

Chapter 8: Solutions

Review Questions

1. The molecules of a compound are composed of one phosphorus atom and multiple chlorine atoms. A molecule of the compound is described as a trigonal pyramid. This gaseous compound dissolves in water to form a hydrochloric acid solution and phosphorus acid (H_3PO_3). What is the molarity of the hydrochloric acid if 750 mL of the gas, measured at STP, dissolves in 250 mL of water?

Solution

The formula must be PCl_3 . The structure is trigonal pyramidal.

The reaction is $\text{PCl}_3(\text{g}) + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3(\text{aq}) + 0.404 \text{ M HCl}$

2. Why do two gases spontaneously mix when they are brought into contact?

Solution

This takes place due to the tendency for all systems to proceed spontaneously towards a state with a higher degree of randomness (disorder).

3. The value of ΔH_{soln} for a soluble compound is, say, $+26 \text{ kJ mol}^{-1}$, and a nearly saturated solution is prepared in an insulated container (e.g., a coffee cup calorimeter). Will the system's temperature increase or decrease as the solute dissolves? Which value for this compound would be numerically larger, its lattice energy or its hydration energy?

Solution

Since the enthalpy of solution is positive, the process is endothermic. The system thus requires heat for the dissolving process, and the heat flow should cause the temperature to decrease as the solute dissolves. The lattice energy is numerically larger since that step is endothermic, that is, it requires energy to separate the particles.

4. Methanol, $\text{CH}_3\text{--O--H}$, and water are miscible in all proportions. What does this mean? Explain how the O–H unit in methanol contributes to this.

Solution

Since water and methanol both have OH groups, there can be hydrogen bonding between a water molecule and a methanol molecule. This allows any proportion of methyl alcohol in water to be nearly as stable as either separate water samples or separate methyl alcohol samples.

5. Show that when the mole fraction of the solvent in the solution is nearly unity, the molarity (C) and molality (m) of the solution are connected by the equation:

$$C = \rho \times m$$

where ρ is the density of the solution.

Solution

Let molarity be M expressed in mol L^{-1} of the solution and molality be m expressed in mol kg^{-1} of the solvent. Then, M/m will be expressed in kg L^{-1} of the solution

$$\text{As,} \quad \text{Mole fraction of solvent} = \frac{\text{Number of moles of solvent}}{\text{Total number of moles of solution}}$$

It is given that mole fraction of the solvent = unity. So, the number of moles of solvent = total number of moles of solution or mass of the solvent = mass of solution. Therefore,

$$\text{Density of solution } (\rho) = \frac{\text{Mass of solution}}{\text{Volume of solution}} = \frac{\text{Mass of solvent (in kg)}}{\text{Volume of solution (in L)}} = \frac{M}{m}$$

6. Hexane (C_6H_{12}) and water are immiscible. What does this mean? Explain why they are immiscible in terms of structural features of their molecules and the forces of attraction between them.

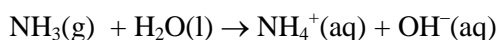
Solution

Water molecules are tightly linked to one another by hydrogen bonding. In hexane, however, which is a non-polar organic substance, we have only weak London forces of attraction. This means that hexane as a solute in water offers no advantage in attraction to individual water molecules, and the solvent is, therefore, not disrupted to allow the solute to dissolve.

7. Why is ammonia so much more soluble in water than in nitrogen? Explain.

Solution

Ammonia is more soluble in water than nitrogen because ammonia is able to form hydrogen bond with solvent molecules, whereas nitrogen cannot. Nitrogen is a non-polar molecular substance, whereas ammonia is a polar substance capable of hydrogen bonding. Also, ammonia reacts with water to form nonvolatile ions:



8. When substances form liquid solutions, what two factors are involved in determining the solubility of the solute in the solvent?

Solution

First, the tendency toward randomness drives the solution process, and second, the new forces of attraction between solute and solvent molecules drive the process. Thus, the relative degree of solute–solute, solvent–solvent, and solute–solvent interactions will determine if a solute is soluble in a solvent or not.

9. Which would be expected to have the larger hydration energy, Al^{3+} or Li^+ ? Why? (Both ions are about the same size.)

Solution

The Al^{3+} ion, having the greater positive charge, should have the larger hydration energy.

10. If a saturated solution of NH_4NO_3 at 70°C is cooled to 10°C , how many grams of solute will separate if the quantity of the solvent is 100 g?

Solution

We can estimate from that the solubility of NH_4NO_3 in 100 g of H_2O is 500 g at 70°C and 150 g at 10°C . The amount of solid that will crystallize is the difference between these two solubilities, namely $500 - 150 = 350$ g.

11. The value of ΔH_{soln} for the formation of an ethanol–hexane solution is positive, while that of acetone–water solution is negative. Explain this in general terms that involve intermolecular forces of attraction.

Solution

The disruption of ethyl alcohol and the disruption of hexane together cost more energy than is gained on formation of the solution. This is because the two liquids are not alike; ethyl alcohol is a polar substance with hydrogen bonding, whereas hexane is a nonpolar liquid having only London forces.

There is a greater attraction between water and acetone molecules in the resulting solution than there is among acetone molecules in the starting pure solute or water molecules in the starting pure solvent.

12. The largest fish are found in deep sinks in lake bottoms. Use the temperature dependence of oxygen solubility in water to explain why.

Solution

Oxygen solubility increases as the temperature decreases. The larger fish will need more oxygen and will be found in the colder areas of lake bottoms.

13. When a solid is *associated* in a solution, what does this mean? What difference does it make to expected colligative properties?

Solution

By the “association of solute particles” we mean that some particles are attracted to others, or that solvent does not perfectly insulate solute particles from attachment to one another. This is another way of saying that there is less than 100% dissociation or dissolution of solute in such a solution.

14. Mountain streams often contain fewer living things than equivalent streams at sea level. Give one reason why this might be true in terms of oxygen solubilities at different pressures.

Solution

The atmospheric pressure on a mountain is less than the atmospheric pressure at sea level. From Henry's law, as the partial pressure of oxygen decreases, the concentration of the oxygen also decreases. Therefore, there is less oxygen to sustain life in mountain streams.

15. When octane is mixed with methanol, the vapor pressure of the octane over the solution is higher than what we would calculate using Raoult's law. Why? Explain the discrepancy in terms of intermolecular attractions.

Solution

A positive deviation indicates that the vapor pressure of the real solution is greater than expected if the solution behaved ideally. Positive deviations result when mixtures with weaker intermolecular forces of attraction between the two substances as compared to the intermolecular forces of the pure substances are formed.

16. Why does a bottled carbonated beverage fizz when you take the cap off?

Solution

When the cap is removed from a bottle of carbonated beverage, the liquid fizzes because CO_2 is being released from the liquid. When the cap is on, the CO_2 fills the space above the liquid until equilibrium is established between the gas and the liquid. After the cap is removed, the equilibrium is disrupted and more of the gas leaves the solution. This is the fizzing.

17. Suppose a 1.0 molal solution of a solute is made using a solvent with a density of 1.15 g mL^{-1} . Will the molarity of this solution be numerically larger or smaller than 1.0? Explain.

Solution

The molarity will be greater than 1.0. Since the density of the solution is greater than one, the mass of the solution in kg will be greater than its volume in liters.

18. What kinds of data would have to be obtained to find out if a solution of two miscible liquids is almost exactly an ideal solution?

Solution

A solution is ideal if the sum of the partial pressures of the components of the solution equals the observed vapor pressure of the solution, that is, if the solution obeys Raoult's law. Also, it should be true that the heat of solution is nearly zero.

19. Explain why a non-volatile solute dissolved in water makes the system have (a) a higher boiling point than water and (b) a lower freezing point than water.

Solution

When a solute is dissolved in a solvent, the vapor pressure is lowered. As a result, the boiling point is increased to a temperature where the vapor pressure is high enough to once again allow boiling to occur. This effect also reduces the triple point, and the entire solid-liquid equilibrium curve on a phase diagram shifts to lower temperatures. The net result is a lowering of the freezing point.

20. What specific fact about a physical property of a solution must be true to call it a colligative property?

Solution

A colligative property of a solution is one that depends only on the molal concentration of the solute particles, and not on the identity of the solute.

21. At a molecular level, explain why in osmosis there is a net migration of solvent from the side of the membrane less concentrated in solute to the side more concentrated in solute.

Solution

The side of the membrane less concentrated in solute will be more concentrated in solvent. Therefore, the escaping tendency of the solvent will be greater than on the side of the membrane less concentrated in solute. The solvent will shift through the membrane from the side less concentrated in solute to the side more concentrated in solute.

22. What is the van't Hoff factor? What is its expected value for all non-dissociating molecular solutes? If its measured value is slightly larger than 1.0, what does this suggest about the solute? What is suggested by a van't Hoff factor of approximately 0.5?

Solution

The van't Hoff factor is the ratio of the value for a colligative property as actually measured to that value of the colligative property that is expected in the complete absence of any solute dissociation. A van't Hoff factor of one is expected for all non-dissociating molecular solutes. A van't Hoff factor greater than one indicates a dissociation of the solute. A van't Hoff factor less than one indicates association of the solute. If the van't Hoff factor is 0.5, then this indicates the formation of dimers.

23. Two glucose solutions of unequal molarity are separated by an osmotic membrane. Which solution will *lose* water, the one with the higher or the lower molarity?

Solution

The solution that loses solvent into the other solution is the one with the lower molarity.

24. What is the key difference between dialyzing and osmotic membranes?

Solution

An osmotic membrane allows only solvent to pass, whereas a dialyzing membrane allows solvated ions of a certain minimum size to pass as well as solvent molecules. A dialyzing membrane prevents the passage of only certain solute particles, usually those of large size, such as colloid particles.

25. Why are colligative properties of solutions of ionic compounds usually more pronounced than those of solutions of molecular compounds of the same molalities?

Solution

Ionic compounds dissociate in solution. The dissociation results in an increase in the number of particles in the solution, that is, one NaCl "molecule" will dissociate creating two ions: Na^+ and Cl^- . Colligative properties depend on the concentration of particles, so any compound that dissociates into multiple particles will have pronounced effects on colligative properties.

26. Which aqueous solution has the higher osmotic pressure, 10% glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, or 10% sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$? (Both are molecular compounds.)

Solution

In each case, the osmotic pressure Π is given by the equation: $\Pi = M \times R \times T$. Since we do not know either the density of the solution or the volume of the solution, we cannot convert values for % by mass into molarities. However, we do know that glucose, having the smaller molecular mass, has the higher molarity, and we conclude that it will have the larger osmotic pressure.

27. Which aqueous solution, if either, is likely to have the higher boiling point, 0.50 molal NaI or 0.50 molal Na_2CO_3 ?

Solution

The solute that dissolves to produce the greater number of ions, Na_2CO_3 , gives the solution with the larger boiling point elevation and, thus, the higher boiling point.

28. To what type of solution does an alloy belong to? Give one example of a solution of liquid in solid.

Solution

Alloy is a solution of solid solute in solid solvent. For example, gold and copper form a solid solution because gold atoms can replace copper atoms in the copper crystal and similarly, copper atoms can replace gold atoms in the gold crystals. Alloys of two or more metals are solid solutions. For example, a solution of liquid in solid is mercury with sodium (amalgam).

Numerical Problems

1. Calculate the freezing point of an aqueous solution of electrolyte having osmotic pressure of 2.0 atm at 300 K. $K_f = 1.86 \text{ K molal}^{-1}$, $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$.

Solution

$$\Pi = CRT \Rightarrow C = \frac{\Pi}{RT} = \frac{2}{0.0821 \times 300} = 0.0812 \text{ M}$$

Colligative properties are defined for dilute solutions by assuming molarity = molality. Therefore,

$$\Delta T_f = K_f \times m = 1.86 \times 0.0812 = 0.15^\circ\text{C}$$

$$\text{Now, } \Delta T_f = T_f^\circ - T_f \Rightarrow 0.15 = 0 - T_f \Rightarrow T_f = -0.15^\circ\text{C}$$

2. At 25°C , the vapor pressure of pure methyl alcohol is 92.0 torr. What is the mole fraction of CH_3OH in a solution in which vapor pressure of CH_3OH is 23.0 torr at 25°C ?

Solution

$$p_1 = p_1^\circ x_1 \Rightarrow 23 = 92 \times x_1 \Rightarrow 23/92 = x_1 \Rightarrow x_1 = 0.25$$

3. The vapor pressure of pure benzene at 25°C is 640.0 mm Hg and vapor pressure of a solution of a solute in benzene is 25°C is 632.0 mm Hg. Find the freezing point of the solution if K_f for benzene is $5.12 \text{ K molal}^{-1}$ ($T_{f(\text{Benzene})}^\circ = 5.5^\circ\text{C}$).

Solution

We know that $p_1 = p_1^\circ x_1$, therefore,

$$632 = 640 \times x_1 \Rightarrow x_1 = 632/640 = 0.9875$$

$$\text{and } \Delta T_f = K_f \times m = 5.12 \times 0.9875 = 5.056^\circ\text{C}$$

$$\text{Now, } \Delta T_f = T_f^\circ - T_f \Rightarrow 5.056 = 5.5 - T_f \Rightarrow T_f = 5.5 - 5.056 = 0.444^\circ\text{C}$$

4. A solution containing 2.7 g of urea per 100 mL of the solution is isotonic with a solution of sucrose. How many grams of sucrose are present in 500 mL of the solution?

Solution

Given that $\Pi_1 = \Pi_2$, therefore

$$C_1RT = C_2RT \Rightarrow \frac{2.7}{60} \times \frac{R \times T}{100} = \frac{x}{342} \times \frac{R \times T}{500}$$

Solving, we get $x = 76.95 \text{ g}$.

5. 2.0 g of benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$ dissolve in 25.0 g of benzene show a depression in freezing point of 1.62 K. K_f of benzene = 4.9 K molal^{-1} . What is the percentage association of the acid?

Solution

$$\text{The molality of the solution is } m = \frac{2.0}{25} \times 1000 = 0.65$$

$$\text{Therefore, } \Delta T_{f(\text{calculated})} = K_f \times m = 4.9 \times 0.65 = 3.21 \text{ K}$$

Given that $\Delta T_{f(\text{observed})} = 1.62 \text{ K}$. Therefore, the van't Hoff factor is found as

$$i = \frac{1.62}{3.21} = 0.504$$

$$\text{The degree of association } (\alpha) = \frac{n(1-i)}{(n-1)} = \frac{2(1-0.504)}{(2-1)} = 0.496 \times 2 = 99.2\%$$

6. What is the percentage by mass of iodine needed to reduce the freezing point of benzene to 3.5°C . The freezing point and cryoscopic constant of pure benzene are 5.5°C and $5.12 \text{ K molal}^{-1}$, respectively.

Solution

$$\text{Given that } \Delta T_f = T_f^\circ - T_f = 5.5 - 3.5 = 2^\circ\text{C}$$

Also, $\Delta T_f = K_f \times m$. Therefore,

$$m = \frac{2}{5.12} = 0.391 \text{ molal}$$

Mass of iodine needed for 1000 g of benzene = $0.39 \times 254 = 99.06$ g or 9.9%.

7. What is the degree of dissociation α of a weak electrolyte in terms of van't Hoff factor i and the number of ions given by 1 mol of the electrolyte, N ?

Solution

Given that the initial number of moles = 1. If we have $1 - \alpha$ moles of undissociated molecules and $n\alpha$ ions (undissociated) then the total number of moles undissociated will be $1 - \alpha + n\alpha$

The van't Hoff factor is given by

$$i = \frac{1 - \alpha + n\alpha}{1}$$

Therefore, the degree of dissociation is

$$\alpha = \frac{i - 1}{n - 1}$$

8. What is the osmotic pressure of a solution made by mixing 100 mL of 0.1 M acetone and 100 mL of 0.2 M solution at 30°C?

Solution

The osmotic pressure is calculated as

$$\Pi = \frac{0.3 \times 0.0821 \times 303 \times 1000}{200} = 37.31 \text{ atm}$$

9. In a cold climate, water gets frozen causing damage to the radiator of cars. Ethylene glycol is used as an anti-freeze. Calculate the amount of glycol to be added to 4.0 kg of water to prevent it from freezing at -6°C . K_f of water = $1.86 \text{ K molal}^{-1}$.

