

विध्न विचारत भीरु जन, नहीं आरम्भे काम, विपति देख छोड़े तुरंत मध्यम मन कर श्याम।
पुरुष सिंह संकल्प कर, सहते विपति अनेक, 'बना' न छोड़े ध्येय को, रघुबर राखे टेक।।

*रचितः मानव धर्म प्रणेता
सद्गुरु श्री रणछोड़दासजी महाराज*

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Subject : CHEMISTRY

Topic : LIQUID SOLUTIONS

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1. Key Concepts
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KEY CONCEPTS

Vapor Pressure. The pressure exerted by the vapors of a liquid which are in equilibrium with it at a given temperature.

Note: It depends only on temperature and on nature of the liquid. It does NOT depend on the surface area

Raoult's Law. The equilibrium vapor pressure of a volatile component is linearly proportional to the mole fraction of that component in liquid phase.

For non-volatile solutes :

or relative lowering of vapor pressure,

A more useful form is

$$P(\text{solution}) = x_{\text{solvent}} P^{\circ}$$

$$(P^{\circ} - P)/P^{\circ} = x_{\text{solute}}$$

$$(P^{\circ} - P)/P = n/N$$

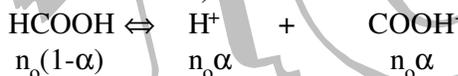
where n = total number of moles of *all the free solute species* in the solution *finally* (i.e. at equilibrium).

Three cases arise.

(i) **Non-electrolyte** is dissolved e.g. glucose or urea. These molecules do not dissociate into ions. If 0.1 mol of urea is dissolved in 50 moles of water, then $n/N = 0.1/50$ simply.

(ii) **Strong electrolyte** is dissolved e.g. NaCl, $\text{Ca}(\text{NO}_3)_2$ etc. These dissociate nearly completely into ions. If 0.1 mol of NaCl is dissolved in 50 moles of water, then $n/N = 0.2/50$ since NaCl dissociates completely into 0.1 mol Na^+ ions and 0.1 mol Cl^- ions. Similarly, for $\text{Ca}(\text{NO}_3)_2$, $n/N = 0.3/50$ if 0.1 mol of it dissociates completely into ions.

(iii) **Weak electrolyte** is dissolved e.g. HCOOH , CH_3NH_2 etc. In such cases, we should determine the *total* number of moles of all the solute species at equilibrium. e.g. if n_0 moles of formic acid considered non-volatile here) are dissolved in N moles of solvent then,



Total number of moles at equilibrium = $n_0(1 + \alpha)$. Hence, $n/N = n_0(1 + \alpha)/N$.

Note : This factor, n (at equilibrium)/ n (original) is referred to as **van't Hoff factor**.

Ideal Solutions. The solutions which obey Raoult's Law are called ideal solution. For ideality :

$$(i) \Delta H_{\text{mix}} = 0, \quad (ii) \Delta V_{\text{mix}} = 0 \text{ as well for liquid-liquid solutions.}$$

Non ideal solution (Deviations From Raoult's Law)

Positive deviation. When the observed vapor pressure is *more than* that expected by Raoult's law.

This is observed when $\Delta H_{\text{mix}} > 0$ i.e. energy is absorbed on mixing. Usually obtained by mixing of polar liquids with non-polar ones. e.g. cyclohexane and ethanol.

Negative deviation. When the observed vapor pressure is *less than* that expected by Raoult's law. This is observed when $\Delta H_{\text{mix}} < 0$ i.e. energy is released on mixing. Attractive forces between unlike molecules are greater than the forces of attraction between like molecules. e.g. chloroform and acetone. (Curve 3 in Fig. 1 and 2).

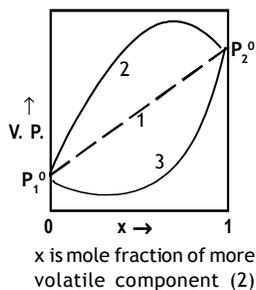


Fig. 1

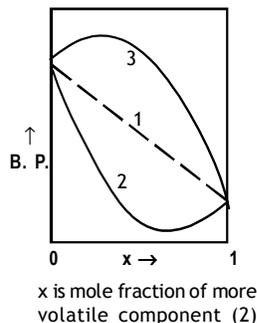


Fig. 2

Azeotropic Solutions. During distillation, the mole fraction of more volatile component in vapor state is higher than that in liquid state. This makes distillation possible. However, there exist some solutions for particular compositions of which the mole fraction of components in liquid and vapor state is same. Thus, no advantage is derived by distilling such a mixture and it is termed as **azeotropic**.

Completely Immiscible Liquids : When they are distilled, they distil in the ratio of their vapor pressure

at that temperature. e.g. When A and B are distilled wt ratio $\frac{w_B}{w_A}$ is given as $\frac{w_B}{w_A} = \frac{P_B^0 \cdot M_B}{P_A^0 \cdot M_A}$

Completely Miscible Liquids. They can be handled by Raoult's Law i.e.

$$y_i P = x_i P_i^0$$

where P = Total pressure of vapors in equilibrium with the liquid solution,

P_i^0 = vapor pressure of component i in pure state

y_i = mole fraction of i th component in vapor state, x_i = mole fraction of i th component in liquid state

This most fundamental expression may be arranged in many useful forms. e.g. for binary solutions :

$$P = x_1(P_1^0 - P_2^0) + P_2^0$$

or

$$1/P = 1/P_2^0 + y_1(1/P_1^0 - 1/P_2^0)$$

Note : Vapor pressure of an ideal solution is always between P_1^0 and P_2^0 (Curve 1 in Fig. 1 and 2)

Bubble Point. When the first bubble of vapor appears in liquid solution.

Dew Point. When the first drop of liquid condenses from a mixture of vapors. OR when the last drop of liquid remains and rest of the liquid is completely vaporised.

