CHAPTER
1

Solutions

NCERT FOCUS ANSWERS

Topic 1

1. A solution is a homogeneous mixture of two or more pure substances which are chemically non-reacting, whose composition can be varied within certain limits. The component which is present in a large proportion in the solution is called solvent and the component present in relatively small proportion is called solute.

Types of solutions : Depending upon the physical state of solvent, solutions can be divided into three main groups :

(a) Gaseous solutions :

(i) Solvent - gas, solute - gas. *e.g.*, air (oxygen and nitrogen).

(ii) Solvent - gas, solute - liquid. *e.g.*, humidity in air.

(iii) Solvent - gas, solute - solid. *e.g.*, camphor in nitrogen.

(b) Liquid solutions :

(i) Solvent - liquid, solute - gas. *e.g.*, aerated drinks.

(ii) Solvent - liquid, solute - liquid. *e.g.*, ethanol in water.

(iii) Solvent - liquid, solute - solid. *e.g.*, salt solution in water.

(c) Solid solutions :

(i) Solvent - solid, solute - gas. *e.g.*, H_2 over palladium.

(ii) Solvent - solid, solute - liquid. *e.g.*, amalgam of Hg with Na.

(iii) Solvent - solid, solute - solid. *e.g.*, alloys.

2. Solution of hydrogen over palladium and dissolved gases in minerals.

3. **(i) Mole fraction :** Mole fraction of a constituent (solute as well as solvent) is the ratio of the number of moles of one component to the total number of moles of all the components present in the solution. If n_A and n_B are the number of moles of solvent and solute respectively then

$$x_A = \frac{n_A}{n_A + n_B} \text{ and } x_B = \frac{n_B}{n_A + n_B}$$

(ii) Molality : Molality of a solution is defined as the number of moles of the solute dissolved in one kilogram of the solvent. It is denoted by m. It is expressed as

$$m = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

$$\text{or } \frac{\text{Number of moles of solute}}{\text{Mass of solvent in grams}} \times 1000$$

(iii) Molarity : Molarity of a solution is defined as the number of moles of the solute dissolved in one litre or one dm^3 of the solution. It is denoted by M and is expressed as

$$M = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litres}}$$

(iv) Mass percentage : It may be defined as mass of solute in grams per 100 g of solution.

$$\frac{w}{W} \text{ or mass percentage} = \frac{\text{Mass of solute}}{\text{Total mass of solution}} \times 100$$

4. Let mass of solution = 100 g

Then mass of nitric acid = 68 g

Molar mass of HNO_3 = 63 g mol^{-1}

Number of moles of $HNO_3 = \frac{68}{63} = 1.079$ mole

Density of solution = 1.504 g mL^{-1}

$\therefore$ Volume of solution $= \frac{100 \text{ g}}{1.504 \text{ g mL}^{-1}}$

$= 66.5 \text{ mL} = 0.0665 \text{ L}$

Molarity of the solution =

$$\frac{\text{Number of moles of the solute}}{\text{Volume of solution in L}} = \frac{1.079}{0.0665}$$

$= 16.23$ M

5. Let mass of solution = 100 g

$\therefore$ Mass of glucose = 10 g

Mass of water = 90 g = 0.09 kg

No. of moles in 10 g glucose $= \frac{10}{180} = 0.0555$ mol

No. of moles in 90g $H_2O = \frac{90}{18} = 5$ moles

Volume of solution $= \frac{100 \text{ g}}{1.2 \text{ gmL}^{-1}} = 83.33 \text{ mL} = 0.0833 \text{ L}$

(a) Molality $= \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}} = \frac{0.0555 \text{ mol}}{0.09 \text{ kg}}$

$= 0.617$ m

(b) Mole fraction of glucose

$$= \frac{\text{Number of moles of solute}}{\text{Number of moles of solution}} = \frac{0.0555}{5.0555}$$

$= 0.01$

$\therefore$ $x(H_2O) = 1 - 0.01 = 0.99$

(c) Molarity $= \frac{\text{Number of moles of solute}}{\text{Volume of solution in L}} = \frac{0.0555}{0.0833}$

$= 0.666$ M

6. **Step 1 :** Calculation of the number of moles of the components in the mixture.

