CHAPTER 12

Solutions

Section-A JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. Given that ΔT_f is the depression in freezing point of the solvent in a solution of a non-volatile solute of molality, m, the quantity $\underset{m \to 0}{Lt}\ (\Delta T_f / m)$ is equal to .... *(1994 - 1 Mark)*

C MCQs with One Correct Answer

1. An azeotropic solution of two liquids has boiling point lower than either of them when it *(1981 - 1 Mark)*
   - (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
2. For a dilute solution, Raoult's law states that : *(1985 - 1 Mark)*
   - (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.
3. When mercuric iodide is added to the aqueous solution of potassium iodide then *(1987 - 1 Mark)*
   - (a) freezing point is raised.
   - (b) freezing point is lowered.
   - (c) freezing point does not change.
   - (d) boiling point does not change.
4. Which of the following 0.1 M aqueous solutions will have the lowest freezing point? *(1989 - 1 Mark)*
   - (a) Potassium sulphate (b) Sodium chloride
   - (c) Urea (d) Glucose
5. The freezing point of equimolal aqueous solutions will be highest for : *(1990 - 1 Mark)*
   - (a) $C_6H_5NH_3Cl$ (aniline hydrochloride)
   - (b) $Ca(NO_3)_2$
   - (c) $La(NO_3)_3$
   - (d) $C_6H_{12}O_6$ (glucose)
6. 0.2 molal acid HX is 20% ionised in solution. $K_f = 1.86$ K molality^{-1}. The freezing point of the solution is : *(1995S)*
   - (a) -0.45 (b) -0.90
   - (c) -0.31 (d) -0.53
7. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to : *(1996 - 1 Mark)*
   - (a) ionization of benzoic acid.
   - (b) dimerization of benzoic acid.
   - (c) trimerization of benzoic acid.
   - (d) solvation of benzoic acid.
8. During depression of freezing point in a solution the following are in equililbrium *(2003S)*
   - (a) liquid solvent, solid solvent
   - (b) liquid solvent, solid solute
   - (c) liquid solute, solid solute
   - (d) liquid solute, solid solvent
9. The elevation in boiling point of a solution of 13.44 g of $CuCl_2$ in 1 kg of water using the following information will be (Molecular weight of $CuCl_2 = 134.4$ and $K_b = 0.52$ K molal^{-1}) *(2005S)*
   - (a) 0.16 (b) 0.05
   - (c) 0.1 (d) 0.2
10. When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene ($K_f = 1.72$ K kg mol^{-1}), a freezing point depression of 2K is observed. The Van't Hoff factor (i) is *(2007)*
    - (a) 0.5 (b) 1
    - (c) 2 (d) 3
11. 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 at 298 K and 5 atm pressure is *(2009)*
    - (a) 4.0×10^{-4} (b) 4.0×10^{-5}
    - (c) 5.0×10^{-4} (d) 4.0×10^{-6}
12. Dissolving 120 g of urea (mol. wt. 60) in 1000 g of water gave a solution of density 1.15 g/mL. The molarity of the solution is *(2011)*
    - (a) 1.78 M (b) 2.00 M
    - (c) 2.05 M (d) 2.22 M

13. The freezing point (in °C) of a solution containing 0.1 g of $K_3[Fe(CN)_6]$ (Mol. wt. 329) in 100 g of water (K_f = 1.86 K kg mol^{-1}) is *(2011)*

(a) -2.3×10^{-2} (b) -5.7×10^{-2}

(c) -5.7×10^{-3} (d) -1.2×10^{-2}

14. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 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

D MCQs with One or More Than One Correct

1. In the depression of freezing point experiment, it is found that the *(1999 - 3 Marks)*

(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

2. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is(are) *(JEE Adv. 2013)*

(a) ΔG is positive (b) ΔS_{system} is positive

(c) $\Delta S_{surroundings} = 0$ (d) $\Delta H = 0$

3. Mixture(s) showing positive deviation from Raoult's law at 35 °C is (are) *(JEE Adv. 2016)*

(a) carbon tetrachloride + methanol

(b) carbon disulphide + acetone

(c) benzene + toluene

(d) phenol + aniline

E Subjective Problems

1. What is the molarity and molality of a 13% solution (by weight) of sulphuric acid with a density of 1.02 g/ml? To what volume should 100 ml of this acid be diluted in order to prepare a 1.5 N solution? *(1978)*

2. A bottle of commercial sulphuric acid (density 1.787 g/ml) is labelled as 86 percent by weight. What is the molarity of the acid. What volume of the acid has to be used to make 1 litre of 0.2 M H_2SO_4? *(1979)*

3. 0.5 gm of fuming H_2SO_4 (Oleum) is diluted with water. This solution is completely neutralized by 26.7 ml of 0.4 N NaOH. Find the percentage of free SO_3 in the sample of oleum. *(1980)*

4. The vapour pressure of pure benzene is 639.7 mm of mercury and the vapour of a solution of a solute in benzene at the same temperature is 631.9 mm of mercury. Calculate the molality of the solution. *(1981 - 3 Marks)*

5. An organic compound $C_xH_{2y}O_y$ was burnt with twice the amount of oxygen needed for complete combustion to CO_2 and H_2O. The hot gases when cooled to 0°C and 1 atm. pressure, measured 2.24 liters. The water collected during cooling weighed 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 - 5 Marks)*

6. 'Two volatile and miscible liquids can be separated by fractional distillation into pure component', is true under what conditions? *(1984 - 1 Mark)*

7. The vapour pressure of ethanol and methanol are 44.5 mm and 88.7 Hg respectively. An ideal solution is formed at the same temperature by 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 - 4 Marks)*

8. 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 solution. *(1989 - 3 Marks)*

9. 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 - 3 Marks)*

10. The degree of dissociation of calcium nitrate in a dilute aqueous solution, containing 7.0 g. 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. *(1991 - 4 Marks)*

11. 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 K kg mol^{-1}, calculate the molecular weight of the compound. *(1992 - 2 Marks)*

12. What weight of the non-volatile solute, urea ($NH_2 - CO - NH_2$) needs to be dissolved in 100g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution? *(1993 - 3 Marks)*

13. The molar volume of liquid benzene (density=0.877 g mL^{-1}) increases by a factor of 2750 as it vaporises at 20°C and that of liquid toluene (density=0.867 g mL^{-1}) increases by a factor of 7720 at 20°C. A solution of benzene and toluene at 20°C has a vapour pressure of 46.0 Torr. Find the mole fraction of benzene in the vapour above the solution. *(1996 - 3 Marks)*

14. A solution of a nonvolatile 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 - 4 Marks)*

15. 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 and determine its molecular and structural formula. (Molal boiling point elevation constant of benzene is 2.53 K kg mol^{-1}.) ***(1999 - 10 Marks)***

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

17. 1.22g of benzoic acid is dissolved in 100 g of acetone and 100 g of benzene separately. Boiling point of the solution in acetone increases by 0.17° C, while that in the benzene increases by 0.13° C; K_b for acetone and benzene is 1.7 K kg mol^{-1} and 2.6 K kg mol^{-1}. Find molecular weight of benzoic acid in two cases and justify your answer. ***(2004 - 2 Marks)***

18. 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 % of phenol that dimerises. ***(2006 - 6M)***

G Comprehension Based Questions

PASSAGE

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Application of colligative properties are very useful in day-to-day life. One of its example is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

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

Given : Freezing point depression constant of water (K_f^{water}) $= 1.86$ K kg mol^{-1}

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

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

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

Standard freezing point of water = 273 K

Standard boiling point of water = 155.7 K

Standard boiling point of water = 373 K

Standard boiling point of ethanol = 351.5 K

Vapour pressure of pure water = 32.8 mm Hg

Vapour pressure of pure ethanol = 40 mm Hg

Molecular weight of water = 18 g mol^{-1}

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

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

1. The freezing point of the solution M is ***(2008 - 3 Marks)***

(a) 268.7 K (b) 268.5 K

(c) 234.2 K (d) 150.9 K

2. The vapour pressure of the solution M is ***(2008 - 3 Marks)***

(a) 39.3 mm Hg (b) 36.0 mm Hg

(c) 29.5 mm Hg (d) 28.8 mm Hg

3. Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is ***(2008 - 3 Marks)***

(a) 380.4 K (b) 376.2 K

(c) 375.5 K (d) 354.7 K

I Integer Value Correct Type

1. 29.2% (w/w) HCl stock solution has a density of 1.25 g mL^{-1}. The molecular weight of HCl is 36.5 g mol^{-1}. The volume (mL) of stock solution required to prepare a 200 mL solution of 0.4 M HCl is : ***(2012)***

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

3. A compound H_2X with molar weight of 80g is dissolved in a solvent having density of 0.4 g ml^{-1}. Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is ***(JEE Adv. 2014)***

4. 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 of water = 1.86 K kg mol^{-1}] ***(JEE Adv. 2015)***

5. The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is 2.0 g cm^{-3} . The ratio of the molecular weights of the solute and solvent, $\left(\frac{MW_{solute}}{MW_{solvent}}\right)$, is ***(JEE Adv. 2016)***

Section-B JEE Main / AIEEE

1. Freezing point of an aqueous solution is (–0.186)°C. Elevation of boiling point of the same solution is K_b = 0.512°C, K_f = 1.86°C, find the increase in boiling point.