Colligative Properties. The properties which depend only on the number of moles of solute (and not on their molecular weights or sizes) are referred to as colligative properties.

e.g. Lowering of vapor pressure, depression of freezing point, elevation of boiling point, osmotic pressure etc.

- Relative lowering of vapour Pressure.** $\frac{P^0 - P}{P^0} = \frac{n}{n + N} = \frac{w/m}{w/m + W/M} = x_{\text{solute}}$
- Elevation in Boiling Point, ΔT_b .** For dilute solutions, $\Delta T_b = K_b m$
where m is molality of the solution (i.e. total number of moles of all the solute particles per kg of solvent).
 K_b is ebullioscopic or boiling point elevation constant which is given by

$$K_b = \frac{R(T_b^0)^2 M_{\text{solvent}}}{1000\Delta H_{\text{vap}}}$$

ΔH_{vap} is the enthalpy of vaporisation of solvent.

3. **Depression in freezing Point (ΔT_f).** For dilute solutions, $\Delta T_f = K_f m$

where,

$$K_f = \frac{R(T_f^0)^2 M_{\text{solvent}}}{1000\Delta H_{\text{fusion}}}$$

Osmosis. Spontaneous flow of solvent molecules through a semipermeable membrane from a pure solvent to the solution (or from a dilute solution to a concentrated solution) is termed as osmosis.

Reverse Osmosis. If a pressure greater than the osmotic pressure is applied on the concentrated solution, the solvent starts to flow from concentrated solution to dilute solution (or pure solvent). This is reverse osmosis. One of its chief uses is desalination of sea water to get pure drinking water.

4. **Osmotic Pressure (π).** The hydrostatic pressure built up on the solution which just stops osmosis. Alternately, it may be defined as the pressure which must be applied to the concentrated solution in order to stop osmosis.

For dilute solutions

$$\pi = cRT = h\rho g$$

where c is the total molar concentration of all the free species present in the solution, h is the height developed by the column of the concentrated solution and ρ is the density of the solution in the column. On the basis of osmotic pressure, the solutions can be classified in three classes.

Isotonic solutions. Two solutions having same osmotic pressures at same temperature. (This implies $c_1 = c_2$).

Hypertonic solution. When two solutions are being compared, then the solution with higher osmotic pressure is termed as hypertonic. The solution with lower osmotic pressure is termed as **hypotonic**.

Important. Osmotic pressures can be determined quite accurately, hence it is used in the determination of molecular weights of large proteins and similar substances.

Van't Hoff Factor (i)

Since colligative properties depends upon the number of particles of the solute, in some cases where the solute associates or dissociates in solution, abnormal results for molecules masses are obtained.

$$i = \frac{\text{Observed colligative property(actual)}}{\text{Theoretical colligative property}}$$

THE ATLAS

Liquid Solutions

- | | |
|--|---|
| 1. Vapour Pressure | Colligative properties (C.P.) |
| 2. Raoult's law | 1. Introduction |
| (i) When volatile solute is added | 2. The various C.P. |
| (a) When solute and solvent; both are miscible | (i) Lowering of V.P. |
| (b) When both are immiscible | (a) Determination of molar masses |
| (ii) When non-volatile solute is added. | (b) It's measurement |
| 3. Condensation of vapours of solution | (ii) Boiling point elevation |
| 4. Ideal and non-ideal solutions | (iii) Depression in freezing point |
| 5. Azeotropic mixtures | (iv) Osmotic pressure |
| | (a) Osmosis |
| | (b) Reverse osmosis |
| | (c) Isotonic solution |
| | 3. Van't Haff factor; Where the solute associates or dissociates in solution. |

EXERCISE I

Raoult's law

- Q.1 At 25°C, the vapour pressure of methyl alcohol is 96.0 torr. What is the mole fraction of CH₃OH in a solution in which the (partial) vapor pressure of CH₃OH is 23.0 torr at 25°C?
- Q.2 The vapour pressure of pure liquid solvent A is 0.80 atm. When a nonvolatile substance B is added to the solvent its vapour pressure drops to 0.60 atm. What is the mole fraction of component B in the solution?
- Q.3 The vapour pressure of pure water at 26°C is 25.21 torr. What is the vapour pressure of a solution which contains 20.0 glucose, C₆H₁₂O₆, in 70 g water?
- Q.4 The vapour pressure of pure water at 25°C is 23.76 torr. The vapour pressure of a solution containing 5.40 g of a nonvolatile substance in 90.0 g water is 23.32 torr. Compute the molecular weight of the solute.

Raoult's law in combinaton with Dalton's law of P.P. and V.P. lowering

- Q.5 The vapour pressure of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is prepared at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate total vapour pressure of the solution.
- Q.6 Calculate the mole fraction of toluene in the vapour phase which is in equilibrium with a solution of benzene and toluene having a mole fraction of toluene 0.50. The vapour pressure of pure benzene is 119 torr; that of toluene is 37 torr at the same temperature.
- Q.7 What is the composition of the vapour which is in equilibrium at 30°C with a benzene-toluene solution with a mole fraction of benzene of 0.40? With a mole fraction of benzene of 0.60?
 $P_b^\circ = 119$ torr and $P_t^\circ = 37$ torr
- Q.8 At 90°C, the vapour pressure of toluene is 400 torr and that of σ -xylene is 150 torr. What is the composition of the liquid mixture that boils at 90°C, when the pressure is 0.50 atm? What is the composition of vapour produced?
- Q.9 Two liquids A and B form an ideal solution at temperature T. When the total vapour pressure above the solution is 400 torr, the mole fraction of A in the vapour phase is 0.40 and in the liquid phase 0.75. What are the vapour pressure of pure A and pure B at temperature T?
- Q.10 Calculate the relative lowering in vapour pressure if 100 g of a nonvolatile solute (mol.wt.100) are dissolved in 432 g water.
- Q.11 What weight of the non-volatile solute, urea needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution?
- Q.12 The vapour pressure of an aqueous solution of glucose is 750 mm Hg at 373 K. Calculate molality and mole fraction of solute.