Let Na_2CO_3 present in the mixture $= x$ g

$\therefore$ $NaHCO_3$ present in the mixture $= (1 - x)$ g

Molar mass of $Na_2CO_3 = 2 \times 23 + 12 + 3 \times 16 = 106 \text{ g mol}^{-1}$

Molar mass of $NaHCO_3 = 23 + 1 + 12 + 3 \times 16 = 84 \text{ g mol}^{-1}$

$\therefore$ No. of moles of Na_2CO_3 in x g $= \dfrac{x}{106}$

No. of moles of $NaHCO_3$ in $(1 - x)$ g $= \dfrac{1-x}{84}$

As mixture contains equimolar amounts of the two,

$$\frac{x}{106} = \frac{1-x}{84} \quad \text{or, } 106 - 106x = 84x$$

or, $x = \dfrac{106}{190}$ g $= 0.558$ g

Thus, moles of $Na_2CO_3 = \dfrac{0.558}{106} = 0.00526$

$\therefore$ Moles of $NaHCO_3 = 0.00526$

Step 2 : To calculate the moles of HCl required.

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

1 mole of Na_2CO_3 requires HCl = 2 moles

$\therefore$ 0.00526 mole of Na_2CO_3 requires HCl

$= 0.00526 \times 2 = 0.01052$ mole

1 mole of $NaHCO_3$ requires HCl = 1 mole

$\therefore$ 0.00526 mole of $NaHCO_3$ requires HCl = 0.00526 mole

$\therefore$ Total HCl required $= 0.01052 + 0.00526 = 0.01578$ mole

Step 3 : To calculate volume of 0.1 M HCl

$$\text{Volume of acid} = \frac{\text{Number of moles}}{\text{Molarity}} = \frac{0.01578}{0.1} \text{ L} = 157.8 \text{ mL}$$

7. 300 g of 25% solution contains solute = 75 g

400 g of 40% solution contains solute = 160 g

Total mass of solute = 160 + 75 = 235 g

Total mass of solution = 300 + 400 = 700 g

$$\% \text{ of solute in the final solution} = \frac{235}{700} \times 100 = 33.5\%$$

% of water in the final solution = 100 – 33.5 = 66.5%

8. Mass of the solute, $C_2H_4(OH)_2 = 222.6$ g

Molar mass of solute, $C_2H_4(OH)_2 = 62 \text{ g mol}^{-1}$

$$\therefore \text{ Moles of the solute} = \frac{222.6 \text{ g}}{62 \text{ g mol}^{-1}} = 3.59 \text{ mol}$$

Mass of the solvent = 200 g = 0.200 kg

$$\text{Volume of solution} = \frac{422.6}{1.072 \text{ g mL}^{-1}} = 394.2 \text{ mL} = 0.3942 \text{ L}$$

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}} = \frac{3.59}{0.2} = 17.95 \text{ m}$$

$$\text{Molarity} = \frac{3.59 \text{ moles}}{0.3942 \text{ L}} = 9.11 \text{ mol L}^{-1}$$

9. (i) 15 ppm means 15 parts in million (10^6) parts by mass in the solution.

$$\% \text{ by mass} = \frac{15}{10^6} \times 100 = 1.5 \times 10^{-3}$$

(ii) Mass of solvent = 10^6 g (Mass of solute is negligible)

Molar mass of $CHCl_3 = 12 + 1 + 3 \times 35.5 = 119.5 \text{ g mol}^{-1}$

$$\text{No. of moles of } CHCl_3 = \frac{\text{Mass (in g)}}{\text{Molar mass}} = \frac{15}{119.5}$$

$$\therefore \text{ Molality} = \frac{15/119.5}{10^6} \times 1000 = 1.25 \times 10^{-4} \text{ m}$$

10. Number of moles in 92 g of Na^+ ions

$$= \frac{92 \text{ g}}{23 \text{ g mol}^{-1}} = 4 \text{ mole (as atomic mass of Na = 23)}$$

