9 Colligative Properties and Solutions

Colligative Properties

The properties of a solution which depend on the number of particles present in solution, *e.g.*, osmotic pressure, lowering in vapour pressure, elevation in boiling point and depression in freezing point.

1. Osmosis and Osmotic pressure

(a) Spontaneous movement of solvent particles from dilute solution to concentrate solution through semipermeable membrane (SPM) is known as **osmosis.**

(b) The osmotic pressure is defined as the hydrostatic pressure developed in a **vertical** column as a result of osmosis, when a solution is separated with its solvent by SPM.

i.e., Osmotic pressure $(\pi) = h \times d \times g$

where h is height developed

	In CGS cm	In MKS metre
d is density of final solution	g/cm^3	kg/m^3
g is gravitational acceleration	$981\,cm/sec^2$	$9.8\,cm/sec^2$

(c) Osmotic pressure is given by solution equation proposed by van't Hoff as

$$\pi V = nST \quad ...(1)$$

or $$\pi = \frac{n}{V} ST \quad ...(2)$$

or $$\pi V = \frac{w}{m} ST \quad ...(3)$$

or $$\pi = CST \quad ...(4)$$

Conditions for validity of Eqs. (1) to (4).

(1) Dilute solutions.

(2) Solute neither dissociate nor associate.

	Litre atm	CGS	MKS
where π is osmotic pressure	atm	$dyne/cm^2$	$Newton/m^2$
V is volume of solution	litre	cm^3	m^2
n is no. of mole of solute	—	—	—
w is mass of solute	g	g	kg
m is M. mass of solute	g	g	kg
S is solution constant	0.0821 litre atm K^{-1} mol^{-1}	8.314×10^7 erg K^{-1} mol^{-1}	8.314 joule K^{-1} mol^{-1}
T is temperature	Kelvin	Kelvin	Kelvin
C is concentration	mol $litre^{-1}$	mol/cm^3	mol/cm^3

Isotonic or iso-osmotic solutions: Two solutions of different substances having same osmotic pressure at same temperature are known as isotonic solutions.

For isotonic solutions

$$\pi_1 = \pi_2 \quad \text{Primary Condition} \quad ...(5)$$

Also, $$C_1 = C_2 \quad \text{Secondary Conditions} \quad ...(6)$$

Eq. (6) holds good only for those solutes which neither possess the tendency to get associate nor dissociate in solution NaCl, Na_2SO_4 etc.

2. Vapour Pressure Lowering

(a) The pressure exerted by the vapours of a solvent when they are in equilibrium with its liquid at a temperature is known as **vapour pressure.**

(b) Vapour pressure varies with:

(1) Temperature—Increases with increase in temperature.

(2) Nature of solvent—High boiling point liquid has low vapour pressure and *vice-versa*.

(3) Addition of a non-volatile solute—Addition of a non-volatile solute to a solvent always lowers the vapour pressure, *i.e.*,

$$\underset{(P^\circ)}{\text{V.P. of solvent}} > \underset{(P_s)}{\text{V.P. of solution}}$$

(c) The decrease in V.P. of a solvent on addition of a non-volatile solute (*i.e.*, $P^\circ - P_s$) is known as lowering in vapour pressure.

$$\Delta P = P^\circ - P_s$$

(d) Raoult's law for mixture of volatile liquids: The vapour pressure of a mixture obtained by mixing two or more volatile liquids is equal to the sum of partial vapour pressure of each component in mixture.

$$P_M = P'_A + P'_B + \ldots \qquad \ldots(7)$$

where partial vapour pressure (P') of a component in a mixture is equal to the product of V.P. of pure component and its mole fraction in liquid mixture, *i.e.*,

$$P'_A = P^\circ_A \cdot X_A\,;\quad P'_B = P^\circ_B \cdot X_B\,; \text{ and so on}$$

$$\therefore \quad P_M = P^\circ_A \cdot X_A + P^\circ_B \cdot X_B + \ldots \qquad \ldots(8)$$

$$\text{or} \quad P_M = P^\circ_A \cdot \frac{n_A}{n_A + n_B + \ldots} + P^\circ_B \cdot \frac{n_B}{n_A + n_B + \ldots} + \ldots \qquad \ldots(9)$$

where, X is mole fraction of that component in mixture

and n is no. of mole of components, *i.e.*, w/m

$$\therefore \quad P_M = P^\circ_A \cdot \frac{w_A/m_A}{\frac{w_A}{m_A} + \frac{w_B}{m_B} + \ldots} + P^\circ_B \cdot \frac{w_B/m_B}{\frac{w_A}{m_A} + \frac{w_B}{m_B} + \ldots} + \ldots \qquad \ldots(10)$$

(e) Raoult's law for non-volatile solute-liquid system: For non-volatile solute-solvent systems, the vapour pressure of a solution $P(s)$ is directly proportional to mole fraction of solvent.

$$P_s \propto \frac{N}{n+N} = P^\circ \times \frac{N}{n+N} \qquad \ldots(11)$$

where, P° is vapour pressure of pure solvent

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

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n}{n+N} \qquad \ldots(12)$$

Thus, the relative lowering in vapour pressure is equal to mole fraction of solute in solution,

where, $\dfrac{P^\circ - P_s}{P^\circ}$ = Relative lowering in vapour pressure.

$$\therefore \text{ By Eq. (12)} \quad \frac{P^\circ - P_s}{P^\circ} = \frac{n}{n+N} \qquad \ldots(13)$$

For dilute solutions: $n << N$

$$\therefore \quad n + N \approx N$$

$$\therefore \quad \frac{P^\circ - P_s}{P^\circ} = \frac{n}{N} = \frac{w \times M}{m \times W} \qquad \ldots(14)$$

Note: (i) It is to be noted that use of Eq. (14) should be made only when solution is reported to be dilute.

(ii) In case dilute solutions are not reported, use Eq. (13) for calculating relative lowering in V.P. and if any other factor is to be calculated, an alternative derivation for Raoult's law given below (a simplified form for the numericals) should be used.

Alternative derivation: According to Raoult's law:

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n}{n+N} \quad \text{or} \quad \frac{P^\circ}{P^\circ - P_s} = \frac{n+N}{n} = 1 + \frac{N}{n}$$

$$\text{or} \quad \frac{P^\circ}{P^\circ - P_s} - 1 = \frac{N}{n} \quad \text{or} \quad \frac{P^\circ - P^\circ + P_s}{P^\circ - P_s} = \frac{N}{n}$$

$$\text{or} \quad \frac{P^\circ - P_s}{P_s} = \frac{n}{N} = \frac{w \times M}{m \times W} \qquad \ldots(15)$$

Eq. (15) gives accurate results whether solution is dilute or concentrated one.

(f) Raoult's law in combination with Dalton's law of partial pressure: Suppose X_A mole fraction of A and X_B mole fraction of B are present in a liquid mixture.

According to Raoult's law for liquid mixtures:

$$P'_A = P^\circ_A \cdot X_A$$

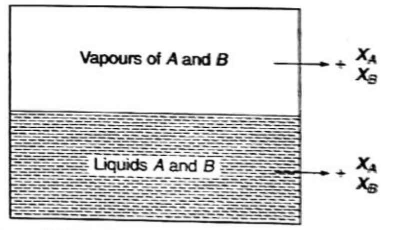
$$P'_B = P^\circ_B \cdot X_B \quad \text{and} \quad P_M = P'_A + P'_B$$

According to Dalton's law of partial pressure:

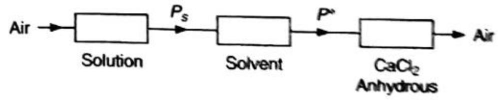
$$P'_A = P_M \cdot X'_A$$

$$P'_B = P_M \cdot X'_B$$

$$\therefore \quad P_M \cdot X'_A = P^\circ_A \cdot X_A \qquad \ldots(16)$$



(g) Ostwald-Walker method for determination of vapour pressure: The method is based on the principle—when air is allowed to pass through a solvent or solution it takes up solvent vapours with it to get itself saturated with vapours at that temperature.



Loss in mass of solution $\propto P_s$

Loss in mass of solvent $\propto P^\circ - P_s$

Gain in mass of $CaCl_2 \propto P^\circ$

(h) Partial pressure of two immiscible liquids: According to Dalton's law:

$$P'_A = P_M \cdot X'_A = P_M \times \frac{n'_A}{n'_A + n'_B}$$

$$P'_B = P_M \cdot X'_B = P_M \times \frac{n'_B}{n'_A + n'_B}$$

where, X'_A and X'_B are mole fractions of A and B in gaseous phase.

$$\therefore \quad \frac{P'_A}{P'_B} = \frac{n'_A}{n'_B} \quad ...(17)$$

3. Elevation in boiling point

(a) B. pt. of a liquid is a characteristic temperature at which its vapour pressure becomes equal to 1 atm pressure or 76 cm or 760 mm pressure.

(b) Addition of a non-volatile solute in a solvent lowers its vapour pressure and thus more heat is required to increase the V.P. of solution up to 1 atm. That is why b. pt. of solution increases. This increase in b. pt. is known as elevation in b. pt.

$$\text{Elevation in b. pt.} = \Delta T_b = T_1 - T_0$$

where, T_1 = b. pt. of solution and T_0 = b. pt. of solvent

(c) The elevation in b. pt. of solution is given by

$$\Delta T_b = K'_b \times \text{molality} = \frac{1000 K'_b w}{mW} = \frac{100 K_b w}{mW} \quad ...(18)$$

where, K'_b = molal elevation constant in K mol^{-1} kg

K_b = molecular elevation constt. in K mol^{-1} 100 kg

and w = mass of solute

W = mass of solvent

m = molar mass of solute

4. Depression in freezing point

(a) F. pt. of a liquid is a characteristic temperature at which vapour pressure of solvent in its liquid and solid phase becomes same.

(b) Addition of a non-volatile solute to a solvent lowers the freezing point. The decrease in freezing point is known as depression in freezing point.

$$\text{Depression in f. pt.} = \Delta T_f = T_0 - T_1$$

where, T_1 = f. pt. of solution

T_0 = f. pt. of solvent

(c) The depression in f. pt. of solution is given by

$$\Delta T_f = K'_f \times \text{molality} = \frac{1000 K'_f w}{mW} = \frac{100 K_f w}{mW} \quad ...(19)$$

where, K'_f = molal depression constant in K mol^{-1} kg

K_f = molecular depression constant in K mol^{-1} 100 g

Rest all terms have usual meanings.

5. Thermodynamic derivation for molal constants

$$K' = \frac{RT^2}{1000l} = \frac{0.002T^2}{l\,(\text{in cal / g})} = \frac{RT^2 \times M}{1000\,\Delta H} = \frac{RT \cdot M}{1000\,\Delta S} \quad ...(20)$$

where, K' is molal elevation or depression constant

T is boiling point or freezing point of solvent

l is latent heat of vaporisation or latent heat of fusion in cal/g

R is molar gas constant

ΔH_V is heat of vaporisation or fusion in cal/mole = $l \times M$

ΔS_V is entropy change of vaporisation or fusion = $\frac{\Delta H}{T}$

Note : (1) Put R in the units of latent heat.

(2) Thus, $K'(K'_b$ or $K'_f)$ are characteristic constants for given solvent and are independent of nature of solute.

(3) K'_b is also known as molal ebullioscopic constant.

(4) K'_f is also known as molal cryoscopic constant.

Abnormal colligative properties

The experimental values of C.P. (*i.e.*, π, ΔP, ΔT_b and ΔT_f) of many solutes in solution resemble to calculated values of C.P.

However, in some cases, the experimental values of C.P. differ widely than those obtained by calculations. Such experimental values of C.P. are known as abnormal values of C.P.

Thus, Exp. values of C.P. $\lesseqgtr$ Calculated values of C.P.

or Observed value or Normal values or Theoretical values

The abnormal behaviour of C.P. has been observed in following cases.

(1) Solutes having dissociation nature: Such solutes, which dissociate in solvent (water), *i.e.*, electrolytes show, an increase in the no. of particles present in solution. This gives rise to higher experimental values since,

$$\text{C.P.} \propto \text{No. of particles in solution}$$

$\therefore$ Exp. C.P. > Normal C.P.

or Exp. π, ΔP, ΔT_b or ΔT_f > Normal π, ΔP, ΔT_b or ΔT_f

Also $\because$ $\quad \text{C.P.} \propto \frac{1}{\text{Molar mass}}$

$\therefore$ Exp. Molar mass < Normal Molar mass

Consider an electrolyte say $A_X B_Y$ in water

$$A_X B_Y\,(aq.) \rightleftharpoons XA^{(+Y)}(aq.) + YB^{(-X)}(aq.)$$

Mole before dissociation	1	0	0
Mole after dissociation	$1-\alpha$	$X \cdot \alpha$	$Y \cdot \alpha$

Let α is degree of dissociation $= \frac{\text{Mole dissociated}}{\text{Total mole added}}$

$\therefore$ Normal C.P. $\propto$ No. of particles before dissociation $\propto 1$

$\therefore$ Exp. C.P. $\propto$ No. of particles after dissociation

$\propto 1 - \alpha + X \cdot \alpha + X \cdot \alpha$

$\propto 1 - \alpha + X \cdot \alpha + X \cdot \alpha$

$$(i) = \frac{\text{Exp. C.P.}}{\text{Normal C.P.}} = 1 - \alpha + X \cdot \alpha + Y \cdot \alpha$$

$$= \frac{\text{Normal Molar mass}}{\text{Exp. Molar mass}} \quad ...(21)$$

where (i) is van't Hoff factor. Also $i > 1$ for electrolytes

$$\therefore \quad \alpha = \frac{i-1}{(X+Y)-1} = \frac{i-1}{n-1} \quad [\text{where } n = (X+Y)] \quad ...(22)$$

$$\text{Further, van't Hoff coefficient } (g) = \frac{i}{n} = \frac{i}{(X+Y)} \quad ...(23)$$

where n is no. of particles furnished by 1 molecule of electrolyte assuming its 100% ionisation.

(2) Solutes showing association nature: Such solutes, which associate in solvent show a decrease in the no. of particles present in solution. This gives rise to lower experimental values of C.P.

$\therefore$ Exp. C.P. < Normal C.P.

or Exp. $\pi, \Delta P, \Delta T_b, \Delta T_f$ < Normal $\pi, \Delta P, \Delta T_b, \Delta T_f$

and Exp. Molar mass > Normal Molar mass

consider a solute having association nature as,

$$nA \rightleftharpoons (A)_n$$

Mole before association	1	0
Mole after assocaition	$1-\alpha$	$\frac{\alpha}{n}$

where α is degree of association and n is no. of associated molecules.

$\therefore$ Normal C.P. $\propto$ No. of particles before association $\propto 1$

$\therefore$ Exp. C.P. $\propto$ No. of particles after association

$$\propto 1 - \alpha + \frac{\alpha}{n}$$

$$\therefore \quad (i) = \frac{\text{Exp. C.P.}}{\text{Normal C.P.}} = 1 - \alpha + \frac{\alpha}{n} = \frac{\text{Normal Molar mass}}{\text{Exp. Molar mass}} \quad ...(24)$$

where i is van't Hoff factor; also $i < 1$ to such solutes.

Note : (1) For solutes having neither dissociation nor association, $i = 1$ because

Experimental C.P. = Normal C.P.

(2) General formulae for any C.P. may be written as

$$\text{C.P.} \propto \text{concentration} \times (1 - \alpha + X \cdot \alpha + Y \cdot \alpha)$$

$$\propto \frac{w \times 1000}{m \times V}(1 - \alpha + X \cdot \alpha + Y \cdot \alpha) \quad \text{(for dissociation)}$$

or $\text{C.P.} \propto \text{concentration} \left(1 - \alpha + \frac{\alpha}{n}\right)$ (for association)

Henry's law : Amount of gas (a) dissolved per unit volume of solvent is directly proportional to pressure of gas (P)

$$a \propto P, \quad a = K_H \cdot P \quad ...(25)$$

where K_H is Henry's law constant in g/atm

Also, $P \propto X_{gas}$, $P = K_H \cdot X_{gas}$ ...(26)

where X_{gas} is mole fraction of gas dissolved at pressure P of gas. K_H is expressed in atm.

• NUMERICAL PROBLEMS •

1. Calculate the osmotic pressure at 17°C of an aqueous solution containing 1.75 g of sucrose per 150 mL solution.
2. The osmotic pressure of a non-volatile solute in C_6H_6 at 25°C is 20.66 Nm^{-2}. If the solution had a concentration of 2 g / dm^3, what is molar mass of solute?
3. At 27°C, 36 g of glucose per litre has an O.P. of 4.92 atm. If the osmotic pressure of solution is 1.5 atm at the same temperature, what should be its concentration?
4. 2.5 g of a substance is present in 200 mL of solution showing the osmotic pressure of 60 cm Hg at 15°C. Calculate the molar mass of substance. What will be the osmotic pressure if temperature is raised to 25°C?
5. Calculate O.P. of a solution obtained by mixing 100 mL of 3.4% solution (mass/vol.) of urea (molar mass 60) and 100 mL of 1.6% solution (mass/vol.) of cane-sugar (molar mass 342) at 20°C.
6. A 10 g mixture of glucose and urea present in 250 mL solution shows the osmotic pressure of 7.4 atm at 27°C. Calculate % composition of mixture.
7. At 25°C, a solution containing 0.2 g of polyisobutylene in 100 mL of benzene developed a rise of 2.4 mm at osmotic equilibrium. Calculate the molar mass of polyisobutylene if the density of solution is 0.88 g/mL.
8. A tube of uniform cross-sectional area 1 cm^2 is closed at one end with semipermeable membrane. A solution of 5g glucose per 100 mL is placed inside the tube and is dipped in pure water at 27°C. What equilibrium is established, calculate:
   (a) Osmotic pressure of solution.
   (b) Height developed in vertical column.
   Assume density of final glucose solution 1 g/mL.
9. A beaker containing 20 g sugar in 100 g water and another containing 10 g sugar in 100 g water are placed under a bell-jar and allowed to stand until equilibrium is reached. How much water will be transferred from one beaker to other?
10. At 300 K, two solutions of glucose in water of concentration 0.01 *M* and 0.001 *M* are separated by semipermeable membrane with respect to water. On which solution, the pressure need be applied to prevent osmosis? Calculate magnitude of this applied pressure.
11. 100 mL of 1.0 g sample of a drug having the compound $C_{21}H_{23}O_5N$ as drug is coated with sugar lactose (molar mass 342) exerts the osmotic pressure of 0.70 atm at 27°C. What is the drug percentage in sample.
12. A 5% solution (mass/vol.) of cane-sugar is isotonic with 0.877% (mass/vol.) of urea solution. Find molar mass of urea, if molar mass of sugar is 342.
13. How many g of glucose must be present in 0.5 litre of a solution for its osmotic pressure to be same as that of solution of 9.2 g glucose per litre?
14. At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be 105.3 mm. Determine extent of dilution.
15. At 300 K, the vapour pressure of an ideal solution containing one mole of *A* and 3 mole of *B*, is 550 mm of Hg. At the same temperature, if one mole of *B* is added to this solution, the vapour pressure of solution increases by 10 mm of Hg. Calculate the V.P. of *A* and *B* in their pure state.
16. Cyclohexane and ethanol at a particular temperature have vapour pressure of 280 mm and 168 mm respectively. If these two solutions having mole fraction value of cyclohexane equal to 0.32 are mixed and the mixture has a total vapour pressure of 376 mm, will the mixture be an ideal solution?
17. The vapour pressure of benzene and toluene at 20°C are 75 mm of Hg and 22 mm of Hg respectively. 23.4 g of benzene and 64.4 g of toluene are mixed. If two form ideal solution, calculate the mole fraction of benzene in vapour phase when vapours are in equilibrium with liquid mixture.
18. Benzene and toluene form two ideal solutions *A* and *B* at 313 K. Solution *A* contains 4 mole of toluene and one mole of C_6H_6. Solution *B* contains equal masses of toluene and benzene. Calculate total pressure in each case. The vapour pressure of C_6H_6 and toluene are 160 and 60 mm respectively at 313 K.
19. The vapour pressures of pure ethylene bromide and propylene bromide are 170 and 127 mm of Hg at a temperature. Find out the vapour pressure of ethylene bromide in a 60% by mass solution of ethylene bromide in propylene bromide at same temperature. Also report the vapour pressure of propylene bromide as well as total vapour pressure of solution.
20. An aqueous solution containing liquid *A* (Molar mass = 128) 64% by mass has a V.P. of 145 mm. Find the V.P. of *A*, if that of water is 155 mm at the same temperature.
21. A mixture of ethyl alcohol and propyl alcohol has a V.P. of 290 mm at 27°C. If mole fraction of ethyl alcohol is 0.65, calculate the vapour pressure of ethyl alcohol, if vapour pressure of propyl alcohol is 210 mm.
22. A solution of *A* and *B* with 30% mole in solution is in equilibrium with its vapour which contains 60% mole of *A*. Assuming ideal nature, calculate the ratio of the vapour pressure of pure *A* to that of pure *B*.
23. The mole fraction of $CCl_4(g)$ in the vapour in equilibrium with liquid mixture of CCl_4 and $SiCl_4$ is

0.3474. The vapour pressure of $SiCl_4$ and CCl_4 is 238.3 and 114.9 mm respectively at the same temperature. Calculate % by mass of CCl_4 in liquid mixture.

24. The molar volume of liquid benzene (density $= 0.877 \text{ g mL}^{-1}$) increases by a factor of 2750 as it vaporises at 20°C and that of liquid toluene (density 0.867 g mL^{-1}) increases by a factor of 7720 at 20°C. A solution of benzene and toluene at 20°C has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution. **(IIT 1996)**

25. At 90°C, the vapour pressure of toluene is 400 mm and that of xylene is 150 mm. What is the composition of liquid mixture that will boil at 90°C when the pressure of mixture is 0.5 atm?

26. An organic liquid *A*, is immiscible with water. When boiled together with water, the boiling point is 90°C at which the partial vapour pressure of water is 526 mm Hg. The superincumbent (atmospheric) pressure is 736 mm Hg. The mass ratio of the liquid and water collected is 2.5 : 1. What is the molar mass of the liquid?

27. A mixture of two immiscible liquids nitrobenzene and water boiling at 99°C has a partial vapour pressure of water 733 mm and that of nitrobenzene 27 mm. Calculate the ratio of the mass of nitrobenzene to the water in distillate.

28. A mixture of chlorobenzene and water (immiscible) boils at 90.3°C at an external pressure of 740.2 mm. The vapour pressure of pure water at 90.3°C is 530.1 mm. Calculate the % composition of distillate.

29. Dichlorodifluoro methane, CCl_2F_2, one of the chlorofluoro refrigerant responsible for destroying part of the earth's ozone layer has $P_{(vap)} = 40.0$ mm Hg at −81.6°C and $P_{(vap)} = 400$ mm Hg at −43.9°C. What is the normal boiling point of CCl_2F_2 in °C?

30. The vapour pressure of pure water at 25°C is 23.62 mm. What will be the vapour pressure of a solution of 1.5 g of urea in 50 g of water? **(Roorkee 2001)**

31. Calculate the vapour pressure of solution having 3.42 g of cane-sugar in 180 g water at 40°C and 100°C. Given that boiling point of water is 100°C and heat of vaporisation is 10 kcal mol^{-1} in the given temperature range. Also calculate the lowering in vapour pressure of 0.2 molal cane-sugar at 40°C.

32. The vapour pressure of pure benzene at 25°C is 639.7 mm of Hg and the vapour pressure of a solution of a solute in C_6H_6 at the same temperature is 631.9 mm of Hg. Calculate molality of solution.

33. What mass of solute (Molar mass 60) is required to dissolve in 180 g of water to reduce the vapour pressure to 4/5th of pure water?

34. The vapour pressure of pure benzene at a certain temperature is 640 mm of Hg. A non-volatile non-electrolyte solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm of Hg. What is the molar mass of solid substance? **(IIT 1990)**

35. The vapour pressure of an aqueous solution of glucose is 750 mm of Hg at 373 K. Calculate molality and mole fraction of solute. **(IIT 1989)**

36. The vapour pressure of water is 92.5 mm at 300 K. Calculate V.P. of 1 molal solution of a solute in it.

37. A solution containing 30 g of a non-volatile solute in exactly 90 g water has a vapour pressure of 21.85 mm of Hg at 25°C. Further 18 g of water is then added to solution, the new vapour pressure becomes 22.15 mm of Hg at 25°C. Calculate,
(a) Molar mass of solute.
(b) Vapour pressure of water at 25°C.

38. The vapour pressure of an aqueous solution at 20°C is 17 mm and that of pure water at same temperature is 17.39 mm. Calculate, (i) Density of water vapours at this temperature, (ii) Osmotic pressure of solution assuming molarity and molality be same.

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

40. Calculate the relative lowering in V.P. if 10 g of a solute (molar mass 100) are dissolved in 180 g water.

41. At 50°C the vapour pressure of pure water and ethyl alcohol are 92.5 and 219.9 mm of Hg respectively. If 6g of non-volatile solute of molar mass 120 are dissolved in 150 g of each of these solvent, what will be the ratio of relative vapour pressure lowering in two solvents?

42. 0.1 *M* solution of glucose was found to be isotonic with a solution of *X* in 100 g water. Calculate relative lowering in vapour pressure of solution of *X* in water.

43. Calculate the mass of a non-volatile solute (molar mass 40), which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

44. What mass of non-volatile solute, urea (NH_2CONH_2) needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of solution?

45. Dry air was successively passed through a solution of 5 g solute in 80 g water and then through pure water. The loss in mass of solution was 2.5 g and that of pure water was 0.04 g. What is molar mass of solute?

46. Calculate the vapour pressure lowering of a 0.10 m aqueous solution of non-electrolyte at 75°C.

47. A very small amount of a non-volatile solute (that does not dissociate) is dissolved in 56.8 cm^3 of benzene (density 0.889 g cm^{-3}). At room temperature, vapour pressure of this solution is 98.88 mm Hg while that of benzene is 100 mm Hg. Find the molality of this solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene, what is the value of molal freezing point depression constant of benzene? **(IIT May 1997)**

48. An aqueous solution of glucose containing 12 g in 100 g of water was found to boil at 100.34° C. Calculate K_b for water in K mol^{-1} kg.

49. 20 mL of ethanol (density 0.7893 g/mL) and 40 mL of H_2O (density 0.9971 g/mL) at 25° C are mixed to have a mixture (density 0.9571 g/mL). Calculate the per cent change in volume after mixing. Also report molality and molarity of alcohol and deviation from Raoult's law.

50. The boiling point of $CHCl_3$ was raised by 0.323° C when 0.5143 g of anthracene was dissolved in 35 g $CHCl_3$. Calculate the molar mass of anthracene. K_b' for $CHCl_3$ = 3.9 K mol^{-1} kg.

51. What will be the boiling point of bromine when 174.5 mg of octa atomic sulphur is added to 78 g of brsomine? K_b' for Br_2 is 5.2 K mol^{-1} kg and *b*. pt. of Br_2 is 332.15 K.

52. 0.48 g of a substance was dissolved in 10.6 g C_6H_6. The freezing point of benzene was lowered by 1.8°C. Calculate molar mass of the substance. Molecular depression constant for benzene is 50 K mol^{-1} 100 g.

53. One mole of triphenyl methanol lowers the freezing point of 1000 g of 100% sulphuric acid twice as much as one mole of methanol. Why?