Solution

The molality is

$$m = \frac{x / 62}{4}$$

Therefore,

$$\Delta T_f = K_f \times m \Rightarrow 6 = 1.86 \times \frac{x / 62}{4} \Rightarrow x = 800 \text{ g}$$

10. 0.6 L of a solute is dissolved in 0.1 L of a solvent, which develops an osmotic pressure of 1.23 atm at 27°C. What is the molecular weight of the solute?

Solution

$$M = \frac{wRT}{\pi V} = \frac{0.6 \times 0.0821 \times 200}{1.23 \times 0.1} = 120 \text{ g mol}^{-1}$$

11. The boiling point elevation of 600 mg of acetic acid in 0.1 kg of benzene is 0.1265 K. What conclusion can you draw about the molecular state of acetic acid in benzene? (K_b of benzene is $2.53 \text{ K molal}^{-1}$).

Solution

Molality is $m = \frac{(600 \times 10^{-3} / 60)}{0.1} = 0.1$

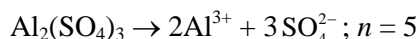
$$\Delta T_{b(\text{calculated})} = 2.53 \times 0.1 = 0.253 \text{ K}$$

$$\text{Given that } \Delta T_{b(\text{observed})} = 0.1265 \text{ K}$$

$$\text{Therefore, } i = 0.1265/0.253 = 0.5$$

12. The van't Hoff factor for a 0.1 M $\text{Al}_2(\text{SO}_4)_3$ solution is 4.20. The degree of dissociation is

Solution



The degree of dissociation is

$$\alpha = \frac{i-1}{n-1} = \frac{4.20-1}{5-1} = 0.8 = 80\%$$

13. The freezing point depression of 0.1 molal NaCl solution is 0.372 K. What conclusion can you draw about the molecular state of NaCl in water. K_f of water = $1.86 \text{ K molal}^{-1}$.

Solution

$$\Delta T_{f(\text{observed})} = 0.372$$

$$\Delta T_{f(\text{calculated})} = 1.86 \times 0.1 = 0.186$$

$$\text{Therefore, } i = 0.372/0.186 = 2 \text{ (dissociation)}$$

14. An aqueous solution containing an ionic salt having molality equal to 0.19 molal freezes at -0.704°C . The van't Hoff factor of the ionic salt is (given K_f for water = $1.86 \text{ K molal}^{-1}$)

Solution

$$\Delta T_{f(\text{observed})} = 0.704$$

$$\Delta T_{f(\text{calculated})} = K_f \times m = 0.19 \times 1.86 = 0.3534$$

$$\text{Therefore, } i = 0.704/0.3534 = 2$$

15. A weak electrolyte XY is 5% dissociated in water. What is the freezing point of a 0.01 molal aqueous solution of XY? The cryoscopic constant of water is $1.86 \text{ K molal}^{-1}$.

Solution

$$\text{Given that } \alpha = 0.05 \text{ and } n = 2. \text{ So, } i = \frac{1+(n-1)\alpha}{1} = 1.05$$

$$\Delta T_f = i \times K_f \times m = 1.05 \times 0.01 \times 1.86 = 0.01953$$

$$\Delta T_f = T_f^\circ - T_f \Rightarrow T_f = T_f^\circ - \Delta T_f = 0 - 0.01953 = -0.01953 \text{ or } -0.2^\circ\text{C}$$

16. Arrange the following solutions in increasing order of

(a) boiling points: (i) 0.001 molal NaCl, (ii) 0.001 molal urea, (iii) 0.001 molal MgCl_2 and (iv) 0.001 molal CH_3COOH .

(b) freezing points: (i) 0.1 M glucose, (ii) 1% urea solution and (iii) 0.1 M common salt.

(c) osmotic pressure: (i) NaNO_3 , (ii) BaCl_2 , (iii) $\text{K}_4[\text{Fe}(\text{CN})_6]$, (iv) $\text{C}_6\text{H}_{12}\text{O}_6$ and (v) CH_3COOH .

Solution

(a) The elevation in boiling point of water for the solutions is given by $\Delta T_b = iK_b m$

Since the molalities are the same, only the van't Hoff factor i of the solution will be considered for finding the order. The values of i for the given solutions are 2, 1, 3, <1, respectively. Therefore, the increasing order of boiling point is

$$\text{ii} < \text{iv} < \text{i} < \text{iii}$$

(b) The depression in the freezing point of water for the solutions is given by $\Delta T_f = iK_f m$

The value of $i = 1$ for both urea and glucose, but molality of glucose solution being more, it will cause greater depression in freezing point as compared to urea. For 0.1 m

common salt solution, $i = 2$, so it will show maximum depression. So the increasing order of freezing point is

$$\text{iii} < \text{i} < \text{ii}$$

(c) Similarly the order of osmotic pressure will be determined by the value of i , higher the value, greater is the osmotic pressure. The value of i for the given solutes are 2, 3, 5, 1 and <1 , respectively. Therefore the order of osmotic pressure is :iv < v < i < ii < iii.

17. The vapor pressure of a solution containing 5.0 g of a non-electrolyte in 100.0 g of water at a particular temperature is 2985 N m^{-2} . If the vapor pressure of pure water is 3000 N m^{-2} , what is the molecular weight of the solution?

Solution

$$\frac{p_o - p_s}{p_s} = \frac{W_2 M_1}{W_1 M_2} \Rightarrow \frac{3000 - 2985}{2985} = \frac{5 \times 18}{100 \times M_2}$$

Solving, we get $M_2 = 179.1 \text{ g mol}^{-1}$.

18. The vapor pressure of pure liquid solvent A is 0.80 atm. When a non-volatile substance B is added to the solvent, its vapor pressure drops to 0.60 atm. What is the mole fraction of the component B in the solution?

Solution

$$\frac{p_o - p_s}{p_s} = x_2 \Rightarrow x_2 = \frac{0.80 - 0.60}{0.80} = 0.25$$

19. The vapor pressure of pure benzene, C_6H_6 at 50°C is 268 torr. How many moles of non-volatile solute per mole of benzene is required to prepare a solution of benzene having a vapor pressure of 167 torr at 50°C ?

Solution

$$\text{The moles of non-volatile solute per mole of benzene} = \frac{268 - 167}{167} = 0.604$$

20. The molal boiling-point constant for water is $0.513 \text{ K molal}^{-1}$. When 0.1 mol of sugar is dissolved in 200.0 g of water, the solution boils under a pressure of 1.0 atm at what temperature?

Solution

$$\text{Molality is } m = \frac{0.1 \times 1000}{200} = 0.5 \text{ molal} \quad m = 0.1 \times 1000 / 200 = 0.5$$

$$\text{Also, } \Delta T_b = 0.513 \times 0.5 = 0.256$$

$$\text{Now, } \Delta T_b = T_b - T_b^\circ \Rightarrow 0.256 = T_b - 100 \Rightarrow T_b = 100 + 0.256 = 100.256^\circ\text{C}$$

21. The vapor pressure at a given temperature of an ideal solution containing 0.2 mol of a non-volatile solute and 0.8 mol of a solvent is 60 mm Hg. What will be the vapor pressure of the pure solvent at the same temperature?

Solution

$$\frac{p_o - p_s}{p_s} = \frac{n_2}{n_1 + n_2} \Rightarrow \frac{p_o - 60}{60} = \frac{0.2}{0.2 + 0.8} \Rightarrow p_o = 72 \text{ mm Hg}$$

22. 10.0 g of glucose (Π_1), 10.0 g of urea (Π_2) and 10.0 g of sucrose (Π_3) are dissolved in 250.0 mL of water at 273 K (where Π = osmotic pressure of a solution). What is the relationship between the osmotic pressures of the solutions?

Solution

We know that $\Pi \propto 1/M$

As $M_{(\text{urea})} = 60 \text{ g mol}^{-1}$, $M_{(\text{glucose})} = 180 \text{ g mol}^{-1}$ and $M_{(\text{sucrose})} = 342 \text{ g mol}^{-1}$

So, $\Pi_2 > \Pi_1 > \Pi_3$

23. A 5% solution of cane sugar (molecular weight = 342 g mol^{-1}) is isotonic with a 1% solution of a substance X. What is the molecular weight of X?

Solution

Given that $\Pi_1 = \Pi_2$, so

$$\frac{5}{342} \times R \times T = \frac{1}{x} \times R \times T \Rightarrow x = 68.4 \text{ g mol}^{-1}$$

24. From the measurement of the freezing-point depression of benzene, the molecular weight of acetic acid in a benzene solution was determined to be 100. What is the percentage association of acetic acid?

Solution

$M_{(\text{calculated})} = 60 \text{ g mol}^{-1}$. Given that $M_{(\text{observed})} = 100 \text{ g mol}^{-1}$. Therefore,

$$i = \frac{60}{100} = 0.6$$

and $n = 2$. Therefore, the degree of dissociation is

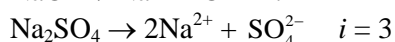
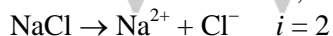
$$\alpha = \frac{(1-i)n}{n-1} = \frac{(1-0.6)2}{1} = 0.8$$

Hence, the percentage dissociation is 80%.

25. What is the ratio of freezing-point depression values of 0.01 M solutions of urea, common salt and Na_2SO_4 ?

Solution

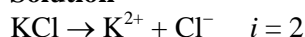
Urea does not dissociate, so $i = 1$.



Hence, the ratio is 1:2:3.

26. What should be the boiling point of 1.0 molal aqueous KCl solution (assuming complete dissociation of KCl) if K_b of H_2O is $0.52 \text{ K molal}^{-1}$?

Solution



$$\Delta T_b = i \times K_b \times m = 2 \times 0.52 \times 1.0 = 1.04$$

$$\text{Now, } \Delta T_b = T_b - T_b^\circ \Rightarrow 1.04 = T_b - 100 \Rightarrow T_b = 101.04^\circ\text{C}$$

Additional Objective Questions

Single Correct Choice Type

1. A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. What will be the mass percentage of the solute and solvent of resulting solution?

- (A) 23% and 77% (B) 12.5% and 87.5% (C) 33.6% and 66.4% (D) 50% and 50%

Solution

$$\text{(C) Weight of solute in 300 g solution} = \frac{300 \times 25}{100} = 75 \text{ g (as 25\% of 300g)}$$

$$\text{Weight of solute in 400 g solution} = \frac{400 \times 40}{100} = 160 \text{ g (as 40\% of 400g)}$$

Therefore, the total weight of solution = 300 + 400 = 700 g

$$\text{Mass percentage of solute in resulting solution} = \frac{235}{700} \times 100 = 33.6\%$$

$$\text{Mass percentage of solvent in resulting solution} = (100 - 33.6\%) = 66.4\%$$

2. An X molal solution of a compound in benzene has mole fraction of solute equal to 0.2. The value of X is

(A) 14

(B) 3.2

(C) 1.4

(D) 2.0

Solution

$$(B) \quad m = \frac{x_A \times 1000}{(1 - x_A) \times m_B} = \frac{0.2 \times 1000}{0.8 \times 78} = 3.2$$

3. 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 L⁻¹.

(A) 1.623 M

(B) 16.23 M

(C) 162.3 M

(D) 0.1623 M

Solution

(B) For 1 L solution, $m = d \times V = 1.504 \times 1000 = 1504$ g. Now,

$$W_{(\text{HNO}_3)} = \frac{1.504 \times 68}{100} = 102.72 \text{ g}$$

$$\text{Molarity} = \frac{W}{M \times V (\text{lit})} = \frac{102.72}{63 \times 1} = 16.23 \text{ M}$$

Therefore,

4. One liter of sea water weighs 1030 g and contains about 6×10^3 g dissolved O₂. What will be the concentration of dissolved oxygen in ppm?

(A) 68 ppm

(B) 5.8 ppm

(C) 580 ppm

(D) 0.58 ppm

Solution

(B) Mass of O₂ in mg = $6 \times 10^3 \times 10^{-3} = 6$ mg

$$\begin{aligned} \text{ppm of O}_2 \text{ in 1030 g sea water} &= \frac{\text{Mass of O}_2 \text{ in mg}}{\text{Mass of sea water in kg}} = \frac{6}{(1030/1000)} \\ &= \frac{6 \times 1000}{1030} = 5.8 \text{ ppm} \end{aligned}$$

5. An antifreeze solution is prepared from 222.6 g of ethylene glycol (C₂H₆O₂) and 200 g of water. What will be the molality and molarity of the solution respectively? (Given that the density of the solution is 1.072 g mL⁻¹)

(A) 17.95, 91.1

(B) 17.95, 9.11

(C) 1.795, 9.11

(D) 1.795, 91.1

Solution

$$(B) \quad \text{Molality of solution} = \frac{\text{Number of moles of ethylene glycol}}{\text{Mass of solvent in kg}} = \frac{222.6}{\frac{62}{200 \times 10^{-3}}} = 17.95 \text{ molal}$$

Now, $d = 1.072 = \frac{422.6}{V} \Rightarrow V = \frac{422.6}{1.072} \text{ cm}^3$. Therefore,

$$\text{Molarity of solution} = \frac{222.6}{\frac{422.6}{1.072} \times 10^{-3}} = 9.11 \text{ M}$$

6. What will be the (A) molality (B) molarity and (C) mole fraction of KI, respectively, if the density of 20% (mass/mass) aqueous KI is 1.202 g mL^{-1} ?

- (A) 1.5, 1.45 and 0.0263 (B) 15, 14.5 and 0.0263
(C) 1.5, 14.5 and 0.0263 (D) 1.5, 1.45 and 0.263

Solution

(A) Density of solution = M/V [Let the volume of solution is 1000 mL]

$$\text{Mass of solution} = \rho \times V = 1.202 \times 1000 = 1202 \text{ g}$$

Now, 20% (w/w) KI means amount of KI is

$$w = \frac{1202 \times 20}{100} = 240.4 \text{ g}$$

Therefore,
$$\text{Molality} = \frac{\frac{240.4}{166}}{(1.202 - 0.2404)} = 1.5 \text{ mol kg}^{-1}$$

$$\text{Molarity} = \frac{\frac{240.4}{166}}{1} = 1.45 \text{ mol L}^{-1}$$

and
$$\text{Mole fraction} = \frac{240.4}{166} = 0.0263$$

$$\frac{240.4}{166} + \frac{961.6}{18}$$

7. Vapor pressure of CCl_4 at 25°C is 143 mm Hg. If 0.5 g of a non-volatile solute (molecular weight 65) is dissolved in 100 mL CCl_4 , find the vapor pressure of the solution. (Given that density of $\text{CCl}_4 = 1.58 \text{ g cm}^{-3}$).

- (A) 141.93 mm Hg (B) 94.39 mm Hg (C) 199.34 mm Hg (D) 143.99 mm Hg

Solution

(A) According to Raoult's law

$$x_{\text{solute}} = \frac{p_0 - p_s}{p_0} = \frac{0.5}{\frac{0.5}{65} + \frac{158}{154}} \Rightarrow \frac{143 - p_s}{143} = 0.00745$$

Solving, we get $p_s = 141.93 \text{ mm of Hg}$.

8. Two liquids A and B are mixed at temperature T in a certain ratio to form an ideal solution; it was found that the partial vapor pressure of A, that is, p_A is equal to p_B the vapor pressure of B for the liquid mixture. What is the total vapor pressure of the liquid mixture in terms of p_A° and p_B° ?

- (A) $\frac{p_A^\circ p_B^\circ}{p_A^\circ + p_B^\circ}$ (B) $\frac{2p_A^\circ p_B^\circ}{p_A^\circ + p_B^\circ}$ (C) $\frac{p_A^\circ}{p_A^\circ + p_B^\circ}$ (D) $\frac{2p_B^\circ}{p_A^\circ + p_B^\circ}$

Solution

(B) $p_A = x_A p_A^\circ$ and $p_B = x_B p_B^\circ = p_B^\circ (1 - x_A)$

If $p_A = p_B$, then
$$x_A = \frac{p_B^\circ}{p_A^\circ + p_B^\circ}; \quad p_T = 2p_A = \frac{2p_A^\circ p_B^\circ}{p_A^\circ + p_B^\circ}$$

For $p_A = p_B$, $x_A = \frac{p_B^\circ}{p_A^\circ + p_B^\circ}$

$$p_{\text{Total}} = p_A + p_B = \frac{2p_A^\circ p_B^\circ}{p_A^\circ + p_B^\circ}$$

9. The partial pressure of ethane over a solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what shall be the partial pressure of the gas?

