Topic 1 Solution and Vapour Pressure of Liquid Solutions

Objective Questions I (Only one correct option)

1. The mole fraction of a solvent in aqueous solution of a solute is 0.8. The molality (in mol kg 1) of the aqueous solution is I)

(2019	Main,	12 A	pril

(a)	13.88	10^{-2}	(b)	13.88	10 1
(c)	13.88		(d)	13.88	10^{-3}

2. What would be the molality of 20% (mass/mass) aqueous solution of KI? (Molar mass of $KI = 166 \text{ g mol}^{-1}$)

(2019 Main, 9 April I)

(a)	1.48	(b)	1.51
(c)	1.35	(d)	1.08

- **3.** Liquid *M* and liquid *N* form an ideal solution. The vapour pressures of pure liquids M and N are 450 and 700 mmHg, respectively, at the same temperature. Then correct statement is (2019 Main, 9 April I)
 - mole fraction of *M* in solution; x_M
 - mole fraction of N in solution; x_N
 - mole fraction of *M* in vapour phase; y_M
 - mole fraction of N in vapour phase y_N

(a)
$$\frac{x_M}{x_N} = \frac{y_M}{y_N}$$

(b)
$$\frac{x_M}{2}$$

$$x_N \quad y_1$$

(c)
$$\frac{x_M}{x_N} = \frac{y_M}{y_N}$$

(d)
$$(x_M \quad y_M) \quad (x_N \quad y_N)$$

4. For the solution of the gases *w*, *x*, *y* and *z* in water at 298 K, the Henry's law constants ($K_{\rm H}$) are 0.5, 2, 35 and 40 K bar, respectively. The correct plot for the given data is

(2019 Main, 8 April II)



5. The vapour pressures of pure liquids A and B are 400 and 600 mmHg, respectively at 298 K. On mixing the two liquids, the sum of their initial volumes is equal to the volume of the final mixture. The mole fraction of liquid *B* is 0.5 in the mixture. The vapour pressure of the final solution, the mole fractions of components A and B in vapour phase, respectively are

(2019 Main, 8 April I)

(a) 450 mmHg, 0.4, 0.6	(b) 500 mmHg, 0.5, 0.5
(c) 450 mmHg, 0.5,0.5	(d) 500 mmHg, 0.4,0.6

6. Liquids A and B form an ideal solution in the entire composition range. At 350 K, the vapour pressures of pure A and pure B are 7 10^3 Pa and 12 10^3 Pa, respectively. The composition of the vapour in equilibrium with a solution containing 40 mole percent of A at this temperature is

(2019 Main, 10 Jan I)

(a) x_A	$0.76; x_B$	0.24	(b) x_A	0.28; x_B	0.72
(c) x_A	0.4; x_B	0.6	(d) x_A	0.37; <i>x_B</i>	0.63

- Which one of the following statements regarding Henry's law is not correct? (2019 Main, 8 Jan I)
 - (a) Different gases have different $K_{\rm H}$ (Henry's law constant) values at the same temperature
 - (b) Higher the value of $K_{\rm H}$ at a given pressure, higher is the solubility of the gas in the liquids
 - (c) The value of $K_{\rm H}$ increases with increase of temperature and $K_{\rm H}$ is function of the nature of the gas
 - (d) The partial pressure of the gas in vapour phase is proportional to the mole fraction of the gas in the solution
- **8.** 18 g of glucose $(C_6H_{12}O_6)$ is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution is (2016 Main)

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

- 9. The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 Torr. The molar mass of the substance is (2015, 1M)
 (a) 32 (b) 64 (a) 128 (b) 488
- **10.** The Henry's law constant for the solubility of N_2 gas in water at 298 K is 1.0 10^5 atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water of 298 K and 5 atm pressure is (2009)
 - (a) $4.0 \quad 10^{-4}$ (b) $4.0 \quad 10^{-5}$ (c) $5.0 \quad 10^{-4}$ (d) $4.0 \quad 10^{-6}$
- **11.** A molal solution is one that contains one mole of a solute in (1986, 1M)

(a)	1000 g of the solvent	(b) 1 L of the solvent
(c)	1 L of the solution	(d) 22.4 L of the solution

- **12.** For a dilute solution, Raoult's law states that (1985, 1M)
 - (a) the lowering of vapour pressure is equal to the mole fraction of solute
 - (b) the relative lowering of vapour pressure is equal to the mole fraction of solute
 - (c) the relative lowering of vapour pressure is proportional to the amount of solute in solution
 - (d) the vapour pressure of the solution is equal to the mole fraction of solvent
- **13.** An azeotropic solution of two liquids has boiling point lower than either of them when it (1981, 1M)
 - (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

Objective Questions II

(One or more than one correct option)

14. For a solution formed by mixing liquids L and M, the vapour pressure of L plotted against the mole fraction of M in solution is shown in the following figure. Here x_L and x_M represent mole fractions of L and M, respectively, in the

solution. The correct statement(s) applicable to this system is (are) (2017 Adv.)



- (a) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed from $x_L = 0$ to $x_L = 1$
- (b) Attractive intermolecular interactions between *L L* in pure liquid *L* and *M M* in pure liquid *M* are stronger than those between *L M* when mixed in solution
- (c) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when $x_L = 0$
- (d) The point Z represents vapour pressure of pure liquid L and Raoult's law is obeyed when $x_L = 1$
- Mixture(s) showing positive deviation from Raoult's law at 35°C is (are) (2016 Adv.)
 - (a) carbon tetrachloride + methanol
 - (b) carbon disulphide + acetone
 - (c) benzene + toluene
 - (d) phenol + aniline

Numerical Value Based Question

16. Liquids A and B form ideal solution over the entire range of composition. At temperature T, equimolar binary solution of liquids A and B has vapour pressure 45 torr. At the same temperature, a new solution of A and B having mole fractions x_A and x_B, respectively, has vapour pressure of 22.5 torr. The value of x_A / x_B in the new solution is _____.

(Given that the vapour pressure of pure liquid A is 20 Torr at temperature T) (2018 Adv. Paper-1)

True/False

 Following statement is true only under some specific conditions. Write the condition for it.
 "Two volatile and miscible liquids can be separated by

fractional distillation into pure components." (1994)

Subjective Questions

18. The vapour pressure of two miscible liquids *A* and *B* are 300 and 500 mm of Hg respectively. In a flask 10 moles of *A* is mixed with 12 moles of *B*. However, as soon as *B* is added, *A* starts polymerising into a completely insoluble solid. The polymerisation follows first-order kinetics. After 100 min, 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. (2001, 4M)

19. The molar volume of liquid benzene (density 0.877 g/mL) increases by a factor of 2750 as it vaporises at 20 C and that of liquid toluene (density 0.867 g mL¹) increases by a factor of 7720 at 20 C. A solution of benzene and toluene at 20 C has a vapour pressure of 45.0 torr. Find the mole fraction of benzene in the vapour above the solution.

(1996, 3M)

- **20.** What weight of the non-volatile solute urea $(NH_2 CO NH_2)$ needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution? (1993, 3M)
- **21.** The degree of dissociation of $Ca(NO_3)_2$ in a dilute aqueous solution, containing 7.0 g of the salt per 100 g of water at 100 C is 70%. If the vapour-pressure of water at 100 C is 760mm, calculate the vapour pressure of the solution.