54. Menthol is a crystalline substance with a peppermint taste. A 6.2% (mass/mass) solution of menthol in cyclohexane freezes at −19.5° C. Determine molar mass of menthol. The freezing point and molal depression constant of cyclohexane are 6.5°C and 20.2 K $molality^{-1}$.

55. How much ethyl alcohol must be added to 1.00 litre of water so that the solution will freeze at 14° F ? (K_f for water = 1.86° C / mol)

56. An aqueous solution containing 5% by mass of urea and 10% by mass of glucose. What will be its freezing point? K_f' for H_2O is 1.86° mol^{-1} kg.

57. An aqueous solution of glucose boils at 100.01° C. The molal elevation constant for water is 0.5 K mol^{-1} kg. What is the number of glucose molecules in the solution containing 100 g water?

58. 1.4 g of acetone dissolved in 100 g of benzene gave a solution which freezes at 277.12 K. Pure benzene freezes at 178.4 K. 2.8 g of a solid (*A*) dissolved in 100 g of benzene gave a solution which froze at 277.76 K. Calculate the molar mass of (*A*). **(Roorkee 2000)**

59. Two elements *A* and *B* form compounds having molecular formula AB_2 and AB_4. When dissolved in 20 g C_6H_6, 1 g of AB_2 lowers the f. pt. by 2.3° C whereas 1.0 g of AB_4 lowers it by 1.3° C. The K_f for C_6H_6 is 5.1 K mol^{-1} kg. Calculate atomic mass of *A* and *B*.

60. The freezing point of a solution containing 50 cm^3 of ethylene glycol in 50 g of water is found to −34°C. Assuming ideal behaviour calculate the density of ethylene glycol.
(K_f' for water = 1.86 K kg mol^{-1}) **(Roorkee 1999)**

61. A solution of 0.643 g of an organic compound in 50 mL of benzene (density 0.879 g/mL) lowered its freezing point from 5.51° C to 5.03° C. Calculate the molar mass of solid. K_f for benzene is 5.12 K mol^{-1} kg. **(IIT 1992)**

62. A motor vehicle radiator was filled with 8 litre of water to which 2 litre of methyl alcohol (density 0.8 g/mL) were added. What is the lowest temperature at which the vehicle can be parked out doors without a danger that the water in radiator will freeze? K_f' for H_2O = 1.86 K mol^{-1} kg.

63. A mixture which contains 0.550 g of camphor and 0.090 g of an organic solute melts at 161° C. The solute contains 93.75% C and 6.25% H by mass. What is the molecular formula of compound? K_f' for camphor is 37.5° C mol^{-1} kg. The m. pt. of camphor is 209° C.

64. If boiling point of an aqueous solution is 100.1° C. 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.

65. Calculate the freezing point of an aqueous solution having mole fraction of water 0.8. Latent heat of fusion of ice is 1436.3 cal mol^{-1}.

66. Two solutions of non-volatile solutes *A* and *B* having molar mass ratio of *A* and *B* (M_A / M_B) as 1/3 are prepared by dissolving 5% (mass/vol.) of each in water. Calculate the ratio of freezing point depression. If the two solutions are mixed to prepare a new solution (S_1) by mixing in the ratio 2 : 3 by volume and another new solution (S_2) is obtained by mixing in the ratio 3 : 2, find out $\frac{(\Delta T_f)_{S_1}}{(\Delta T_f)_{S_2}}$. Assume density of solution *A* and *B* equal to one.

67. Calculate the entropy change for vaporisation of water if latent heat of vaporisation for water is 540 cal/g. Given K_b for H_2O = 0.51 K / molality.

68. Match the following if the molar masss of *X*, *Y* and *Z* are same. **[IIT 2003]**

	b.pt.	K_b
X	100	0.68
Y	27	0.53
Z	253	0.98

69. Calculate the amount of ice that will separate out on cooling *a* solution containing 50 g of ethylene glycol in 200 g water to −9.3°C. (K_f for water $= 1.86 \text{ K mol}^{-1} \text{ kg}$) **(Roorkee 1995)**

70. 1000 g of 1 m sucrose solution in water is cooled to −3.534°C. What mass of ice would be separated out at this temperature? K'_f $H_2O = 1.86 \text{ K mol}^{-1}$ kg.

71. 100 g of sucrose solution in water is cooled to −0.5°C. What mass of ice would be separated out at this temperature, if solution started to freeze at −0.38°C? K'_f for $H_2O = 1.86 \text{ K mol}^{-1}$ kg.

72. Calculate the freezing point of an aqueous solution of non-electrolyte having an osmotic pressure 2.0 atm at 300 K. $K'_f = 1.86 \text{ K mol}^{-1}\text{kg}$ and $S = 0.0821$ litre atm K^{-1} mol^{-1}. Assume molarity and molality same. **(Roorkee 1993)**

73. An aqueous solution of urea has freezing point of −0.52°C. Calculate the osmotic pressure of solution at 27°C. Assume molarity and molality be same. K'_f for H_2O is 1.86 K mol^{-1} kg.

74. The osmotic pressure of an aqueous solution of sucrose is 2.47 atm at 303 K and the molar volume of the water present is 18.10 cm^3. Calculate the elevation in boiling point of the solution. Given $\Delta H_{\text{Vap.}} = 540 \text{ cal / g}$. Assume volume of solvent equal to volume of solution.

75. The molar mass of an organic compound is 58 g / mol. 24 g of this is dissolved in 600 g of water, calculate its boiling point when vapour pressure of water becomes 760 mm at 99.725°C. K_b of H_2O is $0.513 \text{ K kg mol}^{-1}$.

76. A solution of a non-volatile solute in water freezes at −0.30°C. The vapour pressure of pure water at 298 K is 23.51 mm Hg and K_f for water is 1.86 degree/molal. Calculate the vapour pressure of this solution at 298 K. **(IIT 1998)**

77. A decimolar solution of potassium ferrocyanide is 50% dissociated at 300 K. Calculate osmotic pressure of the solution. Given $S = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$. **(Roorkee 1991)**

78. A 1% (mass/vol.) KCl solution is ionised to the extent of 82%. What would be its osmotic pressure at 18°C?

79. Calculate the osmotic pressure of 0.1*N* Na_3PO_4 solution at 300 K.

80. Arrange the osmotic pressures of given solution in increasing order assuming complete ionisation of each salt.
(a) 0.1 *N* glucose (b) 0.1 *N* KNO_3
(c) 0.1 *N* K_2SO_4 (d) 0.1 *N* K_3PO_4

81. A 0.001 molal solution of a complex represented as Pt $(NH_3)_4Cl_4$ in water had a freezing point depression of 0.0054°C. Given K_f for $H_2O = 1.86 \text{ K molality}^{-1}$. Assuming 100% ionisation of the complex, write the ionisation nature and formula of complex.

82. Calculate the osmotic pressure of 20% (mass/vol.) anhydrous $CaCl_2$ solution at 0°C assuming 100% ionisation.

83. A solution of KCl containing 7.45 g of it per litre solution has osmotic pressure 4.68 atm at 300 K. Calculate van't Hoff factor, degree of dissociation and osmotic coefficient (*g*).

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

85. *X* g of a non-electrolyte compound (molar mass = 200) are dissolved in 1.0 litre of 0.05 *M* NaCl aqueous solution. The osmotic pressure of this solution is found to be 4.92 atm at 27°C. Calculate the value of *X*. Assume complete dissociation of NaCl and ideal behaviour of this solution. ($R = 0.082$ litre atm mol^{-1} K^{-1}) **(Roorkee 1998)**

86. Calculate osmotic pressure of a decinormal solution of $BaCl_2$ at 27°C showing 80% degree of ionisation.

87. A 1.2% solution (mass/volume) of NaCl is isotonic with 7.2% solution (mass/volume) of glucose. Calculate degree of ionisation and van't Hoff factor of NaCl.

88. The vapour pressure of a solution containing 2 g of an electrolyte *BA* in 100 g water, which dissociates in one B^+ and one A^- ion in water, is 751 mm, at 100°C. Calculate degree of ionisation of *BA* if its molar mass is 56.

89. When 11.7 g of NaCl are dissolved in 200 g of water the depression in freezing point is doubled than the depression caused by 342 g of cane-sugar in 1000 g of water. From this information what do you infer about the nature of solute particles of NaCl in solution?

90. A storage battery contains a solution of H_2SO_4 38% by mass. At this concentration, van't Hoff factor is 2.50. At what temperature will the battery contents freeze? ($K'_f = 1.86° \text{ mol}^{-1}$ kg)

91. The degree of dissociation of $Ca(NO_3)_2$ in a dilute aqueous solution containing 7 g of salt per 100 g of water at 100°C is 70%. Calculate the vapour pressure of solution. **(IIT 1991)**

92. 1 g of monobasic acid in 100 g of water lowers the freezing point by 0.168°C. If 0.2 g of same acid requires 15.1 mL of *N* / 10 alkali for complete neutralization, calculate degree of dissociation of acid. K'_f for H_2O is 1.86 K mol^{-1} kg.

93. 1 g of a mixture containing NaCl and $CaCl_2$ is dissolved in water. Sodium oxalate on addition to this solution completely converts $CaCl_2$ to CaC_2O_4. The CaC_2O_4 is filtered and dissolved in dil. H_2SO_4. The clear solution requires 22 mL of 0.1 *M* $KMnO_4$. Calculate freezing point of an aqueous solution prepared by dissolving 5 g of same mixture containing $CaCl_2$ and NaCl in 100 g water. K_f of water is $1.86 \text{ K kg}^{-1} \text{ mol}^{-1}$. Assume complete dissociation of $CaCl_2$ and NaCl.

94. What will be the osmotic pressure of 0.1 M monobasic acid if its pH is 2 at 25°C?

95. A complex is represented as $CoCl_3 xNH_3$. Its 0.1 molal solution in water shows $\Delta T_f = 0.558°$. K_f for H_2O is 1.86 K molality^{-1}. Assuming 100% ionisation of complex and coordination number of Co as six, calculate formula of complex.

96. What is the ratio by mass of NaF and NaI which when dissolved in water produces the same osmotic effects as 0.1 molar solution of urea in water at same temperature? The mass of residue obtained on evaporation of the salt solution is 0.48 gram per 100 mL of solution evaporated. Assume complete dissociation of the salts.

97. A 0.025M solution of monobasic acid had a freezing point of −0.06°C. Calculate K_α for the acid. K_f for $H_2O = 1.86°$ molality^{-1}. Assume molality equal to molarity.

98. 0.01 M aqueous solution of weak acids HA and HB shows osmotic pressures equal to 0.30 atm and 0.35 atm respectively at 25°C. Calculate the ratio of their degree of dissociation.

99. Calculate the boiling point of a solution containing 0.61 g of benzoic acid in 50 g of carbon disulphide assuming 84% dimerization of the acid. The boiling point and K_b of CS_2 are 46.2°C and 2.3 K kg mol^{-1}. **(Roorkee 1997)**

100. 1.22 g of benzoic acid is dissolved in 100 g each of acetone and benzene separately. Boiling point of mixture with acetone increase by 0.17°C and boiling point of mixture with benzene increases by 0.13°C. K_b for acetone and benzene are 1.7 and 2.6 K kg mol^{-1} respectively. Find the molar mass of benzoic acid in acetone and benzene. Justify your answer with structure. **(IIT 2004)**

101. To 500 cm^3 of water, 3.0×10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86 K kg mol^{-1} and 0.997 g cm^{-3} respectively. **(IIT 2000)**

102. The freezing point of a solution containing 0.2 g of acetic acid in 20.0 g benzene is lowered by 0.45°C. Calculate the degree of association of acetic acid in benzene. Assume acetic acid dimerizes in benzene. K_f for benzene = 5.12 K mol^{-1} kg. **(Roorkee 1994)**

103. 2 g of benzoic acid dissolved in 25 g of C_6H_6 shows a depression in freezing point equal to 1.62 K. Molal depression constant of C_6H_6 is 4.9 K mol^{-1} kg. What is the percentage association of acid if it forms double molecule in solution? **(Roorkee 1990)**

104. 75.2 g C_6H_5OH (phenol) is dissolved in 1 kg of solvent of $K_f = 14$ K molality^{-1}. If depression in freezing point is 7K, then find the % dimerisation of phenol. **[IIT 2006]**

105. The freezing point of 0.02 mole fraction of acetic acid in benzene is 277.4 K. Acetic acid exists partly as dimer. Calculate the equilibrium constant for dimerisation. Freezing point of benzene is 278.4 K and heat of fusion of benzene is 10.042 kJ mol^{-1}. Assume molarity and molality same.

106. A solution containing 28 g phosphorus in 315 g CS_2 (b.pt. 46.3°C) boils at 47.98°C. K_b' for CS_2 is 2.34 K mol^{-1} kg. Calculate molar mass of phosphorus and deduce its molecular formula. Assume its complete association.

107. Calculate the molal lowering of vapour pressure for H_2O at 100°C.

108. The freezing point of 0.08 molal $NaHSO_4$ is −0.345°C. Calculate the percentage of HSO_4^- ions that transfers a proton to water. Assume 100% ionisation of $NaHSO_4$ and K_f for $H_2O = 1.86$ K molality^{-1}.

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

110. The vapour pressure of a very dilute aqueous solution and pure water are 17 and 17.39 mm at 20°C. Calculate the osmotic pressure at 20°C and density of water vapours at 20°C.

111. A 10% (mass/mass) solution of cane-sugar undergoes partial conversion into glucose and fructose to show inversion of cane-sugar as:

Sucrose + Water ⟶ Glucose + Fructose.

If the solution boils at 100.27°C at this state, calculate the average mass of the dissolved material. What fraction of the sugar has inverted? Given K_b for H_2O is 0.512 K mol^{-1} kg.

112. The vapour pressure of a certain liquid is given by the equation:

$$\log_{10} P = 3.54595 + \frac{313.7}{T} + 1.40655 \log_{10} T,$$

where P is the vapour pressure in mm and T is temperature in K. Determine molar latent heat of vaporisation as a function of temperature and calculate its value at 80K.

113. 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 25°C. The Henry's law constant for CO_2 in water at 25°C is 3.1×10^{-2} mol / litre - atm.

114. If N_2 gas is bubbled through water at 293 K, how many milli moles of N_2 gas would dissolve in 1 litre of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given, that Henry's law constant for N_2 at 293 K is 76.48 k bar.

SOLUTIONS (Numerical Problems)

1. Given that, $w = 1.75\,g$, $m = 342$

$V = \frac{150}{1000}$ litre, $T = 290\,K$

$$\pi V = nST = \frac{w}{m}ST$$

$$\pi \times \frac{150}{1000} = \frac{1.75}{342} \times 0.0821 \times 290$$

$$\pi = \mathbf{0.812\ atm}$$

2. Given that,

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

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

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

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

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

3. Given that, $\pi_1 = 4.92\,atm$, $\pi_2 = 1.5\,atm$

$C_1 = \frac{36}{180\times1}$ $\left(\because C = \frac{w}{m\times V}\right)$ $C_2 = ?$

$$\pi_1 V_1 = n_1 ST_1, \quad \pi_2 V_2 = n_2 ST_2$$

At same temperature,

$$\frac{\pi_1}{\pi_2} = \frac{n_1}{V_1}\times\frac{V_2}{n_2} = \frac{C_1}{C_2} \quad \therefore \quad \frac{4.92}{1.5} = \frac{36}{180\times C_2}$$

$\therefore$ $C_2 = \mathbf{0.061\ mol/L}$

4. Given that, $w = 2.5\,g$, $V = \frac{200}{1000}$ litre, $\pi = \frac{60}{76}$ atm,

$T = 288\,K$

$\because$ $\pi V = \frac{w}{m}ST$ $\quad \frac{60}{76}\times\frac{200}{1000} = \frac{2.5}{m}\times0.0821\times288$

$\therefore$ $m = \mathbf{374.38\ g\ mol^{-1}}$

Also, $\frac{\pi_1}{\pi_2} = \frac{T_1}{T_2}$

$\because$ $\frac{60}{\pi_2} = \frac{288}{298}$

$\therefore$ $\pi_2 = \mathbf{62.08}$

5. $\pi_1 V_1 = \frac{w_1}{m_1}ST_1$ for urea

$\pi_2 V_2 = \frac{w_2}{m_2}ST_2$ for sugar

Since, 100 mL of urea solution are mixed with 100 mL of cane-sugar solution and thus, total volume becomes 200 mL in which 3.4 g urea and 1.6 g sugar is present

$\therefore$ $\pi_1 \times \frac{200}{1000} = \frac{3.4}{60}\times0.0821\times293$

$$\pi_1 = \mathbf{6.82\ atm}$$

$$\pi_2 \times \frac{200}{1000} = \frac{1.6}{342}\times0.0821\times293$$

$\therefore$ $\pi_2 = \mathbf{0.56\ atm}$

$\therefore$ $\pi_{Total} = \pi_1 + \pi_2 = 6.82 + 0.56 = \mathbf{7.38\ atm}$

6. Let mixture contains a g glucose and b g urea.

$\therefore$ $a + b = 10$ ...(1)

From $\pi V = nST$

Also, $7.4\times\frac{250}{1000} = \left[\frac{a}{180}+\frac{b}{60}\right]\times0.0821\times300$

$3a + b = 13.52$ ...(2)

Solving Eqs. (1) and (2), $a = 1.76\,g$

$b = 8.24\,g$

$\therefore$ % of glucose $= \frac{1.76}{10}\times100 = \mathbf{17.6}$

% of urea $= \frac{8.24}{10}\times100 = \mathbf{82.4}$

7. Height developed = 2.4 mm

$\therefore$ Osmotic pressure $= h\cdot d\cdot g = \frac{2.4}{10}\times0.88\times981$

$= 207.187\,dyne\,cm^{-2}$

Now, $\pi V = nST$

$$207.187\times100 = \frac{0.2}{m}\times8.314\times10^7\times298$$

(R in erg; V in mL, using CGS system)

$\therefore$ $m = \mathbf{2.39\times10^5\ g\ mol^{-1}}$

8. (a) $\pi V = \frac{w}{m}ST$

Given that, $w = 5\,g$, $V = \frac{100}{1000}$ litre

$T = 300\,K$, $m = 180$

$$\pi = \frac{5\times1000\times0.0821\times300}{180\times100} = \mathbf{6.842\ atm}$$

(b) $\pi = hdg$

$6.841\times1.01\times10^5 = h\times10^3\times9.81$

$h = \frac{6.841\times1.01\times10^5}{9.81\times10^3}$

$= \mathbf{70.43\ m}$

$\pi = 6.841\,atm$

$= 6.841\times1.01\times10^5\,Nm^{-2}$

$d = 1\,g/cm^3 = 10^3\,kg/m^3$

$g = 9.81\,m/sec^2$

9. 1. At equilibrium the solutions occupy same vapour pressures as well as same concentrations since both are non-electrolyte.

2. Let w g of water passes from dilute solution to concentrate one to attain equilibrium.

Since, $P_s \propto$ mole fraction of solvent and $\frac{P^\circ - P_s}{P_s} = \frac{n}{N}$

$$\frac{P^\circ - P_s}{P_s}\text{ for I} = \frac{P^\circ - P_s}{P_s}\text{ for II}$$

$$\frac{20\times18}{342\times(100+w)} = \frac{10\times18}{342\times(100-w)}$$

$\therefore$ $w = \mathbf{33.3\ g}$

10. For $0.01M$ solution,

$\pi_1 V_1 = n_1 S T_1$ | $n_1 / V_1 = 0.01$

$\therefore \pi_1 = 0.01 \times 0.0821 \times 300$ | $T = 300$ K

$= \mathbf{0.2463\ atm}$

For $0.001M$ solution,

$\pi_2 V_2 = n_2 S T_2$ | $n_2 / V_2 = 0.001$

$\therefore \pi_2 = 0.001 \times 0.0821 \times 300$ | $T = 300$ K

$= \mathbf{0.02463\ atm}$

The movement of solvent particles occurs from dilute to concentrate solution, *i.e.*, $0.001M$ to $0.01M$ solution. Thus, pressure should be applied on concentrated solution, *i.e.*, on **$0.01M$** solution to prevent osmosis.

Also, magnitude of external pressure

$= 0.2463 - 0.0246 = 0.2217$ atm pressure on $0.01M$ solution.

11. Let a, b g be the amount of drug (molar mass 369) and sugar (molar mass 342) respectively.

$$a + b = 1.0 \quad ...(1)$$

$$\therefore \quad \pi V = (n_1 + n_2) \cdot ST$$

$$0.70 \times \frac{100}{1000} = \left[\frac{a}{369} + \frac{b}{342}\right] \times 0.0821 \times 300$$

$$\therefore \quad 342a + 369b = 358.66 \quad ...(2)$$

By Eqs. (1) and (2) $a = 0.617$ g

$b = 0.383$ g

$$\therefore \quad \%\text{ of drug} = \frac{0.617}{1} \times 100 = \mathbf{61.7\%}$$

12. For iostonic solutions, having neither dissociation nor association nature of solutes.

$$C_1 = C_2 \quad \text{or} \quad \frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$$

For sugar For urea

$$\frac{5}{\frac{342 \times 100}{1000}} = \frac{0.877}{\frac{m \times 100}{1000}}$$

$$\therefore \quad m = \frac{0.877 \times 342}{5} = \mathbf{59.99\ g\ mol^{-1}}$$

13. For isotonic solutions of non-electrolytes;

$$C_1 = C_2$$

$$\text{or} \quad \frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2} \quad \text{or} \quad \frac{w_1}{180 \times 0.5} = \frac{9.2}{180 \times 1}$$

$$\therefore \quad w = \mathbf{4.60\ g}$$

14. For initial solution, $\because \pi = \frac{500}{760}$ atm, $T = 283$ K

$$\frac{500}{760} \times V_1 = n \times S \times 283 \quad ...(1)$$

After dilution, let volume becomes V_2 and temperature is raised to 25° C, *i.e.*, 298 K.

$$\pi = \frac{105.3}{760} \text{ atm}$$

$$\frac{105.3}{760} \times V_2 = n \times S \times 298 \quad ...(2)$$

$\therefore$ By Eqs. (1) and (2), we get $\frac{V_1}{V_2} = \frac{283}{298} \times \frac{105.3}{500}$

$$\frac{V_1}{V_2} = \frac{1}{5}$$

$$\therefore \quad V_2 = 5V_1$$

i.e., Solution was **diluted to 5 times.**

15. Initially, $P_M = P_A^\circ \cdot X_A + P_B^\circ \cdot X_B$

$$550 = P_A^\circ \cdot \frac{1}{1+3} + P_B^\circ \cdot \frac{3}{1+3}$$

$$\text{or} \quad P_A^\circ + 3P_B^\circ = 2200 \quad ...(1)$$

When, one mole of B is further added to it

$$P_M = P_A^\circ \cdot X_A + P_B^\circ \cdot X_B$$

$$560 = P_A^\circ \cdot \frac{1}{1+4} + P_B^\circ \cdot \frac{4}{1+4}$$

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

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

$$P_A^\circ = \mathbf{400\ mm}, \quad P_B^\circ = \mathbf{600\ mm.}$$

16. Mole fraction of cyclohexane = 0.32

$\therefore$ Mole fraction of ethanol = $1 - 0.32 = 0.68$

Thus, $P_M = P_C^\circ \cdot X_C + P_E^\circ \cdot X_E$

$$P = 280 \times 0.32 + 168 \times 0.68 = 203.84 \text{ mm}$$

For the solution to be an ideal one, the vapour pressure should be 203.84 but the given value of vapour pressure is 376 mm, the **solution is non-ideal.**

17. Mole of $C_6H_6 = \frac{23.4}{78} = 0.3$

Mole of $C_7H_8 = \frac{64.4}{92} = 0.7$

Mole fraction of $C_6H_6 = \frac{0.3}{0.3 + 0.7} = 0.3$

Mole fraction of $C_7H_8 = \frac{0.7}{0.3 + 0.7} = 0.7$

According to Raoult's law for liquid mixtures

P_M = Partial V.P. of C_6H_6 + Partial V.P. of C_7H_8

$= 75 \times 0.3 + 22 \times 0.7 = 22.5 + 15.4 = 37.9$ mm

Now from Dalton's law of partial pressure,

Partial V.P. of $C_6H_6 = P_M \times$ Mole fraction of C_6H_6 in vapour phase

$22.5 = 37.9 \times$ Mole fraction of C_6H_6 in vapour phase

$\therefore$ Mole fraction of C_6H_6 in vapour phase $= \frac{22.5}{37.9} = \mathbf{0.59}$

$\therefore$ Mole fraction of C_7H_8 in vapour phase $= \mathbf{0.41}$

18. A: $P_M = P_B' + P_T' = P_B^\circ \cdot X_B + P_T^\circ \cdot X_T$ | $X_B = \frac{1}{1+4}$

$= 160 \times \frac{1}{1+4} + 60 \times \frac{4}{1+4} = 32 + 48$ | $X_T = \frac{4}{1+4}$

$= \mathbf{80\ mm}$

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

(Given, equal masss are mixed)

$$= 160 \times \frac{92}{170} + 60 \times \frac{78}{170} = 86.588 + 27.529$$

$= \mathbf{114.117\ mm}$

19. Given that,

Molar mass of $C_2H_4Br_2 = 188$, M. mass of $C_3H_6Br_2 = 202$

Mass of $C_2H_4Br_2 = 60\,g$, Mass of $C_3H_6Br_2 = 40\,g$

$$P'_{C_2H_4Br_2} = P^\circ \times \text{Mole fraction of } C_2H_4Br_2$$

$$= 170 \times \frac{60/188}{\frac{60}{188}+\frac{40}{202}} = \mathbf{104.9\ mm}$$

$$P'_{C_3H_6Br_2} = 127 \times \frac{40/202}{\frac{60}{188}+\frac{40}{202}} = \mathbf{48.63\ mm}$$

$$P_M = 104.9 + 48.63 = \mathbf{153.53\ mm}$$

20. According to Raoult's law for liquid mixtures:

$$P_M = P'_A + P'_B$$

$$\therefore \quad P_M = P^\circ_A \times \frac{\frac{w_A}{m_A}}{\frac{w_A}{m_A}+\frac{w_B}{m_B}} + P^\circ_B \times \frac{\frac{w_B}{m_B}}{\frac{w_A}{m_A}+\frac{w_B}{m_B}}$$

Given that,

$w_A = 64\,g$, $w_{H_2O} = 36\,g$, $P_M = 145$ mm

$P_{H_2O} = 155$ mm, $m_A = 128$, $m_{H_2O} = 18$

$$\therefore \quad P_M = 145 = P^\circ_A \times \frac{\frac{64}{128}}{\frac{64}{128}+\frac{36}{18}} + 155 \times \frac{\frac{36}{18}}{\frac{64}{128}+\frac{36}{18}}$$

$$\therefore \quad P^\circ_A = \mathbf{105\ mm}$$

21. $P_M = P^\circ_{EA} \times MF_{EA} + P^\circ_{PA} \times MF_{PA}$

$= P^\circ_{EA} \times X_{EA} + P_{PA} \times X_{PA}$

$290 = P^\circ_{EA} \times 0.65 + 210 \times 0.35$

P°_{EA} = **333.1 mm**

Given that,

$P^\circ_{PA} = 210$ mm

$X_1 = MF_{EA} = 0.65$

$\therefore \ X_1 + X_2 = 1$

$X_2 = MF_{PA} = 0.35$

$P_M = 290$ mm

22.

$$P^\circ_A \cdot X_{A(LP)} = P_M \cdot X'_{A(VP)}$$

$$P^\circ_A \cdot \frac{30}{100} = P_M \times \frac{60}{100}$$

$$P^\circ_B \cdot \frac{70}{100} = P_M \times \frac{40}{100}$$

$$\therefore \quad \frac{P^\circ_A}{P^\circ_B} \times \frac{30}{70} = \frac{60}{40}$$

$$\therefore \quad \frac{P^\circ_A}{P^\circ_B} = \frac{60 \times 70}{30 \times 40} = \mathbf{3.5}$$

23.

$$X_{CCl_4(g)} = 0.3474$$

$$X_{SiCl_4(g)} = 0.6526$$

$$P^\circ_{SiCl_4} = 238.3 \text{ mm}$$

$$P^\circ_{CCl_4} = 114.9$$

$$P'_{CCl_4} = P^\circ_{CCl_4} \cdot X_{CCl_4(l)} = P_M \times X_{CCl_4(g)}$$

$\therefore \quad 114.9 \times X_{CCl_4(l)} = P_M \times 0.3474$ ...(1)

Also, $238.3 \times X_{SiCl_4(l)} = P_M \times 0.6526$ ...(2)

By Eqs. (1) and (2) $\dfrac{X_{CCl_4(l)}}{X_{SiCl_4(l)}} = \dfrac{0.3474}{0.6526} \times \dfrac{238.3}{114.9} = 1.104$

Let a g CCl_4 and b g $SiCl_4$ be present in liquid and ratio of mole fraction is the ratio of their mole.