- Q.13 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 C₆H₆ at the same temperature is 631.7 mm of Hg. Calculate molality of solution.
- Q.14 The vapour pressure of pure benzene at a certain temperature is 640 mm of Hg. A nonvolatile nonelectrolyte solid weighing 2.175 g is added to 39.0 of benzene. The vapour pressure of the solution is 600 mm of Hg. What is molecular weight of solid substance?
- Q.15 The vapour pressure of water is 17.54 mm Hg at 293 K. Calculate vapour pressure of 0.5 molal solution of a solute in it.
- Q.16 Benzene and toluene form two ideal solution A and B at 313 K. Solution A (total pressure P_A) contains equal mole of toluene and benzene. Solution B contains equal masses of both (total pressure P_B). The vapour pressure of benzene and toluene are 160 and 60 mm Hg respectively at 313 K. Calculate the value of P_A/P_B.

Boiling point elevation and freezing point depression

- Q.17 When 10.6 g of a nonvolatile substance is dissolved in 740 g of ether, its boiling point is raised 0.284°C. What is the molecular weight of the substance? Molal boiling point constant for ether is 2.11°C·kg/mol.
- Q.18 A solution containing 3.24 of a nonvolatile nonelectrolyte and 200 g of water boils at 100.130°C at 1 atm. What is the molecular weight of the solute? (K_b for water 0.513°C/m)
- Q.19 The molecular weight of an organic compound is 58.0 g/mol. Compute the boiling point of a solution containing 24.0 g of the solute and 600 g of water, when the barometric pressure is such that pure water boils at 99.725°C.
- Q.20 An aqueous solution of a nonvolatile solute boils at 100.17°C. At what temperature will this solution freeze? [K_f for water 1.86°C/m]
- Q.21 Pure benzene freeze at 5.45°C. A solution containing 7.24 g of C₂H₂Cl₄ in 115.3 g of benzene was observed to freeze at 3.55°C. What is the molal freezing point constant of benzene?
- Q.22 A solution containing 6.35 g of a nonelectrolyte dissolved in 500 g of water freezes at – 0.465°C. Determine the molecular weight of the solute.
- Q.23 The freezing point of a solution containing 2.40 g of a compound in 60.0 g of benzene is 0.10°C lower than that of pure benzene. What is the molecular weight of the compound? (K_f is 5.12°C/m for benzene)
- Q.24 The elements X and Y form compounds having molecular formula XY₂ and XY₄. When dissolved in 20 gm of benzene, 1 gm XY₂ lowers the freezing point by 2.3°, whereas 1 gm of XY₄ lowers the freezing point by 1.3°C. The molal depression constant for benzene is 5.1. Calculate the atomic masses of X and Y.
- Q.25 Calculate the molal elevation constant, K_b for water and the boiling of 0.1 molal urea solution. Latent heat of vaporisation of water is 9.72 kcal mol⁻¹ at 373.15 K.
- Q.26 Calculate the amount of ice that will separate out of cooling a solution containing 50g of ethylene glycol in 200 g water to –9.3°C. (K_f for water = 1.86 K mol⁻¹ kg)

Q.27 A solution of 0.643 g of an organic compound in 50ml of benzene (density ; 0.879 g/ml) lowers its freezing point from 5.51°C to 5.03°C. If K_f for benzene is 5.12 K, calculate the molecular weight of the compound.

Q.28 The cryoscopic constant for acetic acid is 3.6 K kg/mol. A solution of 1 g of a hydrocarbon in 100 g of acetic acid freezes at 16.14°C instead of the usual 16.60°C. The hydrocarbon contains 92.3% carbon. What is the molecular formula?

Osmotic pressure

Q.29 Find the freezing point of a glucose solution whose osmotic pressure at 25°C is found to be 30 atm. $K_f(\text{water}) = 1.86 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{K}$.

Q.30 At 300 K, two solutions of glucose in water of concentration 0.01 M and 0.001 M are separated by semipermeable membrane. Pressure needs to be applied on which solution, to prevent osmosis? Calculate the magnitude of this applied pressure.

Q.31 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.

Q.32 The osmotic pressure of blood is 7.65 atm at 37°C. How much glucose should be used per L for an intravenous injection that is to have the same osmotic pressure as blood?

Q.33 What would be the osmotic pressure at 17°C of an aqueous solution containing 1.75 g of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) per 150 cm^3 of solution?

Q.34 A 250 mL water solution containing 48.0 g of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, at 300 K is separated from pure water by means of a semipermeable membrane. What pressure must be applied above the solution in order to just prevent osmosis?

Q.35 A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.750 g in 125 cm^3 of an aqueous medium. At 4°C an osmotic pressure rise of 2.6 mm of the solution was observed. The solution had a density of 1.00 g/cm^3 . Determine the molecular weight of the protein.

Q.36 The osmotic pressure of a solution of a synthetic polyisobutylene in benzene was determined at 25°C. A sample containing 0.20 g of solute/100 cm^3 of solution developed a rise of 2.4 mm at osmotic equilibrium. The density of the solution was 0.88 g/cm^3 . What is the molecular weight of the polyisobutylene?

Q.37 A 5% solution (w/v) of cane-sugar (Mol. weight = 342) is isotonic with 0.877% (w/v) of urea solution. Find molecular weight of urea.

Q.38 10 gm of solute A and 20 gm of solute B are both dissolved in 500 ml water. The solution has the same osmotic pressure as 6.67 gm of A and 30 gm of B dissolved in the same amount of water at the same temperature. What is the ratio of molar masses of A and B?