(1991, 4M)

- **22.** The vapour pressure of pure benzene at a certain temperature is 640 mm 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 Hg. What is the molecular weight of the solid substance? (1990, 3M)
- **23.** The vapour pressure of a dilute aqueous solution of glucose $(C_6H_{12}O_6)$ is 750 mm of mercury at 373 K. Calculate (i) molality and (ii) mole fraction of the solute. (1989, 3M)
- **24.** The vapour pressure of ethanol and methanol are 44.5 and 88.7 mm Hg respectively. An ideal solution is formed at the

Topic 2 Colligative Properties

Objective Questions I (Only one correct option)

A solution is prepared by dissolving 0.6 g of urea (molar mass 60 g mol⁻¹) and 1.8 g of glucose (molar mass 180 g mol⁻¹) in 100 mL of water at 27°C. The osmotic pressure of the solution is (*R* 0.08206 L atm K⁻¹ mol⁻¹)

(2019 Main, 12 April II)

II)

(a) 8.2 atm (b) 2.46 atm (c) 4.92 atm (d) 1.64 atm

2. 1 g of a non-volatile, non-electrolyte solute is dissolved in 100 g of two different solvents A and B, whose ebullisocopic constants are in the ratio of 1 : 5. The ratio of the elevation in their heiling points $T_b(A)$ is

their boining points, -	$\overline{T_b(B)}$, is	(2019 Main, 10 April
(a) 5:1	(b)	10:1
(c) 1:5	(d)	1:0.2

3. At room temperature, a dilute solution of urea is prepared by dissolving 0.60 g of urea in 360 g of water. If the vapour pressure of pure water at this temperature is 35 mm Hg, lowering of vapour pressure will be

(Molar mass of urea 60 g mol^{-1}) (2019 Main, 10 April I)

same temperature by the mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour. (1986, 4M)

25. An organic compound $(C_x H_{2y} O_y)$ was burnt with twice the amount of oxygen needed for complete combustion to CO_2 and H_2O . The hot gases when cooled to 0°C and 1 atm pressure, measured 2.24 L. The water collected during cooling weight 0.9 g. The vapour pressure of pure water at 20°C is 17.5 mm Hg and is lowered by 0.104 mm when 50 g of the organic compound are dissolved in 1000 g of water. Give the molecular formula of the organic compound.

(1983, 5M)

- **26.** Two liquids A and B form ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of A and 3 moles of B is 550 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of A and B in their pure states. (1982, 4M)
- 27. The vapour pressure of pure benzene is 639.70 mm of Hg and the vapour pressure of solution of a solute in benzene at the same temperature is 631.9 mm of Hg. Calculate the molality of the solution. (1981, 3M)
- 28. What is the molarity and molality of a 13% solution (by weight) of sulphuric acid with a density of 1.02 g/mL ? To what volume should 100 mL of this solution be diluted in order to prepare a 1.5 N solution ? (1978, 2M)
 - (a) 0.027 mmHg
 - (b) 0.031 mmHg
 - (c) 0.017 mmHg
 - (d) 0.028 mmHg
- 4. Molal depression constant for a solvent is 4.0 K kg mol¹. The depression in the freezing point of the solvent for 0.03 mol kg¹ solution of K₂SO₄ is

(Assume complete dissociation of the electrolyte)

(2019	Main.	9 April II)
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(a)	0.18 K	(b)	0.36 K
(c)	0.12 K	(d)	0.24 K

5. The osmotic pressure of a dilute solution of an ionic compound XY in water is four times that of a solution of 0.01 M BaCl₂ in water. Assuming complete dissociation of the given ionic compounds in water, the concentration of XY (in mol L¹) in solution is (2019 Main, 9 April I)

(a) 4	10 ²	(b) 16 10 ⁴
(c) 4	10 4	(d) 6 10 2

6. Molecules of benzoic acid (C_6H_5COOH) dimerise in benzene. 'w' g of the acid dissolved in 30 g of benzene shows a depression in freezing point equal to 2 K. If the percentage association of the acid to form dimer in the solution is 80, then w is

 (Given that K_f 5 K kg mol⁻¹, molar mass of benzoic

 acid
 122 g mol⁻¹)

 (a)
 1.8 g
 (b)
 1.0 g
 (c)
 2.4 g
 (d)
 1.5 g

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

(2019 Main, 12 Jan I) (b) 2A (c) 3A (d) A

- 8. K₂HgI₄ is 40% ionised in aqueous solution. The value of its van't Hoff factor (*i*) is (2019 Main, 11 Jan II)
 (a) 1.6 (b) 1.8 (c) 2.2 (d) 2.0
- 9. The freezing point of a diluted milk sample is found to be 0.2 C, while it should have been 0.5°C for pure milk. How much water has been added to pure milk to make the diluted sample? (2019 Main, 11 Jan I)
 - (a) 2 cups of water to 3 cups of pure milk

(a) 4A

(a) 32

- (b) 1 cup of water to 3 cups of pure milk
- (c) 3 cups of water to 2 cups of pure milk
- (d) 1 cup of water to 2 cups of pure milk
- **10.** Elevation in the boiling point for 1 molal solution of glucose is 2 K. The depression in the freezing point for 2 molal solution of glucose in the same solvent is 2 K. The relation between K_b and K_f is (2019 Main, 10 Jan II) (a) K_f (b) K_b (c) K_f

$(a) \Lambda_b$	IJK_f	$(0) \mathbf{K}_b$	0.5 1
(c) K_b	K_{f}	(d) K_b	$2K_f$

11. A solution contain 62 g of ethylene glycol in 250 g of water is cooled upto -10° C. If K_f for water is 1.86 K kg mol⁻¹, then amount of water (in g) separated as ice is

ten amount of water (in g) separated as ice is (2019 Main, 9 Jan II)

(b) 48 (c) 64 (d) 16

- 12. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point?(2018 Main)
 (a) [Co(H₂O)₆]Cl₃ (b) [Co(H₂O)₅Cl]Cl₂ H₂O
 (c) [Co(H₂O)₄Cl₂]Cl 2H₂O (d) [Co(H₂O)₃Cl₃] 3H₂O
- **13.** The freezing point of benzene decreases by 0.45°C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be

$(K_f \text{ for ben})$	zene 5.12 K k	kg mol ¹)	(2017 Main)
(a) 64.6 %	(b) 80.4 %	(c) 74.6 %	(d) 94.6 %

14. Pure water freezes at 273 K and 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as 2 K kg mol¹. The figures shown below represent

plots of vapour pressure (V.P.) *versus* temperature (*T*). [Molecular weight of ethanol is 46 g mol¹] (2017 Adv.) Among the following, the option representing change in the freezing point is



- 15. Consider separate solution of 0.500 M C₂H₅OH (*aq*),
 0.100 M Mg₃(PO₄)₂(*aq*), 0.250 M KBr(*aq*) and 0.125 M Na₃PO₄(*aq*) at 25°C. Which statement is true about these solution, assuming all salts to be strong electrolytes?
 - (a) They all have the same osmotic pressure (2014 Main)
 - (b) 0.100 M Mg₃ (PO₄)₂(*aq*) has the highest osmotic pressure
 - (c) $0.125 \text{ M Na}_3\text{PO}_4(aq)$ has the highest osmotic pressure (d) $0.500 \text{ M C}_2\text{H}_5\text{OH}(aq)$ has the highest osmotic pressure
- **16.** 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). (2012)
 - (a) 724 (b) 740 (c) 736 (d) 718
- 17. The freezing point (in C) of solution containing 0.1 g of K₃[Fe(CN)₆] (mol. wt. 329) in 100 g of water

 $(K_f = 1.86 \text{ K kg mol}^{-1})$ is
 (2011)

 (a) 2.3 10 2 (b) 5.7 10 2

 (c) 5.7 10 3 (d) 1.2 10 2

- **18.** When 20 g of naphthoic acid $(C_{11}H_8O_2)$ is dissolved in 50 g of benzene $(K_f \quad 1.72 \text{ K kg mol}^{-1})$, a freezing point depression of 2 K is observed. The van't Hoff factor (*i*) is (2007, 3M) (a) 0.5 (b) 1 (c) 2 (d) 3
- **19.** The elevation in boiling point, when 13.44 g of freshly prepared $CuCl_2$ are added to one kilogram of water, is. [Some useful data, K_b 0.52 K kg mol⁻¹, molecular weight of $CuCl_2$ 134.4 g]. (2005, 1M) (a) 0.05 (b) 0.1 (c) 0.16 (d) 0.21

20. 0.004 M Na₂SO₄ is isotonic with 0.01 M glucose. Degree of dissociation of Na₂SO₄ is (2004, S, 1M)

