

1. An ideal solution was obtained by mixing (MeOH) methanol and (EtOH) ethanol. If the partial vapour pressure of methanol and ethanol are 2.619 K Pa and 4.556 K Pa respectively, the composition of vapour (in terms of mole fraction) will be -

(A) 0.635 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

Applying Raoult's law & Dalton's law;

$$y_{\text{EtOH}} p_{\text{total}} = x_{\text{EtOH}} p^{\circ}_{\text{EtOH}} ;$$

$$y_{\text{mean}} p_{\text{total}} = x_{\text{mean}} \bar{p}_{\text{mean}}$$

$P_{\text{EtOH}}^{\circ}$ ;  $P_{\text{MeOH}}^{\circ}$ : vapour pr. of pure ethanol & methanol, resp.

$y_{\text{MeOH}}$ ;  $y_{\text{EtOH}}$ : vapour phase mole fraction  
of MeOH & EtOH, resp.

$x_{\text{MeOH}}$ ;  $x_{\text{EtOH}} =$  liquid phase mole fraction  
of MeOH & EtOH, resp.

$$\Rightarrow y_{\text{meOH}} + y_{\text{EtOH}} = 1$$

$p_r$ : vapour pressure of the binary soln.

$$\text{Given: } - x_{\text{EtoH}} p^{\circ} = 4.556 \text{ kPa}$$

$$\text{& } x_{\text{meOH}} p^{\circ} = 2.619 \text{ kPa}$$

$$\Rightarrow f_r = (4.556 + 2.619) \text{ kPa} = 7.175 \text{ kPa}$$

$$\therefore y_{\text{EtoH}} = \frac{4.556 \text{ kPa}}{7.175 \text{ kPa}} = 0.635$$

$$y_{\text{meOH}} = 1 - y_{\text{EtoH}} = 0.365$$

2. Molar volume of liquid A ( $d = 0.8 \text{ gm/ml}$ ) increase by factor of 2000 when it vapourises at 200K.  
 Vapour pressure of liquid A at 200K is [ $R = 0.08 \text{ L-atm/mol-K}$ ]  
 (Molar mass of A = 80g/mol)
- (A) 0.4 atm      (B) 8 atm      (C) 0.8 atm      (D) 0.08 atm

Consider 1 mole of liquid A.

$$\Rightarrow \text{mass} = 80 \text{ g/mol} \times 1 \text{ mol} = 80 \text{ gm}$$

$$\Rightarrow \text{volume of liquid A} = \frac{80 \text{ gm}}{0.8 \text{ gm/ml}} = 100 \text{ ml}$$

$\Rightarrow$  Given that volume increases by 2000 times upon vaporisation;

$$\Rightarrow \text{volume of vapour A} = \frac{100 \times 2000}{100} \text{ l} = 200 \text{ l}$$

$\Rightarrow$  If vapour pressure of pure A =  $p_A^{\circ}$  ;  
 applying ideal gas equation;

$$pV = nRT$$

$$\Rightarrow p_A^{\circ} \cdot (200 \text{ l}) = 1 \text{ mol} \times 0.08 \frac{\text{l-atm}}{\text{mol-K}} \times 200 \text{ K}$$

$$\Rightarrow p_A^{\circ} = 0.08 \text{ atm}$$

3. Assuming each salt to be 90 % dissociated, which of the following will have highest boiling point?
- (A) Decimolar  $\text{Al}_2(\text{SO}_4)_3$   
(B) Decimolar  $\text{BaCl}_2$   
(C) Decimolar  $\text{Na}_2\text{SO}_4$   
(D) A solution obtained by mixing equal volumes of (B) and (C)

Applying formula of elevation in boiling point;

$$\Delta T_b = T_b' - T_b = K_b \times \text{molality} \times i$$

$T_b'$  = boiling point of solution;

$T_b$ ' = " " " pure solvent

$K_b$  = molal elevation constant

molality = molality of solution

$i$  = van't Hoff factor =  $1 + (y-1)\alpha$ .