(a) 0.186°C (b) 0.0512°C **[2002]**

(c) 0.092°C (d) 0.2372°C.

2. In mixture *A* and *B* components show -ve deviation as **[2002]**

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

(b) $\Delta H_{mix} < 0$

(c) $A - B$ interaction is weaker than $A - A$ and $B - B$ interaction

(d) $A - B$ interaction is stronger than $A - A$ and $B - B$ interaction.

3. If liquids A and B form an ideal solution **[2003]**

(a) the entropy of mixing is zero

(b) the free energy of mixing is zero

(c) the free energy as well as the entropy of mixing are each zero

(d) the enthalpy of mixing is zero

4. In a 0.2 molal aqueous solution of a weak acid HX the degree of ionization is 0.3. Taking k_f for water as 1.85, the freezing point of the solution will be nearest to **[2003]**

(a) $-0.360°$ C (b) $-0.260°$ C

(c) $+0.480°$ C (d) $-0.480°$ C

5. A pressure cooker reduces cooking time for food because **[2003]**

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

(b) the higher pressure inside the cooker crushes the food material

(c) cooking involves chemical changes helped by a rise in temperature

(d) heat is more evenly distributed in the cooking space

6. Which one of the following aqueous solutions will exihibit highest boiling point ? **[2004]**

(a) 0.015 M urea (b) 0.01 M KNO_3

(c) 0.01 M Na_2SO_4 (d) 0.015 M glucose

7. For which of the following parameters the structural isomers C_2H_5OH and CH_3OCH_3 would be expected to have the same values?(Assume ideal behaviour) **[2004]**

(a) Boiling points

(b) Vapour pressure at the same temperature

(c) Heat of vaporization

(d) Gaseous densities at the same temperature and pressure

8. Which of the following liquid pairs shows a positive deviation from Raoult's law ? **[2004]**

(a) Water - nitric acid

(b) Benzene - methanol

(c) Water - hydrochloric acid

(d) Acetone - chloroform

9. Which one of the following statements is **FALSE**? **[2004]**

(a) The correct order of osmotic pressure for 0.01 M aqueous solution of each compound is $BaCl_2 > KCl > CH_3COOH >$ sucrose

(b) The osmotic pressure (π) of a solution is given by the equation $\pi = MRT$, where M is the molarity of the solution

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

(d) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression

10. Benzene and toluene form nearly ideal solution. At 20°C, the vapour pressure of benzene is 75 torr and that of toluene is 22 torr. The partial vapour pressure of benzene at 20°C for a solution containing 78 g of benzene and 46 g of toluene in torr is **[2005]**

(a) 53.5 (b) 37.5

(c) 25 (d) 50

11. Equimolar solutions in the same solvent have **[2005]**

(a) Different boiling and different freezing points

(b) Same boiling and same freezing points

(c) Same freezing point but different boiling points

(d) Same boiling point but different freezing points

12. Among the following mixtures, dipole-dipole as the major interaction, is present in **[2006]**

(a) KCl and water

(b) benzene and carbon tetrachloride

(c) benzene and ethanol

(d) acetonitrile and acetone

13. 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water. The vapour pressure of water for this aqueous solution at 100°C is **[2006]**

(a) 76.00 Torr (b) 752.40 Torr

(c) 759.00 Torr (d) 7.60 Torr

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

(a) 360 (b) 350

(c) 300 (d) 700

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

(a) 1/2 (b) 2/3

(c) $\frac{1}{3}\times\frac{273}{298}$ (d) 1/3.

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

(a) 210.0 g mol^{-1} (b) 90.0 g mol^{-1}

(c) 115.0 g mol^{-1} (d) 105.0 g mol^{-1}.

17. At 80° C, the vapour pressure of pure liquid 'A' is 520 mm Hg and that of pure liquid 'B' is 1000 mm Hg. If a mixture solution of 'A' and 'B' boils at 80° C and 1 atm pressure, the amount of 'A' in the mixture is (1 atm = 760 mm Hg) **[2008]**

(a) 52 mol percent (b) 34 mol percent

(c) 48 mol percent (d) 50 mol percent

18. The vapour pressure of water at 20° C is 17.5 mm Hg. If 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water at 20° C, the vapour pressure of the resulting solution will be **[2008]**

(a) 17.325 mm Hg (b) 15.750 mm Hg

(c) 16.500 mm Hg (d) 17.500 mm Hg

19. A binary liquid solution is prepared by mixing *n*-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution? **[2009]**

(a) The solution is non-ideal, showing – ve deviation from Raoult's Law.

(b) The solution is non-ideal, showing + ve deviation from Raoult's Law.

(c) n-heptane shows + ve deviation while ethanol shows – ve deviation from Raoult's Law.

(d) The solution formed is an ideal solution.

20. Two liquids *X* and *Y* form an ideal solution. At 300 K, vapour pressure of the solution containing 1 mol of *X* and 3 mol of *Y* is 550 *mm*Hg. At the same temperature, if 1 mol of *Y* is further added to this solution, vapour pressure of the solution increases by 10 *mm*Hg. Vapour pressure (in *mm*Hg) of *X* and *Y* in their pure states will be, respectively: **[2009]**

(a) 300 and 400 (b) 400 and 600

(c) 500 and 600 (d) 200 and 300

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

(a) 0.372 K (b) 0.0558 K

(c) 0.0744 K (d) 0.0186 K

22. On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively. Vapour pressure of the solution obtained by mixing 25.0 g of heptane and 35 g of octane will be

(molar mass of heptane = 100 g mol^{-1} and of octane = 114 g mol^{-1}) **[2010]**

(a) 72.0 kPa (b) 36.1 kPa

(c) 96.2 kPa (d) 144.5 kPa

23. A 5.2 molal aqueous solution of methyl alcohol, CH_3OH, is supplied. What is the mole fraction of methyl alcohol in the solution? **[2011]**

(a) 0.100 (b) 0.190

(c) 0.086 (d) 0.050

24. Ethylene glycol is used as an antifreeze in a cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at –6°C will be : (K_f for water = 1.86 K kg mol^{-1}, and molar mass of ethylene glycol = 62 g mol^{-1}) **[2011]**

(a) 804.32 g (b) 204.30 g

(c) 400.00 g (d) 304.60 g

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

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

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

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

(a) 0.50 M (b) 1.78 M

(c) 1.02 M (d) 2.05 M

27. K_f for water is 1.86 K kg mol^{-1}. If your automobile radiator holds 1.0 kg of water, how many grams of ethylene glycol ($C_2H_6O_2$) must you add to get the freezing point of the solution lowered to –2.8°C ? **[2012]**

(a) 72 g (b) 93 g

(c) 39 g (d) 27 g

28. The molarity of a solution obtained by mixing 750 mL of 0.5(M) HCl with 250 mL of 2(M) HCl will be : **[JEE M 2013]**

(a) 0.875 M (b) 1.00 M

(c) 1.75 M (d) 0.975 M

29. Consider separate solutions of 0.500 M $C_2H_5OH(aq)$, 0.100 M $Mg_3(PO_4)_2\ (aq)$, 0.250 M KBr(aq) and 0.125 M $Na_3PO_4(aq)$ at 25°C. Which statement is true about these solutions, assuming all salts to be strong electrolytes? **[JEE M 2014]**

(a) They all have the same osmotic pressure.

