SOLUTIONS OF SOLUTION & COLLIGATIVE PROPERTIES

EXERCISE # 1

PART - I

B-1. Equivalent of HCl per ml = $\frac{0.0365}{36.5}$ = 0.001 eq. (eq. wt. of HCl = 36.5)

$\therefore$ Normality of HCl = eq. of HCl per 1000 ml = 1 N
$\therefore$ Normality of NaOH = 1 N
$\therefore$ gram per 1000 ml of NaOH = normality × eq. wt. = 1 × 40 = 40 (eq. wt. of NaOH = 40)
$\therefore$ concentration of NaOH solution in g/ml = 0.04 g/ml **(Ans. 0.04 g)**

B-2. (i) Let us consider one litre of $Na_2S_2O_3$ solution.
$\therefore$ wt. of the solution = density × volume (ml) = 1.58 × 1000 = 1580 gram
wt. of $Na_2S_2O_3$ present in 1 litre of the solution = molarity × mol. Wt = 3 × 158 = 474 gram

wt % of $Na_2S_2O_3$ = $\frac{474}{1580}$ × 100 = 30% **(Ans. 30%)**

(ii) wt. of solute ($Na_2S_2O_3$) = 474 gram

moles of solute = $\frac{474}{158}$ = 3

wt. of solvent (H_2O) = 1580 – 474 = 1106 gram, moles of solvent = $\frac{1106}{18}$ = 61.444

$\therefore$ mole fraction of $Na_2S_2O_3$ = $\frac{3}{3+61.44}$ = 0.046 **(Ans. 0.046)**

(iii) Molality of $Na_2S_2O_3$ = $\frac{\text{moles of } Na_2S_2O_3}{\text{wt.of solvent in grams}}$ × 1000 = $\frac{3}{1106}$ × 1000 = 2.71 m

$\because$ 1 mole of $Na_2S_2O_3$ contains 2 moles of Na^+ ions and 1 mole of $S_2O_3^{2-}$ ions.
$\therefore$ molality of Na^+ = 2 × 2.71 = 5.42 m **(Ans. Na^+ = 5.42 m)**
molality of $S_2O_3^{2-}$ = 2.71 m **(Ans. $S_2O_3^{2-}$ = 2.71 m)**

B-3. Suppose that the solution contains 100 ml of each variety of H_2SO_4. Total solution is, 200 ml or 0.2 litre
wt. of 100 ml of H_2SO_4 solution (30%) = 1.20 × 100 = 120 gram
and wt. of 100 ml of H_2SO_4 solution (70%) = 1.60 × 100 = 160 gram

wt. of H_2SO_4 (30%) = 120 × $\frac{30}{100}$ = 36 gram

wt. of H_2SO_4 (70%) = 160 × $\frac{70}{100}$ = 112 gram

Total wt. of H_2SO_4 (solute) = 36 + 112 = 148 gram
$\therefore$ wt. of H_2O (solvent) = wt. of solution – wt. of solute
= (120 + 160) – 148 = 280 – 148 = 132 gram

Moles of H_2SO_4 = $\frac{148}{98}$ = 1.51 (mol. wt. of H_2SO_4 = 98)

Molality = $\frac{1.51}{132}$ × 1000 = 11.44 m

Molarity = $\frac{1.51}{0.2}$ = 7.55 M

C-1. In 100 ml vessel which contained water - saturated oxygen, the pressure of O_2 gas = 760 – 355 = 405 torr.

When the contents of this vessel were pumped into 50 ml vessel, at the same temperature, the pressure of oxygen gets doubled i.e. P_{O_2} = 810 torr.

But pressure of water vapour will remain constant, as some vapour in this 50 ml vessel, gets condensed.

So P_{H_2O} = 355 torr & Total pressure = 810 + 355 = 1165 torr.

C-2. $P_{N_2} + P_{H_2O(v)} = 1$ atm, $\because$ $P_{H_2O} = 0.3$ atm

$\therefore$ $P_{N_2} = 0.7$ atm

Now new pressure of N_2 in another vessel of volume V/3 at same T is given by :

$$P_{N_2} \times \frac{V_1}{3} = 0.70 \times V_1$$

$$\therefore \quad P_{N_2} = 2.1 \text{ atm}$$

Since aqueous tension remains constant, and thus total pressure in new vessel.

= $P_{N_2} + P_{H_2O}$ = 2.1 + 0.3 = 2.4 atm.

D-1. $\frac{6.56 \times 10^{-3}}{5 \times 10^{-2}} = \frac{1}{P} \Rightarrow$ P = 7.62 bar.

D-2. The solubility of gas is related to the mole fraction in aqueous solution. The mole fraction of the gas in the solution is calculated by applying Henry's law. Thus :

$$x \text{ (Nitrogen)} = \frac{p(\text{nitrogen})}{K_H} = \frac{1 \text{bar}}{75{,}000 \text{bar}}$$

if n represents number of moles of N_2 in solution,

$$x \text{ (Nitrogen)} = \frac{n}{n+300} = \frac{n}{300} = \frac{1 \text{bar}}{75{,}000 \text{bar}}$$

(n in denominator is neglected as it is < < 300)

Thus n = 4 × 10^{-3} mol. = 4 mmol

E-1. When the liquid A-water mixture distills, the pressure = 760 mm Hg.

$\therefore$ Partial pressure of A = 760 – 739 = 21 mm Hg.

Mole fraction of A in the distillate = $\frac{21}{760}$ = 0.02764

Mole fraction of water in the distillate = $\frac{739}{760}$ = 0.9723

$\therefore$ mass of A in the distillate = 0.02764 × 123 = 3.399 g

Mass of water in the distillate = 0.9723 × 18 = 17.50 g

Mass of steam condensed per g of liquid A = $\frac{17.5}{3.399}$ = 5.15 g.

E-2. $\frac{n_W}{n_N} = \frac{W_W}{18} \cdot \frac{123}{W_N} = \frac{733}{27} \quad \Rightarrow \quad \frac{W_W}{W_N} = \frac{18 \times 733}{27 \times 123}$ = 3.973 **Ans.**

F-1. In first case, $X_A = \frac{1}{4}$, $X_B = \frac{3}{4}$ & $P_T = 550$

Acoording to Raoult's law,

$$X_A P^o_A + X_B P^o_B = P_T$$

so $\frac{1}{4} P^o_A + \frac{3}{4} P^o_B = 550$ or $P^o_A + 3P^o_B = 2200$ .... (i)

In second case

$X'_A = 1/5$, $X'_B = 4/5$ & $P_T = 560$

$\therefore$ $\frac{1}{5}P^o_A + \frac{4}{5}P^o_B = 560$ or $P^o_A + 4P^o_B = 2800$ .... (ii)

Subtracting (i) from (ii), we get

$P^o_A = 400$ mm, $P^o_B = 600$ mm of Hg.

F-2. $X_A\,P^o_A = P_A = Y_AP_T$ or $X_A \times 200 = 0.5\,P_T =$ .... (i)

Similarly

$X_B\,P^o_B = P_B = Y_BP_T$ or $X_B \times 75 = 0.5\,P_T =$ .... (ii)

Comparing (i) & (ii) we get

$200\,X_A = 75\,X_B = 75\,(1 - X_A)$

Solving we get $X_A = 0.2727 \approx 0.273$

so mol percent of A in liquid = 27.3%

F-3. The data provide the following two expressions for total pressure

$$1 = \frac{1}{4}P^o_A + \frac{3}{4}P^o_B$$

or $4 = P^o_A + 3P^o_B$ and $1 = \frac{1}{5}P^o_A + \frac{1}{5}P^o_B + \frac{3}{5}P^o_C$

or $4 = P^o_A + P^o_B + 2.4$

on solving these two equations simultaneously, one obtains $P^o_B = 0.7$ atm and $P^o_A = 1.9$ atm.

F-4. Given $P^o_{Benzene} = 753$ & $P^o_{toluene} = 290$

$X_BP^o_B = Y_BP_T$ i.e. $X_B(753) = 0.3\,P_T$ ..... (i)

$X_tP^o_t = Y_tP_T$ i.e. $X_t(290) = 0.7\,P_T$ ..... (ii)

Dividing (i) by (ii)

$$\frac{X_B(753)}{X_t(290)} = \frac{3}{7} \quad \text{or} \quad \frac{1-X_t}{X_t} = 0.165$$

$\therefore$ $X_t = 0.8584 = 85.84\%$ so $X_B = 14.16\%$.