Then $\dfrac{\frac{a}{154}}{\frac{b}{170}} = 1.104 \quad \therefore \quad \dfrac{a}{b} = \mathbf{1}$

Thus 50% by mass of CCl_4 liquid is present in mixture.

24. In vapour phase

1 mole or 78 g benzene has volume at 20° C

$$= \frac{78 \times 1}{0.877} \times 2750 \text{ mL}$$

Similarly,

1 mole or 92 g toluene has volume at 20° C

$$= \frac{92 \times 1}{0.867} \times 7720 \text{ mL}$$

Thus, from $PV = nRT$

$$\therefore \quad \frac{P^\circ_B}{760} \times \frac{78 \times 2750}{0.877 \times 1000} = 1 \times 0.0821 \times 293$$

$$P^\circ_B = 74.74 \text{ mm}$$

Similarly, $\dfrac{P^\circ_T}{760} \times \dfrac{92 \times 7720}{0.867 \times 1000} = 1 \times 0.0821 \times 293$

$P^\circ_T = 22.37$ mm

$\because \quad P_M = P^\circ_B X_B + P^\circ_T X_T$

$\therefore \quad P_M = P^\circ_B X_B + P^\circ_T (1 - X_B)$

or $\quad 46 = 74.74\, X_B + 22.37\,(1 - X_B)$

$\therefore \quad X_B = 0.45$ (in liquid phase)

$\because \quad X_B + X_T = 1$

$\therefore \quad X_T = 0.55$ (in liquid phase)

Also, $\quad P'_B = P^\circ_B \cdot X_B = P_M \cdot X'_B$

or $\quad 74.74 \times 0.45 = 46 \cdot X'_B$

$\therefore \quad X'_B$ (in gas phase) $= \mathbf{0.73}$

25. The solution boils at 0.5 atm and thus,

$$\text{V.P. of mixture} = \frac{760}{2} \text{ mm} = 380 \text{ mm}$$

$\because \quad P_M = P^\circ_T \cdot X_T + P^\circ_{xylene} \cdot X_{xylene}$

$380 = 400(X_T) + 150(1 - X_T) \quad (\because \ X_T + X_{xylene} = 1)$

$\therefore \quad X_{toluene} = \mathbf{0.92}$ and $X_{xylene} = \mathbf{0.08}$

26. At boiling point $P_{Mixture} = 736$ mm

Thus, at boiling point $P'_{H_2O} = 526$ mm

$\therefore \quad P'_l = 736 - 526 = 210$ mm

Also, $\quad P' = P_m \times$ m.f. in vapour phase ...(1)

Let a g of liquid and water is collected or this is the amount of vapours at equilibrium

Thus, mass of liquid vapours $= \dfrac{2.5 \times a}{3.5}$

mass of water vapours $= \dfrac{a}{3.5}$

Now for liquid, from Eq. (1)

$$210 = 736 \times \frac{\frac{2.5a}{3.5 \times m}}{\frac{a}{3.5 \times 18} + \frac{2.5a}{3.5 \times m}} \quad ...(2)$$

where m is molar mass of liquid

For H_2O, from Eq. (1)

$$526 = 736 \times \frac{\frac{a}{3.5\times18}}{\frac{a}{3.5\times18}+\frac{2.5a}{3.5\times m}} \qquad ...(3)$$

Thus, from Eqs. (2) and (3) $\frac{210}{526}=\frac{18\times2.5}{m}$

$\therefore$ $m = \mathbf{112.7}$

27. $P' = P_M \cdot X_A$

where X_A is mole fraction in gaseous phase

$\therefore$ $$27 = 760 \cdot \frac{\frac{w_2}{123}}{\frac{w_1}{18}+\frac{w_2}{123}} \quad \text{(for nitrobenzene)}$$

and $$733 = 760 \cdot \frac{w_1/18}{\frac{w_1}{18}+\frac{w_2}{123}} \quad \text{(for water)}$$

$\therefore$ $\frac{w_1}{w_2} = \mathbf{4}$

28. At boiling point $P'_M = 740.2$ mm

$P'_{H_2O} = 530.1$ mm

$\therefore$ $P'_{\text{chlorobenzene}} = 740.2 - 530.1 = 210.1$ mm

Also, $P' = P_M \times$ mole fraction

$530.1 = 740.2 \times$ mole fraction of H_2O

$\therefore$ mole fraction of $H_2O = 0.716$

$\therefore$ mole fraction of $C_6H_5Cl = 0.284$

Let a g H_2O and b g chlorobenzene be present in distillate

or $$\frac{w_{H_2O}/18}{\frac{w_{CB}}{112.5}+\frac{w_{H_2O}}{18}} = 0.716 \qquad ...(1)$$

and $$\frac{w_{CB}/112.5}{\frac{w_{CB}}{112.5}+\frac{w_{H_2O}}{18}} = 0.284 \qquad ...(2)$$

By Eqs (1)/(2)

or $\frac{a}{18}\times\frac{112.5}{b}=\frac{0.716}{0.284}$ or $\frac{a}{b}=\frac{12.89}{31.95}=0.403$ ...(3)

Let total mass of distillate be 100 g, than

$a + b = 100$ ...(4)

By Eqs. (3) and (4) $a = \mathbf{28.73}$

$b = \mathbf{71.27}$

29. $$2.303\log\frac{P_2}{P_1}=\frac{\Delta H}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$\therefore$ $$2.303\log\frac{400}{40}=\frac{\Delta H}{2}\left[\frac{229.1-191.4}{229.1\times191.4}\right]$$

$\therefore$ $\Delta H_{vap} = 5357.35$ cal

Again $$2.303\log\frac{P_2}{P_1}=\frac{\Delta H}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$2.303\log\frac{760}{400}=\frac{5357.35}{2}\left[\frac{T-229.1}{T\times229.1}\right]$$

$\therefore$ $\frac{T-229.1}{T}=0.055$

$\therefore$ $T = 242.43$ K $= \mathbf{-30.57°C}$

30. $$\frac{P°-P_s}{P_s}=\frac{w\times M}{m\times W}$$

$$\frac{23.62-P_s}{P_s}=\frac{1.5\times18}{60\times50}$$

$\therefore$ $P_s = \mathbf{23.41\ mm}$

31. At 100° C: Vapour pressure of pure water ($P°$) = 760 mm

$\because$ $$\frac{P°-P_s}{P_s}=\frac{w\times M}{m\times W} \qquad ...(1)$$

$\therefore$ $$\frac{760-P_s}{P_s}=\frac{3.42\times18}{342\times180}$$

$\therefore$ $P_s = \mathbf{759.2\ mm}$

Also we have, $2.303\log\frac{P_2}{P_1}=\frac{\Delta H}{R}\frac{[T_2-T_1]}{T_1T_2}$ ...(2)

$\because$ $P_2 = 760$ mm; $T_2 = 373$ K; $T_1 = 313$ K

and $\Delta H = 10$ kcal mol^{-1}

$\therefore$ From Eq. (2)

$$2.303\log\frac{760}{P_1}=\frac{10}{2\times10^{-3}}\times\frac{[373-313]}{373\times313}$$

$\therefore$ $P_1 = \mathbf{58.2\ mm}$

Now at 40° C: $\frac{P°-P_s}{P_s}=\frac{w\times M}{m\times W}$

For 0.2 molal solution $P°_{H_2O} = 58.2$ mm at 40° C

$\because$ $\frac{w}{m} = 0.2$ and $W = 1000$ g; $M = 18$

$\therefore$ $$\frac{58.2-P_s}{P_s}=\frac{0.2\times18}{1000}$$

$\therefore$ $P_s = \mathbf{57.99\ mm}$

$\Delta P = P° - P_s = 58.20 - 57.99 = \mathbf{0.21\ mm}$

32. $\because$ $$\frac{P°-P_s}{P_s}=\frac{w\times M}{m\times W}$$

$\therefore$ $$\text{Molality} = \frac{w}{m\times W}\times1000=\frac{P°-P_s}{P_s\times M}\times1000$$

$$=\frac{639.7-631.9}{631.9\times78}\times1000$$

$= \mathbf{0.158\ mol / kg\ of\ solvent}$

33. $\because$ $$\frac{P°-P_s}{P_s}=\frac{w\times M}{m\times W}$$

$P_s=\frac{4P°}{5}$, $m = 60$ g mol^{-1}, $w = ?$, $W = 180$ g, $M = 18$

$\therefore$ $$\frac{P°-\frac{4P°}{5}}{\frac{4P°}{5}}=\frac{w\times18}{60\times180}$$

$\therefore$ $$w=\frac{60\times180}{4\times18}=\mathbf{150\ g}$$

34. Given that,

$P° = 640$ mm, $P_s = 600$ mm, $w = 2.175$ g, $W = 39.0$ g, $M = 78$ g mol^{-1}

$\because$ $$\frac{P°-P_s}{P_s}=\frac{w\times M}{m\times W}$$

$\therefore$ $$\frac{640-600}{600}=\frac{2.175\times78}{m\times39}$$

$\therefore$ $m = \mathbf{65.25\ g\ mol^{-1}}$

35. Given that, temperature is 373 K and b. pt. of $H_2O = 373$ K

$\therefore$ Vapour pressure of $H_2O = 76$cm

We have, $\frac{P^\circ - P_s}{P_s} = \frac{w \times M}{m \times W}$

$\therefore$ $\text{Molality} = \frac{w}{m \times W} \times 1000 = \frac{P^\circ - P_s}{P_s} \times \frac{1}{M} \times 1000$

$= \frac{760 - 750}{750} \times \frac{1}{18} \times 1000$

$= \mathbf{0.741\ mol / kg\ of\ solvent}$

Also we have, $\frac{P^\circ - P_s}{P^\circ} = \frac{n}{n+N}$

$\therefore$ Mole fraction $= \frac{P^\circ - P_s}{P^\circ} = \frac{760-750}{760} = \frac{10}{760} = \mathbf{0.013}$

36. $\frac{P^\circ - P_s}{P_s} = \frac{w \times M}{m \times W} = \frac{w \times M \times 1000}{m \times W \times 1000} = \text{Molality} \times \frac{M}{1000}$

$\therefore$ $\frac{92.5 - P_s}{P_s} = 1 \times \frac{18}{1000}$

$\therefore$ $P_s = \mathbf{90.84\ mm}$

37. We have, $\frac{P^\circ - 21.85}{21.85} = \frac{30 \times 18}{90 \times m}$ for I case ...(1)

Now, Mass of solvent $= 90 + 18 = 108$ g

$\frac{P^\circ - 22.15}{22.15} = \frac{30 \times 18}{108 \times m}$ for II case ...(2)

$\therefore$ By Eq. (1) $P^\circ_M - 21.85m = 21.85 \times 6 = 131.1$

By Eq. (2) $P^\circ_M - 22.15m = 22.15 \times 5 = 110.75$

$\quad - \quad + \quad -$

$\therefore$ $0.30m = 20.35$

$\therefore$ $m = \frac{20.35}{0.30} = 67.83\ \text{g mol}^{-1}$

On substituting the value of m in Eq. (1),

$\frac{P^\circ - 21.85}{21.85} = \frac{30 \times 18}{90 \times 67.83}$

$\therefore$ $P^\circ = \mathbf{23.78\ mm}$

38. For water vapours : $PV = \frac{w}{m} RT$

$\therefore$ $\frac{w}{V} = (d) = \frac{Pm}{RT} = \frac{17.39 \times 18}{760 \times 0.0821 \times 293} = 0.0171$ g / litre

Also, $\frac{P^\circ - P_s}{P_s} = \frac{w \times M \times 1000}{m \times W \times 1000}$

$\therefore$ molality $\left(\frac{w}{m \times W} \times 1000\right) = \frac{17.39 - 17}{17} \times \frac{1000}{18} = 1.275$

$= \text{molarity} \left(\frac{n}{V}\right)$

$\therefore$ $P = \frac{n}{V} \times S \times T = 1.275 \times 0.0821 \times 293 = \mathbf{30.67\ atm}$

39. At 293 K; $\frac{P^\circ - P_s}{P_s} = \frac{n}{N} = \frac{n \times 18}{W}$

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

$\therefore$ $\frac{n}{W} = \frac{42.2}{2295.8} \times \frac{1}{18}$ or $W = 979.25 \times n$ g

$\therefore$ Mass of solution $= 979.25n +$ mass of solute

$= 979.25n + 60n = 1039.25n$ g $= 1.0393n$ kg

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

Now, $PV = nST$

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

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

40. $\frac{P^\circ - P_s}{P^\circ} = \frac{n}{n+N} = \frac{w/m}{\frac{w}{m} + \frac{W}{M}} = \frac{10/100}{\frac{10}{100} + \frac{180}{18}} = \mathbf{0.0099}$

41. $\frac{P^\circ - P_s}{P^\circ} = \frac{n}{n+N} = \frac{w/m}{\frac{w}{m} + \frac{W}{M}}$

For H_2O $\frac{P^\circ - P_s}{P^\circ} = \frac{6/120}{\frac{6}{120} + \frac{150}{18}}$

For C_2H_5OH $\frac{P^\circ - P_s}{P^\circ} = \frac{6/120}{\frac{6}{120} + \frac{150}{46}}$

$\therefore$ Ratio of $\left(\frac{P^\circ - P_s}{P^\circ}\right)$ for H_2O and C_2H_5OH

$= \frac{6/120}{\frac{6}{120} + \frac{150}{18}} \times \frac{6/120 + 150/46}{\frac{6}{120}} = \mathbf{0.3949}$

42. Given that 0.1 M glucose is isotonic with solution of X in 100 g water.

Thus, Conc. of solution of $X = 0.1$ mol per litre

For dilute solution:

Volume of solution = volume of solvent (H_2O)

= weight of H_2O

$\therefore$ Mole of $X = 0.1$; Mole of water $= \frac{1000}{18}$

$\frac{P^\circ - P_s}{P^\circ} = \frac{n}{n+N} = \frac{0.1}{0.1 + \frac{1000}{18}} = \mathbf{0.0018}$

43. Given that, $P_s = \frac{80}{100} P^\circ$, $w = ?$, $m = 40$, $W = 114$ g, $M = 114$

$\because$ $\frac{P^\circ - P_s}{P_s} = \frac{w \times M}{m + W}$

$\frac{P^\circ - \frac{80}{100} P^\circ}{\frac{80}{100} P^\circ} = \frac{w \times 114}{40 \times 114}$

$w = \frac{40}{4} = \mathbf{10\ g}$

44. According to Raoult's law:

$\frac{P^\circ - P_s}{P_s} = \frac{w}{m} \times \frac{M}{W}$

Given if $P^\circ = 100$, then $P_s = 75$ mm, $m = 60$, $M = 18$, $W = 100$ g

$\frac{100 - 75}{75} = \frac{w \times 18}{60 \times 100}$

$\therefore$ $w = \mathbf{111.11\ g}$

Also molality of solution,

$$= \frac{\text{mass of solute}}{\text{molar mass of solute} \times \text{mass of solvent (in kg)}}$$

$$= \frac{111.11}{60 \times \frac{100}{1000}} = \mathbf{18.52\ m}$$

45. $\because$ Loss in mass of solution $\propto P_s$

Loss in mass of solvent $\propto P^\circ - P_s$

$$\therefore \quad \frac{P^\circ - P_s}{P_s} = \frac{\text{Loss in mass of solvent}}{\text{Loss in mass of solution}} \quad ...(1)$$

Also, $$\frac{P^\circ - P_s}{P_s} = \frac{w \times M}{m \times W} \quad ...(2)$$

$\therefore$ By Eqs. (1) and (2), we get $\frac{0.04}{2.5} = \frac{5 \times 18}{80 \times m}$

$\therefore \quad m = \mathbf{70.31\ g\ mol^{-1}}$

46. At 100° C: $P_2 = 760$ mm; $\Delta H_{\text{Vap.}} = 540 \times 18$ cal/mol $= 9720$ cal/mol

$$\therefore \quad 2.303 \log \frac{P_2}{P_1} = \frac{\Delta H}{R} \frac{[T_2 - T_1]}{T_1 T_2}$$

$$\log \frac{P_2}{P_1} = \frac{9720}{1.987 \times 2.303} \times \frac{[373 - 348]}{373 \times 348}$$

$$\therefore \quad \frac{P_2}{P_1} = 2.57$$

$$\therefore \quad P_1 = \frac{760}{2.57} = 295.7 \text{ mm (or } P^\circ)$$

Now, $$\frac{P^\circ - P_s}{P_s} = \frac{n}{N} = \frac{0.1}{1000/18}$$

$$\frac{P^\circ}{P_s} - 1 = \frac{1.8}{1000} \quad \therefore \quad \frac{P^\circ}{P_s} = \frac{1001.8}{1000}$$

$$\therefore \quad P_s = \frac{P^\circ \times 1000}{1001.8} = \frac{295.7 \times 1000}{1001.8} = 295.17$$

$$\therefore \quad \Delta P = 295.7 - 295.17 = \mathbf{0.53\ mm}$$

47. $\frac{P^\circ - P_s}{P_s} = \frac{w}{m} \times \frac{M}{W}$, $\therefore$ $\frac{100 - 98.88}{98.88} = \frac{w \times 78 \times 1000}{m \times W \times 1000}$

or $$\text{molality} \left(\frac{w \times 1000}{m \times W} \right) = \frac{1.12 \times 1000}{78 \times 98.88} = 0.1452$$

Also, $$\Delta T = K'_f \times \text{molality}$$

$$0.73 = K'_f \times 0.1452$$

$$\therefore \quad K'_f = \mathbf{5.028\ K\ molality^{-1}}$$

48. Given, b. pt. of water $= 100°$ C, b.pt. of solution $= 100.34°$ C

$\therefore$ Elevation in b. pt., $\Delta T = 0.34$, $w = 12$ g, $W = 100$ g, $m = 180$

$$\Delta T = \frac{1000 K'_b\, w}{mW}$$

$$0.34 = \frac{1000 \times K'_b \times 12}{180 \times 100}$$

$$\therefore \quad K'_b = \mathbf{0.51\ K\ mol^{-1}\ kg}$$

49. $$w_{\text{EA}} = 20 \times 0.7893 = 15.786 \text{ g}$$

$$w_{\text{H}_2\text{O}} = 40 \times 0.9971 = 39.884$$

$\therefore$ $w_{\text{mixture}} = 55.670$ g $\therefore$ $V_{\text{mixture}} = \frac{55.67}{0.9571} = 58.165$ mL

$$\therefore \quad \% \text{ change in volume} = \frac{[60 - 58.165]}{60} \times 100 = 3.058$$

$$\text{molality of alcohol} = \frac{15.786}{46 \times \frac{39.884}{1000}} = \mathbf{8.6\ m}$$

$$\text{molarity of alcohol} = \frac{15.786}{46 \times \frac{58.165}{1000}} = \mathbf{5.90\ M}$$

$\Delta V_{\text{mixing}} = (58.165 - 60) = -1.835$ mL

$\therefore$ –ve deviation from Raoult's law.

50. Given that, $w = 0.5143$ g, $W = 35$ g

$K'_b = 3.9$ K mol^{-1} kg, $\Delta T = 0.323°$ C

$$\because \quad \Delta T = \frac{1000 K'_b\, w}{mW}$$

$$\therefore \quad 0.323 = \frac{1000 \times 3.9 \times 0.5143}{m \times 35}$$

$$m = \mathbf{177.42\ g\ mol^{-1}}$$

51. Given, $w = 174.5 \times 10^{-3}$ g, $W = 78$ g

$m = 8 \times 32 = 256$ ($\because$ Octa atomic), $K'_b = 5.2$

$$\because \quad \Delta T = \frac{1000 K'_b\, w}{Wm} = \frac{1000 \times 5.2 \times 174.5 \times 10^{-3}}{78 \times 256} = 0.045$$

$\therefore$ Boiling pt. of Br_2 solution $= 332.15 + \Delta T$ $= 332.15 + 0.045 = \mathbf{332.195\ K}$

52. $$\because \quad \Delta T = \frac{100 K_f\, w}{mW}$$

$\because$ $w = 0.48$ g, $W = 10.6$ g, $\Delta T_f = 1.8$, $K_f = 50$

$$\therefore \quad 1.8 = \frac{100 \times 50 \times 0.48}{m \times 10.6}$$

$$\therefore \quad m = \mathbf{125.79\ g\ mol^{-1}}$$

53. $MeOH + H_2SO_4 \rightleftharpoons MeOH_2^+ + HSO_4^-$ (two ions)

$$Ph_3C{\cdot}OH + H_2SO_4 \rightleftharpoons Ph_3COH_2^+ + HSO_4^-$$

$$Ph_3COH_2^+ \rightleftharpoons Ph_3C^+ + H_2O$$

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$$

$$Ph_3COH + 2H_2SO_4 \rightleftharpoons Ph_3C^+ + H_3O^+ + 2HSO_4^-$$

(four ions)

Since, number of ions are doubled in Ph_3COH and so depression is two times more for same number of mole of each.

54. Given, $W_{\text{menthol}} = 6.2$ g; $w_{\text{cyclohexane}} = 100 - 6.2 = 93.8$ g

$\Delta T_f = 6.5 - (-19.5) = 26.0$; $K = 20.2$ K molality^{-1}

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

or $$m = \frac{1000 \times 20.2 \times 6.2}{93.8 \times 26.0} = \mathbf{51.35\ g\ mol^{-1}}$$

55. $\frac{F - 32}{9} = \frac{C}{5}$ (For conversion of ° F scale to ° C scale)

$$\frac{14 - 32}{9} = \frac{C}{5}$$

$\therefore$ $C = -10°$ C $\therefore$ $\Delta T = 10$

Now, $\Delta T = K_f \times \text{molality}$

$$10 = 1.86 \times \frac{w}{46 \times 1}$$

$\therefore$ $w = \mathbf{247.31\ g}$

56. $\because$ Solution has 5% by mass urea and 10% by mass glucose

$\because$ $\% \text{ By mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$

$\therefore$ Mass of water = 85 g; mass of urea = 5 g; mass of glucose = 10 g

$$\Delta T = \Delta T_{Urea} + \Delta T_{Glucose}$$
$$\Delta T = \frac{1000 \times 1.86 \times 5}{60 \times 85} + \frac{1000 \times 1.86 \times 10}{180 \times 85}$$
$$= 1.824 + 1.216 = \mathbf{3.04}$$

$\therefore$ Freezing point $= 0 - 3.04 = \mathbf{-3.04°C}$

57. $\because$ $\Delta T = \frac{1000 K'_b\ w}{mW}$

$$0.01 = \frac{1000 \times 0.5 \times w}{180 \times 100} \quad \therefore\ w = 0.36\text{g}$$

$\because$ 180 g glucose contains $= 6.023 \times 10^{23}$ molecules

$\therefore$ 0.36 g glucose contains

$$= \frac{6.023 \times 10^{23} \times 0.36}{180}$$
$$= \mathbf{1.2 \times 10^{21}\ molecules}$$

58. For acetone + Benzene mixture:

$$\Delta T = \frac{K'_f \times 1000 \times w}{m \times W}$$

$$(278.40 - 277.12) = \frac{1000 \times K_f \times 1.4}{100 \times 58}$$

or $$1.28 = \frac{1000 \times K_f \times 1.4}{100 \times 58} \quad ...(1)$$

For solute (A) + Benzene mixture (Let m be the molar mass of A)

$$(278.40 - 277.76) = \frac{1000 \times K_f \times 2.8}{100 \times m}$$

or $$0.64 = \frac{1000 \times K_f \times 2.8}{100 \times m} \quad ...(2)$$

By Eqs. (1) and (2), $m = \mathbf{232\ g\ mol^{-1}}$

59. $$\Delta T = \frac{1000 \times K'_f\ w}{mW}$$

For AB_2 $\quad 2.3 = \frac{1000 \times K'_f \times 1}{m_1 \times 20} = \frac{1000 \times 5.1 \times 1}{m_1 \times 20}$

For AB_4 $\quad 1.3 = \frac{1000 \times K'_f \times 1}{m_2 \times 20} = \frac{1000 \times 5.1 \times 1}{m_2 \times 20}$

$\therefore$ $m_1 = 110.87\ \text{g mol}^{-1}$; and $m_2 = 196.15\ \text{g mol}^{-1}$

Now, m_1 is molar mass of AB_2 $\therefore$ $a + 2b = 110.87$

m_2 is molar mass of AB_4 $\therefore$ $a + 4b = 196.15$

where a and b are atomic mass of A and B

$\therefore$ $a = \mathbf{25.59\ g/mol}$

$b = \mathbf{42.64\ g/mol}$

60. Given ethylene glycol = 50cm^3; $K'_f = 1.86\ \text{K mol}^{-1}$ kg

$\therefore$ mass of glycol $= 50 \times d$, where d is density of glycol

mass of water = 50 g

$$\Delta T_f = 34°\text{C}$$

Now, $$\Delta T_f = \frac{1000 \times K'_f \times w}{m \times W}$$

$$34 = \frac{1000 \times 1.86 \times 50 \times d}{62 \times 50}$$

$\therefore$ $d = \mathbf{1.133\ g/cm^3}$

61. [Ans. $m = \mathbf{156.06\ g\ mol^{-1}}$**]**

62. $$\Delta T = \frac{1000 \times K'_f \times w}{m \times W}$$

$\therefore$ $\Delta T = \frac{1000 \times 1.86 \times 2000 \times 0.8}{32 \times 8000}$

$= 11.625$

$\therefore$ F. pt. of solution $= 0 - 11.625 = -11.625$

Given,

$w = 2000 \times 0.8\ \text{g}$

$W = 8000 \times 1\ \text{g}$

$K'_f = 1.86\ \text{K mol}^{-1}$ kg

$m = 32$ for CH_3OH

$\therefore$ Vehicle may be parked out door not below $\mathbf{-11.625°C}$.

