SOLUTION & COLLIGATIVE PROPERTIES

CONTENTS

JEE(Advanced) Syllabus

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

JEE(Main) Syllabus

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

Solutions & Colligative Properties

Section (A) : General Introduction & types of solution

1. Introduction :

A solution is a homogeneous mixture of two or more substances which are chemically non-reacting. We come across many types of solutions in our daily life. e.g., solid-liquid, liquid-liquid, gas-gas. In this chapter we will learn several properties of solutions and their applications.

D1 **Solution :** *A homogeneous mixture of two or more substances is known as solution.*

D2 **Solute :** *The substance present in smaller amount in a solution is called solute.*

D3 **Solvent :** *The substance present in larger amount in a solution is called solvent.*

D4 **Binary solutions :** *Those solutions which contain two components are called binary solutions,* e.g., salt solution, benzene and toluene.

D5 **Ternary solutions :** *Those solutions which contain three components are called ternary solutions,* e.g., ethanol + water + acetic acid.

D6 **Aqueous solution :** *When solute is dissolved in water, it is called aqueous solution,* e.g., sugar solution, ethanol in water.

D7 **Non-aqueous solution :** *When solute is dissolved in solvent other than water, it is called non-aqueous solution,* e.g., iodine dissolved in alcohol (Tincture of iodine).

D8 **Miscible liquids :** *Those liquids which mix with each other and form homogeneous mixture are called miscible liquids.*

D9 **Immiscible liquids :** *Those liquids which do not mix with each other are called immiscible liquids.*

D10 **Alloys :** *Solid solutions of the two or more metals are called alloys. One of them can be a non-metal also.*

2. Types of Solutions :

S.No.	Solute	Solvent	Types of Solutions	Examples
Solid Solutions				
1	Solid	Solid	Solid in solid	All alloys like brass, bronze, an alloy of copper and gold, etc.
2	Liquid	Solid	Liquid in solid	Amalgam of mercury with Na, $CuSO_4.5H_2O$. $FeSO_4.7H_2O$
3	Gas	Solid	Gas in solid	Solution of H_2 in Pd, dissolved gases in minerals.
Liquid Solutions				
4	Solid	Liquid	Solid in liquid	Sugar solution, salt solution, I_2 in CCl_4
5	Liquid	Liquid	Liquid in liquid	Benzene in toluene, alcohol in water.
6	Gas	Liquid	Gas in liquid	CO_2 in water, NH_3 in water etc.
Gaseous Solutions				
7	Solid	Gas	Solid in gas	Iodine vapours in air, camphor vapours in N_2.
8	Liquid	Gas	Liquid in gas	Water vapours in air, $CHCl_3$ vapours in N_2.
9	Gas	Gas	Gas in gas	Air ($O_2 + N_2$)

The concentration of a solution can be expressed by different concentration terms which are described as follows.

Resonance®
Educating for better tomorrow

Section (B) : Concentration terms (Revision of mole)
3. Concentration Terms :
3.1 % Concentration
D11 **Mass percentage :** *It is the amount of solute in grams dissolved per 100 g of solution.* e.g., 10% solution of sodium chloride means 10 g of solid sodium chloride present in 100 g of solution.

F1 **% w/w** = $\dfrac{\text{weight of solute(g)}}{\text{weight of solution(g)}} \times 100$

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

= 10 g of urea is present in 90 g of water.

D12 **Mass by volume percentage (% w/v) :** *It is defined as mass of solute dissolved per 100 ml of solution.* It is commonly used in medicine and pharmacy.

F2 **% wt/vol. (w/v)**

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

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

Ex. 10% (w/v) urea solution. = 10 g of urea is present in 100 mL of solution.

But not 10 g of urea present in 90 ml of water

for dilute solution : volume solution = volume solvent.

D13 **Volume percentage (% v/v) :** *It is defined as volume of a solute dissolved per 100 ml of solution.*

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

3.2 Strength of solution in g/L
Weight of solute (in gram) per litre (1000 mL) of solution.

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

100 mL .... 10 g

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

Solved Examples

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

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

6 g in $\dfrac{100}{1.060}$ mL

$\dfrac{100}{1.060}$ mL $\longrightarrow$ 6 g.

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

D14 **Molarity (M) :** *It is expressed as the number of moles of solute per litre of solution.*

3.3 Molarity = No. of moles of solute per litre of solution.
Let n = No. of moles of solute ; N = No. of moles of solvent ; V = volume of solution

F3 $M = \dfrac{n}{V \ (\text{in } L)} = \left(\dfrac{W}{M}\right) \times \dfrac{1000}{V \ (\text{in } mL)}$

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

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

Der.1 If V_1 mL of C_1 molarity solution is mixed with V_2 mL of C_2 molarity solution (same substance or solute)

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

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

D15 **Molality (m) :** *It is defined as number of moles of solute per 1000 g or 1 kg of solvent.*

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

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

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

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

Molality not depends on temperature.

Solved Examples

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

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

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

    (ii) $[H^+] = ?$
         10 m. moles H_2SO_4
         20 m. moles H^+

         $[H^+] = \dfrac{20}{100} = 0.2 \text{ M}$

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

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

Example-3 : **(a)** Derive a relationship between molality & molarity of a solution in which w g of solute of molar mass M g/mol is dissolved in W g solvent & density of resulting solution = 'd' g/ml.
(b) Calculate molality of 1.2 M H_2SO_4 solution ? If its ρ = 1.4 g/mL

Solution : **(a)** Say 1 L solution taken,
     mass of 1 lit solution = (1000 d) g
     moles of solute = (molarity)
     mass of solute = (molarity) x m
     mass of solvent = W = 1000 d – (molarity) × m

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

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

3.5 D16 Normality : *It is defined as number of gram equivalents of solute dissolved per litre of solution.*

F5 $\text{No.of equivalents per litre of solution} = \dfrac{\text{no. of equivalents of solute}}{\text{volume of solution (in L)}}$

     = n-factor × molarity   No. of equivalents = normality × volume (in L)

F6 $\text{Equivalent mass} = \dfrac{\text{Molar mass}}{n-\text{factor}}$

F7 $\text{No. of equivalent} = \dfrac{\text{Mass of the species}}{\text{equivalent mass}} = \dfrac{\text{Mass of the species}}{\dfrac{\text{Molar mass}}{n-\text{factor}}}$

3.6 'n' - factor

(i) For oxidizing/reducing agents : no. of e^- involved in oxidation/reduction half reaction per mole of oxidising agent /reducing agent.

e.g. : $5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + H_2O$ n- factor = 5

(ii) For acid/ base reactions : no. of H^+ ions displaced/ OH^- ions displaced per mole of acid/ base.

e.g. : NaOH   n - factor = 1 H_2SO_4 n - factor = 2

(iii) For salt :

n = Total charge on cations.
       or   } Simple salts
total charge on anions

e.g. : $Al_2(SO_4)_3$ n - factor = charge on the cation = 2 x 3 = 6
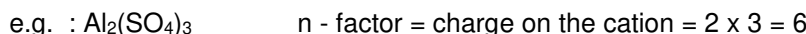
3.7 D17 Mole-fraction (x) : *It is the ratio of number of moles of a particular component to the total number of moles of all the components.* e.g., mole-fraction of component A, $x_A = \dfrac{n_A}{n_A + n_B}$, where n_A is the number of moles of component 'A' and n_B is the number of moles of component 'B'.

For binary mixture.

F8 $X_{solute} = \dfrac{\text{moles of solute}}{\text{total moles in solutions}} = \dfrac{n}{n+N}$

F9 $X_{Solvent} = \dfrac{\text{moles   of   solvent}}{\text{Total   moles   in   solutions}} = \dfrac{N}{n+N}$

F10 $X_{solute} + X_{Solvent} = 1$

3.8 D18 Parts per million (ppm) : *The number of parts of solute present in 1 million parts of solution are called its ppm.* When a solute is present in small quantities (very minute amounts), it is easier to express the concentration in parts per million.

F11   **(a)** $ppm (w/w) = \dfrac{\text{wt. of solute (in g)}}{\text{wt. of solution (in g)}} \times 10^6$

F12   **(b)** $ppm (w/v) = \dfrac{\text{wt. of solute (in g)}}{\text{vol. of solution (in mL)}} \times 10^6$

F13   **(c)** $ppm (moles/moles) = \dfrac{\text{moles of solute}}{\text{moles of solution}} \times 10^6$

Table : 1

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

Note : All volume related concentration terms are temperature dependent.

Solved Examples

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

Solution : 10 moles urea in 1000 g of water

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

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

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

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

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

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

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

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

Section (C) : Vapour Pressure

4. Vapour Pressure of a pure liquid or pure solid :
4.1 The origin of saturated vapour pressure: The evaporation of a liquid
Some of the more energetic particles on the surface of the liquid move fast enough to escape from the attractive forces holding the liquid together. They evaporate. The diagram shows a small region of a liquid near its surface.

Some of the more energetic particles escape.
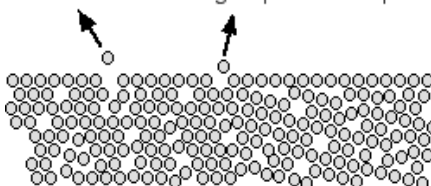
Note: evaporation only takes place on the surface of the liquid. That's quite different from boiling which happens when there is enough energy to disrupt the attractive forces throughout the liquid. That's why, if you look at boiling water, you see bubbles of gas being formed all the way through the liquid.

If you look at water which is just evaporating in the sun, you don't see any bubbles. Water molecules are simply breaking away from the surface layer. Eventually, the water will all evaporate in this way.

The evaporation of a liquid in a closed container: Evaporation and Condensation

Now imagine what happens if the liquid is in a closed container. Common sense tells that water in a sealed bottle doesn't disappear over time. But, there is still constant evaporation from the surface. Particles continue to break away from the surface of the liquid - but this time they are trapped in the space above the liquid.
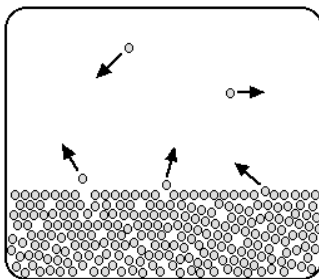
As the gaseous particles bounce around, some of them will hit the surface of the liquid again, and be trapped there. This is called as condensation. There will rapidly be an equilibrium set up in which the number of particles leaving the surface is exactly balanced by the number rejoining it. **At equilibrium, rate of evaporation becomes equal to the rate of condensation.**
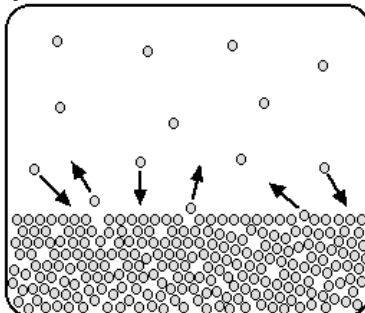
In this equilibrium, there will be a fixed number of the gaseous particles in the space above the liquid. When these particles hit the walls of the container, they exert a pressure. This pressure is called the **saturated vapour pressure** (or just **vapour pressure**) of the liquid.

Suppose, we take 10 gram liquid in a chamber. Initially, there are no molecules in the gaseous phase. Thus, no pressure is exerted on the mercury and the level of mercury in both columns is equal. Suppose, after vapourization of 5 gram of the liquid vapour-liquid equillibrium is established. Now, molecules in the gaseous phase exert pressure on the mercury and level of mercury in the column attached to the chamber decreases.

Note: From the figure, we can see that, Vapour Pressure of the liquid = h mm Hg.
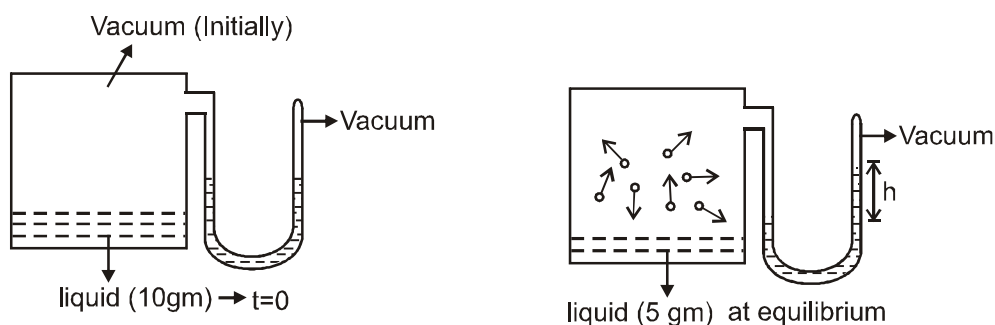
(Imagine no liquid molecule exist in vapour phase)

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

4.2 Important Points related to vapour pressure :

D19 **Vapour pressure of a pure liquid :** *The pressure exerted by the vapours over the liquid surface at equilibrium is called vapour pressure.* It increases with the increase in temperature.

D20 **Vapour pressure of solution :** *The pressure exerted by the vapours of solvent 'A' and solute 'B' in equilibrium with the liquid phase is called the vapour pressure of solution.*

D21 **Partial vapour pressure :** *The pressure of vapours of a component 'A' over a solution of 'A' and 'B' is called partial vapour pressure of component A. It is denoted by p_A.*

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005

Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in

Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029

ADVSCP - 6

(1) **Definition of vapour pressure :** The partial pressure of vapours in equilibrium with pure solid or pure liquid at a given temperature.
At eq. the rate of evaporation = rate of condensation
e.g. $H_2O(l) \rightleftharpoons H_2O(g)$
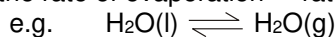
$K_p = p_{H_2O,g}^{eq}$

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

(2) Since vapour pressure is an equilibrium constant. so it's value is dependent only on temperature.

(a) **Nature of liquid :** The value of a liquid's vapour pressure depends on the magnitude of the intermolecular forces in the liquid. The smaller the intermolecular forces, higher the vapour pressure becuause loosely held molecules escape more easily into vapour phase.

(b) **Temperature of the given liquid :** At higher temperature, more molecules from the liquid have enough KE to escape from the surface of the liquid. That will increase the saturated vapour pressure.

liquid $\rightleftharpoons$ vapour ΔH is +ve

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

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

F14 $\ln\left(\dfrac{p_2}{p_1}\right) = -\dfrac{\Delta H_v}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$, where ΔH_v = molar enthalpy of vapourisation of the given liquid,

p_2 = vapour pressure of the liquid at T_2 and p_1 = vapour pressure of the liquid at T_1.

(3) Vapour pressure of a liquid does not depend on :
(i) the amount of liquid taken
(ii) surface area of the liquid
(iii) volume or shape of the container

(4) **Partial pressure of vapours**: If vapours of a liquid are present in a gaseous mixture then,

Partial pressure of vapours of the liquid = $\dfrac{\text{Pressure of vapours}}{\text{Total pressure}}$

Saturation: A gas or gaseous mixture is said to be saturated with the vapours of a liquid if the partial pressure of the liquid vapours is equal to its (saturated) vapour pressure.

(5) (a) Saturated (Equillibrium) Vapour pressure of water, at a given temprature, is called aqueous tension. The value of aqueous tension is different at different temprature.

F15 (b) Relative Humidity (R.H.) = $\dfrac{\text{Partial pressure of water vapour at given temperatue}}{\text{Vapour pressure of water at the same temperatue}} \times 100\%$

(6) **Saturated vapour pressure and boiling point:**
A liquid boils when its saturated vapour pressure becomes equal to the external pressure on the liquid. When that happens, it enables bubbles of vapour to form throughout the liquid. If the external pressure is higher than the saturated vapour pressure, these bubbles are prevented from forming, and we just get evaporation at the surface of the liquid.
* $P_{ext} > P_{sat} \Rightarrow$ evaporation
* $P_{ext} = P_{sat} \Rightarrow$ Boiling

If the liquid is in an open container and exposed to normal atmospheric pressure, the liquid boils when its saturated vapour pressure becomes equal to 1 atmosphere. This happens with water when the temperature reaches 100°C. But at different pressures, water will boil at different temperatures. For example, at the top of Mount Everest the pressure is so low that water will boil at about 70°C.
(a) Boiling point : The boiling point is the temperature at which the vapour pressure of a liquid is equal to the external pressure.
(b) At boiling temperature, vapour pressure of the pure liquid i.e. $P^\circ = P_{ext}$
(c) At normal boiling point, vapour pressure of the pure liquid i.e. $P^\circ = 1$ atm

Resonance® Educating for better tomorrow	**Reg. & Corp. Office :** CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005	
	Website : www.resonance.ac.in	**E-mail :** contact@resonance.ac.in	
	Toll Free : 1800 258 5555	**CIN:** U80302RJ2007PLC024029	**ADVSCP - 7**

(7)   Saturated vapour pressure and solids: Sublimation

Solids can also loose particles from their surface to form a vapour, except that in this case we call the effect sublimation rather than evaporation. Sublimation is the direct change from solid to vapour without going through the liquid stage.

The forces of attraction in many solids are too high to allow much loss of particles from the surface. However, there are some solids which easily form vapours.

Naphthalene (used in "moth balls") has quite a strong smell. Molecules must be breaking away from the surface as a vapour, because otherwise we wouldn't be able to smell it.

Solid carbon dioxide never forms a liquid at atmospheric pressure and always converts directly from solid to vapour. That's why it is known as dry ice.

(8)   If partial pressure of vapours of a liquid is increased beyond the saturated (equillibrium) vapour pressure value (P^o), its vapours begin to condense till their partial pressure becomes equal to the saturated vapur pressure.

(9)   If the partial pressure of vapour is less than v.p. of liquid, the liquid (if present) will vaporize till
(a) its v.p. is attained or (b) the liquid completely gets vaporized

(10)   If a volatile solid/ liquid is brought in contact with a gas (or vaccuum), vapours of that solid/ liquid occupy the gas phase till the gas phase becomes saturated with that solid /liquid vapours.

Solved Examples

Example-6 : The vapor pressure of water at 80º C is 355 torr. A 100 ml vessel contained water–saturated oxygen at 80º C, the total gas pressure being 760 torr. The contents of the vessel were pumped into a 50.0 ml, vessel at the same temperature. What were the partial pressures of oxygen and of water vapor, what was the total pressure in the final equilibrated state ? Neglect the volume of any water which might condense.

Ans. P_{O_2} **= 810 mm Hg,** P_{H_2O} **= 355 mm Hg   , P_{total} = 1165 mm Hg**

Solution : In 100 ml vessel which contained water - saturated oxygen, the pressure of O_2 gas = 760 – 355 = 405 torr when the contents of this vessel were pumped into 50 ml vessel, at the same temperature, the pressure of oxygen gets doubled i.e. P_{O_2} = 810 torr.

But pressure of water vapour will remain constant, as some vapour in this 50 ml vessel, gets condensed.
So, P_{H_2O} = 355 torr & Total pressure = 810 + 355 = 1165 torr.

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

5. D22 Saturated solution : *A solution in which no more solute can be dissolved at the same temperature is called saturated solution.*

D23   Unsaturated solution : *It is a solution in which more amount of solute can be dissolved at the same temperature.*

D24   Supersaturated solution : *It is a solution which contains more mass of the dissolved solute than the saturated solution at the same temperature and pressure.* It should be prepared in a dust-free vessel and at a higher temperature. It is metastable. Mechanical stress, such as shaking or addition of solute, causes deposition of solute.

D25   Solubility : Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent (generally 100 g of solvent) at a specified temperature to form a saturated solution.
Solubility of one substance into another depends on
(i) nature of the solute and solvent.   (ii) Temprature   (iii) Pressure

5.1   Solubility of a solid in a liquid :
Like dissolves like: Polar solutes dissolve in polar solvents and non polar solutes in non-polar solvents.
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.

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

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

At equilibrium, rate of dissolution is equal to rate of crystallisation. At this stage the concentration of solute in solution will remain constant under the given conditions, i.e., temperature and pressure. Such a solution is said to be saturated with the given solute.

$$\text{Solute + Solvent} \rightleftharpoons \text{Solution}$$
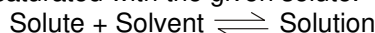
5.2 Effect of temperature on solubility of a solid in a liquid

Consider the equilibrium: Solute + Solvent $\rightleftharpoons$ Solution. By Le Chatelier's Principle:

If above process is exothermic i.e. $\Delta H < 0$, then as T increases, solubility decreases.

If above process is endothermic i.e. $\Delta H > 0$, then as T increases, solubility increases.

5.3 Effect of pressure on solubility of a solid in a liquid (no effect)

Pressure does not have any significant effect on solubility of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

6. Solubility of gases in liquids :

6.1 Factors Affecting Solubility of Gas In Liquid :

(i) Nature of gas　　　　(ii) Nature of liquid　　　(iii) Temperature　　　　(iv) Pressure

6.2 Henry's Law (effect of pressure on solubility of gases in liquids) :

Statement : The solubility of a gas in a liquid at a given temperature is directly proportional to its partial pressure at which it is dissolved.

Der.2 Let　　x = Mole fraction of unreacted gas in solution at a given temperature as a measure of its solubility.
p = Partial pressure of gas in equilibrium with the solution.
By Henry's law:　　　　$x \propto p$　　　　or　　　$p \propto x$
That is;　　**F16**　$p = K_H x$　　　or　　　$x = \dfrac{p}{K_H}$,　　where K_H = Henry's law constant.

6.3 Characteristics of Henry's Law constant (K_H).

(i) Unit same as those of pressure: torr or bar.

(ii) Different gases have different value of K_H for the same solvent.

(iii) The K_H value of a gas is different in different solvents and it increase with the increase in temperature.

(iv) Higher the value of K_H of a gas, lower will be its solubility. Since, $x = \dfrac{p}{K_H}$.

Plot of p Vs x is a straight line passing through the origin with slope equal to K_H.
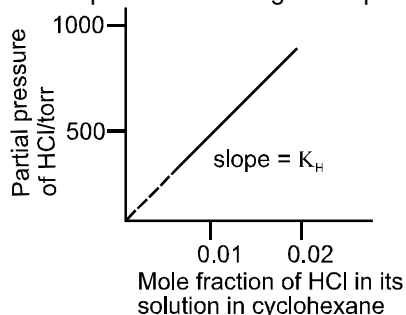
Plot of p Vs x for solution of HCl in cyclohexane.

Note : If a mixture of gases is brought in contact with solvent each constituent gas dissolves in proportion to its partial pressure. It means Henry's law applies to each gas independent of the pressure of other gas.

Resonance® Educating for better tomorrow	**Reg. & Corp. Office :** CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
	Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in
	Toll Free : 1800 258 5555 | **CIN :** U80302RJ2007PLC024029 ADVSCP - 9

Solved Examples

Example-7 : Henry's law constant for O_2 dissolved in water is 4.34×10^4 atm at 25°C. If the partial pressure of oxygen in air is 0.4 atm. Calculate the concentration (M) of dissolved oxygen in water in equilibrium with air at 25°C :

Solution : Given $K_H = 4.34 \times 10^4$ atm

$$p_{O_2} = 0.4 \text{ atm}$$

acc. to Henry's Law

$$p = K_H X$$

$$X_{O_2} = \frac{0.4}{4.34 \times 10^4} = 9.2 \times 10^{-6}$$

Moles of water $(n_{H_2O}) = \frac{1000}{18} = 55.8$ mol

$$X_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{H_2O}}$$

Since n_{O_2} is very small in comparison to n_{H_2O}

$$X_{O_2} = \frac{n_{O_2}}{n_{H_2O}}$$

or $\quad X_{O_2} \times n_{H_2O} = n_{O_2}$

So $\quad n_{O_2} = 9.2 \times 10^{-6} \times 55.55 = 5.11 \times 10^{-4}$ mol

So $\quad M = 5.11 \times 10^{-4}$

Example-8 : A gas 'X' is present with saturated water vapour over water liquid at total pressure of 1.5 atm. Vapour pressure of H_2O at same temperature is 0.5 atm. What is the solubility of gas 'X' in terms of moles in 10 moles $H_2O(\ell)$.

slope=38×10^5 torr

Partial pressure of 'X'

mol. frac. of x in H_2O
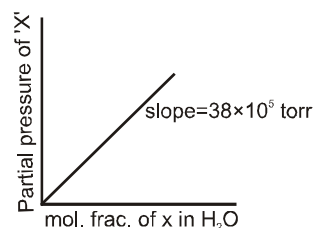
Solution : $P_T = P_x + P_{H2O}$

$P_x = 1.5 - 0.5 = 1$ atm

slope of graph = $K_H = 5 \times 10^3$

$$P_x = K_H \frac{n_x}{n_{H_2O}}$$

$$1 = 5 \times 10^3 \times \frac{n_x}{10}$$

$$n_x = \frac{1}{500} = 2 \times 10^{-3}$$

6.4 **Effect of temperature :** Solubility of gases in liquids decreases with rise in temperature.

Explanation: When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved in this process. We have learnt that dissolution process involves dynamic equilibrium and thus must follow Le Chatelier's principle. As dissolution of gases in liquids is an exothermic process, the solubility should decrease with increase of temperature.

Note : K_H values for both N_2 and O_2 increase with increase of temperature indicating that the solubility of gases increases with decrease of temperature. It is due to this reason that aquatic spcies are more comfortable in cold water rather than warm water.

6.5   Applications of Henry's law :
It has several applications in biological and industrial phenomena.
(i) To increase the solubility of CO_2 in soft drinks and soda water the bottle is sealed under high pressure.
(ii) Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmosphere gases in blood. When the divers come towards surface, the pressure is gradually decreased. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as **bends**, which are painful and dangerous to life. To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).
(iii) At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as **anoxia**.

6.6   Limitation of Henry's law :
Henry's law is valid only under following condition.
(i) The pressure of gas is not too high.   **(ii)** The temperature is not too low.
(iii) The gas should not undergo any chemical reaction with the solvent.
(iv) The gas should not undergo dissociation in solution.