Van't Hoff factor & colligative properties

Q.39 A storage battery contains a solution of H_2SO_4 38% by weight. What will be the Van't Hoff factor if the $\Delta T_{f(\text{experiment})}$ is 29.08. [Given $K_f = 1.86 \text{ mol}^{-1} \text{ Kg}$]

- Q.40 A certain mass of a substance, when dissolved in 100 g C_6H_6 , lowers the freezing point by $1.28^\circ C$. The same mass of solute dissolved in 100g water lowers the freezing point by $1.40^\circ C$. If the substance has normal molecular weight in benzene and is completely ionized in water, into how many ions does it dissociate in water? K_f for H_2O and C_6H_6 are 1.86 and $5.12 K kg mol^{-1}$.
- Q.41 2.0 g of benzoic acid dissolved in 25.0g of benzene shows a depression in freezing point equal to $1.62 K$. Molal depression constant (K_f) of benzene is $4.9 K.kg.mol^{-1}$. What is the percentage association of the acid?
- Q.42 A decimolar solution of potassium ferrocyanide is 50% dissociated at 300K. Calculate the osmotic pressure of the solution. ($R=8.314 JK^{-1} mol^{-1}$)
- Q.43 The freezing point of a solution containing 0.2 g of acetic acid in 20.0g of benzene is lowered by $0.45^\circ C$. Calculate the degree of association of acetic acid in benzene. (K_f for benzene = $5.12 K mol^{-1} kg$)
- Q.44 0.85 % aqueous solution of $NaNO_3$ is apparently 90% dissociated at $27^\circ C$. Calculate its osmotic pressure. ($R= 0.082 l atm K^{-1} mol^{-1}$)
- Q.45 A 1.2% solution (w/v) of $NaCl$ is isotonic with 7.2% solution (w/v) of glucose. Calculate degree of ionization and Van't Hoff factor of $NaCl$.

TEKO

PROFICIENCY TEST

Q.1 *Fill in the blanks with appropriate items :*

1. Lowering of vapour pressure is _____ to the mole fraction of the solute.
2. The ratio of the value of any colligative property for NaCl solution to that of equimolal solution of sugar is nearly _____.
3. Semipermeable membrane allows the passage of _____ through it.
4. A binary solution which has same composition in liquid as well as vapour phase is called _____.
5. The molal elevation constant of solvent is also called _____.
6. The 0.1 M aqueous solution of acetic acid has boiling point _____ than that of 0.1 M aqueous solution of KCl.
7. For ideal solutions, the plot of total vapour pressure v/s composition is _____.
8. A solution of CHCl_3 and acetone shows _____ deviation.
9. Gases which react with water are generally _____ soluble in it.
10. Assuming complete dissociation, Van't Hoff's factor for Na_2SO_4 is equal to _____.
11. The osmotic pressure of a solution _____ with increase in temperature.
12. Water will boil at 101.5°C at pressure of _____ 76 cm of Hg.
13. Vant's Hoff's factor 'i' for dimerisation of CH_3COOH in benzene is _____.
14. $\pi = \frac{n_B}{V} RT$ is known as _____.
15. The molal elevation constant is the ratio of the elevation in boiling point to _____.

Q.2 *True or False Statements :*

16. Relative lowering of vapour pressure is a colligative property.
17. Lowering of vapour pressure of a solution is equal to the mole fraction of the non-volatile solute present in it.
18. The components of an azeotropic solution can be separated by simple distillation.
19. Vapour pressure of a liquid depends on the size of the vessel.
20. Addition of non-volatile solute to water always lowers its vapour pressure.
21. Reverse osmosis is generally used to make saline water fit for domestic use.
22. A 6% solution of NaCl should be isotonic with 6% solution of sucrose.
23. A real solution obeys Raoult's law.
24. Boiling point is a characteristic temperature at which vapour pressure of the liquid becomes higher than the atmospheric pressure.
25. Molal depression constant is independent of the nature of solute as well as that of solvent.
26. The real solutions can exhibit ideal behaviour at high concentrations.
27. The osmotic pressure decreases on addition of solvent to the solution.
28. For urea the value of Vant's Hoff's factor 'i' is equal to 1.
29. The unit of k_b is $\text{kg K}^{-1} \text{mol}^{-1}$.
30. 0.1 M solution of urea would be hypotonic with 0.1 M solution of NaCl.

EXERCISE II

Q.1 An aqueous solution containing 288 gm of a non-volatile compound having the stoichiometric composition $C_xH_{2x}O_x$ in 90 gm water boils at 101.24°C at 1.00 atmospheric pressure. What is the molecular formula?

$$K_b(\text{H}_2\text{O}) = 0.512 \text{ K mol}^{-1} \text{ kg}$$
$$T_b(\text{H}_2\text{O}) = 100^\circ\text{C}$$

Q.2 The degree of dissociation of $\text{Ca}(\text{NO}_3)_2$ in a dilute aqueous solution containing 7 gm of the salt per 100 gm of water at 100°C is 70%. If the vapour pressure of water at 100°C is 760 mm. Calculate the vapour pressure of the solution.

Q.3 The addition of 3 gm of substance to 100 gm CCl_4 ($M = 154 \text{ gm mol}^{-1}$) raises the boiling point of CCl_4 by 0.60°C of $K_b(\text{CCl}_4)$ is $5.03 \text{ kg mol}^{-1} \text{ K}$. Calculate

- (a) the freezing point depression
- (b) the relative lowering of vapour pressure
- (c) the osmotic pressure at 298 K
- (d) the molar mass of the substance

Given $K_f(\text{CCl}_4) = 31.8 \text{ kg mol}^{-1} \text{ K}$ and ρ (density) of solution = 1.64 gm/cm^3

Q.4 A 10% solution of cane sugar has undergone partial inversion according to the reaction:
Sucrose + Water \longrightarrow Glucose + Fructose. If the boiling point of solution is 100.27°C .

