in due course of time

67. (S) Consider the following statements

1. Isotonic solutions have the same molar concentration at a given temperature.
2. The molal elevation constant K_b is characteristic of a solvent, and is independent of the solute added.
3. The freezing point of a 0.1 M aqueous KCl solution is more than that of a 0.1 M aqueous $AlCl_3$ solution.

Which of these statements is correct.

(a) 1 and 2 (b) 2 and 3

(c) 1 and 3 (d) 1, 2 and 3

68. (S) Raoult's law states that for a dilute solution,

(a) the lowering of vapour pressure is equal to the mole fraction of the solute

(b) the relative lowering of vapour pressure is proprotional to the amount of solute in the solution

(c) the relative lowering of vapour pressure is equal to the mole fraction of the solute

(d) the vapour pressure of the solution is equal to the mole fraction of the solvent

69. (S) Which one of the following is not a colligative property ?

(a) Relative Lowering of vapour pressure of a solution

(b) Elevation in boiling point of a solution

(c) Critical point

(d) Osmotic pressure

70. (S) Given that ΔT_f is the depression in freezing point of the solvent in a solution of a nonvolatile solute of molality 1, the quantity $\underset{m\to1}{lt}\left(\frac{\Delta T_f}{m}\right)$ is equal to

(a) L_f (latent heat of fusion)

(b) K_b (ebullioscopic constant)

(c) K_f (cryoscopic constant)

(d) ΔH_{fus} (enthalpy of fusion)

71. (S) An aqueous solution freezes at -2.55^0C. What is its boiling point $\left(K_b^{H_2O} = 0.52\ K/m;\ K_f^{H_2O} = 1.86\ K/m\right)$?

(a) 107.0^0C (b) 100.6^0C

(c) 100.1^0C (d) 100.7^0C

72. (S) Which of the following colligative properties can provide molar mass of proteins (or polymers of colloids) with greater precision ?

(a) Relative lowering to vapour pressure

(b) Elevation of boiling point

(c) Depression in freezing point

(d) Osmotic pressure.

73. (M) Colligative properties of a solution are

(a) independent of the nature of solute

(b) inversely proportional to molecular mass of solute

(c) Proportional to concentration of solute

(d) independent of the amount of solvent.

74. (X) ΔH_f = Molar heat of fusion of ice ; L_f = Latent heat of fusion of ice (g^{-1})

ΔH_v = Molar heat of vaporisation of water ; L_v = Latent heat of vaporisation of water (g^{-1})

Match the following appropriately

COLUMN - I	COLUMN - II
(A) Molal depression	(P) $\frac{18\times 373\times 373\times R}{1000\Delta H_v}$ constant of water
(B) Molal elevation	(Q) $\frac{373\times 373\times R}{1000\ L_v}$ constant of water
(C) ΔT_f of solution	(R) $\frac{18\times 273\times 273\times R}{1000\ \Delta H_f}$ containing 9.0 g of glucose in 50g of water
(D) ΔT_b of solution	(S) $\frac{273\times 273\times R}{1000\ L_f}$ containing 3.0g of urea in 50 g of water

Deviation in Colligative Properties

75. (S) If a solute undergoes dimerization and trimerization, the minimum values of the van't Hoff factors are

(a) 0.50 and 1.50 (b) 1.50 and 1.33

(c) 0.50 and 0.33 (d) 0.25 and 0.67

76. (S) The van't Hoff factors i for an electrolyte which undergoes dissociation and association in solvents are respectively

(a) greater than 1 and greater than 1

(b) less than 1 and greater than 1

(c) less than 1 and less than 1

(d) greater than 1 and less than 1

77. (S) When 1.345 g of $CuCl_2$ is dissolved in 1 kg of water, the elevation in boiling point will be ($K_b = 0.52$, molar mass of $CuCl_2 = 134.5$)

(a) 0.05 (b) 0.30

(c) 0.15 (d) 0.015

78. (S) Which one has the highest b.p. ?

