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 equilibrium ***(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
   (a) $\Delta V_{mix} > 0$ **[2002]**
   (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