As these are present in 1 kg of water, by definition molality = 4 m

11. Given, Mass of aspirin = 6.5 g,

Mass of acetonitrile = 450 g

Mass percent of aspirin

$$= \frac{\text{Mass of aspirin}}{\text{Mass of aspirin + Mass of acetonitrile}} \times 100$$

$$= \frac{6.5}{6.5 + 450} \times 100 = 1.424\%$$

12. Given, $m = 1.5 \times 10^{-3}$

Mass of solvent = 1 kg

Molar mass of $C_{19}H_{21}NO_3 = 19 \times 12 + 21 + 14 + 48$

$= 311 \text{ g mol}^{-1}$

$\therefore$ 1.5×10^{-3} mole of $C_{19}H_{21}NO_3$

$= 1.5 \times 10^{-3} \times 311\text{g} = 0.467 \text{ g} = 467 \text{ mg}$

$\therefore$ Mass of solution = 1000 g + 0.467 g = 1000.467 g

Thus, for 467 mg of nalorphene, solution required = 1000.467 g

For 1.5 mg of nalorphene, solution required

$$= \frac{1000.467}{467} \times 1.5 = 3.21 \text{ g}$$

13. $M = \dfrac{w_2 \times 1000}{M_2 \times V}$

$$0.15 = \frac{w_2 \times 1000}{122 \times 250} \quad \text{or, } w_2 = \frac{0.15 \times 122}{4} = 4.57 \text{ g}$$

Topic 2

1. As the temperature is increased, the equilibrium between a gas and liquid solution shifts in backward direction since dissolution of gas in liquid is an exothermic process. Hence the solubility of the gases decreases.

2. **Henry's law :** The solubility of a gas in a liquid at a particular temperature is directly proportional to the pressure of the gas in equilibrium with the liquid at that temperature.

OR

The partial pressure of a gas in vapour phase is proportional to the mole fraction of the gas (x) in the solution.

$$p = K_H x$$

where K_H is Henry's law constant.

Applications of Henry's law :

(i) To increase the solubility of CO_2 in soft drinks, soda, etc., the bottles are sealed under high pressure.

(ii) In deep sea diving, increased pressure increases the solubility of atmospheric gases in blood. Oxygen is used up in the metabolism but N_2 remains dissolved and forms bubbles in the blood, when diver comes to the surface. To reduce this danger, N_2 is replaced by He which is much less soluble in biological fluids.

3. Applying the relationship

$$m = K_H \times p$$

In the first case, 6.56×10^{-3} g $= K_H \times 1$ bar

or, $K_H = 6.56 \times 10^{-3}$ g bar^{-1}

In the second case,

$$5.00 \times 10^{-2} \text{ g} = (6.56 \times 10^{-3} \text{ g bar}^{-1}) \times p$$

$$\text{or,} \quad p = \frac{5.00 \times 10^{-2} \text{ g}}{6.56 \times 10^{-3} \text{ g bar}^{-1}} = 7.62 \text{ bar}$$

4. Here, $K_H = 4.27 \times 10^5$ mm Hg, $p = 760$ mm Hg

Applying Henry's law, $p = K_H x$

$$\therefore \quad x = \frac{p}{K_H} = \frac{760}{4.27 \times 10^5} = 1.78 \times 10^{-3}$$

i.e., solubility in terms of mole fraction of methane in benzene $= 1.78 \times 10^{-3}$

5. Maximum molarity of CuS in aqueous solution = Solubility of CuS in mol L^{-1}

If S is the solubility of CuS in mol L^{-1}, then

$$CuS \rightleftharpoons Cu^{2+} + S^{2-}, K_{sp} = [Cu^{2+}][S^{2-}] = S \times S = S^2$$

$$\therefore \quad S^2 = 6 \times 10^{-16} \quad \text{or} \quad S = \sqrt{6 \times 10^{-16}}$$

$$= 2.45 \times 10^{-8} \text{ mol L}^{-1}$$

6. Total pressure of air in equilibrium with water = 10 atmosphere

As air contains 20% oxygen and 79% nitrogen by volume,

$\therefore$ Partial pressure of oxygen (p_{O_2})

$$= \frac{20}{100} \times 10 \text{ atm}$$

$$= 2 \text{ atm} = 2 \times 760 \text{ mm Hg} = 1520 \text{ mm Hg}$$

Partial pressure of nitrogen $(p_{N_2}) = \frac{79}{100} \times 10$ atm

$$= 7.9 \text{ atm} = 7.9 \times 760 \text{ mm Hg} = 6004 \text{ mm Hg}$$

$$K_H(O_2) = 3.30 \times 10^7 \text{mm Hg,}$$

$$K_H(N_2) = 6.51 \times 10^7 \text{ mm Hg}$$

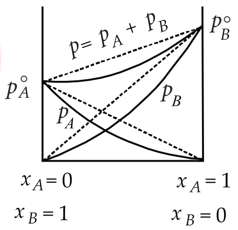
Applying Henry's law, $p_{O_2} = K_H \times x_{O_2}$