(b) 0.100 M $Mg_3(PO_4)_2(aq)$ has the highest osmotic pressure.

(c) 0.125 M $Na_3PO_4(aq)$ has the highest osmotic pressure.

(d) 0.500 M $C_2H_5OH(aq)$ has the highest osmotic pressure.

30. The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 torr. The molar mass (g mol^{-1}) of the substance is : **[JEE M 2015]**

(a) 128 (b) 488

(c) 32 (d) 64

31. 18 g glucose ($C_6H_{12}O_6$) is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution is: **[JEE M 2016]**

(a) 752.4 (b) 759.0

(c) 7.6 (d) 76.0

12 Solutions

Section-A : JEE Advanced/ IIT-JEE

A **1.** K_f

C **1.** (c) **2.** (b) **3.** (a) **4.** (a) **5.** (d) **6.** (a) **7.** (b)
8. (a) **9.** (a) **10.** (a) **11.** (a) **12.** (c) **13.** (a) **14.** (a)

D **1.** (a, d) **2.** (b, c, d) **3.** (a, b)

E **1.** 1.38 M, 1.57 m, 184 ml **2.** 15.81M; 12.65 **3.** 3.84% **4.** 0.156 m/kg
5. $(CH_2O)_5$ or $C_5H_{10}O_5$ **7.** 66.17 mm, 0.65
8. 0.7503 mol/kg, 0.9868 **9.** 65.25 **10.** 746.3 mm Hg
11. 156.056 **12.** 18.52 m **13.** 0.73 **14.** 23.44 mm Hg
15. 168 g, $C_6H_4(NO_2)_2$, m-dinitrobenzene **16.** 0.228 K
17. 122, 224 **18.** 75%

G **1.** (d) **2.** (b) **3.** (b)

I **1.** 8 **2.** 2 **3.** 8 **4.** 1 **5.** 9

Section-B : JEE Main/ AIEEE

1. (b) **2.** (d) **3.** (d) **4.** (d) **5.** (a) **6.** (c) **7.** (d)
8. (b) **9.** (d) **10.** (d) **11.** (d) **12.** (d) **13.** (b) **14.** (b)
15. (d) **16.** (a) **17.** (d) **18.** (a) **19.** (b) **20.** (b) **21.** (b)
22. (a) **23.** (c) **24.** (a) **25.** (a) **26.** (d) **27.** (b) **28.** (a)
29. (a) **30.** (d) **31.** (a)

Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. **K_f ;** Depression in freezing point, $\Delta T_f = K_f \cdot m$, where K_f is the molar depression constant or cryoscopic constant and m is the molality of the solution given by moles of solute per 1000 g of the solvent.

C. MCQs with One Correct Answer

1. **(c)** Lower the B. pt., higher will be the V.P. The V.P. of the mixture is greater than either of the two liquids.
[NOTE : : In case of positive deviation from Roult's law the partial vapour pressure of each liquid and total vapour pressure of solution will be greater as compared to initial solution]

2. **(b)** $$\frac{p^\circ - p}{p^\circ} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}} = \text{mole fraction of solute} = x_B$$

[Mathematical statement of Raoult's law]

3. **(a)** Added HgI_2 forms a complex with KI in the solution as follows
$2KI + HgI_2 \rightarrow K_2[HgI_4]$
As a result, number of particles decreases and so ΔT_f increases.
[NOTE : : Depression in freezing point is a colligative property]

4. **(a)** **NOTE :** The salt producing highest number of ions will have lowest freezing point.

$K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$; K_2SO_4 gives highest number of particles $(2 + 1 = 3)$.
Glucose, being non-electrolyte gives minimum no. of particles and hence minimum ΔT_f or maximum F. pt.

5. (d) **TIPS/Formulae :** The salt that ionises to least extent will have highest freezing point. [i.e., minimum ΔT_f]
Glucose, being non electrolyte, gives minimum no. of particles and hence minimum ΔT_f or maximum F. pt

6. **(a)** Depression in freezing point, $\Delta T_f = i \times K_f \times m$

Van't Hoff factor, $i = \dfrac{1-\alpha+n\alpha}{1}$, where n = no. of ions produced by complete dissociation of 1 mole of HX.

$HX \rightleftharpoons H^+ + X^- \Rightarrow n = 2$

$$\therefore\ i = \frac{1-0.2+2\times 0.2}{1} = 1.2$$

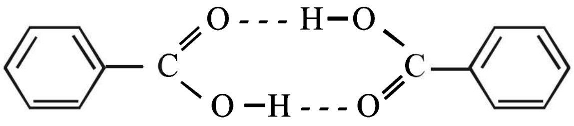
$$\left[\text{For 20 \% ionisation, } \alpha = \frac{20}{100} = 0.2\right]$$

$\therefore\ \Delta T_f = 1.2 \times 1.86 \times 0.2 = 0.45$ [$\because$ m = 0.2]

Hence freezing point of solution is $0 - 0.45 = \mathbf{-0.45}$

[$\because$ F.P of water = 0.0 C]

7. **(b)** Benzoic acid exists as dimer in benzene.



[Normal molecular mass = 122 amu

observed molecular mass = 244 amu, in case of complete association]

$$\alpha = \frac{20}{100} = 0.2 \quad \alpha = \frac{20}{100} = 0.2 \quad \alpha = \frac{20}{100} = 0.2$$

8. **(a)** **NOTE :** At the freezing point liquid and solid remain in equilibrium. If a solution of a non-volatile solute is cooled to a temperature below the freezing point of solution, some of liquid solvent will separate as a solid solvent and thus the concentration of solution will increase.

9. **(a)** TIPS/Formulae :

(i) $i = \dfrac{\text{No. of particles after ionisation}}{\text{No. of particles before ionisation}}$

(ii) $\Delta T_b = i \times K_b \times m$

$$\begin{array}{lll} CuCl_2 \longrightarrow & Cu^{2+} & + 2Cl^- \\ \ 1 & 0 & \ \ 0 \\ (1-\alpha) & \alpha & \ \ 2\alpha \end{array}$$

$$i = \frac{1+2\alpha}{1} \quad i = 1 + 2\alpha$$

Assuming 100% ionization So, i = 1 + 2 = 3

$$\Delta T_b = 3 \times 0.52 \times 0.1 = 0.156 \approx 0.16 \quad \left[m = \frac{13.44}{134.4} = 0.1\right]$$

10. **(a)** Molecular weight of naphthoic acid $C_{11}H_8O_2 = 172\ \text{gmol}^{-1}$.

The theoretical value of depression in freezing point

$$= K_f \times \text{ molality} = 1.72 \times \frac{20\times 1000}{172\times 50} = 4K$$

Van't Hoff factor,

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

$$= \frac{2}{4} = 0.5\,.$$

11. (a) $P_{N_2} = \kappa_H \chi_{N_2}$; $0.8 \times 5 = 1 \times 10^5 \times \chi_{N_2}$

$\therefore\ \chi_{N_2} = 4 \times 10^{-5}$; Solubility in 10 moles $= 4 \times 10^{-4}$.