$\alpha$  = degree of dissociation;

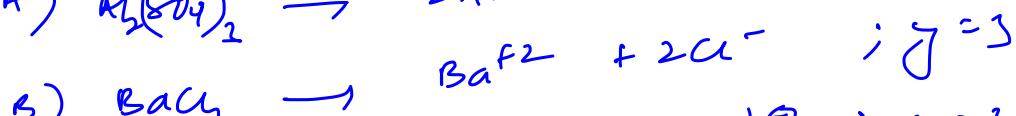
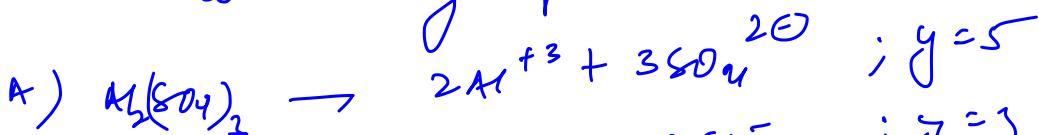
$y$  = no. of moles of product per mole of reactant

Assuming 100% dissociation;  $\alpha = 1$

$$i = y$$

$\therefore$  The more number of ions that a molecule dissociates in, more will

be the value of  $y$  hence more will  
be the boiling point.

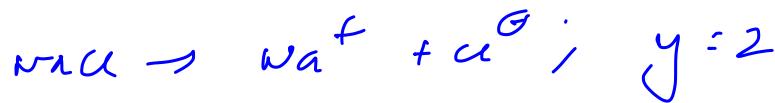


$$0.1\text{M}, \quad 0.1\text{M}, \\ \text{VL} \quad \text{VL}$$

$$\therefore 0.1\text{M} \times 2 = 0.1\text{M}$$

$$2 \times 0.1\text{M}$$

$$\Rightarrow \text{molarity of final soln of NaCl} = \frac{2 \times 0.1\text{M}}{2\text{V}} \\ = 0.1\text{M}$$



(4)

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

(A) 0.200

(B) 0.478

(C) 0.549

(D) 0.786

$X_{\text{Pentane}}$ ;  $X_{\text{Hexane}}$ : mole fraction of pentane  
of hexane in liquid phase

$$X_{\text{Pentane}} : \frac{n_{\text{Pentane}}}{n_{\text{Pentane}} + n_{\text{Hexane}}} = \frac{1}{1+4} = \frac{1}{5}$$

$$\Rightarrow X_{\text{Hexane}} = 1 - X_{\text{Pentane}} = 1 - \frac{1}{5} = \frac{4}{5}$$

$P_T$  = total vapour pressure of sol'n of hexane  
of pentane

acc-to Raoult's law;

$$P_T = P_{\text{hexane}}^{\circ} X_{\text{hexane}} + P_{\text{pentane}}^{\circ} X_{\text{pentane}}$$

$$= (120 \text{ mmHg}) \left( \frac{4}{5} \right) + (440 \text{ mmHg}) \left( \frac{1}{5} \right)$$

$$= 184 \text{ mm Hg}$$

combining Raoult's of Dalton's law;

$$P_{\text{hexane}}^{\circ} X_{\text{hexane}} = P_T \times y_{\text{hexane}}$$

$$P_{\text{pentane}}^{\circ} X_{\text{pentane}} = P_T \times y_{\text{pentane}}$$

where)

$y_{\text{hexane}}$ ;  $y_{\text{pentane}}$  = mole fractions  
of hexane and pentane, resp.  
in vapour phase

$\Rightarrow$  substituting values)

$$120 \times \frac{y}{5} = 184 \times y_{\text{hexane}}$$

$$\Rightarrow y_{\text{hexane}} = 0.52$$

$$\Rightarrow y_{\text{pentane}} = 1 - y_{\text{hexane}} = 0.478$$

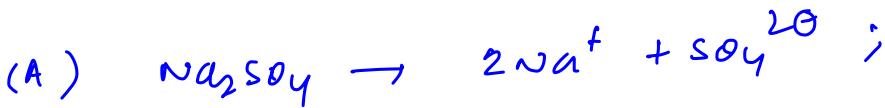
5) For which of the following vant' Hoff's factor is not correctly matched -

Salt	Degree of dissociation ( $\alpha$ )	$i$
(A) $\text{Na}_2\text{SO}_4$	50 %	2
(B) $\text{K}_3[\text{Fe}(\text{CN})_6]$	75%	3.25
(C) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$	80 %	1.8
(D) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$	90 %	2.8