- (A) 76.2 bar (B) 762 bar (C) 0.762 bar (D) 7.62 bar

Solution

(D) According to Henry's Law: $p_1 = k_H \times x_1$ and $p_2 = k_H x_2$

$$p_1 = 1 \text{ bar} : x_1 = \frac{6.56 \times 10^{-3} \text{ g}}{30} \quad \text{(i)}$$

$$p_2 = ? : x_2 = \frac{5.00 \times 10^{-2} \text{ g}}{30} \quad \text{(ii)}$$

From Eqs. (1) and (2), we have

$$\frac{p_1}{p_2} = \frac{x_1}{x_2} \Rightarrow p_2 = \frac{5 \times 10^{-2}}{6.56 \times 10^{-3}} = 7.62 \text{ bar}$$

10. Henry's law constant for the molality of methane in benzene at 298 K is 4.27×10^5 mm Hg. Determine the solubility of methane in benzene at 298 K under 760 mm Hg.

- (A) 178×10^{-3} (B) 178×10^{-5} (C) 356×10^{-5} (D) 356×10^{-3}

Solution

(B) Given that $k_H = 4.27 \times 10^5$ mm Hg, $p = 760$ mm Hg and $x =$ solubility

$$p = k_H \cdot x \Rightarrow x = \frac{p}{k_H} = \frac{760}{4.27 \times 10^5} = 1.78 \times 10^{-5}$$

11. The relative lowering of vapor pressure is equal to the mole fraction of the solute. This law is called

- (A) Henry's law (B) Raoult's law (C) Ostwaki's law (D) Arrhenius law.

Solution

(B) $\frac{p^\circ - p_s}{p^\circ} = x_{\text{solute}}$

12. An aqueous solution of methanol has vapor pressure

- (A) equal to that of water. (B) equal to that of methanol.
(C) more than that of water. (D) less than that of water.

Solution

(C) Due to more volatile nature of methanol, it forms more vapor than H_2O at same T .

13. Which of the following statements is correct, if the intermolecular forces in liquids A, B and C are in the order $A < B < C$?

- (A) B evaporates more readily than A (B) B evaporates less readily than C
(C) A and B evaporate at the same rate (D) A evaporates more readily than C

Solution

(D) Due to weakest intermolecular forces; evaporation is fastest in A.

14. An ideal solution was obtained by mixing methanol and ethanol. If the partial vapor pressure of methanol and ethanol are 2.619 kPa and 4.556 kPa, respectively, the composition of vapor (in terms of mole fraction) will be

- (A) 0.634 MeOH, 0.365 EtOH (B) 0.365 MeOH, 0.635 EtOH
(C) 0.574 MeOH, 0.326 EtOH (D) 0.173 MeOH, 0.827 EtOH.

Solution

(B) As $n \propto p$, we have

$$p_{\text{methanol}} = \frac{p_{\text{methanol}}}{p_{\text{ethanol}} + p_{\text{methanol}}} = \frac{2.619}{2.619 + 4.556} = 0.365 \text{ and } p_{\text{ethanol}} = \frac{4.556}{2.619 + 4.556} = 0.635$$

15. At 35°C the vapor pressure of CS₂ is 512 mm Hg, and of acetone, CH₃COCH₃, is 344 mm Hg. A solution of CS₂ and acetone in which the mole fraction of CS₂ is 0.25 has a total vapor pressure of 600 mm Hg. Which of the following statements about solution of acetone–CS₂ is true?

- (A) A mixture of 100 mL of acetone and 100 mL of CS₂ has a total volume of 200 mL.
(B) When acetone and CS₂ are mixed at 25°C, heat must be absorbed in order to produce a solution at 35°C.
(C) When acetone and CS₂ are mixed at 35°C, heat is released.
(D) Raoult's law is obeyed by both CS₂ and acetone for the solution in which the mole fraction of CS₂ is 0.25.

Solution

(B) For a solution of acetone + CS₂: $\Delta H = +ve.$ Therefore, absorption of heat takes place and endothermic process is favorable.

16. What is the composition of the vapor that is in equilibrium at 30°C with a benzene–toluene solution with a mole fraction of benzene of 0.400? ($p_B^\circ = 119$ torr and $p_T^\circ = 37.0$ torr)

- (A) 1.237 (B) 2.237 (C) 3.237 (D) 0.237

Solution

(D) Total pressure of the solution is given by (Raoult's law)

$$p_{\text{Total}} = X_B p_B^\circ + X_T p_T^\circ = 0.4 \times 119 + 0.6 \times 37 = 47.6 + 22.2 = 69.8 \text{ torr}$$

Applying Dalton's law for mole fraction in vapor phase, we get

$$Y_B = \frac{p_B}{p_{\text{Total}}} = \frac{p_B^\circ X_B}{p_A^\circ X_A + p_B^\circ X_B} = \frac{0.4 \times 119}{69.8} = 0.763$$

$$Y_T = 1 - 0.763 = 0.237$$

17. At a given temperature, total vapor pressure in torr of a mixture of volatile components A and B is given by $p_{\text{total}} = 120 - 75x_B$, hence, vapor pressure of pure A and B, respectively, (in torr) are

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

Solution

(C) We have $p = x_A p_A^\circ + x_B p_B^\circ = p_A^\circ x_A + p_B^\circ (1 - x_A) = x_A (p_A^\circ - p_B^\circ) + p_B^\circ$

Now, $p_T = 120 - 75x_B$. Comparing with the above equation, we get

$$p_A^\circ = 120 \text{ torr and } p_B^\circ = 120 - 75 = 45 \text{ torr}$$

18. Liquids A and B form an ideal solution and the former has stronger intermolecular forces. If x_A and y_A are the mole fractions of A in the solution and vapor phase in equilibrium, then

- (A) $y_A/x_A = 1$ (B) $y_A/x_A > 1$ (C) $y_A/x_A < 1$ (D) $y_A + x_A = 1$

Solution

(C) $Y_A = \frac{p_A}{p} = \frac{p_A^\circ x_A}{p} \Rightarrow \frac{Y_A}{X_A} = \frac{p_A^\circ}{p} < 1$ (Since the liquid A is less volatile, $p_A^\circ < p$)

19. Benzene and toluene form ideal solution over the entire range of composition. The vapor pressure of pure benzene and naphthalene at 300 K are 50.71 mm Hg and 32.06 mm Hg, respectively. What will be the mole fraction of benzene in vapor phase if 80 g of benzene is mixed with 100 g of naphthalene?

- (A) 0.0675 (B) 0.675 (C) 0.35 (D) 0.5

Solution

$$(B) p_T = X_A p_A^0 + x_B p_B^0$$

$$y_A = \frac{p_A}{p_T} \text{ or } y_B = \frac{p_B}{p_T}$$

Solving, we get $Y_B = 0.675$

20. 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 vapor pressure of pure liquid B was found to be 500 torr. What will be the vapor pressure of pure liquid A and its vapor pressure in the solution, respectively, if the total vapor pressure of the solution is 475 torr?

- (A) 28.7 torr and 32 torr (B) 280.7 torr and 32 torr
(C) 28.7 torr and 3.2 torr (D) 280.7 torr and 3.2 torr

Solution

$$(B) p_T = p_A + p_B = p_A^0 x_A + p_B^0 x_B = p_B (1 - x_A) x_A = \frac{100}{\frac{1000}{180} + \frac{100}{140}} = 0.11$$

Therefore, $0.75 = p_A^0 \times 0.11 + 500(1 - 0.11) \Rightarrow p_A^0 = \frac{310}{311} = 280.7 \text{ torr}$

Now, $p_A = p_A^0 \times X_A = 280.7 \times 0.11 = 32 \text{ torr}$

21. Liquids A and B form an ideal solution, then which of the following is true?

- (A) The enthalpy of mixing is zero. (B) The entropy of mixing is zero.
(C) The free energy of mixing is zero. (D) The ΔV_{mix} of mixing is not zero.

Solution

(A) For an ideal solution $\Delta H_{\text{mix}} = 0$; $\Delta S_{\text{mix}} > 0$; $\Delta G_{\text{mix}} < 0$, $\Delta V_{\text{mix}} = 0$

22. 100 mL of liquid A was mixed with 25 mL of liquid B to give a non-ideal solution of A–B mixture. The volume of this mixture would be

- (A) 75 mL. (B) either less or more than 125 mL.
(C) close to 125 mL but not exceeding 125 mL. (D) just more than 125 mL.

Solution

(B) Either less than or more than 125 mL, because $\Delta V_{\text{mix}} \neq 0$ for non-ideal solution.

23. If p_A^0 is the vapor pressure of a pure liquid A and the mole fraction of A in the mixture of two liquids A and B is x , the partial vapor pressure of A is

- (A) $(1-x) p_A^0$ (B) $x p_A^0$ (C) $(x/1-x) p_A^0$ (D) $[(1-x)/x] p_A^0$

Solution

(B) $p_A = x p_A^0$ (Raoult's law)

24. In a mixture of A and B if the mole fraction of the component A in vapor phase is x_1 and mole fraction of component A in liquid mixture is x_2 (p_A° = vapor pressure of pure A; p_B° = vapor pressure of pure B), then total vapor pressure of the liquid mixture is:

- (A) $\frac{p_A^\circ x_2}{x_1}$ (B) $\frac{p_A^\circ x_1}{x_2}$ (C) $\frac{p_B^\circ x_1}{x_2}$ (D) $\frac{p_B^\circ x_2}{x_1}$

Solution

(A) According to Raoult's law, $p_A = p_A^\circ x_2$ and Dalton law, $p_A = p_{\text{Total}} x_1$

Therefore,
$$p_{\text{Total}} = p_A^\circ \times \frac{x_2}{x_1}$$

25. Heptane and octane form an ideal solution. At 373 K, the vapor pressures of the two liquid components are 105.2 kPa and 46.8 kPa, respectively. What will be the vapor pressure of a mixture of 26.0 g of heptane and 35 g of octane?

- (A) 7.308 kPa (B) 73.08 kPa (C) 730.8 kPa (D) 7308 kPa

Solution

(B) We know that $p = x_A p_A^\circ + x_B p_B^\circ$. Given that $p_{\text{Heptane}}^\circ = 105.2$ kPa and $p_{\text{Octane}}^\circ = 46.8$ kPa and

$n_{\text{heptane}} = \frac{26}{100}$ and $n_{\text{octane}} = \frac{35}{114}$. Therefore,

$$p_{\text{Total}} = p_{\text{Heptane}}^\circ x_{\text{Heptane}} + p_{\text{Octane}}^\circ x_{\text{Octane}} = 105.2 \times \left(\frac{\frac{26}{100}}{\frac{26}{100} + \frac{35}{114}} \right) + 46.8 \times \left(\frac{\frac{35}{114}}{\frac{26}{100} + \frac{35}{114}} \right) = 73.08 \text{ kPa}$$

26. At 40°C, the vapor pressure in torr of methanol and ethanol solution is $p = 119x + 135$, where x is the mole fraction of methanol. Hence,

- (A) vapor pressure of pure methanol is 119 torr.
 (B) vapor pressure of pure ethanol is 135 torr.
 (C) vapor pressure of equimolar mixture of each is 127 mm Hg.
 (D) mixture is completely immiscible.

Solution

(B) $p_{\text{Total}} = p_A^\circ x_A + p_B^\circ x_B = p_A^\circ x_A + p_B^\circ (1 - x_A) = p_A^\circ x_A + p_B^\circ - p_B^\circ x_A = x_A (p_A^\circ - p_B^\circ) + p_B^\circ$

Comparing it with $p = 119x + 135$, we get $p_{\text{C}_2\text{H}_5\text{OH}}^\circ = 135$ torr.

27. A solution that obeys Raoult's law is

- (A) non-ideal. (B) colloid. (C) ideal. (D) saturated.

Solution

(C) Ideal solutions obey Raoult's law over a wide range of temperature and pressure.

28. In a mixture, A and B components show negative deviation as

- (A) ΔV_{mix} is positive.
 (B) ΔH_{mix} = negative.
 (C) A–B interaction is weaker than A–A and B–B interaction.
 (D) None of the above reason is correct.

Solution

(B) For non-ideal solution with negative deviation, $\Delta H_{\text{mix}} = -ve$, $\Delta V_{\text{mix}} = -ve$ and $A-B > A-A$ and $B-B$ interactions.

29. The vapor pressure of a solvent decreased by 10 mm Hg when a non-volatile solute was added to the solvent. The mole fraction of the solute in solution is 0.2. What would be mole fraction of the solvent if decrease in vapor pressure is 20 mm Hg?

- (A) 0.8 (B) 0.6 (C) 0.4 (D) 0.2

Solution

(B) According to relative lowering in vapor pressure,

$$\frac{p^\circ - p_s}{p^\circ} = x_{\text{solute}}$$

Case 1: $\frac{10}{p^\circ} = 0.2 \Rightarrow p^\circ = \frac{10}{0.2}$

Case 2: $\frac{20}{p^\circ} = x_{\text{solute}}$

Therefore, $x_{\text{solute}} = \frac{20}{10} \times 0.2 = 0.4$ and $x_{\text{solvent}} = 1 - 0.4 = 0.6$

30. The vapor pressure of ethyl alcohol at 25°C is 59.2 torr. The vapor pressure of a very dilute solution of urea in ethyl alcohol is 51.3 torr. What is the molality of the solution?

- (A) 29 molal (B) 2.9 molal (C) 0.29 molal (D) 1.5 molal

Solution

(B) $m = \left(\frac{p^\circ - p_s}{p^\circ} \right) \times \frac{1000}{M_B} = \left(\frac{59.2 \times 51.3}{59.2} \right) \times \frac{1000}{46} \Rightarrow m = 2.9 \text{ molal}$

31. Which of the following liquid pairs shows a positive deviation from Raoult's law?

- (A) Water–nitric acid (B) Benzene–methanol
(C) Water–hydrochloric acid (D) Acetone–chloroform

Solution

(B) The solutions in which solute has van't Hoff < 1 will exhibit positive deviation. For example, Benzene + Methanol.

32. All form ideal solutions except

- (A) C₂H₅Br and C₂H₅I (B) C₂H₅Cl and C₆H₅Br
(C) C₆H₆ and C₆H₅CH₃ (D) C₂H₅I and C₂H₅OH

Solution

(D) C₂H₅OH will be having intermolecular H-bonding, whereas in case of C₂H₅I no H-bonding is there. Hence, a non-ideal solution is formed as $\Delta H \neq 0$.

33. The vapor pressure of a pure liquid A is 40 mm Hg at 310 K. The vapor pressure of this liquid in a solution with liquid B is 32 mm Hg. Mole fraction of A in the solution, if it obeys Raoult's law, is:

- (A) 0.8 (B) 0.5 (C) 0.2 (D) 0.4

Solution

(A) Given that $p_A^\circ = 40 \text{ mm Hg}$ and $p_A = 32 \text{ mm Hg}$. Hence,

$$p_A = x_A \times p_A^\circ$$

$$32 = x_A \times 40$$

$$x_A = \frac{32}{40} = 0.8$$

34. Mole fraction of the component A in vapor phase is x_1 and mole fraction of component A in liquid mixture is x_2 ($p_A^\circ =$ vapor pressure of pure A), then the total vapor pressure of the liquid mixture is

- (A) $\frac{p_A^\circ x_2}{x_1}$ (B) $\frac{p_A^\circ x_1}{x_2}$ (C) $\frac{p_B^\circ x_1}{x_2}$ (D) $\frac{p_B^\circ x_2}{x_1}$

Solution

(A) According to Raoult's law, $p_A = p_A^\circ x_2$ and Dalton law, $p_A = p_{\text{Total}} x_1$

Therefore,
$$p_{\text{Total}} = p_A^\circ \times \frac{x_2}{x_1}$$

35. Negative deviations from Raoult's law are exhibited by binary liquid mixtures

(A) in which the molecules tend to attract each other and hence their escape into the vapor phase is retarded.

(B) in which the molecules tend to repel each other and hence their escape into the vapor phase is retarded.

(C) in which the molecules tend to attract each other and hence their escape into the vapor phase is speeded up.

(D) in which the molecules tend to repel each other and hence their escape into the vapor phase is speeded up.

Solution

(A)

36. A non-ideal solution was prepared by mixing 30 mL chloroform and 50 mL acetone. The volume of mixture will be

- (A) >80 mL. (B) <80 mL. (C) =80 mL. (D) none of these.