(a)	75%	(b)	50%
(c)	25%	(d)	85%

- **21.** During depression of freezing point in a solution the following are in equilibrium (2003)
 - (a) liquid solvent, solid solvent
 - (b) liquid solvent, solid solute
 - (c) liquid solute, solid solute
 - (d) liquid solute, solid solvent
- **22.** The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to

(1996, 1M)

- (a) ionisation of benzoic acid
- (b) dimerisation of benzoic acid
- (c) trimerisation of benzoic acid
- (d) solvation of benzoic acid
- The freezing point of equimolal aqueous solutions will be highest for (1990, 1M)
 - (a) C₆H₅NH₃Cl (aniline hydrochloride)
 - (b) Ca(NO₃)₂
 - (c) $La(NO_3)_3$
 - (d) $C_6H_{12}O_6$ (glucose)
- 24. Which of the following 0.1 M aqueous solution will have the lowest freezing point? (1989, 1M)
 - (a) Potassium sulphate(b) Sodium chloride(c) Urea(d) Glucose
- **25.** When mercuric iodide is added to the aqueous solution of potassium iodide (1987, 2M)
 - (a) freezing point is raised
 - (b) freezing point is lowered
 - (c) freezing point does not change
 - (d) boiling point does not change

Objective Questions II

(One or more than one correct option)

- 26. In the depression of freezing point experiment, it is found that the (1999, 3M)
 - (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

Numerical Value Based Question

27. The plot given below shows $p \ T$ curves (where p is the pressure and T is the temperature) for two solvents X and Y and isomolal solution of NaCl in these solvents. NaCl completely dissociates in both the solvents.



On addition of equal number of moles of a non-volatile solute S in equal amount (in kg) of these solvents, the elevation of boiling point of solvent X is three times that of solvent Y. Solute S is known to undergo dimerisation in these solvents. If the degree of dimerisation is 0.7 in solvent Y, the degree of dimerisation in solvent X is _____. (2018 Adv.)

Subjective Questions

- **28.** 75.2 g of C_6H_5OH (phenol) is dissolved in a solvent of K_f 14. If the depression in freezing point is 7 K, then find the percentage of phenol that dimerises. (2006, 2M)
- **29.** 1.22 g C₆H₅COOH is added into two solvents and data of T_b and K_b are given as :
 - (i) In 100 g CH₃COCH₃ T_b 0.17, K_b 1.7 K kg/mol (ii) In 100 g benzene, T_b 0.13 and K_b 2.6 K kg/mol Find out the molecular weight of C₆H₅COOH in both the cases and interpret the result. (2004, 2M)
- **30.** Consider the three solvents of identical molar masses. Match their boiling point with their K_b values

Boiling point	K_b values
100°C	0.92
27°C	0.63
283°C	0.53
	Boiling point100°C27°C283°C

(2003)

31. To 500 cm³ of water, 3.0 10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86 K kg⁻¹ mol⁻¹ and 0.997 g cm⁻³, respectively.

(2000, 3M)

32. Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon : 42.86%, hydrogen : 2.40%, nitrogen : 16.67% and oxygen : 38.07%,

(i) Calculate the empirical formula of the minor product.(ii) When 5.5 g of the minor product is dissolved in 45 g of benzene, the boiling point of the solution is 1.84°C higher

than that of pure benzene. Calculate the molar mass of the minor product then determine its molecular and structural formula. (Molal boiling point elevation constant of benzene is 2.53 K kg mol 1). (1999)

- **33.** 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 K kg mol⁻¹. Calculate the vapour pressure of this solution at 298 K. (1998, 4M)
- **34.** Addition of 0.643 g of a compound to 50 mL of benzene (density: 0.879 g/mL) lowers the freezing point from 5.51 C to 5.03 C. If K_f for benzene is 5.12, calculate the molecular weight of the compound. (1992, 2M)

Passage Based Questions

Passage 1

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life.

One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

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

Given, freezing point depression constant of water

 (K_f^{water}) 1.86 K kg mol⁻¹

Freezing point depression constant of ethanol (K_f^{ethanol}) 2.0 K kg mol⁻¹

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

Boiling point elevation constant of ethanol (K_b^{ethanol}) 1.2 K kg mol⁻¹

Standard freezing point of water 273 K

Standard freezing point of ethanol 155.7 K

Standard boiling point of water 373 K

Standard boiling point of ethanol 351.5 K Vapour pressure of pure water 32.8 mm Hg Vapour pressure of pure ethanol 40 mm Hg Molecular weight of water 18 g mol⁻¹

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

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative. (2008,3 4M 12M)

- **35.** The freezing point of the solution *M* is (a) 268.7 K (b) 268.5 K (d) 150.9 K (c) 234.2 K
- **36.** The vapour pressure of the solution *M* is (a) 39.3 mm Hg (b) 36.0 mm Hg (c) 29.5 mm Hg (d) 28.8 mm Hg
- **37.** Water is added to the solution *M* such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is (a) 380.4 K (b) 376.2 K (c) 375.5 K (d) 354.7 K

Fill in the Blank

38. Given that T_f is the depression in freezing point of the solvent in a solution of a non-volatile solute of molality, m, the quantity $\lim_{m \to \infty} (T_f/m)$ is equal to (1994,1M)

Integer Answer Type Question

39. If the freezing point of a 0.01 molal aqueous solution of a cobalt (III) chloride-ammonia complex (which behaves as a strong electrolyte) is 0.0558°C, the number of chloride(s) in the coordination sphere of the complex is

 $[K_f \text{ of water} = 1.86 \text{ K kg mol}^1]$ (2015 Adv.)

38. (K_f)

40. (2)

40. MX_2 dissociates into M^2 and X ions in an aqueous solution, with a degree of dissociation () of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is (2014 Adv.)

To

Answers

Γοι	oic 1							To	pic 2						
1.	(c)	2.	(b)	3.	(a)	4.	(a)	1.	(c)	2.	(c)	3.	(c)	4.	(b)
5.	(d)	6.	(b)	7.	(b)	8.	(b)	5.	(d)	6.	(c)	7.	(c)	8.	(b)
9.	(b)	10.	(a)	11.	(b)	12.	(b)	9.	(c)	10.	(d)	11.	(c)	12.	(d)
13.	(c)	14.	(b, d)	15.	(a, b)	16.	(19)	13.	(d)	14.	(b)	15.	(a)	16.	(a)
17.	Т	19.	(0.72)	20.	(18.5)	21.	(746.32 mm)	17.	(a)	18.	(a)	19.	(c)	20.	(a)
22.	(65.25)	23.	(0.75)	24.	(0.657)	27.	(0.158)	21.	(a)	22.	(b)	23.	(d)	24.	(a)
28.	(180.40 mL)							25.	(a)	26.	(a, d)	27.	(0.05)	28.	(75%)
	()							30.	(0.23°C)	33.	(23.44 mm)	34.	(156 g/mol)	35.	(d)

36. (a)

37. (b)

Hints & Solutions

Topic 1 Solution and Vapour Pressure of Liquid Solutions

1. Key Idea Molality (m) $\frac{\text{Mass of solute } (w_2) \quad 1000}{\text{Molar mass of solute } (M_2)}$ $m = \frac{w_2}{M_2} \quad \frac{1000}{w_1}$ and also, m = n_2 \quad \frac{1000}{n_1 \quad M_1}

 X_{solvent} 0.8 (Given) It means that $n_{\text{solvent}}(n_1)$ 0.8 and $n_{\text{solute}}(n_2)$ 0.2

Using formula $m = n_2 = \frac{1000}{n_1 - M_1} = 0.2 = \frac{1000}{0.8 - 18} = 13.88 \,\mathrm{mol}\,\mathrm{kg}^{-1}$

2. Key Idea Molality is defined as number of moles of solute per kg of solvent.

$$m \quad \frac{w_2}{Mw_2} \quad \frac{1000}{w_1}$$

 w_2 mass of solute, Mw_2 molecular mass of solute w_1 mass of solvent.