$$\text{or,} \quad x_{O_2} = \frac{p_{O_2}}{K_H} = \frac{1520 \text{ mm Hg}}{3.30 \times 10^7 \text{ mm Hg}} = 4.61 \times 10^{-5}$$

$$p_{N_2} = K_H \times x_{N_2}$$

$$x_{N_2} = \frac{p_{N_2}}{K_H} = \frac{6004 \text{ mm Hg}}{6.51 \times 10^7 \text{ mm Hg}} = 9.22 \times 10^{-5}$$

Topic 3



Non-ideal solution with negative deviation

1. **Negative deviation from Roult's law :** When intermolecular forces between A and B are stronger than A-A and B-B, then intermolecular force increases, volume decreases, vapour pressure decreases and heat is released.

Hence, $\Delta V_{mix} = -$ve,

$\Delta H_{mix} = -$ve

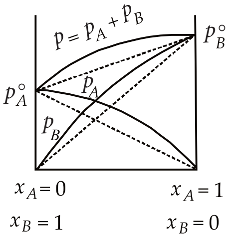
This is why, the solution is known as non-ideal solution with –ve deviation.

$$p_A < x_A p^\circ_A, p_B < x_B p^\circ_B \text{ and } p_S < x_A p^\circ_A + x_B p^\circ_B$$

Examples :

(i) Chloroform + acetone

(ii) Acetone + aniline



Non-ideal solution with positive deviation

(b) Positive deviation from Raoult's law: When intermolecular forces between A and B are weaker than that of A-A and B-B.

In this case intermolecular force decreases, volume increases, vapour pressure increases, enthalpy increases.

$$\Delta V_{mix} = +\text{ve}, \Delta H_{mix} = +\text{ ve},$$

So, it is called non-ideal solution with positive deviation.

$$p_A > x_A p^\circ_A, p_B > x_B p^\circ_B \quad \text{and } p_S > x_A p^\circ_A + x_B p^\circ_B$$

Examples :

(i) Ethanol + water

(ii) Chloroform + ethanol

2 (i) *n*-Hexane and *n*-octane : London dispersion forces as both the molecules are non-polar.

(ii) I_2 and CCl_4 : London dispersion forces as both the molecules are non-polar.

(iii) $NaClO_4$ and water : Ion-dipole interactions as $NaClO_4$ in water gives Na^+ and ClO_4^- ions. These ions interact with polar water molecules.

(iv) Methanol and acetone : Dipole-dipole interactions as both the molecules are polar.

(v) Acetonitrile and acetone : Dipole-dipole interactions as both the molecules are polar.

3. (i) Cyclohexane and *n*-octane both are non-polar. Hence, they mix completely in all proportions.

(ii) KCl is an ionic compound while *n*-octane is non-polar. Hence, KCl will not dissolve at all in *n*-octane.

(iii) CH_3OH and CH_3CN both are polar but CH_3CN is less polar than CH_3OH. As the solvent is non-polar, CH_3CN will dissolve more than CH_3OH in *n*-octane.

Thus, the order of solubility will be $KCl < CH_3OH < CH_3CN <$ cyclohexane.

4. (i) Partially soluble because phenol has polar –OH group and non-polar C_6H_5 group.

(ii) Insoluble because toluene is non-polar while water is polar.

(iii) Highly soluble because formic acid can form hydrogen bonds with water.

(iv) Highly soluble because ethylene glycol can form hydrogen bonds with water.

(v) Insoluble because chloroform is an organic liquid.

(vi) Partially soluble because –OH group is polar but the large hydrocarbon part (C_5H_{11}) is non-polar.