Solution

(B) Chloroform and acetone form a non-ideal solution, CHCl_3 and acetone have greater attraction when mixed together than alone, and hence, show negative deviation from Raoult's law, that is,

$$\Delta V_{\text{mix}} < 0; \quad \Delta H_{\text{mix}} < 0$$

Total volume of solution = < {30 + 50 mL} or < 80 mL

37. A solution of pair of volatile liquids A and B will show positive deviation from Raoult's law if it fulfills the following conditions:

- (A) $p_A > p_A^\circ x_A$ and $p_B > p_B^\circ x_B$ (B) The intermolecular forces of A–A, B–B > A–B.
 (C) $\Delta H_{\text{mix}} > 0$ and $\Delta V_{\text{mix}} > 0$ (D) All of these

Solution

(D)

38. Which of the following is not a colligative property?

- (A) Osmotic pressure (B) Elevation in boiling point.
 (C) Vapor pressure. (D) Depression in freezing point.

Solution

(C) Vapor pressure is not a colligative property; rest are.

39. The colligative properties of a solution depend on

- (A) nature of solute particles present in it. (B) nature of solvent used.
 (C) number of solute particles present in it (D) number of moles of solvent only.

Solution

(C) Conceptual

40. A dry air is passed through the solution, containing the 10 g of solute and 90 g of water and then it is passed through pure water. There is the depression in weight of solution by 2.5 g and of pure solvent by 0.05 g. Calculate the molecular weight of solute.

- (A) 50 (B) 180 (C) 100 (D) 25

Solution

(C) From Ostwald and Walker experiment,

$$\frac{\text{Loss in mass of solvent bulb}}{\text{Loss in mass of solution bulb}} = \frac{n_{\text{solute}}}{n_{\text{solvent}}} \Rightarrow \frac{0.05}{2.5} = \frac{10/M}{90/18} \Rightarrow M = 100$$

41. The vapor pressure of a solvent decreased by 10 mm Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be mole fraction of the solvent if decrease in vapor pressure is 20 mm Hg?

- (A) 0.8 (B) 0.6 (C) 0.4 (D) 0.2

Solution

$$(B) \frac{p^{\circ} - p_s}{p^{\circ}} = x_{\text{solute}}$$

Case 1: $\frac{10}{p^{\circ}} = x_{\text{solute}} \Rightarrow \frac{10}{p^{\circ}} = 0.2$

Case 2: $\frac{20}{p^{\circ}} = x_{\text{solute}} \Rightarrow x_{\text{solute}} = 0.4$ and $x_{\text{solvent}} = 1 - 0.4 = 0.6$

42. The vapor pressure of water is 12.3 kPa at 300 K. What will be the vapor pressure of 1 molal solution if a non-volatile solute is added to it?

- (A) 24.16 kPa (B) 1.208 kPa (C) 2.416 kPa (D) 12.08 kPa

Solution

$$(D) M_{\text{solute}} = \frac{x_{\text{solute}} \times 1000}{x_{\text{solvent}} \times (\text{GMW})_{\text{solvent}}}; \frac{p^{\circ} - p_s}{p^{\circ}} = x_{\text{solute}}$$

From 1 molal solution,

Number of moles of solute = 1

$$\text{Number of moles of solvent} = \frac{1000}{18} = 55.5$$

$$\frac{12.3 - p_s}{12.3} = \frac{1}{1 + 55.5}$$

$$12.3 \times 56.5 - p_s \times 56.5 = 12.3$$

$$p_s = \frac{682.55}{56.5} = 12.08 \text{ kPa}$$

43. What will be the mass of a non-volatile solute (molar mass 40 mol^{-1} which should be dissolved in 114 g octane to reduce its vapor pressure to 80%?

- (A) 8 g (B) 4 g (C) 2 g (D) 16 g

Solution

$$(A) \frac{p^{\circ} - p_s}{p^{\circ}} = \frac{20}{100} = \frac{n_A}{n_A + n_B} = \frac{\frac{w}{40}}{\frac{w}{40} + \frac{114}{114}}$$

Let the vapor pressure of pure octane = p°

Then the vapor pressure of solution, $p_s = \frac{p^\circ \times 80}{100}$

Hence,

$$\frac{p^\circ - p_s}{p^\circ} = x_{\text{solute}} \Rightarrow \frac{p^\circ - p^\circ \times 0.8}{p^\circ} = \frac{w_{\text{solute}}}{114}$$

$$0.2 \times 40 = w_{\text{solute}} \Rightarrow w_{\text{solute}} = 8 \text{ g}$$

44. An aqueous solution freezes at -2.55°C . What is its boiling point? (Given that K_b of $\text{H}_2\text{O} = 0.52 \text{ K molal}^{-1}$ and K_f of $\text{H}_2\text{O} = 1.86 \text{ K molal}^{-1}$.)?

- (A) 107.0°C (B) 100.6°C (C) 100.1°C (D) 100.7°C

Solution

$$(D) \left. \begin{array}{l} \Delta T_f - 2.25^\circ\text{C} = K_f \cdot m \\ \Delta T_b = K_b \cdot m \end{array} \right\} \Delta T_b = 2.25 \times \frac{K_b}{K_f} = 2.25 \times \frac{0.52}{1.86}^\circ\text{C} = 0.7^\circ\text{C}$$

or $T_b = 100 + 0.7 = 100.7^\circ\text{C}$

For a same solution ΔT_b is larger than ΔT_f (pure substances have sharp melting point).

45. Vapor pressure of water at 293 K is 17.535 mm Hg. What will be the vapor pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water?

- (A) 17.44 mm Hg (B) 174.4 mm Hg (C) 34.88 mm Hg (D) 8.72 mm Hg

Solution

(A) Relative lowering of vapor pressure is

$$\frac{p^\circ - p_s}{p^\circ} = \frac{n_A}{n_A + n_B} \Rightarrow \frac{17.5 - p_s}{17.5} = \frac{\frac{25}{180}}{\frac{25}{180} + \frac{450}{18}}$$

Solving, we get $p_s = 17.5 - \frac{25 \times 17.5}{4525} = 17.4 \text{ mm Hg}$

46. The boiling point of an aqueous solution of a non-volatile solute is 100.15°C . What is the freezing point of an aqueous solution obtained by diluting the above solution with an equal volume of water? The values of K_b and K_f for water are $0.412^\circ\text{C molal}^{-1}$ and $1.86^\circ\text{C molal}^{-1}$, respectively.

- (A) -0.544°C (B) -0.512°C (C) -0.272°C (D) -1.86°C

Solution

(C) We know that $\Delta T_b = K_b \times m$ and $\Delta T_f = K_f \times m$

On diluting the above solution with equal volume of water molality becomes approximately half; (as

concentration $\times \frac{1}{\text{dilution}}$)

$$\frac{\Delta T_f}{\Delta T_b} = \frac{K_f}{K_b} \times \frac{1}{2} \Rightarrow \frac{\Delta T_f}{0.15} = \frac{1.86}{0.512} \times \frac{1}{2} \Rightarrow \Delta T_f = 0.272^\circ\text{C}$$

47. The boiling point elevation constant for toluene is $3.32 \text{ K kg mol}^{-1}$, the normal boiling point of toluene is 110.7°C . The enthalpy of vaporization of toluene would be nearly

- (A) 17.0 kJ mol^{-1} (B) 34.0 kJ mol^{-1} (C) 51.0 kJ mol^{-1} (D) 68.0 kJ mol^{-1}

Solution

$$(B) K_b = \frac{R \times T_b^2}{1000 L_v} \text{ or } \frac{MR \times T_b^2}{1000 \Delta_{\text{vap}} H} \left(\text{as } L_v = \frac{\Delta_{\text{vap}} H}{M} \right)$$

$$\text{Therefore, } \Delta_{\text{vap}} H = \frac{M \times R \times T_b^2}{K_b \times 1000} = \frac{92 \times 8.34(383.7)^2}{3.32 \times 1000} \text{ kJ mol}^{-1} = 34.0 \text{ kJ mol}^{-1}$$

48. The molal elevation constant is the ratio of the elevation in boiling point to
(A) molarity. (B) molality. (C) mole fraction of solute. (D) mole fraction of solvent.

Solution

$$(B) \Delta T_b = K_b \times m \Rightarrow K_b = \frac{\Delta T_b}{m}$$

49. 0.15 g of a substance dissolved in 15 g of a solvent is boiled at a temperature higher by 0.216°C than that of the pure solvent. Find out the molecular weight of the substance. (K_f for solvent is 2.16 K kg mol⁻¹).

- (A) 1.01 g mol⁻¹ (B) 10.1 g mol⁻¹ (C) 100 g mol⁻¹ (D) 1000 g mol⁻¹

Solution

$$(D) \Delta T_b = K_b \times m \Rightarrow m = \frac{0.216}{2.16} = 0.1$$

$$\text{where } m = \frac{w_A}{M_A \times w_B} \Rightarrow M_A = \frac{w_A}{m \times w_B} = \frac{15}{0.1 \times 0.15} = 1000 \text{ g mol}^{-1}$$

50. Y g of non-volatile organic substance of molecular mass M is dissolved in 250 g benzene. Molal elevation constant of benzene is K_b . Elevation in its boiling point is given by

- (A) $\frac{M}{K_b Y}$ (B) $\frac{4K_b Y}{M}$ (C) $\frac{K_b Y}{4M}$ (D) $\frac{K_b Y}{M}$

Solution

$$(B) \Delta T_b = K_b \times m$$

$$\text{However, molality is } m = \frac{Y}{M \times \frac{250}{1000}}$$

$$\text{Therefore, } \Delta T = \frac{1000 \times K_b \times Y}{250 \times M} = \frac{4K_b Y}{M}$$

51. The molal boiling point constant of water is 0.573°C kg mol⁻¹. When 0.1 mol of glucose is dissolved in 1000 g of water, the solution boils under atmospheric pressure at

- (A) 100.513°C (B) 100.0573°C (C) 100.256°C (D) 101.025°C

Solution

$$(B) \Delta T_b = K_b m = 0.573 \times 0.1 = 0.0573^\circ\text{C}$$

The boiling point of solution is

$$\text{Boiling point of pure solvent} + \Delta T_b = 100 + 0.0573 = 100.0573^\circ\text{C}$$

52. It is more a convenient to obtain the molecular weight of an unknown solute by measuring the freezing point depression than by measuring the boiling point elevation because

- (A) freezing point depression is a colligative property whereas boiling point elevation is not.
(B) freezing point depressions are larger than boiling point elevations for the same solution.
(C) freezing point depressions are smaller than boiling point elevations for the same solution.
(D) freezing point depression depends more on the amount of the solute than boiling point elevation.

Solution

(B)

53. The freezing point of aqueous solution contains 5% by mass urea, 1.0% by mass KCl and 10% by mass of glucose is: (Given that K_f of $H_2O = 1.86 \text{ K molal}^{-1}$.)

- (A) 290.2 K (B) 285.5 K (C) 269.93 K (D) 250 K

Solution

(C) $\Delta T_f = \Delta T_f$ for glucose + ΔT_f for KCl + ΔT_f for urea for glucose and urea ($i=1$)

Therefore,
$$\Delta T_f = \frac{1000 \times 1.86 \times 10}{100 \times 180} + \frac{1000 \times 1.86 \times 1 \times 2}{74.5 \times 100} + \frac{1000 \times 1.86 \times 5}{100 \times 60} = 3.069 \text{ K}$$
 and for KCl ($i=2$)

Freezing point = $273 - 3.069 = 269.93 \text{ K}$

54. In 100 g of naphthalene, 2.423 g of S was dissolved. Melting point of naphthalene = 80.1°C , $\Delta T_f = 661^\circ\text{C}$ and latent heat of fusion, $L_{\text{fus}} = 35.7 \text{ cal g}^{-1}$ of naphthalene. Then the molecular formula of sulphur added is

- (A) S_2 (B) S_4 (C) S_6 (D) S_8

Solution

(D)
$$M_2 = \frac{1000 K_f w_2}{w_1 \Delta T_f} = \frac{1000 w_2}{w_1 \Delta T_f} \times \frac{RT_0^2}{1000 L_f} = \frac{1000 \times 2.423}{100 \times 0.661} \times \frac{2(353.1)^2}{1000 \times 35.7} = 256 \text{ g mol}^{-1}$$

As $n \times 32 = 256 \Rightarrow n = \frac{256}{32} = 8$.

Hence, the molecule is S_8 .

55. Osmotic pressure of blood is 7.65 atm at 310 K. An aqueous solution of glucose that will be isotonic with blood is _____ % (w/V).

- (A) 5.41% (B) 3.54% (C) 4.53% (D) 53.4%

Solution

(A) We know $pV = nRT$ for glucose and blood. If isotonic, $p_{\text{glucose}} = p_{\text{blood}}$

Thus,
$$7.65 \times V = \frac{W}{180} \times 0.0821 \times 310$$

or
$$\frac{W}{V} = 54 \text{ g L}^{-1} = 5.41\% \text{ (wt vol}^{-1}\text{)}$$

56. A 5% solution (by mass) of cane sugar in water has freezing point of 271 K. What will be the freezing point of 5% glucose in water if freezing point of pure water is 273.15 K?

- (A) 273.15 K (B) 279.07 K (C) 260.07 K (D) 203.07 K

Solution

(C) Let the mass of solution be 100 g, then $\Delta T_f = K_f m$.

Case 1:
$$(273.15 - 271) = K_f \times \frac{5/242}{95 \times 10^{-3}} \quad (1)$$

Case 2:
$$(273.15 - T_{f(\text{glucose})}) = K_f \times \frac{5/180}{95 \times 10^{-3}} \quad (2)$$

Solving Eqs. (1) and (2), we get

$$T_{f(\text{glucose})} = 269.07 \text{ K}$$

57. Two elements A and B form compounds having formulas 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 $5.1 \text{ K kg mol}^{-1}$. What will be the atomic masses of A and B, respectively?

- (A) 26 u, 42.5 u (B) 52 u, 42.5 u (C) 26 u, 85 u (D) 52 u, 85 u

Solution

(A)

Case 1: For compound AB_2 , let the molar mass be M_1 ; then

$$\Delta T_f = K_f m$$

$$2.3 = 5.1 \times \frac{1}{\frac{M}{20 \times 10^{-3}}} \quad (1)$$

Case 2: For compound AB_4 , let the molar mass is M_2 . Then $\Delta T_f = K_f m$

$$1.3 = 5.1 \times \frac{1}{\frac{M}{20 \times 10^{-3}}} \quad (2)$$

Solving Eq. (1), we get: $M_1 = 111 \text{ g mol}^{-1}$ and from Eq. (2), we get $M_2 = 196 \text{ g mol}^{-1}$. Now,

If M_A and M_B are respective atomic masses of A and B, then

$$\text{For } \text{AB}_2: \quad M_A + 2M_B = 111 \quad (3)$$

$$\text{For } \text{AB}_4: \quad M_A + 4M_B = 196 \quad (4)$$

Solving Eqs. (3) and (4), we get $M_B = 42.5 \text{ u}$ (approx.); $M_A = 26 \text{ u}$ (approx.).

58. The molal freezing point constant for water is $1.86 \text{ K molal}^{-1}$. If 34.2 g of cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is dissolved in 1000 g of water, the solution will freeze at

- (A) -1.86°C (B) 1.86°C (C) -3.92°C (D) 3.42°C

Solution

$$(A) \Delta T_f = K_f \times m \text{ where } m = \frac{W_A}{M_A \times W_B (\text{kg})}$$

$$\Delta T_f = \frac{1000 \times K_f \times w}{MW} = \frac{1000 \times 1.86 \times 34.2}{100 \times 342} = 1.86^\circ\text{C}$$

$$T_f = 0 - 1.86 = -1.86^\circ\text{C}$$

59. Which one of the following pairs of solution can we expect to be isotonic at the same temperature?

- (A) 0.1 M urea and 0.1 M NaCl (B) 0.1 M urea and 0.2 M MgCl_2
 (C) 0.1 M NaCl and 0.1 M Na_2SO_4 (D) 0.1 M $\text{Ca}(\text{NO}_3)_2$ and 0.1 M Na_2SO_4

Solution

(D) We know that $\Pi = iCRT$. For $\Pi_1 = \Pi_2$, C_1 should be equal to C_2 at constant T .