Section (E) : Immiscible Liquids
7.   Vapour Pressure of liquid-liquid solution: volatile solute + volatile solvent
7.1   Completely Immiscible Liquids and Steam Distillation
For mixture of two completely immiscible liquids, each liquid exerts its own vapor pressure, independent of the other, and the total vapor pressure is the sum of the separate vapour pressures of the two components in the pure state at the given temperature.
Thus, $p_A = P_A^0$ & $p_B = P_B^0$

F17 $P_T = P_A^0 + P_B^0$; $\dfrac{P_A^0}{P_B^0} = \dfrac{n_A}{n_B}$

where n_A and n_B are the numbers of moles of each component present in the vapor phase, which on condensing form distillate.
The ratio of A to B in the vapor in terms of the actual weights w_A and w_B is

F18 $\dfrac{w_A}{w_B} = \dfrac{n_A M_A}{n_B M_B} = \dfrac{p_A^0 M_A}{p_B^0 M_B}$

(i) A system of two immiscible liquids will boil when the total vapor pressure P is equal to the atmospheric pressure or the given external pressure. The boiling point of the mixture is thus lower than that of either constituent.
(ii) Further, since the total vapor pressure is independent of the relative amounts of the two liquids, the boiling point, and hence the composition of the vapor and distillate, will remain constant as long as the two layers are present. e.g. Water and Benzene has boiling point = 68.9ºC.
But boiling point = H_2O (pure) C_6H_6 (pure)
                            100ºC   80.2ºC

Steam Distillation: The boiling point of a solution of two immiscible liquids is less than the individual boiling points of both the liquids. This concept is used in steam distillation.
A liquid (generally organic) that is immiscible with water, and that has a higher boiling point than water can be boiled (distilled) at a much lower temperature by passing steam through it. In this way, the organic liquid can be purified from impurities using steam distillation.

Section (F) : Completely miscible liquids : Raoult's law
7.2   Statement of Raoult's law (for volatile liq. mixture) : In solution of volatile liquids, the partial vapour pressure of each component is directly proportional to its mole fraction.
$p_A \propto x_A$

F19 $p_A = x_A P_A^0$

p_A = Partial vapour pressure of component A

x_A = Mole fraction of component 'A' in solution.

P_A^0 = Vapour pressure of pure component 'A' at given temperature

---

Der.3 **Derivation of total pressure over solution using Raoult's law and Dalton's law:**

Let A, B be to two volatite liquids in a closed container as shown.
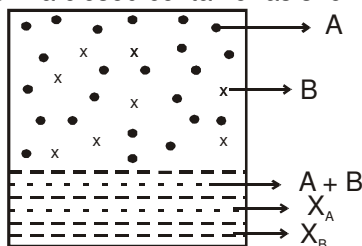
$p_A = x_A P_A^0$

Similarly, for liquid B we have,

$p_B = x_B P_B^0$

Total pressure over the solution P_T , according to Dalton's law is

F20 $P_T = p_A + p_B = x_A P_A^0 + x_B P_B^0$

Determining composition of vapour phase:

Let, y_A = mole fraction of A in vapour phase above the solution and

y_B = mole fraction of B in vapour phase above the solution

Now, we have, $p_A = y_A P_T$ .....Dalton's law of partial pressure for a gaseous mixture

$p_A = x_A P_A^0$ ⋯⋯⋯Raoult's law

Thus, $p_A = y_A P_T = x_A P_A^0$

Also, $p_B = y_B P_T = x_B P_B^0$

$x_A + x_B = 1 = \dfrac{y_A P_T}{P_A^0} + \dfrac{y_b P_T}{P_B^0}$

F21   Thus, $\dfrac{1}{P_T} = \dfrac{y_A}{P_A^0} + \dfrac{y_B}{P_B^0}$

Graphical Representation of Raoult's Law:

$p_A = x_A P_A^0$ & $p_B = x_B P_B^0$

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

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

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

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

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

7.3 Application of Raoult's Law:

(1) Phase Diagrams of Two-Component Ideal Solutions: Bubble and Dew Points

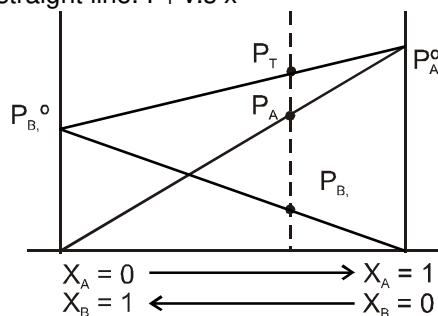The compositions of the liquid and vapour that are in mutual equilibrium are not necessarily the same. Common sense suggests that the vapour should be richer in the more volatile component. This can be easily derived from Raouls's Law.

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

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

From the above equation, the plot of P_T with respect to y is a curve instead of a straight line. We can superimpose this curve on the diagram for graphical representation of Raoult's Law to get following phase diagrams.

(A) Pressure versus Composition Phase Diagram (At constant T): P vs. x and y

In this kind of phase diagram the temperature has a fixed value. The mole fraction of one component is plotted on the horizontal axis and the pressure is plotted on the vertical axis. If A is more volatile than B, then we get following diagram.
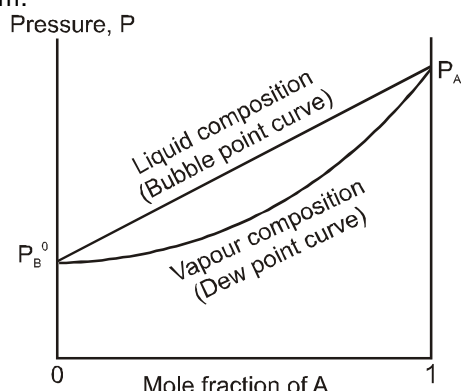
Explanation :

(i) On horizontal-axis we have plotted both x and y that is both liquid composition and vapour composition.

(ii) The lower curve (Dew Point Curve) represents the total pressure as a function of the composition i.e. mole fraction in the vapor phase at equilibrium with the liquid phase. It is plotted using P_T vs. y_A equation:

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

(iii) The upper curve i.e. Bubble Point Curve (a straight line in the case of an ideal solution) represents the total pressure as a function of composition i.e. mole fraction in the liquid. It is plotted using P_T vs. x_A equation: $P_T = (P_A^° - P_B^°) x_A + P_B^0$

(iv) The area between these two curves is vapour-liquid equilibrium region. Vapours cannot exist above the bubble point curve and liquid can not exist below the dew point curve.

(v) Suppose, initially the pressure over the solution is very high so that no vapour exist above the liquid. As we gradually decrease the pressure, a point (Bubble point) comes when we cross the Bubble-Point curve and first bubble of vapour starts forming. Hence, the name bubble point curve. Now we have entered the vapour-liquid equilibrium region. On further decreasing the pressure, a point (Dew Point) comes when we cross the Dew-Point curve when almost all the liquid has evaporated into vapour i.e. only the last drop of liquid (Dew) remains. Beyond this point no liquid exists in the system.

Solved Examples

Example-9 : Benzene and toluene form nearly ideal solutions. At 300 K, $P^0_{toluene}$ = 30 mm Hg and $P^0_{benzene}$ = 100 mm Hg.

A liquid mixture is composed of 3 mol of toluene and 2 mol of benzene.

(a) If the pressure over the mixture at 300 K is reduced. At what pressure does the first vapour form?

(b) What is the composition of the first trace of vapour formed ?

(c) If the pressure is reduced further, at what pressure does the last trace of liquid disappear?

(d) What is the composition of the last trace of liquid?

Ans. (a) 58 mm Hg (b) y_b = 20/29 (c) 250/6 mm Hg (d) x_b = 1/6

Solution : (a) $P = X_A P^0_A + X_B P^0_B = \dfrac{3}{5} \times 30 + \dfrac{2}{5} \times 100 = 58$ mm Hg

(b) Composition of the first trace of vapour formed

$$Y_{benzene} = \frac{X_b P^0_b}{P_{Total}} = \frac{2}{5} \times \frac{100}{58} = \frac{20}{29} \qquad \& \qquad Y_{toluene} = 1 - \frac{20}{29} = \frac{9}{29}$$

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

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

$$\frac{1}{p} = \frac{3}{5 \times 30} + \frac{2}{5 \times 100} \qquad \text{or} \qquad p = \frac{250}{6} \text{ mm Hg}$$

(d) The composition of the last trace of liquid

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

so $\quad X'_{toluene} = \dfrac{5}{6}$.

(B) Temperature versus Composition Phase Diagrams i.e. T vs x and y diagram

(i) In this type of phase diagram the pressure is held fixed. The mole fraction of one component is plotted on the horizontal axis and the boiling temperature is plotted on the vertical axis.
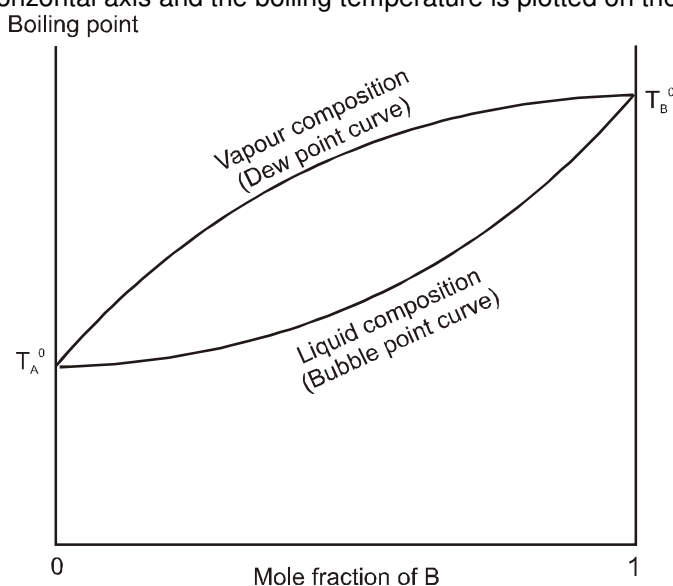
(ii) The upper curve (Dew-Point curve) gives the boiling temperature at the given pressure as a function of the mole fraction in the vapor phase, and the lower curve (Bubble-Point curve) gives the boiling tempera ture at the given pressure as a function of the mole fraction in the liquid phase.

Note: If a liquid has a high vapour pressure at a particular temperature, it means that its molecules can escape easily from the surface. The liquid with the higher vapour pressure at a particular temperature is the one with the lower boiling point. If A is more volatile than B, then we get following diagram.

(2)   Distillation:

(i) The compositions of the liquid and vapour that are in mutual equilibrium are not necessarily the same. Common sense suggests that the vapour should be richer in the more volatile component.

(ii) In a simple distillation, the vapour over a boiling mixture is withdrawn and condensed in a separate container. The liquid collected in the new container is called condensate or distillate and the liquid remaining in the original container is called residue. The condensate has higher mole fraction of the more volatile component than the original mixture. The residue has higher mole fraction of the less volatile component than the original mixture. This is the principle of distillation and is used to separate a more volatile liquid from a less volatile liquid.

(iii) In fractional distillation, the boiling and condensation cycle is repeated successively to get a distillate which gets richer in the more volatile component after each cycle.

Solved Examples

Example-10 :   An equimolar mixture of benzene & toluene is prepared. The total vapour pressure of this mixture as a function of mole fraction of benzene is found to be $P_T = 200 + 400\, X_{ben}$.

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

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

Solution :   (a) $P^0_{Beazene} = 600$ mm of Hg ; $P^0_{Toloune} = 200$ mm of Hg

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

$P_{benz} = x_{ben}\,'\,P^0_{ben} = y_{ben}P_T.$

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

(b)

condensate (Liq. formed after condensation of vapours)
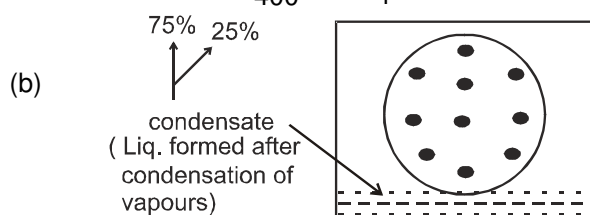
$$P_T = \frac{3}{4} \times 600 + \frac{1}{4} \times 200 = 500 \qquad \Rightarrow \qquad y_{ben} = \frac{3/4 \times 600}{500} = 0.9 = 90\%$$

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

7.4   Limitations of Raoult's Law: Raoult's Law only works for ideal solutions. Very dilute solutions obey Raoult's Law to a reasonable approximation.

(1)   Ideal Solutions : Those solutions which obey Raoult's law over the entire range of conc. are called ideal solutions. When the forces of attraction between A—A, B—B is similar to A—B, then A and B will form ideal solution.

In an ideal solution, the forces between the solvent molecules

.... are exactly the same as those between solvent and solvent and solute.
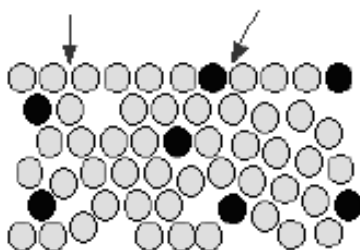
That means that it takes the same amount of energy for solvent molecules to break away from the surface in either case.

Properties of ideal solution :
(i) Raoult's law is obeyed
(ii) $\Delta H_{mix} = 0$, i.e., there should not be enthalpy change when components of ideal solutions are mixed.
(iii) $\Delta V_{mix} = 0$, (1L + 1L = 2L) i.e., there should not be change in volume on mixing. e.g.; n-hexane and n-heptane; ethyl bromide and ethyl iodide; benzene and toluene; chlorobenzene and bromobenzene form ideal solutions.

Section (G) : Non-ideal Solutions
(2)   Non–Ideal Solutions :
Those solutions which do not obey Raoult's over the entire range of concentration are called non-ideal solutions.
When the forces of attraction between A—A, B—B is different from A—B then 'A' and 'B' form non-ideal solutions. For these solutions :
(i) Raoult's law is not obeyed.   (ii) $\Delta H_{mix} \neq 0$;   (iii) $\Delta V_{mix} \neq 0$.

Types of Non-Ideal Solutions:
(A)   Non-Ideal Solutions Showing Positive Deviation From Raoult's Law :
(i) In this case, partial pressure of each component A and B is higher than that calculated from Raoult's law, and hence total pressure over the solution is also higher than if the solution were ideal, as shown in figure.
(ii) Boiling point of such a solution is relatively lower than the boiling points of both A and B.
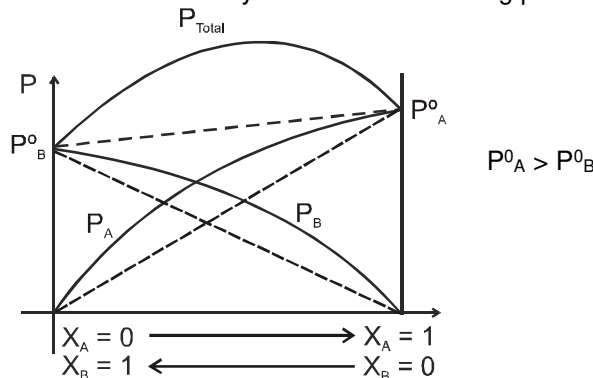
Note: Dashed lines represent vapour pressures and total pressure corresponding to ideal solution

**Examples:** water and ethanol, chloroform and water, ethanol and CCl_4, methanol and chloroform, benzene and methanol, acetic acid and toluene, acetone and ethanol, methanol and H_2O, C_2H_5OH + cyclohexane.
Explanation: The fact that the vapour pressure is higher than ideal in these mixtures means that molecules are breaking away more easily than they do in the pure liquids. That is because the intermolecular forces between molecules of A and B are less than they are in the pure liquids.
You can see this when you mix the liquids. Less heat is evolved when the new attractions are set up than was absorbed to break the original ones. Heat will therefore be absorbed when the liquids mix. The enthalpy change of mixing is endothermic.

Resonance® Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in
Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029
ADVSCP - 16

(B) **Non-Ideal Solutions Showing Negative Deviation From Raoult's Law :**

(i) In this case, partial pressure of each component A and B is lower than that calculated from Raoult's law, and hence total pressure over the solution is also lower than if the solution were ideal, as shown in figure.

(ii) Boiling point of such a solution is relatively higher than the boiling points of both A and B.
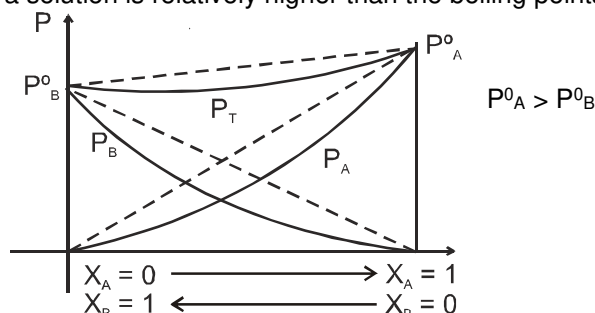
$P^0_A > P^0_B$

Note: Dashed lines represent vapour pressures and total pressure corresponding to ideal solution.

Examples: chloroform and acetone, chloroform and methyl acetate, H_2O and HCl, H_2O and HNO_3, acetic acid and pyridine, Phenol & Aniline.

Explanation: These are cases where the molecules break away from the mixture less easily than they do from the pure liquids. New stronger forces must exist in the mixture than in the original liquids.

You can recognise this happening because heat is evolved when you mix the liquids-more heat is given out when the new stronger bonds are made than was used in breaking the original weaker ones.

Positive deviation solution

(i) $P_T > \left(X_A P^0_A + X_B P^0_B \right)$

(ii) The inter molecular interaction is weaker as interaction found in any one of the pure components.

$$\begin{array}{c} A\ldots\ldots\ldots A \\ B\ldots\ldots\ldots B \end{array} \text{ molecular interaction is Stronger than } A\ldots\ldots\ldots B$$

(iii) There is increase in volume on mixing and absorption of heat.

ΔV_{mix} = positive ΔH_{mix} = positive

ΔS_{mix} = +ive ΔG_{mix} = −ive

Ex. $H_2O + CH_3OH$, C_2H_5OH + Hexane

C_2H_5OH + Cyclohexane, $CHCl_3 + CCl_4$

Negative deviation solution

(i) $P_T < X_A P^0_A + X_B P^0_B$

(ii) The inter molecular interaction is more than the interaction found in any of the pure components

$$A\ldots\ldots\ldots B \text{ molecular interaction is more than } \begin{array}{c} A\ldots\ldots\ldots A \\ B\ldots\ldots\ldots B \end{array}$$

(iii) There is decrease in volume on mixing and evolution of heat takes place on mixing

ΔV_{mix} = −ve ΔH_{mix} = −ive

ΔS_{mix} = +ive ΔG_{mix} = −ive

Ex. $H_2O + HCOOH$, $H_2O + CH_3COOH$

$H_2O + HNO_3$, $CHCl_3 + CH_3OCH_3$

7.5 **Azeotropic Mixtures :** Very large deviations from ideality lead to a special class of mixtures known as azeotropes, azeotropic mixtures, or constant-boiling mixtures.

D26 **Azeotropes :** Liquid mixtures which distill over without changes in composition are called constant boiling mixtures or Azeotropes or Azeotropic mixtures.

A boiling liquid mixture at the azeotropic composition produces a vapour of exactly the same composition, and the liquid does not change its composition as it evaporates. Two types of azeotropes are known.

(1) D27 Minimum Boiling Azeotropes : *Non-ideal solutions showing large positive deviation from Raoult's law form minimum boiling azeotropes which boil at temperature lower than boiling point of its components 'A' and 'B',* e.g., water and benzene, chloroform and methanol.

The figures below show the Temprature vs. composition (at constant pressure) phase diagram on the left side and Pressure vs. composition (at constant temprature) phase diagram for a minimum-boiling azeotropic mixture chloroform and methanol.

Note: The detailed values in the diagram are not important. Only the qualitative shape of the diagram is important.

Temperature-Minimum Azeotrope Mixture of Chloroform and Methanol — Minimum-Boiling Azeotrope — Pressure-Maximum Azeotrope Mixture of Chloroform and Methanol
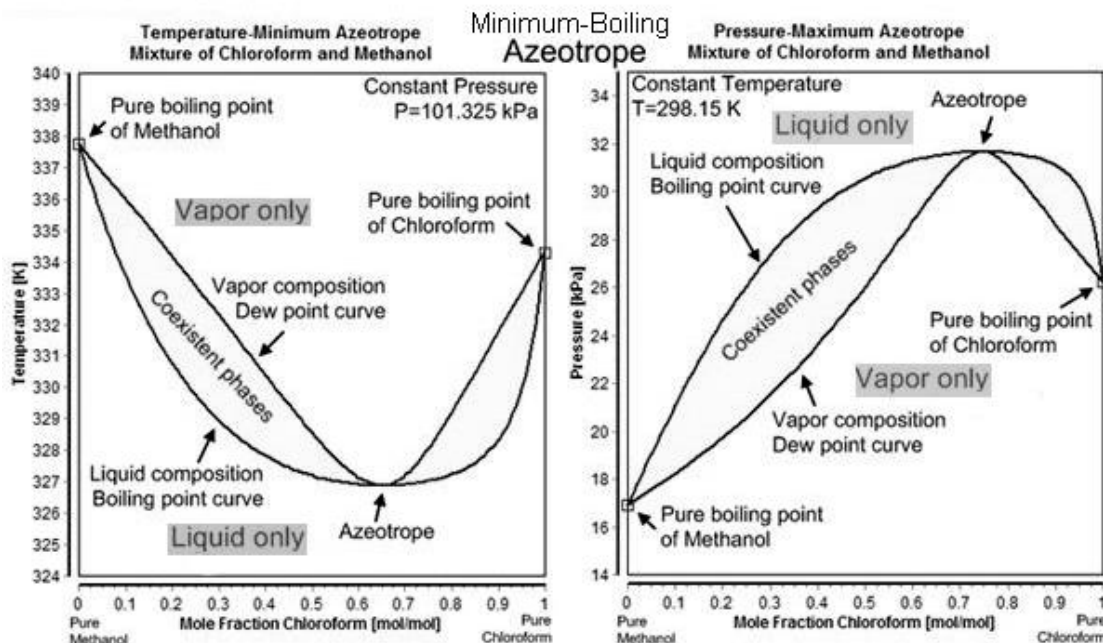
At the lowest point in the temperature vs. composition phase diagram, the concentration in the vapour phase is the same as the concentration in the liquid phase (y = x). This concentration is known as the azeotropic composition. At this point, the mixture boils at a constant temperature and without change in composition.

(2) D28 Maximum Boiling Azeotropes : *Non-ideal solutions showing large negative deviation from Raoult's law form maximum boiling azeotropes which boil at temperature higher than the boiling point of its components A and B respectively,* e.g., a mixture of HCl and H_2O containing 20.2% HCl by weight boils at 108.5ºC higher than either pure HCl (– 85°C) or water (100°C).

The figures below show the Temprature vs. composition (at constant pressure) phase diagram on the left side and Pressure vs. composition (at constant temprature) phase diagram for a maximum-boiling azeotropic mixture water and formic acid.

Note: The detailed values in the diagram are not important. Only the qualitative shape of the diagram is important.

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in
Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029

ADVSCP - 18

Negative Azeotrope

Temperature-Maximum Azeotrope Mixture of Water and Formic Acid

Pressure-Minimum Azeotrope Mixture of Water and Formic Acid

(3)   Separation of Azeotropic Mixtures
When the azeotropic composition has been reached, the condensate has the same composition as the azeotropic liquid. The vapour phase is not richer in any component than the liquid phase. Thus, azeotropic mixtures can't be separated beyond the azeotropic composition using distillation.

Section (H) : Degree of Ionisation/Dissociation for Weak Electrolytes
8. Colligative properties & constitutional properties :

D29   ● Constitutional Properties :
Properties which are dependent on nature of particles are constitutional properties like electrical conductance.

D30   ● Colligative properties :
The properties of the solution which are dependent only on the total no. of particles relative to solvent/solution or total concentration of pa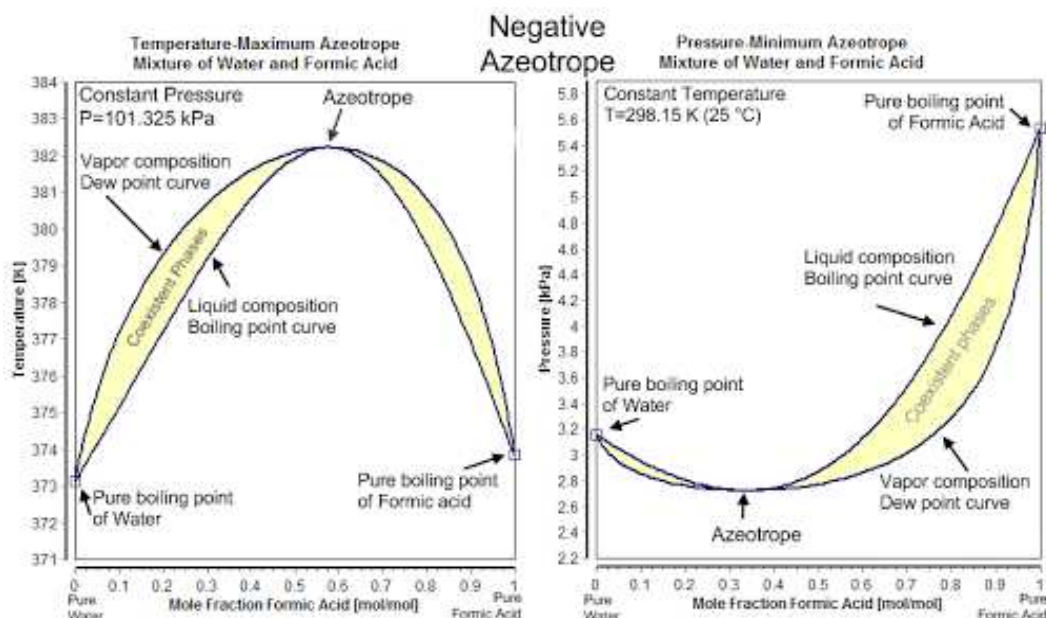rticles in the solution and are not dependent on the nature of particle i.e. shape, size, neutral /charge etc. of the particles.

There are 4 colligative properties of solution.

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

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

8.1   Abnormal Colligative Properties :
Vant–Hoff correction :
● For electrolytic solutes the number of particles would be different from the number of particles actually added, due to dissociation or association of solute.

● The actual extent of dissociation/association can be expressed with a correction factor known as vant Haff factor (i).