F-5. P(mm Hg) = $180X_B + 90$

P^o_B (Benzene) = 180 + 90 ($X_B = 1$) = 270 mm Hg

P^o_T (Toluene) = 90 mm Hg ($X_B = 0$)

moles of $C_6H_6 = 12$, $X_B = 0.6$

moles of $C_6H_5CH_3 = 8$ $X_T = 0.4$

Vapour Pressure of solution $P_S = X_B\,P^o_B + X_T\,P^o_T$

$P_S = 198$ mm Hg

mole fraction of Benzene in vapour state $Y_B = \frac{P_B}{P_S}$

$$Y_B = \frac{X_BP^o_B}{P_S} = \frac{0.6 \times 270}{198} = 0.82$$

Mole fraction of Toluene in vapour state

$Y_T = 0.18$

Now this vapour when condensed

$P_S = Y_T\,P^o_T + Y_B\,P^o_B = 0.18 \times 90 + 0.82 \times 270 = 237.6$ mm Hg.

Now mole fraction of benzene in vapour state is

$$Y'_B = \frac{Y_BP^o_B}{P_S} = \frac{0.82 \times 270}{237.6}$$ **Ans.** $Y'_B = 0.932$.

G-1. Chloroform & acetone form a non-ideal solution, in which A.....B type interaction are more than A......A & B......B type interaction due to H-bonding. Hence, the solution shows, negative deviation from Raoult's Law i.e.,

$\Delta V_{mix} = -ve$; $\Delta H_{mix} = -ve$

total volume of solution = less than (30 + 50 ml)

or $<$ 80 ml

Ans. V < 80ml.

G-2. $P_{ideal} = P^o{}_A x_A + P^o{}_B x_B$;

$$= 100 \times \frac{1}{4} + 80 \times \frac{3}{4} \Rightarrow 85 \text{ mm Hg}$$

P_{actual} = 90 mm Hg ;

Actual v. pr. is greater than ideal solution v. pr. so +ve deviation from Raoult's law.

H-2. $XY_2 \rightleftharpoons X^{2+} + 2Y^-$

Initially 1 0 0

at equilibrium $1-\alpha$ α 2α

Total no. of moles = $1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} ; \frac{1+2\alpha}{1} = \frac{164}{65.6}$$

$\therefore$ $\alpha = 0.75$; %α = 75%.

I-1. (a) Relative lowering of vapour pressure = mole fraction of solute

$$\frac{23.76-22.41}{23.76} = \frac{20/M}{20/M+100/18} = 0.0568$$

so M = 60 g/mol

(b) Let w be the mass of solute reqd.

& $P = \frac{P^o}{2}$

so $$\frac{P^o - P}{P^o} = \frac{w/60}{w/60+100/18} \text{ or } \frac{P^o - P^o/2}{P^o} = \frac{w/60}{w/60+5.56}$$

$\therefore$ w = 333.3 g

I-2. $Ca(NO_3)_2 (aq) \rightleftharpoons Ca^{2+} (aq) + 2NO_3^- (aq)$

1 0 0

$1-\alpha$ α 2α

so $i = 1 + 2\alpha = 1 + 2 \times 0.7 = 2.4$

Now $$\frac{P^0 - P}{P^0} = i \times X_A \quad \text{or} \quad \frac{760-P}{760} = 2.4 \times \frac{7/164}{7/164+100/18}$$

Solving, we get P = 746.2 mm of Hg.

J-1. **(a)** Let the molar mass of the unknown solute is m

Now, for naphthalene solution

$\Delta T_b = K_b$ = molality

$$0.4 = K_b \times \frac{0.5/128}{50/1000} \quad .... (i)$$

for unknown solution

$$0.65 = K_b \times \frac{0.6/m}{50/1000} \quad .... (ii)$$

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

m = **94.5 Ans.**

(b) $\Delta T_b = K_b$ molality

$$0.100 = 2.16 \times \frac{0.1/m}{16/1000}$$

so m = **135 Ans.**

J-2.
$$0.2 = 5.12\left[\frac{\frac{7.32}{244}}{\frac{1000-x}{1000}}\right]$$

$$\Rightarrow \quad 0.2 = 5.12\left[\frac{30}{1000-x}\right] \quad \Rightarrow \quad \frac{30}{1000-x} = \frac{0.2}{5.12}$$

$\Rightarrow$ 1000 – x = 768 $\Rightarrow$ x = 232 g

J-3. Here $K_b = \frac{RT_b^2}{1000L_V} = \frac{2\times(320)^2}{1000\times 84} = 2.438$

& $\Delta T_b = K_b \times$ molality

or $0.474 = \frac{2.438\times 5/m}{100/1000}$

so m = 257

Hence no. of S atoms in the sulphur molecule = $\frac{257}{32} \simeq 8$

so S_8 is the molecular formula of sulphur in this solvent.

J-4. Experimental $\Delta T = 0.02^o$

Theoretical $\Delta T = 1.86 \times 0.01 = 0.0186^o$

i = van't Hoff factor = $\frac{0.02}{0.0186} = 1.075$

Degree of dissociation, $\alpha = \frac{i-1}{v-1}$ (v = no. of species formed on dissociation)

$$= \frac{0.075}{2-1} = 0.075$$

% dissociation = 7.5.

K-1. **(a)** Van't hoff factor value for urea, NaCl, Na_2SO_4 & Na_3PO_4 are 1, 2, 3 & 4 respectively. so for equal concentration of all these, order of osmotic pressure will be

Urea < NaCl < Na_2SO_4 < Na_3PO_4

(b) Total concentration after mixing equal volumes of all these solutions will be :

$$C_{Total} = \frac{\sum i\times C\times V}{\text{Total volume}}$$

$$C_{Total} = \frac{0.1\times 1\times V + 2\times 0.1\times V + 3\times 0.1\times V + 4\times 0.1\times V}{4V} = 0.25$$

Now $P = C_{Total} \times R \times T = 0.25 \times 0.082 \times 300 = 6.15$ atm **Ans.**

K-2. C = Molarity

$$= \frac{\text{no. of moles of } Ca(NO_3)_2}{\text{Vol. of solution (ml)}} \times 1000 = \frac{3\times 1000}{164\times 100} = \frac{30}{164}$$

π = i.CRT

$$11.2 = i \times \frac{30}{164} \times 0.082 \times 285$$

i = 2.62 = 1 + (3 – 1) α

2.62 = 1 + 2α

α = 0.81.

K-3. For isotonic solutions, $i_1 C_1 = i_2 C_2$

for K_2SO_4 and NaCl, $i_1 \times \frac{17.4 \times 1000}{174 \times 100} = \frac{2 \times 5.85 \times 1000}{58.5 \times 100}$

so $i_1 = 2$

Now $K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$

At equilibrium $1 - x$ $2x$ x

or $1 + 2x = 2$

or $x = ½ = 0.5$

$\therefore$ 50% ionisation.

K-4. $T_1 = 2^oC = 275$ K, $P_1 = 500$ mm of Hg $= \frac{500}{760}$ atm

& $T_2 = 27^oC = 300$ K, $P_2 = 109.09$ mm $\frac{109.09}{760}$ atm

Let C_1 & C_2 be the concentrations for these two cases

so $P_1 = C_1RT_1$ & $P_2 = C_2RT_2$

or $\frac{P_1}{P_2} = \frac{C_1T_1}{C_2T_2}$ or $\frac{C_2}{C_1} = \frac{T_1P_2}{T_2P_1} = \frac{275 \times 109.09/760}{300 \times 500/760} = \frac{1}{5}$

Since volume is inversely proportional to concentration of $\frac{V_2}{V_1} = \frac{C_1}{C_2} = 5$,

so volume must have been made 5 times.

PART - II

A-1. It is a fact.

A-2. Certain compounds combine with the moisture of atmosphere and are converted into hydroxides or hydrates. Such substances are called hygroscopic. e.g., anhydrous $CuSO_4$, quick lime (CaO), anhydrous Na_2CO_3 etc.

B-1. 10 μg per decilitre

$\Rightarrow$ 10×10^{-6} g in 100 mL

$\therefore$ 10^9 parts (1 billion) has $= \frac{10 \times 10^{-6}}{100} \times 10^9$ g = 100 g

C-1. (B) V.P. does not depends on surface area of liquid. (it depends on temperature).

C-2. (A) V.P. depends on temperature.

