

Summary

A solution is a homogeneous mixture of two or more substances. Solutions are classified as solid, liquid and gaseous solutions. The concentration of a solution is expressed in terms of mole fraction, molarity, molality and in percentages. The dissolution of a gas in a liquid is governed by **Henry's law**, according to which, at a given temperature, the **solubility of a gas in a liquid is directly proportional to the partial pressure of the gas**. The vapour pressure of the solvent is lowered by the presence of a non-volatile solute in the solution and this lowering of vapour pressure of the solvent is governed by Raoult's law, according to which the **relative lowering of vapour pressure of the solvent over a solution is equal to the mole fraction of a non-volatile solute present in the solution**. However, in a binary liquid solution, if both the components of the solution are volatile then another form of Raoult's law is used. Mathematically, this form of the Raoult's law is stated as: $p_{\text{total}} = p_1^0 x_1 + p_2^0 x_2$. **Solutions which obey Raoult's law over the entire range of concentration are called ideal solutions**. Two types of deviations from Raoult's law, called positive and negative deviations are observed. Azeotropes arise due to very large deviations from Raoult's law.

The properties of solutions which depend on the number of solute particles and are independent of their chemical identity are called colligative properties. These are lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. The process of osmosis can be reversed if a pressure higher than the osmotic pressure is applied to the solution. Colligative properties have been used to determine the molar mass of solutes. Solutes which dissociate in solution exhibit molar mass lower than the actual molar mass and those which associate show higher molar mass than their actual values.

Quantitatively, the extent to which a solute is dissociated or associated can be expressed by van't Hoff factor i . This factor has been defined as ratio of normal molar mass to experimentally determined molar mass or as the ratio of observed colligative property to the calculated colligative property.

Exercises

- 2.1 Define the term solution. How many types of solutions are formed? Write briefly about each type with an example.
- 2.2 Suppose a solid solution is formed between two substances, one whose particles are very large and the other whose particles are very small. What kind of solid solution is this likely to be?
- 2.3 Define the following terms:
(i) Mole fraction (ii) Molality (iii) Molarity (iv) Mass percentage.
- 2.4 Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is 1.504 g mL^{-1} ?

- 2.5** A solution of glucose in water is labelled as 10% w/w, what would be the molality and mole fraction of each component in the solution? If the density of solution is 1.2 g mL^{-1} , then what shall be the molarity of the solution?
- 2.6** How many mL of 0.1 M HCl are required to react completely with 1 g mixture of Na_2CO_3 and NaHCO_3 containing equimolar amounts of both?
- 2.7** A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.
- 2.8** An antifreeze solution is prepared from 222.6 g of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g mL^{-1} , then what shall be the molarity of the solution?
- 2.9** A sample of drinking water was found to be severely contaminated with chloroform (CHCl_3) supposed to be a carcinogen. The level of contamination was 15 ppm (by mass):
- express this in percent by mass
 - determine the molality of chloroform in the water sample.
- 2.10** What role does the molecular interaction play in a solution of alcohol and water?
- 2.11** Why do gases always tend to be less soluble in liquids as the temperature is raised?
- 2.12** State Henry's law and mention some important applications?
- 2.13** The partial pressure of ethane over a solution containing $6.56 \times 10^{-3} \text{ g}$ of ethane is 1 bar. If the solution contains $5.00 \times 10^{-2} \text{ g}$ of ethane, then what shall be the partial pressure of the gas?
- 2.14** What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{\text{mix}}H$ related to positive and negative deviations from Raoult's law?
- 2.15** An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute?
- 2.16** Heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35 g of octane?
- 2.17** The vapour pressure of water is 12.3 kPa at 300 K. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it.
- 2.18** Calculate the mass of a non-volatile solute (molar mass 40 g mol^{-1}) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.
- 2.19** A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further, 18 g of water is then added to the solution and the new vapour pressure becomes 2.9 kPa at 298 K. Calculate:
- molar mass of the solute
 - vapour pressure of water at 298 K.
- 2.20** A 5% solution (by mass) of cane sugar in water has freezing point of 271K. Calculate the freezing point of 5% glucose in water if freezing point of pure water is 273.15 K.
- 2.21** Two elements A and B form compounds having formula AB_2 and AB_4 . When dissolved in 20 g of benzene (C_6H_6), 1 g of AB_2 lowers the freezing point by 2.3 K whereas 1.0 g of AB_4 lowers it by 1.3 K. The molar depression constant for benzene is $5.1 \text{ K kg mol}^{-1}$. Calculate atomic masses of A and B.