- (a) What is the average mass of the dissolved materials?
- (b) What fraction of the sugar has inverted? $K_b(\text{H}_2\text{O}) = 0.512 \text{ K mol}^{-1} \text{ kg}$

Q.5 If 20 ml of ethanol (density = 0.7893 gm/ml) is mixed with 40 ml water (density = 0.9971 gm/ml) at 25°C , the final solution has density of 0.9571 gm/ml . Calculate the percentage change in total volume of mixing. Also calculate the molality of alcohol in the final solution.

Q.6 Mixture of two liquids A and B is placed in cylinder containing piston. Piston is pulled out isothermally so that volume of liquid decreases but that of vapour increases. When negligibly small amount of liquid was remaining, the mole fraction of A in vapour is 0.4. Given $P_A^\circ = 0.4 \text{ atm}$ and $P_B^\circ = 1.2 \text{ atm}$ at the experimental temperature. Calculate the total pressure at which the liquid has almost evaporated. (Assume ideal behaviour).

Q.7 1.5 g of a monobasic acid when dissolved in 150g of water lowers the freezing point by 0.165°C . 0.5 g of the same acid when titrated, after dissolution in water, requires 37.5 ml of N/10 alkali. Calculate the degree of dissociation of the acid (K_f for water = $1.86^\circ\text{C mol}^{-1}$).

Q.8 Sea water is found to contain 5.85% NaCl and 9.50% MgCl_2 by weight of solution. Calculate its normal boiling point assuming 80% ionisation for NaCl and 50% ionisation of MgCl_2 [$K_b(\text{H}_2\text{O}) = 0.51 \text{ kg mol}^{-1} \text{ K}$].

Q.9 The latent heat of fusion of ice is 80 calories per gram at 0°C . What is the freezing point of a solution of KCl in water containing 7.45 grams of solute in 500 grams of water, assuming that the salt is dissociated to the extent of 95%?

Q.10 A complex is represented as $\text{CoCl}_3 \cdot x \text{NH}_3$. It's 0.1 molal solution in aq. solution shows $\Delta T_f = 0.558^\circ\text{C}$. K_f for H_2O is $1.86 \text{ K mol}^{-1} \text{ kg}$. Assuming 100% ionisation of complex and coordination no. of Co is six, calculate formula of complex.

- Q.11 The molar volume of liquid benzene (density = 0.877 g ml^{-1}) increases by a factor of 2750 as it vaporizes at 20°C and that of liquid toluene (density = 0.867 g ml^{-1}) increases by a factor of 7720 at 20°C has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution.
- Q.12 At 100°C , benzene & toluene have vapour pressure of 1375 & 558 Torr respectively. Assuming these two form an ideal binary solution, calculate the composition of the solution that boils at 1 atm & 100°C . What is the composition of vapour issuing at these conditions?
- Q.13 Calculate the boiling point of a solution containing 0.61 g of benzoic acid in 50g of carbon disulphide assuming 84% dimerization of the acid. The boiling point and K_b of CS_2 are 46.2°C and $2.3 \text{ K kg mol}^{-1}$, respectively.
- Q.14 At 25°C , 1 mol of A having a vapor pressure of 100torr and 1 mol of B having a vapor pressure of 300 torr were mixed. The vapor at equilibrium is removed, condensed and the condensate is heated back to 25°C . The vapors now formed are again removed, recondensed and analyzed. What is the mole fraction of A in this condensate?
- Q.15 Phenol associates in benzene to a certain extent to form a dimer. A solution containing $20 \times 10^{-3} \text{ kg}$ phenol in 1 kg of benzene has its freezing point depressed by 0.69 K. Calculate the fraction of phenol that has dimerised. K_f for benzene = $5.12 \text{ kg mol}^{-1}\text{K}$.
- Q.16 30 ml of CH_3OH ($d = 0.7980 \text{ gm cm}^{-3}$) and 70 ml of H_2O ($d = 0.9984 \text{ gm cm}^{-3}$) are mixed at 25°C to form a solution of density $0.9575 \text{ gm cm}^{-3}$. Calculate the freezing point of the solution. $K_f(\text{H}_2\text{O})$ is $1.86 \text{ kg mol}^{-1} \text{ K}$. Also calculate its molarity.
- Q.17 Dry air was drawn through bulbs containing a solution of 40 grams of urea in 300 grams of water, then through bulbs containing pure water at the same temperature and finally through a tube in which pumice moistened with strong H_2SO_4 was kept. The water bulbs lost 0.0870 grams and the sulphuric acid tube gained 2.036 grams. Calculate the molecular weight of urea.
- Q.18 Vapour pressure of C_6H_6 and C_7H_8 mixture at 50°C is given by $P(\text{mm Hg}) = 180 X_B + 90$, where X_B is the mole fraction of C_6H_6 . A solution is prepared by mixing 936g benzene and 736g toluene and if the vapours over this solution 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 the vapour state?
- Q.19 When the mixture of two immiscible liquids (water and nitrobenzene) boils at 372 K and the vapour pressure at this temperature are 97.7 kPa (H_2O) and 3.6 kPa ($\text{C}_6\text{H}_5\text{NO}_2$). Calculate the weight % of nitrobenzene in the vapour.
- Q.20 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 = Kelvin Temperature. Determine the molar latent heat of vaporisation as a function of temperature. Calculate the its value at 80 K.
- Q.21 A very dilute saturated solution of a sparingly soluble salt A_3B_4 has a vapour pressure of 20 mm of Hg at temperature T, while pure water exerts a pressure of 20.0126 mm Hg at the same temperature. Calculate the solubility product constant of A_3B_4 at the same temperature.