F22   Vant–Hoff factor : $i = \dfrac{\text{moles of particles in solution after dissociat ion/ association}}{\text{moles of solute dissolved}}$

D31   ● If solute gets associated or dissociated in solution then experimental / observed / actual value of colligative property will be different from theoretically predicted value so it is also known as **abnormal colligative property.**

● This abnormality can be calculated in terms of Vant-Hoff factor.
$i = \dfrac{\text{exp/observ ed/ actual/ abnormal v alue of colligative property}}{\text{Theoretical v alue of colligative property}}$

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in
Toll Free : 1800 258 5555 | **CIN:** U80302RJ2007PLC024029

ADVSCP - 19

Resonance®
Educating for better tomorrow

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

$i > 1$ dissociation
$i < 1$ association

Der.4 **Case - I : Electrolyte dissociates**

Relation between i & α (degree of dissociation) :

Let the electrolyte be A_xB_y

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

t = 0	C	0	0
t_{eq}	$C(1 - \alpha)$	$xC\alpha$	$yC\alpha$
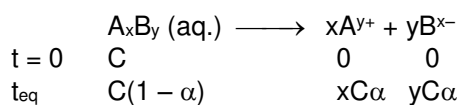
Net concentration $= C - C\alpha + xC\alpha + yC\alpha = C [1 + (x+y-1)\alpha] = C[1 + (n-1)\alpha]$.

$n = x + y$
= no. of particles in which 1 molecule of electrolyte dissociates

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

F23 $\qquad i = 1 + (n - 1)\alpha$

e.g. NaCl (100% ionised), i = 2. ; BaCl$_2$ (100% ionised), i = 3. ; K$_4$[Fe(CN)$_6$] (75% ionised), i = 4.

Der.4 **Case - II : Electrolyte associates**

Relation between degree of association β & i.

$nA \longrightarrow A_n$.

t = 0	C	0
t_{eq}	$C(1-\beta)$	$\dfrac{C\beta}{n}$
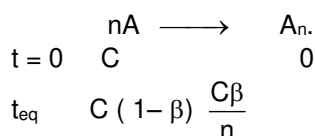
Net concentration $= C - C\beta + \dfrac{C\beta}{n}$

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

F24 $\qquad i = 1 + \left(\dfrac{1}{n} - 1\right)\beta$

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

e.g. CH$_3$COOH 100% dimerise in benzene, $i = \dfrac{1}{2}$; C$_6$H$_5$COOH 100% dimerise in benzene, $i = \dfrac{1}{2}$

Section (I) : Relative lowering of vapour pressure
8.2 Relative lowering in vapour pressure (RLVP) :
Vapour Pressure of a solution of non-volatile solute in a volatile solvent

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

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

Pure solvent

solution of non-volatile solute in volatile solvent
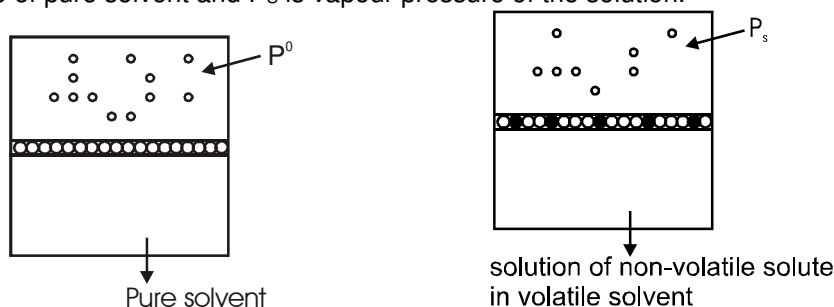
Lowering in VP = $P^0 - P_S = \Delta P$

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

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

Der.6 $P_S = x_{solvent}P^0 = (1 - x_{solute})P^0$

F25 $\quad RLVP = \dfrac{P^0 - P_s}{P^0} = x_{Solute} = \dfrac{n}{n+N}$

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

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

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

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

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

F26 $\quad \dfrac{P^0 - P_s}{P_s}$ **= (molality) ×** $\dfrac{M}{1000}$

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

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

Solved Examples

Example-11 : Calculate weight of urea which must be dissolved in 400 g of water so final solutions has vapour pressure 2% less than vapour pressure of pure water :

Solution : Let vapour pressure be P^0 of water

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

$\qquad P_s = 0.98\ V$

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

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

Example-12 : 10 g of a solute is dissolved in 80 g of acetone. Vapour pressure of this sol = 271 mm of Hg. If vapour pressure of pure acetone is 283 mm of H

$\qquad \dfrac{P^0 - P_s}{P_s} = \dfrac{w}{m} \times \dfrac{M}{W} \qquad \Rightarrow \qquad \dfrac{283 - 271}{271} = \dfrac{10}{m} \times \dfrac{58}{80}$

$\qquad m = 163$ g/mol.

Example-13 : Vapour pressure of solute containing 6 g of non volatile solute in 180 g of water is 20 Torr. If 1 mole of water is further added into it, vapour pressure increases by 0.02 torr. Calculate vapour pressure of pure water and molecular weight of non-volatile solute.

Resonance®
Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in
Toll Free : 1800 258 5555 | **CIN:** U80302RJ2007PLC024029

ADVSCP - 21

Solution :

$$\frac{P^0 - P_s}{P_s} = \frac{w}{m} \times \frac{M}{W} \qquad \Rightarrow \qquad \frac{P^0 - 20}{20} = \frac{6}{m} \times \frac{18}{180}$$

$$\frac{P^0 - 20.02}{20.02} = \frac{6}{m} \times \frac{18}{198} \qquad \Rightarrow \qquad P^0 = 20.22 \text{ Torr.}$$

m = 54 g/mol.

Example-14 :

0.1 mole NaCl   Rigid   0.1 mole urea
100 ml H_2O wall   100 ml H_2O
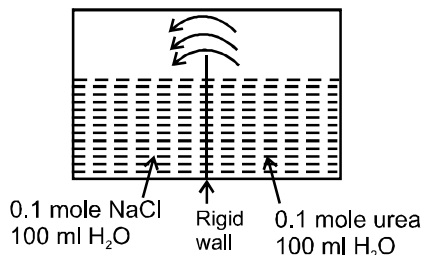
What is the final volume of both container.

Solution : $i_1 C_1 = i_2 C_2$

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

200 − 2x = 100 + x.

x = 33.3 ml.

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

Example-15 : If 0.1 M solutions of $K_4[Fe(CN)_6]$ is prepared at 300 K then its density = 1.2 g/mL. If solute is 50% dissociated calculate ΔP of solution if P of pure water = 25 mm of Hg. (K = 39, Fe = 56)

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

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

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

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

$P_s = 24.82$ mm of Hg

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

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

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

D32   **Boiling point:** The temperature at which vapour pressure of a liquid becomes equal to the external pressure present at the surface of the liquid is called b.p of liquid at that pressure.

D33   **Normal Boiling Point:** The boiling temperature when $P_{ext} = 1$ atm = 760 mm of Hg is called normal boiling point of the liquid (T_b).

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005

Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in

Toll Free : 1800 258 5555 | **CIN:** U80302RJ2007PLC024029

ADVSCP - 22
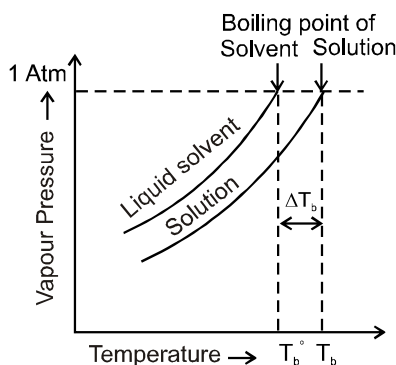
The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that ΔT_B denotes the elevation of boiling point of a solution in comparison to solvent.

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

Der.7	$\Delta T_b = T_b - T_b^{\circ}$ $\Delta T_b \propto m$ m = Molality
F27	$\Delta T_b = K_b m$

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

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

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

D34 *It is equal to elevation in boiling point of 1 molal solution.* It is also called molal elevation constant. The units of K_b, is K/m or °C/m or K kg mol^{-1}.

F28 $K_b = \dfrac{RT_b^2 \ M}{1000 \times \Delta H_{vap}} = \dfrac{RT_b^2}{1000 \times L_{vap}}$

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

F29 $L_{vap} = \left(\dfrac{\Delta H_{vap}}{M} \right)$

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

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

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

Extra Information (Not for Boards)
As only solvent particles are going into vapours,
We have: $\Delta H_{\text{vapourisation of solvent}} = \Delta H_{\text{vapourisation of solution}}$
S means "entropy".
Vapour is always pure solvent
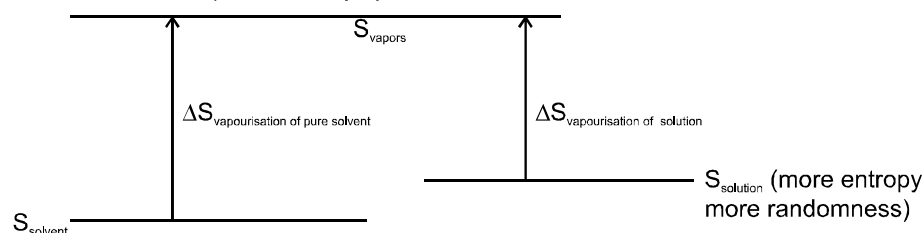
$\Delta S_{\text{vapourisation}} = \dfrac{\Delta H_{\text{vapourisation}}}{T_{b,\text{solvent}}}$

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

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

Resonance® Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in
Toll Free : 1800 258 5555 | **CIN:** U80302RJ2007PLC024029

ADVSCP - 23

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

Due to presence of solute, it is difficult to vapourise the solution, i.e it is difficult to boil the solution. So, there is elevation in boiling point with respect to pure solvent.
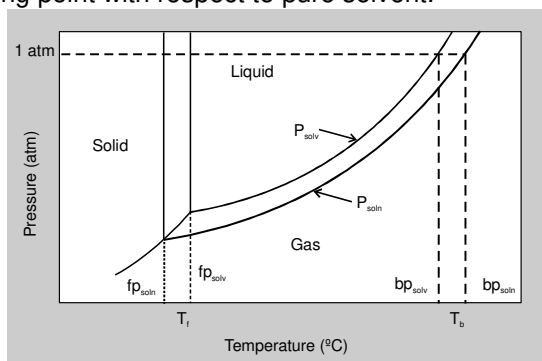
Phase diagram for a pure solvent and a solution of a nonvolatile solute. Because the vapour pressure of the solution is lower than that of the pure solvent at a given temperature, the temperature at which the vapour pressure reaches atmospheric pressure is higher for the solution than for the solvent. Thus, the boiling point of the solution is higher by an amount ΔT_b.

Solved Examples

Example-16 : A solution of 122 g of benzoic acid in 1000 g of benzene shows a boiling point elevation of 1.4º. Assuming that solute is dimerized to the extent of 80 percent, calculate normal boiling point of benzene. Given molar enthalpy of vapourization of benzene = 7.8 Kcal/mole.

Solution :

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

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

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

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

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

$$T_b = 418.33 \ K$$
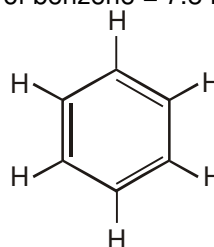
Example-17 : 1 Lit. of aq. solution of urea having density = 1.060 g/mL is found to have $\Delta T_b = 0.5ºC$. If temperature of this solution increase to 101.5ºC, then calculate amount of water which must have gone in vapour state upto this pt. given $K_b = 0.5$ K kg mol^{-1} for water

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

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

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

mass of water = 1060 – 60 = 1000 g

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

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

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

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

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

D35 **Freezing point :** Temperature at which vapour pressure of solid becomes equal to vapour pressure of liquid is called freezing point of liquid or melting point of solid.

→ vacuum

→ ΔH_{sub} = + ve

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

↓ ice cube

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

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

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

= vapour pressure of solid
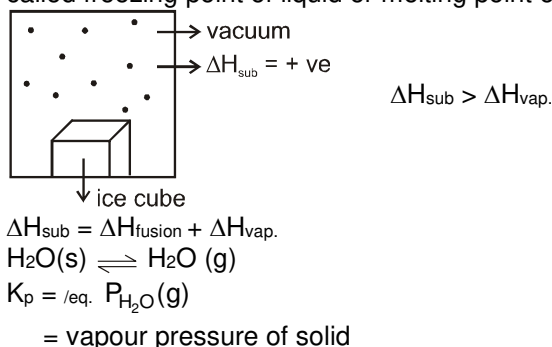
Reason for Depression In Freezing Point :

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

D36 **Depression In Freezing Point :**
The difference between freezing point of pure solvent T_f^0 and freezing point of solution T is called depression in freezing point (ΔT_f) as shown in figure.
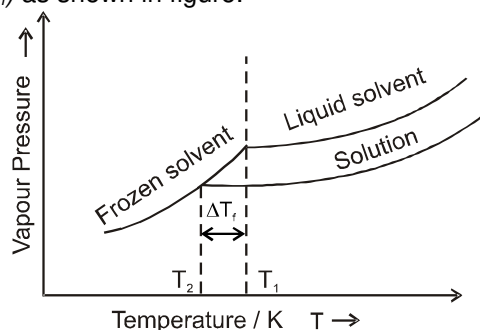
Diagram showing ΔT_f depression of the freezing point of a solvent in a solution.

Der.8	$\Delta T_f = T_f^0 - T_f$
	$\Delta T_f \propto m$
	m = Molality
F30	$\Delta T_f = K_f m$

F31 Cryoscopic constant K_f = molal depression constant = $\dfrac{RT_f^2}{1000 \times L_{fusion}} = \dfrac{RT_f^2 \ M}{1000 \times \Delta H_{fusion}}$

where, ΔH_{fusion} is molar enthalpy of fusion (cal/mol ; J/mol)

L_{fusion} is Latent Heat of fusion in cal/g or J/g

M is molar mass of the solvent in gram

T_f = freezing point of solvent

F32 $L_{fusion} = \left(\dfrac{\Delta H_{fusion}}{M} \right)$

D37 **K_f, Freezing point Depression Constant (Molal Depression Constant) :**
It is equal to depression in freezing point of 1 molal solution. It is also called cryoscopic constant. The units of K_f is K/m or °C/m or K kg mol^{-1}.

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

Note: (i) Depression in freezing point is proportional to the lowering of vapoure pressure i.e. $\Delta T_f \propto \Delta P$

(ii) If solute gets associated/dissociated then $\Delta T_f = i \times K_f \times$ molality

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

(iv) At freezing point or below it, only solvent molecules will freeze not solute molecules (solid will be of pure solvent)

(v) $K_f = $ depression in freezing point of 1 molal solution.

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

ΔH_{Fusion} for solvent and solution is same.

But for entropy, we can see following diagram.
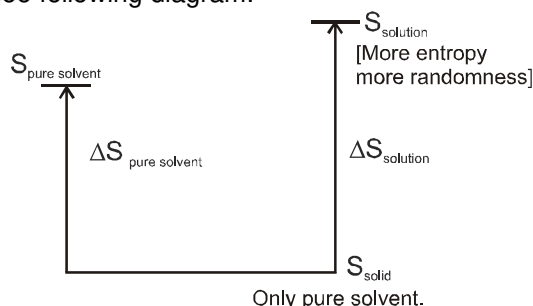
$\therefore \Delta S_{Solution} > \Delta S_{solvent}$ So, freezing point of solution < freezing point of solvent

Solved Examples

Example-18 : Van't Hoff factors of aqueous solutions of X, Y, Z are 1.8, 0.8 and 2.5. Hence, their (assume equal concentrations in all three cases)

        (A) b.p. : X < Y < Z   (B) f. p. Z < X < Y

        (C) osmotic pressure : X = Y = Z   (D) v. p. : Y < X < Z

Solution : As van't Hoff factor increases RLVP increases   i.e.,   V.P. decreases y > x > z

Elevation in b.p. increases i.e., b.p. increases   y < x < z

Depresion in f.p increases i.e., f.p decreases   y > x > z

Osmotic pressure increases   so   y < x < z. **Ans. (B)**

Example-19 : 1000 g H_2O have 0.1 mole urea and its freezing point is $-0.2{^\circ}C$ and now it is freezed upto $-2{^\circ}C$ then how much amount of ice will form.
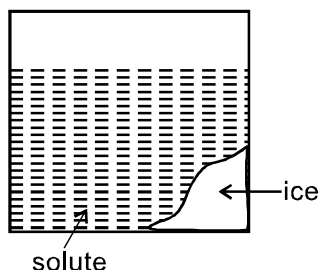
Solution : It is assumed that solute do not freeze and do not vapourise

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

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

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

Example-20 : If boiling point of an aqueous solution is 100.1ºC. What is its freezing point? Given latent heat of fusion and vaporization of water are 80 cal g^{-1} and 540 cal g^{-1} respectively.

Solution : For a given aqueous solution

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

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

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

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

$T_b = 100 + 273 = 373$ K.

$T_f = 0 + 273 = 273$ K.

$l_f = 80$ cal g^{-1}.

$l_v = 540$ cal g^{-1}.

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

$\therefore \qquad \Delta T_f = 0.362$.

$\therefore \qquad T_f = 0.0 - 0.362 = \textbf{– 0.362ºC.}$

Example-21 : A 0.001 molal solution of a complex reprsented as Pt(NH$_3$)$_4$Cl$_4$ in water had a freezing point depression of 0.0054ºC. Given K$_f$ for H$_2$O = 1.86 molality^{-1}. Assuming 100% ionisation of the complex, write the ionisation nature and formula of complex.

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

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

| 1 | 0 | 0 |
| 0 | 1 | (4 – n) |
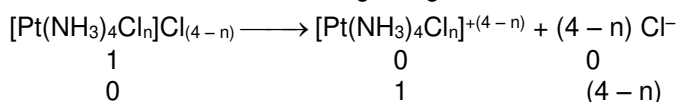
Thus particles after dissocation = 4 – n + 1 = 5 – n

and therefore, van't Hoff factor (i) = 5 – n

Now $\Delta T_f = K'_f \times$ molality $\times$ van't Hoff factor

$0.0054 = 1.86 \times 0.001 \times (5 - n)$

$\therefore$ n = 2.1 $\approx$ 2 (integer value)

Thus complex and its ionisation is :

$$[Pt(NH_3)_4Cl_2]Cl_2 \longrightarrow [Pt(NH_3)_4Cl_2]^{2+} + 2Cl^-$$
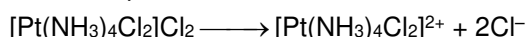
Example-22 : Depression of freezing point of 0.01 molal aq. CH$_3$COOH solution is 0.02046°. 1 molal urea solution freezes at – 1.86°C. Assuming molality equal to molarity, pH of CH$_3$COOH solution is :

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

Solution : For urea

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

Now for CH$_3$COOH

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

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

Now $i = 1 + \alpha$

so $\alpha = 1.1 - 1 = 0.1$

Now CH$_3$COOH $\rightleftharpoons$ CH$_3$COO$^-$ + H$^+$

| C | 0 | 0 |
| C – Cα | Cα | Cα |
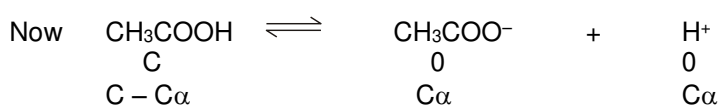
$[H^+] = C\alpha = 0.01 \times 0.1 = 0.001$

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

Section (K) : Osmotic Pressure

8.6   **Osmosis & Osmotic pressure :**

D38   **Diffusion :** Spontaneous flow of particles from high concentration region to lower concentration region is known as diffusion.

Ex.

Figure

D39   **Osmosis :**

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

D40   **Semipermeable Membrane (SPM):** A membrane which allows only solvent particles to move across it.

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

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

Ex.

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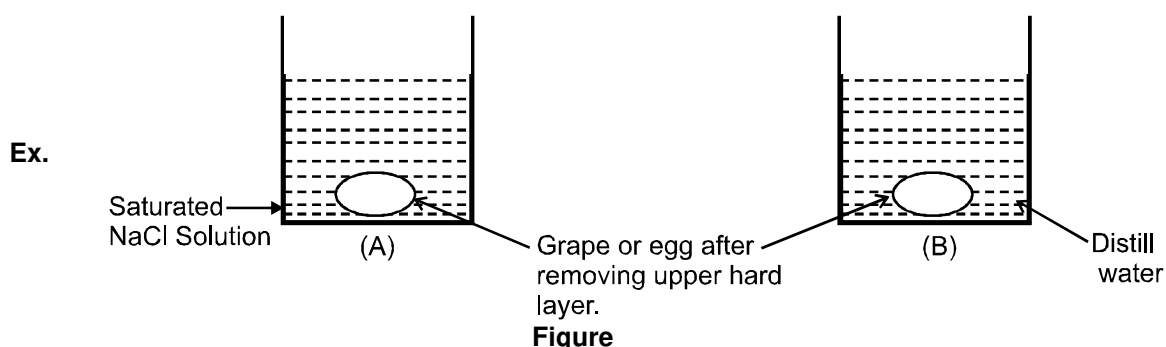
Conclusion : After some time in (A) grape or egg will shrink and in (B) grape or egg will swell.

e.g.   (i) A raw mango placed in concentrated salt solution loses water & shrivel into pickle.
(ii) People taking lot of salt, experience water retention in tissue cells. This results in puffiness or swelling called edema.

Solved Examples

Example-23 :   In which soluton side complex $[Cu(NH_3)_4]^{2+}$ will form and deep blue colour will obtain.

0.1 M $CuSO_4$ (aq)   S.P.M.   0.01 M NH_3(aq)
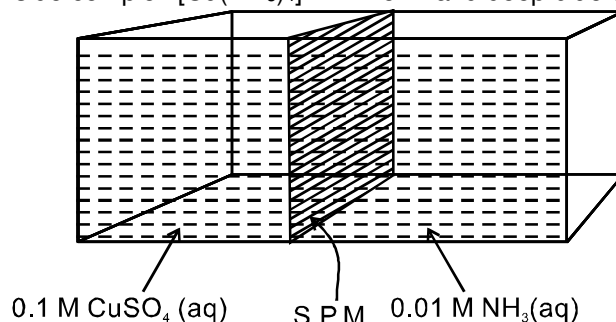
Solution :   In neither of side colour complex will form. No solute particle passes through SPM.

Osmotic Pressure :
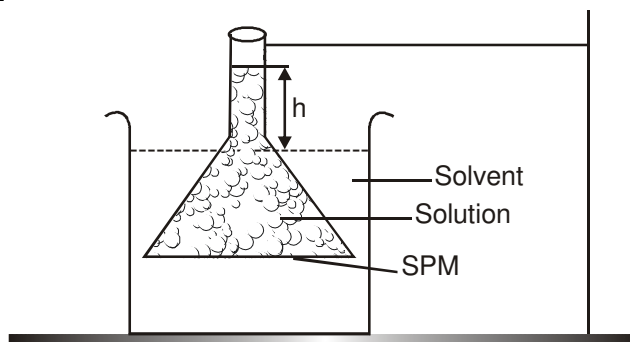
Figure

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

$\pi = \rho gh$; ρ = density of solution
g = acceleration due to gravity ; h = eq. height
1 atm = 1.013×10^5 N/m^2
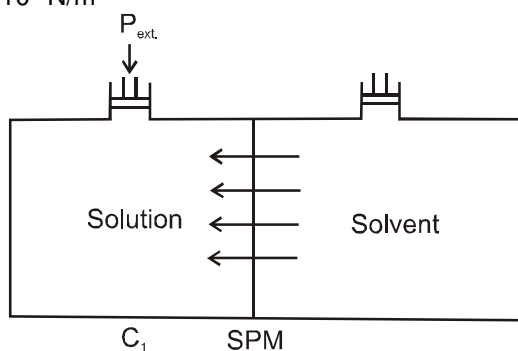
Figure

D41 **Osmotic Pressure :** The external pressure which must be applied on solution side to stop the process of osmosis is called osmotic pressure of the solution.

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

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

D42 **Reverse Osmosis :**

If the pressure applied on the solution side is more than osmotic pressure of the solution then the solvent particles will move from solution to solvent side. This process is known as reverse osmosis.

Berkely : Hartely device/method uses the above pressure to measure osmotic pressure.

e.g. used in desalination of sea-water.

Vant – Hoff Formula (For calculation of osmotic pressure)

● $\pi \propto$ concentration (molarity)
$\propto T$
$\pi = CST$
S = ideal solution constant π = atm. $\left\{ \begin{array}{l} C - mol/lit. \\ R - 0.082 \ lit.atm. \ mol^{-1} K^{-1} \\ T - kelvin \end{array} \right.$
= 8.314 J mol^{-1} K^{-1} (exp value)
= R (ideal gas) constant

F33 $\pi = CRT = \dfrac{n}{V} RT$ (just like ideal gas equation)

● In ideal solution solute particles can be assumed to be moving randomly without any interactions.
C = total concentration of all types of particles.

$= C_1 + C_2 + C_3 + s................. = \dfrac{(n_1 + n_2 + n_3 + ...)}{V}$

Solved Examples

Example-24 : If V_1 mL of C_1 solution + V_2 mL of C_2 solution are mixed together then calculate final concentration of solution and final osmotic pressure. If initial osmotic pressure of two solutions are π_1 and π_2 respectively ?

Solution : $C_f = \dfrac{C_1 V_1 + C_2 V_2}{V_1 + V_2}$

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

$\pi = \left(\dfrac{C_1 V_1 + C_2 V_2}{V_1 + V_2}\right) RT$

$\pi = \left(\dfrac{\pi_1 V_1 + \pi_2 V_2}{V_1 + V_2}\right)$

Type of solutions :

D43 **(a) Isotonic solution :** Two solutions having same osmotic pressure are consider as isotonic solution.

$\pi_1 = \pi_2$ (at same temperature)

D44 **(b) Hypotonic & Hypertonic solutions :** If two solutions 1 and 2 are such that $\pi_2 > \pi_1$, then 2 is called hypertonic solution and 1 is called hypotonic solution.
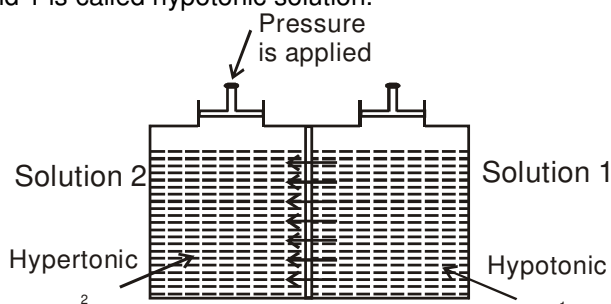
Figure

Conclusion :

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

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

D45 **Plasmolysis :** *When the cell is placed in solution having osmotic pressure greater than that of the cell sap, water passes out of the cell due to osmosis. Consequently, cell material shrinks gradually. The gradual shrinking of the cell material is called plasmolysis.*

Solved Examples

Example-25 : Calculate osmotic pressure of 0.1 M urea aqueous solution at 300 K ,

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

$\pi = CRT$

$\pi = 0.1 \times 0.082 \times 300$

$\pi = 2.46$ atm.