C-3. (B) Non volatile substance has no V.P.

C-4. (B) Atmospheric pressure is low.

D-1. Solubility increases with decrease in temperature. But solubility increases with increase in pressure according to Henry's Law.

D-2. Henry's law is $m = K \cdot P$; where m = mass of gas absorbed by given volume of the solvent.

P = pressure of gas ;

$\therefore$ $\log m = \log K + \log P$

D-4. $CO_2 + H_2O \longrightarrow H_2CO_3 \longrightarrow 2H^+ + CO_3^{2-}$

$NH_3 + H_2O \longrightarrow NH_4OH \longrightarrow NH_4^+ + OH^-$

$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

But CH_4 and H_2 are insoluble gases in water.

D-5. Solubility $\propto$ pressure

$$\frac{S_2}{S_1} = \frac{P_2}{P_1}$$

$$S_2 = 5.3 \times 10^{-4} \times \frac{760}{593} = 6.8 \times 10^{-4}\ \text{M}$$

E-1. For two immiscible liquid ;

$P^o_A = P_{total} - P^o_{H2O} = 748 - 648 \Rightarrow 100$

$$\frac{W_A}{W_B} = \frac{P_A^o M_A}{P_B^o M_B}\ ;\ M_A = \frac{1.25}{1} \times \frac{648 \times 18}{100} \Rightarrow 145.8$$

F-2. $P = P_A^o\, x_A + P_B^o\, x_B \quad \Rightarrow \quad 100 \times \frac{1}{5} + 200 \times \frac{4}{5}$

$\Rightarrow$ 180 torr

y_A (composition of A in vapour phase) = $\frac{P_A^o x_A}{p}$

$\Rightarrow \quad \frac{20}{180} \Rightarrow \frac{1}{9}$, $Y_B = \frac{8}{9}$

For condensation $y_A = x^1_A$; $y_B = x^1_B$

$P_{total} = P_A^o\, x_A^1 + P_B^o\, x_B^1$;

$P_{total} = 100 \times \frac{1}{9} + \frac{8}{9} \times 200 \quad \Rightarrow \quad 188.88$ torr

F-3. As $X_A \longrightarrow 1$. Then we will have pure methanol so $P_T = 120\, X_A + 140 = 120 + 140 = 260$ mm of Hg.

F-4. $760 = 300\, X_A + 800\, (1 - X_A)$

$\Rightarrow \quad 760 = 800 - 500\, X_A$

$\Rightarrow \quad 500\, X_A = 40$

$\therefore \quad X_A = \frac{40}{500} = 0.08.$

F-5. $x_A = \frac{1}{1+3} \Rightarrow \frac{1}{4}$; $x_B = \frac{3}{4}$;

$$\frac{y_A}{y_B} = \frac{P_A^o}{P_B^o} \times \frac{x_A}{x_B}$$

$$\frac{y_A}{(1-y_A)} = \frac{1}{3} \times \frac{1}{3} \quad \Rightarrow \quad \frac{1}{9} \text{ or } y_A = \frac{1}{10}$$

G-1. $P_{Total} = 0.4 \times 80 + 0.6 \times 120 = 104 > 100$ mm of Hg.

G-2. It shows negative deviation from Raoult's law

p_s (actual) = 580 torr

p_s (Raoult) = $0.4 \times 300 + 0.6 \times 800 = 600$ torr.

G-3. Due to H-bonding

G-4. Some solids dissolves exothermically as LiCl (ΔH = –ve) and other dissolved endothermically as KCl (ΔH = +ve). Solvent-solvent interaction and solute-solute interaction are endothermic while solvent-solute interaction is exothermic. The sum of the three interaction determines whether ΔH_{sol} is endothermic or exothermic.

G-5. Solvent-solvent interaction and solute-solute interaction are endothermic while solvent-solute interaction is exothermic. The sum of the three interaction determines whether ΔH_{sol} is endothermic as exothermic.

G-6. (C) for a ideal solution $\Delta G_{mix} < 0$.

H-1. $$i = \frac{C(1-\alpha) + \frac{C\alpha}{n}}{C} \Rightarrow i = 1 - \alpha + \frac{\alpha}{n}$$

H-2. $i = 1 + (n - 1)\alpha$ so $n = \dfrac{i + \alpha - 1}{\alpha}$

H-3.

	$K_3[Fe(CN)_6]$	$\rightleftharpoons$	$3K^+$	+	$[Fe(CN)_6]^{3-}$	
At t = 0	1		0		0	
After ionization	$(1 - \alpha)$		3α		α;	$i = 1 + 3\alpha$

Since, $i = \dfrac{M_{normal}}{M_{abnormal}}$

$$\therefore \quad \frac{1 + 3\alpha}{1} = \frac{M_{normal}}{M_{abnormal}}$$

H-4. i = van't Hoff factor = 1 + (y – 1) x
(y = number of ions, x = degree of ionisation)

		y	i = 1 + (y – 1) x
(a) K_2PtCl_4	$2K^+ + PtCl_4^{2-}$	3	1 + 2 = 3
(b) K_2PtCl_6	$2K^+ + PtCl_6^{2-}$	3	3

In (a) oxidation number of Pt = 2; In (b) oxidation number of Pt = 4

I-1. Acc. of Rault's law $P = P_A + P_B$
for non volatile solute = $P_B = 0$
$P_s = P_A$
$P_s = P^0_A X_A$ X_A = mole fractions of solvent = N_1
so $P = P_0 N_1$ $P^0_A = P_0$.

I-2. $\text{RLVP} = \dfrac{in}{in + N}$

so $$0.167 = \frac{2 \times n}{2n + \frac{180}{18}}$$

so n = 1

I-3. $\dfrac{268 - 167}{167} = x \Rightarrow$ So x = 0.605.

I-4. $\text{RLVP} = \dfrac{i\ \ n_{NaCl}}{i\ \ n_{NaCl} + n_{H_2O}}$; $0.4 = \dfrac{i}{i + 3}$

so i = 2

$\because$ $i = 1 + \alpha$ so $\alpha = 1$ or 100%

I-5. According to question $P_s = 0.95\ P_0$

according raoult's law $P_s = P_0\ X_A$ given $M_A = 0.3\ M_B$

$$0.95\ P_0 = P_0 \left(\frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}} \right)$$

M_A = molecular wt. of solvent

M_B = molecular wt. of solute

$$0.95 = \frac{\frac{W_A}{0.3\ \ M_B}}{\frac{W_A}{0.3\ \ M_B} + \frac{W_B}{M_B}}$$

W_A = gram wt. of solvent

W_B = gram wt. of solute

on solving $\dfrac{W_A}{W_B} = 5.7.$

I-6. $\dfrac{\Delta P}{P} = \dfrac{ni}{ni + N}$

$0.5 = \dfrac{2\ \ i}{2\ \ i + 3}$

$i + 1.5 = 2\ i$

$i = 1.5$

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

$1.5 = 1 + (2 - 1)\ \alpha$

$\alpha = 0.5$

mole of $Cl^- = 1.0$

mole of AgCl ppt. = 1.0 **Ans. (A)**

J-3. $3S \rightleftharpoons S_3$

$\ \ 1 \qquad\quad 0$

$1 - \alpha \quad \dfrac{\alpha}{3} \quad \Rightarrow \qquad i = 1 - \dfrac{2\alpha}{3}$

Now $\quad 0.1 \left(1 - \dfrac{2\alpha}{3}\right) = 0.08$

$\Rightarrow \qquad \alpha = 0.3$. Hence 30% trimerization.

J-4. $\Delta T_b = ik_b\ m$

so $\quad i = \dfrac{2.08}{0.52 \times 1} = 4$ so the compex is $K_3\ [Fe(CN_6)]$

$K_3\ [Fe(CN)_6] \rightleftharpoons 3\ K^+ + [Fe(CN)_6]^{3-}$

J-5. $\Delta T_f = i \times m \times k_f$

$i = \dfrac{3.72}{1.86 \times 1} = 2$

So salt is $(Pt\ (H_2O)_3\ Cl_3)\ Cl.\ 3H_2O$.