5. Number of moles of liquid *A* (solute)

$$= \frac{100\text{ g}}{140\text{ g mol}^{-1}} = \frac{5}{7}\text{ mole}$$

Number of moles of liquid *B* (solvent)

$$= \frac{1000\text{ g}}{180\text{ g mol}^{-1}} = \frac{50}{9}\text{ mole}$$

∴ Mole fraction of *A* in the solution (x_A)

$$= \frac{\frac{5}{7}}{\frac{5}{7}+\frac{50}{9}} = \frac{\frac{5}{7}}{\frac{395}{63}} = \frac{5}{7}\times\frac{63}{395} = \frac{45}{395} = 0.114$$

∴ Mole fraction of *B* in the solution $(x_B) = 1 - 0.114 = 0.886$

Also, given $p^\circ_B = 500$ torr

Applying Raoult's law,

$$p_A = x_A\, p^\circ_A = 0.114 \times p^\circ_A \quad \text{... (i)}$$

$$p_B = x_B\, p^\circ_B = 0.886 \times 500 = 443 \text{ torr}$$

$$p_{Total} = p_A + p_B$$

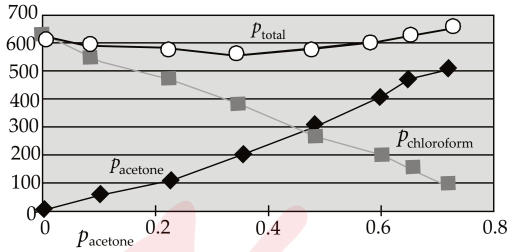
$$475 = 0.114\, p^\circ_A + 443 \;\text{ or }\; p^\circ_A = \frac{475-443}{0.114} = 280.7 \text{ torr}$$

Substituting this value in eqn. (i), we get

$$p_A = 0.114 \times 280.7 \text{ torr} = 32 \text{ torr}$$

6.

$x_{acetone}$	0.0	0.118	0.234	0.360	0.508	0.582	0.645	0.721
$P_{acetone}$/mm Hg	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$P_{chloroform}$/mm Hg	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7
P_{total}	632.8	603.0	579.5	562.1	580.4	599.5	615.3	641.8



As the plot for p_{total} dips downwards, hence the solution shows negative deviation from the ideal behaviour.

7. Molar mass of benzene $(C_6H_6) = 78\text{ g mol}^{-1}$

Molar mass of toluene $(C_7H_8) = 92\text{ g mol}^{-1}$

∴ Number of moles in 80 g of benzene

$$= \frac{80\text{ g}}{78\text{ g mol}^{-1}} = 1.026 \text{ mole}$$

∴ Number of moles in 100 g of toluene $= \dfrac{100\text{ g}}{92\text{ g mol}^{-1}}$

$$= 1.086 \text{ mole}$$

∴ In the solution, mole fraction of benzene

$$= \frac{1.026}{1.026+1.086} = \frac{1.026}{2.112} = 0.486$$

Mole fraction of toluene $= 1 - 0.486 = 0.514$

$$p^\circ_{benzene} = 50.71 \text{ mm Hg},\; p^\circ_{toluene} = 32.06 \text{ mm Hg}$$

Applying Raoult's law of vapour pressure

$$p_{toluene} = x_{benzene} \times p^\circ_{benzene} = 0.486 \times 50.71 \text{ mm Hg}$$
$$= 24.65 \text{ mm Hg}$$

$$p_{toluene} = x_{toluene} \times p^\circ_{toluene}$$
$$= 0.514 \times 32.06 \text{ mm Hg} = 16.48 \text{ mm Hg}$$

∴ From Dalton's law, mole fraction of benzene in the vapour phase

$$= \frac{p_{Benzene}}{p_{Benzene}+p_{toluene}} = \frac{24.65}{24.65+16.48} = \frac{24.65}{41.13} = 0.5993$$

8. Molar mass of heptane $(C_7H_{16}) = 100\text{ g mol}^{-1}$

Molar mass of octane $(C_8H_{18}) = 114\text{ g mol}^{-1}$

Number of moles of heptane $= \dfrac{26.0\text{ g}}{100\text{ g mol}^{-1}} = 0.26$ mol

No. of moles of octane $= \dfrac{35.0\text{ g}}{114\text{ g mol}^{-1}} = 0.31$ mol

$$x\text{ (heptane)} = \frac{0.26}{0.26+0.31} = 0.456$$

x (octane) = 1– 0.456 = 0.544

p(heptane) = 0.456 × 105.2 kPa = 47.97 kPa

p(octane) = 0.544 × 46.8 kPa = 25.46 kPa

p_{Total} = 47.97 + 25.46 = 73.43 kPa

9. There is a strong hydrogen bonding in water as well as in alcohol molecules. When alcohol and water are mixed the intermolecular hydrogen bonding between the alcohol and water molecules in the mixture is weak. Due to weaker interactions, the solution shows positive deviations from ideal behaviour. As a result, the solution will have higher vapour pressure and lower boiling point than alcohol and water separately.