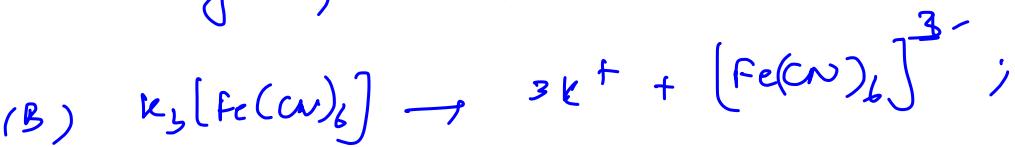
$$i = \text{vant' Hoff factor} = 1 + (y-1) \alpha.$$

$\alpha$  = degree of dissociation;

$y$  = no. of moles of product per mole of reactant



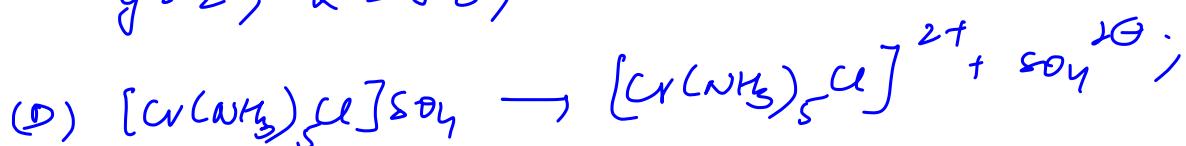
$$y=3; \alpha=0.5 \Rightarrow i = 1 + (3-1) \times 0.5 = 2$$



$$y=4; \alpha=0.75; i = 1 + (4-1)(0.75) = 3.25$$



$$y=2; \alpha=0.8; i = 1 + (2-1)(0.8) = 1.8$$



$$y=2; \alpha=0.9; i = 1 + (2-1)(0.9) = 1.9$$

(6) Theory based

(7) Which of the following is correct for a non-ideal solution of liquids A and B, showing negative deviation?

(A)  $\Delta H_{\text{mix}} = -\text{ve}$

(B)  $\Delta V_{\text{mix}} = -\text{ve}$

(C)  $\Delta S_{\text{mix}} = +\text{ve}$

(D)  $\Delta G_{\text{mix}} = -\text{ve}$

A negative deviation solution would have stronger bonds in the resultant mixture as compared to the bonds in individual components.  $\therefore \Delta H_{\text{mix}} < 0$ ;

$$\Delta V_{\text{mix}} < 0$$

$\therefore$  the mixing is spontaneous;

$$\therefore \Delta G_{\text{mix}} < 0$$

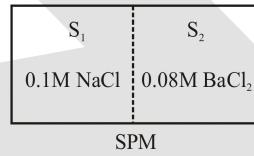
$\therefore$  Entropy increases after mixing;

$$\therefore \Delta S_{\text{mix}} > 0.$$

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Two solutions  $S_1$  and  $S_2$  containing 0.1M NaCl(aq.) and 0.08M BaCl<sub>2</sub>(aq.) are separated by semipermeable membrane. Which among the following statement(s) is/are correct -

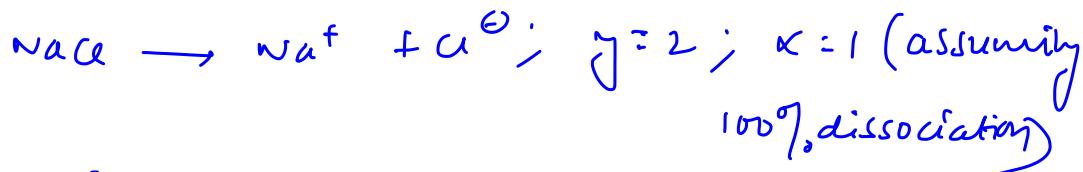
- (A)  $S_1$  and  $S_2$  are isotonic
- (B)  $S_1$  is hypertonic and  $S_2$  is hypotonic
- (C)  $S_1$  is hypotonic and  $S_2$  is hypertonic
- (D) Osmosis will take place from  $S_1$  to  $S_2$



for solution  $S_1$  ;