Now, i of NaCl = 2, i of MgCl_2 = 3; i of Urea = 1; i of Na_2SO_4 = 3; $\text{Ca}(\text{NO}_3)_2$ = 3. Therefore,

$$C = 3 \times 0.1 = 0.3 \text{ for both } \text{Ca}(\text{NO}_3)_2 \text{ and } \text{Na}_2\text{SO}_4.$$

60. What is the percent by mass of iodine needed to reduce the freezing point of benzene to 3.5°C ? The freezing point and cryoscopic constant of pure benzene are 5.5°C and $5.12 \text{ K molal}^{-1}$, respectively, are

- (A) 20% (B) 90.1% (C) 30% (D) 9.01%

Solution

(D) $\Delta T_f = T_f^\circ - T_f = K_f m$. Therefore,

$$m = \frac{\Delta T_f}{K_f} = \frac{2}{5.12} = 0.39 \text{ molal}$$

But, $m = \frac{W_A}{M_A \times W_B} \Rightarrow W_A = m \times M_A \times W_B \text{ (kg)}$

Hence, $\text{mass\%} = \frac{0.39 \times 254 \times 100}{1099.06} = 9.01\%$

61. The amount of ice that will separate on cooling a solution containing 50 g of ethylene glycol in 200 g water to -9.3°C is: [$K_f = 1.86 \text{ K molal}^{-1}$]

- (A) 38.71 g (B) 38.71 mg (C) 42 g (D) 42 mg

Solution

(A) $\Delta T_f = K_f \times m$. During freezing, only solvent freezes and separates out.

$$\Delta T = \frac{1000 \times K_f \times w}{W \times M} \Rightarrow 9.3 = \frac{1000 \times 1.86 \times 50}{62 \times W} = 161.29 \text{ g}$$

Thus, the ice separated is $200 - 161.29 = 38.71 \text{ g}$

62. At 300 K, 36 g of glucose present in a liter of its solution has osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bar at the same temperature, what would be its concentration?

- (A) 0.061 M (B) 0.61 M (C) 0.0061 M (D) 6.1 M

Solution

(A) $\Pi = CRT$, so $\Pi_1 = C_1 R_1 T_1$ and $\Pi_2 = C_2 R_2 T_2$. Given that $V_1 = V_2$ and $T_1 = T_2$, so

$$\frac{\Pi_1}{C_1} = \frac{\Pi_2}{C_2} \Rightarrow C_2 = \frac{\Pi_2 C_1}{C_2} = \frac{1.52 \times 36}{4.98 \times 180} = 0.061 \text{ M}$$

63. Nitrobenzene freezes at 278.98°C , 0.25 molal solution of a solute in nitrobenzene causes freezing point depression of 2°C . K_f for nitrobenzene is

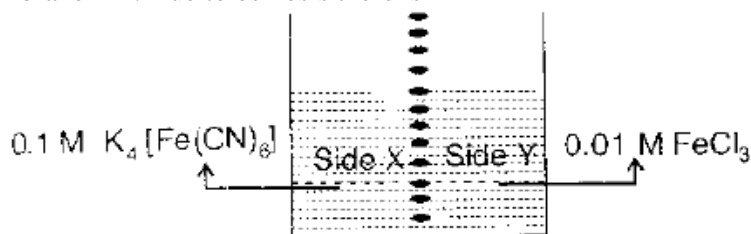
- (A) 2 K molal^{-1} (B) 4 K molal^{-1} (C) 8 K molal^{-1} (D) 12 K molal^{-1}

Solution

$$\Delta T_f = K_f \times m \Rightarrow K_f = \frac{\Delta T_f}{m} = \frac{2}{0.25} = 8 \text{ km}^{-1}$$

(C)

64. FeCl_3 on reaction with $\text{K}_4[\text{Fe}(\text{CN})_6]$ in aqueous solution gives blue color. These are separated by a semipermeable membrane AB. Due to osmosis there is



- (A) blue color formation in side X. (B) blue color formation in side Y.
(C) blue color formation in both sides. (D) no blue color formation.

Solution

(D) Due to osmosis, solvent (i.e., water) from Y side migrates towards X side. Since solute, that is, FeCl_3 , is not migrating, there is no blue color formation.

65. Consider the following cases:

I: 2 M CH₃COOH solution in benzene at 27°C where there is formation to the extent of 100%.

II: 0.5 M KCl aqueous solution at 27°C, which ionizes 100%.

Which is/are true statement(s)?

- (A) Both are isotonic. (B) I is hypertonic.
(C) II is hypertonic. (D) None is correct.

Solution

(A) $\frac{\Pi_1}{\Pi_2} = \frac{C_1}{C_2} = \frac{2/2}{0.5 \times 2} = 1$ (at constant T), $i = 2$ for both (as 100% ionization). Therefore, both the solutions are isotonic.

66. Boiling point of pure H₂O is 373.15 K. If 32.5 g of KCN is dissolved in 100 mL of H₂O, what will the boiling point of solution? (Given K_b for H₂O = 0.52 K kg mol⁻¹ and molar mass of KCN = 65 g mol⁻¹.)

- (A) 105.20°C (B) 100.52°C (C) 373.67 K (D) 273.67 K

Solution

(A) KCN → K⁺ + CN⁻, where $i = 2$. Hence,

$$\Delta T_b = i \times m \times K_b = 2 \times \frac{32.5}{65} \times 0.52 = 5.2^\circ\text{C}$$

Therefore, $T_b^s = 373.15 + 5.2 = 378.35 \text{ K} = 378.35 - 273.15 = 105.20^\circ\text{C}$

67. A 5% solution of cane sugar (molecular weight = 342 g mol⁻¹) is isotonic with 1% solution of substance X. The molecular weight of X is

- (A) 17.12 g mol⁻¹ (B) 68.4 g mol⁻¹ (C) 34.2 g mol⁻¹ (D) 136.2 g mol⁻¹.

Solution

(B) $\Pi_1 = \Pi_2$ means $C_1 = C_2$. Therefore,

$$\frac{5}{100 \times 342} = \frac{1}{M_B \times 100} \Rightarrow M_B = 68.4 \text{ g mol}^{-1}$$

68. Which of the following aqueous solutions will have the lowest freezing point?

- (A) 0.10 M KCl (B) 0.10 M Al₂(SO₄)₃
(C) 0.10 M C₆H₁₂O₆ (D) 0.10 M C₁₂H₂₂O₁₁

Solution

(B) Based on van't Hoff factor values, we find that $i = 2$ for KCl, $i = 5$ for Al₂(SO₄)₃, $i = 1$ for C₆H₁₂O₆ and $i = 1$ for C₁₂H₂₂O₁₁. Hence, the value of ΔT_f will be maximum for Al₂(SO₄)₃ and so it has the lowest freezing point.

69. Which of the following solution (in H₂O) has the highest boiling point elevation?

- (A) 0.2 M urea (B) 0.1 M K₄[Fe(CN)₆] (C) 0.2 M K₂SO₄ (D) 0.3 M glucose

Solution

(C) Since $i = 3$ and $m = 0.2$ are maximum for K₂SO₄, it has the highest value of ΔT_b , and hence the highest boiling point.

70. Arrange the following compounds in order of decreasing the depression in freezing point of water of water for the same molarity:

- (I) Acetic acid (II) Trichloroacetic acid (III) Trifluoroacetic acid
(A) I > II > III (B) II > III > I (C) III > I > II (D) III > II > I

Solution

(D) The value of i value is: CF₃COOH > CCl₃COOH > CH₃COOH. This is because greater the -I effect (electron withdrawing group), more is the ionization.

71. The osmotic pressure of a 5% aqueous solution of cane sugar at 150°C is (molecular weight of cane sugar = 342 g mol⁻¹).

- (A) 4 atm (B) 3.4 atm (C) 5.07 atm (D) 2.45 atm

Solution

$$(C) \Pi = CRT = \frac{5}{342 \times 100 / 1000} \times 0.0821 \times (150 + 273) = 5.07 \text{ atm}$$

72. If 32 g of an unknown molecule (assumed to be unionized in solution) dissolved in 200 g of H₂O, then elevation in boiling point is found to be 1.04°C. Find out the molar mass of the unknown molecule (given that K_b for H₂O = 0.52 K kg mol⁻¹).

- (A) 160 g mol⁻¹ (B) 80 g mol⁻¹ (C) 40 g mol⁻¹ (D) 320 g mol⁻¹

Solution

(B) As the molecule is unionized, therefore, $i = 1$. Hence,

$$\Delta T_b = m \times K_b \Rightarrow 1.04 = \frac{32}{M} \times \frac{0.52}{0.2} \Rightarrow M = 80 \text{ g mol}^{-1}$$

73. The ratio of the value of any colligative property for KCl solution to that for sugar is nearly _____ times (for the same molality and solvent).

- (A) 1 (B) 0.5 (C) 2 (D) 2.5

Solution

(C) Colligative property, CP is given by

$$\frac{CP_1}{CP_2} = \frac{i_1}{i_2}$$

For the reaction $KCl \rightarrow K^+ + Cl^-$ $i = 2$ and for sugar (non-electrolyte), $i = 1$, therefore,

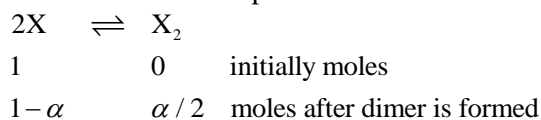
$$\frac{CP_{KCl}}{CP_{sugar}} = \frac{2}{1}$$

74. The freezing point of a solution of acetic acid (mole fraction is 0.02) in benzene is 277.4 K. Acetic acid exists partly as a dimer $2A \rightleftharpoons A_2$. Determine the equilibrium constant for dimerization. Freezing point of benzene is 278.4 K and K_f for benzene is 5 K molal⁻¹.

- (A) 3.19 kg mol⁻¹ (B) 31.9 kg mol⁻¹ (C) 1.6 kg mol⁻¹ (D) 16.0 kg mol⁻¹

Solution

(A) Let acetic acid = X; Benzene = Y. Assume a part of A forms dimer



Therefore,
$$i = \frac{(1 - \alpha) + \alpha / 2}{1} = 1 - \alpha / 2 \Rightarrow i < 1$$

Mole fraction of X = $x_X = 0.02$; mole fraction of Y = $x_Y = 0.98$

$$\text{Molality of X in Y} = \frac{X_A}{m_B} = \frac{0.02}{78} \times \frac{1000}{0.98} = 0.262 \text{ mol kg}^{-1} \text{ of benzene}$$

Since, $\Delta T_f = K_f \times i \times \text{molality}$

$$278.4 - 277.4 = 5 \times i \times 0.262 \Rightarrow 1 = 5 \times i \times 0.262$$

$$i = \frac{1}{5 \times 0.262} = 0.763 \Rightarrow 1 - \frac{\alpha}{2} = 0.763 \Rightarrow \alpha = 0.47$$

Hence, the molality of X after dimer is formed is

$$(1 - \alpha) \times \text{Initial molality} = (1 - 0.47) \times \text{Initial molality} = 0.53 \times 0.262 = 0.13886.$$

$$\text{Molality of } X_2 \text{ after dimer is formed} = \frac{\alpha}{2} \times \text{Molality} \Rightarrow \frac{0.47}{2} \times 0.262 = 0.235 \times 0.262 = 0.0616$$

$$\text{The equilibrium constant } K_{\text{eq}} = \frac{[X_2]}{[X]^2} = \frac{0.0616}{(0.13886)^2} = 3.19 \text{ kg mol}^{-1}$$

75. 0.01 M solution each of urea, common salt, and Na_2SO_4 are taken. The ratio of depression of freezing point is

- (A) 1:1:1 (B) 1:2:1 (C) 1:2:3 (D) 2:2:3

Solution

(C) $\Delta T_f = i K_f \times m \Rightarrow \Delta T_f \propto i$ where $i = 1$ for urea, $i = 2$ for NaCl and $i = 3$ for Na_2SO_4 . Therefore, Ratio of number of molecules after ionization = 1:2:3

76. If the solution of mercuric cyanide of strength 3 g L^{-1} has an osmotic pressure $0.3092 \times 10^5 \text{ Nm}^{-2}$ at 298 K, what is the apparent molecular weight and degree of dissociation of $\text{Hg}(\text{CN})_2$, respectively? (Given atomic masses as Hg = 200.61 u, C = 12 u, N = 14 u.)

- (A) 240.2, 2.45% (B) 480.4, 2.45% (C) 480.4, 24.5% (D) 240.2, 24.5%

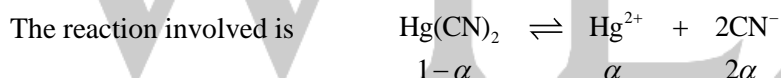
Solution

$$(A) \text{ Osmotic pressure} = \Pi = CRT = \frac{w}{m_o} \times \frac{1}{V} \times RT$$

$$\text{or } 0.3092 \times 10^5 = \frac{3 \times 10^{-3}}{m_o} \times \frac{1}{10^{-3}} \times 8.314 \times 298$$

Therefore, $m_o = 240.2 \times 10^{-3} \text{ kg}$ and $M_{\text{normal}} = 252.61 \text{ g mol}^{-1}$

$$i = \frac{\text{Number of particles after dissociation}}{\text{Number of particles before dissociation}} = \frac{\text{Normal molecular weight}}{\text{Observed molecular weight}}$$



$$\text{Number of particles after dissociation} = (1 - \alpha) + \alpha + 2\alpha = 1 + 2\alpha$$

$$\text{That is, } \frac{1 + 2\alpha}{1} = \frac{252.61 \times 10^{-3}}{240.2 \times 10^{-3}} \Rightarrow \alpha = 0.02454 \text{ or } 2.546\%$$

77. When mercuric iodide is added to the aqueous solution of potassium iodide, the:

- (A) freezing point is raised. (B) freezing point is lowered.
(C) freezing point does not change. (D) boiling point does not change.

Solution

(A) $\Delta T_f = i K_f m$. As ΔT_f decreases, T_f will increase.

As $i < 1$ (as association), $2\text{KI}(\text{aq}) + \text{HgI}_2(\text{s}) \rightarrow \text{K}_2[\text{HgI}_4](\text{aq})$ (due to decrease in the value of i).

78. The freezing point of 1 molal NaCl solution assuming NaCl to be 100% dissociated in water is (K_f for $\text{H}_2\text{O} = 1.86^\circ\text{C molal}^{-1}$)

- (A) -1.86°C (B) -3.72°C (C) $+1.86^\circ\text{C}$ (D) -3.72°C .

Solution

(B) $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$ (for 100% ionization, $i = 2$)

Now, $\Delta T_f = T_f - T_f^\circ = 0 - 3.72$. Therefore,

$$\Delta T_f = i \times \text{molality} \times K_f = 1 \times 2 \times 1.86 = 3.72^\circ\text{C}$$

Therefore, $T_f^\circ = -3.72^\circ\text{C}$

79. When 1000 g of 1 molal sucrose solution in water is cooled to -3.534°C , the mass of ice separated out at this temperature will be (K_f for $\text{H}_2\text{O} = 1.86^{\circ}\text{C molal}^{-1}$)
 (A) 353.19 g (B) 252.9 g (C) 52.98 g (D) 152.98 g

Solution

(A) We know that

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

Therefore, for 1 molal solution

$$\Delta T_f = 1.86 \times 1 = 1.86$$

$$\text{Also, } \Delta T_f = K_f \times \frac{1000 \times w_B}{M_B \times w_A} \Rightarrow 1.86 = 1.86 \times \frac{1000 \times w_{\text{sucrose}}}{342 \times w_{\text{water}}} \Rightarrow \frac{w_{\text{water}}}{w_{\text{sucrose}}} = \frac{342}{1000}$$

Also, $w_{\text{water}} + w_{\text{sucrose}} = 1000$ g. Therefore, using two relations we get

$$w_{\text{water}} = 745.16 \text{ g and } w_{\text{sucrose}} = 254.84 \text{ g}$$

When the solution is cooled to -3.534°C , the amount of sucrose in the solution does not change, so the amount of water in solution can be calculated as

$$\Delta T_f = K_f \times \frac{1000 \times w_B}{M_B \times w_A} \Rightarrow 3.534 = 1.86 \times \frac{1000 \times 254.84}{342 \times w_{\text{water}}} \Rightarrow w_{\text{water}} = 392.18 \text{ g}$$

The amount of ice separated is: $745.16 - 392.18 = 352.98$ g

80. How much is the amount of CaCl_2 ($i = 2.47$) dissolved in 2.5 L of water such that its osmotic pressure is 0.75 atm at 27°C ?