Example-26 : If 10 g of an unknown substance (non-electrolytic) is dissolved to make 500 mL of solution,then osmotic pressure at 300 K is observed to be 1.23 atm find molecular weight?

Resonance®
Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005

Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in

Toll Free : 1800 258 5555 | **CIN:** U80302RJ2007PLC024029

ADVSCP - 30

Solution : $1.23 = \dfrac{10 \times 1000}{M \times 500}$ x 0.082 x 300

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

Example-27 : If 6 g of urea, 18 g glucose & 34.2 g sucrose is dissolved to make 500 mL of a solution at 300 K calculate osmotic pressure ?

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

π = C x 0.082 x 300

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

Example-28 : If 200 mL of 0.1 M urea solution is mixed with 300 mL of 0.2 M glucose solution at 300 K. Calculate osmotic pressure?

Solution : 0.02 moles urea

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

Example-29 : If urea (aq) solution at 500K has O.P. = 2.05 atm. & glucose solution at 300 K has OP = 1.23 atm. If 200 ml of Ist solution & 400 ml of 2nd solution are mixed at 400 K then calculate O.P. of resulting solution at 400 K (assume molarity is not dependent on temp.)

Solution : $C_{urea} = \dfrac{2.05}{R \times 500} = 0.05 \Rightarrow \qquad V_{urea}$ = 200 mL

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

$C_{total} = \dfrac{C_1 V_1 + C_2 V_2}{V_1 + V_2} = \dfrac{0.05 \times 200 + 0.05 \times 400}{600} = 0.05$

π = CRT = 0.05 × 0.082 × 400

π = 1.64 atm

Example-30 $\dfrac{0.1\,M\,urea}{(A)}$, $\dfrac{0.1\,M\,NaCl}{(B)}$, $\dfrac{0.1\,M\,BaCl_2}{(C)}$

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

(Calculating osmotic pressure when reaction is not taking place)

Example-31 : Calculate osmotic pressure of a solutions having 0.1 M NaCl & 0.2 M Na$_2$SO$_4$ and 0.5 MHA. (Given : Weak acid is 20% dissociated at 300 K).

Soluiton : $\pi = \pi_{NaCl} + \pi_{Na2SO4} + \pi_{HA}$

= 0.1 RT × 2 + 0.2 RT × 3 + 0.5 RT × 1.2

= 0.0821 × 300 (0.2 + 0.6 + 0.6) = 34.482 atm.

Example-32 : If 0.04 M Na$_2$SO$_4$ solutions at 300 K is found to be isotonic with 0.05 M NaCl (100 % disscociation) solutions. Calculate degree of disscociation of sodium sulphate ?

Soluiton : $i_1 C_1 RT = i_2 C_2 RT$

$i_1 C_1 = i_2 C_2$

0.04 (1 + 2α) = 0.05 × 2

α = 0.75 = 75%.

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005	
Website : www.resonance.ac.in	E-mail : contact@resonance.ac.in	
Toll Free : 1800 258 5555	CIN: U80302RJ2007PLC024029	ADVSCP - 31

Resonance® Educating for better tomorrow

Example-33 : If 6 g of CH_3COOH is dissolved in benzene to make 1 litre at 300 K. Osmotic pressure of solution is found to be 1.64 atm. If it is known that CH_3COOH in benzene forms a dimer. Calculate degree of association of acetic acid in benzene ?

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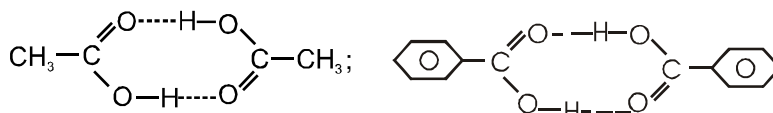
$$i = 1 + \left(\frac{1}{n} - 1\right)\beta.$$

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

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

$$\frac{1.64}{0.0821 \times 30} = \frac{2-\beta}{2}$$

$$\frac{1.64}{2.46} = \frac{2-\beta}{2} \qquad\qquad 4 = 6 - 3\beta$$

$3\beta = 2$

$\beta = 2/3$

(Calculating osmotic pressure when reaction is taking place)

Example-35 : If 200 ml of 0.2 M $BaCl_2$ solution is mixed with 500 ml of 0.1 M Na_2SO_4 solution. Calculate osmotic pressure of resulting solutions ?

Solution :

$$BaCl_2 \;+\; Na_2SO_4 \rightarrow BaSO_4 + 2\,NaCl$$

0.04 moles	0.05	0	0
0	0.01	No effect	0.08
	$\dfrac{0.01}{0.7}$	No effect	$\dfrac{0.08}{0.7}$
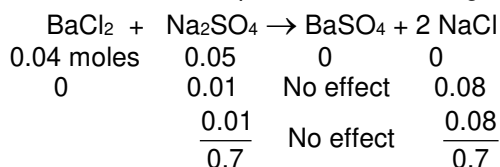
$$\pi = (i_1C_1 + i_2C_2)\,RT.$$

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

Example-36 : If 200 ml of 0.2 M $HgCl_2$ solution is added to 800 ml of 0.5 M KI (100% dissociated) solution. Assuming that the following complex formation taken place to 100% extent.

$$Hg^{2+} + 4I^- \longrightarrow [HgI_4]^{2-}$$
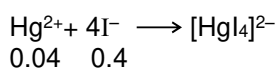
0.04   0.4

Calculate osmotic pressure of resulting initially solution at 300K ?

Solution :

$$HgCl_2 \;+\; 4KI \longrightarrow K_2[HgI_4] \;+\; 2KCl.$$

40	400	0	0
0	400 −160	40	80
	240	40	80
	1000	1000	1000
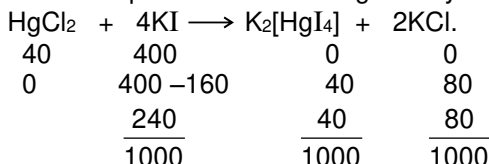
$$\pi = (i_1C_1 + i_2C_2 + i_3C_3)\,RT.$$

$$= (0.24 \times 2 + 3 \times 0.04 + 0.08 \times 2)\,0.082 \times 300. = \textbf{18.69 atm.}$$

Example-37 : (**Note:** Attempt this problem after you have studied co-ordination compounds)
Ba^{2+} ions, CN^- & Co^{2+} ions form a water soluble complex with Ba^{2+} ions as free cations. For a 0.01 M solution of this complex, osmotic pressure = 0.984 atm & degree of dissociation = 75%. Then find coordination number of Co^{2+} ion in this complex (T=300 K, R=0.082 L atm. mol^{-1} k^{-1})

Solution : Say C.N. = x

$$0.984 = i \, CRT$$

$$0.984 = i \, 0.01 \times 0.082 \times 300 = i \times 0.246$$

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

$\Rightarrow$ n = 5

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

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

Charge on Barium ion is +2

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

$$x - 2 + 2 = 5$$

$$x = 5$$

$\therefore$ CN = 5

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

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005

Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in

Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029

Resonance®
Educating for better tomorrow

ADVSCP - 33

Summary

```
                              Mixtures
                                 │
                              can be
                    ┌────────────┴────────────┐
                    ▼                          ▼
              Homogeneous              Heterogeneous
                    │
             classified by
           particle size as
              ┌──────┴──────────────────────────────────┐
              ▼         ▼                                 │
          Colloids   Solutions  ──formation──▶  Intermolecular
              │          │       depends on          force
              │          │                             │
        comprised of   can be                       between
       ┌─────┴─────┐  ┌──┴───────────────┐            │
       ▼           ▼  ▼        ▼          ▼            ▼
    Solute    Solvent  Not saturated  Saturated  Supersaturated   1) Solvent-
       │         │                 │                                  solvent
       └────┬────┘            for which                            2) Solute-
            │            solute:solvent ratio                         solute
   in relative amounts       is the                                3) Solvent-
   expressed using             │                                      solute
            │                  ▼                                       │
      Concentration        Solubility                          as reflected in
         units                 │                               ┌──────┴──────┐
            │            which depends on                       ▼             ▼
     which include        ┌────┴────┐                        Heat of     Entropy of
            │             ▼         ▼                         solution    solution
       Molarity       Pressure  Temperature                  ΔH_soln      ΔS_soln
         M                │
            │        expressed in
       Molality           │
         m              Henry's
            │            law
      Mass percent
       mass %                      Colligative  ──exhibit──
            │                      properties
      Mole fraction                     │
         X                          such as
```

$$\Delta H_{soln} \qquad \Delta S_{soln}$$

Colligative properties such as:

- Vapor-pressure lowering — expressed by **Raoult's law**
$$\frac{P - P_s}{P_s} = \frac{w}{m} \times \frac{M}{W}$$

- Boiling-point elevation
$$\Delta T_b = i\,K_b\ \text{molality}$$
$$K_b = \frac{RT_b^2}{1000 \times L_{vap}}$$

- Freezing-point depression
$$\Delta T_f = i\,K_f\ \text{molality}$$
$$K_f = \frac{RT_f^2}{1000 \times L_{fus}}$$

- Osmotic pressure
$$\pi = i\,CRT$$

ADVSCP - 34

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

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

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

wt of solute = 6.9 × 56 gm

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

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

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

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

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

$2 \times 0.184 = \dfrac{2.5 \times V}{1000}$ 　　　　V = **147.2**

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

Sol. Let V = 1lt = 1000 ml

So mass of solution = 1800 gm

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

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

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

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

Ans. (a) 37.92 　(b) 0.065

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

Mass of $Na_2S_2O_3 = 3 \times 158 = $ **474**

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

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

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

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

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

Ans. 3.94 atm

Sol. $C_{net} = \dfrac{C_1 V_1 + C_2 V_2}{V_1 + V_2}$

Now 　$\pi = C_{net} RT$

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

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

Ans. P_2 = 6.66 atm.

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

Resonance® Educating for better tomorrow
Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in
Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029
ADVSCP - 35

Check List

Definitions (D)

D1	**Solution** ☐
D2	**Solute** ☐
D3	**Solvent** ☐
D4	**Binary solutions** ☐
D5	**Ternary solutions** ☐
D6	**Aqueous solution** ☐
D7	**Non-aqueous solution** ☐
D8	**Miscible liquids** ☐
D9	**Immiscible liquids** ☐
D10	**Alloys** ☐
D11	**Mass percentage** ☐
D12	**Mass by volume percentage** ☐
D13	**Volume percentage** ☐
D14	**Molarity (M)** ☐
D15	**Molality (m)** ☐
D16	**Normality** ☐
D17	**Mole-fraction (x)** ☐
D18	**Parts per million (ppm)** ☐
D19	**Vapour pressure of a pure liquid** ☐
D20	**Vapour pressure of solution** ☐
D21	**Partial vapour pressure** ☐
D22	**Saturated solution** ☐
D23	**Unsaturated solution** ☐
D24	**Supersaturated solution** ☐
D25	**Solubility** ☐
D26	**Azeotropes** ☐
D27	**Minimum Boiling Azeotropes** ☐
D28	**Maximum Boiling Azeotropes** ☐
D29	**Constitutional Properties** ☐
D30	**Colligative properties** ☐
D31	**Abnormal colligative property** ☐
D32	**Boiling Point** ☐
D33	**Normal Boiling Point** ☐
D34	**Elevation Of Boiling Point** ☐
D35	**Freezing Point** ☐
D36	**Depression In Freezing Point** ☐
D37	**K_f, Freezing point Depression Constant (Molal Depression Constant)** ☐ ☐
D38	**Diffusion** ☐
D39	**Osmosis** ☐
D40	**Semi-permeable Membrane** ☐
D41	**Osmotic Pressure** ☐
D42	**Reverse Osmosis** ☐
D43	**Isotonic solution** ☐
D44	**Hypotonic & Hypertonic solutions** ☐
D45	**Plasmolysis** ☐

Formule (F)

F1	**% w/w** ☐
F2	**% wt/vol. (w/v)** ☐
F3	**molarity** ☐
F4	**molality** ☐
F5	**No. of equivalents per litre of solution** ☐
F6	**Equivalent mass** ☐
F7	**No. of equivalent** ☐
F8	**X_{solute}** ☐
F9	**$X_{Solvent}$** ☐
F10	**$X_{solute} + X_{Solvent} = 1$** ☐
F11	**ppm (w/w)** ☐
F12	**ppm (w/v)** ☐
F13	**ppm (moles/moles)** ☐
F14	**Clausius-Clapeyron equation** ☐
F15	**Relative Humidity (R.H.)** ☐
F16	**Henry's Law** ☐

F17	**Distillation of Immiscible liquids** ☐
F18	**Composition of distillate obtained from distillation of Immiscible liquids** ☐
F19	**Raoult's Law**
F20	**Total pressure of vapour in ideal solutions of two miscible liquids** ☐
F21	**relation between total pressure and vapour composition over an ideal solution of two miscible liquids** ☐
F22	**Vant–Hoff factor** ☐
F23	**Relation of i with α** ☐
F24	**Relation of i with β** ☐
F25	**RLVP** ☐
F26	**Relation of ΔP with molality** ☐
F27	**ΔT_b** ☐
F28	**K_b** ☐
F29	**L_{vap}** ☐
F30	**Formula for Depression of freezing point** ☐
F31	**Cryoscopic constant K_f** ☐
F32	**L_{fusion}** ☐
F33	**Osmotic Pressure** ☐

Derivations (Der.)

Der1	**Molarity of mixture of two solutions of known molarity and volume of same solute** ☐
Der2	**Henry's Law** ☐
Der3	**Total pressure over solution using Raoult's law and Dalton's law** ☐
Der4	**Relation of i with α** ☐
Der5	**Relation of i with β** ☐
Der6	**RLVP** ☐
Der7	**ΔT_b** ☐
Der8	**ΔT_f** ☐

Exercise-1

✎ **Marked questions are recommended for Revision.**

PART - I : SUBJECTIVE QUESTIONS

Section (A) : General Introduction & types of solution

A-1.✎ What are the characteristics of the supersaturated solution.

A-2.✎ What do you mean by Hygroscopic compound ?

A-3. Why are some solution processes exothermic whereas others are endothermic ?

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

Commit to memory :

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

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

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

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

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

B-2.✎ The density of 3M solution of sodium thiosulphate ($Na_2S_2O_3$) is 1.58 g/ml. Calculate
(i) amount of $Na_2S_2O_3$ in % w/w
(ii) mole fraction of $Na_2S_2O_3$
(iii) molality of Na^+ and $S_2O_3^{2-}$ ions.

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

Section (C) : Vapour Pressure

Commit to memory :
* The partial pressure of vapours of X in equilibrium with X at a given temperature is called as its vapour pressure. (X is given pure solid or pure liquid)
* A gas is said to be saturated with vapours of a liquid if the partial pressure of liquid vapours is equal to its (saturated) vapour pressure.
* Partial pressure of vapours of X (pure solid or liquid) will remain equal to its vapour pressure till the vapours of X are in equilibrium with X.

C-1.✎ The vapour pressure of water at 80ºC is 355 torr. A 100 ml vessel contained water−saturated oxygen at 80º C, the total gas pressure being 760 torr. The contents of the vessel were pumped into a 50.0 ml, vessel at the same temperature. What were the partial pressures of oxygen and of water vapour and the total pressure in the final equilibrium state? Neglect the volume of any water which might condense.

C-2. A vessel has nitrogen gas and water vapours in equilibrium with liquid water at a total pressure of 1 atm. The partial pressure of water vapours is 0.3 atm. The volume of this vessel is reduced to one third of the original volume, at the same temperature, then find total pressure of the system. (Neglect volume occupied by liquid water)

Resonance®
Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in
Toll Free : 1800 258 5555 | **CIN:** U80302RJ2007PLC024029

ADVSCP - 37

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

Commit to memory :

*   **Henry's law :** The solubility of gas in a liquid at a given temperature is directly proportional to its partial pressure above liquid in which it is dissolved.

$P = K_H x$ (where x is mole fraction of unreacted, dissolved gas and P is its partial pressure above liquid.)

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

D-2. If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 300 mole of water, if N_2 exerts a partial pressure of 1 bar. Given that Henry's law constant for N_2 at 293 K is 75.00 kbar.

Section (E) : Immiscible Liquids

Commit to memory :

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

* $P_T = P^\circ_A + P^\circ_B$ (P_T = Total pressure above mixture of A and B, P°_A = vapour pressure of A, P°_B = vapour pressure of B)

$\dfrac{P^\circ_A}{P^\circ_B} = \dfrac{n_A}{n_B}$ (n_A and n_B are moles of A and B in distillate)

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

E-1. A mixture of an organic liquid A and water distilled under one atmospheric pressure at 99.2ºC. How many grams of steam will be condensed to obtain 1.0 g of liquid A in the distillate ? (Vapour pressure of water at 99.2ºC is 739 mm Hg. Molecular weight of A = 123)

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

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

Commit to memory :

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

$p_A \propto x_A$

$p_A = x_A P_A^\circ$ .... (1)

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

Hence $P_T = x_A P_A^\circ + x_B P_B^\circ$ .... (2)

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

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

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

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

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

F-3. Two solutions of A and B are available. The first is known to contain 1 mole of A and 3 moles of B and its total vapour pressure is 1.0 atm. The second is known to contain 2 moles of A and 2 moles of B; its vapour pressure is greater than 1 atm, but it is found that this total vapour pressure may be reduced to 1 atm by the addition of 6 moles of C. The vapour pressure of pure C is 0.80 atm. Assuming ideal solutions and that all these data refer to 25°C, calculate the vapour pressure of pure A and of pure B.

F-4. At 80°C, the vapour pressure of pure benzene is 753 mm Hg and of pure toluene 290 mm Hg. Calculate the composition of a liquid in mole per cent which at 80°C is in equilibrium with the vapour containing 30 mole per cent of benzene.

F-5. Vapour pressure of C_6H_6 and C_7H_8 mixture at 50°C is given P (mm Hg) = $180X_B + 90$, where X_B is the mole fraction of C_6H_6. A solution is prepared by mixing 12 mol benzene and 8 mol toluene and if vapours over this solution are removed and condensed into liquid and again brought to the temperature 50°C, what would be mole fraction of C_6H_6 in the vapour state. (At. wt. of C = 12, H = 1)

Section (G) : Non-ideal Solutions

Commit to memory :

* **+ve deviation**	**–ve deviation**
$P_{T.exp} > (x_A P^o_A + x_B P^o_B)$	$P_{T.exp} < (x_A P^o_A + x_B P^o_B)$
(where $P_{T.exp}$ is experimental total pressure above mixture of volatile liquids A and B).	
$\Delta H_{mix} = +ve$	$\Delta H_{mix} = -ve$
$\Delta V_{mix} = +ve$	$\Delta V_{mix} = -ve$
$\Delta S_{mix} = +ve$	$\Delta S_{mix} = +ve$
$\Delta G_{mix} = -ve$	$\Delta G_{mix} = -ve$

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

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

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

Commit to memory :

* For dissociation/association $\quad i = 1 + (n - 1)\alpha$
(where n is total number of particles produced per solute particle after association/dissociation, i = vant Hoff factor, α = degree of dissociation / association.

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

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

H-1. Complete the following table.

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

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

Section (I) : Relative lowering of vapour pressure

Commit to memory :

* $\quad$ RLVP $= \dfrac{P^\circ - P_S}{P^\circ} = x_{solute}$; $\qquad \dfrac{P^\circ - P_s}{P_s} = \dfrac{n}{N}$

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

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

$\dfrac{P^\circ - P_s}{P_s} = (\text{molality}) \times \dfrac{M_{solvent}}{1000}$

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

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

I-1. Twenty grams of a solute are added to 100 g of water at 25ºC. The vapour pressure of pure water is 23.76 mmHg; the vapour pressure of the solution is 22.41 Torr.
(a) Calculate the molar mass of the solute.
(b) What mass of this solute is required in 100 g of water to reduce the vapour pressure to one-half the value for pure water ?

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

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

Commit to memory :

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

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

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

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

J-1. (a) A solution containing 0.5 g of naphthalene in 50 g CCl_4 yield a boiling point elevation of 0.4 K, while a solution of 0.6 g of an unknown solute in the same mass of the solvent gives a boiling point elevation of 0.65 K. Find the molar mass of the unknown solute.
(b) The boiling point of a solution of 0.1 g of a substance in 16 g of ether was found to be 0.100ºC higher that of pure ether. What is the molecular mass of the substance. K_b(ether) = 2.16 K kg mol^{-1}.

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

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

[Hint : $K_b = \dfrac{RT_b^2}{1000 L_v} = \dfrac{2 \times (320)^2}{1000 \times 84} = 2.438$]

J-4. A 0.01 molal solution of ammonia freezes at –0.02ºC. Calculate the van't Hoff factor, i and the percentage dissociation of ammonia in water. ($K_{f(H_2O)}$) = 1.86 deg molal^{-1}.

Section (K) : Osmotic Pressure

Commit to memory :

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

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

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

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

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

K-3. 17.4% (w/v) K_2SO_4 solution at 27ºC is isotonic with 5.85% (w/v) NaCl solution at 27ºC. If NaCl is 100% ionised, what is % ionisation of K_2SO_4 in aq. solution ?

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

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : General Introduction & types of solution

A-1. Which statement best explains the meaning of the phrase "like dissolves like " ?
(A) A Solute will easily dissolve a solute of similar mass
(B) A solvent and solute with similar intermolecular forces will readily form a solution
(C) The only true solutions are formed when water dissolves a non-polar solute
(D) The only true solutions are formed when water dissolves a polar solute

A-2. An ionic compound that attracts atmospheric water so strongly that a hydrate is formed is said to be :
(A) Dilute   (B) Hygroscopic   (C) Immiscible   (D) Miscible

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

B-1. Persons are medically considered to have lead poisoning if they have a concentration greater than 10 micrograms of lead per decilitre of blood. Concentration in parts per billion is :
(A) 1000   (B) 100   (C) 10   (D) 1

Section (C) : Vapour Pressure

C-1. A liquid is kept in a closed vessel. If a glass plate (negligible mass) with a small hole is kept on top of the liquid surface, then the vapour pressure of the liquid in the vessel is :
(A) More than what would be if the glass plate were removed
(B) Same as what would be if the glass plate were removed
(C) Less than what would be if the glass plate were removed
(D) Cannot be predicted

C-2. The vapour pressure of water depends upon :
(A) Surface area of container   (B) Volume of container
(C) Temperature   (D) All

C-3. Among the following substances, the lowest vapour pressure is exerted by :
(A) Water   (B) Mercury   (C) Acetone   (D) Ethanol

C-4. At higher altitudes, water boils at temperature < 100ºC because
(A) temperature of higher altitudes is low   (B) atmospheric pressure is low
(C) the proportion of heavy water increases   (D) atmospheric pressure becomes more.

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

D-1. The solubility of gases in liquids :
(A) increases with increase in pressure and temperature
(B) decreases with increase in pressure and temperature
(C) Increases with increase in pressure and decrease in temperature
(D) decreases with increase in pressure and increase in temperature

D-2. Which of the following curves represents theHenry'slaw?
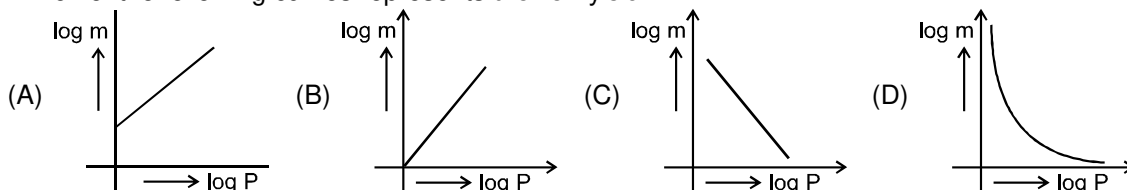
D-3. According to Henry's law, the solubility of a gas in a given volume of liquid increases with increase in :
(A) Temperature   (B) Pressure   (C) Both (A) and (B)   (D) None of these

D-4. Some of the following gases are soluble in water due to formation of their ions :
I : CO_2 ;   II : NH_3 ;   III : HCl ;   IV : CH_4 ;   V : H_2
Water insoluble gases can be :
(A) I, IV , V   (B) I, V   (C) I, II, III   (D) IV, V

D-5. The solubility of N_2(g) in water exposed to the atmosphere, when its partial pressure is 593 mm is 5.3×10^{-4} M. Its solubility at 760 mm and at the same temperature is :
(A) 4.1×10^{-4} M   (B) 6.8×10^{-4} M   (C) 1500 M   (D) 2400 M

Section (E) : Immiscible Liquids

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

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

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

F-2. An ideal solution contains two volatile liquids A (p^o = 100 torr) and B (p^o = 200 torr). If mixture contain 1 mole of A and 4 mole of B then total vapour pressure of the distillate is:
(A) 150   (B) 180   (C) 188.88   (D) 198.88

F-3. At 323 K, the vapour pressure in millimeters of mercury of a methanol-ethanol solution is represented by the equation p = 120 X_A + 140, where X_A is the mole fraction of methanol.Then the value of

$\lim\limits_{x_A \to 1} \dfrac{p_A}{X_A}$ is

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

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

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

Resonance® Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in
Toll Free : 1800 258 5555 | **CIN:** U80302RJ2007PLC024029

ADVSCP - 42

Section (G) : Non-ideal Solutions

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

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

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

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

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

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

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

H-1. One mole of a solute A is dissolved in a given volume of solvent. The association of the solute take place as follows : $nA \rightleftharpoons A_n$
If α is the degree of association of A, the van't Hoff factor i is expressed as :

(A) $i = 1 - \alpha$ (B) $i = 1 + \dfrac{\alpha}{n}$ (C) $i = \dfrac{1 - \alpha + \dfrac{\alpha}{n}}{1}$ (D) $i = 1$

H-2. The degree of dissociation of an electrolyte is α and its van't Hoff factor is i. The number of ions obtained by complete dissociation of 1 molecule of the electrolyte is :
(A) $\dfrac{i + \alpha - 1}{\alpha}$ (B) $i - \alpha - 1$ (C) $\dfrac{i - 1}{\alpha}$ (D) $\dfrac{i + 1 + \alpha}{1 - \alpha}$

H-3. If M_{normal} is the normal molecular mass and α is the degree of ionization of $K_3[Fe(CN)_6]$, then the abnormal molecular mass of the complex in the solution will be :
(A) $M_{normal} (1 + 2\alpha)^{-1}$ (B) $M_{normal} (1 + 3\alpha)^{-1}$ (C) $M_{normal} (1 + \alpha)^{-1}$ (D) equal to M_{normal}

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

Resonance® Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in
Toll Free : 1800 258 5555 | **CIN :** U80302RJ2007PLC024029

ADVSCP - 43

Section (I) : Relative lowering of vapour pressure

I-1. If P_0 and P are the vapour pressures of a solvent and its solution respectively and N_1 and N_2 are the mole fractions of the solvent and non-volatile solute respectively, then correct relation is :

(A) $P = P_0N_2$ (B) $P = P_0N_1$ (C) $P_0 = PN_1$ (D) $P = P_0(N_1/N_2)$

I-2. Relative decrease in vapour pressure of an aqueous NaCl is 0.167. Number of moles of NaCl present in 180g of H_2O is :

(A) 2 mol   (B) 1 mol   (C) 3 mol   (D) 4 mol

I-3. The vapour pressure of pure benzene, C_6H_6 at 50°C is 268 Torr. How many moles of non-volatile solute per mol of benzene is required to prepare a solution of benzene having a vapour pressure of 167 Torr at 50°C?