$$\pi_1 = C_1 RT \times i ; \quad C_1 = 0.1 \text{ M}$$

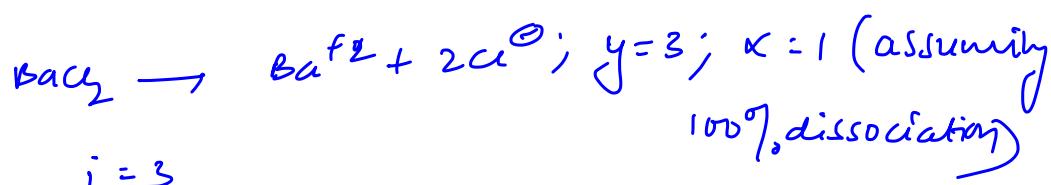
$$i = 1 + (y-1)\kappa ;$$



$$\Rightarrow i = 2$$

$$\Rightarrow \pi_1 = 0.1 \times RT \times 2 = 0.2RT$$

for solution  $S_2$  ;



$$\Rightarrow \pi_2 = (0.08)RT \times 3 = 0.24RT$$

$\therefore \pi_2 > \pi_1 \Rightarrow S_2$  is hypertonic as compared to  $S_1$

(q) For an ideal binary liquid solution with  $P_A^\circ > P_B^\circ$ , which relation between  $X_A$  (mole fraction of A in liquid phase) and  $Y_A$  (mole fraction of A in vapour phase) is correct?

- (A)  $Y_A < Y_B$       (B)  $X_A > X_B$       (C)  $\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$       (D)  $\frac{Y_A}{Y_B} < \frac{X_A}{X_B}$

combining results of Dalton's law;

$$y_A p_T = x_A p_A^\circ \quad \text{--- ①}$$

$$y_B p_T = x_B p_B^\circ \quad \text{--- ②}$$

Dividing ① & ②;

$$\frac{y_A}{y_B} = \frac{x_A}{x_B} \frac{p_A^\circ}{p_B^\circ}$$

$$\therefore p_A^\circ > p_B^\circ \Rightarrow \frac{p_A^\circ}{p_B^\circ} > 1 \Rightarrow \frac{y_A}{y_B} > \frac{x_A}{x_B}$$

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**Column-I**

(Colligative properties)

(A)  $\Delta T_f = 0.3 \times K_f$

(B)  $\Delta T_b = 0.28 \times K_b$

(C)  $\pi = 0.19 \times RT$

(D) 
$$\frac{P^0 - P}{P^0} = \frac{\left( \frac{\Delta T_f}{K_f} \right)}{\left( \frac{1000}{18} \right) + \left( \frac{\Delta T_f}{K_f} \right)}$$

**Column-II**

(Aqueous solution)

(Assume  $m = M$ )

(P)  $0.1 \text{ m} - \text{Ca}(\text{NO}_3)_2$

(Q)  $0.14 \text{ m} - \text{NaBr}$

(R)  $0.1 \text{ m} - \text{MgCl}_2 (\alpha = 0.9)$

(S)  $0.28 \text{ m} - \text{Urea}$

(T)  $0.1 \text{ m} - \text{HA} \text{ (monobasic acid, } K_a = 0.81\text{)}$

21. Ans. (A)  $\rightarrow$  P ; (B)  $\rightarrow$  Q, R, S ; (C)  $\rightarrow$  T ; (D)  $\rightarrow$  P, Q, R, S, T

$$(A) \Delta T_f = K_f \times m \times i$$

$\Delta T_f$  = depression in freezing point

$K_f$  = molal depression constant ;

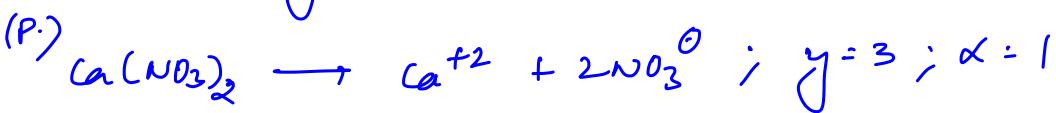
molality = molality of solution

$i$  = van't Hoff factor =  $1 + (y-1)\alpha$ .