- Q.22 The molar volume of liquid benzene (density = 0.877 g ml^{-1}) increases by a factor of 2750 as it vaporises at 20°C while in equilibrium with liquid benzene. At 27°C when a non-volatile solute (that does not dissociate) is dissolved in 54.6 cm^3 of benzene vapour pressure of this solution, is found to be 98.88 mm Hg . Calculate the freezing point of the solution.
 Given : *Enthalpy of vaporization of benzene(l) = 394.57 J/gm*
Molal depression constant for benzene = $5.0 \text{ K kg. mol}^{-1}$.
Freezing point of benzene = 278.5 K .
- Q.23 If the apparent degree of ionization of KCl ($KCl=74.5 \text{ gm mol}^{-1}$) in water at 290 K is 0.86 . Calculate the mass of KCl which must be made up to 1 dm^3 of aqueous solution to the same osmotic pressure as the 4.0% solution of glucose at that temperature.
- Q.24 An ideal solution was prepared by dissolving some amount of cane sugar (non-volatile) in 0.9 moles of water. The solution was then cooled just below its freezing temperature (271 K), where some ice get separated out. The remaining aqueous solution registered a vapour pressure of 700 torr at 373 K . Calculate the mass of ice separated out, if the molar heat of fusion of water is 6 kJ .
- Q.25 The freezing point depression of a 0.109 M aq. solution of formic acid is -0.21°C . Calculate the equilibrium constant for the reaction,
 $\text{HCOOH (aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{HCOOH}^-(\text{aq})$
 K_f for water = $1.86 \text{ kg mol}^{-1} \text{ K}$
- Q.26 10 gm of NH_4Cl (mol. weight = 53.5) when dissolved in 1000 gm of water lowered the freezing point by 0.637°C . Calculate the degree of hydrolysis of the salt if its degree of dissociation of 0.75 . The molal depression constant of water is $1.86 \text{ kg mol}^{-1} \text{ K}$.
- Q.27 The freezing point of 0.02 mol fraction solution of acetic acid (A) in benzene (B) is 277.4 K . Acetic acid exists partly as a dimer $2A = A_2$. Calculate equilibrium constant for the dimerisation. Freezing point of benzene is 278.4 K and its heat of fusion ΔH_f is $10.042 \text{ kJ mol}^{-1}$.
- Q.28 A saturated solution of a sparingly soluble salt, MCl_2 has a vapour pressure of 31.78 mm of Hg at 30°C , while pure water exerts a pressure of 31.82 mm of Hg at the same temperature. Calculate the solubility product of the compound at this temperature.
- Q.29 The vapour pressure of two pure liquids, A and B that form an ideal solution are 300 and 800 torr respectively, at temperature T . A mixture of the vapour of A and B for which the mole fraction of A is 0.25 is slowly compressed at temperature T . Calculate
 (a) the composition of the first drop of the condensate,
 (b) the total pressure when this drop is formed,
 (c) the composition of the solution whose normal boiling point is T ,
 (d) the pressure when only the last bubble of vapour remains, and
 (e) the composition of the last bubble.
- Q.30 Tritium, T (an isotope of H) combines with fluorine to form weak acid TF, which ionizes to give T^+ . Tritium is radioactive and is a β -emitter. A freshly prepared aqueous solution of TF has pT (equivalent of pH) of 1.5 and freezes at -0.372°C . If 600 ml of freshly prepared solution were allowed to stand for 24.8 years. Calculate (i) ionization constant of TF. (ii) Number of β -particles emitted.
 (Given K_f for water = $1.86 \text{ kg mol}^{-1} \text{ K}^{-1}$, $t_{1/2}$ for tritium = 12.4 years)

EXERCISE III

Q.1 For an ideal binary liquid solution with $P_A^\circ > P_B^\circ$, which relation between X_A (mole fraction of A in liquid phase) and Y_A (mole fraction of A in vapour phase) is correct?

- (A) $Y_A < Y_B$ (B) $X_A > X_B$ (C) $\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$ (D) $\frac{Y_A}{Y_B} < \frac{X_A}{X_B}$

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

[Given : $P_A^\circ = 100$ mm Hg and $P_B^\circ = 200$ mm Hg]

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

Q.3 The exact mathematical expression of Raoult's law is

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

Q.4 A mixture contains 1 mole of volatile liquid A ($P_A^\circ = 100$ mm Hg) and 3 moles of volatile liquid B ($P_B^\circ = 80$ mm Hg). If solution behaves ideally, the total vapour pressure of the distillate is

- (A) 85 mm Hg (B) 85.88 mm Hg (C) 90 mm Hg (D) 92 mm Hg

Q.5 Which of the following aqueous solution will show maximum vapour pressure at 300 K?

- (A) 1 M NaCl (B) 1 M CaCl₂ (C) 1 M AlCl₃ (D) 1 M C₁₂H₂₂O₁₁

Q.6 The Van't Hoff factor for a dilute aqueous solution of glucose is

- (A) zero (B) 1.0 (C) 1.5 (D) 2.0

Q.7 The correct relationship between the boiling points of very dilute solution of AlCl₃ (T_1 K) and CaCl₂ (T_2 K) having the same molar concentration is

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

Q.8 A 0.001 molal solution of a complex $[MA_n]$ in water has the freezing point of -0.0054°C . Assuming 100% ionization of the complex salt and K_f for H₂O = 1.86 km^{-1} , write the correct representation for the complex

- (A) $[MA_8]$ (B) $[MA_7]A$ (C) $[MA_6]A_2$ (D) $[MA_5]A_3$

Q.9 The vapour pressure of a solution of a non-volatile electrolyte B in a solvent A is 95% of the vapour pressure of the solvent at the same temperature. If the molecular weight of the solvent is 0.3 times the molecular weight of solute, the weight ratio of the solvent and solute are

- (A) 0.15 (B) 5.7 (C) 0.2 (D) 4.0

Q.10 At a given temperature, total vapour pressure in Torr of a mixture of volatile components A and B is given by

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

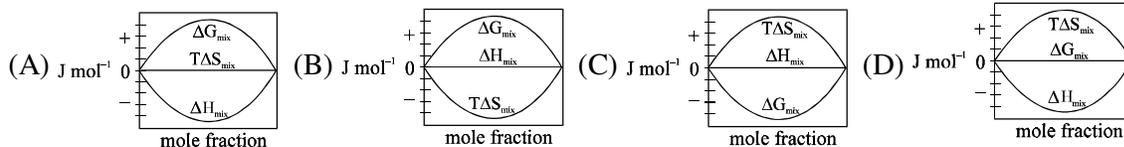
hence, vapour pressure of pure A and B respectively (in Torr) are

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

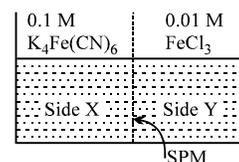
Q.11 Assuming each salt to be 90% dissociated, which of the following will have highest boiling point?