(A) 0.377   (B) 0.605   (C) 0.623   (D) 0.395

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

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

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

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

I-6. Relative decrease in vapour pressure of an aqueous solution containing 2 moles $[Cu(NH_3)_3Cl]Cl$ in 3 moles H_2O is 0.50. On reaction with $AgNO_3$, this solution will form(assuming no change in degree of ionisation of substance on adding $AgNO_3$)

(A) 1 mol AgCl   (B) 0.25 mol AgCl   (C) 0.5 mol AgCl   (D) 0.40 mol AgCl

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

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

(A) 100.75 °C   (B) 100.5 °C   (C) 100°C   (D) 100.25°C

J-2. Elevation in boiling point was 0.52 °C when 6 g of a compound x was dissolved in 100 g of water. Molecular weight of x is : (K = 0.52 kg mol^{-1})

(A) 120   (B) 60   (C) 100   (D) 342

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

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

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

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

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

(A) $[Pt(H_2O)_6]Cl_4$ (B) $[Pt(H_2O)_4Cl_2]Cl_2 . 2H_2O$

(C) $[Pt(H_2O)_3Cl_3]Cl . 3H_2O$ (D) $[Pt(H_2O)_2Cl_4] . 4H_2O$

J-6. How many moles of sucrose should be dissolved in 500 g of water so as to get a solution which has a difference of 104°C between boiling point and freezing point.

($K_f = 1.86$ K Kg mol^{-1}, $K_b = 0.52$ K Kg mol^{-1})

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

Resonance® Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005

Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in

Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029

ADVSCP - 44

J-7. Which of the following has been arranged in order of decreasing freezing point?
(A) 0.05 M KNO_3 > 0.04 M $CaCl_2$ > 0.140 M sugar > 0.075 M $CuSO_4$
(B) 0.04 M $BaCl_2$ > 0.140 M sucrose > 0.075 M $CuSO_4$ > 0.05 M KNO_3
(C) 0.075 M $CuSO_4$ > 0.140 M sucrose > 0.04 M $BaCl_2$ > 0.05 M KNO_3
(D) 0.075 M $CuSO_4$ > 0.05 M $NaNO_3$ > 0.140 M sucrose > 0.04 M $BaCl_2$

J-8. A solution of x moles of sucrose in 100 grams of water freezes at −0.2ºC. As ice separates the freezing point goes down to − 0.25ºC. How many grams of ice would have separated?
(A) 18 grams (B) 20 grams (C) 25 grams (D) 23 grams

J-9. Sea water is found to contain 5.85 % NaCl and 9.50% $MgCl_2$ by weight of solution. Calculate its normal boiling point assuming 80% ionisation for NaCl and 50% ionisation of $MgCl_2$ ($K_b(H_2O)$ = 0.51 $kgmol^{-1}$ K).
(A) T_b = 101.9°C (B) T_b = 102.3°C (C) T_b = 108.5°C (D) T_b = 110.3°C

Section (K) : Osmotic Pressure

K-1. The relationship between osmotic pressure at 273 K when 10 g glucose (P_1), 10 g urea (P_2) and 10 g sucrose (P_3) are dissolved in 250 mL of water is :
(A) $P_1 > P_2 > P_3$ (B) $P_3 > P_1 > P_2$ (C) $P_2 > P_1 > P_3$ (D) $P_2 > P_3 > P_1$

K-2. Osmotic pressure of blood is 7.40 atm at 27°C. Number of moles of glucose to be used per litre for an intravenous injection that is to have the same osmotic pressure as blood is :
(A) 0.3 (B) 0.2 (C) 0.1 (D) 0.4

K-3. The total concentration of dissolved particles inside red blood cells is approximately 0.30 M and the membrane surrounding the cells is semipermeable. What would the osmotic pressure (in atmosphere) inside the cells become if the cells were removed from the blood plasma and placed in pure water at 298 K ?
(A) 7.34 atm (B) 1.78 atm (C) 2.34 atm (D) 0.74 atm

K-4. Consider following cases :
I : 2M CH_3COOH solution in benzene at 27°C where there is dimer formation to the extent of 100%
II : 0.5 M KCl aq. solution at 27°C, which ionises 100%
Which is/are true statements(s) :
(A) both are isotonic (B) I is hypertonic (C) II is hypotonic (D) none is correct

PART - III : MATCH THE COLUMN

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

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

2. Match the following column-

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

Exercise-2

PART - I : ONLY ONE OPTION CORRECT TYPE

1. All of the water in a 0.20 M solution of NaCl was evaporated and a 0.150 mol of NaCl was obtained. What was the original volume of the sample ?
(A) 30 mL   (B) 333 mL   (C) 750 mL   (D) 1000 mL

2.☜ A 20.0 mL sample of $CuSO_4$ solution was evaporated to dryness, leaving 0.967 g of residue. What was the molarity of the original solution ? (Cu = 63.5)
(A) 48.4 M   (B) 0.0207 M   (C) 0.0484 M   (D) 0.303 M

3.☜ The vapour pressure of water at 20°C is 17.54 mmHg. What will be the vapour pressure of the water in the apparatus shown after the piston is lowered, decreasing the volume of the gas above the liquid to one half of its initial volume (assume temperature constant).
(A) 8.77 mmHg   (B) 17.54 mmHg
(C) 35.08 mmHg   (D) between 8.77 and 17.54 mmHg

4.☜ A sample of air is saturated with benzene (vapor pressure = 100 mm Hg at 298 K) at 298K, 750mm Hg pressure. If it is isothermally compressed to one third of its initial volume, the final pressure of the system is
(A) 2250 torr   (B) 2150 torr   (C) 2050 torr   (D) 1950 torr

5. Water and chlorobenzene are immiscible liquids. Their mixture boils at 89ºC under a reduced pressure of 7.7×10^4 Pa. The vapour pressure of pure water at 89ºC is 7×10^4 Pa. Weight percent of chlorobenzene in the distillate is:
(A) 50   (B) 60   (C) 78.3   (D) 38.46

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

7.☜ Given P-x curve for a non-ideal liquid mixture (Fig.). Identify the correct T-x curve for the same mixture.
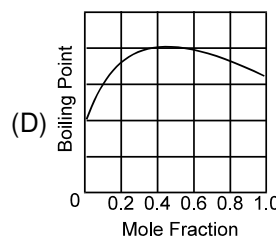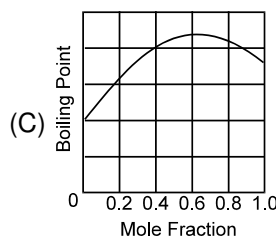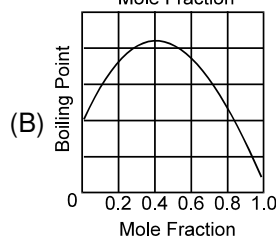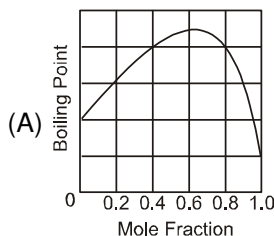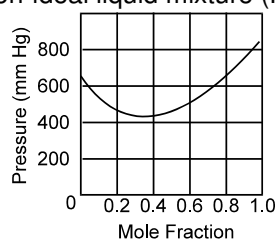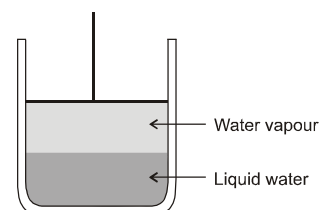
8.☜ If vapour pressures of pure liquids 'A' & 'B' are 300 and 800 torr respectively at 25°C. When these two liquids are mixed at this temperature to form a solution in which mole percentage of 'B' is 92, then the total vapour pressure is observed to be 0.95 atm. Which of the following is true for this solution.
(A) $\Delta V_{mix} > 0$ (B) $\Delta H_{mix} < 0$ (C) $\Delta V_{mix} = 0$ (D) $\Delta H_{mix} = 0$

9. Barium ions, CN^- and Co^{2+} form an ionic complex. If that complex is supposed to be 75% ionised in water with vant Hoff factor 'i' equal to four, then the coordination number of Co^{2+} in the complex can be:
(A) Six   (B) Five   (C) Four   (D) Six and Four both

10. In the following aqueous solutions (a) 1 m sucrose, (b) 1 m potassium ferricyanide and (c) 1 m potassium sulphate
Maximum value of vapour pressure of solution is that of :
(A) a   (B) b   (C) c   (D) equal

11. When only a little quantity of $HgCl_2(s)$ is added to excess KI(aq) to obtain a clear solution, which of the following is true for this solution? (no volume change on mixing).
The reaction is $4KI(aq.) + HgCl_2(s) \longrightarrow K_2[HgI_4]$ (aq.) + 2KCl (aq.)
(A) Its boiling and freezing points remain same   (B) Its boiling point is lowered
(C) Its vapour pressure become lower   (D) Its boiling point is raised
(E) Its freezing point is lowered.

12. x mole of KCl and y mole of $BaCl_2$ are both dissolved in 1 kg of water. Given that x + y = 0.1 and K_f for water is 1.85 K/molal, what is the observed range of ΔT_f, if the ratio of x to y is varied ?
(A) 0.37º to 0.555º   (B) 0.185º to 0.93º   (C) 0.56º to 0.93º   (D) 0.37º to 0.93º

13. $FeCl_3$ on reaction with $K_4[Fe(CN)_6]$ in aq. solution gives blue colour. These are separated by a semipermeable membrane PQ as shown. Due to osmosis there is-
(A) blue colour formation in side X
(B) blue colour formation in side Y
(C) blue colour formation in both of the sides X and Y
(D) no blue colour formation

14. Two beakers, one containing 20 ml of a 0.05 M aqueous solution of a non volatile, non electrolyte and the other, the same volume of 0.03 M aqueous solution of NaCl, are placed side by side in a closed enclosure. What are the volumes in the two beakers when equilibrium is attained ? Volume of the solution in the first and second beaker are respectively.
(A) 21.8 ml and 18.2 mL   (B) 18.2 mL and 21.8 mL
(C) 20 mL and 20 mL   (D) 17.1 mL and 22.9 mL
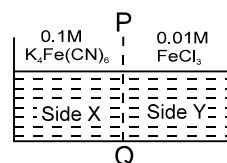
PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

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

2. At 300 K, 40 mL of O_3 (g) dissolves in 100 g of water at 1.0 atm. What mass of ozone (in gram) dissolved in 1600 g of water at a pressure of 4.0 atm at 300 K?

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

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

5. The vapour pressure of pure liquid A at 300 K is 577 Torr and that of pure liquid B is 390 Torr. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.35. Find the mole % of A in liquid.

6. How many facts related to $CHCl_3$ + ethylmethylketone solution are correct ?
(a) It shows negative derivation.   (b) It forms maximum boiling azeotropic mixture
(c) $\Delta S > 0$ (d) $\Delta G < 0$
(e) Components can be separated by fractional distillation.

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in
Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029   ADVSCP - 47

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

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

8. 0.1 mole XY_2 is dissolved in 2L water, where it ionizes to give X^{2+} and Y_2^{2-}. Observed osmotic pressure is 3 atm. Molar mass of X is 24 and Y is 32. Find $M_{observed}$ + 2i (where $M_{observed}$ is observed molar mass of XY_2). (Use R = 1/12 L-atm/mol.K and temperature is 87°C)

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

10. 1.22 g of a monobasic acid is dissolved in 100 g of benzene. Boiling point of solution increases by 0.13ºC with respect to pure benzene. Find the molecular mass of acid in benzene solvent (in u). Report your answer after dividing it by 100 and Round it off to nearest integer.
(K_b of benzene = 2.6 K kg mol^{-1}).

11. 1 g of a monobasic acid dissolved in 200 g of water lowers the freezing point by 0.186ºC. On the other hand when 1 g of the same acid is dissolved in water so as to make the solution 200 mL, this solution requires 125 mL of 0.1 M NaOH for complete neutralization. Calculate % dissociation of acid ? (K_f $=1.86 \dfrac{K-kg}{mol}$)

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

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

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

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

2. Which of the following concentration factors can be calculated if the mole fraction and density of an aqueous solution of HCl are known ?
(A) Molality
(B) Molarity
(C) Percent by mass
(D) Normality

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

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

Resonance® Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in
Toll Free : 1800 258 5555 | **CIN:** U80302RJ2007PLC024029

ADVSCP - 48

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

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

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

8. At 40ºC, vapour pressure in Torr of methanol and ethanol solution is P = 119x + 135 where x is the mole fraction of methanol. Hence
(A) vapour pressure of pure methanol is 119 Torr
(B) vapour pressure of pure ethanol is 135 Torr
(C) vapour pressure of equimolar mixture of each is 127 Torr
(D) mixture is completely immiscible

9. Which is/are correct statement(s) ?
(A) When mixture is more volatile than both pure components, there is positive deviation from Raoult's law.
(B) When mixture is less volatile than both pure components, there is negative deviation from Raoult's law.
(C) Ethanol and water form ideal solution
(D) $CHCl_3$ and water form ideal solution

10. At 35°C, the vapour pressure of CS_2 is 512 mm Hg, and of acetone is 344 mm Hg. A solution of CS_2 and acetone in which the mole fraction of CS_2 is 0.25, has a total vapour pressure of 600 mm Hg. Which of the following statements is/are correct ?
(A) A mixture of 100 mL of acetone and 100 mL of CS_2 has a volume of 200 mL
(B) When acetone and CS_2 are mixed at 35°C, heat must be absorbed in order to produce a solution at 35°C.
(C) Process of mixing is exothermic
(D) Entropy of mixing is zero

11. For the given electrolyte A_xB_y, the degree of dissociation 'α' can be given as
(A) $\alpha = \dfrac{i-1}{x+y-1}$ (B) $i = (1-\alpha) + x\alpha + y\alpha$ (C) $\alpha = \dfrac{1-i}{1-x-y}$ (D) None

12. In which of the following pairs of solutions will the values of the vant Hoff factor be the same?
(A) 0.05 M $K_4[Fe(CN)_6]$ and 0.10 M $FeSO_4$
(B) 0.10 M $K_4[Fe(CN)_6]$ and 0.05 M $FeSO_4 (NH_4)_2SO_4$. $6H_2O$
(C) 0.20 M NaCl and 0.10 M $BaCl_2$
(D) 0.05 M $FeSO_4 (NH_4)_2SO_4.6H_2O$ and 0.02 M $KCl.MgCl_2.6H_2O$

13. 2 g of non-volatile hydrocarbon solute dissolved in 100 g of hypothetical organic solvent (molar mass = 50) was found to lower vapour pressure from 75.50 to 75 mm of Hg at 20°C. Given that hydrocarbon contains 96% of C. Then which of the following are true ?
(A) molecular wt of solute = 150   (B) molecular formula = $C_{12}H_6$
(C) molecular wt. of solute = 132   (D) none of these

14. In the depression of freezing point experiment, it is found that the :
(A) Vapour pressure of the solution is less than that of pure solvent
(B) Vapour pressure of the solution is more than that of pure solvent
(C) Only solute molecules solidify at the freezing point
(D) Only solvent molecules solidify at the freezing point

Resonance®
Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in
Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029

ADVSCP - 49

15. Consider following solutions :
I : 1 M aqueous glucose solution
II : 1M aqueous sodium chloride solution
III : 1M aqueous ammonium phosphate solution
IV : 1M benzoic acid in benzene
Select correct statements for the above solutions :
(A) All are isotonic solutions   (B) III is hypertonic of I, II and IV
(C) IV is hypotonic of I, II and III   (D) II is hypotonic of III but hypertonic of I and IV

16. Which facts are true when we use van't Hoff equation PV = nST for osmotic pressure P of dilute solutions?
(A) The equation is identical to that of ideal gas equation
(B) The solute particles in solution are analogous to the gas molecules and the solvent is analagous to the empty space between the gas molecules
(C) Solute molecules are dispersed in the solvent the way the gas molecules are dispersed in empty space
(D) The equation is not identical to that of ideal gas equation

PART - IV : COMPREHENSIONS

Read the following passage carefully and answer the questions.

Comprehension # 1

$$P_A = x_A P_A^{\circ} \qquad \& \qquad P_B = x_B P_B^{\circ}$$

$$P_T = x_A P_A^{\circ} + x_B P_B^{\circ} \qquad \text{(Note : } P_A^{\circ} > P_B^{\circ} \text{ ; A is more volatile than B)}$$
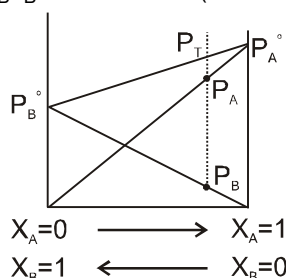
Vapour pressure of mixtures of Benzene (C_6H_6) & toluene (C_7H_8) at 50ºC are given by $P_M = 179\, X_B + 92$, where X_B is mole fraction of C_6H_6.

1. What is vapour pressure of pure liquids ?
(A) $P_B^{\circ} = 92$ mm, $P_T^{\circ} = 179$ mm   (B) $P_B^{\circ} = 271$ mm, $P_T^{\circ} = 92$ mm
(C) $P_B^{\circ} = 180$ mm, $P_T^{\circ} = 91$ mm   (D) none of these

2. Vapour pressure of liquid mixture obtained by mixing 936 g C_6H_6 & 736 g tolene is :
(A) 300 mm Hg   (B) 250 mm Hg   (C) 199.4 mm Hg   (D) 180.6 mm Hg

Comprehension # 2

Answer the questions (given below) which are based on the following diagram. Consider some facts about the above phase diagram: Vapour pressure diagram for real solutions of two liquids A and B that exhibit a positive deviation from Raoult's law. The vapour pressure of both A and B are greater than predicted by Raoult's law. The dashed lines represented the plots for ideal solutions.
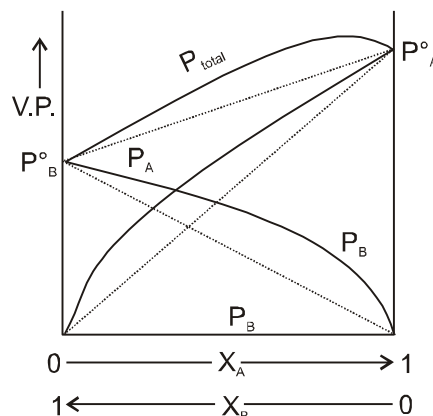
3. A : This is observed when A...B attractions are greater than average of A...A and B...B attraction:

B : ΔH_{mix} = +ve, ΔV_{mix} = +ve

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

D : Mixture can form azeotropic mixture

Select correct facts

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

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

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

(B) Boiling point has been lowered

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

(D) All the above statements are correct.

Comprehension # 3

Addition of non-volatile solute to a solvent always increases the colligative properties such as osmotic pressure, ΔP, ΔT_b and ΔT_f. All these colligative properties are directly proportional to molality if solutions are dilute. The increases in colligative properties on addition of non-volatile solute is due to increase in number of solute particles.
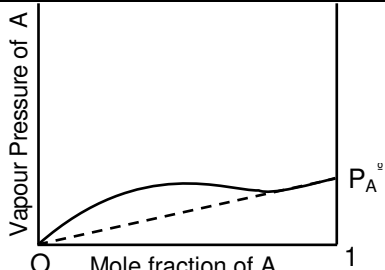
5. For different aqueous solutions of 0.1 M NaCl, 0.1 M urea, 0.1 M Na_2SO_4 and 0.1 M Na_3PO_4 solution at 27ºC, the correct statements are : (Consider the solutions to be dilute)

1. The order of osmotic pressure is, NaCl > Na_2SO_4 > Na_3PO_4 > urea

2. $\pi = \dfrac{\Delta T_b}{K_b}$ × ST for urea solution

3. Addition of salt on ice increases its melting point

4. Addition of salt on ice brings in melting of ice earlier

(A) 2, 3, 4   (B) 2, 4   (C) 1, 2, 3   (D) 3, 4

6. 1 g mixture of glucose and urea present in 250 mL aqueous solution shows the osmotic pressure of 0.74 atm at 27ºC. Assuming solution to be dilute, which are correct ?

1. Percentage of urea in mixture is 17.6.

2. Relative lowering in vapour pressure of this solution is 5.41×10^{-4}.

3. The solution will boil at 100.015ºC, if K_b of water is 0.5 K molality^{-1}.

4. If glucose is replaced by same amount of sucrose, the solution will show higher osmotic pressure at 27ºC.

5. If glucose is replaced by same amount of NaCl, the solution will show lower osmotic pressure at 27ºC.

(A) 1, 2, 3   (B) 1, 2, 3, 5   (C) 2, 4, 5   (D) 1, 4, 5

Comprehension # 4

Let us consider a binary solution of two volatile liquids 'A' and 'B', when taken in a closed container. Both the components would evaporate and an equilibrium would be established between vapour phase and liquid phase. Let the total vapour pressure at this stage be p_{total} and p_A and p_B are partial pressures of A and B. Mole fractions of these components in liquid solution are x_A and x_B, that of vapour phase are y_A and y_B respectively p_A° & p_B° are vapour pressure of pure A & pure B.

Column-I	Column-II	Column-III
(i) Ideal solution	(a) $p_T = p_A^{\circ} x_A + p_B^{\circ} x_B$	(P)

(ii) Non ideal solution (Positive deviation)	(b) A—A interactions, B—B interactions $\neq$ A—B interactions	(Q) $P_T = P°_A + P°_B$
(iii) Non ideal solution (negative deviation)	(c) Form azeotropic mixture	(R) $\Delta S_{surrounding} = +ve$
(iv) Immiscible liquids	(d) solution having vapours of fixed composition	(S)

7. For Hexane + Heptane $\rightarrow$ solution correct set is :
   (A) (i) (a) (R)   (B) (ii) (b) (P)   (C) (ii) (d) (R)   (D) (i) (a) (P)

8. For water + ethanol $\rightarrow$ solution correct set is :
   (A) (ii) (b) (Q)   (B) (ii) (c) (S)   (C) (iv) (d) (S)   (D) (iv) (c) (R)

9. For water + H_2SO_4 $\rightarrow$ solution correct set is
   (A) (i) (a) (P)   (B) (ii) (b) (Q)   (C) (iii) (b) (R)   (D) (iv) (c) (P)

10. For a mixture of water and chlorobenzene correct set is
    (A) (i) (a) (P)   (B) (ii) (b) (Q)   (C) (iii) (b) (R)   (D) (iv) (d) (Q)

Exercise-3

* Marked Questions may have more than one correct option.

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

1. In the depression of freezing point experiment, it is found that : **[JEE 1999, 3/80]**
   I. The vapour pressure of the solution is less than that of pure solvent.
   II. The vapour pressure of the solution is more than that of pure solvent.
   III. Only solute molecules solidify at the freezing point.
   IV. Only solvent molecules solidify at the freezing point.
   (A) I, II   (B) II, III   (C) I, IV   (D) I, II, III.