The molality of 20% (mass/mass) aqueous solution of KI can be calculated by following formula.

$$m \quad \frac{w_2 \quad 1000}{Mw_2 \quad w_1}$$

20% aqueous solution of KI means that 20 gm of KI is present in 80 gm solvent.

$$m = \frac{20}{166} = \frac{1000}{80} = 1.506 = 1.51 \text{ mol/kg}$$

3. Key Idea For a solution of volatile liquids the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution. This is known as Raoult's law.

Liquid M and N form an ideal solution. Vapour pressures of pure liquids M and N are 450 and 700 mm Hg respectively.

$$p^{o}{}_{N} p^{o}{}_{M}$$

So, by using Raoult's law
 $v_{N} = x_{N}$

and $x_M \quad y_M$ Multiplying (i) and (ii) we get

$$\begin{array}{ccc} y_N x_M & y_M x_N \\ \frac{x_M}{x_N} & \frac{y_M}{y_N} \end{array}$$

Thus, correct relation is (a).

4. According to Henry's law (at constant temperature)

 $\begin{array}{cccc} p_{\rm gas} & K_{\rm H} & _{\rm gas \ (solute)} & K_{\rm H} & \begin{bmatrix} 1 & _{\rm H_2O \ (solvent)} \end{bmatrix} \\ p_{\rm gas} & K_{\rm H} & K_{\rm H \ H_2O} \end{array}$

 p_{gas} partial pressure of the gas above its solution with a liquid (solvent) say water.

 $_{\rm gas}$ mole fraction of the gas (solute) in the solution. $_{\rm H_{2}O}$ mole fraction of water (solvent).



[i.e. $p_{\text{gas}} = K_{\text{H}}$]Higher the value of K_{H} , higher will be the partial pressure of the gas (p_{gas}) , at a given temperature. The plot of $p_{\text{gas}} vs_{\text{H}_2\text{O}}$ gives a (ve) slope.

$$p_{\rm gas}$$
 $K_{\rm H}$ $K_{\rm H}$ $_{\rm H_2O}$

Comparing the above equation with the equation of straight line y mx c

Slope $K_{\rm H}$, intercept $K_{\rm H}$

So, (i) Higher the value of $K_{\rm H}$, more (ve) will be the slope and it is for z ($K_{\rm H}$ 40 K bar)

(ii) Higher the value of $K_{\rm H}$, higher with the value of intercept, i.e. partial pressure and it is also for *z*.

5. (d) According to Dalton's law of partial pressure

Given, p_A° 400 mm Hg, p_B° 600 mm Hg

$$B = 0.5, A = B = 1$$

A = 0.5

On substituting the given values in Eq. (i). We get, p_{total} 400 0.5 600 0.5 500 mm Hg Mole fraction of *A* in vapour phase,

 $Y_A = \frac{p_A}{p_{\text{total}}} = \frac{p_{A-A}^\circ}{p_{\text{total}}} = \frac{0.5 - 400}{500} = 0.4$

$$Y_A \quad Y_B = 1$$

 $Y_B = 1 \quad 0.4 \quad 0.6$

6. For ideal solution,

...(i)

...(ii)

 $\begin{array}{ccccccc} p & x_A p_A & x_B p_B \\ \therefore & x_A & 0.4, x_B & 0.6 \\ p_A & 7 & 10^3 \text{Pa}, p_B & 12 & 10^3 \text{Pa} \\ \end{array}$ On substituting the given values in Eq. (i), we get

In vapour phase,

7. At constant temperature, solubility of a gas (S) varies inversely with Henry's law constant $(K_{\rm H})$

$$K_{\rm H} = \frac{\rm Pressure}{\rm Solubility of a gas in a liquid} = \frac{P}{S}$$

Thus, higher the value of $K_{\rm H}$ at a given pressure, the lower is the solubility of the gas in the liquid.

8. Key Idea Vapour pressure of water (p) 760 torr

Number of moles of glucose
$$\frac{\text{Mass (g)}}{\text{Molecular mass (g mol^{-1})}}$$

$$\frac{18 \text{ g}}{180 \text{ gmol}^{-1}} = 0.1 \text{ mol}$$

Molar mass of water 18 g/mol Mass of water (given) 178.2g Number of moles of water

vulliber of moles of water

Mass of water Molar mass of water 178. 2g 18 g/mol 9.9 mol

Total number of moles (0.1 9.9) moles 10 moles Now, mole fraction of glucose in solution Change in pressure with respect to initial pressure

i.e. $\frac{p}{p} = \frac{0.1}{10}$

or p 0.01p 0.01 760 7.6 torr Vapour pressure of solution (760 7.6) torr 752.4 torr

9. Given, p = 185 Torr at 20°C

 p_s 183 Torr at 20°C

Mass of non-volatile substance, m = 1.2 g Mass of acetone taken = 100 g

we have
$$\frac{p - p_s}{p_s}$$

As

Putting the values, we get,

$$\frac{185 \ 183}{183} \quad \frac{\frac{1.2}{M}}{\frac{100}{58}} \quad \frac{2}{183} \quad \frac{1.2 \ 58}{100 \ M}$$
$$M \quad \frac{183 \ 1.2 \ 58}{2 \ 100}$$

Ν

10. Give, $K_{\rm H} = 1 - 10^5$ atm, $_{\rm N_2} = 0.8$

 $\begin{array}{ll} n_{\rm H_{2O}} & 10 \text{ moles}, p_{\rm total} & 5 \text{ atm} \\ p_{\rm N_2} & p_{\rm total} & _{\rm N_2} & 5 & 0.8 & 4 \text{ atm} \\ \text{According to Henry's law,} \end{array}$

$$p_{\mathrm{N}_2}$$
 K_{H} $_{\mathrm{N}_2}$

$$\begin{array}{ccccc} 4 & 10^{5} & _{N_{2}} \\ & _{N_{2}} & 4 & 10^{-5} \\ \hline \frac{n_{N_{2}}}{n_{N_{2}} & n_{H_{2}O}} & 4 & 10^{-5} \\ \hline \frac{n_{N_{2}}}{n_{N_{2}} & 10} & 4 & 10^{-5} \\ & & n_{N_{2}} & 4 & 10^{-4} \end{array}$$

- **11.** Molality = moles of solute present in 1.0 kg of solvent.
- **12.** The relative lowering of vapour pressure :

 $\frac{p}{p}$ 2 (mole fraction of solute)

- **13.** In case of positive deviation from Raoult's law, the observed vapour pressure is greater than the ideal vapour pressure and boiling point of azeotrope becomes lower than either of pure liquid.
- 14. The graph shown indicates that there is positive deviation because the observed vapour pressure of L is greater than the ideal pressure



Since, deviation is positive, the intermolecular force between L and M is smaller than the same in pure L and pure M.

Also as $x_L = 1$, $x_M = 0$, the real curve approaching ideal curve where Raoult's law will be obeyed.

15. When intermolecular attraction between two components *A* and *B* in the mixture is same as between *A* and *A* or *B* and *B*, hence it is a case of ideal solution.

When intermolecular attraction between A and B in a mixture is smaller than that between A and A or B and B, then mixture is more vaporised, bp is lowered. It is a case of positive deviation from Raoult's law.

When intermolecular attraction between A and B is higher than that between A and A or B and B, then mixture is less vaporised, bp is increased. It is a case of negative deviation.

- (a) Methanol molecules (CH₃OH) are hydrogen bonded. In a mixture of CCl₄ and CH₃OH, extent of H-bonding is decreased. Mixture is more vaporised thus, positive deviation from Raoult's law.
- (b) Acetone molecules have higher intermolecular attraction due to dipole-dipole interaction. With CS₂, this interaction is decreased thus, positive deviation.
- (c) Mixture of benzene and toluene forms ideal solution.
- (d) Phenol and aniline have higher interaction due to intermolecular H-bonding. Hence, negative deviation.