- 2.22** At 300 K, 36 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bars at the same temperature, what would be its concentration?
- 2.23** Suggest the most important type of intermolecular attractive interaction in the following pairs.
- n-hexane and n-octane
 - I₂ and CCl₄
 - NaClO₄ and water
 - methanol and acetone
 - acetonitrile (CH₃CN) and acetone (C₃H₆O).
- 2.24** Based on solute-solvent interactions, arrange the following in order of increasing solubility in n-octane and explain. Cyclohexane, KCl, CH₃OH, CH₃CN.
- 2.25** Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water?
- phenol
 - toluene
 - formic acid
 - ethylene glycol
 - chloroform
 - pentanol.
- 2.26** If the density of some lake water is 1.25 g mL⁻¹ and contains 92 g of Na⁺ ions per kg of water, calculate the molality of Na⁺ ions in the lake.
- 2.27** If the solubility product of CuS is 6 × 10⁻¹⁶, calculate the maximum molarity of CuS in aqueous solution.
- 2.28** Calculate the mass percentage of aspirin (C₉H₈O₄) in acetonitrile (CH₃CN) when 6.5 g of C₉H₈O₄ is dissolved in 450 g of CH₃CN.
- 2.29** Nalorphene (C₁₉H₂₁NO₃), similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is 1.5 mg. Calculate the mass of 1.5 × 10⁻³ m aqueous solution required for the above dose.
- 2.30** Calculate the amount of benzoic acid (C₆H₅COOH) required for preparing 250 mL of 0.15 M solution in methanol.
- 2.31** The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order given above. Explain briefly.
- 2.32** Calculate the depression in the freezing point of water when 10 g of CH₃CH₂CHClCOOH is added to 250 g of water. K_a = 1.4 × 10⁻³, K_f = 1.86 K kg mol⁻¹.
- 2.33** 19.5 g of CH₂F₂COOH is dissolved in 500 g of water. The depression in the freezing point of water observed is 1.0^o C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.
- 2.34** Vapour pressure of water at 293 K is 17.535 mm Hg. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water.
- 2.35** Henry's law constant for the molality of methane in benzene at 298 K is 4.27 × 10⁵ mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.
- 2.36** 100 g of liquid A (molar mass 140 g mol⁻¹) was dissolved in 1000 g of liquid B (molar mass 180 g mol⁻¹). The vapour pressure of pure liquid B was found to be 500 torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 Torr.

- 2.37** Vapour pressures of pure acetone and chloroform at 328 K are 741.8 mm Hg and 632.8 mm Hg respectively. Assuming that they form ideal solution over the entire range of composition, plot p_{total} , $p_{\text{chloroform}}$, and p_{acetone} as a function of x_{acetone} . The experimental data observed for different compositions of mixture is:

$100 \times x_{\text{acetone}}$	0	11.8	23.4	36.0	50.8	58.2	64.5	72.1
$p_{\text{acetone}} / \text{mm Hg}$	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{\text{chloroform}} / \text{mm Hg}$	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7

Plot this data also on the same graph paper. Indicate whether it has positive deviation or negative deviation from the ideal solution.

- 2.38** Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and naphthalene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in vapour phase if 80 g of benzene is mixed with 100 g of naphthalene.
- 2.39** The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% is to 79% by volume at 298 K. The water is in equilibrium with air at a pressure of 10 atm. At 298 K if the Henry's law constants for oxygen and nitrogen at 298 K are 3.30×10^7 mm and 6.51×10^7 mm respectively, calculate the composition of these gases in water.
- 2.40** Determine the amount of CaCl_2 ($i = 2.47$) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27° C.
- 2.41** Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litre of water at 25° C, assuming that it is completely dissociated.

Answers to Some Intext Questions

- 2.1** $\text{C}_6\text{H}_6 = 15.28\%$, $\text{CCl}_4 = 84.72\%$
- 2.2** 0.459, 0.541
- 2.3** 0.024 M, 0.03 M
- 2.4** 37.5 g
- 2.5** 1.5 mol kg^{-1} , 1.45 mol L^{-1} 0.0263
- 2.9** 289.5 bar
- 2.10** 1.86 g
- 2.11** $x_A = 0.4$, $y_A = 0.3$; $x_B = 0.6$, $y_B = 0.7$
- 2.12** 23.4 mm Hg, 0.017