J-6. Boiling point of solution = boiling point + $\Delta T_b = 100 + \Delta T_b$

Freezing point of solution = freezing point – $\Delta T_f = 0 - \Delta T_f$

Difference in temperature (given) = $100 + \Delta T_b - (-\Delta T_f)$

$104 = 100 + \Delta T_b + \Delta T_f = 100 +$ molality $\times K_b +$ molality $\times K_f = 100 +$ molality $(0.52 + 1.86)$

$\therefore \qquad$ Molality $= \dfrac{104 - 100}{2.38} = \dfrac{4}{2.38} = 1.68$ m and $\quad$ molality = $\dfrac{\text{moles} \times 1000}{W_{\text{gm (solvent)}}}$; $1.68 = \dfrac{\text{moles} \times 1000}{500}$

∴ $\quad$ Moles of solute = $\dfrac{1.68 \times 500}{1000}$ = 0.84 moles.

J-7. Higher freezing point ⇒ lesser ΔT_f ⇒ lesser molality ⇒ lesser number of particles

J-8. (i) $\Delta T_f = m \times K_f$

$0.2 = \dfrac{X \times 1000}{100} \times 1.86 \qquad X = \dfrac{0.2}{10 \times 1.86}$

after freezing

$\Delta T_f = m \times K_f$

$\Delta T_f = \dfrac{X \times 1000}{(100 - y)} \times 1.86 \qquad \Delta T_f = 0.25$

On solving, Amount of ice y = 20 g ice

J-9. $\Delta T_b = K_b.m.i$

In 100 g of solution

moles of NaCl = 0.1 $\qquad (\alpha = 0.8)$

moles of $MgCl_2$ = 0.1 $\qquad (\alpha = 0.5)$

$NaCl \longrightarrow Na^+ + Cl^-$

$i_{NaCl} = 1 + (2 - 1)\ 0.8 = 1.8$

Effective no. of moles of NaCl = 0.1 × 1.8 = 0.18

$i_{MgCl_2} = 1 + (3-1)\ 0.5 = 2$

Effective no. of moles of $MgCl_2$ = 0.1 ×2 = 0.2

Total no.of mole = 0.18 + 0.2 = 0.38

$\Delta T_b = \dfrac{0.38}{84.65} \times 1000 \times 0.51 = 3.8 \times 0.51 = 2.28$

So, $T_b = 100 + 2.28 = 102.28 \approx 102.3$

K-1. p = CRT order of conc is urea > glucose > sucrose

K-2. $\pi = CRT \qquad 7.40 = n \times 0.0821 \times 300$

$\pi = \dfrac{n}{v}RT \qquad n = \dfrac{7.4}{0.0821 \times 300} = 0.3.$

K-3. Osmotic pressure = CRT = 0.30 × 0.082 × 298 = 7.34 atm

K-4. $\pi_I = 2R \times 300 \times \left(1 + \left(\dfrac{1}{2} - 1\right) \quad 1\right) \multimap = 300\ R$

$\pi_{II} = 0.5\ R \times 300 \times 2 = 300\ R$

PART - III

2.	(A) Acetone + $CHCl_3$ $\Delta H < 0 \quad \Delta V < 0$ Maximum Boiling Azeotropes.	–ve devation from Raoult's law $\Delta S > 0$
	(B) Ethanol + Water $\Delta H > 0 \quad \Delta V > 0$	+ve Deviation from Raoult's law $\Delta S > 0$ Minimum Boiling Azeotropes
	(C) $C_2H_5Br + C_2H_5I$ $\Delta H = 0 \quad \Delta V = 0$	Ideal solution No Azeotropes
	(D) Acetone + Benzene $\Delta H > 0 \quad \Delta V > 0$ Minimum Boiling Azeotropes	+ve Deviation from Raoults law $\Delta S > 0$

EXERCISE # 2

PART - I

1. Let V_{ml} be the original volume of the sample,

$$\therefore \quad 0.20 = \frac{0.150}{V/1000} \quad \Rightarrow \quad V = 750 \text{ ml.}$$

2. $$\text{Molarity} = \frac{0.967/159.5}{20/1000} \qquad \begin{Bmatrix} \text{Mol.wt.of } CuSO_4 \\ 159.5 \end{Bmatrix}$$

$= 0.303$ M

3. Vapour pr. depends on temperature not volume.

4. Pressure of air = 750 – 100 = 650 mm of Hg

on compressing P_f = Hg 650 × 3 mm of Hg = 1950 mm of Hg

so P_T = (1950 + 100) = 2050 mm of Hg

5. $$\frac{W_A}{W_B} = \frac{P_A^o}{P_B^o} \times \frac{M_A}{M_B} \Rightarrow \frac{0.7}{7} \times \frac{112.5}{18} \Rightarrow 0.625$$

$$\% \ \frac{W_A}{W_A + W_B} \times 100 = \frac{0.625}{1.625} \times 100 \Rightarrow 38.46$$

6. $P_T = P^o_A + P^o_B = 100 + 200 = 300$ torr

8. According to Raoult's law

P_T = (0.08 × 300 + 0.92 × 800) torr = (24 + 736) torr = 760 torr = 1 atm

$P_{exp.}$ = 0.95 atm < 1 atm

Hence solution shows -ve deviation

so $\Delta H_{mix} < 0$, and $\Delta V_{mix} < 0$.

9. $i = 1 + \alpha (n – 1)$ or $4 = 1 + 0.75 (n – 1)$

$\therefore$ n = 5 , so complex will be $Ba_3[Co(CN)_5]_2$.

10. Less is the no. of moles of solute present in the solution, Less is the lowering in vapour pressure, here least no of moles are of sucrose.

11. Due to this addition a complex $[HgI_4]^{2-}$ will get formed as follows

$$Hg^{2+} + 4I^- \rightleftharpoons [HgI_4]^{2-}$$

or $$Hg^{2+} + 2Cl^- + 4I^- \rightleftharpoons [HgI_4]^{2-} + 2Cl^-$$

on adding we can see that $4I^-$ ions are consumed but resultant number of particles are three. Hence boiling point gets decreased. Freezing point gets increased.

12. x + y = 0.1

$$\Delta T_f = \frac{x + x + y + 2y}{1000} \times 1000 \times 1.85$$

if only KCl is used then

$$\Delta T_f = \frac{0.2}{1000} \times 1000 \times 1.85 = 0.37$$

if only $BaCl_2$ is used then

$\Delta T_f = 0.3 \times 1.85 = 0.555$

13. Semipermeable membrane allows the solvent particles only to pass through it.

14. Mole of solute in first beaker = $\frac{0.05 \times 20}{1000}$ = 0.001

mole of solute (Na^+ & Cl^-) in other beaker = $\frac{2 \times 0.03 \times 20}{1000}$ = 0.0012

conc. of IInd beaker is higher then Ist beaker so water flowes from Ist beaker to IInd beaker till both beaker achieved equal conc. let v volume of water flows from Ist to IInd beaker

so $\frac{0.001}{20 - v} = \frac{0.0012}{20 + v}$

v = 1.8 ml

volume of Ist beaker = 20 – 1.8 = 18.2 ml

volume of IInd beaker = 20 + 1.8 = 21.8 ml.

PART - II

1. It is a case of dilution , simplest way is to determine normality of the 98% and 15% H_2SO_4 .

(i) For 98% H_2SO_4 : 100 g H_2SO_4 solution = $\frac{100}{1.88}$ cm^3 solution has H_2SO_4 = 98 g

$$N_1\ (98\%) = \frac{1000\ \ w_1}{E_1 V} = \frac{1000\ \ \times 98}{49 \times \frac{100}{1.88}} = 37.6\ N$$

where w_1 is the weight of solute of equivalent weight E_1 in V mL solution

(ii) For 15% H_2SO_4 : 100 g H_2SO_4 solution = $\frac{100}{1.12}$ cm^3 has H_2SO_4 = 15 g

$$N_2\ (15\%) = \frac{1000\ \ w_1}{E_1 V} = \frac{1000\ \ \times 15}{49 \times \frac{100}{1.12}} = 3.43$$

Using $N_1V_1 = N_2V_2$

$37.6 \times V_1 = 3.43 \times 200$

V_1 = 18.2 mL

2. 40 mL O_3 dissolve in 100 g water at 300 K and 1 atm

40 × 4 mL O_3 dissolve in 400 g water at 300 K and 1 atm

∵ $m \propto P$ so (40 × 4) × 4 mL O_3 dissolve in 400 g water at 300 K and 4 atm

n_{O_3} dissolve = $\frac{4 \times 640 \times 10^{-3}}{0.0821 \times 300}$ = 0.1 or mass of O_3 = 4.8 g.