12. **(c)** Number of moles of urea $= \dfrac{120}{60} = 2$

Total mass of solution = 1000 + 120 = 1120 g

Total volume of solution (in L) $= \dfrac{\text{Mass}}{\text{Density}}$

$$= \frac{1120}{1.15\times 10^3} = \frac{112}{115}\text{L}$$

Molarity of the solution $= \dfrac{\text{Number of moles}}{\text{Volume in L}}$

$$= \frac{2\times 115}{112} = 2.05 \text{ mol L}^{-1}$$

13. **(a)** $\Delta T_f = i \times K_f \times m$

Where m = Molality of the solution

(*i.e.* number of moles of solute per 1000 g of the solvent)

Here $m = \dfrac{0.1}{329} \times 100$

Thus $\Delta T_f = 4 \times 1.86 \times \dfrac{0.1\times 100}{329} = 2.3 \times 10^{-2}$

Thus $T_f = 0 - 2.3 \times 10^{-2} = -2.3 \times 10^{-2}$ °C

14. **(a)** From Raoult law relation,

$$\frac{p^\circ - p}{p^\circ} = \frac{\text{No.of moles of solute}}{\text{No. of moles of solvent + No. of moles of solute}}$$

When the concentration of solute is much lower than the concentration of solvent,

$$\frac{p^\circ - p}{p^\circ} = \frac{\text{No.of moles of solute}}{\text{No. of moles of solvent}}$$

$$\frac{760-p}{760} = \frac{2.5/m}{100/18} \qquad \text{...(i)}$$

From elevation in boiling point, $\Delta T_b = K_b \times m$

$2 = 0.76 \times m$

$$m = \frac{2}{0.76} \qquad \text{...(ii)}$$

From (i) and (ii), $p = 724$ mm

D. MCQs with One or More Than One Correct

1. **(a, d)** The freezing point of a solvent depresses as a non-volatile solute is added to a solvent. According to Raoult's law, when a non-volatile solute is added to a solvent the vapour pressure of the solvent decreases. At the freezing point it will be only the solvent molecules which will solidify.

2. **(b, c, d)**

For ideal solution, $\Delta S_{system} > 0$

$\Delta S_{surrounding} = 0$; $\Delta H_{mixing} = 0$

3. **(a, b)**

(A) H-bonding of methanol breaks when CCl_4 is added so bonds become weaker, resulting positive deviation.

(B) Mixing of polar and non-polar liquids will produce a solution of weaker interaction, resulting positive deviation

(C) Ideal solution

(D) –ve deviation because stronger H-bond is formed.

E. Subjective Problems

1. **TIPS/Formulae :**

(i) $$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in L}}$$

(ii) $N_1V_1 = N_2V_2$

A 13% solution (by weight) contains 13g of solute (i.e. H_2SO_4) per 100 gm of solution

$$\text{Moles of solute} = \frac{\text{Mass of } H_2SO_4}{\text{M. wt. of } H_2SO_4} = \frac{13}{98} = 0.1326$$

Volume of solution in L

$$= \frac{\text{Mass of solution}}{\text{density of solution} \times 1000} = \frac{100}{1.02 \times 1000} = 0.0980 \text{ Litre}$$

$$\therefore \quad \text{Molarity of solution} = \frac{0.1326}{0.0980} = \mathbf{1.35\ M}$$

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

Mass of solute in 100 ml of solution = 13 g [13 % solution]

Mass of solvent = Mass of solution – Mass of solvent

= 100 – 13 = 87 g

$$\therefore \text{Molality} = \frac{13/98}{87/1000} = \mathbf{1.57\ m}$$

$$\text{Normality} = \text{Molarity} \times \frac{\text{Mol. wt.}}{\text{Eq. wt.}} \text{ or } 1.35 \times \frac{98}{2 \cdot 49} \cdots$$

$$\text{Normality} = \text{Molarity} \times \frac{\text{Mol. wt.}}{\text{Eq. wt.}} \text{ or } 1.35 \times \frac{98}{49} = 2.70\text{ N}$$

$$N_1 = 2.70,\ V_1 = 100\text{ ml},\ N_2 = 1.5,\ V_2 = ? \quad \begin{bmatrix} \because \text{Eq. wt} = \dfrac{98}{2} \\ 2H_2SO_4 = 49 \end{bmatrix}$$

$N_1V_1 = N_2V_2;\ 2.70 \times 100 = 1.5 \times V_2$

$$\text{or } V_2 = \frac{2.70 \times 100}{1.5} = 180\text{ ml.}$$

∴ 100 ml of this acid should be diluted to 180 ml to prepare 1.5 N solution.

2. $$M = \frac{86/98}{100/1.787} \times 1000 = \frac{0.8775}{55.5} \times 1000 = \mathbf{15.81\ M}$$

$M_1V_1 = M_2V_2$

$M_1 = 15.81,\ V_1 = ?$

$M_2 = 0.2,\ V_2 = 1\ L = 1000\text{ ml}$

$\therefore 15.81 \times V_1 = 0.2 \times 1000$

$$\text{or } V_1 = \frac{0.2 \times 1000}{15.81} = 12.65\text{ ml}$$

∴ Amount of acid to be used to make 1 L of 0.2 M H_2SO_4 = **12.65.**

3. $N_1 = 1,\ V_1 = ?,\ N_2 = 26.7,\ V_2 = 0.4$

$N_1V_1 = N_2V_2;\ 1 \times V_1 = 26.7 \times 0.4$

$$V_1 = \frac{26.7 \times 0.4}{1} = 10.68$$

49g (∵ eq wt of $H_2SO_4 = 49$) of H_2SO_4 will be neutralised by = 1N 1000 ml NaOH

∴ 0.5g of H_2SO_4 will be neutralised by

$$= \frac{1000}{49} \times 0.5 = 10.20\text{ ml 1N NaOH}$$

Volume of 1 N NaOH used by dissolved $SO_3 = 10.68 - 10.20 = 0.48$ ml

$$SO_3 + 2NaOH \longrightarrow Na_2SO_4 + H_2O$$

$$\therefore \text{ Eq wt of } SO_3 = \frac{\text{Mol wt}}{2} = \frac{80}{2} = 40$$

Wt of SO_3 in 0.48 ml of 1 M solution

$$= \frac{40}{1000} \times 0.48 = 0.0192\text{ g}$$

$$\%\text{ of } SO_3 = \frac{0.0192}{0.5} \times 100 = \mathbf{3.84\%}$$

4. **TIPS/Formulae :** $\dfrac{P^o - P}{P^o} = \dfrac{n}{N}$ [Roults Equation]

Let the molality of the solution = m

Now the solution contains '*m*' moles of solute per 1000 gm of benzene

Vapour pressure of benzene, $P^o = 639.7$ mm

Vapour pressure of solution, $P = 631.9$ mm

$$\text{Moles of benzene (Mol. wt. 78), } N = \frac{1000}{78}$$

Moles of solute, $n = ?$

Substitute these values in the Raoult's equation

$$\frac{P^o - P}{P^o} = \frac{n}{N} \text{ or } \frac{639.7 - 631.9}{639.7} = \frac{n \times 78}{1000}$$

$$\text{or } \frac{7.8}{639.7} = \frac{78\,n}{1000} \quad \therefore\ n = \frac{1000 \times 7.8}{78 \times 639.7} = \mathbf{0.156}$$

Hence, molality of solution = **0.156 m**

5. The chemical equation for the combustion of organic compound $C_xH_{2y}O_y$ can be represented as :

$C_xH_{2y}O_y + 2xO_2 = x\,CO_2 + y\,H_2O + x\,O_2$

The gases obtained after cooling $= x + x = 2x$

$\therefore 2x = 2.24$ litres [∵ H_2O is in liquid state]

$$\text{or } x = \frac{2.24}{2} = 1.12 \text{ litres}$$

$$\text{Number of moles of } CO_2 = \frac{1.12 \text{ litres}}{22.4 \text{ litres mole}}$$

[∵ 22.4 L at NTP = 1 mole]

$$= \frac{1}{20}\text{ mole} = 0.05\text{ mole}$$

The empirical formula of the organic compound is $C(H_2O)$ ...(1)

The mole fraction of the solute (A)
= relative decrease in vapour pressure of the solvent (B)

$$\frac{p^\circ - p}{p^\circ} = \frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

or $\frac{0.104}{17.5} = \frac{\frac{50}{M_A}}{\frac{50}{M_A} + \frac{1000}{18}}$ $[M_A = \text{mol.wt.g } A]$

or $\frac{0.104}{17.5} = \frac{50}{M_A\left(\frac{50 \times 18 + 1000M_A}{18M_A}\right)}$

or $\frac{104}{17500} = \frac{50 \times 18}{900 + 1000M_A}$ or $M_A = 150.6$

Molecular wt. of the organic compound
$(CH_2O)_n = 150$
Molecular wt. of $CH_2O = 12 + 2 + 16 = 30$

$\therefore 30 \times n = 150$ $[\because (CH_2O)_n = \text{mol. formula}]$

or $n = \frac{150}{30} = 5$

$\therefore$ Molecular formula of the given organic compound is $\mathbf{(CH_2O)_5}$ or $\mathbf{C_5H_{10}O_5}$.