16. Key Idea Use the formula

 $P_{\text{Total}} \quad P_A \quad A \quad P_B \quad B$ and for equimolar solutions $A \quad P \quad \frac{1}{-}$

Given, p_{Total} 45 torr for equimolar solution p_4 20 torr

So,
$$45 \quad p_A \quad \frac{1}{2} \quad p_B \quad \frac{1}{2} \quad \frac{1}{2} \quad (p_A \quad \frac{1}{2} \quad \frac{1}{2})$$

or $p_A p_B$ 90 torr

But we know $p_A = 20$ torr

so, p_B 90 20 70 torr (From Eq. (i)) Now, for the new solution from the same formula

 $p_B)$

...(i)

500

Given, p_{Total} 22.5 torr So, 22.5 20 $_A$ 70(1 $_A$) (As $_A$ $_B$ 1) or 22.5 70 50 $_A$ So, $A = \frac{70 22.5}{50} 0.95$ Thus $_B = 1 0.95 0.05$ (as $_A = B = 1$) Hence, the ratio

$$\frac{-A}{B} = \frac{0.95}{0.05} = 19$$

- **17.** It will be true only if boiling points of two liquids are significantly different.
- **18.** Let after 100 min, x moles of A are remaining unpolymerised moles of B 12

Moles of non-volatile solute = 0.525

Mole fraction of A
$$-\frac{12}{12}$$
 0.525
Mole fraction of B $-\frac{12}{12}$ 0.525
 $400 -\frac{12}{12.525}$ $300 -\frac{12}{12.525}$

9.9
Moles of A polymerised in 100 min =
$$10 - 9.9 = 0.10$$

$$k = \frac{1}{t} \ln \frac{10}{9.9} + \frac{1}{100} \ln \frac{10}{9.9} \min^{-1}$$

1.005 = 10⁻⁴ min⁻¹

19. Volume of 1.0 mole liquid benzene $=\frac{78}{0.877}$ mL = 88.94 mL Molar volume of benzene vapour at 20°C

VP of pure benzene at 20°C
$$\frac{0.082 \quad 293}{244.58}$$
 760 mm
74.65 mm

Similarly; molar volume of toluene vapour $= \frac{92}{0.867} - \frac{7720}{1000} L = 819.2L$

VP of pure toluene
$$\frac{0.082 \ 293}{819.2}$$
 760 mm = 22.3mm
Now, let mole fraction of benzene in the liquid phase
 $4.65 \ + 22.3 \ (1 -)$ 45

0.43

Mole fraction of benzene in vapour phase

$$\frac{74.65 \quad 0.43}{45} \quad 0.72$$

20. Vapour pressure of solution = 0.75 VP of water

75 100 1: 1 mole fraction of solute
1
$$\frac{3}{4}$$
 and 2 1 1 $\frac{1}{4}$
 $\frac{-2}{1}$ $\frac{n_2}{n_1}$ $\frac{1}{3}$
 n_2 $\frac{n_1}{3}$ $\frac{100}{18 3} = 1.85$
Weight of urea 1.85 60 = 111 g
Molality $\frac{n_2}{n_1}$ $\frac{1000}{M_1}$
 $\frac{1}{3}$ $\frac{1000}{18} = 18.5$
21. Ca(NO₃)₂ \Longrightarrow Ca²⁺ + 2NO₃
1 $\frac{1}{12}$ where, 0.7
 $\frac{1}{12}$ 0.7= 2.4
Mole fraction of solvent $\frac{n_1}{n_1 in_2}$
 $\frac{\frac{100}{18}}{\frac{100}{18} 2.4 \frac{7}{164}} = 0.982$
(VP of H₂O at 100°C = 760 mm of Hg)
746.32 mm

22. According to Raoult's law :

$$p \quad p_{0-1}$$

$$600 \quad 640 \quad \frac{n_1}{n_1 \quad n_2}$$

$$\frac{n_2}{n_1} \quad \frac{64}{60} \quad 1 \quad \frac{1}{15}$$

$$n_2 \quad \frac{39}{78} \quad \frac{1}{15} \quad 0.033$$

$$\frac{2.175}{M} \quad 0.033$$

$$M = 65.25$$

23. At 373 K (bp) of H_2O , Vapour pressure = 760 mm VP of solution at 373 K 750 mm

 $p \quad p_{0-1}$

or 750 760
$$_{1}$$

 $1 \frac{75}{76}$ mole fraction of H₂O
 $2 1 \frac{75}{76} \frac{1}{76}$ mole fraction of solute
Now $\frac{n_2}{n_1 n_2} \frac{1}{76}$
 $\frac{n_1}{n_2}$ 75
Molality $\frac{n_2}{n_1 M_1}$ 1000 $\frac{1000}{75 18}$ 0.74 molal
24. Moles of ethanol $\frac{60}{46} = 1.3$
Moles of methanol $= \frac{40}{32} = 1.25$
Mole fraction of ethanol $= \frac{1.3}{1.3 1.25} = 0.51$
Vapour pressure of solution p_{ethanol} p_{methanol}
 $0.51 44.5 + 0.49 88.7$
 66.16 mm
Mole fraction of methanol in vapour phase
 $\frac{p_{\text{methanol}}}{\text{Total vapour pressure}}$
 $\frac{43.463}{66.16} 0.657$

25. From lowering of vapour pressure information :

$$\frac{0.104}{17.5} = 2 - \frac{n_2}{n_1 - n_2}$$

$$\frac{n_1}{n_2} = 1 - 1 - 1 - 168.27$$

$$\frac{n_1}{n_2} = 167.27$$

$$\frac{1000}{18} - \frac{M}{50} - 167.27$$

$$M - 150 \text{ g/mol}$$
Also, the combustion reaction is :

$$C_x H_{2y} O_y \quad xO_2 \quad xCO_2 \quad yH_2O$$

$$\therefore 18 \ y \ g \ of \ H_2O \ is \ produced \ from \ 1.0 \ mole \ of \ compound.$$

$$0.9 \ g \ of \ H_2O \ will \ be \ produced \ from \ \frac{0.9}{18 \ y} = \frac{1}{20 \ y} \ mol$$

$$At \ the \ end, \ moles \ of \ O_2 \ left \quad \frac{x}{20 \ y}$$

$$moles \ of \ CO_2 \ formed \ \frac{x}{20 \ y}$$

$$Total \ moles \ of \ gases \ at \ STP \ \frac{2x}{20 \ y} \ \frac{2.24}{22.4}$$

$$Molar \ mass; \ 150 \ 12x \ 2x \ 16x \ 30x$$

$$x \ \frac{150}{30} \ 5$$
Formula \ C_5H_{10}O_5

26. When 1.0 mole of A is mixed with 3 moles of B. 550 0.25 p_A + 0.75 p_B ...(i) When 1.0 mole of A is mixed with 4 moles of B. 560 0.20 $p_A + 0.80 p_B$...(ii) Now, solving (i) and (ii) $p_A = 400 \text{ mm}$ $p_B = 600 \,\mathrm{mm}.$ **27.** According to Raoult's law : $p \quad p_{0-1} \quad 631.9 = 639.7 \quad _1$ $_{1}$ 0.9878 $_{2} = 0.0122$ Molality = $\frac{0.0122}{0.9878 - 78}$ 1000 0.158 **28.** Let us consider 1.0 L of solution. Weight of solution = $1000 \quad 1.02 = 1020 \text{ g}$ Weight of H_2SO_4 1020 $\frac{13}{100} = 132.60 \text{ g}$ Weight of $H_2O = 1020 - 132.60 = 887.40$ g Molarity 132.60 1.353 M 98 132.60 $\frac{1000}{887.40}$ Molality 1.525 m 98 Normality 2 M = 2.7062.706 100 1.5 V V 180.40 mL

Topic 2 Colligative Properties

1. Key Idea Osmotic pressure is proportional to the molarity
(C) of the solution at a given temperature (T).
Thus, C, CRT (for dilute solution)

$$\frac{n}{V}RT$$

For the relation, CRT $\frac{n}{V}RT$
Given, mass of urea 0.6 g
Molar mass of urea 60 g mol⁻¹
Mass of glucose 1.8 g
Molar mass of glucose 180 g mol⁻¹
 $\frac{[n_2 \text{ (urea)} \quad n_2(\text{glucose})]}{V}RT$
 $\frac{0.6}{60} \quad \frac{1.8}{180}}{100} \quad 1000 \quad 0.0821 \quad 300$
(0.01 0.01) 10 0.0821 300
4.92 atm