(a) 0.1 N Na_2SO_4 (b) 0.1 N $MgSO_4$

(c) 0.1 M $Al_2(SO_4)_3$ (d) 0.1 M $BaSO_4$

79. (S) Which of the following aqueous solutions has the highest boiling point ?

(a) 0.1 M KNO_3 (b) 0.1 M Na_3PO_4

(c) 0.1 M $BaCl_2$ (d) 0.1 M K_2SO_4

80. (S) The freezing point of 1 molal NaCl solution assuming NaCl to be 100% dissociated in water is

(a) -1.86^0C (b) -3.72^0C

(c) $+1.86^0C$ (d) $+3.72^0C$

81. (S) The molal freezing point constant for water is 1.86^0C/mole. Therefore, the freezing point of 0.1M NaCl solution in water is expected to be

(a) -1.86^0C (b) -0.186^0C

(c) -0.372^0C (d) $+0.337^0C$

82. (S) 0.01 M solution each of urea, common salt and Na_2SO_4 are taken, the ratio of depression of freezing point is

(a) 1 : 1 : 1 (b) 1 : 2 : 1

(c) 1 : 2 : 3 (d) 2 : 2 : 3

83. (S) The osmotic pressures of equimolar solutions of $Al_2(SO_4)_3$, KCl and sugar will be in the order

(a) $KCl < Al_2(SO_4)_3 <$ sugar

(b) sugar $< KCl < Al_2\,(SO_4)_3$

(c) sugar $> KCl > Al_2\,(SO_4)_3$

(d) $KCl <$ sugar $< Al_2\,(SO_4)_3$

84. (S) Solutions A, B, C and D are respectively 0.1 M glucose, 0.05 M NaCl, 0.05 M $BaCl_2$ and 0.1 M $AlCl_3$. Which of the following pairs is isotonic ?

(a) A and B (b) B and C

(c) A and D (d) A and C

85. (S) 0.004 M Na_2SO_4 is isotonic with 0.01 M glucose. The degree of dissociation of Na_2SO_4 is

(a) 75% (b) 50%

(c) 25% (d) 85%

86. (S) The average osmotic pressure of human blood is 7.8 bar at 37^0C. What is the concentration of an aqueous NaCl solution that could be introduced in the bloodstream ?

(a) 0.16 mol L^{-1} (b) 0.32 mol L^{-1}

(c) 0.45 mol L^{-1} (d) 0.65 mol L^{-1}

87. (S) An aqueous solution of NaCl freezes at -0.186^0C. Given that $K_b^{H_2O} = 0.512$ K kg mol^{-1} and $K_f^{H_2O} = 1.86$ K kg mol^{-1}, the elevation in boiling point of this solution is

(a) 0.0585 K (b) 0.0512 K

(c) 1.864 K (d) 0.0265 K

88. (S) Among 0.1 M solutions of urea, Na_3PO_4 and $Al_2(SO_4)_3$, which is incorrect

(a) the vapour pressure and freezing point are the lowest for urea

(b) the vapour pressure and freezing point are the highest for urea

(c) the boiling point is the highest for $Al_2(SO_4)_3$

(d) the depression in freezing point is the highest for $Al_2(SO_4)_3$

89. (A) **Assertion (A) :** The boiling point of 0.1 M urea solution is less than that of 0.1 M KCl solution.

Reason (R) : Elevation of boiling point is directly proportional to the number of species present in the solution.

(a) A (b) B

(c) C (d) D

90. (A) **Assertion (A) :** NaCl in water and organic acids in benzene show abnormal molecular mass

Reason (R) : Abnormal molecular mass is obtained when the substance in the solution undergoes dissociation or association.