3. According to Raoult's law for liquid mixtures $P = P_A + P_B$

$$P = P_A{}^0 x \frac{\frac{w_A}{M_A}}{\frac{w_A}{M_A} + \frac{w_B}{M_B}} + P_B{}^0 x \frac{\frac{M_B}{m_B}}{\frac{w_A}{M_A} + \frac{w_B}{M_B}}$$

Given that,

w_A = 64 g $w_{H_2O} = 36$ g P_M = 145 mm

$P_{H_2O} = 155$ mm M_A = 128 $M_{H_2O} = 18$

$$P = 145 = P_A{}^0 x \frac{\frac{64}{128}}{\frac{64}{128} + \frac{36}{18}} + \frac{\frac{36}{18}}{\frac{64}{128} + \frac{36}{18}}$$

$P_A{}^0$ = 105 mm $\Rightarrow \frac{P_A^\circ}{5} = 21$

4. We can write immediately : 1(atm) = $0.2\ P_A^0 + 0.8\ P_B^0$ and, further

$$1 = 0.2 \times \frac{P_B^o}{2} + 0.8\ P_B^o \text{ so } P_B^o = \frac{1}{0.9} = 1.11 \text{ atm. } P_A^o \text{ must then be } 0.55 \text{ atm.}$$

$\Rightarrow$ $2 \times P_A^o = 1.10$

5. A and B are volatile liquids, given P_A^0 = 575 Torr , P_B^0 = 390 Torr
let mole fraction of A in solution = X_A
hence, $P_{total} = P_A^0\ X_A + P_B^0\ (1 - X_A)$
also X_A' = mole fraction of A in the vapour = 0.35

$$X_A' = \frac{P_A^0\ X_A}{P_A^0\ X_A + P_B^0\ (1 - X_A)} = 0.35$$

$$= \frac{575\ X_A}{575\ X_A + 390\ (1 - X_A)}$$

this gives $X_A = 0.27$
Composition of liquid mixture, A = 27 mol % , B = 73 mol %.

7. Positive deviation = I, II, III, IV, V, IX
Negative deviation = VI, VIII

8. T = 87 + 273 = 360 K

$$\Pi_{Theoretical} = \frac{0.1}{2} \times \frac{1}{12} \times 360 = 1.5 \text{ atm.}$$

$$\Pi_{observed} = 3 \text{ atm}$$

$$\Rightarrow \quad i = \frac{3}{1.5} = 2 \Rightarrow i = \frac{M_T}{M_{ob}}$$

$$\Rightarrow \quad M_{observed} = \frac{M_T}{i} = \frac{24 + 2 \times 32}{2} = 12 + 32 = 44 \Rightarrow 44 + 2i = 44 + 2 \times 2 = 48$$

9. Let P° be the vapour pressure of water, now if relative humidity is 80% after dissolving $C_{12}H_{22}O_{11}$, then the new pressure of solution will be P (let).

$$\text{so } \frac{P}{P_0} = 0.8 \quad \text{or} \quad P = 0.8\ P_0$$

Now Relative lowering of pressure = $\frac{P_0 - P}{P_0} = X_A$

$$\text{So} \quad \frac{P_0 - 0.8P_0}{P_0} = \frac{\frac{x}{342}}{\frac{x}{342} + \frac{90}{18}} \quad \{\text{Let x be the wt. of } C_{12}H_{22}O_{11} \text{ dissolved}\}$$

$\therefore$ x = 427.5 g.

10. $\Delta T_b = K_b \times m$

$$0.13 = 2.6 \times \frac{1.22/M}{0.1}$$

$\therefore$ M = 244 u
$\therefore$ Reported answer = 2

11. $\frac{1}{M_{acid}} = \frac{125}{1000} \times 0.1 \quad \Rightarrow \quad M_{acid} = 80 \text{ g mol}^{-1}$

$$0.186 = (1 + \alpha) \times 1.86 \times \left[\frac{\frac{1}{80}}{0.2}\right] \quad \Rightarrow \quad \alpha = 0.6 \Rightarrow 60 \text{ percent}$$

12. 1.2% solution (wt./vol) of glucose is isotonic with 4 g/litre of solution of X at 27ºC, so

$C_1 = C_2$

$$\frac{1.2\times1000}{180\times100} = \frac{4}{M_X}$$

so M_X = 60 g/mole.

13. Let M_A and M_B are the molar masses of A & B respectivey when 10 g of A and 20 g of B are both dissolved in 500 ml of water, then concentration of this solution will be $C_1 = \left(\frac{10}{M_A} + \frac{20}{M_B}\right)\times\frac{1000}{500}$ moles/lt.

In second case, when 6.67 g of A and 30 g of B are dissolved in same volume of water then concentration of this solution will be $C_2 = \left(\frac{6.67}{M_A} + \frac{30}{M_B}\right)\times\frac{1000}{500}$ M.

As both solution have same osmotic pressure at same temperature.

$\pi_1 = \pi_2$

$C_1RT = C_2RT$

$C_1 = C_2$ or $\frac{M_A}{M_B} = \frac{1}{3}$

PART - III

1. Initial moles of KCl = $\frac{100}{1000} \times 0.1 = 0.01$

Let x moles of KCl are added , so

$$0.2 = \frac{0.01 + x}{100/1000} \text{ or } x = 0.01$$

2. Molality, Molarity, Percent by mass and Normality all can be related to mole fraction (by using density).

3. Temperature ↑ , vapour pressure ↑.

4. $P_{gas} = K_{gas} . X_{gas}$

So, Temperature ↑ , K_{gas} ↑ , X_{gas} ↓

5. a↑, Force of attraction↑, Liquifaction↑, Solublity↑, So gas form ion are more soluble.

6. $p_x^0 + p_y^0$ = Total vapour pressure (as X and Y are perfectly immiscible)

400 + 200 = 600 Torr.

7. For ideal solutions :

$\Delta V_{mix} = 0$ and $\Delta H_{mix} = 0$

$\Delta S_{mix} = -$ ve

8. P = 119 x + 135

x = 1 for pure methanol.

so $P^o_{methanol} = 119 + 135 = 254$ Torr

But for pure ethanol x = 0

so $P^o_{ethanol} = 135$ Torr

9. When mixture is more volatile, total pressure increases so there is a positive deviation from Raoult's law , and vice–versa.

10. $X_AP_A^0 + X_BP_B^0 = 0.25 \times 512 + 0.75 \times 344 = 386$ mm

Now $P_A + P_B = 600$ mm Hg (Given)

so $P_A + P_B > X_AP_A^0 + X_BP_B^0$

therefore, there is positive devition from Raoult's law

$\Delta H > 0$ i.e., heat is absorbed.

11. $A_xB_y \rightleftharpoons xA^{y+} + yB^{x+}$

	A_xB_y	xA^{y+}	yB^{x+}
Initial moles	n	o	o
At eq b.	$n(1-\alpha)$	$nx\alpha$	$ny\alpha$

$$i = \frac{\text{Total mol at equilirium}}{\text{Initial mol}} = \frac{n[(1-\alpha)+x\alpha+y\alpha]}{n}$$

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

It can also seen that all other expressions imply the same thing.

(A) $\alpha = \frac{i-1}{x+y-1}$ (B) $i = (1 - \alpha) + x\alpha + y\alpha$. (C) $\frac{1-i}{1-x-y}$

12. Number of particles from $K_4[Fe(CN)_6] = 5$

number of particles from $FeSO_4(NH_4)_2SO_4.6H_2O = 5$

number of particles from $KCl.MgCl_2.8H_2O = 5$

13. $$\frac{\Delta P}{P_s} = \frac{2/MM}{100/50} = \frac{T}{MM} \Rightarrow \frac{0.5}{75} = \frac{1}{MM} \Rightarrow MM = 150$$

If formula is C_xH_y, then $\frac{12x}{150} \times 100 = 96$

$\Rightarrow$ $x = 12$ and $\frac{y}{150} \times 100 = 4.$ so, $y = 6$

14. In solution, lesser number of solvent molecules have tendency to form vapour. Only solvent molecule under go phase transition.

15. As concentration values are same for all solutions , so osmotic pr. will depend on van't hoff factor (i).

	I	II	III	IV
	glucose (aq.)	NaCl (aq.)	$(NH_4)_3PO_4$ (aq)	Benzoic acid in benzene
Value of i	1	2	4	0.5

more the value of i , more is the osmotic pressure.

16. Ideal gas equation, PV = nRT

Solute particle is similar as gas molecule.