63. $$\Delta T = \frac{1000 \times K'_f \times w}{m \times W}$$

$$48 = \frac{1000 \times 37.5 \times 0.09}{m \times 0.55}$$

$\therefore$ $m = \mathbf{127.84\ g\ mol^{-1}}$

Given,

$\Delta T = 209 - 161 = 48°\text{C}$

$w = 0.09\text{g}$

$W = 0.55\text{g}$

$K'_f = 37.5°\text{C mol}^{-1}$ kg

Now %	$\frac{\%}{\text{Atomic mass}}$ value	Value/Lowest value
C = 93.75	$\frac{93.75}{12} = 7.8125$	$\frac{7.8125}{6.25} = 1.25$
H = 6.25	$\frac{6.25}{1} = 6.25$	$\frac{6.25}{6.25} = 1$

$\therefore$ C : H :: 1.25 : 1 or 5 : 4

$\therefore$ Empirical formula is C_5H_4 and empirical formula mass = 64

$\therefore$ Molecular formula is $(C_5H_4)_n$ and $n = \frac{127.84}{64} \approx 2$

$\therefore$ Molecular formula of solute is $(C_5H_4)_2 = \mathbf{C_{10}H_8}$

64. For a given aqueous solution

$$\Delta T_b = K'_b \times \text{molality}$$
$$\Delta T_f = K'_f \times \text{molality}$$

$\therefore$ $$\frac{\Delta T_b}{\Delta T_f} = \frac{K'_b}{K'_f} = \frac{RT_b^2}{1000 l_v} \times \frac{1000 l_f}{RT_f^2}$$

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

$\because$ $T_b = 100 + 273 = 373\ \text{K}$

$T_f = 0 + 273 = 273\ \text{K}$

$l_f = 80\ \text{cal g}^{-1}$

$l_v = 540\ \text{cal g}^{-1}$

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

$\therefore \quad T_f = 0.0 - 0.362 = -\mathbf{0.362°\,C}$

65. Given, $l_f = 1436.3\text{ cal/mole} = \frac{1436.3}{18}\text{ cal/g}$

$$K'_f = \frac{RT^2}{1000 l_f} = \frac{2\times 273\times 273}{1000\times\frac{1436.3}{18}}$$

$$K'_f = \frac{2\times 273\times 273\times 18}{1000\times 1436.3} = 1.87$$

Now, Mole fraction of $H_2O = 0.8 = \frac{N}{n+N}$

$\therefore$ Now, Mole fraction of solute $= 0.2 = \frac{n}{n+N}$

$\therefore \quad \frac{n}{N} = \frac{0.2}{0.8} = \frac{1}{4}$

or $\quad \frac{w\times M}{m\times W} = \frac{1}{4}$ or $\frac{w}{m\times W} = \frac{1}{4\times 18}$

$\therefore \quad \Delta T = \frac{1000\times K'_f\times w}{m\times W} = 1000\times 1.87\times\frac{1}{4\times 18}$

$= 25.97°\,C$

$\therefore$ F. pt. $= 0 - 25.97 = -\mathbf{25.97°\,C}$

66. For 5% solution of A :

$$(\Delta T_f)_A = \frac{K_f\times 5\times 1000}{m_A\times 95} \quad ...(1)$$

For 5% solution of B :

$$(\Delta T_f)_B = \frac{K_f\times 5\times 1000}{m_B\times 95} \quad ...(2)$$

By Eqs. (1) and (2), $\therefore \quad \frac{(\Delta T_f)_A}{(\Delta T_f)_B} = \frac{m_B}{m_A} = \frac{3}{1} \left(\because \frac{m_A}{m_B} = \frac{1}{3}\right)$

For solution S_1 : Let $2V$ mL solution of A is mixed with $3V$ mL solution of B.

Mass of A in $2V$ mL or $2V$ g $= \frac{5\times 2V}{100}$ g $= \frac{10V}{100}$ g

Mass of B in $3V$ mL or $3V$ g $= \frac{5\times 3V}{100}$ g $= \frac{15V}{100}$ g

Total mass of solution $= 5V$ g

$$(\Delta T_f)_{S_1} = \frac{K_f\times 1000\times\left[\frac{0.1V}{m_A} + \frac{0.15V}{m_B}\right]}{\left[5V - \frac{10V}{100}\right]}$$

$$= \frac{1000K_f\,[0.1m_B + 0.15m_A]}{4.9\times m_A\times m_B}$$

For solution S_2 : Similarly, we have

$$(\Delta T_f)_{S_2} = \frac{1000\times K_f\,[0.15m_B + 0.10m_A]\times 0.9898}{4.85\times m_A\times m_B}$$

Thus, $\frac{(\Delta T_f)_{S_1}}{(\Delta T_f)_{S_2}} = \frac{(0.1m_B + 0.15m_A)\times 0.9898}{(0.10m_A + 0.15m_B)}$

$$= \frac{(0.1\times 3m_A + 0.15m_A)\times 0.9898}{(0.10m_A + 0.15\times 3m_A)}$$

$$= \frac{0.45\times 0.9898}{0.55} = \mathbf{0.81}$$

67. $K_b = \frac{RT_b^2\cdot M}{1000\,\Delta H_V} = \frac{RT_bM}{1000\,\Delta S_V} \quad \left(\because \Delta S_V = \frac{\Delta H_V}{T_b}\right)$

$\therefore \quad \Delta S_V = \frac{RT_b^2\cdot M}{1000\,\Delta K_b} = \frac{2\times 373\times 18}{1000\times 0.51} = \mathbf{26.33\ cal/mol}$

68. $K_b = \frac{RT_b^2}{1000\,l_V} = \frac{RT_b\cdot M}{1000\,\Delta H_V} = \frac{RT_b^2\cdot M}{1000\,\Delta S_V}$

Where, ΔS_V is change in entropy during vaporisation at T_b. Since, during vaporisation entropy increases because randomness increases. Also ΔS_V may be taken as almost constant as for liquid $\rightleftharpoons$ vapour even if the extent of disorderness varies from liquid to liquid since, entropy in vapour state is abnormally higher. Thus, $S_V - S_L = \Delta S_V$ is almost constant. If M and R are constant, $K_b \propto T_b$.

Thus, values reported in table are in accordance with X, Y and Z.

69. Given, $\Delta T = 9.3$, $\quad w = 50$ g; $\quad K_f$ for $H_2O = 1.86\text{ K mol}^{-1}\text{ kg}$, $m_{\text{Glycol}} = 62$

$\because \quad \Delta T = \frac{1000\times K_f\times w}{m\times W} \quad \therefore 9.3 = \frac{1000\times 1.86\times 50}{62\times W}$

$\therefore \quad W_{\text{Water}} = 161.29$ g

Thus, mass of ice separated $= 200 - 161.29 = \mathbf{38.71\ g}$

70. $\quad \Delta T = K'_f\times\text{molality} = 1.86\times 1 = 1.86$

$\therefore$ Solution starts freezing at $-1.86°$ C. Thus, on cooling up to $-3.534°$ C, freezing continues,

Let molality of solution left at $-3.534°$ C be m'

$\therefore \quad \Delta T = K'_f\times m'$

$\therefore \quad m' = \frac{3.534}{1.86} = 1.9$ m

Initially 1000 g solvent contains 342 g Sucrose

or 1342 g solution contains 342 g Sucrose

$\therefore$ 1000 g solution contains

$= \frac{342\times 1000}{1342}$ g sucrose $= 254.84$ g sucrose

Finally,

$\therefore$ Mass of water $= 1000 - 254.84 = 745.16$ g

Since, sucrose remains same in solution before and after freezing

Now, 1.9×342 g sucrose is in 1000 g water $(\because m' = 1.9)$

254.84 g sucrose should be in

$\frac{1000\times 254.84}{1.9\times 342} = 392.18$ g H_2O

Thus, mass of ice separated out

$= 745.16 - 392.18$ g $= \mathbf{352.98\ g}$

Alternate Solution

$$\Delta T_f = \frac{1000\times K'_f\times w}{W\times m} \quad ...(1)$$

or $\quad \Delta T_f = K'_f\times\text{molality} \quad ...(2)$

$\Delta T_f = 1.86\times 1 = 1.86$

Now using Eq. (1) again to obtain $\frac{w}{W}$ for sucrose

$$\frac{w}{W} = \frac{1.86\times 342}{1.86\times 1000} = 0.342 \quad ...(3)$$

Also, $w + W = 1000$ ...(4)

(mass of solution = 1000 g)

$\therefore$ By Eqs. (3) and (4), we get $w = 254.84$ g

$W = 745.16$ g

(*i.e.*, mass of water)

Now if solution has been freezed up to -3.534, the mass of sucrose remains same and therefore, using Eq. (1) again

$$3.534 = \frac{1.86\times 1000\times 254.84}{342\times W_1}$$

$\therefore$ $W_1 = 392.18$ g (*i.e.*, new mass of water)

Thus, Ice separated = 745.16 − 392.18

= 352.98 g

71. Let 100 g solution contains w g solute in W g solvent

$\therefore$ $w + W = 100$ ...(1)

Now, $\Delta T_f = \frac{1000\times K'_f \times w}{W\times m}$

$$0.38 = \frac{1000\times 1.86\times w}{W\times 342} \quad \therefore \quad \frac{w}{W} = 0.07 \quad ...(2)$$

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

$w = 6.6$ g

$W = 93.40$ g

Now at −0.5° C, some water separates out as ice and solute exists as 6.6 g.

$\therefore$ $0.5 = \frac{1000\times 1.86\times 6.6}{W\times 342}$ $\therefore$ $W = 71.78$ g

$\therefore$ Mass of ice separated out is (93.40 − 71.78) g = **21.62 g**

72. $\because$ $\pi V = nST$ | Given, $\pi = 2$ atm, $S = 0.0821$ litre atm K^{-1} mol^{-1} and $T = 300$ K

$\therefore$ $\frac{n}{V} = \frac{\pi}{ST} = \frac{2}{0.0821\times 300}$

$\therefore$ Molarity $\left(\frac{n}{V}\right) = 0.0812$ mol $litre^{-1}$

Since, $\Delta T = K'_f \times$ molality

$\because$ molarity = molality

and thus, molality = 0.0812

$\therefore$ $\Delta T = 1.86\times 0.0812 = 0.151$

$\therefore$ Freezing point $= T_0 - \Delta T$ $(\because T_0 = 0° C)$

$= 0 - 0.151 = $ **− 0.151° C**

73. $\because$ $\Delta T = \frac{1000\times K'_f \times w}{m\times W} = K'_f \times$ molality

$\therefore$ $0.52 = 1.86\times$ molality

$\therefore$ Molality $= \frac{0.52}{1.86}$ = molarity $\left(\frac{n}{V}\right)$ (given)

Now, $\pi V = nST$

$\therefore$ $\pi = \frac{n}{V}\cdot ST = \frac{0.52}{1.86}\times 0.0821\times 300 =$ **6.886 atm**

74. $\pi = CST$

$2.47 = C\times 0.0821\times 303$

$\therefore$ $C = 9.93\times 10^{-2}$ M

Thus, 1 litre solution of sucrose contains 9.93×10^{-2} mole of sucrose or $9.93\times 10^{-2}\times 342$ g of sucrose.

$\because$ Volume of solution = Volume of solvent = 1000 mL

$\therefore$ Mole of water $= \frac{1000}{18.10}$

$\therefore$ Mass of water $= \frac{1000}{18.10}\times 18 = 994.475$ g

Thus, molality of solution $= \frac{9.93\times 10^{-2}}{994.475\times 10^{-3}}$

$= 9.985\times 10^{-2}$ M

$$\Delta T_b = K_b \times \text{molality} = \frac{RT_b^2}{1000l}\times \text{molality}$$

$$= \frac{2\times 373\times 373}{1000\times 540}\times 9.985\times 10^{-2}$$

$= \mathbf{5.145\times 10^{-2}}$

75. b.pt. of $H_2O = 99.725° C$

Given, $w_{\text{organic compound}} = 24$ g, $w_{H_2O} = 600$ g,

$m_{\text{organic compound}} = 58$

Also, $\Delta T_b = \frac{1000\times K_b \times w}{W\times m} = \frac{1000\times 0.513\times 24}{600\times 58} = 0.354$

$\therefore$ b.pt. of solution = 99.725 + 0.354 = **100.079° C**

76. We have, $\Delta T = K_f \times$ molality

Also from Raoult's law,

$$\frac{P° - P_s}{P_s} = \frac{w\times M}{m\times W} = \frac{w\times 1000\times M}{m\times W\times 1000}$$

$$\frac{P° - P_s}{P_s} = \text{molality}\times \frac{M}{1000}$$

$$\frac{P° - P_s}{P_s} = \frac{\Delta T}{K_f}\times \frac{M}{1000}$$

Given, $P° = 23.51$ mm of Hg; $\Delta T = 0.3$

$K_f = 1.86$ K molality^{-1}; $M = 18$

$\therefore$ $\frac{23.51 - P_s}{P_s} = \frac{0.3}{1.86}\times \frac{18}{1000}$ $\therefore$ $P_s =$ **23.44 mm Hg**

77. Given, Molarity $= \frac{n}{V} = 0.1$ mol $litre^{-1}$

$= \frac{0.1}{10^{-3}}$ mol $m^{-3} = 10^2$ mol m^{-3}

$\because$ $\pi_N \times V = nST$

$\pi_N = \frac{n}{V}ST$

$\pi_N = 10^2\times 8.314\times 300$ Nm^{-2}

For

$$\underset{\substack{1\\1-\alpha}}{K_4Fe(CN)_6} \rightleftharpoons \underset{\substack{0\\4\alpha}}{4K^+} + \underset{\substack{0\\\alpha}}{Fe(CN)_6^{4-}}$$

where 'α' is degree of dissociation.

Given, $\alpha = 0.5$

$\frac{\pi_{exp}}{\pi_N} = 1 + 4\alpha$ $\therefore$ $\pi_{exp} = \pi_N\,(1 + 4\alpha)$

$= 10^2\times 8.314\times 300\times (1 + 4\times 0.5)$

$= 10^2\times 8.314\times 300\times (1 + 2)$

$= \mathbf{7.483\times 10^5\ Nm^{-2}}$

78. Given, $w = 1\,g$, $m = 74.5$, $V = \frac{100}{1000}$ litre,

$T = 18 + 273 = 291\,K$

$\because \quad \pi_N = \frac{n}{V}ST = \frac{w}{m \cdot V}ST$

$= \frac{1 \times 1000}{74.5 \times 100} \times 0.0821 \times 291 = 3.21\,atm$

For	$KCl \rightleftharpoons$	K^+	+ Cl^-
Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	α	α

$\therefore \quad \frac{\pi_{exp}}{\pi_N} = 1 + \alpha$

$\therefore \quad \pi_{exp} = 3.21(1 + 0.82) = \mathbf{5.842\ atm}$

79. Given, $N_{Na_3PO_4} = 0.1$

$\therefore$ Molarity of $Na_3PO_4 = \frac{0.1}{3}M \quad \left(\because M = \frac{N}{V}\right)$

Thus, using $\pi V = nST$

or $\pi = \frac{n}{V}ST = \frac{0.1}{3} \times 0.0821 \times 300 = \mathbf{0.821\ atm}$

80. $\because$ Molarity = Normality × Valence factor

$\therefore \quad M_{Glucose} = \frac{0.1}{1} = 0.1$

$M_{KNO_3} = \frac{0.1}{1} = 0.1$

$M_{K_2SO_4} = \frac{0.1}{2} = 0.05$

$M_{K_3PO_4} = \frac{0.1}{3} = 0.033$

Also $\pi \propto$ Molarity $\times (1 - \alpha + x\alpha + y\alpha)$

$\therefore \quad \pi_{Glucose} \propto 0.1 \propto 0.1$

$\pi_{KNO_3} \propto 0.1 \times 2 \propto 0.2$

$\pi_{K_2SO_4} \propto 0.05 \times 3 \propto 0.15$

$\pi_{K_3PO_4} \propto 0.033 \times 4 \propto 0.132$

$\therefore \quad \pi_{order}$ is : $\pi_{KCl} > \pi_{K_2SO_4} > \pi_{K_3PO_4} > \pi_{Glucose}$

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

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

$\quad 1 \qquad\qquad\qquad 0 \qquad\qquad 0$

$\quad 0 \qquad\qquad\qquad 1 \qquad\qquad (4-n)$

Thus, particles after dissociation $= 4 - n + 1 = 5 - n$

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

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

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

$\therefore \quad n = 2.1 \simeq 2$ (integer value)

Thus, complex and its ionisation is:

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

82.	$CaCl_2 \longrightarrow$	Ca^{2+}	+ $2Cl^-$
Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	α	2α

Given, $w = 20\,g$, $V = 100\,mL$, $T = 273\,K$

Formula mass of $CaCl_2 = 111\ g\ mol^{-1}$

$\pi_N = \frac{w}{mV} \times S \times T = \frac{20 \times 1000 \times 0.0821 \times 273}{111 \times 100} = 40.38\,atm$

Now, $\frac{\pi_{exp}}{\pi_N} = 1 + 2\alpha = 1 + 2 = 3 \qquad \because \alpha = 1$

$\therefore \quad \pi_{exp} = 40.38 \times 3 = \mathbf{121.14\ atm}$

83. $\because \pi_N = \frac{w}{m \times V} \times ST = \frac{7.45}{74.5 \times 1} \times 0.0821 \times 300 = 2.463\,atm$

Now,	$KCl \rightleftharpoons$	K^+	+ Cl^-
Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	α	α

$\therefore \quad i = \frac{\pi_{exp}}{\pi_N} = \frac{4.68}{2.463} = 1 + \alpha \quad \therefore \quad i = \mathbf{1.90}$

$\therefore \quad \alpha = \mathbf{0.90}$ or **90%**

Also, $g = \frac{i}{n} = \frac{1.90}{2} = \mathbf{0.95}$

84. $\because \quad \Delta T = \frac{1000 \times K'_f \times w}{W \times m}$

In C_6H_6 : $1.28 = \frac{1000 \times 5.12 \times w}{m_N \times 100}$ ...(1)

In H_2O : $1.40 = \frac{1000 \times 1.86 \times w}{m_{exp} \times 100}$ ...(2)

(Since, given that solute behaves as normal in C_6H_6 and dissociates in water.) By Eqs. (1) and (2),

$\frac{m_N}{m_{exp}} = \frac{1.40}{1.28} \times \frac{5.12}{1.86} = 3.01 \quad \therefore \quad i = 3.01 \approx 3.0$

Since, solute is 100% ionised, *i.e.*, $\alpha = 1$;

Let solute be A_xB_y

$A_xB_y \rightleftharpoons$	xA^+	+ yB^-
1	0	0
$(1-\alpha)$	$x\alpha$	$y\alpha$

$\therefore \quad i = 1 - \alpha + x\alpha + y\alpha$

$\because \quad i = 3$ and $\alpha = 1$

$\therefore \quad x + y = 3$

or No. of ions given = **3**

85. Given that,

$\pi = 4.92\,atm$; $T = 27 + 273 = 300\,K$; $V = 1$ litre

n_1 = mole of non-electrolyte $= \frac{x}{200}$

n_2 = mole of NaCl = 0.05

Using $\pi V = nST$ for a solution containing non-electrolyte and NaCl

$\pi V = n_1ST + n_2(1 + \alpha)]ST$

$\pi V = [n_1 + n_2(1 + \alpha)]ST$; where $\alpha = 1$ given for NaCl

$\therefore \quad 4.92 \times 1 = \left[\frac{X}{200} + 0.05 \times 2\right] \times 0.082 \times 300 \quad \therefore \quad X = \mathbf{20\ g}$

86. Given, Normality $= \frac{1}{10}$ for $BaCl_2$

$\therefore$ Molarity $= \frac{1}{20}$ for $BaCl_2 \quad \left(\because M = \frac{N}{\text{Valency}}\right)$

$\because \quad \pi_N = \frac{n}{V} \times ST = \frac{1}{20} \times 0.0821 \times 300 = 1.2315\,atm$

	$BaCl_2 \rightleftharpoons$	Ba^{2+}	+ $2Cl^-$
Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	α	2α

Total mole at equilibrium $= 1 + 2\alpha$

and $\alpha = 80\%$ or 0.8

Now, $\dfrac{\pi_{exp}}{\pi_N} = 1 + 2\alpha$

$\therefore$ $\pi_{exp} = \pi_N \times (1+2\alpha) = 1.2315 \times (1 + 2 \times 0.8)$
$= 1.2315 \times 2.6 = \mathbf{3.20\ atm}$

87. $\because$ % of mass/volume $= \dfrac{\text{mass of solute}}{\text{volume of solution}} \times 100$

$\therefore$ Mass of glucose = 7.2 g
Volume of solution = 100 mL

For glucose: π_{exp} or $\pi_N = \dfrac{w}{m \times V} \times ST$ (V in litre)

$\because$ π_{exp} or $\pi_N = \dfrac{7.2 \times 1000 \times 0.0821 \times T}{180 \times 100}$

For NaCl: $\pi_N = \dfrac{w}{m \times V} \times ST = \dfrac{1.2 \times 1000 \times 0.0821 \times T}{58.5 \times 100}$

Now, since two solutions are isotonic and therefore,

$\pi_{exp_{NaCl}} = \pi_{N_{Glucose}}$

$\therefore$ **For NaCl:** $\dfrac{\pi_{exp}}{\pi_N} = 1 + \alpha$

$$\frac{7.2 \times 1000 \times 0.0821 \times T}{180 \times 100} \times \frac{58.5 \times 100}{1.2 \times 1000 \times 0.0821 \times T} = 1 + \alpha = (i)$$

$\therefore$ $\alpha = 0.95$ and $i = \mathbf{1.95}$

88. $\because$ $\dfrac{P° - P_s}{P_s} = \dfrac{w \times M}{m \times W}$

$\dfrac{760 - 751}{751} = \dfrac{2 \times 18}{m \times 100}$ $\therefore$ $m_{exp} = 30.04$

For $BA \rightleftharpoons B^+ + A^-$

	BA	B^+	A^-
Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	α	α

Now, $\dfrac{m_n}{m_{exp}} = 1 + \alpha$

$\therefore$ $\dfrac{56}{30.04} = 1 + \alpha$

$\therefore$ $\alpha = \mathbf{0.8641}$ or **86.41%**

89. For NaCl:

Given, $2\Delta T = \dfrac{1000 \times K'_f \times 11.7}{200 \times m}$

(Let depression in f. pt. for sugar = ΔT)

For Sugar: $\Delta T = \dfrac{1000 \times K'_f \times 342}{1000 \times 342}$

($\therefore$ depression in f. pt. for NaCl = $2 \times \Delta T$)

$\therefore$ $m_{NaCl} = 29.25$ (experimental)

Now m_{Normal} for NaCl = 58.5 g mol^{-1}

For NaCl: $NaCl \rightleftharpoons Na^+ + Cl^-$

	NaCl	Na^+	Cl^-
Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	α	α

$\therefore$ $\dfrac{m_{Normal}}{m_{exp}} = 1 + \alpha$

$\dfrac{58.5}{29.25} = 1 + \alpha$ $\therefore$ $\alpha = 1$

That is NaCl is 100% ionised in solution.

90. Given, $w_{H_2SO_4} = 38\,g$, $W_{H_2O} = 100 - 38 = 62\,g$

$\therefore$ $\Delta T = \dfrac{1000 \times K'_f \times w}{mW}$

$\Delta T = \dfrac{1000 \times 1.86 \times 38}{98 \times 62}$ $\therefore$ $\Delta T_{Normal} = 11.633$

Now, $\dfrac{\Delta T_{exp}}{\Delta T_N} = i = 2.50$

$\therefore$ $\Delta T_{exp} = 11.633 \times 2.50 = 29.08$

$\therefore$ f. pt. $= 273 - 29.08 = \mathbf{243.92\ K}$

91. $Ca(NO_3)_2 \rightleftharpoons Ca^{2+} + 2NO_3^-$

	$Ca(NO_3)_2$	Ca^{2+}	$2NO_3^-$
Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	α	2α

$\therefore$ Total mole at equilibrium $= (1 + 2\alpha) = (1 + 2 \times 0.7) = 2.4$
($\because \alpha = 0.7$)

For $Ca(NO_3)_2$: $\dfrac{m_N}{m_{exp}} = 1 + 2\alpha$

$\therefore$ $m_{exp} = \dfrac{m_N}{(1 + 2 \times 0.7)} = \dfrac{164}{2.4} = 68.33$

Also at 100° C, $P°_{H_2O} = 760$ mm, $w = 7$ g, $W = 100$ g

Now, $\dfrac{P° - P_s}{P_s} = \dfrac{7 \times 18}{68.33 \times 100} = 0.0184$

or $\dfrac{P°}{P_s} - 1 = 0.0184$

$\therefore$ $P_s = \dfrac{760}{1.0184} = \mathbf{746.27\ mm}$

92. $\because$ $\Delta T = \dfrac{1000 \times K'_f \times w}{m \cdot W}$

and $\Delta T = 0.168$, $w = 1$ g, $W = 100$ g and $K'_f = 1.86$

$\therefore$ $m_{acid} = 110.71$ (This is exp. molar mass)

Now, Meq. of acid = Meq. of alkali

$\dfrac{0.2}{E} \times 1000 = 15.1 \times \dfrac{1}{10}$

$\therefore$ Eq. mass of acid $= \dfrac{0.2 \times 1000 \times 10}{15.1} = 132.45$

$\therefore$ Normal Molar mass of acid $= 132.45 \times 1$
(Since monobasic)

$HA \rightleftharpoons H^+ + A^-$

	HA	H^+	A^-
Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	α	α

Now, $\dfrac{m_N}{m_{exp}} = \dfrac{132.45}{110.71} = 1 + \alpha$ $\therefore$ $\alpha = \mathbf{19.6\%}$

93. Let NaCl and $CaCl_2$ be a, b g respectively in 1 g mixture

$\therefore$ $a + b = 1$

Also, Meq. of $CaCl_2$ = Meq. of CaC_2O_4
= Meq. of $KMnO_4 = 22 \times 0.1 \times 5 = 11$

$\therefore$ mass of $CaCl_2 = 11 \times \dfrac{111}{2} \times \dfrac{1}{1000} = 0.61$ g

$\therefore$ mass of NaCl = 0.39 g

$\therefore$ mass of $CaCl_2$ in 5 g mixture $= 0.61 \times 5 = 3.05$ g
mass of NaCl in 5 g mixture $= 0.39 \times 5 = 1.95$ g

Now, $\Delta T = \frac{1000\,K_b}{W}\left[\underset{\text{for NaCl}}{(1+\alpha)\frac{w}{m}} + \underset{\text{for CaCl}_2}{(1+2\alpha)\frac{w}{m}}\right]$

$= \frac{1000\times1.86}{100}\left[(1+1)\times\frac{1.95}{58.5}+(1+2)\times\frac{3.05}{111}\right]$

$= \frac{1000\times1.86}{100}\times0.149 = 2.77\text{ K}$

$\therefore$ Freezing point = $273 - 2.77 =$ **270.23 K**

94. $HA \rightleftharpoons H^+ + A^-$

$[H^+] = C\alpha = 10^{-2}$

$\therefore \quad \alpha = \frac{10^{-2}}{0.1} = 10^{-1} = 0.1$

$\therefore$ Total particles in solution $= 1+\alpha = 1+0.1 = 1.1$

Now, $P = CST\,(1+\alpha)$

$= 0.1\times0.0821\times298\times1.1 =$ **2.69 atm**

95. $\underset{\substack{1\\(1-\alpha)}}{CoCl_3\cdot xNH_3} \longrightarrow \underset{\substack{0\\ \alpha}}{CoCl_{3-n}\cdot xNH_3} + \underset{\substack{0\\ n\alpha}}{nCl^-}$

Assume nCl^- are attached with Co through primary valencies which undergo ionisation. All the NH_3 molecules are attached with Co through secondary valencies.