(a) A (b) B

(c) C (d) D

Comprehension

A Protein has been isolated as sodium salt with their molecular formula Na_xP (this notation means xNa^+ ions are associated with a negatively charged protein P^{-x}). A solution of this salt was prepared by dissolving 0.25g of this sodium salt of protein in 10g of water and ebullioscopic analysis revealed that solution boils at temperature 6.78×10^{-3} °C higher than the normal boiling point of pure water. K_b of water of 0.52 K kg mol^{-1}. Also elemental analysis revealed that the salt contain 1% sodium metal by weight.

91. (C) Deduce molecular formula of protein.

(a) NaP (b) Na_2P

(c) Na_4P (d) Na_5P

92. (C) Determine molecular weight of sodium salt of protein.

(a) 2300 (b) 4600

(c) 9200 (d) 11500

93. (C) Determine molecular weight of acidic form of protein :

(a) 11390 (b) 2278

(c) 9112 (d) 4556

94. (X) M_n = Normal molecular mass of solute

M_o = Observed molecular mass of solute from colligative property measurement

Match the following :

COLUMN - I	**COLUMN - II**
(A) $M_o < M_n$	(P) 0.1 M CH_3COOH is benzene
(B) $M_o \approx M_n/3$	(Q) 0.1 M urea in water
(C) $M_o > M_n$	(R) 0.05 M barium chloride in water
(D) $M_o = M_n$	(S) 0.1 M CH_3COOH in water

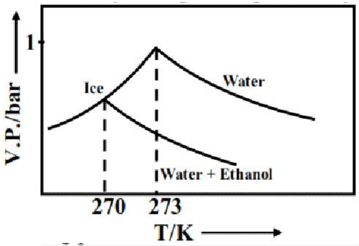
95. (I) A mixture of NaCl and sucrose of combined mass 10.2 g is dissolved in enough water to make up a 250 mL solution. the osmotic pressure of the solution is 7.32 atm at 23°C. Calculate the mass percentage of NaCl in the mixture.

96. (I) A non-volatile organic compound X was used to make-up two solution. Solution A contains 5.0 g of X in 100 g of water and solution B contains 2.0 g of X in 100 g of benzene. Solution A has vapour pressure of 754.5 mm of Hg at normal boiling point of water and solution B has the same vapour pressure at the normal boiling point of benzene. Assuming X undergo partial dimerization in benzene, determine percentage of X dimerized in benzene solution.

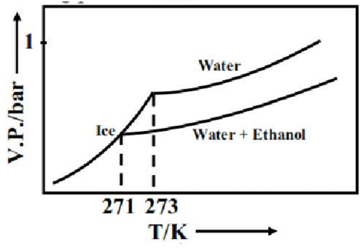
EXERCISE - 4 : PREVIOUS YEAR JEE ADVANCED QUESTION

1. 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.) versus temperature (T). [molecular weight of ethanol is 46 g mol^{-1}] Among the following, the option representing change the freezing point is **(2017)**

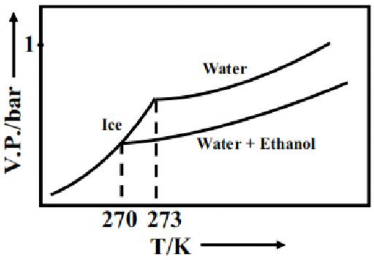
(a)



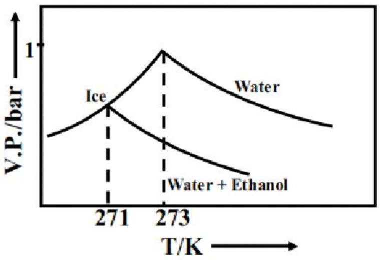
(b)



(c)



(d)



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

(a) 724 (b) 740

(c) 736 (d) 718

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

(a) -2.3×10^{-2} (b) -5.7×10^{-2}

(c) -5.7×10^{-3} (d) -1.2×10^{-2}

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

(a) 4.0×10^{-4} (b) 4.0×10^{-5}

(c) 5.0×10^{-4} (d) 4.0×10^{-6}

5. When 20 g of naphthoic 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 2K is observed. The Van't Hoff factor (i) is **(2007)**