2. The expression of elevation of boiling point,

$$\begin{array}{cccc} T_b & K_b & m & i \\ & k_b & \frac{w_2 & 1000}{M_2 & w_1} & i \end{array}$$

where, *m* molality *i* van't Hoff factor 1(for non-electrolyte/non-associable) W_2 mass of solute in g 1 g (present in both of the solutions) M_2 molar mass of solute in g mol⁻¹ (same solute in both of the solutions) mass of solvent in g 100 g (for both of the w_1 solvents A and B) K_{h} ebullioscopic constant So, the expression becomes, $T_b = K_b$ $\frac{T_b(A)}{T_b(B)} \quad \frac{K_b(A)}{K_b(B)} \quad \frac{1}{5}$ Given $\frac{K_b(A)}{K_b(B)} = \frac{1}{5}$ Key Idea For dilute solution, lowering of vapour pressure 3. (p) p^0 p and relative lowering of vapour pressure $\frac{p}{p^0}$ which is a colligative property of solutions. $_B$ i p $_B$ i p^0 where, p^0 vapour pressure of pure solvent i van't Hoff factor mole fraction of solute R Given. p vapour pressure of pure water of 25° C 35 mm Hg mole fraction of solute (urea) В 0.60 $\frac{n_B}{n_A \quad n_B} \quad \frac{\overline{60}}{\underline{360} \quad \underline{0.60}}$ 0.01 20 0.01 18 60 0.01 0.0005 20.01 *i* van't Hoff factor = 1 (for urea)

Now, according to Raoult's law

p $_B$ i p° On substituting the above given values, we get p 0.0005 1 35 0.0175 mm Hg

4. Key Idea Depression in freezing point (T_f) is given by $T_f \quad iK_fm$ *i* vant Hoff factor $K_f \quad \text{molal depression constant}$ *m* molality $K_f \quad 4.0 \text{K kg mol}^{-1}$ (Given) *m* 0.03 mol kg^{-1} (Given) $T_f \quad ?$ For $K_2 \text{SO}_4$, *i* 3It can be verified by the following equation : $K_s \text{SO}_4 \implies 2\text{K}^+ + \text{SO}_4^2$

Using formula $\begin{array}{rrrr} T_{f} & iK_{f} & m \\ T_{f} & 3 & 4 & 0.03 & 0.36\,\mathrm{K} \end{array}$ Key Idea Osmotic pressure is proportional to the molarity (C) 5. of the solution at a given temperature, CRT Concentration of BaCl₂ 0.01M (Given) $_{XY}$ 4 $_{\mathrm{BaCl}_2}$ (Given) i CRT 4 i CRT ...(i) For the calculation of *i*, XY X = Y(Here, i = 2) Ba² 2Cl BaCl₂ (Here, i = 3) Putting the values of *i* in (i) 2 [XY] 4 3 [BaCl₂]2 [XY] 12 0.01 $[XY] \frac{12 \quad 0.01}{2}$ So, the concentration of $XY = 0.06 \text{ mol } \text{L}^{-1}$ 6 10 2 mol L 1 6. Molecules of benzoic acid dimerise in benzene as: $2(C_6H_5COOH) \iff (C_6H_5COOH)_2$ Now, we know that depression in freezing point (T_f) is given by following equation: T_f i K_f m $\frac{i - K_f - w_{solute} - 1000}{M w_{solute} - w_{solvent}}$...(i) Given, w_{solute} (benzoic acid) wg $w_{\rm solvent}$ (benzene) 30 g Mw_{Solute} (benzoic acid) 122 g mol⁻¹, T_f 2 K K_f 5 Kkg mol⁻¹, % 80 or 0.8 $2(C_6H_5COOH) \longrightarrow (C_6H_5COOH)_2$ Initial 1 0 Final / 2 1 0.8 0.2 0.8 / 2 0.4 Total number of moles at equilibrium 0.2 0.4 0.6 Number of moles at equilibrium Number of moles present initially $i \quad \frac{0.6}{1} \quad 0.6$ On substituting all the given values in Eq. (i), we get $2 \frac{0.6 5 w 1000}{0.2 c c}$, w 2.44 g 122 30 Thus, weight of acid (w) is 2.4 g. 7. Given, Freezing point of 4% aqueous solution of *X*.

Freezing point of 12% aqueous solution of Y or $(T_f)_X$ $(T_f)_Y$ [:: T_f T_f T_f] K_f m_X $K_f m_Y$ where, m_X and m_Y are molality of X and Y, respectively.

 $m_X m_Y$

or

Now,	molality	Number of moles of solute (
		Mass of solvent (in kg)					
	12	Weight					
	п	Molecular mass					
	WX	<i>W_Y</i>					
M_X	$(w_{\text{solvent}})_1$	$M_Y (w_{ m solvent})_2$					
Given,	W_X	4 and $w_{(\text{solvent})_1} = 96$					
	w_Y	12 and $w_{(\text{solvent})_2} = 88$					
	M_X	A					
	4 1000	12 1000					
	$\overline{M_X}$ 96	M_Y 88					
Thus,	M_Y	$\frac{12\ 1000\ M_X\ 96}{4\ 1000\ 88}$					
		$\frac{96 \ 12}{4 \ 88} \ A \ 3.27A \ 3A$					

8. The ionisation of K_2HgI_4 in aqueous solution is as follows: $K_2[HgI_4] \longrightarrow 2K \quad [HgI_4]^2$

van't Hoff factor (i) for ionisation reaction is given as, $i \ 1 \ n \ 1$) where,

viicie,

n number of ions,

degree of ionisation or dissociation

From above equation, it is clear that n = 3

i 1 0.4 (3 1) [Given, %

40% or

0.4]

9. We know that,

Depression in freezing points (T_f)

 $T_f T_f K_f m i$ where, K_f molal depression constant

m molality
$$\frac{w_{\text{solute}}}{M_{\text{solute}}} \frac{1000}{w_{\text{solvent (in g)}}}$$

i van't Hoff factor

For diluted milk

$$\begin{array}{cccc} T_{f_1} & K_f & m_1 & i \\ 0 & (0.2) & 0.2 & K_f & \frac{w_{\text{milk}} & 1000}{M_{\text{milk}} & w_1(\text{H}_2\text{O})} & 1 \end{array}$$

For pure milk

$$T_{f_{2}} \quad K_{f} \quad m_{2} \quad i$$

$$0 \quad (0.5) \quad 0.5 \quad K_{f} \quad \frac{w_{\text{milk}} \quad 1000}{M_{\text{milk}} \quad w_{2}(\text{H}_{2}\text{O})} \quad 1$$
So,
$$\frac{0.2}{0.5} \quad \frac{K_{f}}{K_{f}} \quad \frac{w_{\text{milk}} \quad 1000}{M_{\text{milk}} \quad w_{1}(\text{H}_{2}\text{O})} \quad \frac{M_{\text{milk}} \quad w_{2}(\text{H}_{2}\text{O})}{w_{\text{milk}} \quad 1000} \quad \frac{w_{2}(\text{H}_{2}\text{O})}{w_{1}(\text{H}_{2}\text{O})}$$

$$\frac{w_{2}(\text{H}_{2}\text{O}) \text{ (in pure milk)}}{w_{1}(\text{H}_{2}\text{O}) \text{ (in diluted milk)}} \quad \frac{2}{5}$$

i.e. 3 cups of water has to be added to 2 cups of pure milk.