6. If they form an ideal solution which obeys' Raoult's Law and for which
$\Delta H_{mixing} = 0$ and $\Delta V_{mixing} = 0$
Thus we can separate two volatile and miscible liquids by fractional distillation if, they should not form azeotropic solutions.

7. **TIPS/Formulae :**
$P_{total} = p_A + p_B$
Molecular weight of $CH_3OH = 12 + 3 + 16 + 1 = 32$
Molecular weight of $C_2H_5OH = 24 + 5 + 16 + 1 = 46$
According to Raoult's law
$P_{total} = p_1 + p_2$
where P_{total} = Total vapour pressure of the solution
p_1 = Partial vapour pressure of one component
p_2 = Partial vapour pressure of other component
Again, p_1 = Vapour pressure (p_1°) × mole fraction
Similarly, p_2 = Vapour pressure (p_2°) × mole fraction

Mole fraction of $CH_3OH = \frac{\frac{40}{32}}{\frac{40}{32} + \frac{60}{46}} = 0.49$

Mole fraction of ethanol $= \frac{\frac{60}{46}}{\frac{60}{46} + \frac{40}{32}} = 0.51$

NOTE THIS STEP : Thus now let us first calculate the partial vapour pressures, i.e., p_1 and p_2 of the two component.
Partial vapour pressure of $CH_3OH(p_1)$
$= 88.7 \times 0.49 = 43.48$ mm
Partial vapour pressure of $C_2H_5OH(p_2)$
$= 44.5 \times 0.51 = 22.69$ mm
$\therefore$ Total vapour pressure of the solution
$= 43.48 + 22.69$ mm $=$ **66.17 mm**

Mole fraction of CH_3OH in vapour $= \frac{43.48}{66.17} = \mathbf{0.65}$

8. **TIPS/Formulae :**

Molality, $M = \frac{\text{moles of solute}}{\text{kg of solvent}}$

Mole fraction, $x_A = \frac{n_A}{n_A + n_B}$, $x_B = \frac{n_B}{n_A + n_B}$

$p_1 = x_1 p_1^\circ$

$\therefore x_1 = \frac{p_1}{p_1^\circ} = \frac{750}{760} = 0.9868$

$x_2 \text{ (solute)} = 1 - 0.9868 = 0.0132$

Molality, $m = \frac{x_2}{x_1 M_1} \times 1000 = \frac{0.0132 \times 1000}{0.9868 \times 18}$
$= \mathbf{0.7503 \text{ mol kg}^{-1}}$

9. **TIPS/Formulae :**
According to Raoult's law,

$$\frac{p^\circ - p}{p^\circ} = \frac{w/m}{w/m + W/M}$$

Here, $p^\circ = 640$ mm $p = 600$ mm
$w = 2.175$ g $W = 39.0$
$m = ?$ $M = 78$
Substituting the various values in the above equation for Roult's law :

$$\frac{640 - 600}{640} = \frac{2.175/m}{2.175/m + 39/78}$$

$$\frac{1}{16} = \frac{2.175}{2.175 + 0.5m} \Rightarrow m = \mathbf{65.25}$$

10. **TIPS/Formulae :** First find moles of $Ca(NO_3)_2$ and water.

Then use the expression $\frac{p^\circ - p}{p^\circ} = \frac{n}{n + N}$ to find vapour pressure of solution.
Let initially 1 mole of $Ca(NO_3)_2$ is taken
Degree of dissociation of $Ca(NO_3)_2 = \frac{70}{100} = 0.7$
Ionisation of $Ca(NO_3)_2$ can be represented as

	$Ca(NO_3)_2$	$\rightleftharpoons$	Ca^{2+}	+	$2NO_3^-$
At start	1		0		0
At equilibrium	1 – 0.7		0.7		2 × 0.7

$\therefore$ Total number of moles in the solution at equilibrium
$= (1 - 0.7) + 0.7 + 2 \times 0.7 = 2.4$

No. of moles when the solution contains 1 gm of calcium nitrate instead of 1 mole of the salt

$= \frac{2.4}{164}$ (164 is the mol. wt. of Cal. nitrate)

∴ No. of moles of the solute in the solution containing 7 g of salt, i.e.,

$$n = \frac{2.4}{164} \times 7 = 0.102$$

$$\text{No. of moles of water (N)} = \frac{\text{Wt. of water}}{\text{Mol. wt. of water}} = \frac{100}{18} = 5.55$$

$$\text{Applying Raoult's law, } \frac{p^0 - p}{p^0} = \frac{n}{n+N}$$

$$\frac{760 - p}{760} = \frac{0.102}{0.102 + 5.55} \Rightarrow \frac{760 - p}{760} = 0.0180$$

$\Rightarrow p = 760 - (760 \times 0.0180) = \mathbf{746.3\ mm\ Hg}$

11. TIPS/Formulae :

Given Wt. of benzene (solvent),

$W = \text{Volume} \times \text{density} = 50 \times 0.879 = 43.95$ g

Wt. of compound (solute), $w = 0.643$ g

Mol. wt. of benzene, $M = 78$; Mol. wt. of solute, $m = ?$

Depression in freezing point, $\Delta T_f = 5.51 - 5.03 = 0.48$

Molal freezing constant, $K_f = 5.12$

Now we know that,

$$m = \frac{1000 \times K_f \times w}{W \times \Delta T_f} = \frac{1000 \times 5.12 \times 0.643}{43.95 \times 0.48} = \mathbf{156.056}$$

12. TIPS/Formulae :

$$\frac{p^\circ - p}{p^\circ} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}$$

Here, w and m are wt. and molecular wt. of solute, W and M are wt. and molecular weight of solvent

p = Pressure of solution; p° = Normal vapour pressure

Let the initial (normal) pressure (p°) = p

$$\therefore \text{Pressure of solution} = \frac{75}{100} \times p = \frac{3}{4}p$$

$m = 60$, $M = 18$, $W = 100$ gm

$$\therefore \frac{p - \frac{3}{4}p}{p} = \frac{w/60}{\frac{w}{60} + \frac{100}{18}} \Rightarrow \frac{1}{4} = \frac{w/60}{(w/60) + 5.55}$$

$$\frac{4w}{60} = \frac{w}{60} + 5.55 \Rightarrow \frac{3w}{60} = \frac{w}{20} = 5.55 \text{ or } w = \mathbf{111\ g}$$

$$\text{Molality} = \frac{\text{No. of moles of solute}}{\text{Wt. of solvent}} \times 1000$$

$$= \frac{111 \times 1000}{60 \times 100} = \mathbf{18.52\ m}$$

13. TIPS/Formulae :

(i) $\text{Volume} = \frac{\text{No. of moles} \times \text{molar mass}}{\text{density}}$

(ii) $PV = nRT$ or $P = \frac{nRT}{V}$

Volume of 1 mole of liq. benzene $= \frac{78}{0.877}$

Volume of 1 mole of toluene $= \frac{92}{0.867}$

In vapour phase,

At 20°C, for 1 mole of benzene,

$$\text{Volume} = \frac{1 \times 78 \times 2750}{0.877} = 244583.80\ \text{mL} = 244.58\ \text{L}$$

Similarly for 1mole of toluene,

$$\text{volume} = \frac{1 \times 92}{0.867} \times 7720 = 819192.61\ \text{mL} = 819.19\ \text{L}$$

As we know that, $PV = nRT$

$$\text{For benzene, } P_B^o = \frac{nRT}{V} = \frac{1 \times 0.0821 \times 293}{244.58}\ \text{atm} = 0.098\ \text{atm}$$

$$\text{For toluene, } P_T^o = \frac{nRT}{V} = \frac{1 \times 0.0825 \times 293}{819.19}\ \text{atm} = 0.029\ \text{atm}$$

$$P = P_B^o . X_B + P_T^o . X_T$$

$$\because \quad X_B + X_T = 1 \quad \therefore \quad X_T = 1 - X_B$$

$$P = P_B^o . X_B + P_T^o (1 - X_B)$$

$$\text{Total vapour-pressure} = 46 \text{ torr} = \frac{46}{760} = 0.060 \text{ atm}$$