PART - IV

1. Given , $P_M = 179\,X_B + 92$

For pure C_6H_6; X_B i.e., mole fraction of benzene = 1

$\therefore$ $P^0_B = 179 + 92 = 271$ mm

For pure C_7H_8 ; $X_B = 0$

$\therefore$ $P^0_T = 179 \times 0 + 92 = 92$ mm

2. $$X_B = \frac{\frac{936}{78}}{\frac{936}{78}+\frac{736}{92}} = \frac{12}{12+8} = 0.6$$

$P_M = 179 \times 0.6 + 92 = 107.4 + 92 = 199.4$ mm

3. B, C and D are the conditions and facts for positive deviation from Raoult's law.
(A) is incorrect.
Because A–B attractive force should be weaker than A–A and B–B attractive forces.

4. $X_AP_A^0 + X_BP_B^0 = \frac{1}{4} \times 100 + \frac{3}{4} \times 60 = 70$ mm of Hg
Now $P_A + P_B > X_AP_A^0 + X_BP_B^0$
i.e., positive deviation from Raoult's law.
for positive deviation, B.P. < expected value
$F_{A...B} < F_{A...A}$
$F_{A...B} < F_{B...B}$

5. $\pi = MRTi$
Hence,
$\Delta T_b = mK_bi$, $\Delta T_f = mK_f \times i$

6. (1) $0.74 = \frac{0.0821}{250 \times 10^{-3}} \times 300 \left(\frac{x}{60} + \frac{1-x}{180}\right)$

$x = 0.176$

% urea $= \frac{0.176}{1} \times 100 = 17.6$

(2) $\frac{dP}{P} = X_{solute} = \frac{\frac{0.176}{60} + \frac{0.824}{180}}{\frac{0.176}{60} + \frac{0.824}{180} + \frac{250}{18}} = 5.4 \times 10^{-4}$

(3) $\Delta T_b = mK_b = \left(\frac{0.176}{60} + \frac{0.824}{180}\right) \times \frac{1000}{250} \times 0.5 = 0.015$

$\Delta T_b = 100.015$.

7. Hexane + Heptane → ideal solution correct code for ideal solution are → (i) (a),(P)

8. water + ethanol → non ideal solution with +ve derivation correct code for this solution are (ii), (iv), b, c, d, S

9. water + H_2SO_4 → non ideal solution with -ve deviation correct codes for this solution are (iii), iv, b, c, R

10. (iv) (d) (Q) is a correct match.

EXERCISE # 3

PART - I

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

2. Van't Hoff factor, $i = 1 + (n - 1)\alpha$
Here $n = 3$
So, $2.74 = 1 + (3 - 1)\alpha$
So, $\alpha = 0.87$ i.e. 87%

3. Weight of water = 500 × 0.997 = 498.5 g

No. of moles of acetic acid = $\dfrac{\text{Wt. of } CH_3COOH \text{ (in gm)}}{\text{Mol.wt.of } CH_3COOH} = \dfrac{3\times10^{-3}\times10^{3}}{60} = 0.05$

Since 498.5 g of water has 0.05 moles of CH_3COOH

1000 g of water has = $\dfrac{0.05\times1000}{498.5} = 0.1$

Determination of van`t Hoff factor, i

$$CH_3COOH \longrightarrow CH_3COO^- + H^+$$

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

$\Delta T_f = (1 - 0.23 + 0.23 + 0.23) \times 1.86 \times 0.1 = 0.228K.$

4. Only solvent molecule under go solidification. So liquid solvent and solid solvent remain in equilibrium.

5. $(\pi_{obs})_{Na_2SO_4} = \pi_{glucose}$

or $\dfrac{10}{4} = \dfrac{1+2\alpha}{1}$ or $10 = 4 + 8\alpha$

$\alpha = \dfrac{10-4}{8} = 0.75$ % of α = 75%

6. (i) In first case,

$$\Delta T_b = K_b \times m = K_b \times \frac{\text{Wt. of solute}}{\text{Mol. wt. of solute}} \times \frac{1000}{\text{wt. of solvent}}$$

or $0.17 = 1.7 \times \dfrac{1.22}{M\times100\times10^{-3}}$ or **M = 122 g/mole**

Thus the benzoic acid exists as a monomer in acetone
(ii) In second case,

$$\Delta T_b = K_b \times \frac{\text{Wt.of solute}}{\text{Mol.wt.of solute}} \times \frac{1000}{\text{wt. of solvent}}$$

or $0.13 = 2.6 \times \dfrac{1.22}{M`\times100\times10^{-3}}$ or **M` = 224**

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

7. $\Delta T_b = i\, K_b\, m$ i (vant Haff factor) of $CuCl_2$ = 3

$\Delta T_b = 3 \times 0.52 \times \dfrac{13.44}{134.4\times1} = 0.156 = 0.16.$

8. $\Delta T_f = i \times K_f \times \text{molality} \Rightarrow 2 = i \times 1.72 \times \dfrac{20}{172} \times \dfrac{1000}{50}$

$\Rightarrow 2 = 4i$

$\Rightarrow i = 1/2 = 0.5$

9. $\Delta T_f = K_f\, .\, m$

$= 2 \times \dfrac{0.1}{0.9\times46} \times 1000 = \dfrac{2000}{414} = \dfrac{1000}{207} = 4.83$

$\Delta T'_f = T_f - 4.83$

$\Delta T'_f = 155.7 - 4.83$

$\Delta T'_f = 150.9$ K

10. Total vapour pressure

$P = P^o_A X_A$ (considering solute to be non-volatile as given in the question)

$P = 40 \times 0.9 = 36$ mm Hg

11. $\Delta T_b = K_b \cdot m$

$= 0.52 \times \dfrac{0.1}{0.9 \times 18} \times 1000 = \dfrac{520}{9 \times 18} = 3.20$

$T_b = 373 + 3.20$

$T_b = 376.2$ K

12. $P_{N2} = K_H \times x_{N_2}$

$x_{N_2} = \dfrac{1}{10^5} \times 0.8 \times 5 = 4 \times 10^{-5}$ per mole

In 10 mole solubility is 4×10^{-4}.

13. $\Delta T_f = i \times K_f \times m = 4 \times 1.86 \times \dfrac{0.1}{329 \times 0.1} = 2.3 \times 10^{-2}$

$\Rightarrow \quad T_f = 0 - 2.3 \times 10^{-2} = -2.3 \times 10^{-2}$ ºC.

14. $\Delta T_b = 2$ºC; $\quad m_a = 2.5$ g

$m_{solvent} = 100$ g

$K_b = 0.76$ K. kg. mol^{-1}

$P_{solution} = ?$

$\Delta T_b = K_b \times m$

$2 = 0.76 \times m \qquad \therefore \qquad m = \dfrac{2}{0.76}$

$\dfrac{P^0 - P}{P} = m \times MM \times 10^{-3} \qquad \therefore \qquad \dfrac{760 - P}{P} = \dfrac{2}{0.76} \times 18 \times 10^{-3}$

$760 - P = \dfrac{36}{760} P \qquad \therefore \qquad 760 = \dfrac{796}{760} P$

$\therefore \; P = 760 \left(\dfrac{796}{760}\right)$ torr $= 725.6$ torr ≈ 724 torr

15. $\Delta G = -$ ve, $\quad \Delta S_{system} = +$ ve $\quad$ Always for solution formation.

$\Delta S_{surr.} = 0 \quad$ No heat exchange between solution and surrounding.

$\Delta H = 0 \quad$ For ideal solution.

16. $MX_2 \rightleftharpoons M^{2+} + 2X^-$

$m_0(1 - \alpha) \qquad m_0\alpha \qquad 2m_0\,\alpha \qquad ; m = m_0(1 + 2\alpha)$

$\therefore \; m = m_0(1 + 2 \times 0.5) = 2m_0$ (as given)

$\dfrac{(-\Delta T_f)_{observed}}{(-\Delta T_f)_{undissociated}} = i = \dfrac{m}{m_0} = 2$

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

$0.0558 = 1.86 \times i \times 0.01$

$i = 3$

Given complex behaves as a strong electrolyte

$\alpha = 100$ %

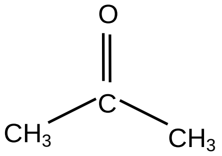
n = 3 (no. of particles given by complex)

$\therefore$ complex is $[Co(NH_3)_5Cl]Cl_2$

no. of Cl^- ions in the co-ordination sphere of the complex = 1

18. (A) $CCl_4 + CH_3OH \Rightarrow$ Positive deviation from Raoult's law

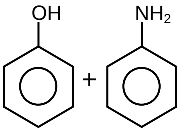
(B) CS_2 +



$\Rightarrow$ Positive deviation from Raoult's law

(C) $C_6H_6 + C_7H_8$ $\Rightarrow$ Ideal solution

(D)



$\Rightarrow$ Negative deviation from Raoult's law.