10. Elevation in boiling point (T_b) K_b m iDepression is freezing point (T_f) K_f m i

where, *m* molality

For the glucose solution (van't Hoff factor, i 1), T_b^{1m} T_f^{2m} 2KSo, K_b 1 1 K_f 2 1 K_b $2K_f$

11. Considering the expression of the depression in freezing point of a solution,

$$T_f \quad K_f \quad m \quad i$$

$$T_f \quad T_f \quad K_f \quad \frac{w_B \quad 1000}{M_B \quad w_A(\text{in g})} \quad i \qquad \dots(i)$$

Here, $T_f = 0$ C, $T_f = 10$ C

- w_B mass of ethylene glycol 62 g
- M_B molar mass of ethylene glycol

$$CH_2 - CH_2$$

 62 g mol^{-1}

- w_A mass of water in g as liquid solvent,
- i van't-Hoff factor 1 (for ethylene glycol in water)

 K_f 1.86 K kg mol⁻¹

On substituting in Eq. (i), we get

0

(10) 1.86
$$\frac{62}{62} \frac{1000}{w_A}$$
 1
 $w_A = \frac{1.86}{10} \frac{62}{62} \frac{1000}{62}$ 186 g

So, amount of water separated as ice (solid solvent) $250 \quad w_A \quad (250 \quad 186)g \quad 64g$

12. Key idea "Addition of solute particles to a pure solvent results to depression in its freezing point." All the compounds given in question are ionic in nature so, consider their van't Hoff factor (*i*) to reach at final conclusion.

The solution with maximum freezing point must have minimum number of solute particles. This generalisation can be done with the help of van't Hoff factor (i) i.e.

Number of solute particles van't Hoff factor (i)

Thus, we can say directly

Solution with maximum freezing point will be the one in which solute with minimum van't Hoff factor is present

Now, for $Co(H_2O)_6$]Cl₃ \iff [Co(H₂O)₆]³⁺ + 3Cl

van't Hoff factor (i) is 4. Similarly for,

$$[\operatorname{Co}(\operatorname{H}_2\operatorname{O})_5\operatorname{Cl}]\operatorname{Cl}_2 \operatorname{H}_2\operatorname{O} \rightleftharpoons [\operatorname{Co}(\operatorname{H}_2\operatorname{O})_5\operatorname{Cl}]^{2^+} + 2\operatorname{Cl} \quad `i' \text{ is } 3$$
$$[\operatorname{Co}(\operatorname{H}_2\operatorname{O})_4\operatorname{Cl}_2]\operatorname{Cl} \operatorname{2H}_2\operatorname{O} \rightleftharpoons [\operatorname{Co}(\operatorname{H}_2\operatorname{O})_4\operatorname{Cl}_2]^+ + \operatorname{Cl} \quad `i' \text{ is } 2$$

and for $[Co(H_2O)_3Cl_3]$ 3H₂O, '*i*' is 1 as it does not show ionisation. Hence, $[Co(H_2O)_3Cl_3]$ 3H₂O have minimum number of particles in the solution.

So, freezing point of its solution will be maximum.

13. Let the degree of association of acetic acid (CH₃COOH) in benzene is , then

 $\begin{array}{c} \text{2CH}_3\text{COOH} \rightleftharpoons (\text{CH}_3\text{COOH})_2 \\ \text{Initial moles} & 1 & 0 \\ \text{Moles at equilibrium} & 1 & -\frac{1}{2} \end{array}$

Total moles
$$1 \quad \frac{1}{2} \quad \frac{1}{2} \quad \text{or } i \quad 1 \quad \frac{1}{2}$$

Now, depression in freezing point (T_f) is given as
 $T_f \quad iK_fm \qquad \dots(i)$
where, K_f molal depression constant or
cryoscopic constant.
 m molality

Molality
$$\frac{\text{number of moles of solute}}{\text{weight of solvent (in kg)}} \frac{0.2}{60} \frac{1000}{20}$$

Putting the values in Eq. (i)

Thus, percentage of association 94.6%

14.
$$T_f \quad ik_f m_2$$

1 2 $\frac{34.5}{46500}$ 1000 3

Vapour pressure curves shown in (b) is in agreement with the calculated value of T_{f} . (a) is wrong, vapour pressure decreases on cooling.

15. PLAN This problem includes concept of colligative properties (osmotic pressure here) and van't Hoff factor. Calculate the effective molarity of each solution.

i.e. effective molarity van't Hoff factor m	olarity	
0.5 M C ₂ H ₅ OH (<i>aq</i>)	i	1
Effective molarity 0.5		
0.25 M KBr (aq)	i	2
Effective molarity 0.5 M		

 $\begin{array}{rcr} 0.1 \ \mathrm{M} \ \mathrm{Mg}_3(\mathrm{PO}_4)_2(aq) & i & 5 \\ \mathrm{Effective \ molarity} & 0.5 \ \mathrm{M} & \\ & 0.125 \ \mathrm{M} \ \mathrm{Na}_3 \mathrm{PO}_4(aq) & i & 4 \end{array}$

Effective molarity 0.5 M

Molarity is same hence, all colligative properties are also same.

NOTE This question is solved by assuming that the examiner has taken $Mg_3(PO_4)_2$ to be completely soluble. However, in real it is insoluble (sparingly soluble).

16. The elevation in boiling point is

$$T_b$$
 K_b m : m molality $\frac{n_2}{w_1}$ 1000

 $[n_2$ Number of moles of solute, w_1 Weight of solvent in gram]

$$\begin{array}{cccc} 2 & 0.76 & \frac{n_2}{100} & 1000 \\ n_2 & \frac{5}{19} \end{array}$$

Also, from Raoult's law of lowering of vapour pressure :

$$\frac{p}{p} \quad x_2 \quad \frac{n_2}{n_1 \quad n_2} \quad \frac{n_2}{n_1} \qquad [\because n_1 \quad n_2]$$

$$p \quad 760 \quad \frac{5}{19} \quad \frac{18}{100} \quad 36 \text{ mm of Hg}$$

$$p \quad 760 \quad 36 \quad 724 \text{ mm of Hg}$$
17. van't Hoff factor (i) = 4 $\{3K^+ + [Fe(CN)_6]^{3^-}$
Molality $\quad \frac{0.1}{329} \quad \frac{1000}{100} \quad \frac{1}{329}$

$$- T_f \quad iK_f \cdot m$$

$$4 \quad 1.86 \quad \frac{1}{329} \quad 2.3 \quad 10^{-2}$$

$$T_f \quad -2 \cdot 3 \quad 10^{-2} \text{ C}$$
(As % freezing point of water is 0%C)

(As % freezing point of water is 0°C)

18. Molality
$$\frac{20}{172} = \frac{1000}{50} = 2.325 \text{ m}$$

 $T_f = 2 = iK_f = m$
 $i = \frac{2}{1.72} = 2.325 = 0.5$
19. Molality $\frac{13.44}{134.1} = 0.1$
 $T_b = iK_b = m = 3 = 0.52 = 0.1 = 0.156$

20. For isotonic solutions, they must have same concentrations of ions, Therefore,

$$0.004 \ i \ (Na_2SO_4) \quad 0.01 \\ i \quad \frac{0.01}{0.004} = 2.5$$
Also $Na_2SO_4 \Longrightarrow 2Na^+ \quad SO_4^2 \quad i$

$$1 \quad 2 \quad 2.5 \\ 0.75 \quad 75\%$$

- **21.** During freezing, liquid solvent solidify and solid solvent remains in equilibrium with liquid solvent.
- 22. In benzene, benzoic acid dimerises as :

$$C_6H_5COOH \Longrightarrow \frac{1}{2}(C_6H_5COOH)_2$$

23. $C_6H_5NH_3Cl: i = 2;$

Ca(NO₃)₂:
$$i = 3$$

La(NO₃)₃: $i = 4$;
C₆H₁₂O₆: $i = 1$

Lower the value of *i*, smaller will be the depression in freezing point, higher will be the freezing temperature, if molalities are equal. Hence, glucose solution will have highest freezing temperature.

24. K_2SO_4 : *i* 3 NaCl : *i* = 2 Urea : *i* = 1 Glucose : *i* = 1

Greater the value of *i*, greater the lowering in freezing point, lower will be the freezing temperature, if molarity in all cases are same. Therefore, K_2SO_4 solution has the lowest freezing point.