2. The van't Hoff factor for 0.1 M $Ba(NO_3)_2$ solution is 2.74. The degree of dissociation is : **[JEE 1999, 3/80]**
   (A) 91.3%   (B) 87%   (C) 100%   (D) 74%

3. 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 kgmole^{-1} and 0.997 g cm^{-3} respectively **[JEE 2000, 3/35]**
   (A) 0.186 K   (B) 0.228 K   (C) 0.372 K   (D) 0.556 K

4. During depression of freezing point in a solution, the following are in equilibrium : **[JEE 2003, 3/84]**
   (A) Liquid solvent-solid solvent   (B) Liquid solvent-solid solute
   (B) Liquid solute-solid solute   (D) Liquid solute-solid solvent

5. A 0.004 M solution of Na_2SO_4 is isotonic with 0.010 M solution of glucose at same temperature. The apparent percentage dissociation of Na_2SO_4 is : **[JEE 2004, 3/84]**
   (A) 25%   (B) 50%   (C) 75%   (D) 85%

Resonance® Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in
Toll Free : 1800 258 5555 | **CIN:** U80302RJ2007PLC024029

ADVSCP - 52

6. 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 of, 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}. Find molecular weight of benzoic acid in two cases and justify your answer. **[JEE 2004, 4/60]**

7. The elevation in boiling point of a solution of 13.44 g of $CuCl_2$ in 1kg of water using the following information, will be (Molecular weight of $CuCl_2$ = 134.4 and K_b = 0.52 K molal^{-1}) : **[JEE 2005, 3/84]**
(A) 0.16   (B) 0.05   (C) 0.1   (D) 0.2

8. 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 2 K is observed. The van't Hoff factor (i) is : **[JEE-2007, 3/162]**
(A) 0.5   (B) 1   (C) 2   (D) 3

Comprehension #

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. Application of colligative properties are very useful in day-to-day life. One of its example 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 K kg mol^{-1}
Freezing point depression constant of ethanol ($K_f^{ethanol}$) = 2.0 K kg mol^{-1}
Boiling point elevation constant of water (K_b^{water}) = 0.52 K kg mol^{-1}
Boiling point elevation constant of ethanol ($K_b^{ethanol}$) = 1.2 K kg mol^{-1}
Standard freezing point of water = 273 K
Standard freezing point of ethanol = 155.7 K
Standard boiling point of water = 373 K
Standard boiling point of ethanol = 351.5 K
Vapour pressure of pure water = 32.8 mm Hg
Vapour pressure of pure ethanol = 40 mm Hg
Molecular weight of water = 18 g mol^{-1}
Molecular weight of ethanol = 46 g mol^{-1}

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

9. The freezing point of the solution **M** is **[JEE 2008, 3/163]**
(A) 268.7 K   (B) 268.5 K   (C) 234.2 K   (D) 150.9 K

10. The vapour pressure of the solution **M** is **[JEE 2008, 3/163]**
(A) 39.3 mm Hg   (B) 36.0 mm Hg   (C) 29.5 mm Hg   (D) 28.8 mm Hg

11. Water is added to the solution **M** such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is **[JEE 2008, 3/163]**
(A) 380.4 K   (B) 376.2 K   (C) 375.5 K   (D) 354.7 K

12. The Henry's law constant for the solubility of N_2 gas in water at 298 K is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water of 298 K and 5 atm pressure is : **[JEE 2009, 3/160]**
(A) 4×10^{-4} (B) 4.0×10^{-5} (C) 5.0×10^{-4} (D) 4.0×10^{-6}

13. The freezing point (in ºC) of a solution containing 0.1 g of $K_3[Fe(CN)_6]$ (Mol. Wt. 329) in 100 g of water (K_f = 1.86 K kg mol^{-1}) is : **[JEE 2011, 3/180]**
(A) -2.3×10^{-2} (B) -5.7×10^{-2} (C) -5.7×10^{-3} (D) -1.2×10^{-2}

14. For a dilute solution containing 2.5 g of a non- volatile non- electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2ºC. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take K_b = 0.76 K kg mol^{-1}) **[IIT 2012, 3/136]**
(A) 724   (B) 740   (C) 736   (D)718

Resonance® Educating for better tomorrow	**Reg. & Corp. Office :** CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005	
	Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in	**ADVSCP - 53**
	Toll Free : 1800 258 5555 | **CIN:** U80302RJ2007PLC024029	

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

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

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

18. * Mixture(s) showing positive deviation from Raoult's law at $35^{\circ}C$ is(are) **[JEE(Advanced) 2016, 4/124]**
(A) carbon tetrachloride + methanol
(B) carbon disulphide + acetone
(C) benzene + toluene
(D) phenol + aniline

19.* For a solution formed by mixing liquids **L** and **M**, the vapour pressure of **L** plotted against the mole fraction of **M** in solution is shown in the following figure. Here x_L and x_M represent mole fractions of **L** and **M**, respectively, in the solution. The correct statement(s) applicable to this system is (are) **[JEE(Advanced) 2017, 4/122]**
(A) The point **Z** represents vapour pressure of pure liquid **M** and Raoult's law is obeyed from $x_L = 0$ to $x_L = 1$.
(B) Attractive intermolecular interactions between **L-L** in pure liquid **L** and **M-M** in pure liquid **M** are stronger than those between **L-M** when mixed in solution
(C) The point **Z** represents vapour pressure of pure liquid **M** and Raoult's law is obeyed when $x_L \rightarrow 0$
(D) The point **Z** represents vapour pressure of pure liquid **L** and Raoult's law is obeyed when $x_L \rightarrow 1$

20. Pure water freezes at 273 K and 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as 2 K kg mol^{-1}. The figures shown below represent plots of vapour pressure (V.P.) versus temperature (T). [Molecular weight of ethanol is 46 g mol^{-1}] **[JEE(Advanced) 2017, 3/122]**
Among the following, the option representing change in the freezing point is

21. Liquids **A** and **B** form ideal solution over the entire range of composition. At temperature T, equimolar binary solution of liquids **A** and **B** has vapour pressure 45 Torr. At the same temperature, a new solution of **A** and **B** having mole fractions x_A and x_B, respectively, has vapour pressure of 22.5 Torr. The value of x_A / x_B in the new solution is _____. **[JEE(Advanced) 2018, 3/120]**

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

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in
Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029
Resonance®
Educating for better tomorrow
ADVSCP - 54

22. The plot given below shows P–T curves (where P is the pressure and T is the temperature) for two solvents X and Y and isomolal solutions of NaCl in these solvents. NaCl completely dissociates in both the solvents.
On addition of equal number of moles of a non-volatile solute **S** in equal amount (in kg) of these solvents, the elevation of boiling point of solvent **X** is three times that of solvent **Y**. Solute **S** is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent **Y**, the degree of dimerization in solvent **X** is ____.
[JEE(Advanced) 2018, 3/120]

1. Solvent **X**
2. Solution of NaCl in solvent **X**
3. Solvent **Y**
4. Solution of NaCl in solvent **Y**
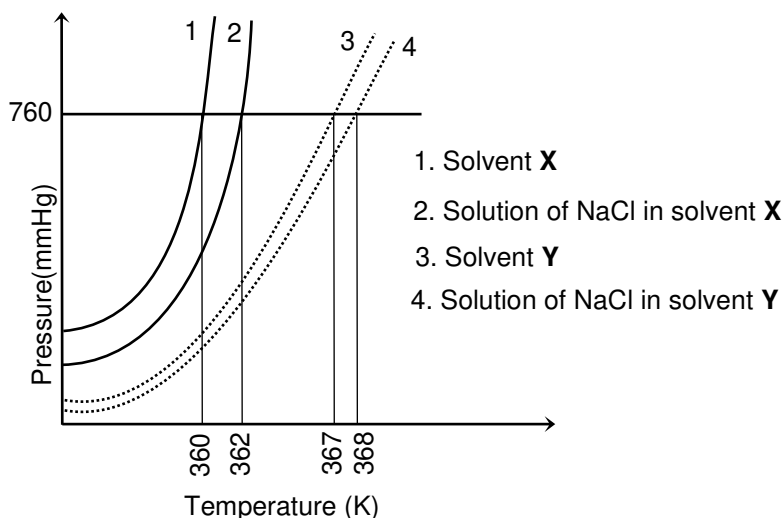
PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

JEE(MAIN) OFFLINE PROBLEMS

1. 6.02×10^{20} molecules of urea are present in 100 ml of its solution. The concentration of urea solution is:
[AIEEE-2004, 3/225]
(1) 0.001 M   (2) 0.01 M   (3) 0.02 M   (4) 0.1 M.

2. Which one of the following aqueous solutions will exhibit highest boiling point ?   **[AIEEE-2004, 3/225]**
(1) 0.01 M Na_2SO_4 (2) 0.01 M KNO_3 (3) 0.015 M urea   (4) 0.015 M glucose

3. If α is the degree of dissociation of Na_2SO_4, the vant Hoff's factor (i) used for calculating the molecular mass is :   **[AIEEE-2005, 1½/225]**
(1) $1 + \alpha$ (2) $1 - \alpha$ (3) $1 + 2\alpha$ (4) $1 - 2\alpha$.

4. Equimolar solutions in the same solvent have :   **[AIEEE-2005, 3/225]**
(1) same boiling point but different freezing point
(2) same freezing point but different boiling point
(3) same boiling and same freezing points
(4) differnet boiling and freezing points

5. Two solutions of a substance (non electrolyte) are mixed in the following manner. 480 ml of 1.5 M first solution + 520 mL of 1.2 M second solution. What is the molarity of the final mixture?
[AIEEE-2005, 3/225]
(1) 1.20 M   (2) 1.50 M   (3) 1.344 M   (4) 2.70 M

6. 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 :   **[AIEEE-2005, 3/225]**
(1) 50   (2) 25   (3) 37.5   (4) 53.5

7. Density of a 2.05 M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is
[AIEEE-2005, 3/165]
(1) 3.28 mol Kg^{-1} (2) 2.28 mol Kg^{-1} (3) 0.44 mol Kg^{-1} (4) 1.14 mol Kg^{-1}

8. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be :   **[AIEEE-2007, 3/120]**
(1) 700   (2) 360   (3) 350   (4) 300

Resonance® Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in
Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029

ADVSCP - 55

9. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60g mol^{-1}) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 g cm^{-3}, molar mass of the substance will be **[AIEEE-2007, 3/120]**
(1) 105.0 g mol^{-1} (2) 210.0 g mol^{-1} (3) 90.0 g mol^{-1} (4) 15.0 g mol^{-1}

10. The vapour pressure of water at 20°C is 17.5 mm Hg. If 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water at 20°C, the vapour pressure of the resulting solution will be : **[AIEEE-2008, 3/105]**
(1) 15.750 mm Hg   (2) 16.500 mm Hg   (3) 17.325 mm Hg   (4) 17.675 mm Hg

11. 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 80º C and 1 atm pressure, the amount of 'A' in the mixture is (1 atm = 760 mm Hg) **[AIEEE-2008, 3/105]**
(1) 34 mol percent   (2) 48 mol percent   (3) 50 mol percent   (4) 52 mol percent

12. A binary liquid solution is prepared by mixing n-heptane and ethanol. Which one of the following statement is correct regarding the behaviour of the solution ? **[AIEEE-2009, 4/144]**
(1) The solution is non-ideal, showing +ve deviation from Raoult's Law.
(2) The solution in non-ideal, showing –ve deviation from Raoult's Law.
(3) n-heptane shows +ve deviation while ethanol shows –ve deviation from Raoult's Law.
(4) The solution formed is an ideal solution.

13. Two liquids X and Y form an ideal solution. At 300K, vapour pressure of the solution containing 1 mol of X and 3 mol of Y is 550 mmHg. At the same temperature, if 1 mol of Y is further added to this solution, vapour pressure of the solution increases by 10 mmHg. Vapour pressure (in mmHg) of X and Y in their pure states will be, respectively : **[AIEEE-2009, 8/144]**
(1) 300 and 400   (2) 400 and 600   (3) 500 and 600   (4) 200 and 300

14. If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (ΔT_f), when 0.01 mole of sodium sulphate is dissolved in 1 kg of water, is (K_f = 1.86 K kg mol^{-1}) **[AIEEE-2010, 4/144]**
(1) 0.0372 K   (2) 0.0558 K   (3) 0.0744 K   (4) 0.0186 K

15. On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively. Vapour pressure of the solution obtained by mixing 25.0 g of heptane and 35 g of octane will be (molar mass of heptane = 100 g mol^{-1} and of octane = 114 g mol^{-1}) **[AIEEE-2010, 4/144]**
(1) 72.0 kPa   (2) 36.1 kPa   (3) 96.2 kPa   (4) 144.5 kPa

16. K_f for water is 1.86 K kg mol^{-1}. If your automobile radiator holds 1.0 kg of water, how may grams of ethylene glycol ($C_2H_6O_2$) must you add to get the freezing point of the solution lowered to –2.8ºC ? **[AIEEE 2012, 4/120]**
(1) 72 g   (2) 93 g   (3) 39 g   (4) 27 g

17. Consider separate solution of 0.500 M C_2H_5OH(aq), 0.100 M $Mg_3(PO_4)_2$(aq), 0.250 M KBr(aq) and 0.125 M Na_3PO_4(aq) at 25°C. Which statement is **true** about these solution, assuming all salts to be strong electrolytes ? **[AIEEE 2014, 4/120]**
(1) They all have the same osmotic pressure.
(2) 0.100 M $Mg_3(PO_4)_2$(aq) has the highest osmotic pressure.
(3) 0.125 M Na_3PO_4(aq) has the highest osmotic pressure.
(4) 0.500 M C_2H_5OH(aq) has the highest osmotic pressure.

18. The vapour pressure of acetone at 20ºC is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20ºC, its vapour pressure was 183 torr. The molar mass (g mol^{-1}) of the substance is: **[JEE(Main) 2015, 4/120]**
(1) 32   (2) 64   (3) 128   (4) 488

19. 18 g glucosse ($C_6H_{12}O_6$) is added to 178.2 g water. The vapor pressure of water (in torr) for this aqueous solution is. **[JEE(Main) 2016, 4/120]**
(1) 76.0   (2) 752.4   (3) 759.0   (4) 7.6

Resonance®
Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in
Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029

ADVSCP - 56

20. The freezing point of benzene decreases by 0.45ºC when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be : (K_f for benzene = 5.12 K kg mol^{-1}) **[JEE(Main) 2017, 4/120]**
(1) 80.4% (2) 74.6% (3) 94.6% (4) 64.6%

21. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point ? **[JEE(Main) 2018, 4/120]**
(1) $[Co(H_2O)_4Cl_2]Cl.2H_2O$ (2) $[Co(H_2O)_3Cl_3].3H_2O$
(3) $[Co(H_2O)_6]Cl_3$ (4) $[Co(H_2O)_5Cl]Cl_2.H_2O$

JEE(MAIN) ONLINE PROBLEMS

1. Choose the correct statement with respect to the vapour pressure of a liquid among the following :
[JEE(Main) 2014 Online (19-04-14), 4/120]
(1) Increases linearly with increasing temperature
(2) Increase non-linearly with increasing temperature
(3) Decreases linearly with increasing
(4) Decreases non-linearly with increasing temperature

2. The observed osmotic pressure for a 0.10 M solution of $Fe(NH_4)_2(SO_4)_2$ at 25ºC is 10.8 atm experimental (observed) and theoritical values of Van't Hoff factor (i) will be respectively : (R = 0.082 L atm k^{-1} mol^{-1}) **[JEE(Main) 2014 Online (19-04-14), 4/120]**
(1) 5 and 4.42 (2) 4 and 4.00 (3) 5 and 3.42 (4) 3 and 5.42

3. For an ideal solution of two components A and B, which of the following is true ?
[JEE(Main) 2014 Online (19-04-14), 4/120]
(1) $\Delta H_{mixing} < 0$ (zero)
(2) $\Delta H_{mixing} > 0$ (zero)
(3) A–B interaction is stronger than A–A and B–B interactions
(4) A–A, B–B and A–B interactions are identical

4. A solution at 20ºC is composed of 1.5 mol of benzene and 3.5 mol of toluene. If the vapour pressure of pure benzene and pure toluene at this temperature are 74.7 torr and 22.3 torr, respectively, then the total vapour pressure of the solution and the benzene mole fraction in equilibrium with it will be, respectively : **[JEE(Main) 2015 Online (10-04-15), 4/120]**
(1) 35.0 torr and 0.480 (2) 30.5 torr and 0.389
(3) 38.0 torr and 0.589 (4) 35.8 torr and 0.280

5. Determination of the molar mass of acetic acid in benzene using freezing point depression is affected by : **[JEE(Main) 2015 Online (10-04-15), 4/120]**
(1) partial ionization (2) dissociation
(3) complex formation (4) association

6. The solubility of N_2 in water at 300 K and 500 torr partial pressure is 0.01 g L^{-1}. The solubility (in g L^{-1}) at 750 torr partial pressure is : **[JEE(Main) 2016 Online (09-04-16), 4/120]**
(1) 0.02 (2) 0.015 (3) 0.0075 (4) 0.005

7. An aqueous solution of a salt MX_2 at certain temperature has a van't Hoff factor of 2. The degree of dissociation for this solution of the salt is : **[JEE(Main) 2016 Online (10-04-16), 4/120]**
(1) 0.67 (2) 0.33 (3) 0.80 (4) 0.50

8. 5 g of Na_2SO_4 are was dissolved in x g of H_2O. The change in freezing point was found to be 3.82ºC. If Na_2SO_4 is 81.5% ionised, the value of x (K_f for water = 1.86ºC kg mol^{-1}) is approximately :
(molar mass of S = 32 g mol^{-1} and that of Na = 23 g mol^{-1}) **[JEE(Main) 2017 Online (08-04-17), 4/120]**
(1) 45 g (2) 65 g (3) 25 g (4) 15 g

9. A solution is prepared by mixing 8.5 g of CH_2Cl_2 and 11.95 g of $CHCl_3$. If vapour pressure of CH_2Cl_2 and $CHCl_3$ at 298 K are 415 and 200 mmHg respectively, the mole fraction of $CHCl_3$ in vapour form is :
(Molar mass of Cl = 35.5 g mol^{-1}) **[JEE(Main) 2017 Online 09-04-17), 4/120]**
(1) 0.675 (2) 0.162 (3) 0.486 (4) 0.325

Resonance®
Educating for better tomorrow
Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in
Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029
ADVSCP - 57

10. Two 5 molal solutions are prepared by dissolving a non-electrolyte non-volotatile solute separately in the solvents X and Y. The molecular weights of the solvents are M_X and M_Y, respectively where $M_X = \frac{3}{4} M_Y$. The relative lowering of vapour pressure of the solution in X is "m" times that of the solution in Y. Given that the number of moles of solute is very small in comparison to that of solvent, the value of "m" is : **[JEE(Main) 2018 Online 15-04-18), 4/120]**

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

11. 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 %, is : **[JEE(Main) 2018 Online 16-04-18), 4/120]**
(1) 37.5 g   (2) 75 g   (3) 150 g   (4) 50 g

12. Which one of the following statements regarding Henry's law is not correct ?
[JEE(Main) 2019 Online 09-01-19), 4/120]
(1) Different gases have different K_H (Henry' law constant) values at the same temperature.
(2) The value of K_H increases with increase of temperature and K_H is function of the nature of the gas
(3) The partial pressure of the gas in vapour phase is proportional to the mole fraction of the gas in the solution.
(4) Higher the value of K_H at a given pressure, higher is the solubility of the gas in the liquids.

13. A solution containing 62 g ethylene glycol in 250 g water is cooled to -10°C. If K_f for water is 1.86 K kg mol^{-1}, the amount of water (in g) separated as ice is: **[JEE(Main) 2019 Online 09-01-19), 4/120]**
(1) 16   (2) 32   (3) 48   (4) 64

14. Liquids A and B form an ideal solution in the entire composition range. At 350 K, the vapor pressures of pure A and pure B are 7×10^3 Pa and 12×10^3 Pa, respectively. The composition of the vapor in equilibrium with a solution containing 40 mole percent of A at this temperature is :
[JEE(Main) 2019 Online 10-01-19), 4/120]
(1) $x_A = 0.28$; $x_B = 0.72$ (2) $x_A = 0.76$; $x_B = 0.24$
(3) $x_A = 0.37$; $x_B = 0.63$ (4) $x_A = 0.4$; $x_B = 0.6$

15. Elevation in the boiling point for 1 molal solution of glucose is 2 k. The depression in the freezing point for 2 molal solution of glucose in the same solvent is 2 k. the relation between k_b and K_f is :
[JEE(Main) 2019 Online 10-01-19), 4/120]
(1) $K_b = 0.5 K_f$ (2) $K_b = K_f$ (3) $K_b = 1.5 K_f$ (4) $k_b = 2 k_f$

16. The freezing point of a diluted milk sample is found to be -0.2°C, while it should have been -0.5°C for pure milk. How much water has been added to pure milk to make the diluted sample ?
[JEE(Main) 2019 Online 11-01-19), 4/120]
(1) 1 cup of water to 3 cups of pure milk   (2) 1 cup of water of 2 cups of pure milk
(3) 2 cups of water to 3 cups of pure milk   (4) 3 cups of water to 2 cups of pure milk

17. K_2HgI_4 is 40% ionised in aqueous solution. The value of its van't Hoff factor (i) is :
[JEE(Main) 2019 Online 11-01-19), 4/120]
(1) 1.8   (2) 1.6   (3) 2.0   (4) 2.2

18. Freezing point of a 4% aqueous solution of X is equal to freezing point of 12% aqueous solution of Y. If molecular weight of X is A, then molecular weight of Y is: **[JEE(Main) 2019 Online 12-01-19), 4/120]**
(1) 4A   (2) 2A   (3) 3A   (4) A

19. Molecules of benzoic acid (C_6H_5COOH) dimerise in benzene. 'w' g of the acid dissolved in 30 g of benzene shows a depression in freezing point equal to 2 K. If the percentage association of the acid to form dimer in the solution is 80, then w is : **[JEE(Main) 2019 Online 12-01-19), 4/120]**
(Given that $K_f = 5$ kg mol^{-1}, Molar mass of benzoic acid = 122 g mol^{-1})
(1) 2.4 g   (2) 1.8 g   (3) 1.0 g   (4) 1.5 g

Resonance®
Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in
Toll Free : 1800 258 5555 | **CIN:** U80302RJ2007PLC024029

ADVSCP - 58

Answers

EXERCISE - 1

PART - I

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

A-2. Certain compounds combine with the moisture of atmosphere and are converted into hydroxides or hydrates. Such substances are called hygroscopic. e.g., anhydrous $CuSO_4$, quick lime (CaO), anhydrous Na_2CO_3 etc.

A-3. The overall energy change associated with dissolution depends on the relative magnitude of the solute–solute, solvent–solvent and solute–solvent interactions. The process is exothermic if the new interaction release more energy than disrupting the old interactions requires, it is endothermic if opposite is true.

B-1. 0.04 g/mL **B-2.** (i) 30%, (ii) 0.046 (iii) Na^+ = 5.42 m, $S_2O_3^{2-}$ = 2.71 m

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

C-1. P_{O_2} = 810 mm Hg, P_{H_2O} = 355 mm Hg , P_{total} = 1165 mm Hg **C-2.** 2.4 atm

D-1. 7.62 bar **D-2.** 4 mmol. **E-1.** 5.15 g **E-2.** $\dfrac{W_W}{W_N}$ = 3.973

F-1. p_A^0 = 400 mm of Hg, p_B^0 = 600 mm of Hg **F-2.** 27.3 mole %

F-3. P_B^0 = 0.7 atm & P_A^0 = 1.9 atm **F-4.** 14.16 mole percent benzene

F-5. Y'_B = 0.932. **G-1.** V < 80ml. **G-2.** There is positive deviation from Raoult's law, ΔS > 0.

H-1.

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

H-2. 75% **I-1.** (a) 60 g/mol, (b) 333.3 g **I-2.** 746.2 mm of Hg

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

J-4. 1.075, 7.5. **K-1.** (a) Urea < NaCl < Na_2SO_4 < Na_3PO_4 (b) 6.15 atm

K-2. α = 0.81 **K-3.** 50% K_2SO_4 **K-4.** Volume must have been made 5 times

PART - II

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

Resonance® Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in
Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029

ADVSCP - 59

J-7.	(A)	**J-8.**	(B)	**J-9.**	(B)	**K-1.**	(C)	**K-2.**	(A)
K-3.	(A)	**K-4.**	(A)						

PART - III

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

EXERCISE - 2

PART - I

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

PART - II

1.	18	**2.**	5	**3.**	21	**4.**	20	**5.**	27
6.	4 (A,B,C,D)	**7.**	2	**8.**	48	**9.**	43	**10.**	2
11.	60	**12.**	60	**13.**	4				

PART - III

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

PART - IV

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

EXERCISE - 3

PART - I

1.	(C)	**2.**	(B)	**3.**	(B)	**4.**	(A)	**5.**	(C)
6.	122, 224	**7.**	(A)	**8.**	(A)	**9.**	(D)	**10.**	(B)
11.	(B)	**12.**	(A)	**13.**	(A)	**14.**	(A)	**15.**	(BCD)
16.	2	**17.**	(1)	**18.**	(AB)	**19.**	(BD)	**20.**	(A)
21.	19	**22.**	0.05						

PART - II
JEE(MAIN) OFFLINE PROBLEMS

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

JEE(MAIN) ONLINE PROBLEMS

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

Resonance® Educating for better tomorrow	**Reg. & Corp. Office :** CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005	
	Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in	**ADVSCP - 60**
	Toll Free : 1800 258 5555 | **CIN:** U80302RJ2007PLC024029	

Additional Problems for Self Practice (APSP)

✎ **Marked questions are recommended for Revision.**

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

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Marks : 120   **Max. Time : 1 Hr.**

Important Instructions :
1. The test is of **1 hour** duration.
2. The Test Booklet consists of **30** questions. The maximum marks are **120.**
3. Each question is allotted **4 (four)** marks for correct response.
4. Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question.
    ¼ (one fourth) marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
5. There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.