$\Delta T_f = K_f \times \text{molality}\times(1-\alpha+\alpha+n\alpha)$

$0.558 = 1.86\times0.1\times(1+n) \qquad (\because \alpha = 1)$

$\therefore \quad n = 2$

Thus, complex is $[CoCl\cdot xNH_3]\cdot Cl_2$. Since, coordination number of Co is six, thus complex is $\mathbf{[Co(NH_3)_5Cl]Cl_2}$.

96. Let NaF and NaI be a and b g respectively

Thus, $a + b = 0.48$ ...(1)

Thus, for NaF + NaI solution in water

$\pi\times\frac{100}{1000} = \left(\frac{a}{42}+\frac{b}{150}\right)\times2\times0.0821\times T$ ...(2)

For urea in water $\pi\times1 = 0.1\times0.0821\times T$ ...(3)

By Eqs. (2) and (3), $\frac{\left(\frac{a}{42}+\frac{b}{150}\right)\times2}{0.1} = \frac{100}{1000}$

$\therefore \quad 150a + 42b = 31.5$ ...(4)

By Eqs. (1) and (4), $a = 0.105$

$b = 0.375$

Thus, $\frac{a}{b} = \frac{0.105}{0.375} =$ **0.28**

97. For monobasic acid HA

$\underset{\substack{1\\(1-\alpha)}}{HA} \rightleftharpoons \underset{\substack{0\\ \alpha}}{H^+} + \underset{\substack{0\\ \alpha}}{A^-}$

From Ostwald dilution law,

$K_\alpha = \frac{C\alpha^2}{(1-\alpha)}$ ...(1)

Now, $\Delta T_{nor.} = K'_f\times\text{molality} = 1.86\times0.025 = 0.0465$

$\therefore \quad i = \frac{\text{Observed }\Delta T}{\text{Calculated }\Delta T} = 1+\alpha$

$i = \frac{0.06}{0.0465} = 1+\alpha$

$\therefore \quad \alpha = 0.29$ and $C = 0.025M$

$\therefore$ By Eq. (1), $K_\alpha = \frac{0.025\times(0.29)^2}{(1-0.29)} = \mathbf{2.96\times10^{-3}}$

98. $\pi_1 = C_1S_1T_1\times(1+\alpha_1)$ (for HA)

$\pi_2 = C_2S_2T_2\times(1+\alpha_2)$ (for HB)

$\therefore \quad (1+\alpha_1) = \frac{0.30}{0.01\times0.0821\times300}$

$\therefore \quad \alpha_1 = 0.218$

$(1+\alpha_2) = \frac{0.35}{0.01\times0.0821\times300} \quad \therefore \alpha_2 = 0.421$

$\therefore \quad \frac{\alpha_1}{\alpha_2} = \frac{0.218}{0.421} = \mathbf{0.52}$

99. $\Delta T = \frac{1000\times K_b\times w}{m\times W}$

$\Delta T_N = \frac{1000\times2.3\times0.61}{122\times50}$

(molar mass of $C_6H_5COOH = 122$)

$\Delta T_N = 0.23$

$\Delta T_{exp} = \Delta T_N\left(1-\alpha+\frac{\alpha}{n}\right) = 0.23\times\left(1-0.84+\frac{0.84}{2}\right)$

$= 0.23\times\left(1-\frac{0.84}{2}\right) = 0.1334$

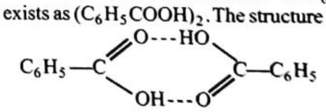
b.pt. $= 46.2 + 0.1334 =$ **46.3334° C**

100. $m = \frac{1000K_b\cdot w}{W\cdot\Delta T}$

In acetone: $m = \frac{1000\times1.7\times1.22}{0.17\times100} = 122\text{ g mol}^{-1}$

In benzene: $m = \frac{1000\times2.6\times1.22}{0.13\times100} = 244\text{ g mol}^{-1}$

Molar mass of C_6H_5COOH is 122 and thus it is evident that benzoic acid remains as normal molecular species in acetone but shows 100% dimerisation in C_6H_6, *i.e.*, in C_6H_6 it exists as $(C_6H_5COOH)_2$. The structure of dimer is:



101. $\Delta T = K_f\times\text{molality}\times(1+\alpha)$

For acetic acid: $\underset{\substack{1\\(1-\alpha)}}{CH_3COOH} \rightleftharpoons \underset{\substack{0\\ \alpha}}{CH_3COO^-} + \underset{\substack{0\\ \alpha}}{H^+}$

Given, $\alpha = 0.23$; Also, molality $= \frac{\text{mole of acetic acid}}{\text{mass of water in kg}}$

$= \frac{3\times10^{-3}\times10^3}{60\times\frac{500\times0.997}{10^3}} = 0.10$

$\Delta T = K_f\times\text{molality}\,(1+\alpha)$

$\Delta T = 1.86\times0.1\times1.23$

$\therefore \quad$ **= 0.229**

102. Given, $w = 0.2\text{ g}$, $W = 20\text{ g}$, $\Delta T = 0.45°\text{ C}$

$\because \quad \Delta T = \frac{1000\times K'_f\times w}{m\times W}$ or $0.45 = \frac{1000\times5.12\times0.2}{20\times m}$

$\therefore \quad m\text{ (observed)} = 113.78\text{ g mol}^{-1}$

Now for $2CH_3COOH \rightleftharpoons (CH_3COOH)_2$

Before association	1	0
After association	$(1-\alpha)$	$\frac{\alpha}{2}$

where α is degree of association

$\therefore \quad \frac{m_{normal}}{m_{observed}} = 1-\alpha+\frac{\alpha}{2}$

or $\quad \frac{60}{113.78} = 1-\alpha+\frac{\alpha}{2}$

or $\quad$ **$\alpha = 0.945$ or 94.5%**

103. Given, $w = 2\,g$, $W = 25\,g$, $\Delta T = 1.62$, $K'_f = 4.9$

$\because \quad \Delta T = \frac{1000\times K'_f \times w}{m\times W}$

$1.62 = \frac{1000\times 4.9\times 2}{25\times m}$

$\therefore \quad m_{exp} = 241.98\,g\,mol^{-1}$

$nC_6H_5COOH \rightleftharpoons (C_6H_5COOH)_n$

Before association	1	0
After association	$(1-\alpha)$	$\frac{\alpha}{n}$

$\therefore$ Total number of mole at equilibrium $= 1-\alpha+\frac{\alpha}{n}$

$\frac{m_N}{m_{exp}} = 1-\alpha+\frac{\alpha}{n}$

For dimer formation $n = 2$

$\frac{122.0}{241.98} = 1-\alpha+\frac{\alpha}{2}$ ($m_N = 122.0$ for C_6H_5COOH)

or $\quad 1-\frac{\alpha}{2} = 0.504$

$\therefore \quad$ **$\alpha = 0.992$ or 99.2%**

104. $2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$

$\quad$ 1 $\quad$ 0

$\quad (1-\alpha) \quad \frac{\alpha}{2}$

$\because \quad \Delta T_f = \frac{1000K_f\times w}{m\times W}\left(1-\alpha+\frac{\alpha}{2}\right)$

$7 = \frac{1000\times 14\times 75.2}{94\times 1000}\left(1-\frac{\alpha}{2}\right)$

$\therefore \quad$ **$\alpha = 0.75$ or 75%**

105. For benzene $K'_f = \frac{RT^2}{1000 l_{f(cal/g)}} = \frac{8.314\times(278.4)^2}{1000\times\frac{10.042\times 10^3}{78}}$

$= 5.0$ K molality

Also, $\quad \Delta T = 278.4 - 277.4 = 1$

For acetic acid in benzene

$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$

Before association	C	0
After association	$C(1-\alpha)$	$\frac{C\alpha}{2}$

$\therefore K_C = \frac{\frac{C\alpha}{2}}{C^2(1-\alpha)^2}$; where α is degree of association ...(1)

Also, $\quad \Delta T = K'_f \times \text{molality} \times \left(1-\frac{\alpha}{2}\right)$ ...(2)

($\because$ total particles at equilibrium $= 1-\alpha+\frac{\alpha}{2} = 1-\frac{\alpha}{2}$)

Given mole fraction of acetic acid $= 0.02 = \frac{n}{n+N}$

$\therefore \quad$ Mole fraction of benzene $= 0.98 = \frac{N}{n+N}$

$\frac{n}{N} = \frac{0.02}{0.98}$

$\therefore$

molality $= \frac{n}{W}\times 1000 = \frac{n\times 1000}{N\times M} = \frac{0.02\times 1000}{0.98\times 78} = 0.262\,m$

$\therefore$ From Eq. (2), $\quad 1 = 5\times 0.262\times\left(1-\frac{\alpha}{2}\right) \quad \therefore \alpha = 0.48$

From Eq. (1), $\quad$ Assuming molarity = molality

$K_C = \frac{0.262\times 0.48}{2\times(0.262)^2\times(1-0.48)^2}$ **= 3.39**

106. $\Delta T = \frac{1000\times K'_b\times w}{m\times W}$

$1.68 = \frac{1000\times 2.34\times 28}{m\times 315}$

$\therefore \quad m_{exp} = 123.80\,g\,mol^{-1}$

$\frac{m_N}{m_{exp}} = 1-\alpha+\frac{\alpha}{n}$

$\because \alpha = 1 \therefore \frac{m_N}{m_{exp}} = \frac{1}{n}$ $\qquad$ (m_N of $P = 31$)

$\therefore \quad \frac{31}{123.80} = \frac{1}{n}$

$\therefore \quad$ **$n \approx 4$**, *i.e.*, **P_4**

107. $\frac{P^\circ - P_s}{P^\circ} = \frac{n}{n+N}$

$P^\circ - P_s = P^\circ\left[\frac{n}{n+N}\right]$

Let 1 mole of solute is dissolved in 1000 g solvent water.

Thus, $\quad n = 1$ and $N = \frac{1000}{18}$

Also, $P^\circ = 760$ mm for water at 100° C

$\therefore \quad P^\circ - P_s = \left[\frac{1}{1+\frac{1000}{18}}\right]\times 760$

= 13.43 mm

108. $NaHSO_4 \longrightarrow Na^+ + HSO_4^-$

$\quad$ 1 $\quad$ 0 $\quad$ 0

$\quad$ 0 $\quad$ 1 $\quad$ 1

$HSO_4^- + H_2O \longrightarrow H_3O^+ + SO_4^{-2}$

$\quad$ 1 $\quad$ 0 $\quad$ 0

$\quad 1-h \quad h \quad h$

$\therefore$ Total particles after dissolution of $NaHSO_4$

$= 1+1-h+h+h = 2+h$

Now, $\quad \Delta T_f = K_f \times \text{molality} \times (i)$

$0.345 = 1.86\times 0.08\times(2+h)$

$\therefore \quad 2+h = 2.319$

$\therefore \quad$ **$h = 0.319$**

i.e., 31.9% of HSO_4^- shows proton transfer to H_2O.

109. $A(l)+B(l) \longrightarrow \underset{\text{Insoluble}}{(A)_n} + B(l)$

$$P_M = P_A^\circ \cdot X_A + P_B^\circ \cdot X_B$$

$$P_M = 300\left(\frac{a}{12+a}\right)+500\left(\frac{12}{12+a}\right) \quad ...(1)$$

where a mole of A are left after polymerisation after 100 minute

Also rate constant, $K = \frac{2.303}{t}\log\frac{10}{a}$

$$K = \frac{2.303}{100}\log\frac{10}{a} \quad ...(2)$$

after 100 minute polymerisation is checked

After 100 minute solute is added and final vapour pressure is 400 (*i.e.*, $P_s = 400$)

$$\therefore \quad \frac{P_M - 400}{400} = \frac{0.525}{(a+12)} \quad ...(3)$$

Solving Eqs. (1) and (3), $a = 9.9$

Using this value of a in Eq. (2),

$$K = \frac{2.303}{100}\log\frac{10}{9.9}$$

$$\mathbf{K = 1.0 \times 10^{-4}}$$

110. $\frac{P^\circ - P_s}{P_s} = \frac{n}{N} = \frac{n \times M \times 1000}{W \times 1000}$

$$\frac{17.39-17.0}{17.0} = \frac{\text{molality} \times M}{1000}$$

$$\therefore \quad \text{molality} = \frac{0.39\times1000}{17\times18} = 1.275$$

For dilute solution molarity = molality

$$\therefore \quad \pi = CST = 1.275\times0.0821\times293 = 30.66\ \textbf{atm}$$

Also, for water vapours $PV = nRT$

$$P = \frac{w}{V}\cdot\frac{RT}{m}$$

$$\frac{w}{V} = \frac{Pm}{RT} = \frac{17.0\times18}{760\times0.0821\times293}$$

density of $H_2O_V = 1.673\times10^{-2}$ g / litre

$$= 1.673\times10^{-5} \text{ g / mL}$$

111. $\Delta T_b = \frac{1000\times w\times K_b}{m\times W}\times(1+\alpha)$

$\because \quad w = 10\,g;\ W = 100-10 = 90\,g$

$$0.27 = \frac{1000\times10\times0.512}{342\times90}\times(1+\alpha) \quad \therefore \alpha = \mathbf{0.623}$$

Also, $\frac{m_N}{m_{exp}} = 1+\alpha$

$$\therefore \quad m_{exp} = \frac{342}{1.623} = \mathbf{210.7\ g\ mol^{-1}}$$

112. $\log_{10} P = 3.54595 + \frac{313.7}{T} + 1.40655\log_{10} T$

$$\ln P = (3.54595\times2.303) - \frac{313.7\times2.303}{T} + 1.40655\ln T$$

$$\therefore \quad \frac{d}{dT}\ln P = \frac{313.7\times2.303}{T^2} + \frac{1.40655}{T} \quad \left[\frac{d}{dT}\ln P = \frac{\Delta H}{RT^2}\right]$$

$$\therefore \quad \Delta H = [313.7\times2.303 + 1.40655T]R$$

at 80K $\quad \Delta H = \mathbf{1670\ cal}$

113. According to Henry's law,

$$\frac{a}{P} = K$$

$$\therefore \quad a = 3.1\times10^{-2}\times4 = \mathbf{0.124\ mol / litre}$$

114. $x_{N_2} = \frac{P_{N_2}}{K_H} = \frac{0.987}{76480} = 1.29\times10^{-5}$

If n represents number of mole of N_2 in 1 litre H_2O or $\left(\frac{1000}{18}\text{ mole}\right)$ 55.6 mole H_2O, then

$$x_{N_2} = \frac{n}{n+55.6} = \frac{n}{55.6} = 1.29\times10^{-5}$$

Thus, $n = 1.29\times10^{-5}\times55.6$ mol

$$= 7.18\times10^{-4} \text{ mol}$$

$$= \mathbf{0.718\ milli\ mol.}$$

• SINGLE INTEGER ANSWER PROBLEMS •

1. The vapour pressure of a mixture of two volatile liquids is expressed as $P_m = 6.0 + 1.5\,X_B$, where X_B is mole fraction of B in mixture. The vapour pressure of 'A' at the same temperature is :
2. van't Hoff factor of a mixture of two mole of KI with 1 mole HgI_2, in a solution of water is ......
3. The freezing point depression of 10^{-3} molal aqueous solution of a compound $K_x[Fe(CN)_6]$ is 7.44×10^{-3} K. Given K_f of $H_2O = 1.86$ k mol^{-1}kg, the value of X is ......
4. The boiling point of a solution of 5 g sulphur in 100 g CS_2 is 0.5°C above pure solvent. If the K_b of CS_2 is 2.56 K $molality^{-1}$ then the atomicity of sulphur in this solvent is ......
5. A solution of 6.2 g ethylene glycol in 55 g H_2O is cooled to −3.72°C. The ice separated from solution is : ($K_f H_2O = 1.86$ K $molality^{-1}$)
6. A complex is represented as $CoCl_3 \cdot XNH_3$. Its 0.1 molal solution in water shows $\Delta T_F = 0.558°C$. K_f of H_2O is 1.86 K $molality^{-1}$. Assuming 100% ionisation, calculate the no. of NH_3 molecules associated with Co.
7. A 0.4 molal aqueous solution of $M_X A$ has freezing point 3.72°C. The K_f of H_2O is 1.86 K $molality^{-1}$. The value of X is ......
8. 3 mole of liquid A (V.P. = 60 mm) and a mole of B (V.P. = 40 mm) results in a solution having V.P. of 50 mm. The value of a is ......
9. An aqueous solution of a substance molar mass 240 has osmotic pressure 0.2 atm at 300 K. The density of solution in g / dm^3 is : ($R = 0.08$ litre atm K^{-1} mol^{-1}).
10. The osmotic pressure of a solution in atm obtained on mixing each 50 mL of 1.2% mass/vol. urea solution and 2.4% mass/vol. glucose solution at 300 K ($R = 0.08$ litre atm K^{-1} mol^{-1}).
11. How many g of glucose must be present in 0.5 litre of a solution for its osmotic pressure be same as that of 8 g glucose in 1 litre?
12. The osmotic pressure of a solute is 600 mm at 300 K. The solution is diluted and the temperature is raised to 400 K and the solution shows an osmotic pressure of 200 mm. The solution was diluted to ...... times.
13. 'n' mole of a non electrolyte are added to 'N' mole of solvent. The addition causes a lowering in vapour pressure of solvent by 20%. The ratio of mole of solvent and its solute is ......
14. A solution of liquids A and B having vapour pressure in pure state P_A^0 and P_B^0. The solution contains 30% mole of A which is in equilibrium with 60% mole of A in vapour phase. If P_B^0 is 2 cm, the P_A^0 is ...... cm.
15. A mixture of two immiscible liquids nitrobenzene and water boiling at 99°C has a partial pressure of water 733 mm and of nitrobenzene 27 mm. The ratio of masss of water and nitrobenzene in mixture is ......
16. How much of the following will not show abnormal colligative properties in aqueous medium. Urea, $NaNO_3$, Thiourea, Glucose, Benzoic acid, Acetic acid.
17. Solute A is binary electrolyte and solute B is non electrolyte. If 0.2M solution of solute B produces an osmotic pressure of 2 atm then 0.1M solution of A at the same temperature will produce an osmotic pressure equal to.....
18. A 0.1m aqueous solution of complex represented as $CoCl_3 \cdot XNH_3$ shows a freezing point of 0.558°C. If K_f of water is 1.86 K $molality^{-1}$, how much Cl atoms are outside the co-ordination sphere, assuming co-ordination number of Co as six and 100% ionisation of complex ?
19. 9 g of a metal fluoride MF_x (molar mass 180) is dissolved in 100 g water to register an increase in b.pt by 1.00 K. Assuming complete dissociation of M F_x and 100% ionisation and K_b for water 0.50 K mol^{-1} kg calculate the value of x.
20. 20 g of solute A present in 500 mL solution exerts same osmotic pressure as 2500 mL of 40 g of solute A and 60g of solute B solution at same temperature. Assuming A and B non electrolytes, calculate the ratio of molar masses of B and A.
21. The vapour pressure of two liquids A and B are 50 and 100 mm respectively. The ratio of mole fractions of B and A in vapour phase over the liquid if they are mixed in 1 : 1 ratio is.....
22. 4 g of solutes A and B each are dissolved separately in 100 g H_2O to produce depression in freezing pt 0.1° and 0.2° respectively. If both A and B are nonelectrolyte, then what is the ratio of molar masses of A and B?
23. How many of the following are natural semipermeable membrane.

    Gall bladder, Plant cell, Phenol layer, $Cu_2Fe(CN)_6$, Root hair
24. 100 g solution of 10% (mass/mass) urea solution is placed together with 200 g of 10% mass/mass glucose solution in closed jar to attain equilibrium. The number of mole of water transferred from one solution to other in order to attain equilibrium is ....
25. Osmotic pressure of an aqueous solution of a non-volatile solute which neither associates nor dissociates at 300 K is 4.737 atm. If K_f of water 0.52,

$\therefore$ $31.2 + 4.8\,n = 151.2 - 25.2\,a$

$\therefore$ $30a = 120$ $(\because\ n = a)$

or $a = +4$

Thus oxide is $\mathbf{CrO_2}$.

81. $10e + (Mn^{7+})_2 \longrightarrow 2Mn^{2+}] \times 61$

$(Fe^{2+}) \longrightarrow Fe^{3+} + e$

$(C^{2+})_6 \longrightarrow 6C^{4+} + 12e$

$(N^{3-})_6 \longrightarrow 6N^{5+} + 48e$

$Fe^{2+} + C^{2+} + N^{3-} \longrightarrow Fe^{3+} + C^{4+} + N^{5+} + 61e] \times 10$

$61Ba(MnO_4)_2 + 10K_4[Fe(CN)_6] \longrightarrow 122Mn^{2+} + Fe^{3+} + 6C^{4+} + 6N^{5+}$

$\because$ 10 mole $K_4Fe(CN)_6 \equiv 61$ mole $Ba(MnO_4)_2$

$\therefore$ 1 mole $K_4Fe(CN)_6 \equiv$ **6.1 mole $Ba(MnO_4)_2$**

• SINGLE INTEGER ANSWER PROBLEMS •

1. 'n' factor of FeC_2O_4 during its oxidation by acidified $KMnO_4$ is ....
2. An element A in a compound has oxidation state A^{n-}. If 1.68×10^{-3} mole of $K_2Cr_2O_7$ are required for complete oxidation of 3.26×10^{-3} mole of ABD for oxidation to A^{n-} to elemental state. The value of n is ....
3. 1.6 g pyrolusite ore was titrated with 50 cm^3 of 1.0 N oxalic acid and some sulphuric acid. The oxalic acid left was raised to 250 mL in a flask 25 mL of this solution when treated with 0.1 N $KMnO_4$ required 32 mL of the solution. The percentage of available oxygen in pyrolusite is :
4. 1 g sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with Zn dust. The resultant solution is cooled and made upto 100 mL. An aliquot of 25 mL of this solution requires 17 mL of 0.0167M solution of an oxidant for titration. The number of electrons taken up by oxidant in the above titration is ....
5. 0.31 g of an alloy of Fe + Cu was dissolved in excess dilute H_2SO_4 and the solution was made upto 100 mL. 20 mL of this solution required 3 mL of $\frac{N}{30}K_2Cr_2O_7$ solution for exact oxidation. The % purity (in closest value) of Fe in wire is :
6. The reaction $Cl_2(g) + S_2O_3^{2-} \longrightarrow SO_4^{2-} + Cl^-$ to be carried out in basic medium. 1.5 mole of Cl_2 are allowed to react can with 0.1 mole of $S_2O_3^{2-}$ in presence of 3.0 mole of OH^-. Mole of OH^- left after the reaction is ....
7. Equivalent mass of O_3 in the reaction : $2O_3 \longrightarrow 3O_2$ is ....
8. 'n' factor for H_2S during its oxidation to SO_2 is ....
9. 'n' factor for Cu_2S in the reaction
   $Cu_2S + KMnO_4 \longrightarrow Cu^{2+} + SO_2 + Mn^{2+}$ is:
10. A 5.6 g sample of limestone is dissolved in acid and calcium is precipitated as calcium oxalate. The precipitate is filtered, washed with water and dissolved in dil. H_2SO_4. The solution required 40 mL of 0.25 N $KMnO_4$ solution for titration. The % of CaO in limestone is ....
11. 80 mL of $M/24$ $K_2Cr_2O_7$ solution oxidises 22.4 mL H_2O_2 solution. The volume strength of H_2O_2 solution is ....
12. 10 mL of 0.2 M solution of $K_xH(C_2O_4)_y$ requires 8 mL of 0.2 M acidified $KMnO_4$ solution. The value of x is ....
13. 'n' factor for SO_2 in $FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$ is ....
14. 30 mL of 0.3 M $MnSO_4$ is completely oxidised by 3 mL of $KMnO_4$ of unknown normality, each forming Mn^{4+} oxidation state. The normality of $KMnO_4$ is ....
15. 2 M solution of HNO_3 is reduced to NO by suitable reductant. The normality of HNO_3, if HNO_3 is used like this is ....
16. 'n' factor for S in SO_2 is 4 and in SO_3 is 6. The 'n' factor of S in $SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$ is ....
17. 'n' factor of C_2H_5OH in the reactions is....
    $C_2H_5OH \longrightarrow CH_3CHO$
18. 4 mole each of Hg^{2+} and I^- will form how much mole of $[HgI_4]^{2-}$.
19. 2.5 mole of $Fe_2(C_2O_4)_3$ requires how much mole of $KMnO_4$ for its complete oxidation in acidic medium?
20. C_3H_8 is completely oxidised to CO_2 and H_2O, the ratio of equivalent mass of CO_2 formed and C_3H_8 taken is.....
21. The number of mole of $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$ oxidised by 4 mole of acidified $KMnO_4$ is.....
22. CrO_5 reacts with H_2SO_4 to give $Cr_2(SO_4)_3$, H_2O and O_2. The mole of O_2 released during the reaction of 4 mole of CrO_5 with excess of H_2SO_4.
23. 2 mole of FeC_2O_4 are oxidised by 'X' mole of $KMnO_4$ whereas 2 mole of $FeSO_4$ are oxidised by 'Y' mole of $KMnO_4$. The ratio of $X : Y$ is.....

24. Number of H_2O_2 mole needed to convert two mole of $Cr(OH)_3$ in alkaline medium to sodium chromate is.....

25. 6×10^{-3} mole $K_2Cr_2O_7$ reacts completely with 9×10^{-3} mole X^{n+} to give XO_3^- and Cr^{3+}. The value of n is ......

26. Mole of $KMnO_4$ required to oxidise a mixture of 2 mole each of $FeSO_4$, FeC_2O_4 and $Fe_2(C_2O_4)_3$ in acid medium.

27. Mole of $K_2Cr_2O_7$ required to oxidise one mole of $Fe_2(C_2O_4)_3$ in acid medium.

28. Equivalent mass of nitrogen in the reaction :

$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$ is $\frac{M}{X}$. The value of X is ....

29. A 1.10 g sample of copper ore is dissolved and Cu^{2+} formed are titrated with excess of KI. The liberated iodine requires 12.12 mL of 0.10 N $Na_2S_2O_3$ solution for titration. The % of copper by mass in sample is ....

30. 9.824 g of $FeSO_4.(NH_4)_2SO_4.X\,H_2O$ were dissolved in 250 mL of solution. 20 mL of this solution required 20 mL of $KMnO_4$ containing 3.52 g of 90% by mass $KMnO_4$ dissolved per litre. The value of 'X' is ....

31. A 0.56 g sample of limestone is dissolved in acid and calcium is precipitated as calcium oxalate. The precipitate is filtered, washed and dried and then dissolved in H_2SO_4. The solution required 4mL of 0.25 N $KMnO_4$ for oxidation of oxalate. The % of CaO in limestone is ....

32. Hydrogen peroxide in aqueous solution decomposes on warming to give oxygen according to the equation.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

under conditions where 1 mole of gas occupies 50 dm^3, 100 cm^3, of XM solution of H_2O_2 produces 5 dm^3 of O_2. Thus X is ....