Topic 4

1. Vapour pressure of pure water at the boiling point ($p°$) = 1 atm = 1.013 bar

Vapour pressure of solution (p_s) = 1.004 bar

Let mass of solution = 100 g, then, mass of solute (w_2) = 2 g

Mass of solvent (w_1) = 100 – 2 = 98 g

Applying Raoult's law for dilute solution,

$$\frac{p°-p_s}{p°}=\frac{n_2}{n_1+n_2}=\frac{n_2}{n_1}=\frac{w_2/M_2}{w_1/M_1}=\frac{w_2}{M_2}\times\frac{M_1}{w_1}$$

$$\frac{1.013-1.004}{1.013}=\frac{2\text{ g}}{M_2}\times\frac{18\text{ g mol}^{-1}}{98\text{ g}}$$

or, $M_2=\frac{2\times18}{98}\times\frac{1.013}{0.009}$ g mol^{-1}

= 41.35 g mol^{-1}

2. Given $p°$ = 12.3 kPa, p_s = ? m = 1

m = 1 molal means 1 mol of solute present in 1000 g of water.

No. of moles of solute = 1,

No. of moles of water $=\frac{1000}{18}$ = 55.5

∴ Mole fraction of solute $=\frac{1}{1+55.5}$ = 0.0177

From Raoult's law, $\frac{p°-p_s}{p°}=x_2$,

i.e., $\frac{12.3-p_s}{12.3}=0.0177$

or p_s = 12.08 kPa

3. Number of moles of solute $=\frac{w}{40}$ mol

Let $p°$ = 100 then p_s = 80

Δp = 20

No. of moles of solvent (octane) = $\frac{114\text{ g}}{114\text{ g mol}^{-1}}$ = 1 mol

[molar mass of C_8H_{18} = 114 g mol^{-1}]

Now, $\frac{\Delta p}{p°}=x_2$ ∴ $\frac{20}{100}=\frac{w/40}{\frac{w}{40}+1}$

or, $0.2\left(\frac{w}{40}+1\right)=\frac{w}{40}$ or, $\frac{0.8w}{40}=0.2$

or, w = 10 g

4. (i) Suppose the molar mass of the solute = M g mol^{-1}

No. of moles of solute, $n_2=\frac{30}{M}$ moles

No. of moles of solvent, H_2O, $n_1=\frac{90\text{ g}}{18\text{ g mol}^{-1}}$ = 5 moles

From Raoult's law, $\frac{p°-p_s}{p°}=\frac{n_2}{n_1+n_2}$,

i.e., $\frac{p°-2.8}{p°}=\frac{\frac{30}{M}}{5+\frac{30}{M}}$

or, $1-\frac{2.8}{P°}=\frac{\frac{30}{M}}{5+\frac{30}{M}}$

or, $\frac{2.8}{p°}=1-\frac{\frac{30}{M}}{5+\frac{30}{M}}=\frac{5+\frac{30}{M}-\frac{30}{M}}{5+\frac{30}{M}}=\frac{5}{5+\frac{30}{M}}$

or, $\frac{p°}{2.8}=\frac{5+\frac{30}{M}}{5}=1+\frac{6}{M}$ ... (i)

After adding 18 g of water, n_1 = 6 moles

$\frac{p°-2.9}{p°}=\frac{\frac{30}{M}}{6+\frac{30}{M}}$ or, $1-\frac{2.9}{p°}=\frac{\frac{30}{M}}{6+\frac{30}{M}}$

or, $\frac{2.9}{p°}=1-\frac{\frac{30}{M}}{6+\frac{30}{M}}=\frac{6+\frac{30}{M}-\frac{30}{M}}{6+\frac{30}{M}}=\frac{6}{6+\frac{30}{M}}$

or, $\frac{p°}{2.9}=\frac{6+\frac{30}{M}}{6}=1+\frac{5}{M}$ ...(ii)