---

1. Mole fraction of $C_3H_5(OH)_3$ in a solution of 36 g of water and 46 g of glycerine is :
    (1) 0.46   (2) 0.36   (3) 0.20   (4) 0.40

2.✎ Colligative properties have many practical uses, some of them may be :
    I : Melting of snow by salt
    II : Desalination of sea water
    III : Determination of molar mass
    IV : Determination of melting point and boiling point of solvent
    Actual practical uses are :
    (1) I, II   (2) III, IV   (3) I, II, III   (4) II, III, IV

3. Select correct statement(s) :
    (1) When solid $CaCl_2$ is added to liquid water, the boiling temperature rises
    (2) When solid $CaCl_2$ is added to ice at 0°C, the freezing temperature falls
    (3) Both (1) and (2)
    (4) None of the above

4.✎ If $pK_a = - \log K_a = 4$, and $K_a = Cx^2$ then Van't Hoff factor for weak monobasic acid when C = 0.01 M is :
    (1) 1.01   (2) 1.02   (3) 1.10   (4) 1.20

5. Consider following terms (m = molality) :

    I : mK_b ;   II : $mK_b i$ III : $\dfrac{\Delta T_b}{i}$ IV : K_b

    Terms which can be expressed in degree (temperature) are
    (1) III, IV   (2) I, II   (3) I, II, IIII   (4) I, III

6. Elevation in b.p. of an aqueous urea solution is 0.52°. ($K_b = 0.52° \ mol^{-1} \ kg$) Hence, mole-fraction of urea in this solution is :
    (1) 0.982   (2) 0.567   (3) 0.943   (4) 0.018

7.✎ Insulin $(C_2H_{10}O_5)_n$ is dissolved in a suitable solvent and the osmotic pressure π of the solution of various concentration (in kg/m^3) is measured at 20ºC. The slope of a plot of π against c is found to be 8.134 × 10^{-3} (SI units) The molecular weight of the insulin (in kg/mol) is :
    (1) 4.8×10^5 (2) 9×10^5 (3) 293×10^3 (4) 8.314×10^5

---

8. What is the normal boiling point of the solution represented by the phase diagram ?
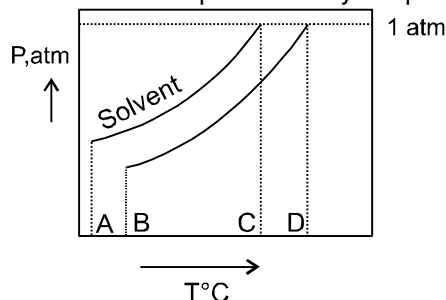
(1) A   (2) B   (3) C   (4) D

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

10. Density of 1M solution of a non-electrolyte $C_6H_{12}O_6$ is 1.18 g/mL. If K_f (H_2O) is 1.86° mol^{-1} kg, solution freezes at :
(1) – 1.58°C   (2) – 1.86°C   (3) – 3.16°C   (4) 1.86°C

11. Mole fraction of a non-electrolyte in aqueous solution is 0.07. If K_f is 1.86° mol^{-1} kg, depression in f.p., ΔT_f, is:
(1) 0.26°   (2) 1.86°   (3) 0.13°   (4) 7.78°

12. What is the normal freezing point of the solution represented by the phase diagram ?
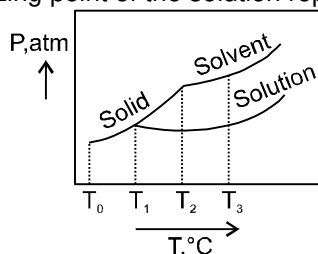
(1) T_1 (2) T_2 (3) T_3 (4) T_0

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

14. A colligative property of a solution depends on the :
(1) arrangement of atoms in solute molecule   (2) total number of molecules of solute and solvent
(3) number of molecules of solute in solution   (4) mass of the solute molecules

15. Which has maximum freezing point ?
(1) 6g urea solution in 100 g H_2O (2) 6g acetic acid solution in 100g H_2O
(3) 6g sodium chloride in 100 g H_2O (4) All have equal freezing point

16. Select correct statements :
(1) The fundamental cause of all colligative properties is the higher entropy of the solution relative to that of the pure solvent
(2) The freezing point of hydrofluoride solution is larger than that of equimolal hydrogen chloride solution
(3) 1M glucose solution and 0.5 M NaCl solution are isotonic at a given temperature
(4) All are correct statements

17. The vapour pressure of a pure liquid A is 40 mmHg at 310 K. The vapour pressure of this liquid in a solution with liquid B is 32 mmHg. Mole fraction of A in the solution, if it obeys Raoult's law is :
(1) 0.8   (2) 0.5   (3) 0.2   (4) 0.4

18. Mole fraction of the toluene in the vapour phase which is in equilibrium with a solution of benzene ($p° = 120$ Torr) and toluene ($p° = 80$ Torr) having 2.0 mol of each is
(1) 0.50   (2) 0.25   (3) 0.60   (4) 0.40

19. An azeotropic solution of two liquids has a boiling point lower than either of them when it :
(1) shows negative deviation from Raoult's law   (2) shows positive deviation from Raoult's low
(3) shows ideal behaviour   (4) is saturated

20. Depression of freezing point of 0.01 molal aq. CH_3COOH solution is 0.02046°. 1 molal urea solution freezes at $– 1.86°C$. Assuming molality equal to molarity, pH of CH_3COOH solution is :
(1) 2   (2) 3   (3) 3.2   (4) 4.2

21. Which of the following azeotropic solutions has the boiling point more than boiling point of the constituents A and B ?
(1) CH_3CH_2OH and CH_3COCH_3 (2) CS_2 and CH_3COCH_3
(3) $CHCl_3$ and CH_3COCH_3 (4) CH_3CHO and CS_2

22. A 0.50 molal solution of ethylene glycol in water is used as coolant in a car. If the freezing point constant of water is 1.86° per molal, at which temperature will the mixture freeze ?
(1) 1.56°C   (2) – 0.93°C   (3) – 1.86°C   (4) 0.93°C

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

24. On mixing 10 mL of acetone with 40 mL of chloroform , the total volume of the solution is :
(1) < 50 mL   (2) > 50 mL   (3) = 50 mL   (4) Cannot be predicted

25. Select correct statement ?
(1) Heats of vaporisation for a pure solvent and for a solution are similar because similar intermolecular forces between solvent molecules must be overcome in both cases
(2) Entropy change between solution and vapour is smaller than the entropy change between pure solvent and vapour
(3) Boiling point of the solution is larger than that of the pure solvent
(4) All are correct statements

26. What will be the molecular weight of NaCl determined experimentally from elevation in the boiling point or depression in freezing point method ?
(1) < 58.5   (2) > 58.5   (3) = 58.5   (4) None of these

27. Which characterises the weak intermolecular forces of attraction in a liquid ?
(1) High boiling point   (2) High vapour pressure
(3) High critical temperature   (4) High heat of vaporization

28. On the basis of intermolecular forces predict the correct order of decreasing boiling points of the compounds:
(1) $CH_3OH > H_2 > CH_4$ (2) $CH_3OH > CH_4 > H_2$ (3) $CH_4 > CH_3OH > H_2$ (4) $H_2 > CH_4 > CH_3OH$

29. During depression of freezing point in a solution the following are in equilibrium :
(1) Liquid solvent, solid solvent   (2) Liquid solvent, solid solute
(3) Liquid solute, solid solute   (4) Liquid solute, solid solvent

30. Which of the following liquid pairs shows a positive deviation from Raoult's law ?
(1) Acetone – chloroform   (2) Benzene – methanol
(3) Water – nitric acid   (4) Water – hydrochloric acid

# Practice Test-1 (IIT-JEE (Main Pattern))
OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27	28	29	30
Ans.										

PART - II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

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

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

3. Consider 1 M solutions of the following salts. State which solution will have the lowest freezing point.
   [NSEC-2000]
   (A) Na_2SO_4 (B) $BaCl_2$ (C) $NaCl$ (D) $Al(NO_3)_3$

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

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

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

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

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

9. Which gas is mixed with oxygen by sea-divers at the high underwater pressure ? **[NSEC-2002]**
   (A) Nitrogen   (B) Neon   (C) Helium   (D) Argon.

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

11. For water, the maximum number of phases that can be in equilibrium is **[NSEC-2004]**
    (A) 1   (B) 2   (C) 3   (D) 4.

12. The boiling point of a glucose solution is higher than that of water because **[NSEC-2004]**
(A) glucose forms extensive hydrogen bonding with water
(B) glucose does not dissociate in water
(C) its vapour pressure is higher than that of water at a given temperature
(D) its vapour pressure is lower than that of water at a given temperature.

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

14. From among the following, the aqueous solution which has the highest freezing point depression is : **[NSEC-2005]**

(A) 0.1 M $Sr(NO_3)_2$ (B) 0.1 M KCl   (C) 0.1 M HNO_3 (D) 0.1 M glucose.

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

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

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

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

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

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

21. According to this phase diagram, which phases can exist at pressures lower than the triple point pressure ?
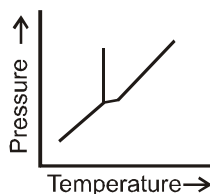
(A) gas only   (B) solid and gas only
(C) liquid only   (D) solid and liquid only

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

23. 20 g of Compound X are dissolved in 500 mL of water and the osmotic pressure of the resulting solution is 500mm of Hg of 10°C. The average molecular mass of X is **[NSEC-2010]**
(A) 1115.42   (B) 1150.70   (C) 1412.84   (D) 1163.88

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

Resonance®
Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in
Toll Free : 1800 258 5555 | **CIN:** U80302RJ2007PLC024029

ADVSCP - 65

25. The aqueous solution having osmotic pressure nearest to that of an equimolar solution of $K_4[Fe(CN)_6]$ is
[NSEC-2010]

(A) K_2SO_4 (B) Na_3PO_4 (C) $Al_2(SO_4)_3$ (D) $C_6H_{12}O_6$

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

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

28. The inorganic precipitate which acts as a semipermeable membrane is   **[NSEC-2012]**
(A) Calcium phosphate   (B) Nickel phosphate   (C) Plaster of paris   (D) Copper ferrocyanide

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

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

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

32. The vapor pressure of benzene is 53.3 kPa at 60.3ºC, but it fall to 51.5 kPa when 19 g of a nonvolatile organic compound is dissolved in 500g benzene. The molar mass of the nonvolatile compound is
[NSEC-2015]

(A) 82   (B) 85   (C) 88   (D) 92

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

34. In cold climate, the water in a radiator of car gets frozen causing damage to the radiator. Ethylene glycol is used as an antifreezing agent. The amount of ethylene glycol that should be added to 5 kg of water to prevent it from freezing at –7ºC is :   **[NSEC-2016]**
(Given : K_f for water = 1.86 K mol^{-1} kg ; Molar mass of ethylene gycol = 62 g mol^{-1})
(A) 1165 g   (B) 46.7 g   (C) 116.7 g   (D) 93.4 g

35. Which of the following is correct ?   **[NSEC-2017]**
A liquid with
(A) low vapour pressure will have a low surface tension and high boiling point
(B) high vapour pressure will have high intermolecular forces and high boiling point
(C) low vapour pressure will have high surface tension and high boiling point
(D) low vapour pressure will have low surface tension and low boiling point
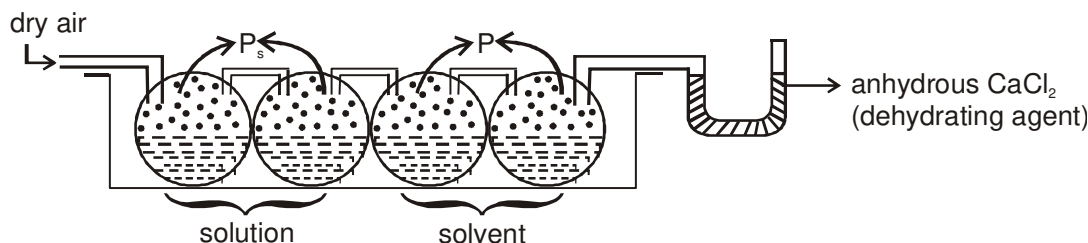
PART - III : HIGH LEVEL PROBLEM (HLP)

THEORY

Ostwald–Walker Method :

Experimental or lab determination of relative lowering of vapoure pressure i.e. $\dfrac{\Delta P}{P^0}$ **or** $\dfrac{\Delta P}{P_s}$.

(i) Initially note down the weights of the solution set, solvent set containers & of dehydrating agent before start of experiment.

(ii) Note down the same weights after the experiment is complete.

Loss of weight of solution containers $\propto P_s$.

Loss of in weight of solvent containers $\propto (P^\circ - P_s)$

gain in weight of dehydriating agent $\propto P^\circ$.

$$\frac{P^\circ - P_s}{P^\circ} = \frac{\text{loss in weight of solvent}}{\text{loss in weight of solution}}$$

$$\frac{P^\circ - P_s}{P_s} = \frac{\text{loss is weight of solvent}}{\text{gain is weight of dehydrating agent}} = \frac{w}{m} \times \frac{M}{W} = (\text{molality}) \times \frac{M}{1000}$$

Suppose, dry air was passed through a solution of 5 g of a solute in 80 g of water & then it is passed through pure water. Loss in weight of solution was 2.50 g & loss in weight of pure water was 0.04 g. Then, to find molecular weight of the solute, we have

$$\frac{P^\circ - P_s}{P_s} = \frac{\text{loss in wt. of solvent}}{\text{loss in wt. of solution}}$$

$$\frac{P^\circ - P_s}{P_s} = \frac{0.04}{2.50} = \frac{w}{m} \times \frac{M}{W} = \frac{5}{m} \times \frac{18}{80}.$$ Thus. m = molecular weight of the solute = 70 g/mol.

Solved Examples

Example-1 :
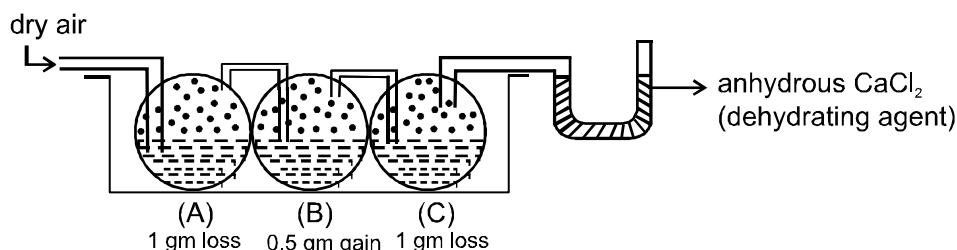
If same volume solution of different solute is used then what is order of (a) vapour pressure (b) moles of solute (c) molar mass of solute.

Solution : $P_A \propto 1$ g.   ; $P_A - P_B \propto 0.5$ g, $P_B \propto 0.5$ g.

$P_C - P_B \propto 1$ g   ; $P_C \propto 1.5$ g.

$P_C > P_A > P_B$; $n_C < n_A < n_B$.   ; $M_C > M_A > M_B$.

SUBJECTIVE QUESTIONS

1. Dry air was passed through bulbs containing a solution of 40 grams of non-volatile electrolytic solute in 360 grams of water, then through bulbs containing pure water at the same temperature and finally through a tube in which pumice moistened with strong H_2SO_4 was kept. The water bulbs lost 0.0870 grams and the sulphuric acid tube gained 2.175 grams. Calculate the molecular weight of solute.

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

ONLY ONE OPTION CORRECT TYPE

**3.** The vapour pressure of two pure liquids A and B, that form an ideal solution are 100 and 900 torr respectively at temperature T. This liquid solution of A and B is composed of 1 mole of A and 1 mole of B. What will be the pressure, when 1 mole of mixture has been vapourized ?
(A) 800 torr   (B) 500 torr   (C) 300 torr   (D) None of these

4. A maxima or minima obtained in the temperature composition curve of a mixture of two liquids indicates
(A) an azeotropic mixture
(B) an eutectic formation
(C) that the liquids are immiscible with one another
(D) that the liquids are partially miscible at the maximum or minimum

5. At a constant temperature, ΔS will be maximum for which of the following processes :
(A) Vaporisation of a pure solvent
(B) Vaporisation of solvent from a solution containing nonvolatile and nonelectrolytic solute in it
(C) Vaporisation of solvent from a solution containing nonvolatile but electrolytic solute in it
(D) Entropy change will be same in all the above cases

6. The freezing point of aqueous solution that contains 3% urea, 7.45% KCl and 9% of glucose is (given K_f of water = 1.86 and asume molarity = molality).
(A) 290 K   (B) 285.5 K   (C) 267.42 K   (D) 250 K

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

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

9. Pressure cooker reduces cooking time because
(A) the heat is more evenly distributed inside the cooker.
(B) a large flame is used.
(C) boiling point of water is elevated.
(D) whole matter is converted into steam.

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

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

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

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

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

Resonance® Educating for better tomorrow	**Reg. & Corp. Office :** CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
	Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in
	Toll Free : 1800 258 5555 | **CIN:** U80302RJ2007PLC024029

ADVSCP - 68

11. Assuming the formation of an ideal solution, determine the boiling point of a mixture containing 1560 g benzene (molar mass = 78) and 1125 g chlorobenzene (molar mass = 112.5) using the following against an external pressure of 1000 Torr.
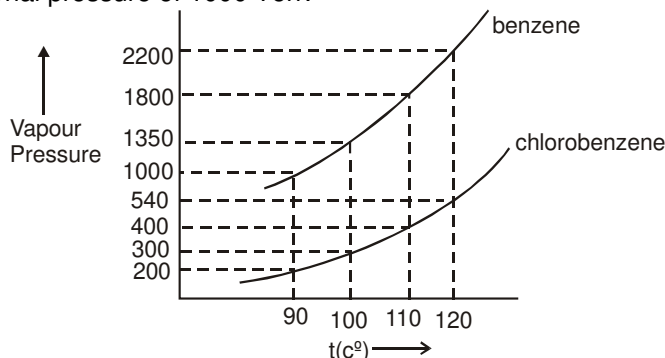
(A) 90ºC   (B) 100ºC   (C) 110º   (D) 120ºC

12. Dry air is slowly passed through three solutions of different concentrations, c_1, c_2 and c_3 ; each containing (non volatile) NaCl as solute and water as solvent, as shown in the Fig. If the vessel 2 gains weight and the vessel 3 loses weight, then
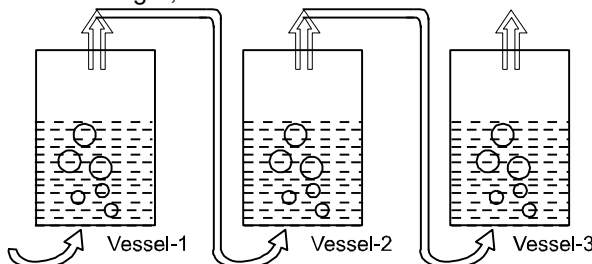
(A) $c_2 > c_3$ (B) $c_1 < c_2$ (C) $c_1 < c_3$ (D) Both (A) and (B)

13. For a solution of 0.849 g of mercurous chloride in 50 g of $HgCl_2(\ell)$ the freezing point depression is 1.24ºC. K_f for $HgCl_2$ is 34.3. What is the state of mercurous chloride in $HgCl_2$? (Hg – 200, Cl – 35.5)
(A) as Hg_2Cl_2 molecules   (B) as HgCl molecules
(C) as Hg^+ and Cl^- ions   (D) as Hg_2^{2+} and Cl^- ions

14. The vapor pressures of chlorobenzene and water at different temperatures are

t/ºC	90	100	110
$P^o(\phi Cl)$/mm Hg	204	289	402
$P^o(H_2O)$/mm Hg	526	760	1075

At what temperature will ϕCl steam-distillation under a total pressure of 800 mmHg?
(A) ≈ 95ºC   (B) ≈ 92ºC   (C) ≈ 94ºC   (D) ≈ 89ºC

MATCH THE COLUMN

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

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

Resonance® Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | **E-mail :** contact@resonance.ac.in
**Toll Free :** 1800 258 5555 | **CIN:** U80302RJ2007PLC024029

ADVSCP - 69

SINGLE AND DOUBLE VALUE INTEGER TYPE

16. The vapour pressure of fluorobenzene at t°C is given by the equation

$$\log p \text{ (mm Hg)} = 7.0 - \frac{1250}{t + 220}$$

Calculate the boiling point of the liquid in ºC if the external (applied) pressure is 5.26% more than required for normal boiling point. ($\log 2 = 0.3$)

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

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

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

20. Dry air was successively passed through a solution of 5g solute in 80 g water and then through pure water. The loss in weight of solution was 2.5 g and that of pure water was 0.04 g. What is mol. wt of solute ?

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

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

22. The diagram given below represents boiling point composition diagram of solution of components A and B, which is/are incorrect among the following?
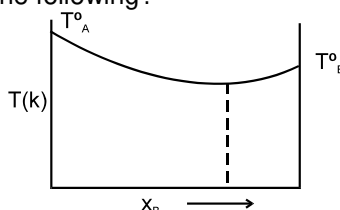
(A) The solution shows negative deviation
(B) A-B-interactions are stronger than A-A and B-B
(C) The solution is ideal solution
(D) The solution shows positive deviation.

23. For a dilute solution having molality m of a given solute in a solvent of mol.wt. M, b.pt. T_b and heat of

vaporisation per mole ΔH; $\left[\dfrac{\partial T_b}{\partial m}\right]_{m \to 0}$ is equal to :

(A) Molal elevation constant of solvent

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

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

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

PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.   **Max. Marks : 66**

Important Instructions
A.   General :
1.   The test is of 1 hour duration.
2.   The Test Booklet consists of 22 questions. The maximum marks are 66.
B.   Question Paper Format :
3.   Each part consists of five sections.
4.   Section 1 contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
5.   Section 2 contains 5 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
6.   Section 3 contains 6 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
7.   Section 4 contains 1 paragraphs each describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a partcular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
8.   Section 5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.
**C.   Marking Scheme :**
9.   For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (– 1) mark will be awarded.
10.   For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
11.   For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

SECTION-1 : (Only One option correct Type)
This section contains 7 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

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

2.   The melting points of most of the solid substances increases with an increase of pressure acting on them. However, ice melts at a temperature lower than its usual melting point , when the pressure increases. This is because :
(A) Ice is less dense than water   (B) Pressure generates heat
(C) The bonds break under pressure   (D) Ice is not a true solid

3.   The phase diagrams for the pure solvent (solid lines) and the solution (non-volatile solute, dashed line) are recorded below : The quantity indicated by L in the figure is :
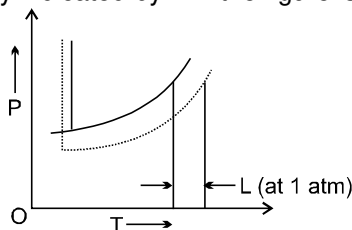
(A) Δp (B) ΔT_f (C) $K_b m$ (D) $K_f m$

---

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

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

5. A teacher one day pointed out to his students the peculiar fact that water is unique liquid which freezes exactly at 0^0 C and boils exactly at 100^0 C. He asked the students to find the correct statement based on this fact :

(A) Water dissolves anything however sparingly the dissolution may be

(B) Water is a polar molecule

(C) Boiling and freezing temperatures of water were used to define a temperature scale

(D) Liquid water is denser than ice

6. Three different ideal solutions (I, II, III) each containing total 10 moles of A & B in different composition are taken as shown in figure and pressure over the solutions is gradually reduced.

Initially external pressure is same for all three solutions. At a particular external pressure (P_1), II solution is found to have

$X_A = 0.4$ & $Y_A = 0.8$

(liq composition)   (Vap. composition)

Then select correct statement :

(A) At the same external pressure, for solution I, $X_A < 0.4$, $Y_A < 0.8$.

(B) At the same external pressure, for solution III, $X_A > 0.4$, $Y_A > 0.8$.

(C) For all three solutions at same external pressure (P_1) liquid & vapour composition will be same

(D) None of these.

7. For an ideal binary solution with P^o_A / P^o_B which relation between X_A (mole fraction of A in liquid phase) and Y_A (mole fraction of A in vapour phase) is correct , X_B and Y_B are mole fraction of B in liquid and vapour phase respectively : (Given : $P^o_A > P^o_B$)

(A) $X_A = Y_A$ (B) $X_A > Y_A$

(C) $\dfrac{X_A}{X_B} < \dfrac{Y_A}{Y_B}$ (D) X_A, Y_A, X_B and Y_B cannot be correlated
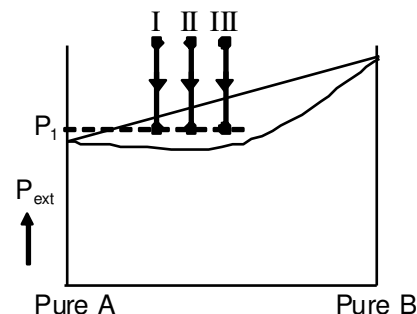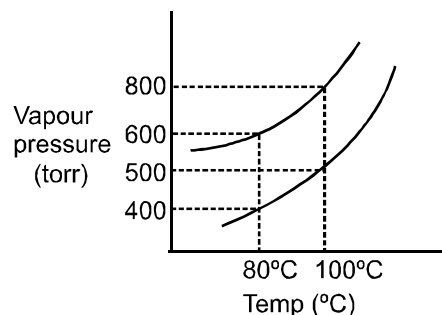

Section-2 : (One or More than one options correct Type)
This section contains 5 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

---

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

(A) K_H is characteristic constant for a given gas–solvent system.

(B) Higher is the value of K_H, lower is solubility of gas for a given partial pressure of gas.

(C) K_H has temperature dependence.

(D) K_H increases with temperature.

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

(A) Vapour pressure of solution = 725 torr.

(B) at 725 torr pressure at 90ºC, no vapour form

(C) Composition of vapour is $\dfrac{2}{11}$ and $\dfrac{9}{11}$

(D) Composition of liquid remain same at equilibrium condition at any temp.

Resonance® Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005

Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in

Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029

ADVSCP - 72

10. Select incorrect statement :
(A) Na^+ and K^+ ions are responsible for maintaining isotonic property inside and outside of the cell of organism.
(B) Aquatic species are more comfortable in lakes present at sea level in comparison to lakes present at high altitude.
(C) Solubility of N_2 decreases, in presence of He when oxygen cylinder is utilised by Scuba divers.
(D) The K_H value of CO_2 is higher than K_H of N_2.

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

(A) $\dfrac{P_A^0 - P_B^0}{P_A} = \dfrac{n_B}{n_A}$ (B) $\dfrac{P_A^0 - P_B^0}{P_A} = \dfrac{n_B}{n_A + n_B}$ (C) $P_A^0 = \dfrac{P_A}{1 - X_B}$ (D) $\dfrac{P_A^0 - P_A}{P_A} = \dfrac{n_B}{n_A}$

12. 0.2 moles of A and 0.3 moles of B are taken in separate beakers and enclosed in chamber I. Another 0.2 moles of A and 0.3 moles of B are mixed in a beaker and enclosed in chamber II. At equilibrium. Which of the following are not true. (A and B are volatile liquids and they form ideal solution on mixing)
(A) The vapour pressure in chamber I is greater than vapour pressure in chamber II.
(B) The vapour pressure in chamber I is less than vapour pressure in chamber II.
(C) The vapour pressure in both chambers are equal.
(D) The vapour pressure in chamber II can not be determined.

Section-3 : (One Integer Value Correct Type.)
This section contains 6 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

---

13. A very small amount of a non-volatile solute (non-associative, non-dissociative) is dissolved in 100 cm³ of a solvent. At room temperature, vapour pressure of this solution is 98.7 mm of Hg while that of pure solvent is 100 mm of Hg. If the freezing temperature of this solution is 0.72 K lower than that of pure solvent, what is the value of cryoscopic constant of solvent (in K Kg/mol) ? Round off your answer to the nearest whole number. Report your answer as 0 (zero) if you find data insufficient.
Given : Molar mass of solvent = 78 g/mol.