- (A) Decimolar Al₂(SO₄)₃
(B) Decimolar BaCl₂
(C) Decimolar Na₂SO₄
(D) A solution obtained by mixing equal volumes of (B) and (C)

- Q.12 The vapour pressure of a solvent decreased by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be mole fraction of the solvent if decrease in vapour pressure is 20 mm of Hg
 (A) 0.2 (B) 0.4 (C) 0.6 (D) 0.8
- Q.13 Elevation of boiling point of 1 molar aqueous glucose solution (density = 1.2 g/ml) is
 (A) K_b (B) $1.20 K_b$ (C) $1.02 K_b$ (D) $0.98 K_b$
- Q.14 What will be the molecular weight of CaCl_2 determined in its aq. solution experimentally from depression of freezing point?
 (A) 111 (B) < 111 (C) > 111 (D) data insufficient
- Q.15 1.0 molal aqueous solution of an electrolyte A_2B_3 is 60% ionised. The boiling point of the solution at 1 atm is ($K_{b(\text{H}_2\text{O})} = 0.52 \text{ K kg mol}^{-1}$)
 (A) 274.76 K (B) 377 K (C) 376.4 K (D) 374.76 K
- Q.16 Which of the following plots represents an ideal binary mixture?
 (A) Plot of P_{total} v/s $1/X_B$ is linear (X_B = mole fraction of 'B' in liquid phase).
 (B) Plot of P_{total} v/s Y_A is linear (Y_B = mole fraction of 'A' in vapour phase)
 (C) Plot of $\frac{1}{P_{\text{total}}}$ v/s Y_A is linear
 (D) Plot of $\frac{1}{P_{\text{total}}}$ v/s Y_B is non linear
- Q.17 Pressure over ideal binary liquid mixture containing 10 moles each of liquid A and B is gradually decreased isothermally. If $P_A^0 = 200 \text{ mm Hg}$ and $P_B^0 = 100 \text{ mm Hg}$, find the pressure at which half of the liquid is converted into vapour.
 (A) 150 mm Hg (B) 166.5 mm Hg (C) 133 mm Hg (D) 141.4 mm Hg
- Q.18 The lowering of vapour pressure in a saturated aq. solution of salt AB is found to be 0.108 torr. If vapour pressure of pure solvent at the same temperature is 300 torr. Find the solubility product of salt AB
 (A) 10^{-8} (B) 10^{-6} (C) 10^{-4} (D) 10^{-5}
- Q.19 Which of the following represents correctly the changes in thermodynamic properties during the formation of 1 mol of an ideal binary solution.



- Q.20 FeCl_3 on reaction with $\text{K}_4[\text{Fe}(\text{CN})_6]$ in aqueous solution gives blue colour. These are separated by a semipermeable membrane AB as shown. Due to osmosis there is
 (A) blue colour formation in side X.
 (B) blue colour formation in side Y.
 (C) blue colour formation in both of the sides X and Y.
 (D) no blue colour formation.



EXERCISE IV

OBJECTIVE

Q.1 The van't Hoff factor for 0.1 M $\text{Ba}(\text{NO}_3)_2$ solution is 2.74. The degree of dissociation is
(A) 91.3% (B) 87% (C) 100% (D) 74% [JEE 1999]

Q.2 In the depression of freezing point experiment, it is found that
(I) The vapour pressure of the solution is less than that of pure solvent.
(II) The vapour pressure of the solution is more than that of pure solvent.
(III) Only solute molecules solidify at the freezing point.
(IV) Only solvent molecules solidify at the freezing point.
(A) I, II (B) II, III (C) I, IV (D) I, II, III [JEE 1999]

Q.3 During depression of freezing point in a solution, the following are in equilibrium
(A) liquid solvent-solid solvent (B) liquid solvent-solid solute
(C) liquid solute-solid solute (D) liquid solute-solid solvent [JEE 2003]

Q.4 A 0.004 M solution of Na_2SO_4 is isotonic with a 0.010 M solution of glucose at same temperature. The apparent degree of dissociation of Na_2SO_4 is
(A) 25% (B) 50% (C) 75% (D) 85% [JEE 2004]

Q.5 The elevation in boiling point, when 13.44 g of freshly prepared CuCl_2 are added to one kilogram of water, is [Some useful data, $K_b(\text{H}_2\text{O}) = 0.52 \text{ kg K mol}^{-1}$, mol. wt. of $\text{CuCl}_2 = 134.4 \text{ gm}$]
(A) 0.05 (B) 0.1 (C) 0.16 (D) 0.21 [JEE 2005]

SUBJECTIVE

Q.6 A very small amount of a nonvolatile 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? [JEE 1997]

Q.7 A solution of a nonvolatile solute in water freezes at -0.30°C . The vapor pressure of pure water at 298K is 23.51 mmHg and K_f for water is 1.86 degree/molal. Calculate the vapor pressure of this solution at 298K. [JEE 1998]

Q.8 To 500 cm^3 of water, $3 \times 10^{-3} \text{ kg}$ 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 $1.86 \text{ K kg}^{-1} \text{ mol}^{-1}$ and 0.997 g cm^{-3} respectively. [JEE 2000]

Q.9 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. [JEE 2001]

Q.10 Match the boiling point with K_b for x, y and z, if molecular weight of x, y and z are same. [JEE 2003]

	b.pt.	K_b
x	100	0.68
y	27	0.53
z	253	0.98

Q.11 1.22 g of benzoic acid is dissolved in (i) 100 g acetone (K_b for acetone = 1.7) and (ii) 100 g benzene (K_b for benzene = 2.6). The elevation in boiling points T_b is 0.17°C and 0.13°C respectively.