$\alpha$  = degree of dissociation ;

$y$  = no. of moles of product per mole of reactant

substituting values ;



$$i = 1 + (3-1)(\gamma) = 3.$$

$$\Rightarrow \Delta T_f = k_f \times 0.1 \times 3 = 0.3 k_f$$

$$(B) : \Delta T_b = 0.28 \times k_b$$

Q.) 0.14M - NaBr

Applying formula for elevation in boiling point;

$$\Delta T_b = T_b' - T_b = k_b \times \text{molality};$$

$T_b'$  = boiling point of solution;

$T_b$  = " " " pure solvent

$k_b$  = molal elevation constant

molality = molality of solution

$$i = \text{van't Hoff factor} = 1 + (y-1)\alpha.$$

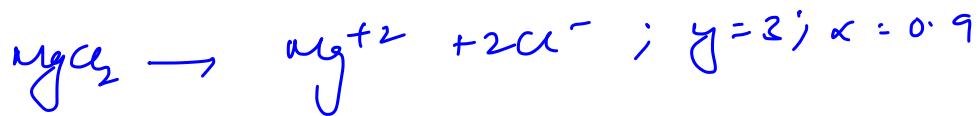
$\alpha$  = degree of dissociation;

$y$  = no. of moles of product per mole of reactant



$$\Rightarrow \Delta T_b = k_b \times (0.14)(2) = 0.28 k_b$$

(R.) 0.1m  $\text{MgCl}_2$  ( $\kappa = 0.9$ )



$$\Rightarrow i = 1 + (3 \cdot 1)(0.9) = 2.8$$

$$\Rightarrow \Delta T_b = k_b \times 0.1m \times 2.8 = 0.28 k_b$$

(S.) 0.28m urea.

$$\kappa = 0 \text{ for urea} \Rightarrow i = 1$$

$$\Delta T_b = k_b \times m \times i = 0.28 k_b$$

(C.)  $\pi = 0.19 RT$  ;

(T.) 0.1m - HA ( $K_a = 0.81$ )



$$0.1(1-\alpha) \quad 0.1\alpha \quad 0.1\alpha$$

$$\Rightarrow \frac{0.1\alpha^2}{1-\alpha} = 0.81$$

$$\Rightarrow \alpha^2 = 8.1 - 8.1\alpha$$

$$\Rightarrow \alpha^2 + 8.1\alpha - 8.1 = 0$$

$$\Rightarrow \alpha = \frac{-8.1 + \sqrt{(8.1)^2 + 4 \times 8.1}}{2}$$

$$= 0.9$$

$$\Rightarrow i = 1 + (y-1)\alpha = 1 + (2-1)(0.9) = 1.9$$

∴ Applying formula of osmotic pressure;

$$\pi = CRT(i) = 0.1 RT(1.9) = 0.19 RT$$

$$(D) \frac{P^0 - P}{P^0} = \frac{\left(\frac{\Delta T_f}{K_f}\right)}{\left(\frac{1000}{18}\right) + \left(\frac{\Delta T_f}{K_f}\right)}$$

(D)  $\frac{P^0 - P}{P^0} = \frac{\left(\frac{\Delta T_f}{K_f}\right)}{\left(\frac{1000}{18}\right) + \left(\frac{\Delta T_f}{K_f}\right)}$

$$R \cdot M \cdot S \cdot = \frac{\frac{\Delta T_f}{K_f}}{\left(\frac{1000}{18}\right) + \frac{\Delta T_f}{K_f}}$$

$$= \frac{\text{molality}}{\left(\frac{1000}{18}\right) + \text{molality}}$$

$$= \frac{\frac{n_{\text{solute}}}{w_{\text{solvent}} \text{ (in g)}}}{\frac{1000}{18} + \frac{n_{\text{solute}}}{w_{\text{solvent}} \text{ (in g)}}}$$

$\because$  solvent is water;

$$= \frac{\frac{n_{\text{solute}}}{\text{wt}_{\text{H}_2\text{O}}(\text{kg})}}{\left(\frac{\text{Molar mass}}{18}\right) + \frac{n_{\text{solute}}}{\text{wt}_{\text{H}_2\text{O}}(\text{kg})}}$$

$$= \frac{\frac{n_{\text{solute}}}{\text{wt}_{\text{H}_2\text{O}}(\text{kg})}}{\left(\frac{\text{Molar mass}}{18}\right) \times \text{wt}_{\text{H}_2\text{O}}(\text{kg}) + n_{\text{solute}}}$$

$$= \frac{\frac{n_{\text{solute}}}{\left(\frac{\text{wt}_{\text{H}_2\text{O}}(\text{gm})}{18}\right)}}{+ n_{\text{solute}}} = \frac{n_{\text{solute}}}{n_{\text{H}_2\text{O}} + n_{\text{solute}}}$$

$$= X_{\text{solute}}$$

$$\Rightarrow \frac{p^0 - p}{p^0} = X_{\text{solute}}$$