- (A) 0.3 mol (B) 0.03 mol (C) 3 mol (D) 0.003 mol

Solution

(B) Osmotic pressure, $\Pi = iCRT$ or $\Pi = i \frac{n}{V} RT$, $C = \text{Molarity} = \frac{n}{V}$. Therefore,

$$0.75 = \frac{n}{2.5} \times 0.0821 \times 300 \times 2.47$$

$$n = \frac{0.75 \times 2.5}{0.0821 \times 300 \times 2.47} = 0.03 \text{ mol}$$

81. What will be the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 L of water at 25°C , assuming that it is completely dissociated?

- (A) 5.27×10^{-3} atm (B) 52.7×10^{-3} atm (C) 26.3×10^{-3} atm (D) 2.03×10^{-3} atm

Solution

(A) $\text{K}_2\text{SO}_4 \rightarrow 2\text{K}^+ + \text{SO}_4^{2-}$; van't Hoff factor, $i = 3$ (as 100% ionization)

Given that $V = 2$ L, $T = 25 + 273 = 298$ K. So, the osmotic pressure is

$$\Pi = i \frac{n}{V} RT = 3 \times \frac{25 \times 10^{-3}}{174 \times 2.0} \times 0.0821 \times 298 = 5.27 \times 10^{-3} \text{ atm}$$

82. The values of observed and calculated molecular weights of silver nitrate are 92.64 g mol^{-1} and 170 g mol^{-1} , respectively. The degrees of dissociation of silver nitrate is

- (A) 60% (B) 83.5% (C) 46.7% (D) 60.23%

Solution

(B) i for $\text{AgNO}_3 = \frac{\text{Normal molecular weight}}{\text{Observed molecular weight}} = 1 + \alpha$

$$\alpha = \frac{170}{92.64} - 1 = 0.835$$

So, the percentage dissociation is 83.5%.

83. Which of the following solutions will have the highest boiling point?

- (A) 1% glucose (B) 1% sucrose (C) 1% NaCl (D) 1% CaCl₂

Solution

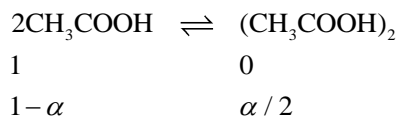
(D) Elevation of boiling point $\propto i$ (as CaCl₂, $i = 3$). Hence, it is highest for CaCl₂.

84. Acetic acid exists in benzene solution in the dimeric form. In an actual experiment, the van't Hoff factor was found to be 0.52. Then the degree of dissociation of acetic acid is

- (A) 0.48 (B) 0.88 (C) 0.96 (D) 0.52

Solution

(C) The reaction involved is



$$i = 1 - \frac{\alpha}{2} \text{ or } \alpha = 2(1 - i) = 2(1 - 0.52) = 0.96$$

Hence, degree of dissociation = 96%

85. The average osmotic of human blood is 7.8 bar at 37°C. What is the concentration of an aqueous NaCl solution that could be used in the blood stream?

- (A) 0.15 mol L⁻¹ (B) 0.30 mol L⁻¹ (C) 0.60 mol L⁻¹ (D) 0.45 mol L⁻¹

Solution

(A) NaCl solution used should be isotonic with blood stream. For NaCl, $i = 2$

$$\Pi = iCRT \Rightarrow C = \frac{7.8}{2 \times 0.083 \times 310} = 0.15 \text{ mol L}^{-1}$$

86. Three particles of a solute, A, associate in benzene to form species A₃. Determine the freezing point of 0.25 molal solution. The degree of association of solute A is found to be 0.80. The freezing point of benzene and its cryoscopic constant are 5.5°C and 5.12 K molal⁻¹, respectively.

- (A) 49°C (B) 4.9°C (C) 25°C (D) 2.5°C

Solution



Number of moles dissolved 3 0

Number of moles after association $m(1 - \alpha)$ $m\alpha / 3$

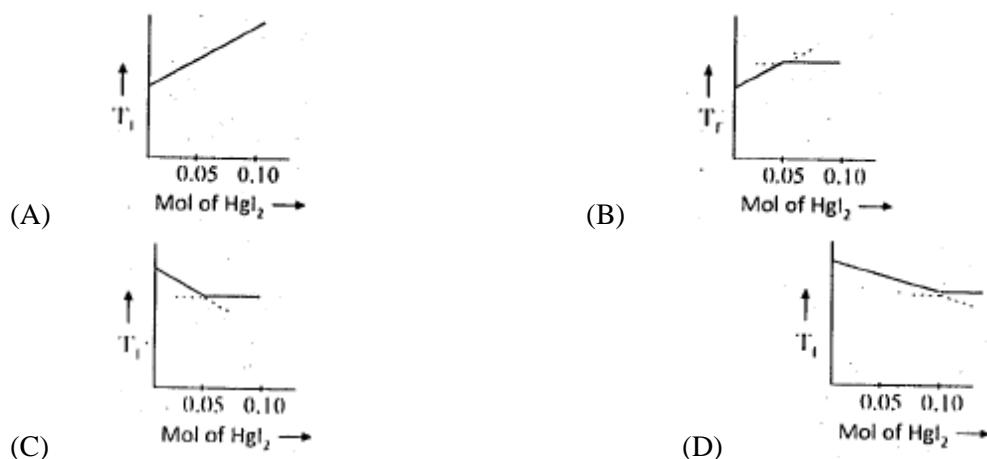
Total moles present after association is

$$m(1 - \alpha) + m \frac{\alpha}{3} = m \left(1 - \alpha + \frac{\alpha}{3} \right) = m \left(1 - \frac{2\alpha}{3} \right) = 0.25m \left[\frac{3 - 2 \times 0.8}{3} \right] = 0.177m$$

$$\Delta T_f = K_f m \Rightarrow T_f^\circ - T_f = 5.12 \text{ K molal}^{-1} \times 0.177 m = 0.6$$

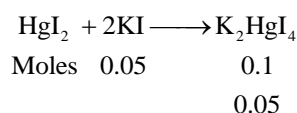
$$T_f = T_f^\circ - 0.6^\circ\text{C} = 5.5 - 0.6 = 4.9^\circ\text{C}$$

87. Increasing amount of solid HgI₂ is added to 1 L of an aqueous solution containing 0.1 mol KI. Which of the following graphs represents the variation of freezing point of the resulting with the amount of HgI₂ added?



Solution

(B) When HgI_2 is added to KI:



This is the case of association in which 2 moles of KI combine with one mole of HgI_2 to form the complex K_2HgI_4 . Hence, 0.05 mol of HgI_2 are required to react completely with 0.1 solution of KI.

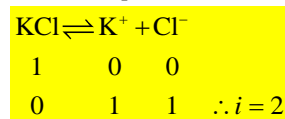
Thus, as HgI_2 is being added, the number of solute molecules will decrease ($i < 1$) causing ΔT_f to decrease, that is, causing T_f to increase. When whole of KI has been converted into K_2HgI_4 , further addition of HgI_2 does not change the T_f , since it is a sparingly soluble salt.

88. Equimolal solutions KCl and compound X in water show depression in freezing point in the ratio of 4:1. Assuming KCl to be completely ionized, the compound X in solution must

- (A) dissociate to the extent of 50%. (B) hydrolyze to the extent of 80%.
 (C) dimerize to the extent of 50%. (D) trimerize to the extent of 75%.

Solution

(D) KCl and X
 (p moles) (p moles)



$$\Delta T_f(\text{KCl}) = iK_f m = 2K_f m$$

$$\Delta T_f(\text{X}) = i_x K_f m = \frac{1}{4}(2K_f m) \quad \Rightarrow \quad i_x = \frac{1}{2} (< 1) \quad (\therefore \text{association})$$



$$i = 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2} = \frac{1}{2} \Rightarrow \alpha = 100\% \quad i = 1 - \alpha + \frac{\alpha}{3} = 1 - \frac{2\alpha}{3} = \frac{1}{2} \Rightarrow \alpha = \frac{3}{4} = 75\%$$

89. Among the following, the solution which shows the lowest osmotic pressure is:

- (A) 0.10 M NaCl (B) 0.05 M CaCl_2 (C) 0.04 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ (D) 0.03 M FeCl_3

Solution

(D) $\Pi = iCRT$. From the given values, $i \times C$ product is lowest for FeCl_3 . Therefore, osmotic pressure is lowest for 0.03 M FeCl_3 .

90. Calculate the boiling point of a one molar aqueous solution (density = 1.04 g mL^{-1}) of potassium chloride, K_b for water = $0.52 \text{ K kg mol}^{-1}$. (Atomic masses of K = 39 u, Cl = 35.5 u)

- (A) 107.28°C (B) 103.68°C (C) 101.078°C (D) None of these

Solution

(C) Volume of solution = 1000 mL

Mass of the solution = $V \times d = 1000 \text{ mL} \times 1.04 \text{ g mL}^{-1} = 1040 \text{ g}$

Amount of solute in 1000 mL solution = $1 \text{ M} = 1 \text{ M} \times \text{Molecular mass} = 1 \text{ M} \times 74.5 \text{ g mol}^{-1} = 74.5 \text{ g}$

Mass of water = Mass of solution – Mass of KCl = $1040 \text{ g} - 74.5 \text{ g} = 965.5 \text{ g}$

Molality of the solution = $m = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} = \frac{1 \text{ mol}}{(965.5/1000)\text{kg}} = 1.0357$

$\Delta T_b = i K_b m = 2 \times 0.52 \text{ K kg mol}^{-1} \times 1.0357 = 1.078^\circ\text{C}$

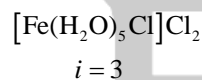
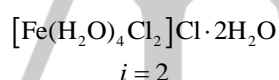
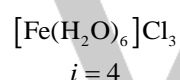
Boiling point of the solution is $100^\circ\text{C} + 1.078^\circ\text{C} = 101.078^\circ\text{C}$

91. Maximum freezing point will be for 1 molal solution of (assuming equal ionization in each case),

- (A) $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_3$ (B) $[\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
 (C) $\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2 \cdot \text{Cl} \cdot 2\text{H}_2\text{O}$ (D) $[\text{Fe}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$

Solution

(D) Smaller the value of i , higher will be the freezing point. Therefore, in the case of non-electrolytes, $i = 1$.



Multiple Correct Choice Type

1. When a solute is added to a pure solvent, the

- (A) vapor pressure of the solution becomes lower than that of the pure solvent.
 (B) rate of evaporation of the pure solvent is reduced.
 (C) solute does not affect the rate of condensation.
 (D) rate of evaporation of the solution is equal to the rate of condensation of the solution at a lower vapor pressure than that in the case of the pure solvent.

Solution

(A, B, C, D) When a non-volatile solute is added to a pure solvent, the solution vapor pressure decreases than that of pure solvent.

2. An ideal solution is formed, when

- (A) its components have the same intermolecular attractions in solution as in pure components.
 (B) $\Delta H_{\text{mix}} = 0$.
 (C) $\Delta V_{\text{mix}} > 0$.
 (D) $\Delta S_{\text{mix}} > 0$.

Solution

(A, B, D) In an ideal solution

- (i) the solute–solute and solvent–solvent interactions are identical to those of solute–solvent.
 (ii) $\Delta H_{\text{mix}} = 0$
 (iii) $\Delta S_{\text{mix}} > 0$

3. Which is/are correct statement(s)?

- (A) When mixture is less volatile, there is positive deviation from Raoult's law.
- (B) When mixture is more volatile, there is negative deviation from Raoult's law.
- (C) When mixture is less volatile, there is negative deviation from Raoult's law.
- (D) When mixture is more volatile, there is positive deviation from Raoult's law.

Solution

(C, D) If a mixture is less volatile, then the solution exhibits negative deviation and if the mixture is more volatile, then the solution exhibits positive deviation from Raoult's law.

4. Identify the correct statements.

- (A) The solution formed by mixing equal volumes of 0.1 M urea and 0.1 M glucose will have the same osmotic pressure.
- (B) 0.1 M $K_4[Fe(CN)_6]$ and 0.1 M $Al_2(SO_4)_3$ are isotonic solutions.
- (C) For association of a solute in a solution, $i > 1$.
- (D) The ratio of van't Hoff factors for 0.2 M glucose and 0.1 M sucrose is 2:1.

Solution

(A, B)

For both urea and glucose $i = 1$

For both $K_4[Fe(CN)_6]$ and $Al_2(SO_4)_3$, $i = 1 + 4\alpha$

For association of a solute in a solution $i < 1$

Glucose and sucrose undergo neither association or dissociation.

5. In the depression of freezing point experiment, it is found that the

- (A) vapor pressure of the solution is less than that of pure solvent.
- (B) vapor pressure of the solution is more than that of pure solvent.
- (C) only ionic molecules solidify at the freezing point.
- (D) only solvent molecules solidify at the freezing point.

Solution

(A, D) When a non-volatile solute is added to a pure solvent to form a solution, vapor pressure of the solution decreases compared to that of a solution. At freezing point, only solvent freezes in a solution.

6. 1 mol benzene ($p_{benzene}^{\circ} = 42$ mm Hg) and 2 mol toluene ($p_{toluene}^{\circ} = 36$ mm Hg) will have:

- (A) total vapor pressure 38 mm Hg.
- (B) mole fraction of vapors of benzene above liquid mixture is 7/19.
- (C) positive deviation from Raoult's law.
- (D) negative deviation from Raoult's law.

Solution

(A, B) $p = x_A p_A^{\circ} + x_B p_B^{\circ}$

$$p_T = p_{benzene}^{\circ} x_{benzene} + p_{toluene}^{\circ} x_{toluene} = 42 \times \frac{1}{3} + 36 \times \frac{2}{3} = 38 \text{ mm Hg}$$

7. Which of the following are correct about Henry's constant, K_H ?

- (A) Greater the value of K_H , lower is the solubility of the gas at the same pressure and temperature.
- (B) K_H decreases with increase of temperature.
- (C) The unit of K_H is bar.
- (D) All noble gases have the same value of K_H at the same temperature.

Solution

(A, C)

(B) is wrong because K_H increases with increase of temperature.

(D) is wrong because different noble gases have different value for K_H at the same temperature.

8. The azeotropic solutions of two miscible liquids

- (A) can be separated by simple distillation.
- (B) may show positive or negative deviation from Raoult's law.
- (C) are supersaturated solutions.
- (D) behave like a single component and boil at a constant temperature.

Solution

(B, D) In azeotropic mixture, both components will boil at the same temperature.

9. Solution showing positive deviation from Raoult's law include

- (A) Acetone + Carbon disulphide
- (B) Acetone + Ethyl alcohol
- (C) Acetone + Benzene
- (D) Acetone + Aniline

Solution

(A, B, C)

(D) shows negative deviation. All other given mixtures, show +ve deviations.

10. Which of the following is/are incorrect (M is assumed to be equal to m)

- (A) 1 M NaCl solution has higher freezing point than 1 M glucose solution.
- (B) 1 M glucose solution has same boiling point as 1 M sucrose solution.
- (C) Molecular weight of benzoic acid in benzene will be doubled than expected.
- (D) van't Hoff factor $i > 1$ if solute undergoes association.

Solution

(A,D) 1 molal NaCl will have greater depression in freezing point, and hence, lower actual freezing point. So (A) is false. If solute undergoes association, $i < 1$.

11. Which of the following aqueous solution are isotonic ($R = 0.082 \text{ atm K}^{-1} \text{ mol}^{-1}$)?

- (A) 0.01 M glucose
- (B) 0.01 M NaNO_3
- (C) 500 mL solution containing 0.3 g urea
- (D) 0.04 N HCl

Solution

(A, C) Both are having same molar concentration as well non-electrolytes.

12. Which of the following statements are correct about the solubility of gases in liquids?

- (A) Mole fraction of the gas in the solution is directly proportional to the partial pressure of the gas above the solution.
- (B) Volume of the gas dissolved measured at the pressure used is independent of the pressure of the gas.
- (C) Solubility of gas is always an exothermic process.
- (D) Gibbs energy change of dissolution of a gas may be positive or negative.

Solution

(A, B, C) Henry's law states that the mole fraction of the gas in the solution is directly proportional to the partial pressure of the gas above the solution, that is, $p_A = k_H \times a$ (where k_H is the Henry's constant).

The solubility of gas does not depend on its volume, but it decreases with increase in temperature. The enthalpy change for solubility of gas is negative, so Gibbs energy change is also negative ($\Delta G = \Delta H - T\Delta S$).