33. 15g sample of an alloy containing Cu (at mass 63.6) and Zn reacts completely with $3M$ HNO_3 as :

$$Cu + HNO_3 \longrightarrow Cu^{2+} + NO_2(g) + H_2O$$

$$Zn + HNO_3 \longrightarrow Zn^{2+} + NH_4^+ + H_2O$$

The liberated $NO_2(g)$ was found to occupy 4.647 litre at 1 atm and 300 K. The mass of Zn (to the closest value) in alloy is ....

34. n-factor of Mn_2O_7 in the change :

$2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$ is ....

35. n-factor for Fe_3O_4 in its reaction during its oxidation to Fe_2O_3 is ....

36. Number of mole of As_2S_3 required to reduce 56 mole of HNO_3 according to equation :

$As_2S_3 + HNO_3 \longrightarrow H_3AsO_4 + H_2SO_4 + NO$

37. Reaction of Br_2 with Na_2CO_3 in aqueous solution gives sodium bromide and sodium bromate with evolution of CO_2 gas. The number of sodium bromide molecules involved in the balanced chemical equation is :

[IIT 2011]

38. In neutral or faintly alkaline solution, 8 moles of permanganate anion quantitatively oxidize thiosulphate anions to produce X moles of a sulphur containing product, the magnitude of X is:

[JEE (Advanced) I 2016]

ANSWERS

1. Three	**2.** Three	**3.** Nine	**4.** Six	**5.** Nine	**6.** Two	**7.** Eight	**8.** Six	**9.** Eight	**10.** Five	**11.** Five	**12.** Three
13. Five	**14.** Two	**15.** Six	**16.** Two	**17.** Two	**18.** One	**19.** Three	**20.** Three	**21.** Five	**22.** Seven	**23.** Three	**24.** Three
25. One	**26.** Four	**27.** One	**28.** Six	**29.** Seven	**30.** Six	**31.** Five	**32.** Two	**33.** Nine	**34.** Six	**35.** One	**36.** Six
37. Five	**38.** Six										

OBJECTIVE PROBLEMS (One Answer Correct)

1. Which of the following is not colligative property?
(a) Molarity (b) Vapour pressure
(c) Osmotic pressure (d) Elevation in b.pt.

2. Pick up the wrong statement :
(a) Hygroscopic and deliquescent salts are highly soluble in water.
(b) Vapour pressure of water in hygroscopic substances in their solution state is lower than humidity of air.
(c) Efflorescent crystals have higher vapour pressure of water than humidity of air.
(d) For isotonic solution concentrations of two solutions must be always same.

3. A 20 mL urea solution of 2% (mass by vol.) is mixed with 80 mL of glucose solution of 4% (mass by vol.) at 300 K. Calculate the osmotic pressure of solution :
(a) 6.02 atm (b) 1.642 atm
(c) 4.378 atm (d) 3.01 atm

4. In two solutions of same solute-solvent system exerts osmotic pressures of 6 atm and 2 atm at 300 K respectively. If these are separated by a semipermeable membrane, which would be observed :
(a) solvent will move from 6 atm solution to 2 atm solution
(b) solute will move from 6 atm solution to 2 atm solution
(c) solvent will move from 2 atm solution to 6 atm solution
(d) no movement of solute or solvent

5. Two liquids A and B are mixed. The partial vapour pressures of A and B in pure state are 100 and 200 mm respectively. If they are mixed in 1 : 4 mole ratio, then at equilibrium pressure of the mixture, assuming that mixture obeys Raoult's law, the mole fractions of A and B present in gaseous state are :
(a) $\frac{1}{5}, \frac{4}{5}$ (b) $\frac{1}{3}, \frac{2}{3}$
(c) $\frac{1}{7}, \frac{6}{7}$ (d) $\frac{1}{9}, \frac{8}{9}$

6. A solution of an organic compound develops an osmotic pressure of 2.07×10^{-2} Nm^{-2}. If the density of solution is 0.88 g dm^{-3}, the height which it will develop on separating with its solvent through semipermeable membrane is :
(a) 2.40×10^{-5} m (b) 2.40×10^{-3} m
(c) 2.4 m (d) 2.40×10^{-4} m

7. Two solutions each in 100 mL having 4 g glucose and 10 g sucrose respectively. Which one is correct to develop isotonic character in them (Assume T constant)?
(a) 0.42 g urea in glucose solution
(b) 0.42 g glucose in glucose solution
(c) 0.42 g sucrose in glucose solution
(d) 0.42 g urea in sucrose solution

8. The vapour pressure of two volatile liquid mixtures is $P_T = 5.3 + 2X_B$ (in cm of Hg), where X_B is mole fraction of B is mixture. What is the ratio of X_A and X_B in vapour phase?
(a) $\frac{73}{53}$ (b) $\frac{73}{53} \times \frac{P'_A}{P'_B}$
(c) $\frac{53}{73}$ (d) $\frac{53}{73} \times \frac{P'_B}{P'_A}$

9. 25 g ethylene glycol is present in 100 g of water. The solution is cooled to $-10°C$. K_f for H_2O is 1.86 K kg mol^{-1}. The amount of ice separated on cooling is :
(a) 25 g (b) 50 g
(c) 75 g (d) 20 g

10. The solution having highest vapour pressure is : (Assume 100% ionisation of electrolytes)
(a) 1 N KNO_3 (b) 1 N $Ba(NO_3)_2$
(c) 1 N $Al_2(SO_4)_3$ (d) 1 N Th $(NO_3)_4$

11. Elevation in b.pt. of an aqueous glucose solution is $0.6 K_b$ for water is 0.52 K molality^{-1}. The mole fraction of glucose in the solution is :
(a) 0.02 (b) 0.03
(c) 0.01 (d) 0.04

12. Normal boiling point (T_N) is defined as the temperature when V.P. of liquid becomes equal to 1 atm and standard boiling point (T_S) is defined as the temperature when V.P. of liquid becomes equal to 1 bar. Which one is not correct if water is considered?
(a) $T_N = 100°C$ (b) $T_S > 100°C$
(c) $T_S < 100°C$ (d) $T_S < T_N$

13. The vapour pressure of a solution at 373 K is 700 mm of Hg. The molality and mole fraction of solute in solution is :
(a) 0.0789, 4.76 (b) 0.789, 2.38
(c) 0.0789, 4.76×10^{-3} (d) 0.789, 4.76×10^{-1}

14. The ratio of vapour pressures of two liquids A and B in pure state are 1 : 2. If the two liquids are mixed and the ratio of their mole fraction in vapour phase are 2 : 1, the liquids A and B were mixed in the ratio of their mole :
(a) 1 : 2 (b) 2 : 1
(c) 4 : 1 (d) 1 : 4

15. During the freezing of a solution at its f.pt., which of the equilibrium exists?
(a) $\text{Solution}_{(l)} \rightleftharpoons \text{Solid solution}_{(s)}$
(b) $\text{Solvent}_{(l)} \rightleftharpoons \text{Solvent}_{(s)}$
(c) $\text{Solution}_{(l)} \rightleftharpoons \text{Solute}_{(s)} + \text{Solvent}_{(s)}$
(d) $\text{Solution}_{(l)} \rightleftharpoons \text{Solute}_{(s)} + \text{Solvent}_{(l)}$

16. A solution of 6% (mass/vol.) urea is isotonic with $NaCl_{aq}$. What is the mass/vol. % of NaCl in solution?
(a) 5.85% (b) 2.925%
(c) 11.7% (d) 1.463%

17. Which of the aqueous equimolal solution will have its vapour pressure near to solvent?
(a) Urea (b) $Ba(NO_3)_2$
(c) $NaNO_3$ (d) $Al(NO_3)_3$

18. Which of the following semipermeable membrane does not at all allow the solute particles to pass through it?
(a) Gelatinous $Cu_2Fe(CN)_6$
(b) Hair root of plants
(c) Bladder of pig
(d) All of these

19. A saturated aqueous solution of sparingly soluble salt AB_3 has the vapour pressure 0.08 mm lesser than the vapour pressure 17.33 mm of solvent at 25°C. The solubility product of AB_3 is :
(a) 1.087×10^{-2} (b) 1.48×10^{-4}
(c) 5.35×10^{-5} (d) 4.56×10^{-4}

20. 30 mL of 0.1 M KI_{aq} and 10 mL of 0.2 M $AgNO_3$ are mixed. The solution is then filtered out. Assuming no change in total volume, the resulting solution will freeze at : (Given, K_f for $H_2O = 1.86$ K kg mol^{-1} assume molarity = molality)
(a) 0.28 (b) 0.22
(c) 0.0744 (d) 0.149

21. Select the incorrect statement :
(a) If ΔT is depression in freezing point and m is molality, then $\left(\text{limit}\ \frac{\Delta T}{m}\right)_{T\to 0}$ = molal depression constant
(b) On dissolution of Fe in aqueous HCl, work is done by the system
(c) Osmosis is bilateral process
(d) For isotonic solutions C_1 must be equal to C_2.

22. 38.2 g of $Na_2B_4O_7 \cdot nH_2O$ dissolved in 250 g water shows an elevation in b.pt by 0.582°C. If K_f of water is 0.52 kg molality^{-1}, then n is :
(a) 6 (b) 5
(c) 8 (d) 10

23. 100 g of 10% by mass/mass urea solution is placed together with 200g of 10% (mass/mass) glucose solution in closed jar and allowed to attain equilibrium, the new (mass/mass)% of urea in its solution at equilibrium is :
(a) 4.26 (b) 6.17
(c) 5.43 (d) 7.68

24. A 0.2 mole fraction of non-electrolyte in water shows vapour pressure of solution equal to 10 mm of Hg. The mole fraction of solute of same electrolyte when it shows a vapour pressure of 5 mm of Hg is :
(a) 0.4 (b) 0.52
(c) 0.8 (d) 0.48

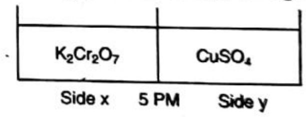
25. Benzoic acid undergoes dimerisation to 60% in benzene. The observed mass of benzoic acid will be :
(a) = 61 (b) > 122
(c) < 122 (d) = 244

26. A non-ideal solution obtained by mixing 30 mL chloroform and 50 mL acetone will show :
(a) ΔH = –ve and total volume < 80 mL
(b) ΔH = –ve and total volume = 80 mL
(c) ΔH = +ve and total volume > 80 mL
(d) ΔH = +ve and total volume = 80 mL

27. A commercial sample of cyclohexane freezes at 6.0°C. If freezing point of cyclohexane is 6.5° and $K_f = 20.0$ K molality^{-1}, then purity of sample is :
(a) 99.8% (b) 98%
(c) 90.9% (d) 99.5%

28. The slope of π vs C was made against insulin concentration (C) in g mL^{-1} and temperature 27°C. If C is in g litre^{-1} and the slope of line obtained is 4.65×10^{-3} g/mL, the molar mass (in g mol^{-1}) of insulin is :
(a) 9×10^5 (b) 3×10^5
(c) 4.5×10^5 (d) 5.30×10^6

29. 0.05 M $CuSO_4$ when treated with 0.01 M $K_2Cr_2O_7$ gives green colour solution of $Cu_2Cr_2O_7$. The two solutions are separated as shown in figure. Due to osmosis :



(a) Green colour formation inside Y
(b) Green colour formation inside X
(c) Molarity of $K_2Cr_2O_2$ is lowered
(d) Molarity of $CuSO_4$ solution is lowered

30. When an immiscible liquid with water was steam distilled at 95°C at a total pressure of 748 mm, the distillate obtained contain 1.25g of liquid per g of water. The vapour pressure of water is 648 mm at 95°C. The molar mass in g mol^{-1} of liquid is :
(a) 145.8 (b) 166
(c) 176 (d) 8

31. An ideal solution has two components A and B. If A is more volatile than B and also $P_A^\circ > P_T$, then the correct relation between mole fractions of A in liquid (X) and vapour (Y) phase is :
(a) $X_A = Y_A$ (b) $X_A > Y_A$
(c) $X_A < Y_A$ (d) nothing can be said

32. The incorrect relationship according to Raoult's law for two miscible liquid mixture is :
(a) $P_T = P_A^0 + (P_B^0 - P_A^0) X_B$

(b) $P_A^{'} + P_B^{'} = P_T$

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

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

33. The ratio of vapour pressure of two miscible liquids A and B in pure state are in the ratio 1 : 3 respectively at a temperature. n_A mole of A and n_B mole of B are mixed to form an ideal solution. If the ratio of mole of A and B in vapour phase was found to be 4 : 3, the ratio of mole of A and B in which they are mixed was :

(a) $\frac{4}{5}$ (b) 4

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

34. The boiling point of water and HCl are 100°C and 86°C respectively. An azeotropic mixture boils at about 120°C. Fractional distillation of this solution will give :

(a) Pure HCl first at 86°C

(b) Pure H_2O then at 100°C

(c) A mixture of HCl and H_2O in the ratio $\frac{373}{359}$

(d) A mixture of HCl in the ratio in which they are present in mixture

35. How many mole of $Th(NO_3)_4$ should be dissolved in 15 mole of water so that vapour pressure of water is reduced by 40% :

(a) 1 (b) 2

(c) 3 (d) 4

36. The boiling point elevation constant for toluene (b.pt = 110.7°C) is 3.32 K molality^{-1}. The entropy of vaporisation of toluene in J K^{-1}ml^{-1} is :

(a) 33.02×10^3 (b) 88.5

(c) 0.885 (d) 33.02

37. A solution of complex salt, $CrCl_3 \cdot 6H_2O$ having co-ordination no. 6 shows an osmotic pressure 73.89 atm at 300 K, when 1.0 molar solution of complex is used. One litre of this solution on treatment with excess of $AgNO_3$ solution ($\alpha_{AgNO_3} = 1$) leads to the formation of AgCl :

(a) 1 (b) 2

(c) 3 (d) 1.5

38. An ideal solution contains two volalite liquid $A\,(P° = 100$ torr$)$ and $B\,(P° = 200$ torr$)$. If liquid mixture contains 1 mole of A and 4 mole of B then total vapour pressure of the mixture obtained by condensing the vapour above this solution in a beaker is :

(a) 180 (b) 188.8

(c) 178.8 (d) 198.8

39. 0.2 M $AgNO_3$ and 0.1 M KI are mixed in the 1 : 3 volume ratio. The osmotic pressure of resultant solution at 300 K is :

(a) 4.93 atm (b) 3.69 atm

(c) 2.93 atm (d) 3.93 atm

40. The relationship which describes the variation of vapour pressure of a liquid with temperature is called :

(a) Hess's law

(b) Clausius Clapeyron equation

(c) Kirchhoff equation

(d) Arrhenius equation

41. An azeotropic solution of two liquids has boiling point lower than either of them when it :

(a) shows negative deviation from Raoult's law

(b) shows no deviation from Raoult's law

(c) shows positive deviation from Raoult's law

(d) is saturated

42. For a dilute solution, Raoult's law states that :

(a) the lowering of vapour pressure is equal to the mole fraction of solute

(b) the relative lowering of vapour pressure is equal to mole fraction of solute

(c) the relative lowering of vapour pressure is proportional to the mass of solute in solution

(d) the vapour pressure of the solution is equal to the mole fraction of solvent.

43. When mercuric iodide is added to the aqueous solution of potassium iodide then :

(a) freezing point is raised

(b) freezing point is lowered

(c) freezing point does not change

(d) boiling point does not change

44. Which of the following 0.1M aqueous solution will have the lowest freezing point?

(a) Potassium sulphate (b) Sodium chloride

(c) Urea (d) Glucose

45. The freezing point of equimolal aqueous solution will be highest for :

(a) $C_6H_5\overset{+}{N}H_3Cl^-$ (aniline hydrochloride)

(b) $Ca(NO_3)_2$

(c) $La(NO_3)_3$

(d) $C_6H_{12}O_{16}$ (glucose)

46. 0.2 molal acid HX is 20% ionised in solution. $K_f = 1.86$ K molality^{-1}. The freezing point of the solution is :

(a) − 0.45°C (b) − 0.90°C

(c) − 0.31°C (d) − 0.53°C

47. The molar mass of benzoic acid in benzene as determined by depression if freezing point method corresponds to :

(a) ionization of benzoic acid

(b) dimerization of benzoic acid

(c) trimerization of benzoic acid

(d) solvation of benzoic acid

48. A liquid mixture containing two immiscible liquids water and an alkyl bromide (molar mass 137 g mol^{-1}) is distilled at 90°C. The ratio of the vapour pressure of water and alkyl bromide in the distillate is 5 : 1, the mass ratio of distillate is :

(a) 1.52 : 1 (b) 0.657 : 1
(c) 1 : 5 (d) 5 : 1

49. The plots of osmotic pressure π (in atm) *vs.* concentration (in g/cm^3) of a polymer at 300 K gives a straight line having slope 2×10^{-3}. The molar mass of polymer is :

(a) 1.23×10^6 (b) 1.23×10^7
(c) 4×10^7 (d) 4×10^6

50. Assuming 100% ionisation of each complex osmotic pressures of equimolar solutions of $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, $Fe_4[Fe(CN)_6]_3$ and $Fe_3[Fe(CN)_6]_2$ at 300 K are in the order :

(a) 5 : 4 : 7 : 5 (b) 4 : 5 : 7 : 5
(c) 7 : 5 : 5 : 4 (d) 4 : 5 : 5 : 7

51. What mass of solute (molar mass = 60 g mol^{-1}) should be dissolved in 180 g water to reduce the vapor pressure to $\frac{4}{5}$ th of pure water :

(a) 120 g (b) 175 g
(c) 150 g (d) 100 g

52. The degree of association for a solute undergoing a change $4P \longrightarrow P_4$ can be given by

(a) $\frac{4[m\times K_f-\Delta T_f]}{3K_f\times m}$ (b) $\frac{2[m\times K_f-\Delta T_f]}{K_f\times m}$

(c) $\frac{[m\times K_f-\Delta T_f]}{K_f\times m}$ (d) $\frac{[K_f-\Delta T_f]}{\Delta T_f}$

53. During depression of freezing point in a solution, the following are in equilibrium : **(IIT 2003)**

(a) liquid solvent, solid solvent
(b) liquid solvent, solid solute
(c) liquid solute, solid solute
(d) liquid solute, solid solvent

54. A 0.004 *M* solution of Na_2SO_4 is isotonic with a 0.01 *M* solution of glucose at same temperature. The apparent degree of dissociation of Na_2SO_4 is : **(IIT 2004)**

(a) 25% (b) 50%
(c) 75% (d) 85%

55. The elevation in boiling point of a solution of 13.44g of $CuCl_2$ assuming 100% ionisation in 1 kg of water using the following information will be (formula mass of $CuCl_2=134.4$ and $K_b=0.52$ K $molal^{-1}$) **(IIT 2005)**

(a) 0.16 (b) 0.05
(c) 0.1 (d) 0.2

56. 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene ($K_f=1.72$ K mol^{-1} kg), a freezing point depression of 2 K is observed. The van't Hoff factor is : **(IIT 2007)**

(a) 0.5 (b) 1
(c) 2 (d) 3

57. 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 mole of N_2 from air dissolved in 10 mole of water at 298 K and 5 atm pressure is : **(IIT 2009)**

(a) 4.0×10^{-4} (b) 4.0×10^{-5}
(c) 5.0×10^{-4} (d) 4.0×10^{-6}

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

(a) -2.3×10^{-2} (b) -5.7×10^{-2}
(c) -5.7×10^{-3} (d) -1.2×10^{-2}

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

(a) 724 (b) 740
(c) 736 (d) 718

SOLUTIONS (One Answer Correct)

1. (b) Vapour pressure lowering is colligative property and not vapourpressure.

2. (d) $c_1 = c_2$ or $c_1 > c_2$ or $c_1 < c_2$ for isotonic solution depending on the nature of solute.

3. (a) $\because \ \pi_T = \frac{w}{mV}ST = \pi_T = \left[\left(\frac{w}{m}\right)_{\text{urea}} + \left(\frac{w}{m}\right)_{\text{glucose}}\right] \times \frac{ST}{V}$

Now, w_{urea} in 20 mL $= \frac{2\times 20}{100} = 0.4$ g,

w_{glucose} in 80 mL $= \frac{4\times 80}{100} = 3.2$ g,

$\therefore \ \pi_T = \left[\frac{0.4}{60} + \frac{3.2}{180}\right] \times \frac{0.0821\times 300\times 1000}{100}$

$\left(V = 20+80 = 100\text{ mL} = \frac{100}{1000} l\right)$

$= 6.02$ atm

4. (c) Osmosis movement of solvent occurs from dil. (low O.P.) to conc. (higher O.P.) solution.

5. (d) $P_M = 100\times\frac{1}{5} + 200\times\frac{4}{5}$

$\because \ \frac{n_A}{n_A+n_B} = \frac{1}{5}$ and

$\frac{n_B}{n_A+n_B} = \frac{4}{5} = 20+160 = 180$ mm

Also, $P'_A = P_M \cdot (X_A)_{\text{V.P.}} = P^\circ \cdot (X_A)_{\text{L.P.}}$

$180 \cdot (X_A)_{\text{V.P.}} = 100\times\frac{1}{5}$

$\therefore \ (X_A)_{\text{V.P.}} = \frac{1}{9}$

$\therefore \ \frac{n'_A}{n'_A+n'_B} = \frac{1}{9}$ and $\frac{n'_B}{n'_A+n'_B} = \frac{8}{9}$

6. (b) $d = 0.88\text{ g/mL} = 0.88\text{ g/cm}^3 = \frac{0.88\times 10^{-3}}{10^{-3}\text{ m}^3}$

$= 0.88\text{ kg/m}^3$

$\therefore \ \pi = h\cdot d\cdot g,$

$2.07\times 10^{-2} = h\times 0.88\times 9.8$

$\therefore \ h = 2.40\times 10^{-3}$

7. (a) $\pi_G = \frac{4}{180}\times 0.1\times 0.0821\times T = 1.82\times 10^{-4}\ T$

$\pi_S = \frac{10}{342}\times 0.1\times 0.0821\times T = 2.40\times 10^{-4}\ T,$

$(2.40-1.82)\times 10^{-4}\ T = \frac{w_{\text{urea}}}{60}\times 0.1\times 0.0821\times T$

$w = 0.42$ g

8. (b) $P_T = P'_A\cdot X_A + P'_B\cdot X_B, \quad P_T = 5.3+2X_B$

if $X_B = 0$ $P^\circ_A = P_T = 5.3$ cm and if $X_B = 1$

$P^\circ_B = P_T = 7.3$

Now mole fraction in mixture : $P'_A = P^\circ_A\cdot X_A$

$P'_B = P_B\cdot X_B$

$\therefore \ \frac{X_A}{X_B} = \frac{73\,P'_A}{53\,P'_B}$

9. (a) $\Delta T = \frac{1000\times K_f\times w}{m\times W}$

$10 = \frac{100\times 1.86\times 25}{62\times W}$

(W_{glycol} remains constant on cooling; only water freezes.)

$\therefore \ W = 75$ g

$\therefore$ Ice separated $= 100 - 75 = 25$ g

10. (c)

	No. of particles
$1N\ KNO_3 = 1M\ KNO_3$	$= 1\times 2 = 2$
$1N\ Ba(NO_3)_2 = \frac{1}{2}M\ Ba(NO_3)_2$	$= \frac{1}{2}\times 3 = 1.5$
$1N\ Al_2(SO_4)_3 = \frac{1}{6}M\ Al_2(SO_4)_3$	$= \frac{1}{6}\times 5 = 0.83$
$1N\ Th(NO_3)_4 = \frac{1}{4}M\ Th(NO_3)_4$	$= \frac{1}{4}\times 5 = 1.25$

Thus, more is the No. of particles furnished more will be lowering or minimum will be V.P.

11. (a) $\Delta T = \frac{1000\times K_b\times n\times M}{W\times M} = \frac{1000\times K_b\times n}{N\times M}$

or $\frac{n}{N} = \frac{\Delta T\times M}{1000\times K_b} = \frac{0.6\times 18}{1000\times 0.52} = 0.02$

$\therefore \ \frac{N}{n} = 50$ or $1+\frac{N}{n} = 51$

$\therefore \ \frac{n+N}{n} = 51 \ \therefore \ \frac{n}{n+N} = 0.02$

12. (b) $T_S = 372.6$ K for water since 1 bar < 1 atm

(1 bar = 0.998 atm)

13. (a) $\frac{P^\circ - P_s}{P^\circ} = \frac{n}{n+N}$

$\frac{760-700}{760}$ = m.f. of solute = 0.0789 (b.pt. of water is 373 K, thus $P_{H_2O} = 760$ mm)

Also, $\frac{P^\circ - P_s}{P_s} = \frac{n}{N} = \frac{n\times M\times 1000}{W\times 1000}$

$\therefore$ Molality $= \frac{760-700}{700}\times\frac{1000}{18} = 4.76$

14. (c) $P'_A = P^\circ_A\cdot X_{A(l)} = P_M\cdot X_{B(G)},$

$P'_B = P^\circ_B\cdot X_{B(l)} = P_M\cdot X_{B(G)},$

$\therefore \ \frac{P^\circ_A}{P^\circ_B}\cdot\left[\frac{X_A}{X_B}\right]_l = \left[\frac{X_A}{X_B}\right]_G$

$\therefore \ \left[\frac{X_A}{X_B}\right]_l = \frac{2}{1}\times\frac{2}{1} = 4:1$

15. (b) At f.pt. only solvent freezes out.

16. (b) $\pi_{\text{urea}} = \pi_{\text{NaCl}}$

$\frac{w}{m}\times\frac{ST}{V} = \frac{w}{m}\times\frac{ST}{V}\times(1+\alpha)$

$\frac{6}{60}\times\frac{1000}{100}\times ST = \frac{w\times 1000\times ST}{58.5\times 100}\times 2$

($\because \alpha = 1$ for NaCl)

$\therefore \ w = 2.925$ g $\quad \therefore$ % by mass/vol. = 2.925%

17. (a) $\frac{P^\circ - P_s}{P^\circ} = \frac{n}{n+N}(1+\alpha)$ ΔP is minimum since $\alpha = 0$ for urea. Thus, urea solution will have its V.P. closer to solvent.

18. (a) Only artificially prepared semipermeable membranes are perfectly semipermeable.

19. (d) For dilute solution :

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n}{N}(1+\alpha) = \frac{n \times M \times 1000}{W \times 1000} \times (1+\alpha)$$

$$= \text{molality} \times \frac{M}{1000} \times (1+3\alpha) \quad (\alpha = 1)$$

$$\text{molality} = \frac{0.08}{17.33} \times \frac{1000}{18 \times 4} = 0.0641\,\text{m}$$

$\therefore$ Molarity $= 0.0641$ M

(since molarity = molality for dilute solution)

$$AB \rightarrow A^{3+} + 3B^-$$

$\therefore K_{sp}$ of $AB_3 = 27 \times S^4 = 27 \times (0.0641)^4 = 4.56 \times 10^{-4}$

20. (a)

	KI +	$AgNO_3 \longrightarrow$	KNO_3 +	AgI
millimole	30×0.1	10×0.2		
	3	2	0	0
mm left	1	0	2	2

$\therefore$ [KI] in solution $= \frac{1}{40}$ and $[KNO_3] = \frac{2}{40}$

(molarity = molality)

$\therefore \Delta T_f = \Delta T_f$ (by KI) $+ \Delta T_f$ by (KNO_3)

$= \text{molality} \times 1.86 \times (1+\alpha_1) + \text{molality} \times 1.86 \times (1+\alpha_2)$

$= \frac{1}{40} \times 1.86 \times 2 + \frac{2}{40} \times 1.86 \times 2$

$= 0.093 + 0.186 = 0.279$

21. (d) $C_1 = C_2$ is valid only when solute neither dissociates nor associates.