19. For a mixture of two liquids L and M,

For ideal solution obey Raoult's law

$P_L = (1 - X_M)P_L^o = P_L^o - X_M P_L^o$

Graph between P_L & X_M has intercept = P_L^o & slope = –ve

But graph representing +ve deviation from Raoult's law therefore M – L < M – M or L – L

Point Z represents intercept which is P_L^o when $X_L \to 1$

20. As T increase, V.P. increases. So C & D options get rejected.

$\Delta T_f = K_f \times m$

$$273 - T'_f = 2 \times \frac{34.5/46}{0.5}$$

$\therefore$ $T'_f = 270$ K

21. $\mathbf{p_T = p^o_A X_A + p^o_B X_B}$

$45 = 20(0.5) + P^{\circ}_B(0.5)$

$P^{\circ}_B = 70$

$22.5 = 20\,X_A + 70(1 - X_A)$

$50X_A = 47.5$

$X_A = \frac{4.75}{5} = 0.95$

$X_B = 0.05$

$\frac{X_A}{X_B} = 19$

22. $2 = 2\,(K_b)_x\,m$

$1 = 2\,(K_b)_y\,m$

$\frac{(K_b)_x}{(K_b)_y} = 2$

$\Delta(T_b)_x = \left(1 - \frac{\beta}{2}\right)(K_b)_x\,m$ …(1)

$\Delta(T_b)_y = \left(1 - \frac{0.7}{2}\right)(K_b)_y\,m$ …(2)

On taking the ratio of eq. no. (1) & (2)

$$\Rightarrow \quad 3 = \frac{1 - \frac{\beta}{2}}{0.65} \times 2$$

$$1 - \frac{\beta}{2} = 1.5 \times 0.65$$

$\beta = 0.05$

23. $\dfrac{P^0 - P_s}{P_s} = i\left[\dfrac{n_{solute}}{n_{solvent}}\right]$ $\dfrac{P^0 - P_s}{P_s} = i\,\dfrac{n_{\text{विलेय}}}{n_{\text{विलायक}}}$

$\dfrac{650-640}{640} = 1 \times \dfrac{0.5\times78}{M\times39} \Rightarrow M_{solute} = 64\text{ g}$

$\Delta T_f = K_f \times m = 5.12 \times \dfrac{0.5\times1000}{64\times39} \Rightarrow \Delta T_f = 1.02564$

PART - II

SOLUTION OF OFFLINE PROBLEMS

1. Moles of urea = $\dfrac{6.02\times10^{20}}{6.02\times10^{23}} = 10^{-3}$ moles

Concentration (molarity) of solution = $\dfrac{10^{-3}}{100} \times 1000 = 0.01$ M.

2. Elevation in boiling point is a colligative property which depends upon the number of solute particles. Greater the number of solute particles in a solution, higher the extent of elevation in boiling point.

$$Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-}$$

3.
$$\begin{array}{lccc} Na_2SO_4 & \rightleftharpoons & 2Na^+ & + & SO_4^{2-} \\ 1 & & 0 & & 0 \\ 1-\alpha & & 2\alpha & & \alpha \end{array}$$

Vant Hoff factor (i) = $\dfrac{1-\alpha+2\alpha+\alpha}{1} = 1+2\alpha.$

4. According to Raoult's law equimolal solutions of all the substances in the same solvent will show equal elevation in boiling points as well as equal depression in freezing point.

5. $P_B = P^o_B\,X_B \quad P^o_B = 75$ torr

$X_B = \dfrac{78/78}{(78/78)+(46/92)} = \dfrac{1}{1+0.5} = P_B = 75 \times \dfrac{1}{1.5} = 50$ torr.

6. According to Raoult's law

$P = P_A + P_B = P^o_A x + P^o_B x_B$ or $290 = P^o_A \times (0.6) + 200 \times (1 - 0.6)$

or $290 = 0.6 \times P^o_A + 0.4 \times 200$ or $P^o_A = 350$ mm.

7. Isotonic solutions have same osmotic pressure.

$\pi_1 = C_1 RT$, $\pi_2 = C_2 RT$

For isotonic solution, $\pi_1 = \pi_2$

$\therefore \quad C_1 = C_2.$

or $\dfrac{1.5/60}{V} = \dfrac{5.25/M}{V}$ [where M = molecular weight of the substance]

or $\dfrac{1.5}{60} = \dfrac{5.25}{M}$ or M = 210.

8. $P_A = P^0_A\,x_A = 17.5 \times \dfrac{178.2/18}{\dfrac{178.2}{18}+\dfrac{18}{180}} = 17.325$

9. $P_{total} = P^0_A\, x_A + P^0_B\, x_A$

$760 = 520\, x_A + 1000\, (1 - x_A)$

$760 = 520\, x_A + 1000 - 1000\, x_A$

$x_A = 0.5$

mol % = 50%

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

11. $P_{total} = P^o_A\, X_A + P^o_B\, X_B = P^o_A \times \frac{1}{4} + P^o_B \times \frac{3}{4} = 550 \Rightarrow P^o_A + 3P^o_B = 550 \times 4$ .....(i)

Similary, $560 = P^o_A \times \frac{1}{5} + P^o_B \times \frac{4}{5} \Rightarrow P^o_A + 4P^o_B = 560 \times 5$ .....(ii)

eq. (ii) – eq.(i)

$P^o_B = 560 \times 5 - 550 \times 4 = 600$

so, $P^o_A = 400.$

12. $Na_2SO_4\,(s) \xrightarrow{H_2O} 2Na^+\,(aq.) + SO_4^{2-}\,(aq.)$

$\Delta T_f = i\, K_f m = 3 \times 1.86 \times 0.01 = 0.0558$ K.

13. $P_T = X_{Heptane}\, P^o_{Heptane} + X_{Octane}\, P^o_{Octane}$

$= \frac{0.25}{0.557} \times 105 + \frac{0.307}{0.557} \times 45$

$47.127 + 24.80 = 71.92 \approx 72$ kPa

14. $\Delta T_f = i \times k_f \times m$

$2.8 = 1 \times 1.86 \times \frac{x}{62 \times 1}$ $\quad x = \frac{2.8 \times 62}{1.86} = 93$ g

15. 0.5 M C_2H_5OH (aq)
i = 1
effective molarity = 0.5

0.1 M $Mg_3(PO_4)_2$ (aq)
i = 5
effective molarity = 0.5 m

0.25 M KBr (aq)
i = 2
effective molarity = 0.5 M

0.125 M Na_3PO_4 (aq)
i = 4
effective molarity = 0.5 M

Hence all colligative properties are same.

Note : This equation is solved by assuming that the examinar has taken $Mg_3(PO_4)_2$ to be completely soluble. However the fact is that it is insoluble (sparingly soluble).

16. $\frac{P_0 - P_S}{P_S} = \frac{n}{N}$

$\frac{185 - 183}{183} = \frac{1.2/M}{100/58}$

$M \approx 64$ g/mol

17. Moles of glucose = $\frac{18}{180} = 0.1$ (Assume that glucose is added at boiling point of water)

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

$\Rightarrow \quad n_{Total} = 10$

$\Rightarrow \quad \frac{\Delta P}{P^o} = \frac{0.1}{10}$

$\Delta P = 0.01\, P^o = 0.01 \times 760 = 7.6$ torr

$P_S = 760 - 7.6 = 752.4$ torr

18. $\Delta T_f = 0.45$

$$m = \frac{\left(\frac{0.2}{60}\right)\times 1000}{20} = \frac{1}{6}$$

$K_f = 5.12$ k kg/mol

$i = 1 + \left(\frac{1}{n} - 1\right)\beta$ (n = 2) = $1 - \frac{\beta}{2}$

Now, $\Delta T_f = i\, K_f\, m$

$$0.45 = \left(1 - \frac{\beta}{2}\right)(5.12)\left(\frac{1}{6}\right)$$

$\Rightarrow$ $\beta = 0.94$

$\therefore$ % Association $\approx$ 94%

19. The complex having minimum value of vant Hoff's factor (i) will give minimum concentration and highest freezing point.