13. Which relations are correct for an aqueous dilute solution of K_3PO_4 if its degree of dissociation is α ?

- (A) $\frac{\Delta p}{p^\circ} = \frac{m \times 18 \times (1 + 3\alpha)}{1000}$
- (B) $\frac{\Delta p}{p^\circ} = \frac{\Pi_{\text{obs.}} \times 18 \times (1 + 3\alpha)}{ST \times 1000}$
- (C) $\frac{\Delta p}{p^\circ} = \frac{\Delta T_{\text{f obs.}} \times 18}{K_f \times 1000}$
- (D) Molecular weight of $\text{K}_3\text{PO}_4 = \text{Molecular weight}_{\text{obs}} \times (1 + 3\alpha)$

Solution

$$(A, C, D) \frac{\Delta p}{p^\circ} = \frac{n}{N} = \frac{n \times M \times 1000}{W \times 1000} = \frac{\text{Molality} \times M}{1000}$$

$$\text{For electrolyte } \frac{\Delta p}{p^\circ} = \frac{\text{Molality} \times M}{1000} \times (1 + 3\alpha) \quad (\text{where } M = 18 \text{ for } H_2O)$$

Also,

$$\begin{aligned} \Pi_{\text{obs}} &= C \times R \times T (1 + 3\alpha) \\ \Delta M_{\text{f(obs.)}} &= K_f \times \text{Molality} \times (1 + 3\alpha) \\ i = (1 + 3\alpha) &= \frac{\text{Calculated molecular weight}}{\text{Observed molecular weight}} \\ \text{Molecular weight of } K_2PO_4 &= M_{\text{obs}} \times (1 + 3\alpha) \end{aligned}$$

14. Two liters of 1 M solution of a complex salt $CrCl_3 \cdot 6H_2O$ (molecular weight = 266.5 g mol^{-1}) shows an osmotic pressure of 98.52 atm. The solution is now treated with 1 L of 6 M $AgNO_3$. Which of the following are correct?

- (A) Weight of $AgCl$ precipitated is 861 g.
 (B) The clear solution will show an osmotic pressure = 98.52 atm.
 (C) The clear solution will show an osmotic pressure = 65.68 atm.
 (D) 2 mol of $[Cr(H_2O)_6](NO_3)_3$ will be present in solution.

Solution

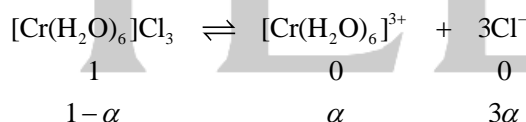
(A, C, D) $CrCl_3 \cdot 6H_2O$

$$\Pi = CRT(1 - \alpha + x\alpha + y\alpha)$$

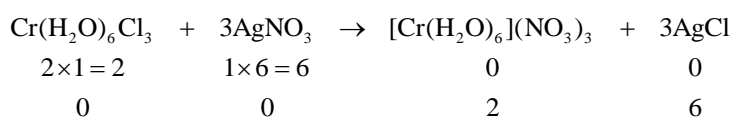
$$93.52 = 1 \times 0.0821 \times 300 \times (x + y) \quad (\text{as } \alpha = 1)$$

Solving, we get $x + y = 4$.

The reactions involved are



and



Weight of $AgCl$ formed = $6 \times 143.5 = 861 \text{ g}$

$$\Pi = CRT \times (1 + 3\alpha) = \frac{2}{3} \times 0.0821 \times 300 \times 4 = 65.68 \text{ atm}$$

15. Two miscible liquids A and B having vapor pressure in pure state p_A° and p_B° are mixed in mole fraction x_A and x_B to get a mixture having total vapor pressure of mixture p_{total} . Which of the following relations are correct?

- (A) $x_A = \frac{p_{\text{total}} - p_B^\circ}{p_A^\circ - p_B^\circ}$ (B) $\frac{x_{A(l)}}{x'_{A(v)}} = \frac{p_{\text{total}}}{p_A^\circ}$ (C) $\frac{x_{A(l)}}{x'_{A(v)}} = \frac{p_{\text{total}}}{p_B^\circ}$ (D) all of these

Solution

(A, B) $p_M = p_A^\circ x_A + p_B^\circ x_B$

Also,

$$p' = p_M x_{A(v)} = p_A^\circ x_{A(l)} = p_A^\circ x_A + p_B^\circ (1 - x_A)$$

Therefore,

$$x_A = \frac{P_M - P_B^{\circ}}{P_A^{\circ} - P_B^{\circ}}$$

16. 1 mol benzene ($p_{\text{benzene}}^{\circ} = 42 \text{ mm Hg}$) and 2 mol toluene ($p_{\text{toluene}}^{\circ} = 36 \text{ mm Hg}$) will have

- (A) total vapor pressure 38 mm Hg.
- (B) mole fraction of vapors of benzene above liquid mixture of 7/19.
- (C) positive deviation from Raoult's law.
- (D) negative deviation from Raoult's law.

Solution

(A, B) Benzene and toluene form an ideal solution, as A–A and B–B attractions are similar to A–B attractions.

$$P_{\text{Total}} = P_A^{\circ}x_A + P_B^{\circ}x_B = 42 \times \frac{1}{3} + 36 \times \frac{2}{3} = 38 \text{ mm Hg}$$

$$x_A = \frac{1}{3} \text{ and } x_B = 1 - \frac{1}{3} = \frac{2}{3}$$

Now, mole fraction of vapors of benzene above liquid mixture is

$$x_{\text{Benzene}}^{\text{Vap}} = \frac{P_{\text{Benzene}}}{P_{\text{Total}}} = \frac{42 \times \frac{1}{3}}{38} = \frac{7}{19}$$

17. Dry air is passed through a set of interconnected air-tight vessel containing a solution of non-volatile solute and then through another set of vessels containing pure solvent. If the solution and the solvent suffer losses of mass to be w_1 and w_2 , respectively, then

- (A) $w_1 \propto p_s$
- (B) $w_2 \propto p^{\circ}$
- (C) $w_2 \propto p^{\circ} - p_s$
- (D) $(w_1 + w_2) \propto p^{\circ}$

Solution

(A, C, D)

Loss in weight of solvent $\propto p_0 - p_s$ } Ostwald and Walker
Loss in weight of solution $\propto p_s$ } experiment

18. Which pair(s) of liquids on mixing are expected to show no net volume change and no heat effect?

- (A) Acetone and ethanol
- (B) Chlorobenzene and bromobenzene
- (C) Chloroform and benzene
- (D) *n*-Butyl chloride and *n*-butyl bromide

Solution

(B, D) $\Delta V_{\text{mixing}} = 0$; $\Delta H_{\text{mixing}} = 0 \Rightarrow$ Look for ideal solutions.

If $\Delta V_{\text{mix}} = +ve$, $\Delta H_{\text{mix}} = +ve$, positive deviation
and $\Delta V_{\text{mix}} = -ve$, $\Delta H_{\text{mix}} = -ve$, negative deviation

19. Which of the following statements is correct?

- (A) The freezing point of water is depressed by the addition of glucose.
- (B) The degree of dissociation of a weak electrolyte decreases as its concentration decreases.
- (C) Energy is released when a substance dissolves in water provided that the hydration energy of the substance is more than its lattice energy.
- (D) If two liquids have form an ideal solution are mixed, the change in entropy is positive.

Solution

(A, C, D)

- (A) There will be a depression in freezing point by the addition of glucose in water.
- (B) α increases as concentration decreases. (Ostwald's law)

$$(C) \Delta_{\text{sol}} H = \Delta H_{\text{Lattice}} + \Delta H_{\text{Hydration}}$$

(+ve)
(-ve)
Endothermic
Exothermic

(D) Mixing of solution is always accompanied by an increase in entropy (randomness).

20. What does not change on changing temperature?

- (A) Mole fraction (B) Normality (C) Molality (D) None of these

Solution

(A, C) Both the mole fraction and molality do not change on changing the temperature because both do not involve any volume term.

Assertion–Reasoning Type

Choose the correct option from the following:

- (A) Statement 1 and Statement 2 are True; Statement 2 is the correct explanation for Statement 1.
 (B) Statement 1 and Statement 2 are True; Statement 2 is NOT the correct explanation for Statement 1.
 (C) Statement 1 is True but Statement 2 is False.
 (D) Statement 1 is False; Statement 2 is True.

1. Statement 1: Gases always tend to be less soluble in liquids as the temperature is raised.

Statement 2: Vapor pressure of liquids increase with increase in temperature.

Solution

(B) Follow Henry's Law, for dissolution of gases.

2. Statement 1: The vapor pressure of a liquid is the equilibrium constant of liquid–vapor equilibrium at the given temperature.

Statement 2: The ratio of the lowering of vapor pressure of a solvent upon dissolution of a non-volatile solute to the vapor pressure of pure solvent increases with temperature.

Solution

(C) $p_{\text{solution}} \propto x_{\text{solvent}} \Rightarrow p_{\text{solution}} = p^{\circ} x_{\text{solvent}}$ where p° = vapor pressure of pure solvent.

3. Statement 1: Ebullioscopy or cryoscopy cannot be used for the determination of molecular weight of polymers.

Statement 2: High molecular weight solute leads to very low value of ΔT_b or ΔT_f .

Solution

(A) Only osmotic pressure is most suitable for determination molecular weights of polymers because ΔT_f and ΔT_b are very low.

4. Statement 1: Reverse osmosis is used to purify saline water.

Statement 2: Solvent molecules pass from concentrated to dilute solution through semipermeable membrane if high pressure is applied on solution.

Solution

(A) In the process of reverse osmosis, solvent flows from concentrated side to dilute side of the solution. Therefore, saline water can be purified.

5. Statement 1: If a solution is heated such that keeping rest of all things unchanged, volume is changed, then it also brings changes to colligative properties related with it.

Statement 2: The molarity of solution changes on changing the volume of solution for the same amount of solute

Solution

(D) On heating a solution, volume decreases and molarity increases. Therefore, colligative property also changes. (Molality does not involve volume term.)

6. Statement 1: The boiling point of 0.1 M urea solution is less than that of 0.1 M KCl solution.

Statement 2: Elevation of boiling point is directly proportional to the number of species present in the solution.

Solution

(A) KCl ($i = 2$), urea ($i = 1$). As $\Delta T_b = i \times k_b \times m \Rightarrow \Delta T_b \propto i$, so ΔT_b for urea is less than KCl.

7. Statement 1: Vapor above a mixture of two liquids that does not obey Raoult's law is always richer in more volatile liquid.

Statement 2: Azeotropic mixture gives off a vapor of same composition as that of liquid.

Solution

(D) Azeotropes are constant boiling mixtures having the same composition throughout.

8. Statement 1: Out of the various colligative properties, osmotic pressure is used for determination of molecular masses of polymers.

Statement 2: Polymer solutions do not possess constant boiling point or freezing point.

Solution

(C) Since molecular weight of polymers is very high, ΔT_f and ΔT_b will be very small so that accurate values cannot be obtained. But osmotic pressure of polymer solution can be measured accurately.

9. Statement 1: Azeotropic mixtures are formed only by non-ideal solutions.

Statement 2: Boiling point of an azeotrope is either higher than both the components or lower than both the components.

Solution

(B) For azeotropes, the boiling point of solution is either lower or higher than that of pure components (depending on the type of deviation).

10. Statement 1: Only temperature can change the vapor pressure of a pure liquid.

Statement 2: Equilibrium constant does not change unless temperature is changed.

Solution

(A) Equilibrium constant changes with temperature, so vapor pressure also will change because vapor pressure is defined at equilibrium state.

Comprehension Type

Read the paragraphs and answer the questions that follow.

Paragraph I

On dissolving 68.4 g of sucrose in 1 kg of water, a solution of sucrose with molar mass 342 g mol^{-1} is formed. K_f for water is $1.86 \text{ K kg mol}^{-1}$ and vapor pressure of water at 298 K is 0.024 atm.

1. The vapor pressure of the solution at 298 K will be

- (a) 0.230 atm. (b) 0.233 atm. (c) 0.236 atm. (d) 0.0239 atm.

Solution

(D) According to relative lowering in vapor pressure,

$$\frac{p^\circ - p_s}{p_s} = \frac{(w_2 / m_2)}{(w_1 / m_1)}$$

where p° is the vapor pressure of the pure solvent, that is, water = 0.024 atm (given) and p_s is the vapor pressure of the solution; w_2 is the mass of sucrose, that is, 68.4 g (given); m_2 is the molar mass of sucrose, that is, 342 g/mol; w_1 is the mass of water, that is, 1000 g (given); m_1 is the molar mass of water, that is, 18 g/mol.

Substituting all the values and solving for p_s , we get

$$\frac{0.024 - p_s}{0.024} = \frac{(68.4 / 342)}{(1000 / 18)} \Rightarrow p_s = 0.0239 \text{ atm}$$

2. The osmotic pressure of the solution at 298 K will be

- (a) 4.29 atm. (b) 4.49 atm. (c) 4.69 atm. (d) 4.89 atm.

Solution

(D) Given that $\Pi = CRT = 0.2 \times 0.0821 \times 298 = 4.89 \text{ atm}$.

3. The freezing point of the solution will be

- (a) -0.684°C . (b) -0.342°C . (c) -0.372°C . (d) -0.186°C .

Solution

(C) $\Delta T_f = 0.2 \times 1.86 = 0.372^\circ\text{C}$. Therefore, freezing point is $= -0.372^\circ\text{C}$.

4. The mass of sodium chloride that should be dissolved in the same amount of water to get the same freezing point will be

- (a) 136.8 g. (b) 32.2 g. (c) 5.85 g. (d) 11.60 g.

Solution

(C) We know that $\Delta T_f = i \times m \times K_f$. Now, for the reaction $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$, $i = 1 - \alpha + \alpha + \alpha = 1 + \alpha = 2(\text{max})$. Therefore, $0.372 = 2 \times m \times 1.86 \Rightarrow m = 0.1 \text{ molal}$.

So, 0.1 mol dissolve per kg of water. Molar mass of NaCl = 58.5 g mol^{-1} . Therefore,

$$m_{\text{NaCl}} = 0.1 \times 58.5 = 5.85 \text{ g}$$

5. If on dissolving the above amount of NaCl in 1 kg of water, the freezing point is found to be -0.344°C , the percentage dissociation of NaCl in the solution is

- (a) 75% (b) 80% (c) 85% (d) 90%

Solution

$$(C) \Delta T_{f(\text{calculated})} = K_f \times m = 1.86 \times \left(\frac{5.85}{58.5} \right) = 0.186^\circ\text{C}$$

Given that $\Delta T_{f(\text{observed})} = 0.344^\circ\text{C}$. Now,

$$i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}} = \frac{0.344}{0.186} = 1.85$$

Also, $i = 1 + \alpha$, so $\alpha = i - 1 = 0.85 = 85\%$

Paragraph II

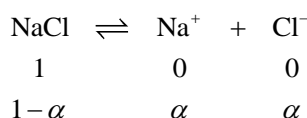
Colligative properties of solution depend only on the total number of solute particles present in solution. In the ionization of electrolytes, more particles are present per unit in solution due to dissociation. The colligative properties of such electrolytes are correlated with the number of particles by means of a factor called van't Hoff factor, denoted by i .

6. The van't Hoff factor for NaCl is 1.4. The degree of dissociation is

- (A) 40% (B) 100% (C) 90% (D) 60%

Solution

(A) For NaCl

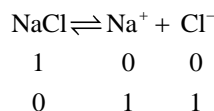


Initially, at equilibrium $i = 1 - \alpha + \alpha + \alpha = 1 + \alpha$. Now, $i = \frac{1 + \alpha}{1} = 1.4$. Therefore, $\alpha = 0.4$ or 40%.

7. The ratio of elevation of boiling point for NaCl solution to that for sugar of same concentration is
 (A) 1 (B) 2 (C) 3 (D) 0.5

Solution

(B) For NaCl, $i = 2$ and the reaction is



Sugar is non-electrolyte ($i = 1$).