Thus, $0.060 = 0.098\, X_B + 0.029\,(1 - X_B)$

$\Rightarrow 0.060 = 0.098\, X_B + 0.029 - 0.029\, X_B \Rightarrow 0.031 = 0.069\, X_B$

$$\therefore X_B = \frac{0.031}{0.069} = 0.45 \text{ (in liquid phase)}$$

$X_B + X_T = 1$

$X_T = 1 - 0.45 = 0.55$ (in liquid phase)

Also, $P_B' = P_B^o X_B = P X_B'$

So, $0.098 \times 0.045 = 0.060 \times X_B'$

$$X_B' = \frac{0.098 \times 0.45}{0.060} = \mathbf{0.735\ (in\ gas\ phase)}$$

14. TIPS/Formulae :

$\Delta T_t = K_f . m$

$$\frac{P^o - p}{p^o} = \frac{\text{moles of solute}}{\text{moles of solvent}}$$

Depression in freezing point, $\Delta T_f = 0 - (-0.30) = 0.30$

Now we know that $\Delta T_f = K_f m$

$$\therefore m = \frac{\Delta T_f}{K_f} = \frac{0.30}{1.86} = 0.161$$

According to Raoult's law

$$\frac{p^\circ - p}{p^\circ} = \frac{\text{No. of moles of solute}}{\text{No. of moles of solvent}}$$

$$\frac{23.51 - p}{23.51} = \frac{0.161}{1000/18} = \frac{0.161 \times 18}{1000}$$

$$\left(\because \text{No. of moles of } H_2O = \frac{1000}{18} \right)$$

On usual calculations,

$$\frac{23.51 - p}{23.51} = .0020898$$

$$p = 23.51 - 23.51 \times 0.0020898 = 23.51 - .068$$

$p = 23.44$ mm Hg

15. **TIPS/Formulae :** $\Delta T_b = k_b \times m$

Element	**%**	**Relative no. of atoms**	**Simplest ratio**
C	42.86	$\frac{42.86}{12} = 3.57$	$\frac{3.57}{1.19} = 3$
H	2.40	$\frac{2.40}{1} = 2.40$	$\frac{2.40}{1.19} = 2$
N	16.67	$\frac{16.67}{14} = 1.19$	$\frac{1.19}{1.19} = 1$
O	38.07	$\frac{38.07}{16} = 2.38$	$\frac{2.38}{1.19} = 2$

$\therefore$ Empirical formula of the minor product is $C_3H_2NO_2$

Molar empirical formula mass of the minor prodouct

$= 3 \times 12 + 2 \times 1 + 1 \times 14 + 2 \times 16 = 84 \text{ g mol}^{-2}$

Let M be the molar mass of the minor product. For 5.5 g of the minor product dissolved in 45 g benzene, the molality

$$(m) \text{ of the solution} = \frac{5.5\text{g/M}}{0.045\text{kg}}$$

Substituting this in the expression of elevation of boiling point,

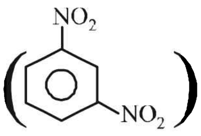
$$\Delta T_b = K_b m \Rightarrow 1.84\text{K} = (2.53\text{K kg mol}^{-1})\left(\frac{5.5\text{g/M}}{0.045\text{kg}}\right)$$

or **$M = 168 \text{ g mol}^{-1}$**

No. of unit of empirical formula in molecular formula

$$= \frac{168 \text{ g mol}^{-1}}{84 \text{ g F}} = 2$$

Hence the molecular formula of the minor product is **$2\,(C_3H_2NO_2)$, i.e., $C_6H_4(NO_2)_2$.**

The product is **m - dinitrobenzene** ().

16. **TIPS/Formulae :**

$$\Delta T_f = i \times K_f \times m$$

Weight of water $= 500 \times 0.997 = 498.5$ g

(weight = volume × denisty)

No. of moles of acetic acid

$$= \frac{\text{Wt. of } CH_3COOH \text{ in g}}{\text{Mol. wt. of } CH_3COOH} = \frac{3 \times 10^{-3} \times 10^3}{60} = 0.05$$

Since 498.5 g of water has 0.05 moles of CH_3COOH

$$1000 \text{ g of water has} = \frac{0.05 \times 1000}{498.5} = 0.1$$

Therefore molality of the solution = 0.1

Determination of van't Hoff factor, i

	$CH_3COOH \longrightarrow$	CH_3COO^- +	H^+
No. of moles at start	1	0	0
No. of moles at equb.	1 – 0.23	0.23	0.23

Therefore vant Hoff factor

$$= \frac{\text{No. of particles before dissociation}}{\text{No. of particles after dissociation}}$$

$$= \frac{1 - 0.23 + 0.23 + 0.23}{1} = 1.23$$

Now we know that

$\Delta T_f = i \times K_f \times m = 1.23 \times 1.86 \times 0.1 =$ **0.228K**

17. (i) **TIPS/Formulae :**

$\Delta T_b = K_b \times M$

In first case,

$$\Delta T_b = K_b \times m = K_b \times \frac{\text{Wt. of solute}}{\text{Mol. wt. of solute}}$$

$$\text{or } 0.17 = 1.7 \times \frac{1.22}{M \times 100 \times 10^{-3}} \text{ or } \mathbf{M = 122}$$

Thus the benzoic acid exists as a monomer in acetone

(ii) In second case,

$$\Delta T_b = K_b \times \frac{\text{Wt. of solute}}{\text{Mol. wt. of solute}}$$

$$\text{or } 0.13 = 2.6 \times \frac{1.22}{M' \times 100 \times 10^{-3}} \Rightarrow \boldsymbol{M' = 224}$$

NOTE : Double the expected molecular weight of benzoic acid (244) in acetone solution indicates that benzoic acid exists as a dimer in acetone.

18.

	$2C_6H_5OH \rightleftharpoons$	$(C_6H_5OH)_2$
Initial no. of moles	1	0
No. of moles at equilibrium	$1 - \alpha$	$\alpha / 2$

$$\text{Total number of moles at equilibrium} = 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$$

$$\Delta T_f = iK_f \times (\text{molality})$$

$$\Rightarrow 7 = 14 \times \frac{75.2}{94} \times \left(1 - \frac{\alpha}{2}\right) \left[\begin{array}{l}\text{weight of phenol} = 75.2\text{g} \\ \text{mol.wt of phenol} = 94\end{array}\right]$$

$\therefore \alpha = 0.75$

So the percentage of phenol that dimerises = **75%.**

G. Comprehension Based Questions

1. **(d)** The solution M is a mixture of ethanol and water. In it the mole fraction of ethanol is 0.9 and mole fraction of water is 0.1 $(1.0-0.9=0.1)$ Also given are:-

Standard freezing point of ethanol = 155.7K.

Freezing point depression constant (K_f) for ethanol = 2.0 kg mol^{-1}

Molecular weight of ethanol (C_2H_5OH) = 46

now molality (m) of solution $= \dfrac{0.1\times1000}{0.9\times46}$

Using the formula :-

Depression in freezing point $(\Delta T_f) = K_f \times m$,

Substituting various values, we get

$$\Delta T_f = \frac{2\times0.1\times1000}{0.9\times46} = \frac{2000}{414} = 4.83\text{ K}.$$

∴ Freezing point of solution 'M' = (155.7 − 4.83) K

= 150.9 K

i.e. (d) is the correct answer.

2. **(b)** **Given :** vapour pressure of pure ethanol (P_A^o) = 40 mmHg

Mole fraction (X_A) of ethanol in solution = 0.9

Using the formula : Total pressure (P) = $P_A^o\ X_A^o$

Substituting the given values, we get

$P = 40\times0.9 = 36.0$ mm Hg

i.e. (b) is the correct answer.

3. **(b)** **Given:** Standard boiling poing of water = 373K

Boiling point elevation constant of water (K_b) = 0.52 Kg mol^{-1}

Molecular weight of water (H_2O) = 18

Mole fraction of water in solution = 0.1 $(1.0-0.9=0.1)$

molality (m) $= \dfrac{0.1\times1000}{0.9\times18}$

using the relation $\Delta T_b = K_b \times m$

Substituting the given values, we get

$$\Delta T_b = 0.52\times\frac{0.1\times1000}{0.9\times18} = \frac{520}{9\times18} = 3.20\text{ K}$$

∴ Boiling point of solution = (373 + 3.20) K

= 376.2 K

i.e. option (b) is correct answer.