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

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

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

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

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

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

SECTION-4 : Comprehension Type (Only One options correct)
This section contains 1 paragraphs, each describing theory, experiments, data etc. 3 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

Resonance® Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in
Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029

ADVSCP - 73

Paragraph for Questions 19 to 21

A solution is made by mixing 1 mole benzene (P_B° = 100 mm Hg) & 1 mole toluene (P_T° = 40 mm Hg).Suppose, initially the pressure over the solution is very high so that no vapour exist above the liquid. As we gradually decrease the pressure, a point (bubble point) comes when we aross the bubble point curve & first bubble of vapour starts forming (hence called bubble point curve). Now we have entered the vapour-liquid equilibrium region. On further decreasing the pressure, a point (dew point) comes when we cross the dew point curve then almost all the liquid has evaporated into vapour i.e. only the last drop of liquid (dew) remains. Beyond this point no liquid exist in the system. Then answer the following questions :

19. If the pressure over the mixture at 300 K is reduced, at what pressure does the first bubble form :
(A) 140 mm Hg   (B) 90 mm Hg   (C) 65 mm Hg   (D) 70 mm Hg

20. What is the composition of first bubble formed ?
(A) Y_A = 2/7, Y_B = 5/7   (B) Y_A = 3/7, Y_B = 4/7
(C) Y_A = 1/7, Y_B = 6/7   (D) none of these

21. What will be the pressure when 1 mole of mixture has been vapourised ?
(A) 70 mm Hg   (B) 63.25 mm Hg   (C) 100 mm Hg   (D) 40 mm Hg

---

SECTION-5 : Matching List Type (Only One options correct)
This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

---

22. Match each List-I with an appropriate pair of characteristics from List-II and select the correct answer using the code given below the lists.
0.1 mol of each solute in the list-I are dissolved in 10 mole water separately.

	List-I		List-II
P.	$AlCl_3$ if α = 0.8	1.	i = 3.4
Q.	$BaCl_2$ if α = 0.9	2.	has minimum osmotic pressure among the given solutions.
R.	Na_3PO_4 if α = 0.9	3.	has minimum freezing point among the given solutions.
S.	$K_4[Fe(CN)_6]$ if α = 0.7	4.	has RLVP = 37/1037.

Code :

	P	Q	R	S		P	Q	R	S
(A)	4	2	3	1	(B)	1	2	4	3
(C)	2	1	3	4	(D)	1	2	3	4

Practice Test-2 ((IIT-JEE (ADVANCED Pattern))
OBJECTIVE RESPONSE SHEET (ORS)

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

Resonance®
Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in
Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029

ADVSCP - 74

APSP Answers

PART - I

1.	(3)	**2.**	(3)	**3.**	(3)	**4.**	(3)	**5.**	(3)
6.	(4)	**7.**	(3)	**8.**	(4)	**9.**	(2)	**10.**	(2)
11.	(4)	**12.**	(1)	**13.**	(4)	**14.**	(3)	**15.**	(1)
16.	(4)	**17.**	(1)	**18.**	(4)	**19.**	(2)	**20.**	(2)
21.	(3)	**22.**	(2)	**23.**	(3)	**24.**	(1)	**25.**	(4)
26.	(1)	**27.**	(2)	**28.**	(2)	**29.**	(1)	**30.**	(2)

PART - II

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

PART - III

1.	M = 48	**2.**	10.33°C	**3.**	(C)	**4.**	(A)	**5.**	(A)
6.	(C)	**7.**	(C)	**8.**	(C)	**9.**	(C)	**10.**	(B)
11.	(B)	**12.**	(D)	**13.**	(A)	**14.**	(B)		

15. (A) – q, s; (B) – q, s; (C) – q, s; (D) – q, s   **16.** 85

17.	12 mol/litre.	**18.**	14	**19.**	3	**20.**	70	**21.**	(AB)
22.	(ABC)	**23.**	(ABD)						

PART - IV
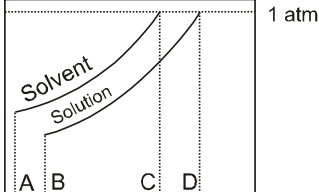
1.	(A)	**2.**	(A)	**3.**	(C)	**4.**	(A)	**5.**	(C)
6.	(C)	**7.**	(C)	**8.**	(ABCD)	**9.**	(AB)	**10.**	(CD)
11.	(AB)	**12.**	(ABD)	**13.**	4	**14.**	5	**15.**	9

16. 2   **17.** 4   **18.** $\dfrac{x}{y} = \dfrac{2}{1}$ Hence x + y = 3   **19.** (D)

20. (A)   **21.** (B)   **22.** (B)

APSP Solutions

PART - I

1. Mole of $H_2O = \dfrac{36}{18} = 2$; Mole of glycerine $= \dfrac{46}{92} = 0.5$

total mole $= 2 + 0.5 = 2.5$; Mole fractions of glycerine $= \dfrac{n_1}{n_1 + n_2} = \dfrac{0.5}{2.5}$ $X_0 = 0.2$ Ans.

2. I. Melting of snow by salt : Depression in freezing point
II. Desalination of sea water : Reverse osmosis
III. Osmosis is used to determine the molar mass.

3. When non volatile solute added to solvent. Due to elevation in boiling point↑ boiling pointand due to dispression in freezing point, freezing temperature ↓

4. $HA \rightleftharpoons H^+ + A^-$
$i = [1 + (y - 1)\, x] = 1 + x$
$pK_a = 4 = - \log K_a$
∴ $K_a = 10^{-4} = Cx^2$
$1 \times 10^{-4} = 0.01 \times x^2 \Rightarrow x = 0.1$ ∴ $i = 1 + x = 1.1$

5. As $\Delta T_b = i\, K_b m$
so $iK_b\, m$ can be expressed in degree (Unit of temperature)
and $K_b\, m$ can be expressed in degree (Unit of temperature)
and $\dfrac{\Delta T_b}{i}$ can be expressed in degree (Unit of temperature)
But unit of K_b is $mol^{-1}\, kg\, K$

6. As $\Delta T_b = $ molality $\times K_b$
$0.52 = m \times 0.52$
molality $= 1\, mol\, kg^{-1}$
∴ urea $= 1\, mol$
moles of water $= \dfrac{1000}{18} = 55.55$; mole fraction of urea $= \dfrac{1}{1 + 55.55} = \mathbf{0.018}$

7. $\pi = CRT$
$\pi = \dfrac{c}{M} RT$ $C = $ moles/liter, $c = kg/m^3$
$\dfrac{\pi}{c} = \dfrac{RT}{M}$
$M = \dfrac{RT}{\pi / c}$ $[\pi/c = 8.314 \times 10^{-3}]$
  $[T = 293\, k]$
$M = \dfrac{8.314 \times 293}{8.314 \times 10^{-3}} = 293 \times 10^3$

8.

Normal boiling point of the solution is that temperature at which vapour pressure of solution equals to 1 atm.

9. Given $\Delta T_b = 1.08ºC$, i = 2 at boiling pt. of solution.

and $\Delta T_f = 1.80ºC$, and $\dfrac{k_b}{k_f} = 0.3$ so $\dfrac{\Delta T_b}{\Delta T_f} = \dfrac{i_b k_b m}{i_f k_f m}$ so $i_f = 1$

i.e., AB behaves as non–electrolyte at the f.p of the solution.

10. 1M $C_6H_{12}O_6$ (molar mass = 180 g mol^{-1})

1000 mL solution has = 180 g solute
1180 g solution has = 180 g solute
1000 g solvent has = 180 g solute
Thus, molality = 1 molal

∴ $\Delta T_f = K_f$ molality = 1.86 × 1 = 1.86º   ∴   F.P. = – 1.86ºC

11. Firstly we have to convert mole fraction into molality.

$$\text{Molality} = \dfrac{x_{solute}}{x_{solvent} \; M_{solvent}/1000} = \dfrac{0.07 \times 1000}{0.93 \times 18} = 4.18$$

Now, $\Delta T_f = k_f m = 1.86 \times 4.18 = 7.78º$.

12. From given graph, we can say T_1 is that temp at which solid state and liquid (solution) are in equilibrium.

13. $P = P_A°X_A + P_B°X_B$

$$\dfrac{100}{4} + \dfrac{60 \times 3}{4} = 70 \text{ mm} < 75 \text{ mm (experimental)}$$

Thus, there is positive deviation (1) is true, mixture is more volatile due to decrease in b.p. Thus, (2) is true also force of attraction is decreased thus (3) is true.

14. Colligative property of a solution depends on no. of particles of solute in solution.

15. Value of van't Hoff factor is least for urea solution, so there will be least depression in freezing point i.e., maximum freezing point.

16. In HF hydrogen bonding is present so there is association of molecules due to this van't hoff factor is less, so depression in f.p decreases therefore f.p. value is larger than HCl. Similarly value of i = 2 for NaCl and i = 1 for Glucose.

17. $p_A = X_A p°_A$; $32 = X_A \; 40$ ∴ $X_A = \dfrac{32}{40} = 0.8$.

18. $P_T = X_A p°_A + X_B p°_B$ $= \left(\dfrac{2}{4}\right) \times 80 + \left(\dfrac{2}{4}\right) \times 120 = 100$ Torr

Now mole fraction in vapour phase = $\dfrac{X_A P_A^0}{P_T} = \dfrac{40}{100} = 0.4$.

19. Boiling point get lowered when vapour pr. increases and it happens when there is a positive deviation from Raoult's law.

20. For urea, $\Delta T_f = k_f \times m$ or $k_f = \dfrac{\Delta T_f}{m} = \dfrac{1.86}{1} = 1.86$

Now for CH_3COOH

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

so   i = = 1.1   Now   i = 1 + α   so   α = 1.1 – 1 = 0.1

Now CH_3COOH CH_3COO^- + H^+

    C   0   0

C – Cα   Cα   Cα

$[H^+] = C\alpha = 0.01 \times 0.1 = 0.001$ so   pH = 3.

21. Mixtures of $CHCl_3$ and CH_3COCH_3 shows negative deviation from Raoult's law, so vapour pressure decreases and boiling point increases.

| Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005 |
| Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in |
| Toll Free : 1800 258 5555 | CIN : U80302RJ2007PLC024029 | ADVSCP - 77 |

Resonance®
Educating for better tomorrow

22. $\Delta T_f = k_f\,m.$; $\Delta T_f = 1.86 \times 0.5 = 0.93.$ so $T_f = -0.93^0C.$

23. More the value of van't hoff factor, more will be the depression in freezing point.

24. Acetone and chloroform forms hydrogen bonding so volume decreases.

25. All are facts.
We should remember that, Entropy of solution is more than entropy of pure solvent. So the difference in entropy change will be less in case of solution.

26. $M_{observed} = \dfrac{58.5}{i}$; $i > 1.$

27. Due to weak force of attraction more vapour will be forrmed so vapour pressure will be high.

28. The order of force attraction and boiling point is $CH_3OH > CH_4 > H_2$.

29. At freezing point liquid solvent and solid solvent are in equilibrium.

30. There is very weak attraction between benzene and methanol as compare to attraction between molecules of methanol.

PART - III

1. $\dfrac{P-P_S}{P} = \dfrac{0.087}{2.175} = \dfrac{\frac{40}{M}}{\frac{40}{M}+\frac{360}{18}}$ $\Rightarrow$ $\dfrac{2.175}{0.087} = 1 + \dfrac{360}{18} \times \dfrac{M}{40}$ $\Rightarrow 25 = 1 + \dfrac{M}{2}$ **Ans.**   M = 48

2. $\because$ $K_f = \dfrac{MRT_f^2}{1000\ \Delta H_f} = \dfrac{2\times300\times300\times30}{1000\times\ 2700} = 2.00$ K kg mol^{-1}

$\because$ mole fraction of water = 0.8 $\therefore$ mole fraction of solute = 0.2

or $0.2 = \dfrac{n}{n+N}$ and $0.8 = \dfrac{N}{n+N}$

$\therefore$ $\dfrac{n}{N} = \dfrac{0.2}{0.8} = \dfrac{1}{4} = \dfrac{wM}{mW}$

or $\dfrac{1}{4} = \dfrac{w\times30}{mW}$ $\therefore$ $\dfrac{w}{mW} = \dfrac{1}{4\times30}$

$\therefore$ $\Delta T_f = \dfrac{1000\times w\times K_f}{m\times W} = \dfrac{1000\times2.0}{4\times30} = 16.67$ $\therefore$ F.P. of solution. = **10.33°C.**

3. Let n_B mole of B present in 1 mole of mixture that has been vaporized. Thus, $y_B = \dfrac{n_B}{1}$

Mole fraction of B in the remaining liquid phase will be $x_B = \dfrac{1-n_B}{1}$

$x_B = \dfrac{P-P_T^\circ}{P_B^\circ-P_T^\circ}$ .... (1) $[\because\ P = P_T^\circ + (P_B^\circ - P_T^\circ)\,x_B]$

and $y_B = \dfrac{P_B}{P} \Rightarrow \dfrac{P_B^\circ x_B}{P}$ .... (2)

After substitution of values of x_B and y_B in (1) and (2)

we get $1 - n_B = \dfrac{P-P_T^\circ}{P_B^\circ-P_T^\circ}$ .... (3)

and $n_B = \dfrac{(1-n_B)P_B^\circ}{P}$ .... (4)

Resonance®
Educating for better tomorrow

or $n_B = \dfrac{P_B^{\circ}}{P + P_B}$

so $1 - \dfrac{P_B^{\circ}}{P + P_B} = \dfrac{P - P_T^{\circ}}{P_B^{\circ} - P_T^{\circ}}$ $\Rightarrow$ $P = \sqrt{P_B^{\circ} \cdot P_T^{\circ}} = \sqrt{100 \times 900}$ $\Rightarrow$ 300 torr

4.   (a) An azeotropic mixture boil at perticular temperture without changing its composition.

5.   Entropy of solvent is less than that of solution.

6. $\Delta T_f = i.m. K_f$
$\Delta T_f = i_1 m_1 K_f + i_2 m_2 K_f + i_3 m_3 K_f = (m_1 + 2m_2 + m_3) K_f$
$\Delta T_f = \dfrac{\dfrac{3}{60} + \dfrac{7.45 \times 2}{74.5} + \dfrac{9}{180}}{100} \times 1000 \times 1.86$
$\Delta T_f = 3 \times 1.86 \qquad = 5.58$
T_f of solution = 273 − 5.58 = 267.42 K Ans.

7.   Desalination is an application of reverse osmosis.

8. $\pi_f V_f = \pi_1 V_1 + \pi_2 V_2$; $\pi_f = \dfrac{1.2V + 2.5V}{2V} = \dfrac{3.7V}{2V}$; $\pi_f = 1.85$ atm.

9.   (C) B.P. of water is elevated.

10. $P'_A = P_A^{\circ} X_A$ and $P'_B = P_B^{\circ} X_B$
$P'_A = P_M \cdot Y_A$ and $P'_B = P_M \cdot Y_B$
$\therefore \qquad \dfrac{P'_A}{Y_A} = \dfrac{P'_B}{Y_B}$

or $\dfrac{P_A^{\circ} X_A}{Y_A} = \dfrac{P_B^{\circ} X_B}{Y_B} = \dfrac{P_B^{\circ}(1 - X_A)}{(1 - Y_A)}$ or $\dfrac{P_A^{\circ} X_A}{Y_A}(1 - Y_A) = P_B^{\circ} - P_B^{\circ} X_A$

or $\dfrac{P_B^{\circ}}{X_A} = \dfrac{P_A^{\circ}}{Y_A} + (P_B^{\circ} - P_A^{\circ})$ or $\dfrac{1}{X_A} = \dfrac{1}{Y_A} \cdot \dfrac{P_A^{\circ}}{P_B^{\circ}} + \dfrac{(P_B^{\circ} - P_A^{\circ})}{P_B^{\circ}}$

or $y = mx + C$ $\therefore$ Slope = $m = \dfrac{P_A^{\circ}}{P_B^{\circ}}$ and intercept $C = \dfrac{(P_B^{\circ} - P_A^{\circ})}{P_B^{\circ}}$.

11.   20 mole C_6H_6, 10 mole C_6H_5Cl $\Rightarrow$ $X_B = \dfrac{2}{3}$, $X_C = \dfrac{1}{3}$

at t = 100°C $\Rightarrow$ $p_s = 300 \times \dfrac{1}{3} + 1350 \times \dfrac{2}{3} = 100 + 900$ (=1000).

12.   Wt gain means   weight loss means
V.P$_{incoming}$ > V.P$_{outgoing}$ V.P$_{incoming}$ < V.P$_{outgoing}$ So $p_1 > p_2 < p_3$ and $c_1 < c_2 > c_3$

13. $1.24 = 34.3 \left[\dfrac{0.849/M}{0.05} \right] \Rightarrow$ M = 469.68 $\therefore$ as Hg_2Cl_2 molecules.

14.   At 90ºC,   Total P_T = 730 mm Hg
At 100ºC total P_T = 289 + 760 = 1049 mm Hg
so for 800 mm Hg, temperature will lie in between 90º −100ºC
Using extrapolation method, Temperature = 90 + $\dfrac{(800 - 730)}{(1049 - 730)} \times (100 - 90) = 92.19$ºC.

15.   No of particles ↓, so vapour pressure ↑, i ↓
$\Delta T_f = mK_f i$; ΔT_f ↓ , freezing point ↑.

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in
Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029
Resonance®
Educating for better tomorrow
ADVSCP - 79

16. $1.0526 \times 760 = p_{ext}$; $p_{ext} = 799.976 \simeq 800$ Torr

∴ $\log 800 = 7 - \dfrac{1250}{t+220}$ ⇒ $2.9 = 7 - \dfrac{1250}{t+220}$ ⇒ $t = 84.878\ °C$ **Ans. 85**

17.   According to Henry's law, $\dfrac{a}{P} = K_H$ ∴ $a = 3.1 \times 10^{-2} \times 4 = 0.12$ mol/litre.
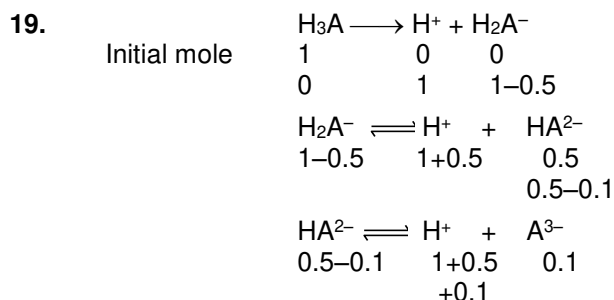
18. $P_T = \dfrac{6}{10} \times 24 + \dfrac{0.4}{10} \times 12 = \dfrac{16 \times 12}{10} = \dfrac{192}{10} = 19.2$ kPa

$P_A' = X_A P_A = \dfrac{6}{10} \times 24 = \dfrac{144}{10} = 14.4 = X_A' \times 19.2$

so $X_A' = \dfrac{144}{192} = 75\%$ $X_B' = 25\%$

so $P_T = \dfrac{3}{4} \times 24 + \dfrac{1}{4} \times 12 = 18 + 3 = 21$ k Pa   & $P_A = \dfrac{3}{4} \times 24 = 18 = X_A'(21)$

so $X_A' = \dfrac{18}{21} = \dfrac{6}{7} = 85.7\%$ of $A \Rightarrow X_B' = 14.3\%$

19. $H_3A \longrightarrow H^+ + H_2A^-$
Initial mole   1   0   0
            0   1   1–0.5

$H_2A^- \rightleftharpoons H^+ + HA^{2-}$
1–0.5   1+0.5   0.5
                0.5–0.1

$HA^{2-} \rightleftharpoons H^+ + A^{3-}$
0.5–0.1   1+0.5   0.1
        +0.1

$i = \dfrac{\text{observed mole of all the species}}{\text{Theoretical moles}} = \dfrac{\text{moles of }\left(H^+ + H_2A^- + HA^{2-} + A^{3-}\right)}{1} = \dfrac{1.6 + 0.5 + 0.4 + 0.1}{1} = 2.6\ 3$

20.   Loss in weight of solution $\propto P_S$;   Loss in weight of solution $\propto P^0 - P_S$

Also, $\dfrac{P^0 - P_s}{P_s} = \dfrac{w \times M}{m \times W}$ By. eq (1) and (2) we get $\dfrac{0.04}{2.5} \times \dfrac{5 \times 18}{80 \times m} \Rightarrow m = 70.31$

21. $P_T = P_A + P_B \neq P_A^0 + P_B^0$
boiling point of the solution will be in between the boiling point of two liquids.

22.   For – ve deviation $A – – B > A – – A$
                    $A – – B > B – – B$
– ve deviation solution are non ideal solution.

23. $\Delta T_b = mK_b\, i$; $K_b = \dfrac{RT^2}{1000\ \Delta H_{vapour}}$

PART - IV

1. $\pi = MRT\, i$: $y \uparrow, i \uparrow, \pi \uparrow$

2.   This is due to cage like structure ice.

3.   L indicates elevation in boiling pt. i.e., $k_b m$.

4.   Let volumes taken by 'x' & 'y' litres, so $\dfrac{0.1x + 0.4y}{x + y} = 0.34$ & $V_g = (x + y)$ (to be maximised) so $y = 4x$ so

for maximum volume $y = 2L$ & $x = \dfrac{1}{2}L$

5.   Freezing point and boiling point are used in temperature scale.

6.   On the same tie line liquid & vapour composition will be same.

7.   Mole fraction of more volatile substance is greater in vapour phase.

9. $P = P_A^° X_A + \dfrac{500}{760} X_B$ (X_B = mole fraction of benzene)

$550 = 400 \times (1 \times X_B) + 600(X_B)$
$150 = (600 - 400) X_B$

$= \dfrac{150}{200} = \dfrac{3}{4} X_B$

$X_A = \dfrac{1}{4}$

At 100ºC mole fraction will be same initially but get change at equilibrium.

$P = \dfrac{1}{4} \times 500 + \dfrac{3}{4} \times 800 = 125 + 600 = 725$ torr

$X_A P_A^° = Y_A P$

$\dfrac{1}{4} \times 500 = Y_A = 725$

$\dfrac{125}{725} = Y_A$

So $Y_A = \dfrac{5}{29}$ $Y_B = \dfrac{24}{29}$

At 90ºC mole fraction will be same initially but get change at equilibrium.
$550 < P < 725$
So at P = 725 only liquid state exist.

11. $\dfrac{P_A^0}{P_A^0 - P_A} = \dfrac{n_A}{n_B} + 1$ or $\dfrac{P_A^0 - P_A}{P_A} = \dfrac{n_B}{n_A}$

12.   In both chamber vapour compositions are same so vapour pressure are equal.

13. $\dfrac{P_o - P_s}{P_o} = X_{solute}$

$\therefore$ $\dfrac{100 - 98.7}{100} = X_{solute} = 0.013$

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

$0.72 = K_f \times \dfrac{0.013 \times 1000}{0.978 \times 78}$

$\therefore$ $K_f \approx 4.2$ K Kg/mol
$\therefore$ Reported answer = 4

14.   Initially P = $\dfrac{500}{760}$ atm, T = 283 K

Let V = V_1 $\therefore$ pV = nRT

Or $\left(\dfrac{500}{760}\right) \times V_1 = R \times 5 \times 283$ ...(1)

Let on dilution the volume becomes V_2 and temp is raised to 25ºC i.e. 298 K

$\pi = \left(\dfrac{105.3}{760}\right)$ atm

Resonance®
Educating for better tomorrow

Reg. & Corp. Office : CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.) – 324005
Website : www.resonance.ac.in | E-mail : contact@resonance.ac.in
Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029

ADVSCP - 81

$$\therefore \quad \left(\frac{105.3}{760}\right) \times V_2 = n \times R \times 298 \qquad \ldots(2)$$

(1)/(2)

$$\frac{V_1}{V_2} = \frac{283}{298} \times \frac{105.3}{500} \qquad \text{Or } V_2 = 5V_1$$

15. $\Delta T_f = iK_f m$

$7.2 \times 10^{-3} = i \times 1 \times 10^{-3} \times 1.8$

$i = \dfrac{7.2}{1.8} = 4$

now , $i = 1 + (x + 1 - 1)\,\alpha = 1 + x$

$\qquad\quad 4 - 1 = x$

$\qquad\qquad x = 3$

So oxidation number of Fe $3 + y - 6 = 0, y = +3$

Sum of primary and sec valency = 3 + 6 = 9

16.   Molarity of I solution $= \dfrac{12.6 \times 1.5 \times 10}{63} = 3$

Molarity of II solution $= \dfrac{6.3 \times 10 \times 10}{63} = 10$

$M = \dfrac{M_1 V_1 + M_2 V_2}{V_1 + V_2} = \dfrac{3 \times 5 + 1 \times 5}{5 + 5} = \dfrac{4}{2} = 2$

17. $P_A = K_H X_A$

$4 \times \dfrac{25}{100} = 2.5 \times 10^3\, X_A \Rightarrow \qquad X_A = \dfrac{2}{5000}$;   Number of moles of water $= \dfrac{2}{1} = 2$

Number of moles of gas A dissolved $\approx \dfrac{2}{5000} \times 2 = 0.8 \times 10^{-3} = 8 \times 10^{-4}$

19. $P = X_A P_A^0 + X_B P_B^0 = 0.5 \times 40 + 0.5 \times 100 = 70$

20. $Y_A = \dfrac{0.5 \ \times \ 40}{70} = \dfrac{2}{7}$; $Y_B = \dfrac{5}{7}$

21.

1− x	x
B = x	T = 1 − x

$$P = 40\,(1 - x) + 100\,x$$

$$\frac{1}{P} = \frac{Y_A}{P_A^0} + \frac{Y_A}{P_B} \Rightarrow \frac{1}{P} = \frac{x}{40} + \frac{1 - x}{100} = \frac{100x + (1 - x)40}{40 \ \times \ 100}$$

So $p^2 = 40 \times 100$

$\qquad p = 20\sqrt{10} = 63.25$

22.   P. $AlCl_3 \rightarrow i = 1 + (4 - 1) \times 0.8 = 1 + 2.4 = 3.4$

Q. $BaCl_2 \rightarrow i = 1 + (3 - 1) \times 0.9 = 1 + 1.8 = 2.8$

R. $Na_3PO_4 \rightarrow i = 1 + (4 - 1) \times 0.9 = 1 + 2.7 = 3.7$

S. $K_4[Fe(CN)_6] \rightarrow i = 1 + (5 - 1) \times 0.7 = 1 + 2.8 = 3.8$

so, $K_4[Fe(CN)_6]$ has highest colligative property and hence minimum freezing point and $BaCl_2$ has lowest colligative property, so lowest osmotic pressure.

$$RLVP = \frac{0.1 \times i}{0.1 \times i + 10} = \frac{0.1 \times 3.7}{0.1 \times 3.7 + 10} = \frac{3.7}{10.37} = \frac{37}{1037}$$