22. (d) $Na_2B_4O_7 \longrightarrow 2Na^+ + B_4O_7^{2-}$

$i = 3$; $\quad w = \frac{38.2}{202 + 18n}$

$$\therefore \Delta T_b = \frac{1000 \times K_f \times w}{m \times w} \cdot i$$

w = mass of water from borax + mass of water

$$w = \frac{38.2 \times 18\,n}{202 + 18\,n} + 250$$

$$0.582 = \frac{1000 \times 0.52 \times 38.2 \times 3}{(250 + 18\,n) \times \left[\frac{38.2 \times 18\,n}{202 + 18n} + 250\right]}$$

$\therefore \quad n = 10$

23. (b) Initial mole fraction of water in urea $= \frac{\frac{90}{18}}{\frac{10}{60} + \frac{90}{18}} = 0.96$

(mass of water = mass of solution – mass of solute)

Initial mole fraction of water in glucose

$$= \frac{\frac{180}{18}}{\frac{20}{180} + \frac{180}{18}} = 0.98$$

$\therefore P_s \propto$ mole fraction of solvent

$\therefore$ V.P. of glucose > V.P. of urea;

Thus to attain equilibrium some mole of water will flow from glucose solution to urea solution. At eq. both solution have same mole fraction of solvent.

For urea $\qquad$ For glucose

$$\frac{\frac{90}{18} + X}{\frac{10}{60} + \frac{90}{18} + X} = \frac{\frac{180}{18} - X}{\frac{20}{180} + \frac{180}{18} - X}$$

$\therefore X = 4$ mole $= 72$ g H_2O

$\therefore$ New mass of water in urea = 90 + 72 = 162 g

$\therefore$ % of urea $= \frac{10}{162} \times 100 = 6.17$

24. (b) $P_s \propto$ mole fraction of solvent

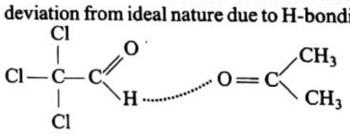
$10 \propto 0.8$

$6 \propto a \quad \therefore \quad a = 0.48$

$\therefore$ mole fraction of solute = 0.52

25. (b) Due to 60% dimerisation the molar mass of benzoic acid > molar mass 122 g mol^{-1} and < 244 g mol^{-1}.

26. (a) Chloroform and acetone mixture show negative deviation from ideal nature due to H-bonding



27. (a) $0.5 = \frac{1000 \times 20 \times w}{m \times W}$

$\therefore \frac{w}{m} = \frac{0.5\,W}{20 \times 1000} = 2.5 \times 10^{-5}\,W$

Let 1000g of cyclohexane contains $\frac{w}{m}$ mole of impurity

Mole of W g of cyclohexane $= \frac{W}{84} = 1190 \times 10^{-5}\,W$

Mole of pure cyclohexane

$= (1190 \times 10^{-5} - 2.5 \times 10^{-5})\,W$

$= 1187 \times 10^{-5}\,W$

$\therefore$ % purity $= \frac{1187 \times 10^{-5}}{1190 \times 10^{-5}} \times 100 = 99.8$

28. (d) $\pi = CRT = \frac{w}{V}\frac{RT}{m}$

$\pi = C\,(\text{in g / mL})\,\frac{RT}{m}$

$\therefore$ slope $= \frac{RT}{m} = 4.65 \times 10^{-3} \times 10^{-3}$ (in g / L)

$\therefore m = \frac{0.0821 \times 300}{4.65 \times 10^{-6}} = 5.3 \times 10^6$ g mol^{-1}

29. (d) During osmosis only solvent particles migrate from $K_2Cr_2O_7$ (dil.) to $CuSO_4$ (conc.) side.

30. (a) At boiling point $P_M = 748\text{ mm} = P'_{H_2O} + P'_l$

$\because P'_{H_2O} = 648\text{ mm} \quad \therefore P'_l = 100\text{ mm}$

Now $P'_{H_2O} = P_m \times \text{m.f. of } H_2O_V$

$P'_l = P_m \times \text{m.f. of liq}_V$

$$\therefore \frac{P'_{H_2O}}{P'_l} = \frac{\text{mole of } H_2O_V}{\text{mole of liq.}_V} = \frac{w \times M}{m \times W} = \frac{1 \times M}{1.25 \times 18} = \frac{648}{100}$$

$\therefore \quad M = 145.8\text{ g mol}^{-1}$

31. (c) $P_A^0 X_A = P_T \cdot Y_A$

$$\therefore \frac{X_A}{Y_A} = \frac{P_T}{P_A^0} < 1 \qquad (\because P_T < P_A^0)$$

$X_A < Y_A$

32. (d) $P_M = P'_A + P'_B$

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

$= P_A^0 \cdot X_A + P_B^0 (1 - X_A) = (P_A^0 - P_B^0) \cdot X_A + P_B^0$

$= P_A^0 (1 - X_B) + P_B^0 \cdot X_B = (P_B^0 - P_A^0) X_B + P_A^0$

33. (b) $P_M = P_A^0 \cdot X_A + P_B^0 \cdot X_B$

Also, $\quad P'_A = P_A^0 \cdot X_A = P_M \cdot X'_A$

$P'_B = P_B^0 \cdot X_B = P_M \cdot X'_B$

where X'_A and X'_B are mole fraction of A and B in vapour phase.

$$\therefore \quad \frac{P'_A}{P'_B} = \frac{P_A^0 \cdot X_A}{P_B^0 \cdot X_B} = \frac{X'_A}{X'_B}$$

or $\quad \frac{1}{3} \times \frac{X_A}{X_B} = \frac{4}{3}$

$\therefore \quad \frac{X_A}{X_B} = 4$

34. (d) Azeotropic mixture remains unchanged in their composition at their b.pt.

35. (b) $\frac{P^0 - P_s}{P_s} = \frac{n}{N} \times i = \frac{5n}{15}$

(1 mole of Th $(NO_3)_4$ gives 5 mole)

$\frac{100 - 60}{60} = \frac{5n}{15}$

$\therefore \quad n = 2$

36. (b) $$\Delta H_V = \frac{M_{C_7H_8} \times R \times T^0_{C_7H_8}}{1000 \times K}$$

$$= \frac{92 \times 8.314 \times (383.7)^2}{1000 \times 3.32} = 33.92\text{ kJ ml}^{-1}$$

Now, $\Delta s = \frac{\Delta H_V}{T_b} = \frac{33.92 \times 11^3}{383.2} = 88.5\text{ JK}^{-1}\text{mol}^{-1}$

37. (b) $\pi = CRT \times i$

$i = \frac{73.89}{1 \times 0.0821 \times 300} = 3$

Thus, $[Cr(H_2O)_5Cl]Cl_2.H_2O \longrightarrow$

$[Cr(H_2O)_5.Cl]_{aq.} + 2Cl^-_{aq.}$

or, 1 mole (mole $= M \times V_{\text{in L}}$) of complex will give 2 mol of Cl^-

2 mole of Cl^- will give 2 mole of AgCl

38. (b) $P_T = P_A^0 \cdot X_A + P_A^0 \cdot X_B$

$= 100 \times \frac{1}{5} + 200 \times \frac{4}{5} = 180$

Now, $X'_{A\,(V.P)} = \frac{P_A^0 \cdot X_A}{P_T} = \frac{100 \times 1}{180 \times 5} = \frac{1}{9}$

$\therefore \quad X'_B = \frac{8}{9}$

$\therefore P_T = 100 \times \frac{1}{9} + 200 \times \frac{8}{9} = \frac{1700}{9} = 188.8\text{ torr}$

39. (b)

	$AgNO_3$	+ KI	$\longrightarrow AgI\downarrow$	$+ KNO_3$
mm	$0.2 \times V$	$0.1 \times 3V$	0	0
	0	$0.1V$	$0.2V$	$0.2V$

Two solution contains $0.1V$ milli mole of KI and $0.2V$ m mole of KNO_3

$[KI] = \frac{0.1V}{4V} = \frac{0.1}{3}$; $[KNO_3] = \frac{0.2V}{4} = \frac{0.2}{4}$

$\pi = (C_1 + C_2)RT \times i$ (i = for KNO_3 and KI both)

$= \left(\frac{0.1}{4} + \frac{0.2}{4}\right) \times 0.0821 \times 300 \times 2$

$= 3.69$ atm

40. (b) $2.303 \log \frac{P_2}{P_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$ is Clausius – Clapeyron equation

41. (c) Lower b. pt means higher vapour pressure of mixture *i.e.*, positive deviation from Raoult's law.

42. (b) $\frac{P^0 - P_S}{P^0} = \frac{n}{n + N}$

43. (a) $2KI_{aq} \rightarrow 2K^+ + 2I^-$ (four particles)

$2KI + HgI_2 \rightarrow K_2HgI_4 \rightarrow 2K^+ + [HgI_4]^{2-}$

(insoluble in water) (three particles)

44. (a) 1 molecule of K_2SO_4 furnishes three ions and thus ΔT_f will be more or T_f will be low.

45. (d) Lower is the number of particles furnished in solution lower will be ΔT_f or higher will be T_f. Glucose does not ionise.

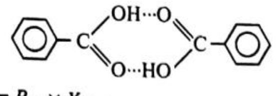
46. (a) $\Delta T_f = K_f \times \text{molality} \times (1 + \alpha)$ $\quad \underset{1-\alpha}{HA} \rightleftharpoons \underset{\alpha}{H^+} + \underset{\alpha}{A^-}$

$\Delta T_f = 1.86 \times 0.2 \times 1.2$ $\quad (\alpha = 0.2)$

$\Delta T_f = 0.45$

$\therefore \quad T_f = -0.45°\,C$

47. (b) Benzoic acid forms dimer in benzene.



48. (b) $P'_{H_2O} = P_M \times X_{H_2O}$

$P'_{AB} = P_M \times X_{AB}$

$\therefore \quad \frac{P'_{H_2O}}{P'_{AB}} = \frac{n_{H_2O}}{n_{AB}} = \frac{w_{H_2O} \times m_{AB}}{m_{H_2O} \times w_{AB}}$

$\frac{5}{1} = \frac{w_{H_2O} \times 137}{w_{AB} \times 18}$

or $\frac{w_{H_2O}}{w_{AB}} = \frac{5 \times 18}{1 \times 137} = \frac{90}{137} = 0.657 : 1$

49. (b) $\pi = \frac{CRT}{V} = \frac{wRT}{m.V_{\text{in L}}}$

$= \frac{w \times RT \times 1000}{m \times V_{\text{in mL}}}$

$\pi = \frac{1000RT}{m} \times C_{\text{g/cm}^3}$

$\therefore$ slope $= \frac{1000RT}{m} = 2 \times 10^{-3}$

$\therefore \quad m = \frac{1000 \times 0.0821 \times 300}{2 \times 10^{-3}} = 1.23 \times 10^7 \text{ g mol}^{-1}$

50. (a) $\pi \propto i$ *i.e.*, van't Hoff factor.

51. (c) $\frac{P^\circ - P_S}{P_S} = \frac{w \times M}{m \times W}$

$\frac{P^\circ - \frac{4P^\circ}{5}}{\frac{4P^\circ}{5}} = \frac{w \times 18}{60 \times 180}$

$\therefore w = 150$ g

52. (a) $\underset{1-\alpha}{4P} \longrightarrow \underset{\frac{\alpha}{4}}{P_4}$

$\therefore i = 1 - \alpha + \frac{\alpha}{4} = \frac{4 - 3\alpha}{4}$

Now $\Delta T_f = K_f \times \text{molality} \times i$

$= K_f \times m \times \frac{(4-3\alpha)}{4}$

$\therefore \quad \frac{4-3\alpha}{4} = \frac{\Delta T_f}{K_f \times m}$

$4 - 3\alpha = \frac{4\Delta T_f}{K_f \times m}$

$\therefore \quad \alpha = \frac{4 - \frac{4\Delta T_f}{K_f \times m}}{3} = \frac{4K_f \times m - 4\Delta T_f}{3K_f \times m}$

$= \frac{4[m \times K_f - \Delta T_f]}{3K_f \times m}$

53. (a) Only liquid freezes at freezing point. Thus equilibrium between solid and liquid forms of solvent exist at freezing point.

54. (c) $\pi_{Na_2SO_4} = \pi_{\text{Glucose}}$

$CRT\,(1 + 2\alpha) = CRT$

$0.004\,(1 + 2\alpha) = 0.01$

$\therefore \quad \alpha = 0.75$ or $= 75\%$

55. (a) $\Delta T_b = K_b \times \text{molality}\,(1 + 2\alpha)$

$\underset{1-\alpha}{CuCl_2} \rightleftharpoons \underset{\alpha}{Cu^{2+}} + \underset{2\alpha}{2Cl^-}$ $\quad (\because \alpha = 1)$

$= 0.52 \times \frac{13.44}{134.4 \times 1} \times (1 + 2)$

$\Delta T_b = 0.156 \simeq 0.16$

56. (a) $\Delta T_f = K_f \times \text{molality} \times i$

$\therefore \quad i = \frac{2 \times 172 \times 50}{1.72 \times 20 \times 1000} = 0.5$

57. (a) $P' = P_T\, X_{N_2}$ (From Dalton's law)

$\therefore \quad P'_{N_2} = 5 \times 0.8 = 4.0$ atm

From Henry's law $P_{N_2} = K_H \cdot X_{N_2}$ dissolved

$\therefore \quad X_{N_2} = \frac{4}{1 \times 10^5} = 4 \times 10^{-5}$

or $\frac{n_{N_2}}{n_{N_2} + N_{H_2O}} = \frac{n_{N_2}}{n_{N_2} + 10} = 4 \times 10^{-5}$

$\therefore \quad n_{N_2} = 4 \times 10^{-5} \times 10 = 4 \times 10^{-4}$

58. (a) $K_3[Fe(CN)_6] \longrightarrow 3K^+ + Fe(CN)_6^{3-}$

	$K_3[Fe(CN)_6]$	$3K^+$	$Fe(CN)_6^{3-}$
Before dissociation	1	0	0
After dissociation	0	3	1

Total no. of particles furnished by

$K_3[Fe(CN)_6] = n = 4$

$\therefore$ van't Hoff factor, $i = 4$

Now $\Delta T_f = \frac{1000 \times K_f \times w}{m \times W} \times i$

$= \frac{1000 \times 1.86 \times 0.1 \times 4}{329 \times 100}$

$= 2.3 \times 10^{-2}\,^\circ C$

$\therefore \quad T'_f = 0 - 2.3 \times 10^{-2}$

$= -2.3 \times 10^{-2}\,^\circ C$

59. (a) $w_{\text{solute}} = 2.5\text{g}, W_{\text{solvent}} = 100\text{g}$

$\Delta T_b = 2^\circ$

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

or $2 = \frac{1000 \times 0.76 \times 2.5}{100 \times m}$

$\therefore \quad m = 9.5$

Now, $\frac{P^0 - P_s}{P^0} = \frac{w \times m}{m \times W}$ (Given dilute solution)

$\frac{760 - P_s}{760} = \frac{2.5 \times 18}{9.5 \times 100} = 0.047$

$\therefore \quad P_s = 724$ mm

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Two miscible liquids A and B having vapour pressure in pure state P_A° and P_B° are mixed in mole fraction X_A and X_B to get a mixture having total vapour pressure of mixture P_M. Which of the following relations are correct?
   (a) $X_A = \dfrac{P_M - P_B^\circ}{P_A^\circ - P_B^\circ}$
   (b) $\dfrac{X_{A(l)}}{X'_{A(V)}} = \dfrac{P_M}{P_A^\circ}$
   (c) $\dfrac{X_{A(l)}}{X'_{A(V)}} = \dfrac{P_M}{P_B^\circ}$
   (d) all of these

2. A mixture of two immiscible liquids A and B, having vapour pressure in pure state obey's the following relationships if X_A and X_B are mole fractions of A and B in vapour phase over the solution :
   (a) $P'_A = P_M \cdot X'_A$
   (b) $\dfrac{P'_A}{P'_B} = \dfrac{w_A \times m_B}{m_A \times w_B}$
   (c) if $P'_A > P'_B$ then $X'_A < X'_B$
   (d) if $P'_A > P'_B$ then $n_A > n_B$

3. Which relations are correct for an aqueous dilute solution of K_3PO_4 if its degree of dissociation is α?
   (a) $\dfrac{\Delta P}{P^\circ} = \dfrac{\text{molality} \times 18 \times (1+3\alpha)}{1000}$
   (b) $\dfrac{\Delta P}{P^\circ} = \dfrac{\pi_{obs.} \times 18 \times (1+3\alpha)}{ST \times 1000}$
   (c) $\dfrac{\Delta P}{P^\circ} = \dfrac{\Delta T_{f\,obs.} \times 18}{K_f \times 1000}$
   (d) Molar mass of K_3PO_4 = Molar mass$_{obs.} \times (1+3\alpha)$

4. 1.2575 g sample of $[Cr(NH_3)SO_4 \cdot Cl]$ (molar mass $251.5\ g\ mol^{-1}$) is dissolved to prepare 250 mL solution showing an osmotic pressure of 1.478 atm of Hg at 27°C. Which are correct about this solution ?
   (a) Each molecule furnishes three ions in solution
   (b) The van't Hoff factor is = 3
   (c) Equilibrium molarity of $[Cr(NH_3)_6SO_4Cl] = 0$
   (d) Equilibrium molarity of $[Cr(NH_3)_6^+]^{3+} = 0.02\ M$

5. 2 litre of 1 molar solution of a complex salt $CrCl_3 \cdot 6H_2O$ (molar mass $266.5\ g\ mol^{-1}$) shows an osmotic pressure of 98.52 atm. The solution is now treated with 1 litre of 6 M $AgNO_3$, which of the following are correct?
   (a) Mass of AgCl precipitated is 861 g
   (b) The clear solution will show an osmotic pressure = 98.52 atm
   (c) The clear solution will show an osmotic pressure = 65.68 atm
   (d) 2 mole of $[Cr(H_2O)_6](NO_3)_3$ will be present in solution

6. 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

7. To 10 mL of 0.5 M $BaCl_2$ solution, 5mL of 0.5M K_2SO_4 is added. $BaSO_4$ precipitates with. What will happen with respect to original solution of $BaCl_2$?
   (a) f.pt will decrease
   (b) f.pt will increase
   (c) b.pt will increase
   (d) b.pt will decrease

8. Salinity of water can be removed by :
   (a) Desalination
   (b) Boiling
   (c) Osmosis
   (d) Reverse osmosis

9. The vapour pressure of a solution depends upon :
   (a) Surface area
   (b) Temperature
   (c) Mole fraction of solvent
   (d) Degree of dissociation of solute

10. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is (are) : **[JEE (Advanced) II 2013]**
    (a) ΔG is positive
    (b) ΔS_{system} is positive
    (c) $\Delta S_{surroundings} = 0$
    (d) $\Delta H = 0$

SOLUTIONS (More Than One Answer Correct)

1. (a,b) $P_M = P_A^\circ \cdot X_A + P_B^\circ \cdot X_B$;

Also, $P' = P_M \cdot X_{A(V)} = P_A^\circ \cdot X_{A(l)}$

$$= P_A^\circ \cdot X_A + P_B^\circ (1 - X_A)$$

$$\therefore \quad X_A = \frac{P_M - P_B^\circ}{P_A^\circ - P_B^\circ}$$

2. (a,b,d) For immiscible liquids

$$P_A' = P_M \cdot X_A'$$

$$P_B' = P_M \cdot X_B'$$

$$\therefore \quad \frac{P_A'}{P_B'} = \frac{X_A'}{X_B'} = \frac{n_A}{n_B} = \frac{w_A \times m_B}{m_A \times w_B},$$

if $P_A' > P_B'$ then $n_A > n_B$

3. (a,c,d) $\frac{\Delta P}{P^\circ} = \frac{n}{N} = \frac{n \times M \times 1000}{W \times 1000} = \frac{\text{molality} \times M}{1000}$

For electrolyte $\frac{\Delta P}{P^\circ} = \frac{\text{molality} \times M}{1000} \times (1 + 3\alpha)$

($M = 18$ for H_2O)

Also, $\pi_{\text{obse.}} = C \times S \times T\ (1 + 3\alpha)$

$$\therefore \quad \frac{\Delta P}{P^\circ} = \frac{\pi_{\text{obse.}}}{ST} \times \frac{18}{1000}$$

$$\Delta T_{f\ \text{obse.}} = K_f \times \text{molality} \times (1 + 3\alpha)$$

$$\frac{\Delta P}{P^\circ} = \frac{\Delta T_{f\ \text{obse.}} \times 18}{K_f \times 100}$$

$$i = (1 + 3\alpha) = \frac{\text{Cal. Molar mass}}{\text{Obser. Molar mass}}$$

$\therefore$ Molar mass of $K_3PO_4 = M_{\text{obse.}} \times (1 + 3\alpha)$

4. (a,b,c,d) Molarity $= \frac{1.2575 \times 1000}{251.5 \times 250} = 0.02M$, $\pi = CST$

$$\therefore \quad \pi_{\text{obse.}} = 0.02 \times 0.0821 \times 300 = 0.4926\,\text{atm}$$

$$= 374.38\ \text{mm.}$$

$$\frac{\pi_{\text{obse.}}}{\pi_{\text{cal.}}} = i = \frac{1478 \times 760}{374.38} = 3$$

$$\because \quad \alpha = \frac{i-1}{n-1} \text{ and } \alpha = 1, \quad \therefore \quad n = 3$$

Also,

$$[Cr(NH_3)_6]SO_4 \cdot Cl \rightleftharpoons [Cr(NH_3)_6^{3+}] + SO_4^{-2} + Cl^-$$

	$[Cr(NH_3)_6]SO_4 \cdot Cl$	$[Cr(NH_3)_6^{3+}]$	SO_4^{-2}	Cl^-
	0.02	0	0	0
Eq. conc.	0	0.02	0.02	0.02

5. (a,c,d) $CrCl_3 \cdot 6H_2O$

$$\pi = CST\ (1 - \alpha + x\alpha + y\alpha)$$

$$98.52 = 1 \times 0.0821 \times 300 \times (x + y)\ (\alpha = 1)$$

$$\therefore (x + y) = 4$$

$\therefore$ $CrCl_3 \cdot 6H_2O$ can be written as :

$$[Cr(H_2O)_6]Cl_3 \rightleftharpoons [Cr(H_2O)_6]^{3+} + 3Cl^{-1}$$

$[Cr(H_2O)_6]Cl_3$	$[Cr(H_2O)_6]^{3+}$	$3Cl^{-1}$
1	0	0
$1-\alpha$	α	3α

3 mole of $AgNO_3$ will react 1 mole of $Cr(H_2O)_6Cl_3$

$$Cr(H_2O)_6Cl_3 + 3AgNO_3 \longrightarrow [Cr(H_2O)_6](NO_3)_3 + 3AgCl$$

	$Cr(H_2O)_6Cl_3$	$3AgNO_3$	$[Cr(H_2O)_6](NO_3)_3$	$3AgCl$
mole	$2 \times 1 = 2$	$1 \times 6 = 6$	0	0
	0	0	2	6

$\therefore$ Mole of AgCl formed = 6;

Mass of AgCl formed $= 6 \times 143.5 = 861\,g$

$[Cr(H_2O)_6](NO_3)_3 = \frac{2}{3}$

$$\therefore \quad \pi = CST \times (1 + 3\alpha) = \frac{2}{3} \times 0.0821 \times 300 \times 4 = 65.68\,\text{atm}$$

6. (a,d) Addition of solute to a solvent lowers the f.pt.

7. (b, d) $BaCl_2 + K_2SO_4 \longrightarrow BaSO_4 + 2KCl$

$BaCl_2$	K_2SO_4	$BaSO_4$	$2KCl$
5	2.5	0	0
2.5	0	2.5	5.0

$$\Delta T = \frac{1000K \times n \times i}{W}$$

initially for $BaCl_2$: $\frac{n \times i}{W} = \frac{0.5 \times 3}{1000} = 1.5 \times 10^{-3}$

Finally for mixture : $\frac{n \times i}{W} = \underset{\text{(For BaCl}_2\text{)}}{\frac{2.5 \times 10^{-3} \times 3}{15}} + \underset{\text{(For KCl)}}{\frac{5 \times 10^{-3} \times 2}{15}}$

$$= \frac{17.5 \times 10^{-3}}{15} = 1.16 \times 10^{-3}$$

Thus $\frac{n \times i}{W}$ decreases on mixing, therefore ΔT_b and ΔT_f of mixture are lowered. Thus T_b decreases and T_f increases.

8. (a, d) Follow text.

9. (b, c, d) $P_S \propto \frac{N}{n+N}$

and $\frac{P^\circ - P_S}{P_S} = \frac{n}{(n+N)} \times i$

10. (b,c,d)

For ideal solution

$\Delta H_{\text{mixing}} = 0$

$\Delta S_{\text{mixing}} = +\text{ve}$

$\therefore \Delta G_{\text{mixing}} = -\text{ve}$

$\Delta S_{\text{surrounding}} = 0$

COMPREHENSION BASED PROBLEMS

Comprehension 1 : Mixing of two liquids may or may not bring in ideal solution nature, (*i.e.*, $\Delta H_{\text{mixing}} = 0$; $\Delta V_{\text{mixing}} = 0$) and the solution obeys Raoult's law or not. If either of the liquid disturbs the forces of attractions among the molecules, ideal nature disappeares, Benzene and toluene mixture however provides ideal solution. Vapour pressure of C_6H_6 and C_7H_8 mixture at 50°C are given by $P = 179X_B + 92$, where X_B is mole fraction of C_6H_6.

[1] Vapour pressure of pure liquids in mm are :
(a) $P_{C_6H_6} = 271, P_{C_7H_8} = 92$
(b) $P_{C_6H_6} = 92, P_{C_7H_8} = 271$
(c) $P_{C_6H_6} = 179, P_{C_7H_8} = 92$
(d) $P_{C_6H_6} = 92, P_{C_7H_8} = 179$

[2] Vapour pressure of liquid mixture obtained by mixing 936 g C_6H_6 and 736 g toluene.
(a) 200 (b) 201.4
(c) 199.4 (d) 198.4

[3] If the vapours are removed and condensed into liquid and again brought to the temperature of 50°C, what would be mole fraction of C_6H_6 in vapour state?
(a) 0.072 (b) 0.064
(c) 0.928 (d) 0.936

Comprehension 2 : A solution containing 0.1 mole of naphthalene and 0.9 mole of benzene is cooled out until some benzene freezes out. The solution is then decanted off from the solid and warmed upto 353 K where its vapour pressure was found to be 670 torr. The freezing point and boiling point of benzene are 278.5 K and 353 K respectively and its enthalpy of fusion is 10.67 kJ mol^{-1}.

[1] The temperature to which the solution was cooled originally:
(a) 279.39°C (b) 278.39°C
(c) 8.11°C (d) 270.39 K

[2] The amount of benzene that must have frozen out. Assume ideal behaviour:
(a) 70.2 (b) 58.06
(c) 12.14 (d) 48.06

[3] The mass of benzene present after cooling the original solution at −2.61°C is:
(a) 58.06 (b) 12.14
(c) 70.2 (d) 48.06

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 decrease in colligative properties on addition of non-volatile solute is due to increase in number of particles.