(a) 0.5 (b) 1

(c) 2 (d) 3

6. 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 = 0.52 kg K mol^{-1}, molecular weight of $CuCl_2$ = 134.4 g]. **(2005)**

(a) 0.05 (b) 0.1

(c) 0.16 (d) 0.21

7. The elevation in boiling point of a solution of 13.44g of $CuCl_2$ in 1 kg of water using the following information will be (Molecular weight of $CuCl_2$ = 134.4 and K_b = 0.52 K molal^{-1}) **(2005)**

(a) 0.16 (b) 0.05

(c) 0.1 (d) 0.2

8. 0.004 M Na_2SO_4 is isotonic with 0.01 M glucose. Degree of dissociation of Na_2SO_4 is **(2004)**

(a) 75% (b) 50%

(c) 25% (d) 85%

9. During depression of freezing point in a solution the following are in equilibrium **(2003)**

(a) liquid solvent, solid solvent

(b) liquid solvent, solid solute

(c) liquid solute, solid solute

(d) liquid solute, solid solvent

10. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to : **(1996)**

(a) ionization of benzoic acid.

(b) dimerization of benzoic acid.

(c) trimerization of benzoic acid.

(d) solvation of benzoic acid.

11. 0.2 molal acid HX is 20% ionised in solution. $K_f = 1.86$ K molality^{-1}. The freezing point of the solution is : **(1995)**

(a) -0.45 (b) -0.90

(c) -0.31 (d) -0.53

12. The freezing point of equimolal aqueous solutions will be highest for **(1990)**

(a) $C_6H_5NH_3Cl$ (aniline hydrochloride)

(b) $Ca(NO_3)$

(c) $La(NO_3)_3$

(d) $C_6H_{12}O_6$ (glucose)

13. Which of the following 0.1 M aqueous solutions will have the lowest freezing point ? **(1989)**

(a) Potassium sulphate (b) Sodium chloride

(c) Urea (d) Glucose

14. When mercuric iodide is added to the aqueous solution of potassium iodide then **(1987)**

(a) freezing point is raised (b) freezing point is lowered

(c) freezing point does not change

(d) boiling point does not change

15. For a dilute solution, Raoult's law states that **(1985)**

(a) the lowering of vapour pressure is equal to the mole fraction of solute

(b) the relative lowering of vapour pressure is equal to the mole fraction of solute

(c) the relative lowering of vapour pressure is proportional to the amount of solute in solution

(d) the vapour pressure of the solution is equal to the mole fraction of solvent.

16. An azeotropic solution of two liquids has boiling point lower than either of them when it **(1981)**

(a) shows negative deviation from Raoult's law

(b) shows no deviation from Raoult's law

(c) show positive deviation from Raoult's law

(d) is saturated

Objective Questions (One or more than one correct option

17. In the depression of freezing point experiment, it is found that the **(1999)**

(a) vapour pressure of the solution is less than that of pure solvent

(b) vapour pressure of the solution is more than that of pure solvent

(c) only solute molecules solidify at the freezing point

(d) only solvent molecules solidify at the freezing point

18. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statements is (are) **(2013)**