- (a) What are the molecular weights of benzoic acid in both the solutions?
 (b) What do you deduce out of it in terms of structure of benzoic acid?

[JEE 2004]

Q.12 72.5 g of phenol is dissolved in 1 kg of a solvent ($k_f = 14$) which leads to dimerization of phenol and freezing point is lowered by 7 kelvin. What percent of total phenol is present in dimeric form?

[JEE 2006]

TEKO

ANSWER

EXERCISE I

- Q.1 0.24 Q.2 0.25 Q.3 24.5 torr Q.4 57.24 g/mol
- Q.5 66.13 mm Hg Q.6 0.237 Q.7 0.682, 0.318; 0.829, 0.171
- Q.8 92 mol% toluene; 96.8 mol % toluene Q.9 $P_A^\circ = 213.33$ torr, $P_B^\circ = 960.0$ torr
- Q.10 0.04 Q.11 111.1g, 18.52 molal Q.12 0.741 m, 0.013
- Q.13 0.162 m Q.14 65.25 Q.15 17.38 Q.16 0.964
- Q.17 106 g/mol Q.18 64.0 g/mol Q.19 100.079°C Q.20 -0.62°C
- Q.21 5.08°C/m Q.22 50.8 g/mol Q.23 2050 g/mol Q.24 $x = 25.6, y = 42.6$
- Q.25 $K_b = 0.512 \text{ kg mol K}^{-1}, T_b = 373.20 \text{ K}$ Q.26 38.71 g Q.27 156.06
- Q.28 C_6H_6 Q.29 $T_f = -2.28^\circ\text{C}$ Q.30 $P = 0.2217$ atm should be applied
- Q.31 ($V_{\text{final}} = 5 \cdot V_{\text{original}}$) Q.32 54.2 g Q.33 0.81 atm Q.34 13.8 atm
- Q.35 $5.4 \times 10^5 \text{ g/mol}$ Q.36 $2.4 \times 10^5 \text{ g/mol}$ Q.37 59.99
- Q.38 $M_A/M_B = 0.33$ Q.39 $i = 2.5$ Q.40 3 ions Q.41 $\alpha = 99.2\%$
- Q.42 $7.482 \times 10^5 \text{ Nm}^{-2}$ Q.43 94.5 % Q.44 4.64 atm Q.45 0.95; 1.95

PROFICIENCY TEST

1. proportional 2. 2 : 1 3. solvent molecules 4. azeotropic mixture
5. Ebullioscopic constant 6. lesser 7. straight line with slope $\neq 0$
8. negative 9. more 10. 3 11. increases
12. greater than 13. less than 1
14. Van't Hoff's solution equation 15. molality 16. T
17. F 18. F 19. F 20. T
21. T 22. F 23. F 24. F
25. F 26. F 27. T 28. T
29. F 30. T

EXERCISE II

- Q.1 $C_{44}H_{88}O_{44}$ Q.2 746.24 mm/Hg
- Q.3 (a) 3.79°C, (b) 0.018, (c) 4.65 atm, (d) 251.5 Q.4 (a) 210, (b) 64.1%
- Q.5 % change in volume = 3.05, 8.604 m Q.6 0.66 atm Q.7 18.34%
- Q.8 $T_b = 102.3^\circ\text{C}$ Q.9 $T_f = -0.73^\circ\text{C}$ Q.10 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ Q.11 0.73
- Q.12 $x_b = 0.2472, Y_b = 0.4473$ Q.13 46.33°C Q.14 $x_a'' = 0.1$
- Q.15 $\alpha = 0.7333$ Q.16 $-19.91^\circ\text{C}, 7.63 \text{ M}$ Q.17 $M = 53.8$
- Q.18 0.93 Q.19 20.11 %
- Q.20 ΔH_v at 80 K is 1659.1 calorie; $\Delta H_v = R [2.303 \times 313.7 + 1.40655T]$
- Q.21 5.4×10^{-13} Q.22 $T_f = 277.5 \text{ K}$ Q.23 8.9 gm
- Q.24 12.54 Q.25 $K_a = 1.46 \times 10^{-4}$ Q.26 $h = 0.082$ Q.27 $K = 3.36$
- Q.28 $4.9 \times 10^{-5} \text{ M}^3$
- Q.29 (a) 0.47, (b) 565 torr, (c) $x_A = 0.08, x_B = 0.92$, (d) 675 torr, (e) $x'_A = 0.11, x'_B = 0.89$
- Q.30 (i) $K_a = 7.3 \times 10^{-3}$ (ii) 4.55×10^{22}

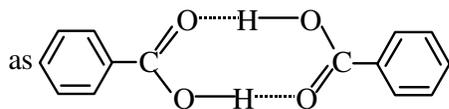
EXERCISE III

- | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|
| Q.1 C | Q.2 C | Q.3 C | Q.4 B | Q.5 D | Q.6 B | Q.7 B |
| Q.8 C | Q.9 B | Q.10 C | Q.11 A | Q.12 C | Q.13 D | Q.14 B |
| Q.15 D | Q.16 C | Q.17 D | Q.18 C | Q.19 C | Q.20 D | |

EXERCISE IV

- Q.1 B Q.2 C Q.3 A Q.4 C
- Q.5 C Q.6 0.1452, 5.028 K m^{-1}
- Q.7 23.44 mm Hg Q.8 0.229 Q.9 1.0×10^{-4}
- Q.10 $K_b(x) = 0.68, K_b(y) = 0.53, K_b(z) = 0.98$

- Q.11 (a) 122, (b) It means that benzoic acid remains as it is in acetone while it dimerises in benzene



- Q.12 35% phenol is present in dimeric form