I. Interger Value Correct Type

1. **(8)** Molarity of stock solution of HCl

$$= \frac{29.2\times1000\times1.25}{100\times36.5}$$

Let the volume of stock solution required = V mL

$$\text{Thus, } V \times \frac{29.2\times1000\times1.25}{100\times36.5} = 200\times0.4 = 8\text{ mL}$$

2. **(2)**

$$\begin{matrix} MX_2 & \rightleftharpoons & M^{2+} & + & 2X^- \\ 1-\alpha & & \alpha & & 2\alpha \end{matrix}$$

$$i = \frac{\text{obser. depression in f.pt of aq. solution}}{\text{depression of f.p.t. in absence of ionic dissociation}}$$

$$= \frac{1-\alpha+\alpha+2\alpha}{1} = 1+2\alpha = 1+2\times0.5 = 2$$

3. **(8)**

$$\text{Molality} = \frac{\text{wt. of solute in 1 L of solution}\times1000}{\text{wt. of solvent in 1 L of solution}\times\text{mol. wt. of solute}}$$

Calculation of wt. of solvent

1 mL of solvent = 0.4 g

1000 mL of solvent = 400 g

Calculation of wt. of solute

1000 mL of solution contain = 3.2 × 80 g solute = 256 g

$$\therefore \quad \text{Molality} = \frac{256\times1000}{400\times80} = 8$$

4. **(1)** Given $\Delta T_f = 0.0558°C$

as we know, $\Delta T_f = i\times K_f\times m$

$\Rightarrow \quad 0.0558 = i\times1.86\times0.01$

$$\boxed{i=3}$$

Therefore the complex will be $[Co(NH_3)_5Cl]Cl_2$

Hence number of chloride in co-ordination sphere is 1.

5. **(9)** 1 mole solution has 0.1 mole solute and 0.9 mole solvent.

Let M_1 = Molar mass solute

M_2 = Molar mass solvent

$$\text{Molality, } m = \frac{0.1}{0.9M_2}\times1000 \quad \text{.......(1)}$$

$$\text{Molarity, } M = \frac{0.1}{0.1M_1+0.9M_2}\times2\times1000 \quad \text{.......(2)}$$

$\because \quad m = M$

$$\Rightarrow \frac{0.1\times1000}{0.9M_2} = \frac{200}{0.1M_1+0.9M_2}$$

$$\Rightarrow \frac{M_1}{M_2} = 9$$

Section-B JEE Main/ AIEEE

1. **(b)** $\Delta T_b = K_b \dfrac{W_B}{M_B \times W_A} \times 1000;$

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

$\dfrac{\Delta T_b}{\Delta T_f} = \dfrac{K_b}{K_f} = \dfrac{\Delta T_b}{-0.186} = \dfrac{0.512}{1.86} = 0.0512°C.$

2. **(d)** In solution containing A and B component showing negative deviation A–A and B–B interactions are weaker than that of A–B interactions. For such solutions.
$\Delta H = -ve$ and $\Delta V = -ve$

3. **(d)** When A and B form an ideal solution, $\Delta H_{mix} = 0$

4. **(d)** $\Delta T_f = K_f \times m \times i;$
$\Delta T_f = 1.85 \times 0.2 \times 1.3 = 0.480°C$
$\therefore T_f = 0 - 0.480°C = -0.480°C$

$(\underset{1-0.3}{HX} \rightleftharpoons \underset{0.3}{\overset{+}{H}} + \underset{0.3}{X^-}, i = 1.3)$

5. **(a)** **NOTE :** On increasing pressure, the temperature is also increased. Thus in pressure cooker due to increase in pressure the b.p. of water increases.

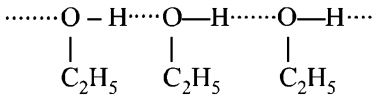
6. **(c)** $\because \Delta T_b° = T_b - T_b°$
Where T_b = b.pt of solution
$T_b°$ = b.pt of solvent or $T_b = T_b° + \Delta T_b$
NOTE : Elevation in boiling point is a colligative property, which depends upon the no. of particles. Thus greater the number of particles, greater is it elevation and hence greater will be its boiling point.

$$Na_2SO_4 \rightleftharpoons 2\overset{+}{Na} + SO_4^{2-}$$

Since Na_2SO_4 has maximum number of particles (3) hence has maximum boiling point.

7. **(d)** Gaseous densities of ethanol and dimethyl ether would be same at same temperature and pressure. The heat of vaporisation, V.P. and b.pts will differ due to H-bonding in ethanol.

8. **(b)** **NOTE :** Positive deviations are shown by such solutions in which solvent-solvent and solute-solute interactions are stronger than the solvent interactions. In such solution, the intcractions among molecules becomes weaker. Therefore their escaping tendency increases which results in the increase in their partial vapour pressures.
In a solutions of benzene and methanol there exists inter molecular H– bonding.



$$\cdots\cdots \underset{C_2H_5}{\underset{|}{O}} - H\cdots\cdots \underset{C_2H_5}{\underset{|}{O}} — H\cdots\cdots \underset{C_2H_5}{\underset{|}{O}} — H\cdots$$

In this solution benzene molecules come between ethanol molecules which weaken intermolecular forces. This results in increase in vapour pressure.

9. **(d)** $\Delta T_f = K_f \times m \times i$. Since K_f has different values for different solvents, hence even if the m is the same ΔT_f will be different

10. **(d)** Given, Vapour pressure of benzene = 75 torr
Vapour pressure of benezene = 22 torr
mass of benzene in = 78g

hence moles of benzene $= \dfrac{78}{78} = 1$mole
(mol.wt of benzene = 78)
mass of toluence in solution = 46g

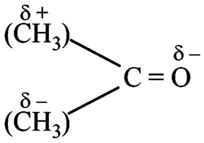
hence moles of toluene $= \dfrac{46}{92} = 0.5$ mole

now partial pressure of benezene

$$= P^o_b . X_b = 75 \times \frac{1}{1+0.5} = 50 \text{ torr} = 75 \times \frac{1}{1.5} = 75 \times \frac{2}{3}$$
$$= 50$$

11. **(d)** Equimolar solutions of normal solutes in the same solvent will have the same b. pts and same f. pts.

12. **(d)** Acetonitrile $(\overset{\delta+}{C}H_3 - C \equiv \overset{\delta-}{N})$ and acetone



both are polar molecules, hence dipole-dipole interaction exist between them. Between KCl and water ion-dipole interaction is found and in Benzene ethanol and Benzene–Carbon tetra chloride dispersion force is present

13. **(b)** Moles of glucose $= \dfrac{18}{180} = 0.1$

Moles of water $= \dfrac{178.2}{18} = 9.9$

Total moles = 0.1 + 9.9 = 10

p_{H_2O} = Mole fraction × Total pressure $= \dfrac{9.9}{10} \times 760$

= 752.4 Torr

14. **(b)** $p_A^\circ = ?$, Given $p_B^\circ = 200$mm, $x_A = 0.6$,
$x_B = 1 - 0.6 = 0.4, P = 290$
$P = P_A + P_B = P_A^\circ x_A + P_B^\circ x_B$
$\Rightarrow 290 = P_A^\circ \times 0.6 + 200 \times 0.4 \qquad \therefore p_A^\circ = 350$ mm

15. **(d)** Let the mass of methane and oxygen = m gm.
Mole fraction of O_2

$$= \frac{\text{Moles of } O_2}{\text{Moles of } O_2 + \text{Moles of } CH_4}$$

$$= \frac{m/32}{m/32 + m/16} = \frac{m/32}{3m/32} = \frac{1}{3}$$

Partial pressure of O_2 = Total pressure × mole fraction of O_2, $P_{O_2} = P \times \dfrac{1}{3} = \dfrac{1}{3}P$

16. (a) TIPS/FORMULAE:

Osmotic pressure (π) of isotonic solutions are equal.