(a) ΔG is positive (b) ΔS_{system} is positive

(c) $\Delta S_{surroundings} = 0$ (d) $\Delta H = 0$

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

(a) carbon tetrachloride + methanol

(b) carbon disulphide + acetone

(c) benzene + toluene

(d) phenol + aniline

Comprehension-I

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

$(k_f^{water}) = 1.86\ \text{K kg mol}^{-1}$

Freezing point depression constant of ethanol

$$(k_f^{\text{ethanol}}) = 2.0\text{ K kg mol}^{-1}$$

Boiling point elevation constant of water

$$(k_b^{\text{water}}) = 0.52\text{ K kg mol}^{-1}$$

Boiling point elevation constant of ethanol

$$(k_b^{\text{ethanol}}) = 1.2\text{ K kg mol}^{-1}$$

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 = 46g mol^{-1}

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative. **(2008)**

20. The freezing point of the solution M is

(a) 268.7 K (b) 268.5 K

(c) 234.2 K (d) 150.9 K

21. The vapour pressure of the solution M is

(a) 39.3 mm Hg (b) 36.0 mm Hg

(c) 29.5 mm Hg (d) 28.8 mm Hg

22. 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

(a) 380.4 K (b) 376.2 K

(c) 375.5 K (d) 354.7 K

Fill in the Blanks

23. Given that ΔT_f is the depression in freezing point of the solvent in a solution of a non-volatile solute of molality, m, the quantity $\lim\limits_{m\to 0}(\Delta T_f / m)$ is equal to .... **(1994)**

True/False

24. Following statement is true only under some specific conditions. Write the condition, for it "Two volatile and miscible liquids can be separated by fractional distillation into pure components." **(1994)**

Subjective Questions

25. What is the molarity and molality of a 13% solution (by weight) of sulphuric acid with a density of 1.02 g/ml ? To what volume should 100 ml of this acid be diluted in order to prepare a 1.5 N solution ? **(1978)**

26. The vapour pressure of pure benzene is 639.70 mm of Hg and the vapour pressure of solution of a solute in benzene at the same temperature is 631.9 mm of Hg. Calculate the molality of the solution. **(1981)**

27. Two liquids A and B form ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of A and 3 moles of B is 550 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of A and B in their pure states. **(1982)**

28. An organic compound ($C_xH_{2y}O_y$) was burnt with twice the amount of oxygen needed for complete combustion to CO_2 and H_2O. The hot gases when cooled to 0ºC and 1 atm pressure, measured 2.24 L. The water collected during cooling weigh 0.9g. The vapour pressure of pure water at 20ºC is 17.5 mm Hg and is lowered by 0.104 mm when 50g of the organic compound are dissolved in 1000 g of water.
Given the molecular formula of the organic compound. **(1983)**

29. The vapour pressure of ethanol and methanol are 44.5 and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by the mixing 60g of ethanol with 40g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour. **(1986)**

30. The vapour pressure of a dilute aqueous solution of glucose ($C_6H_{12}O_6$) is 750 mm of mercury at 373 K. Calculate (i) molality and (ii) mole fraction of the solute. **(1989)**

31. The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile, non-electrolyte solid weighing 2.175g is added to 39.0g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular weight of the solid substance ? **(1990)**

32. The degree of dissociation of $Ca(NO_3)_2$ in dilute aqueous solution, containing 7.0g of the salt per 100g of water at 100°C is 0.7, calculate the vapour pressure of the solution. **(1991)**

33. Addition of 0.643g of a compound to 50 mL of benzene (density : 0.879 g/mL) lowers the freezing point from 5.51ºC to 5.03º C. If k_f for benzene is 5.12, calculate the molecular weight of the compound. **(1992)**

34. What weight of the non-volatile solute urea (NH_2–CO–NH_2) 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 ? **(1993)**

35. The molar volume of liquid benzene (density = 0.877 g/mL) increases by a factor of 2750 as it vaporises at 20ºC and that of liquid toluene (density = 0.867g mL^{-1}) increases by a factor of 7720 at 20ºC. A solution of benzene and toluene at 20ºC has a vapour pressure of 45.0 torr. Find the mole fraction of benzene in the vapour above the solution. **(1996)**

36. A solution of a non-volatile solute in water freezes at – 0.30ºC. The vapour pressure of pure water at 298K is 23.51 mm Hg and k_f for water is 1.86 K kg mol^{-1}. Calculate the vapour pressure of this solution at 298 K. **(1998)**

37. Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon : 42.86%, hydrogen : 2.40%, nitrogen : 16.67% and oxygen : 38.07%,

(i) Calculate the empirical formula of the minor product.