25. Addition of HgI_2 to KI solution establishes the following equilibrium :

 $HgI_2 + 2KI \implies K_2[HgI_4]$

The above equilibrium decreases the number of ions (4 ions on left side of reactions becomes three ions on right side), hence rises the freezing point.

- **26.** In depression of freezing point experiment, vapour pressure of solution is less than that of pure solvent as well as only solvent molecules solidify at freezing point.
- **27.** From the graph we can note

 T_b for solution X i.e., $T_{b(X)}$ 362 360 2 Likewise, T_b for solution Y i.e., $T_{b(Y)}$ 368 367 1

Now by using the formula

 T_b *i* molality of solution× K_b

For solution X

 $\begin{array}{cccc} 2 & i & m_{\text{NaCl}} & K_{b(X)} & & \dots(\text{i}) \\ \text{Similarly for solution } y & & \end{array}$

 $1 \quad i \quad m_{\text{NaCl}} \quad K_{b(i)} \qquad \qquad \dots \dots (\text{ii})$

from Eq. (i) and (ii) above

 $\frac{K_{b(X)}}{K_{b(Y)}} \quad \frac{2}{1} \text{ or } 2 \quad \text{ or } \quad K_{b(X)} \quad 2K_{b(Y)}$

For solute S

	2.2	5	S_2	(given due to dimerisation)
Initial			0	
Final	(1)	2	

So, here

$$T_{b[X](s)} = 1 - \frac{1}{2} K_{b(X)}$$
$$T_{b[Y](s)} = 1 - \frac{2}{2} K_{b(Y)}$$

 $i \quad 1 \quad -2$

Given,

or

or

$$T_{b(X)(s)} \quad \begin{array}{cccc} 3 & T_{b(Y)(s)} \\ 1 & -\frac{1}{2} & K_{b(X)} & \begin{array}{cccc} 3 & 1 & -\frac{2}{2} & K_{b(Y)} \end{array}$$

 $2 \ 1 \ \frac{-1}{2} \quad 3 \ 1 \ \frac{-2}{2} \qquad [\because K_{b(X)} \quad 2K_{b(Y)}]$ $2 \ 1 \ \frac{-1}{2} \quad 3 \ 1 \ \frac{0.7}{2} \qquad (as given, \ _2 \ 0.7)$

or $4 \ 2 \ _{1} \ 6 \ 2.1$ or $2 \ _{1} \ 0.1$ so, $1 \ 0.05$

28. Molar mass of solute (M_B) $\frac{1000 \ K_f \ W_B}{W_A \ T_f}$ $M_B \ \frac{1000 \ 14 \ 75.2}{1000 \ 7}$ $M_B \ 150.4 \text{ g per mol}$ Actual molar mass of phenol94 g/molNow, van't Hoff factor, iCalculated molar mass
Observed molar massi $\frac{94}{150.4}$ 0.625Dimerisation of phenol can be shown as :
 $2C_6H_5OH \Longrightarrow (C_6 H_5OH)_2$ Initial10At equilibrium1 - $\frac{1}{2}$

Total number of moles at equilibrium, i = 1

 $i \quad 1 \quad -\frac{1}{2}$

But *i* 0.625, thus, 0.625 1 $\frac{1}{2}$

 $\frac{-}{2}$ 1 0.625 0.75

Thus, the percentage of phenol that dimerises is 75%.

29. (i)
$$T_b \quad K_b \quad m_2$$

 $0.17 \quad 1.7 \quad \frac{1.22}{M} \quad \frac{1000}{100} \quad M \quad 122$
(ii) $0.13 \quad 2.6 \quad \frac{1.22}{M} \quad \frac{1000}{100} \quad M \quad 244$

The above molar masses suggests thapt benzoic acid is monomeric in acetone while dimeric in benzene.

30. Higher the value of K_b of a solvent suggest that there is larger polarity of solvent molecules, which in turn implies higher boiling point due to dipole-dipole interaction. Therefore, the correct order of K_b values of the three given solvents is

Solvents	Boiling point	K_b
X	100°C	0.63
Y	27°C	0.53
Z	283°C	0.92

31. Mass of water 500 0.997 g = 498.5 g

Also
$$CH_3COOH \rightleftharpoons CH_3COO + H^2$$

$$i$$
 1 1.23
 T_f iK_f m 1.23 1.86 $\frac{3}{60}$ $\frac{1000}{498.5}$ 0.23°C

32. (i) Empirical formula determination

	Elements	С	Н	N	0	
	Weight %	42.86	2.40	16.67	38.07	
	Moles	3.57	2.40	1.19	2.38	
	Simplest ratio	3	2	1	2	
(ii)	Empirical fo T_b 1.84 = 2.53 M 168	$rmula = C_3$ $\frac{5.5}{M} = \frac{10}{4}$	$_{3}H_{2}NO_{2}$ $\frac{000}{45}$			

: Empirical formula weight (84) is half of molar mass, molecular formula is $C_6H_4N_2O_4$ a dinitrobenzene :



33.

Also,

$$m_{2} \quad \frac{n_{2}}{n_{1}} \quad \frac{1000}{M_{1}} = 0.1613$$

$$\frac{n_{2}}{n_{1}} \quad \frac{0.1613 \quad 18}{1000} = 2.9 \quad 10^{-3}$$

$$\frac{n_{2}}{n_{1}} \quad 1 \quad \frac{n_{2} \quad n_{1}}{n_{1}} \quad 2.9 \quad 10^{-3} \quad 1$$

$$\frac{n_{1}}{n_{1}} \quad n_{2} \quad 1 \quad \frac{1}{1 \quad 2.9 \quad 10^{-3}} = 0.997$$

$$p \quad p_{0-1} = 23.51 \quad 0.997 \quad 23.44 \text{ mm}$$
34.

$$T_{f} \quad 5.51 \quad 5.03 \quad 0.48$$

$$T_{c} \quad 0.48 \quad K_{c} \quad m$$

$$T_{f} = 5.51 = 5.03 = 0.48$$

$$T_{f} = 0.48 = K_{f} = m$$

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

$$M = 156 \text{ g/mol}$$

35. In the given solution '*M*', H₂O is solute.
Therefore, molality of H₂O
$$\frac{0.1}{0.9 \ 46}$$
 1000 = 2.4
 $T_f \ K_f^{\text{ethanol}}$ 2.4 2 2.4 4.8
 $T_f \ 155.7 - 4.8 = 150.9 \text{ K}$

36. Vapour pressure $p(H_2O) = p(ethanol)$ 32.8 0.1 40 0.9 3.28 + 36= 39.28 mm

37. Now ethanol is solute.

Molality of solute $\frac{0.1}{0.9 \ 18}$ 1000 = 6.17 T_b 6.17 0.52 = 3.20 T_b 373 + 3.2

= 376.2 K

38.
$$\lim_{m \to 0} \frac{T_f}{m} = K_f$$
 (Cryoscopic constant)

39. 1
$$T_f \ iK_f m$$

 $T_f \ 0 - (-0.0558 \text{ C})$
 0.0558 C
 $i \text{ (vant Hoff's factor)} \quad \frac{0.0558}{1.86 \quad 0.01} \quad 3$

This indicates that complex upon ionisation produces three ions as: $[Co(NH_3)_5Cl]Cl_2$ $[Co(NH_3)_5Cl]^{2+}(aq)$ 2Cl (aq)

Thus, only one Cl is inside the coordination sphere.

40.
$$MX_2$$
 M^2 $2X$

van't Hoff factor for any salt can be calculated by using equation *i* 1 (*n* 1)

where, n number of constituent ions

$$\frac{i(MX_2)}{(T_f)_{\text{observed}}} = i \quad (3 \quad 1) \quad 1 \quad 2$$

$$\frac{(T_f)_{\text{observed}}}{(T_f)_{\text{theoretical}}} = i \quad 1 \quad 2$$

$$i \quad 1 \quad 2 \quad 0.5 \qquad i \quad 2$$