Dividing eqn. (i) by eqn. (ii), we get

$\frac{2.9}{2.8}=\frac{1+\frac{6}{M}}{1+\frac{5}{M}}$ or, $2.9\left(1+\frac{5}{M}\right)=2.8\left(1+\frac{6}{M}\right)$

or, $2.9+\frac{14.5}{M}=2.8+\frac{16.8}{M}$ or, $\frac{2.3}{M}=0.1$

or, $M = 23$ u

(ii) Putting $M = 23$ in eqn. (i) we get

$$\frac{p^\circ}{2.8}=1+\frac{6}{23}=\frac{29}{23} \quad \text{or,} \quad p^\circ=\frac{29}{23}\times 2.8 = 3.53 \text{ kPa}$$

5. Molality of sugar solution $=\frac{5}{342}\times\frac{1000}{100} = 0.146$ m

ΔT_f for sugar solution $= 273.15 - 271 = 2.15$

$\Delta T_f = K_f \times m \quad \therefore \; K_f = \frac{\Delta T_f}{m} = \frac{2.15}{0.146}$

Molality of glucose solution $=\frac{5}{180}\times\frac{1000}{100} = 0.278$ m

$\therefore \quad \Delta T_f \text{ (Glucose)} = \frac{2.15}{0.146}\times 0.278 = 4.09°\text{C}$

$\therefore$ Freezing point of glucose solution

$= 273.15 - 4.09 = 269.06$ K

6. For AB_2, $\Delta T_f = K_f \times \frac{w_2 \times 1000}{M_2 \times w_1}$

or, $2.3 = 5.1 \times \frac{1 \times 1000}{M_2 \times 20}$

$\therefore \; M_2 = \frac{50 \times 5.1}{2.3} = 110.86 \text{ g mol}^{-1}$

Similarly for AB_4, $1.3 = 5.1 \times \frac{1\times 1000}{M_2 \times 20}$

$\therefore \quad M_2 = \frac{50\times 5.1}{1.3} = 196.15 \text{ g mol}^{-1}$

Now, molecular weight of $AB_2 = 110.86$, molecular weight of $AB_4 = 196.15$

$AB_4 = A + 4B = 196.15$ ... (i)

$AB_2 = A + 2B = 110.86$ ... (ii)

On subtracting eqn. (ii) from (i), $2B = 85.29$

$\therefore \; B = 42.645$ u

Putting the value of B in equation (ii),

$A + 2 \times 42.645 = 110.86$

or, $A = 110.86 - 85.29 = 25.57$ u

7. $\pi = CRT$

$\therefore$ In the first case, $4.98 = \frac{36}{180} \times R \times 300 = 60R$ ... (i)

In the second case, $1.52 = C \times R \times 300$ ... (ii)

Dividing (ii) by (i) we get, $C = 0.061$ M

8. The depression in freezing point is in the order :

Acetic acid (CH_3-COOH) < trichloroacetic acid ($Cl_3C-COOH$) < trifluoroacetic acid ($F_3C-COOH$)

Fluorine, being most electronegative, has the highest electron withdrawing inductive effect. Consequently, trifluoroacetic acid is the strongest acid while acetic acid is the weakest acid. Hence, trifluoroacetic acid ionizes to the largest extent while acetic acid ionizes to the minimum extent to give ions in their solutions in water. Greater the ions produced, greater is the depression in freezing point. Hence, the depression in freezing point is the maximum for the fluoroacetic acid and minimum for acetic acid.

9. Number of moles of $CH_3CH_2CH(Cl)COOH$

$= \frac{10}{122.5}$ mole $= 8.16 \times 10^{-2}$ mole

$\therefore$ Molality of the solution (m)

$= \frac{8.16\times 10^{-2} \text{ mol}}{250}\times 1000 \text{ kg}^{-1} = 0.3264$ m

If α is the degree of dissociation of $CH_3CH_2CH(Cl)COOH$, then

	$CH_3CH_2CH(Cl)COOH$ ⇌	$CH_3CH_2CH(Cl)COO^-$ +	H^+
Initial conc.	C mol L^{-1}	0	0
At equilibrium	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$\therefore \quad K_a = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = C\alpha^2$

or, $\alpha = \sqrt{K_a / C} = \sqrt{\frac{1.4\times 10^{-3}}{0.3264}} = 0.065$

To calculate van't Hoff factor:

	$CH_3CH_2CH(Cl)COOH$ ⇌	$CH_3CH_2CH(Cl)COO^-$ +	H^+
Initial moles	1	0	0
Moles at eqm.	$1-\alpha$	α	α