(ii) When 5.5g of the minor product is dissolved in 45g of benzene, the boiling point of the solution is 1.84ºC higher than that of pure benzene. Calculate the molar mass of the minor product then determine its molecular and structural formula. (Molal boiling point elevation constant of benzene is 2.53 K kg mol^{-1}.) **(1999)**

38. To 500 cm^3 of water, 3.0×10^{-3} kg of acetic acid is added. if 23% of acetic acid is dissociated, what will be the depression in freezing point ? K_f and density of water are 1.86 K kg^{-1} mol^{-1} and 0.997 g cm^{-3}, respectively. **(2000)**

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

40. Consider the three solvents of identical molar masses. Match their boiling point with their k_b values **(2003)**

Solvents	Boiling point	k_b values
X	100ºC	0.92
Y	27ºC	0.63
Z	283ºC	0.53

41. 1.22 g of benzoic acid is dissolved in 100 g of acetone and 100 g of benzene separately. Boiling point of the solution in acetone increases by 0.17ºC, while that in the benzene increases by 0.13ºC; K_b for acetone and benzene is 1.7 K Kg mol^{-1} and 2.6 K kg mol^{-1} respectively. Find molecular weight of benzoic acid in two cases and justify your answer. **(2004)**

42. 75.2 g of C_6H_5OH (phenol) is dissolved in 1kg of solvent of k_f = 14. If the depression in freezing point is 7K, then find the percentage of phenol that dimerises. **(2006)**

43. 29.2% (w/W) HCl stock solution has density of 1.25 g mL^{-1}. The molecular weight of HCl is 36.5g mol^{-1}. The volume (mL) of stock solution required to prepare a 200 mL solution 0.4 M HCl is **(2012)**

44. Liquids A and B form ideal solution over the entire range of composition. At temperature T, equimolar binary solution of liquids A and B has vapour pressure 45 Torr. At the same temperature, a new solution of A and B having mole fractions x_A and x_B, respectively, has vapour pressure of 22.5 Torr. The value of x_A/x_B in the new solution is ....

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

Match the column

45. Match the thermodynamic processes given under Column-I with the expressions given under Column-II. **(2015)**

Column–I	**Column–II**
(A) Freezing of water at 273 K and 1 atm	(P) q = 0
(B) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	(Q) w = 0
(C) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	(R) $\Delta S_{sys} < 0$
(D) Reversible heating of H_2(g) at 1 atm from 300K to 600 K, followed by reversible cooling to 300 K at 1 atm.	(S) $\Delta U = 0$
	(T) $\Delta G = 0$

ANSWER KEY

EXERCISE - 1 : BASIC OBJECTIVE QUESTIONS

1. (a)	**2.** (c)	**3.** (b)	**4.** (b)	**5.** (a)	**6.** (d)	**7.** (b)	**8.** (b)	**9.** (a)	**10.** (a)
11. (a)	**12.** (d)	**13.** (a)	**14.** (c)	**15.** (c)	**16.** (c)	**17.** (c)	**18.** (c)	**19.** (c)	**20.** (a)
21. (c)	**22.** (d)	**23.** (b)	**24.** (c)	**25.** (d)	**26.** (b)	**27.** (d)	**28.** (a)	**29.** (a)	**30.** (d)
31. (c)	**32.** (b)	**33.** (a)	**34.** (a)	**35.** (c)	**36.** (d)	**37.** (c)	**38.** (b)	**39.** (b)	**40.** (d)
41. (b)	**42.** (a)	**43.** (a)	**44.** (b)	**45.** (b)	**46.** (a)	**47.** (a)	**48.** (a)	**49.** (b)	**50.** (a)
51. (b)	**52.** (b)	**53. (a)**	**54. (b)**	**55. (c)**	**56.** (a)	**57. (d)**	**58.** (a)	**59.** (a)	**60.** (d)
61. (d)	**62.** (c)								