(1) $[Co(H_2O)_4Cl_2]Cl.\ 2H_2O \longrightarrow [Co(H_2O)_4Cl_2]^+ + Cl^-$ (i = 2)

(2) $[Co(H_2O)_3Cl_3]3H_2O \longrightarrow$ No dissociation (i = 1)

(3) $[Co(H_2O)_6]Cl_3 \longrightarrow [Co(H_2O)_6]^{+3} + 3Cl^-$ (i = 4)

(4) $[Co(H_2O)_5Cl]Cl_2.H_2O \longrightarrow [Co(H_2O)_5Cl]^{+2} + 2Cl^-$ (i = 3)

SOLUTION OF ONLINE PROBLEMS

4. $x_{Benzene} = \frac{1.5}{5} = 0.3,\ x_{toluene} = 0.7$

$\Rightarrow$ $P_T = 74.7 \times 0.3 + 0.7 \times 22.3 = 22.41 + 15.61 = 38.02$ torr

and $y_{benzene} = \frac{22.41}{38.02} = 0.589$

5. Benzene is non-polar solvent.

6. According to Henery law

$\frac{P_1}{P_2} = \frac{S_1}{S_2}$ $\therefore$ S_1 & S_2 are solubility of gas (g/L)

$\frac{500}{750} = \frac{0.01}{S_2}$

$\therefore$ $S_2 = \frac{750 \times 0.01}{500} = 0.015$ g/L

7. For MX_2 type salt

Vant factor (i) = $1 + 2\alpha = 2$ $\Rightarrow$ $\alpha = 0.5$

8. $\Delta T_f = imk_f$

$3.82 = [1+(3-1).815]m \times 1.86$

$= \frac{3.82}{2.63 \times 1.86}$

$= \frac{3.82}{2.63 \times 1.86} = \frac{5}{142} \times \frac{1000}{x}$

x = 45 g

9. Apply raoult's law :

$$P_{Total} = X_AP_A^o + X_BP_B^o$$

$$= \left(\frac{0.1}{0.1+0.1}\right)\times 415 + \left(\frac{0.1}{0.1+0.1}\right)\times 200$$

= 307.5 mm Hg

Mole fraction of $CHCl_3$ in vapour form (Y_B) = $\frac{X_BX_B^o}{P_{Total}} = \frac{0.5\times 200}{307.5}$

10. Mol fraction in x solvent

$$x_{solute} = \frac{5}{5+\frac{1000}{M_x}} = \frac{5M_X}{1000}$$

mol fraction in Y solvent

$$x_{solute} = \frac{5}{5+\frac{1000}{M_y}} = \frac{5M_y}{1000}$$

Ratio of RLVP in both solutions $\frac{m}{1} = \frac{M_X}{M_y} = \frac{3}{4}$

11. $\frac{P^o - P_s}{P_s} = \frac{n}{N}$

$$\frac{100P - 75P}{75P} = \frac{\frac{W}{50}}{1}$$

$$\frac{25}{75} = \frac{W}{50}$$

$$W = \frac{50}{3}g$$

12. Value of K_H decrease when solubility of gas increases

13. Let x gram water is separated out

$\Delta T_f = K_fm$

$10 = 1.86 \times \frac{1\times 1000}{(250-x)}$

or, $2500 - 10x = 1860$

or, $10x = 640$

or, $x = 64$ g.

14. $\frac{x_A}{x_B} = \frac{P_A{}^0x'_A}{P_B{}^0x'_B} = \frac{7\times 10^3(0.4)}{12\times 10^3(0.6)} = \frac{28}{72} = \frac{7}{18}$

x'_A & x'_B are mole fraction in liquid state

$x_A = \frac{7}{25} = 0.28$; $x_B = \frac{18}{25} = 0.72$

15. $\Delta T_b = ik_b\, m \Rightarrow 2 = ik_b \times 1$ ....(1)

$\Delta T_f = ik_f\, m \Rightarrow 2 = ik_f \times 2$ ....(2)

1 / 2

$1 = \frac{k_b}{2k_f}$

$k_b = 2\ k_f$

16. Freezing point of milk = –0.5ºC $\because \Delta T_f = 0.5ºC$

Freezing point of diluted milk = –0.2ºC $\because \Delta T_f = 0.2ºC$

$$\frac{(\Delta T_f)_i}{(\Delta T_f)_{ii}} = \frac{0.5}{0.2} = \frac{K_f m}{k_f m}$$

Both has same amount of solute. Let that is x mole.

$$\frac{0.5}{0.2} = \frac{x\,\text{mole} \times W_2}{W_1 \times x\,\text{mole}}$$

$$\frac{5}{2} = \frac{W_2}{W_1}$$

$W_2 = \frac{5}{2} W_1$

17. $K_2[HgI_4] \longrightarrow 2K^+ + [HgI_4]^{-2}$; n = 3

$i = 1 + (3 - 1) \times 0.4$

$= 1 + 2 \times 0.4 = 1.8$

18. $(\Delta T_f)_X = (\Delta T_f)_Y$

$k_f m_X = k_f m_Y$

$$\frac{4 \times 1000}{A \times 96} = \frac{12 \times 1000}{M \times 88}$$

M = 3.27A ≈3A

19.

$2A$	$\longrightarrow$	$(A)_2$
1		–
1–0.8		$\frac{0.8}{2}$

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

$2 = 5 \times 0.6 \times \frac{w}{122} \times \frac{1000}{30} \quad \Rightarrow \quad w = 2.44\ g$

20. $P_T = X_A P_A° + X_B P_B°$

$= 0.5 \times 400 + 0.5 \times 600$

= 500 mm of Hg

$$\frac{1}{P_T} = \frac{y_A}{P_A^{\circ}} + \frac{1 - y_A}{P_B^{\circ}}$$

$$\frac{1}{500} = \frac{y_A}{400} + \frac{1 - y_A}{600}$$

$y_A = 0.4$ & $y_B = 1 - 0.4 = 0.6$

21. $P_{gas} = K_H.\ x_{gas}$

$P_{gas} = K_H.\ (1 - x_{H_2O})$

$P_{gas} = K_H - K_H.\ x_{H_2O}$

y = c + mx

22. Mass of fatty acid which is added over watch glass = $\frac{0.27\times0.1}{100}$ = 2.7×10^{-2}

Volume of fatty acid = $\frac{2.7\times10^{-2}}{0.9}$ = 3×10^{-2}

Total Area of glass plate = $\pi r^2 = 3 \times [10]^2 = 300$ cm^2
Volume = Area × hight
$3\times10^{-2} = 300 \times$ hight
Hight of the layer = 10^{-4} cm = 10^{-6} m

23. $\pi_{xy} = 4\pi_{BaCl_2}$
$i[XY] = 4 \times i \times [BaCl_2]$
$\Rightarrow 2 \times [XY] = 4 \times 3 \times 0.01$
$\Rightarrow [XY] = 0.06M$

24. Mole fraction of more volatile component increase in vapour phase. $\left(P_N^\circ < P_M^\circ\right)$

25. $\Delta T_f = iK_f m$
$= 3 \times 4 \times 0.03$
$= 0.36$ K

26. $$\frac{P^0 - Ps}{P^0} = \frac{n}{n+N}$$

Lowering in V.P.= $P^0 \times \frac{n}{n+N}$

$$= 35 \times \frac{\frac{0.6}{60}}{\frac{0.6}{60}+\frac{360}{18}} = 0.017 \text{ mm of Hg.}$$

27. $(\Delta T_b)_A = (K_b)_A \times m_A$
$(\Delta T_b)_B = (K_b)_B \times m_B$

$$\frac{(\Delta T_b)_A}{(\Delta T_b)_B} = \frac{1}{5} \times \frac{\frac{1}{M.W.}\times\frac{1000}{100}}{\frac{1}{M.W.}\times\frac{1000}{100}} = \frac{1}{5}$$

28. $\pi = CRT$

$$= \left[\frac{(n_1+n_2)\times1000}{V}\right]RT = \left[\left(\frac{0.6}{60}+\frac{1.8}{180}\right)\times\frac{1000}{100}\right]\times0.082\times300$$

$= [(0.01 + 0.01) \times 10] \times 0.082 \times 300 = 4.92$ atm