For solution of unknown substance ($\pi = CRT$)

$$C_1 = \frac{5.25/M}{V}$$

For solution of urea, C_2 (concentration) $= \frac{1.5/60}{V}$

Given, $\pi_1 = \pi_2$ $\quad \because \pi = CRT$

$\therefore C_1RT = C_2RT$ or $C_1 = C_2$ or $\frac{5.25/M}{V} = \frac{1.8/60}{V}$

$\therefore M = 210$ g/mol

17. (d) At 1 atmospheric pressure the boiling point of mixture is 80°C.
At boiling point the vapour pressure of mixture, $P_T = 1$ atmosphere = 760 mm Hg.
Using the relation,

$P_T = P_A^o X_A + P_B^o X_B$, we get

$P_T = 520X_A + 1000(1 - X_A)$

$\{\because P_A^o = 520 \text{mm Hg},$

$P_B^o = 1000 \text{ mm Hg}, X_A + X_B = 1\}$

or $760 = 520X_A + 1000 - 1000X_A$ or $480X_A = 240$

or $X_A = \frac{240}{480} = \frac{1}{2}$ or 50 mol. percent

i.e., The correct answer is (d)

18. (a) NOTE : On addition of glucose to water, vapour pressure of water will decrease. The vapour pressure of a solution of glucose in water can be calculated using the relation

$$\frac{P^o - P_s}{P_s} = \frac{\text{Moles of glucose in solution}}{\text{moles of water in solution}}$$

or $\frac{17.5 - P_s}{P_s} = \frac{18/180}{178.2/18}$ $\quad [\because P^o = 17.5]$

or $17.5 - P_s = \frac{0.1 \times P_s}{9.9}$ or $P_s = 17.325$ mm Hg.

Hence (a) is correct answer.

19. (b) For this solution intermolecular interactions between *n*-heptane and ethanol aare weaker than *n*-heptane - *n*-heptane & ethanol-ethanol interactions hence the solution of *n*-heptane and ethanol is non-ideal and shows positive deviation from Raoult's law.

20. (b) $P_{total} = \overset{\circ}{P}_A X_A + \overset{\circ}{P}_B X_B$; $550 = \overset{\circ}{P}_A \times \frac{1}{4} + \overset{\circ}{P}_B \times \frac{3}{4}$

$\overset{\circ}{P}_A + 3\overset{\circ}{P}_B = 550 \times 4$ ...(i)

In second case

$P_{total} = \overset{\circ}{P}_A \times \frac{1}{5} + \overset{\circ}{P}_B \times \frac{4}{5}$

$\overset{\circ}{P}_A + 4\overset{\circ}{P}_B = 560 \times 5$ ...(ii)

Subtract (i) from (ii)

$\therefore \overset{\circ}{P}_B = 560 \times 5 - 550 \times 4 = 600$ $\quad \because \overset{\circ}{P}_A = 400$

21. (b) Sodium sulphate dissociates as

$Na_2SO_4(s) \longrightarrow 2Na^+ + SO_4^{--}$

hence van't hoff factor $i = 3$

Now $\Delta T_f = i k_f . m = 3 \times 1.86 \times 0.01 = 0.0558$ K

22. (a) $P_{Total=} = P^\circ_A x_A + P^\circ_B x_B$

$= P^\circ_{Heptane}\, x_{Heptane} + P^\circ_{Octane}\, x_{Octane}$

$$= 105 \times \frac{25/100}{\frac{25}{100} + \frac{35}{114}} + 45 \times \frac{35/114}{\frac{25}{100} + \frac{35}{114}}$$

$$= 105 \times \frac{0.25}{0.25 + 0.3} + 45 \times \frac{0.3}{0.25 + 0.3}$$

$$= \frac{105 \times 0.25}{0.55} + \frac{45 \times 0.3}{0.55} = \frac{26.25 + 13.5}{0.55} = 72 \text{ kPa}$$

23. (c) 5.2 molal solution means 5.2 moles of methyl alcohol in 1000 gm water or in $\frac{1000}{18}$ mole of water.

$\therefore$ mole fraction of methyl alcohol

$$= \frac{\text{moles of methyl alcohol}}{\text{moles of methyl alcohol + moles of water}}$$

$$= \frac{5.2}{5.2 + \frac{1000}{18}} = 0.086$$

24. (a) Given $K_f = 1.86$ K kg mol^{-1}

$\Delta T_f = 0 - (-6) = 6°C$

As we know that

$\Delta T_f = K_f \times$ molality

$$= \frac{K_f \times 1000 \times \text{mass of solute}}{\text{molar mass of solute} \times \text{mass of solvent in kg}}$$

Substituting given values in formula

$6 = \frac{1.86 \times 1000 \times w}{62 \times 4}$; $w = 0.8$ kg $= 800$ gm

25. (a)

$$\begin{array}{llll} & A_xB_y & \rightleftharpoons xA^{y+} & + yB^{x-} \\ t = 0 & 1 & 0 & 0 \\ t_{eq} & 1 - \alpha & x\alpha & y\alpha \end{array}$$

Total no. of moles (i) $= 1 - \alpha + x\alpha + y\alpha$

$i - 1 = x\alpha + y\alpha - \alpha = \alpha(x + y - 1)$

$$\therefore \alpha = \frac{i - 1}{(x + y - 1)}$$

26. (d) Molarity $= \frac{\text{moles of solute}}{\text{volume of solution}(\ell)}$

Mass of solution = 1000 + 120 = 1120

$d = \frac{M}{v}; v = \frac{M}{d} = \frac{1120}{1.15}$ mL $= \frac{120 \times 1.15}{60 \times 1120} \times 1000 = 2.05$ M

27. (b) $\Delta T_f = i \times K_f \times m$

Given $\Delta T_f = 2.8$, $K_f = 1.86$ K kg mol^{-1} $i = 1$

(ethylene glygol is a non- electrolyte)

wt. of solvent = 1 kg; Let of wt of solute = x

Mol. wt of ethylene glycol = 62

$$2.8 = 1 \times 1.86 \times \frac{x}{62 \times 1} \text{ or } x = \frac{2.8 \times 62}{1.86} = 93 \text{ gm}$$

28. (a) From Molarity equation :

$M_1V_1 + M_2V_2 = M \times V$

$$M = \frac{M_1V_1 + M_2V_2}{V} \text{ where V = total volume}$$

$$= \frac{750 \times 0.5 + 250 \times 2}{1000} = 0.875 \text{ M}$$

29. **(a)** $\pi = iCRT$

$$\pi_{C_2H_5OH} = 1 \times 0.500 \times R \times T = 0.5RT$$

$$\pi_{Mg_3(PO_4)_2} = 5 \times 0.100 \times R \times T = 0.5RT$$

$$\pi_{KBr} = 2 \times 0.250 \times R \times T = 0.5RT$$

$$\pi_{Na_3PO_4} = 4 \times 0.125 \times RT = 0.5RT$$

Since the osmotic pressure of all the given solutions is equal. Hence all are isotonic solution.

30. **(d)** Using relation,

$$\frac{p^\circ - p_s}{p_s} = \frac{w_2M_1}{w_1M_2}$$

where w_1, M_1 = mass in g and mol. mass of solvent

w_2, M_2 = mass in g and mol. mass of solute

Let $M_2 = x$

$p^\circ = 185$ torr ; $p_s = 183$ torr

$$\frac{185 - 183}{183} = \frac{1.2 \times 58}{100x} \text{ (Mol. mass of acetone = 58)}$$

$x = 64$

∴ Molar mass of substance = 64

31. **(a)** According to Raoult's Law

$$\frac{P^\circ - P_s}{P_s} = \frac{W_B \times M_A}{M_B \times W_A} \quad \ldots(i)$$

Here P° = Vapour pressure of pure solvent,

P_s = Vapour pressure of solution

W_B = Mass of solute, W_A = Mass of solvent

M_B = Molar mass of solute, M_A = Molar Mass of solvent

Vapour pressure of pure water at 100° C (by assumption = 760 torr)

By substituting values in equation (i) we get,

$$\frac{760 - P_s}{P_s} = \frac{18 \times 18}{180 \times 178.2} \quad \ldots(ii)$$

On solving (ii) we get

$P_s = 752.4$ torr