Total moles $= 1 + \alpha \;\; \therefore \; i = 1 + 0.065 = 1.065$

$\Delta T_f = iK_f m = (1.065)(1.86)(0.3264) = 0.65$

10. Given, $w_2 = 19.5$ g, $w_1 = 500$ g,

$K_f = 1.86$ K kg mol^{-1}, $(\Delta T_f)_{obs} = 1.0°$C, $M_2 = ?$

$\therefore \; M_2 \text{ (observed)} = \frac{1000 K_f w_2}{w_1 \Delta T_f}$

$= \frac{1000 \times 1.86 \times 19.5}{500 \times 1.0} = 72.54 \text{ g mol}^{-1}$

M_2 (calculated) for $CH_2FCOOH = 78$ g mol^{-1}

van't Hoff factor $(i) = \frac{(M_2)_{cal}}{(M_2)_{obs}} = \frac{78}{72.54} = 1.0753$

Calculation of dissociation constant :

Suppose degree of dissociation at the given concentration is a. Then,

	$CH_2FCOOH \rightarrow$	CH_2FCOO^- +	H^+
Initial	C	0	0
At eqm.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

Total moles $= C(1+\alpha)$

$\therefore \quad i = \frac{C(1+\alpha)}{C} = 1 + \alpha$ or, $\alpha = i - 1 = 1.0753 - 1$

$= 0.0753$

Again $K_a = \frac{[CH_2FCOOH][H^+]}{[CH_2FCOOH]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$

Taking volume of the solution as 500 mL,

$$C = \frac{19.5}{78} \times \frac{1}{500} \times 1000 = 0.5 \text{ M}$$

$$\therefore \; K_a = \frac{C\alpha^2}{1-\alpha} = \frac{(0.5)(0.0753)^2}{1-0.0753} = 3.07 \times 10^{-3}$$

11. Given, p° = 17.535 mm Hg, w_2 = 25 g, w_1 = 450 g, p_s = ?

For solute (glucose, $C_6H_{12}O_6$), M_2 = 180 g mol^{-1},

For solvent (H_2O), M_1 = 18 g mol^{-1}

Applying Raoult's law,

$$\frac{p^\circ - p_s}{p^\circ} = \frac{n_2}{n_1 + n_2},$$

$$\frac{p^\circ - p_s}{p^\circ} = \frac{n_2}{n_1} = \frac{\frac{w_2}{M_2}}{\frac{w_1}{M_1}} \qquad (\because \; n_2 << n_1)$$

or, $1 - \frac{p_s}{p^\circ} = \frac{w_2 M_1}{w_1 M_2}$

Substituting the given value, we get

$$1 - \frac{p_s}{17.535} = \frac{25 \times 18}{450 \times 180} \quad \text{or,} \quad 1 - \frac{p_s}{17.535} = \frac{1}{180}$$

$$1 - \frac{1}{180} = \frac{p_s}{17.535} \qquad \text{or,} \quad \frac{179}{180} = \frac{p_s}{17.535}$$

or, $p_s = 17.535 \times \frac{179}{180} = 17.437$ mmHg

12. From the expression, $\pi = iCRT = i\frac{n}{V}RT$

or, $n = \frac{\pi \times V}{i \times R \times T}$

$$= \frac{0.75 \text{ atm} \times 2.5 \text{ L}}{2.47 \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}$$

$$= 0.0308 \text{ mole}$$

Molar mass of $CaCl_2$ = 40 + 2 × 35.5 = 111g mol^{-1}

$\therefore$ Amount of $CaCl_2$ dissolved = 0.0308 × 111 = 3.42 g

13. K_2SO_4 dissolved = 25 mg = 0.025 g

Volume of solution = 2 L, T = 25°C = 298 K

Molar mass of K_2SO_4 = 2 × 39 + 32 + 4 × 16 = 174 g mol^{-1}

K_2SO_4 dissociates completely as

$K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$

i.e., ions produced = 3, $\therefore$ $i = 3$

$$\therefore \; \pi = iCRT = i\frac{n}{V}RT = i \times \frac{w}{M} \times \frac{1}{V}RT$$

$$= 3 \times \frac{0.025 \text{ g}}{174 \text{ g mol}^{-1}} \times \frac{1}{2 \text{ L}} \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$\times 298 \text{ K} = 5.27 \times 10^{-3} \text{ atm}$$

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