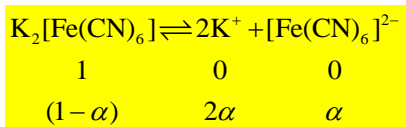
$$\frac{\Delta T_{b, \text{NaCl}}}{\Delta T_{b, \text{sugar}}} = \frac{i_{\text{NaCl}}}{i_{\text{sugar}}} = \frac{2}{1}$$

8. A 0.01 M solution of $\text{K}_2[\text{Fe}(\text{CN})_6]$ is 50% dissociated at 27°C. Then the osmotic pressure of solution will be

(A) 0.02 atm (B) 0.61 atm (C) 0.78 atm (D) 1.29 atm

Solution

(B) The reaction involved is



Thus,

$$i = 1(n - 1)\alpha = 1 + 3\alpha = 2.5$$

$$\Pi = iCST = 2 \times 0.01 \times 0.0821 \times 300 = 0.4926 \text{ atm}$$

Now, $\alpha = 0.5$, so

$$i = 1 - \alpha + 2\alpha + \alpha = +2\alpha = 2$$

Paragraph III

A solution is said to be ideal if each of its components obey Raoult's law for the entire composition range. The law states that the vapor pressure of any component in the solution depends on the mole fraction of that component in the solution and vapor pressure of that component in the pure state. Solutions are non-ideal if they do not obey Raoult's law over the entire composition range. The vapor pressure of the solution is either higher or lower than that predicted by Raoult's law. Depending on the type of deviation from ideal behavior, non-ideal solutions may be classified as showing negative deviation (lower vapor pressure than predicted). However, in either case, corresponding to particular composition, they form constant boiling mixture called azeotropes.

9. Which of the following mixtures do you expect will show positive deviation from Raoult's law?

- (a) Benzene + Acetone (b) Benzene + Chloroform
 (c) Benzene + Carbon tetrachloride (d) Benzene + Ethanol

Solution

(A) Only benzene and acetone show positive deviation because the interactions present in the benzene molecule and the acetone molecules will be stronger than that present in the solution of benzene + acetone. All others show negative deviation as the solutions formed by them have greater forces of interactions than the individual molecules.

10. An azeotropic solution of two liquids has boiling point higher than either of the two liquids when it

- (A) is saturated. (B) shows a negative deviation from Raoult's law.
 (C) shows a positive deviation from Raoult's law. (D) shows no deviation from Raoult's law.

Solution

(B) Boiling point of solution is lower than either of the liquid, which means that the vapor pressure is higher than as predicted by Raoult's law, $p_A > p_A^\circ x_A$, so there is positive deviation from Raoult's law. Solutions that show negative deviation from Raoult's law form maximum boiling azeotropes.

11. A solution has a 1:4 mole ratio of heptane to hexane. The vapor pressures of the pure hydrocarbons at 20°C are 440 mm Hg for heptane and 120 mm Hg for hexane. The mole fraction of pentane in the vapor phase would be

- (a) 0.200 (b) 0.478 (c) 0.549 (d) 0.786

Solution

(B) Mole fraction of pentane = $\frac{1}{1+4} = 0.2$ and that of hexane = $1 - 0.2 = 0.8$. Now substituting these in the equation $p = p_p^\circ x_p + p_H^\circ x_H$, we get

$$p = 0.2 \times 440 + 0.8 \times 120 = 88 + 96 = 184 \text{ mm Hg}$$

Therefore, vapor pressure of pentane in vapor phase is

$$x_{p(\text{vap})} = \frac{88}{184} = 0.478$$

Integer Answer Type

1. van't Hoff factor of an electrolyte A_2B_3 assuming that it ionizes 75% in the solution is ____.

Solution

(4) $i = 1 + (5 - 1) 0.75 = 4$

2. At 20°C, the osmotic pressure of urea solution is 400 mm Hg. The solution is diluted and the temperature is raised to 35°C, when the osmotic pressure is round to be 105.3 mm Hg. Determine extent of dilution.

Solution

(4) $\Pi_1 = C_1 RT$ and $\Pi_2 = C_2 RT$. Therefore,

$$\frac{\Pi_1}{\Pi_2} = \frac{C_1}{C_2}$$

Now, $C = \frac{n}{V} \Rightarrow C \propto \frac{1}{V}$ (dilution)

For initial solution, $\Pi = \frac{400}{760}$ atm and $T = 293$ K

$$\frac{400}{760} \times V_1 = n \times R \times 293 \tag{1}$$

After dilution, let volume becomes V_2 and temperature is raised to 35°C, that is, 308 K.

$$\Pi = \frac{105.3}{760} \text{ atm}$$

$$\frac{105.3}{760} \times V_2 = n \times R \times 308 \tag{2}$$

From Eqs. (1) and (2), we get

$$\frac{V_1}{V_2} = \frac{293}{308} \times \frac{105.3}{400} = \frac{1}{4} \Rightarrow V_2 = 4V_1$$

That is, solution was diluted to 4 times.

3. An aqueous solution containing 5% by weight of urea and 10% by weight of glucose. What will be the ΔT_f of solution? (Given that K_f for H_2O is $1.86^\circ C \text{ kg mol}^{-1}$).

Solution

(3) $\Delta T_f = K_f \times m$. Since solution has 5% by weight urea and 10% by weight glucose, so

$$\% \text{ by weight} = \frac{\text{Weight of solute}}{\text{Weight of solution}} \times 100$$

If total weight = 100 g, then weight of water = 85 g; weight of urea = 5 g; weight of glucose = 10 g

Now, $\Delta T_f = \Delta T_{\text{urea}} + \Delta T_{\text{Glucose}}$

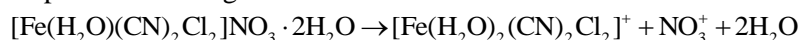
As both are non-electrolytes, $i = 1$, so

$$\Delta T = \frac{100 \times 1.86 \times 5}{60 \times 85} + \frac{1000 \times 1.86 \times 10}{180 \times 85} = 3.04^\circ C$$

4. The van't Hoff factor i for the species $[Fe(H_2O)_2(CN)_5]NO_3 \cdot 2H_2O$.

Solution

(2) $i = 2$, as the complex ionizes to give



5. The freezing point of an aqueous solution of KCN containing $0.189 \text{ mol kg}^{-1}$ was $-704^\circ C$. On adding 0.095 mol of $Hg(CN)_2$. (The freezing point of the solution became $-0.53^\circ C$. What will be new “ i ” factor of the resulting solution? (Assuming that $Hg(CN)_2$ and KCN are produced the complex.)

Solution

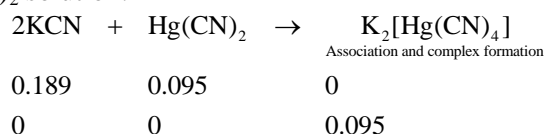
(3) $\Delta T_f = iK_f m$. In aqueous KCN solution, $i = 1$, and the reaction involved is



$$\begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array}$$

$$0.704 = 2 \times k_f \times 0.189 \quad (1)$$

In aqueous KCN + $Hg(CN)_2$ solution:



As, $\Delta T_f = iK_f m$, we have

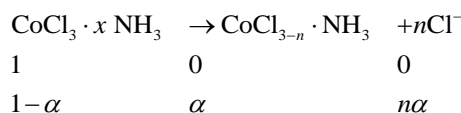
$$0.53 = i \times K_f \times 0.095 \quad (2)$$

From Eqs. (1) and (2), we get $i = 3$.

6. A complex is represented as $CoCl_3 \cdot xNH_3$. Its 0.1 molal solution in aqueous solution shows $\Delta T_f = 0.558^\circ C$. K_f for H_2O is $1.86 \text{ K molal}^{-1}$. Assuming 100% ionization of complex and coordination number of Co as 6, find the value of x .

Solution

(5) $\Delta T_f = iK_f m$. Common coordination number of Co is 6, hence



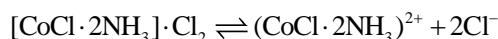
$$i = 1 - \alpha + \alpha + n\alpha = 1 + n\alpha$$

Let n ions of Cl^- are attached with Co through primary valencies that undergo dissociation. All the NH_3 molecules are attached through secondary valencies (which do not undergo ionization).

$$\Delta T_f = K_f \times \text{Molality} \times (1 - \alpha + \alpha + n\alpha)$$

Now $\alpha = 1$ (as 100% dissociation). Therefore,

$$0.558 = 1.86 \times 0.1 \times (1 - 1 + 1 + n) \Rightarrow n = 2$$



Thus, complex is $[\text{CoCl} \cdot x\text{NH}_3] \cdot \text{Cl}_2$. Since co-ordination number of Co is six, thus $x + 1 = 6$ or $x = 5$.

7. The molal lowering of vapor pressure of a liquid is 1.008 mm Hg at 25°C in a very dilute solution containing non-volatile solute. The vapor pressure of liquid at 25°C is $Z \times 10$ mm Hg. The value of Z is (molecular weight of liquid = 18 g mol^{-1})

Solution

$$(6) m = \left(\frac{p^0 - p_s}{p^0} \right) \times \frac{1000}{M_{\text{solvent}}} \quad (\text{Raoult's law})$$

$$p^0 = \frac{1.08}{1} \times \frac{1000}{18} \quad (\text{as molar lowering of vapor pressure} = 1.008 \text{ given})$$

$$\text{Hence, } p^0 = 60 = 6 \times 10 \Rightarrow Z = 6.$$

8. The depression in freezing point for 1 M urea, 0.5 M glucose, 1 M NaCl and 1 M K_2SO_4 are in the ratio $x:1:y:z$. The value of $x + z$ is _____.

Solution

(8)

Urea – 1	Glucose – 0.5	NaCl – 25
K_2SO_4 – 3	1:0.5:2:3	$x + 2 = 2 + 6 = 8$
	2:1:4:6	
	$x:0:y:z$	

9. The elevation in boiling point for 0.3 molal $\text{Al}_2(\text{SO}_4)_3$ solution as compared to elevation in boiling point of 0.1 molal solution of Na_2SO_4 is _____ times.

Solution

$$(5) \text{Elevation in boiling point for } \text{Al}_2(\text{SO}_4)_3 \text{ is } = 0.3 \times 5 \times K_b = 1.5K_b$$

$$\text{Elevation in boiling point for } \text{Na}_2\text{SO}_4 \text{ is } = 0.1 \times 3 \times K_b = 0.3K_b$$

Hence, it is five times.

Matrix–Match Type

1. Match the solutions with their characteristics.

Column I	Column II
(A) CH_3COOH in H_2O	(p) Neither association nor dissociation
(B) CH_3COOH in benzene	(q) When a non-volatile solute is added
(C) Polymer in water	(r) Molecular mass observed greater than molecular mass actual
(D) Vapor pressure of a liquid decreases	(s) $\Delta T_{f(\text{obs.})} > \Delta T_{f(\text{calc.})}$
	(t) van't Hoff factor, $i > 1$

Solution

A → (s, t); B → (r); C → (p); D → (q)

(A) CH₃COOH in H₂O undergoes dissociation (∴ $i > 1$).

(B) CH₃COOH in C₆H₆ undergoes dimerization (∴ $i < 1$).

(C) Polymer in water undergoes neither association nor dissociation (so, $i = 1$).

2. For a solution containing 25% ethanol, 25% acetone, 25% acetic acid and 25% water, match the mole fractions of the substances with their values.

Column I	Column II
(A) Mole fraction of ethanol	(p) 0.500
(B) Mole fraction of acetone	(q) 0.150
(C) Mole fraction of acetic acid	(r) 0.155
(D) Mole fraction of water	(s) 0.195

Solution

A → (s); B → (r); C → (q); D → (p)

It is given that the solution contains 25 g ethanol, 25 g acetone, 25 g acetic acid, and 25 g of water.

Number of moles of ethanol = $25/46 = 0.543$ mol

Number of moles of acetone = $25/58 = 0.431$ mol

Number of moles of acetic acid = $25/60 = 0.417$ mol

Number of water = $25/18 = 1.389$ mol

(A) Mole fraction of ethanol = Number of moles of ethanol/Total number of moles
 $= 0.543/(0.543 + 0.431 + 0.417 + 1.389) = 0.543/2.78 = 0.195$

(B) Mole fraction of acetone = $0.431/2.78 = 0.155$

(C) Mole fraction of acetic acid = $0.417/2.78 = 0.150$

(D) Mole fraction of water = $1.389/2.78 = 0.50$

3. Match the columns I and II.

Column I	Column II
(A) Azeotropes	(p) Molality
(B) A mixture of CHCl ₃ and benzene shows	(q) Intermolecular attraction negative deviation from ideal behavior
(C) The ratio of observed molecular mass to theoretical molecular mass	(r) van't Hoff factor
(D) The number of moles of solute dissolved in 1000 g of solvent	(s) Solutions with same composition in vapor and liquid phase
	(t) Constant boiling mixtures

Solution

A → (s, t); B → (q); C → (r); D → (p)

(A) Azeotropes or constant boiling mixtures with equal composition in both vapor phase and liquid phase.

(B) CHCl₃ in benzene shows negative deviation because of increase in molecular interactions.

(C) $i = \frac{\text{Observed molecular mass}}{\text{Theoretical molecular mass}}$

(D) $m = \frac{\text{Weight of solute}}{\text{GMW}} \times \frac{1000}{\text{Weight of solvent}}$ (as gram moles of solute dissolved per kilogram of solvent).

4. Match the columns I and II using the information below:

ΔH_{fus} = Molar heat of fusion of ice; L_{fus} = Latent heat of fusion of ice (g^{-1})

ΔH_{vap} = Molar heat of vaporization of water; L_{vap} = Latent heat of vaporization of water (g^{-1})

Column I	Column II
(A) Molal depression constant of water	(p) $\frac{18 \times 373 \times 373 \times R}{1000 \Delta H_{\text{vap}}}$
(B) Molal elevation constant of water	(q) $\frac{373 \times 373 \times R}{1000 L_{\text{vap}}}$
(C) ΔT_f of solution containing 9.0 g of glucose in 50 g of water	(r) $\frac{18 \times 273 \times 273 \times R}{1000 \Delta H_{\text{fus}}}$
(D) ΔT_b of solution containing-3.0g of urea in 50 g of water	(s) $\frac{273 \times 273 \times R}{1000 \Delta H_{\text{fus}}}$
	(t) K_f

Solution

A \rightarrow (r, t); B \rightarrow (p); C \rightarrow (r, s, t); D \rightarrow (p, q)

Matrix matching – conceptual

$$(A) K_f = \frac{RT_f^{02}}{1000L_f} = \frac{RT_f^{02} M}{1000 \Delta H_f}; T_f^0 (\text{water}) = 273 \text{ K}, M = 18$$

$$(B) K_b = \frac{RT_b^{02}}{1000L_v} = \frac{RT_b^{02} M}{1000 \Delta H_v}; T_b^0 (\text{water}) = 373 \text{ K}, M = 18$$

$$(C) \Delta T_f = K_f \times m = K_f \times \frac{9 \times 1000}{180 \times 50} = K_f$$

$$(D) \Delta T_b = K_b \times m = K_b \times \frac{3 \times 1000}{60 \times 50} = K_b$$

5. For a 5% solution of H_2SO_4 ($\rho = 1.01 \text{ g mL}^{-1}$), match the quantities with their values.

Column I	Column II
(A) Molarity of the solution	(p) 0.537
(B) Molality of the solution	(q) 0.0096
(C) Mole fraction of H_2SO_4	(r) 0.05
(D) Mass fraction of H_2SO_4	(s) 0.515

Solution

A \rightarrow (s); B \rightarrow (p); C \rightarrow (q); D \rightarrow (r)

5% H_2SO_4 means 5 g of H_2SO_4 in 100 g of solution or 95 g of solvent.

Density = mass/volume = 1.01 g/mL \Rightarrow Mass of solution = 100 g.

So, volume of solution = mass/density = 0.099 L

(A) Molarity = Number of moles of H_2SO_4 /Volume of solution = (5/98)/0.099 = 0.515 M.

(B) Molality = Number of moles of H_2SO_4 /Weight of solvent in kg = (5/98)/0.095 = 0.537 molal.

(C) Mole fraction = Number of moles of H_2SO_4 /Total number of moles of H_2SO_4 + Water
 $= (5/98)/(5/98) + (95/18) = 0.0096$

(D) Mass fraction = Mass of H_2SO_4 /Mass of solution = 5/100=0.005

6. Match the columns I and II. Consider constant pressure of 1 atm.

Column I	Column II
(A) Mixture of two immiscible liquids	(p) Composition dependent
(B) Solution of two miscible liquids	(q) Constant. Independent to the relative amounts of the liquids
(C) Maximum B.pt. azeotrope	(r) Constant along with composition
(D) Minimum B.pt azeotrope	(s) Constant, composition of solution and vapor being identical

	(t) Can be basis of separation of liquid from mixture
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Solution

A \rightarrow (q, t); B \rightarrow (p, t); C \rightarrow (r, s); D \rightarrow (r, s)

$\Pi = iCRT$, where $i = 1+3$

So, the maximum boiling point of azeotrope is when there is a -ve deviation from Raoult's law, and the minimum boiling point of azeotrope is when there is a +ve deviation from Raoult's law.

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