[1] For different aqueous solutions of 0.1 *N* urea, 0.1 *N* NaCl, 0.1 *N* Na_2SO_4 and 0.1 *N* Na_3PO_4 solution at 27°C the correct statements are :
1. The order of osmotic pressure is NaCl > Na_2SO_4 > Na_3PO_4 > urea
2. $\pi = \dfrac{\Delta T_b}{K_b} \times ST$ 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) 1, 2, 4
(c) 1, 2, 3 (d) 3, 4

[2] 1 g mixture of glucose and urea present in 250 mL aqueous solution shows the osmotic pressure of 0.74 atm at 27°C. 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 100.015, if K_b of water is 0.5 K molality^{-1}
4. If glucose is replaced by same mass of sucrose, the solution will show higher osmotic pressure at 27°C
5. If glucose is replaced by same mass of NaCl, the solution will show lower osmotic pressure at 27°C

(a) 1, 2, 3 (b) 1, 2, 3, 5
(c) 2, 4, 5 (d) 1, 4, 5

Comprehension 4 : Addition of a non-volatile solute to a solvent lowers its vapour pressure. Therefore, the vapour pressure of a solution (*i.e.*, V.P. of solvent in a solution) is lower than that of pure solvent, at the same temperature. A higher temperature is needed to raise the vapour pressure upto one atmosphere pressure, when boiling point is attained. However increase in b.p. is small. For example 0.1 molal aqueous sucrose solution boils at 100.05°C.

Sea water, an aqueous solution, which is rich in Na^+ and Cl^- ions, freezes about 1°C lower than frozen water. At the freezing point of a pure solvent, the rates at which two molecules stick together to form the solid and leave it to return to liquid state are equal when solute is present. Fewer solvent molecules are in contact with surface of solid. However, the rate at which the solvent molecules leave the surface of solid remains unchanged. That is why temperature is lowered to restore the equilibrium. The freezing point depression in a dilute solution is proportional to molality of the solute.

[1] An aqueous solution of 0.1 molal concentration of sucrose should have freezing point of ($K_f = 1.86$ K molality^{-1}) :
(a) +0.186°C (b) 1.86°C
(c) −1.86°C (d) −0.186°C

[2] When 250 mg of eugenol is added to 100 g of camphor ($K_f = 39.7$ K molality^{-1}), it lowered the freezing point by 0.62°C. The molar mass of equenol is :

(a) 1.6×10^2 g/mol (b) 1.6×10^4 g/mol
(c) 1.6×10^3 g/mol (d) 200 g/mol

[3] The freezing point of a 5% by mass $CH_3COOH(aq)$ solution is $-1.576°C$. The van't Hoff factor is:
(K_f of water = 1.86 Km^{-1})
(a) 0.996 (b) 2
(c) 0.5 (d) 1.016

[4] The freezing point of benzene solution was 5.4°C. The osmotic pressure of same solution at 10°C is (boiling point of benzene = 5.5°C). Assume solution to be dilute.
[K_f for C_6H_6 is 4.9 K molality^{-1}]
(a) 0.274 atm (b) 0.474 atm
(c) 0.674 atm (d) 0.874 atm

[5] The freezing point of a solution containing 50 cm^3 of ethylene glycol in 50 g water is found to be $-34°C$. Assuming dilute solution, the density of solution is :
[K_f for H_2O = 1.86 K molality^{-1}]
(a) 1.133 g/cm^3 (b) 2.133 g/cm^3
(c) 0.133 g/cm^3 (d) 1.62 g/cm^3

[6] The amount of ice separated out on cooling a solution containing 50 g ethylene glycol in 200 g water to $-9.3°C$ is : [K_f for H_2O = 1.86 K molality^{-1}]
(a) 38.71 g (b) 61.29 g
(c) 138.71 g (d) 161.29 g

[7] 2 g of benzoic acid dissolved in 25 g of C_6H_6 shows a depression in f.pt. equal to 1.62 K. K_f for C_6H_6 is 4.9 K molality^{-1}. The percentage association of acid, if it forms double molecules in solution is :
(a) 0.8% (b) 99.2%
(c) 90.2% (d) 9.8%

Comprehension 5 : Colligative properties of a solution depends upon number of ions furnished by the solute in solution measured in terms of van't Hoff factor i.

$$i = \frac{\text{Exp. colligative property}}{\text{Cal. colligative property}}$$

The van't Hoff factor 'i' is $1-\alpha+x\alpha+y\alpha$ for solutes showing dissociation where $(x+y)$ is the number of particles furnished by 1 mole of solute on 100% ionisation. Also van't Hoff coefficient $(g) = \dfrac{i}{(x+y)}$ ...(i)

For associated solute $i = 1-\alpha+\dfrac{\alpha}{n}$; where '$n$' is association number ...(ii)

The term osmomolarity is expressed as :
osmomolarity = g × no. of particle furnished by 1 molecule on complete dissociation × molarity ...(iii)
or osmomolality = g × no. of particle furnished by 1 molecule on complete dissociation × molality ...(iv)

[1] Osmomolarity of 0.2 M K_2SO_4 is :
(a) 0.3 (b) 0.4
(c) 0.5 (d) 0.6

[2] Osmomolality of 0.2 m benzoic acid in benzene, assuming 100% association is :
(a) 0.4 m (b) 0.1 m
(c) 0.05 m (d) 0.3 m

[3] Osmomolarity of KCl solution in water is 0.2 M. What will be its osmotic pressure at 300 K.
(a) 60 R (b) 30 R
(c) 40 R (d) 50 R

Comprehension 6 : 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}	Standard boiling point of water = 373 K
Freezing point depression constant of ethanol ($K_f^{ethanol}$) = 2.0 K kg mol^{-1}	Standard boiling point of ethanol = 351.5 K
Boiling point elevation constant of water (K_b^{water}) = 0.52 K kg mol^{-1}	Vapour pressure of pure water = 32.8 mm Hg
Boiling point elevation constant of ethanol ($K_b^{ethanol}$) = 1.2 K Kg mol^{-1}	Vapour pressure of pure ethanol = 40 mm Hg
Standard freezing point of water = 273 K	Molar mass of water = 18 g mol^{-1}
Standard freezing point of ethanol = 155.7 K	Molar mass of ethanol = 46 g mol^{-1}

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative. **(IIT 2008)**

[1] The freezing point of the solution M is :
(a) 268.7 K (b) 268.5 K
(c) 234.2 K (d) 150.9 K

[2] The vapour pressure of the solution M is :
(a) 39.3 mmHg (b) 36.0 mmHg
(c) 29.5 mmHg (d) 28.8 mmHg

[3] Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is :
(a) 380.4 K (b) 376.2 K
(c) 375.5 K (d) 354.7 K

SOLUTIONS

Comprehension 1

[1] (a) Given, $P = 179X_B + 92$

For pure C_6H_6, $X_B = 1$

$\therefore$ $P_B^\circ = 179 + 92 = \mathbf{271\ mm}$

For pure C_7H_8, $X_B = 0$

$\therefore$

$P_T^\circ = 179 \times 0 + 92 = \mathbf{92\ mm}$

[2] (c) Now,

$$P_M = P_B^\circ \cdot X_B + P_T^\circ \cdot X_T$$
$$= 271 \times \frac{12}{12+8} + 92 \times \frac{8}{12+8}$$
$$= 162.6 + 36.8$$
$$= \mathbf{199.4\ mm}$$

Mole of C_6H_6 $= \frac{936}{78} = 12$

Mole of C_7H_8 $= \frac{736}{92} = 8$

[3] (c) Now mole fraction of C_6H_6 in vapour phase of initial mixture (X_B')

$$X_B' = \frac{P_B'}{P_M} = \frac{162.6}{199.4} = \mathbf{0.815}$$

Mole fraction of C_7H_8 in vapour phase of initial mixture (X_T')

$$X_T' = \frac{P_T'}{P_M} = \frac{36.8}{199.4} = \mathbf{0.185}$$

These fractions are taken out and condensed into liquid. The liquid is again brought to 50° C to get again vapour-liquid equilibrium.

Thus, mole fraction of C_6H_6 in vapour phase of initial mixture

= Mole fraction of C_6H_6 in liquid phase of II mixture X_B'

Similarly, mole fraction of C_7H_8 in vapour phase of initial mixture

= Mole fraction of C_7H_8 in liquid phase of II mixture X_T'

New $P_M = P_B' + P_T'$

Therefore, new $P_M = P_B^\circ \cdot X_B' + P_T^\circ \cdot X_T'$

$$= 271 \times 0.815 + 92 \times 0.185$$
$$= 220.865 + 17.02 = 237.885 \text{ mm}$$

$\therefore$ New mole fraction of C_6H_6 in vapour phase

$$= \frac{\text{New } P_B'}{\text{New } P_M} = \frac{220.865}{237.885} = \mathbf{0.928}$$

Comprehension 2

$P^\circ = 760$ mm at boiling point of benzene (353 K)

$$\therefore \quad \frac{760-670}{670} = \frac{W_N \times M_B}{M_N \times W_B} = \frac{0.1 \times 78}{W_B}$$

$$\left(\text{or } N = \frac{W_N}{M_N} = 0.1\right)$$

$\therefore$ $W_B = \mathbf{58.06\ g}$

Also in original solution $W_B = 0.9 \times 78 = 70.2$ g

$\therefore$ C_6H_6 frozen out $= 70.2 - 58.06 = \mathbf{12.14\ g}$

Now ΔT (for original solution)

$$= K_f \times \text{molality} = \frac{RT_0^2}{1000l} \times \text{molality}$$
$$= \frac{8.314 \times 278.5 \times 278.5}{1000 \times \frac{10.67 \times 10^3}{78}} \times \frac{1000 \times 0.1}{58.06}$$
$$= 8.11 \text{ K}$$

Thus, original solution must have been cooled to

$$= 278.5 - 8.11 = \mathbf{270.39\ K} = -2.61° \text{ C}$$

[1] (d)

[2] (c)

[3] (a)

Comprehension 3

[1] (b) 1. Molar concentrations are 0.1 M urea, 0.1 M NaCl, $\frac{0.1}{2} M$ Na_2SO_4 and $\frac{0.1}{3} M$ Na_3PO_4

$\therefore$ $\pi \propto CX(1-\alpha+X\alpha+Y\alpha) \propto C(X+Y)$, if $\alpha = 1$

$\therefore$ $\pi_{urea} \propto 0.1 \times 1$; $\pi_{NaCl} \propto 0.1 \times 2$;

$\pi_{Na_2SO_4} \propto \frac{0.1}{2} \times 3$; $\pi_{Na_3PO_4} \propto \frac{0.1}{3} \times 4$

2. Also $\pi = C_M \times S \times T$ and ΔT_b = Molality $\times K_b$

if Molarity = Molality (for dilute solution)

$$\pi = \frac{\Delta T_b}{K_b} \times S \times T$$

3. Addition of salt on ice lowers the freezing point.

4. Also addition of salt on ice lowers its melting point and thus, ice melts earlier.

[2] (a) 1. Let a g glucose, b g urea be present in 1 g

$$\therefore \quad a + b = 1 \quad \text{...(i)}$$

$$\text{Thus,} \quad 0.74 \times \frac{250}{1000} = \left[\frac{a}{180} + \frac{b}{60}\right] \times 0.0821 \times 300 \quad \text{...(ii)}$$

By eqs. (i) and (ii), $b = 0.176$, $a = 0.824$

2. $$\frac{P^0 - P_S}{P^0} = \frac{w \times M \times 1000}{m + W \times 1000}$$

$$\therefore \quad \text{Molality} = \frac{P^0 - P_S}{P^0} \times \frac{1000}{M}$$

$$\text{or} \quad \frac{\pi}{ST} = \frac{P^0 - P_S}{P^0} \times \frac{1000}{M}; \quad (\because M = m)$$

$$\therefore \quad \frac{P^0 - P_S}{P^0} = \frac{0.74 \times 18}{0.0821 \times 300 \times 1000} = 5.41 \times 10^{-4}$$

3. $$\Delta T = \text{molality} \times K_b = \frac{\pi}{ST} \times K_b$$
$$= \frac{0.74}{0.0821 \times 300} \times 0.5 = 0.015$$

$\therefore$ b.pt. = 100.015°

4. On replacing glucose (Molar mass 180 g mol^{-1}) by sucrose (Molar mass 342 g mol^{-1}), π will decrease as $\pi \propto \frac{1}{\text{Molar mass}}$

5. On replacing glucose (Molar mass 180 g mol^{-1}) by NaCl (Molar mass 58.5 g mol^{-1}), π will increase as

$$\pi \propto \frac{1}{\text{Molar mass}} \times 2 \text{ for NaCl}$$

Comprehension 4

[1] (d) $\Delta T_f = \frac{1000 \times K_f \times w}{m \times W} = K_f \times \text{molality}$

$= 1.86 \times 0.1 = 0.186;$

Thus, f.pt. $= 0 - 0.186° C = -0.186° C$

[2] (a) $m = \frac{1000 \times K_f \times w}{W \times \Delta T}$

$= \frac{1000 \times 39.7 \times 250 \times 10^{-3}}{100 \times 0.62} = 160 \text{g/mol}$

[3] (d) $\Delta T_f = \frac{1000 \times K_f \times w}{m \times W} = \frac{1000 \times 1.86 \times 5}{60 \times 100} = 1.55$

$i = \frac{\Delta T_{f_{exp}}}{\Delta T_{f_{cal}}} = \frac{1.576}{1.55} = 1.016$

Acetic acid ionises in water and thus, $i > 1$

[4] (b) $\Delta T_f = 5.5 - 5.4 = 0.1° C$

$\pi = C_M ST$ (C_M = molarity)

$\Delta T_f = C_m \times K_f$ (C_m = molality)

For dilute solutions $C_M = C_m$

$\therefore \quad \pi = \frac{\Delta T_f}{K_f} \times ST = \frac{0.1}{4.9} \times 0.0821 \times 283 = 0.474 \text{ atm}$

[5] (a) $\Delta T_f = \frac{1000 \times K_f \times w}{m \times W}$

$\therefore \; 34 = \frac{1000 \times 1.86 \times 50 \times d}{62 \times 50}$

$\therefore \quad d = 1.133 \text{ g / cm}^3$

[6] (a) $\Delta T = \frac{1000 \times K_f \times w}{m \times W}$

$9.3 = \frac{1000 \times 1.86 \times 50}{62 \times W}$

$\therefore \quad W_{\text{water}} = 161.29 \text{ g}$

$\therefore$ Ice separated $= 200 - 161.29 = 38.71$ g

[7] (b) $\Delta T = \frac{1000 \times K_f \times w}{m \times W} = \frac{1000 \times 4.9 \times 2}{122 \times 25} = 3.213$

$i = \frac{\Delta T_{\text{exp}}}{\Delta T_{\text{cal}}} = 1 - \alpha + \frac{\alpha}{n}$

$\therefore \quad \frac{1.62}{3.213} = 1 - \alpha + \frac{\alpha}{2}$

$\therefore \quad \alpha = 0.992 \text{ or } 99.2\%$

Comprehension 5

$\text{Osmomolarity} = \frac{i}{(x+y)} \times (x+y) \times \text{molarity}$

$= i \times \text{molarity}$

[1] (d) osmomolarity $= 3 \times 0.2 = 0.6M$

[2] (b) osmomolality $= i \times \text{molality} = \frac{1}{2} \times 0.2 = 0.1\, m$

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

[3] (a) $\pi = c \times R \times T \times i$

$= c \times i \times RT$

$= 0.2 \times RT$

$= 0.2 \times 300 \times R = 60R$

Comprehension 6

[1] (d) $\Delta T_f = K_f \times \text{molality} = K_f \times \frac{n \times 1000}{W}$

$= \frac{K_f \times n \times 1000 \times M_{\text{ethanol}}}{W \times M_{\text{ethanol}}}$

$= \frac{K_f \times n_w \times 1000}{N_{\text{ethanol}} \times M_{\text{ethanol}}} = \frac{2.0 \times 0.1 \times 1000}{0.9 \times 46} = 4.83$

$\therefore \; T_f = 155.7 - 4.83 = 150.86° C$

[2] (a) $P_m = P^{\circ}_{H_2O} \cdot X_{H_2O} + P^{\circ}_{\text{ethanol}} \cdot X_{\text{ethanol}}$

$= 32.8 \times 0.1 + 40 \times 0.9 = 39.28$ mm

[3] (b) $\Delta T_b = K_f \times \frac{n_{\text{ethanol}} \times 1000}{N_{\text{ethanol}} \times M_{H_2O}} = \frac{0.52 \times 0.1 \times 1000}{0.9 \times 18}$

$= 3.20$

$\therefore \; T_b = 373 + 3.20 = 376.20° C$

Note : Non-volatile nature of solute should be assumed only for 1 and 3 otherwise the formula cannot be used. For problem 2, see that V.P. of ethanol is given.

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement (**S**) and explanations (**E**) is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) **S** is correct but **E** is wrong
(b) **S** is wrong but **E** is correct
(c) Both **S** and **E** are correct and **E** is correct explanation of **S**
(d) Both **S** and **E** are correct but **E** is not correct explanation of **S**

1. S : Evaporation and vapour pressure depends upon available surface area of solvent.
E : Larger is surface area of solvent for evaporation more is evaporation.

2. S : Formation of semipermeable membrane between the walls of porous pot on hanging pot filled with $CuSO_4(aq.)$ partially dipped in $K_4Fe(CN)_6$ is due to osmosis.
E : The ions moves through the walls of porous pot and between the walls Cu^{2+} and $Fe(CN)_6^{4-}$ gives insoluble gelatinous mass of $Ca_2[Fe(CN)_6]_4$.

3. S : Addition of HgI_2 to KI(*aq.*) shows an increase in freezing point.
E : HgI_2 (insoluble) reacts with KI(*aq.*) to form complex K_2HgI_4 and thus, number of particles present in solution decreases.

4. S : Osmosis is one sided movement of solvent particles.
E : In osmosis, the net movement of solvent particles from dil. to conc. solution and from conc. to dil. solution takes place through semipermeable membrane, showing finally the direction of dil. to conc.

5. S : van't Hoff factor for solute showing dissociation is always greater than for solute showing association.
E : Dissociation leads to increase in number of particles whereas, association leads to a decrease in number of particles.

6. S : At equilibrium of Liquid $\rightleftharpoons$ Vapour, kinetic energy of liquid phase and vapour phase is same.
E : Kinetic energy of liquid or vapour is given by $\frac{3}{2}RT$ for 1 mole.

7. S : Osmotic pressure of 1 *M* glucose is lesser than 1 *M* NaCl(*aq.*) but vapour pressure of 1 *M* glucose is higher than 1 *M* NaCl.
E : Osmotic pressure is colligative property but vapour pressure is not colligative property however, lowering in V.P. is colligative property.

8. S : For rubber and water, $V(l) > V(s)$.
E : The density of both rubber and water is more in liquid state.

9. S : Hoar frost is reverse of sublimation.
E : Formation of snow by freezing of clouds or vapours is called Hoar frost, *i.e.*, to reduce pressure over ice so that its external pressure becomes equal to vapour pressure.

10. S : Hot water extinguishes fire more quickly than cold water.
E : Hot water being at higher temperature is converted to steam in lesser time which by stopping combustion extinguishes the fire.

11. S : Water in a beaker cannot be made to boil by placing it in a bath of boiling water.
E : Water in the beaker will be heated to 100°C but will not boil as for boiling it requires latent heat of steam which is not provided by water bath as both attains 100°C.

12. S : Water can be made boiling without heating.
E : A decrease in external pressure to the vapour pressure of water at room temperature causes boiling of water.

13. S : Addition of a non-volatile solute causes a depression in vapour pressure.
E : Vapour pressure of a solution is directly proportional to mole fraction of solvent.

14. S : Osmosis is a bilateral process.
E : In osmosis net flow from dilute to concentrated solution is noticed.

15. S : Raoult's law for solute-solvent systems can be written as $\frac{P^o - P_s}{P_s} = \frac{n}{N}$
E : For dilute solutions Raoult's law may be written as

$$\frac{P^o - P_s}{P_s} = \frac{n}{N}.$$

16. S : Boiling point of water is 100°C although water boils below 100°C on mountains.
E : Boiling point of a liquid is the temperature at which V.P. of liquid becomes equal to 1 atm.

17. S : An ideal solution is one which obey Raoult's law.
E : $KCl_{(aq)}$ is an ideal solution.

18. S : Ebullioscopy or cryoscopy cannot be used for the determination of molar mass of polymers.
E : High molar mass solute leads to very low value of ΔT_b or ΔT_f.

19. S : For isotonic solutions $C_1 = C_2$
E : For isotonic solutions $\pi_1 = \pi_2$

20. S : Osmotic pressure of non aqueous solutions can be determined by Berkeley-Hartley method.

E : The semipermeable membrane used in Berkeley-Hartley method is $Cu_2[Fe(CN)_6]$.

21. S : Near the freezing point of an aqueous solution of a nonvolatile solute only ice separates out.

E : The remaining solution shows equilibrium between solid solvent-liquid solvent.

22. S : van't Hoff factor for electrolytes is always greater than unity.

E : The number of particles increases in solution due to electrolytic dissociation.

23. S : Addition of solvent to a solution always lowers the V.P.

E : The increase in relative surface area give rise to an increase in V.P. for a given solution.

24. S : A cook cries more in cutting onion rather than cutting an onion taken out from refrigerator.

E : The cold onion has lower vapour pressure of its volatile content.

25. S : At low concentration, benzene and toluene forms ideal solution.

E : Components with structural similarity forms ideal solution.

26. S : Addition of HgI_2 to aqueous solution of KI shows an increase in vapour pressure.

E : The number of particles present in solution decreases due to formation of complex K_2HgI_4.

27. S : Great care is taken in intra-venous injections to have comparable concentration of solutions to be injected to patient.

E : By not controlling the concentration the red blood cells may shrink or swell.

28. S : Ice melts earlier if NaCl is poured on it.

E : The freezing point of water is lowered on addition of NaCl.

29. S : A mixture of cyclohexane and ethanol shows -ve deviation from Raoult's law.

E : Cyclohexane reduces the intermolecular attraction between ethanol molecules.

ANSWERS (Statement Explanation Problems)

1. (b) Vapour pressure is independent of surface area.
2. (b) Diffusion occurs and not osmosis.
3. (c) Explanation is correct reason for statement.
4. (b) Osmosis is net movement of solvent particles from dil. to conc. and conc. to dil., *i.e.*, a bilateral process; The more movement is from dil. to conc. thus net flow from dil. to conc. is noticed.
5. (c) Explanation is correct reason for statement.
6. (c) —do—
7. (c) —do—
8. (c) —do—
9. (c) —do—
10. (c) —do—
11. (c) —do—
12. (c) —do—
13. (c) $P_s \propto \frac{N}{n+N}$ or $P_s = P^o \frac{N}{n+N}$ or $\frac{P_s}{P^o} = \frac{N}{n+N}$

    or $1 - \frac{P_s}{P^o} = 1 - \frac{N}{n+N}$ or $\frac{P^o - P_s}{P^o} = \frac{n}{n+N}$
14. (c) Explanation is correct reason for statement.
15. (d) $\frac{P^o - P_s}{P^o} = \frac{n}{n+N}$ or $\frac{P^o}{P^o - P_s} = \frac{n+N}{n} = 1 + \frac{N}{n}$

    or $\frac{P^o - P^o + P_s}{P^o - P_s} = \frac{N}{n}$ or $\frac{P^o - P_s}{P_s} = \frac{n}{N}$

    [For dilute solution $n + N \approx N$ $\therefore \frac{P^o - P_s}{P^o} = \frac{n}{N}$]
16. (c) Water boils at low temperature at mountains where atmospheric pressure is low, *i.e.*, when P^o = atmospheric pressure.
17. (a) KCl is ionic salt and it dissociates in solution.
18. (c) If molar mass is low, ΔT_b or ΔT_f being low cannot be read out accurately. A little error in measurement of ΔT_b will cause abnormal values of molar mass.
19. (b) For isotonic solutions osmotic pressures are same. Concentrations are same only when solute neither dissociates nor associates.
20. (b) $Cu_2[Fe(CN)_6]$ is soluble in non-aqueous solutions.
21. (c) Explanation is correct reason for statement.
22. (c) Explanation is correct reason for statement.
23. (b) Note that addition of solute to solvent (and not solvent to solute which will show reverse effect) shows a lowering in V.P. due to decrease in relative surface area.
24. (c) Vapour pressure decreases with decrease in temperature.
25. (c) Explanation is correct reason for statement.
26. (c) Explanation is correct reason for statement.
27. (c) Explanation is correct reason for statement.
28. (c) Explanation is correct reason for statement.
29. (b) The given explanation is correct and a reduction in molecular attraction will increase vaporisation nature and lead for higher vapour pressure than that calculated by Raoult's law. Thus, mixture will show positive deviation.

MATCHING TYPE PROBLEMS

Type I : Only One Match Is Possible

1.

List A	List B
(a) 0.1 *N* NaCl	(i) OP = 0.125 ST
(b) 0.2 *N* Na_2SO_4	(ii) OP = 0.133 ST
(c) 0.1 *N* $Ca(NO_3)_2$	(iii) OP = 0.15 ST
(d) 0.1 *N* $Al(NO_3)_3$	(iv) OP = 0.30 ST
(e) 0.1 *N* $Th(NO_3)_4$	(v) OP = 0.20 ST

2.

List A	List B
(a) Additive property	(i) Molarity
(b) Constitutive property	(ii) Dipole moment
(c) Additive and constitutive property	(iii) Optical activity
(d) Colligative property	(iv) Molar mass

3.

List A	List B
(a) Hygroscopic	(i) RBC neither contracts nor swells
(b) Efflorescent	(ii) RBC swells up
(c) Hypertonic	(iii) RBC shrinks
(d) Hypotonic	(iv) Loosing water
(e) Isotonic	(v) Gaining water

4.

List A	List B
(a) Plasmolysis	(i) Swelling of RBC
(b) Haemolysis	(ii) Shrinking of RBC
(c) Reverse osmosis	(iii) Osmosis from plant cell sap to soil
(d) Wilting up of plants	(iv) Desalination of water
(e) Growth of plants	(v) Osmosis from soil to plant cell sap.

5.

List A	List B
(a) Vapour pressure of solution	(i) Mole fraction of solute
(b) Lowering in vapour pressure of solution	(ii) Mole fraction of solvent
(c) Acetone-$CHCl_3$ solution	(iii) ΔH_{mixing} = +ve
(d) Hexane-ethanol solution	(iv) ΔH_{mixing} = −ve
(e) van't Hoff factor	(v) Greater than unity
(f) van't Hoff factor for glucose–H_2O	(vi) Equal to unity
(g) van't Hoff factor for NaCl–H_2O	(vii) Lesser than unity

Type II : More Than One Match Are Possible

6.

List A	List B
1. Gases	a. Victor Meyer's method
2. Volatile liquids	b. Hoffmann's method
3. Non volatile solids	c. Duma's method
4. Solids of low molar mass	d. Ebullioscopy or cryoscopy
5. Solids of high molar mass such as polymers	e. Osmotic pressure
	f. Raoult's law

ANSWERS

1. a–v; b–iv; c–iii; d–ii; e–i
2. a–iv; b–iii; c–ii; d–i
3. a–v; b–iv; c–iii; d–ii; e–i
4. a–ii; b–i; c–iv; d–iii; e–v
5. a–ii; b–i; c–iv; d–iii; e–vii; f–vi; g–v
6. 1–a, b, c; 2–a, b, c, f; 3–d, e, f; 4–d, f; 5–e