EXERCISE - 2 : PREVIOUS YEAR JEE MAINS QUESTIONS

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

JEE Mains Online

1. (c)	**2.** (b)	**3.** (a)	**4.** (d)	**5.** (b)	**6.** (b)	**7.** (c)	**8.** (c)	**9.** (b)	**10.** (c)

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

1. (d)	**2.** (a)	**3.** (c)	**4.** (a)	**5.** (b)	**6.** (c)	**7.** (b)	**8.** (d)	**9.** (d)	**10.** (c)
11. (a)	**12.** (a)	**13.** (a)	**14.** (b)	**15.** (b)	**16.** (b)	**17.** (a)	**18.** (c)	**19.** (c)	**20.** (b)
21. (a)	**22.** (c)	**23.** (a)	**24.** (d)	**25.** (c)	**26.** (c)	**27.** (d)	**28.** (b)	29. (c)	30. (a,b,d)
31. (b,d)	**32.** (b,c)	**33.** (b,d)	**34.** (a,c)	**35.** (a)	**36.** (b)	**37.** (a)	**38.** (c)	**39.** (c)	**40.** (b)
41. (a)	**42.** (c)	**43.** (b)	**44.** (b, c, d)	**45.** (b)	**46.** (b)	**47.** (c)	**48.** (a)	**49.** (b)	**50.** (c)
51. (a)	**52.** (c)	**53.** (b)	**54.** (a,d)	**55.** (b)	**56.** 0034	**57.** (c)	**58.** (d)	**59.** (c)	**60.** (a)
61. (c)	**62.** (a)	**63.** (a)	**64.** (a)	**65.** (b)	**66.** (c,d)	**67.** (d)	**68.** (c)	**69.** (c)	**70.** (c)
71. (d)	**72.** (d)	**73.** (abc)	**74.** (A–R, S; B–P, Q; C–R, S; D–P, Q)						
75. (c)	**76.** (d)	**77.** (d)	**78.** (c)	**79.** (b)	**80.** (b)	**81.** (c)	**82.** (c)	**83.** (b)	**84.** (a)
85. (a)	**86.** (a)	**87.** (b)	**88.** (a)	**89.** (a)	**90.** (a)	**91.** (d)	**92.** (d)	**93.** (a)	
94. (A–R, S; B–R; C–P; D–Q)			**95.** (0020)	**96.** (0085)					

EXERCISE - 4 : (PREVIOUS YEAR JEE ADVANCED QUESTIONS)

1. (c) **2.** (a) **3.** (a) **4.** (a) **5.** (a) **6.** (c) **7.** (a) **8.** (a) **9.** (a) **10.** (b)

11. (a) **12.** (d) **13.** (a) **14.** (a) **15.** (b) **16.** (c) **17.** (a,d) **18.** (bcd) **19.** (a,b) **20.** (d)

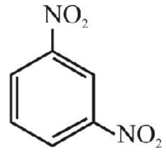
21. (a) **22.** (b) **23.** k_f **24.** (T) **25.** 1.52m, 1.35M, 180 ml **26.** 0.158

27. $p_A^o = 400\text{mm}, p_B^o = 600\text{mm}.$

28. $C_5H_{10}O_5$ **29.** 66.16 mm, 0.657 **30.** 0.74 molal; 1/76 **31.** 65.25 **32.** 746.32

33. 156 g/mol **34.** 111g, 18.5 **35.** 0.72 **36.** 23.44 mm

37. (i) $C_3H_2NO_2$ (ii) 168g/mol; $C_6H_4N_2O_4$;



38. 0.23°C **39.** $1.005 \times 10^{-4}\ \text{min}^{-1}$

40.

Solvents	Boiling point	k_b values
X	100°C	0.63
Y	27°C	0.53
Z	283°C	0.92

41. 122; 244 **42.** (0075) **43.** (0008) **44.** (19) **45.** (A–R,T; B–P,Q,S; C–P,Q,S; D–P,Q,S,T)

Dream on !!

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