PHYSICAL CHEMISTRY CRASH COURSE

SOLUTIONS IN 1 SHOT

Full Chapter REVISION

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Practice Sheet on PW App

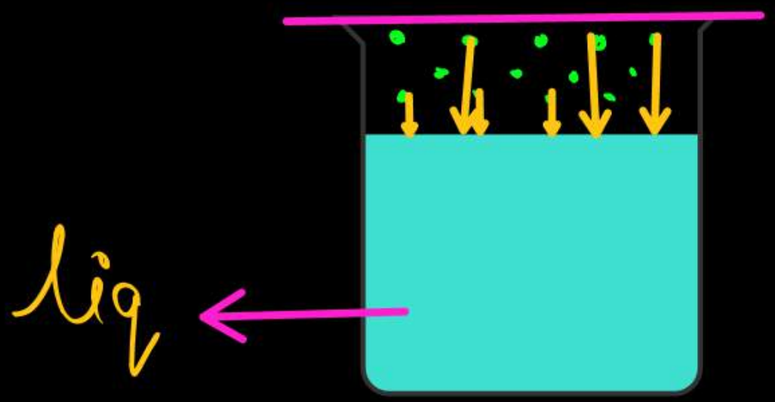
Today's GOAL

Solutions

1. Vapour Pressure

The pressure Exerted by the vapours over the surface of liquid

Rate of evaporation = Rate of condensation



Factors affecting Vapour Pressure

1. Temperature

$$V.P \propto T$$

2. Intermolecular forces

$$V.P \propto \frac{1}{IMF}$$

Q. Compare V.P and B.P

$\left[V.P \propto \frac{1}{B.P}\right]$

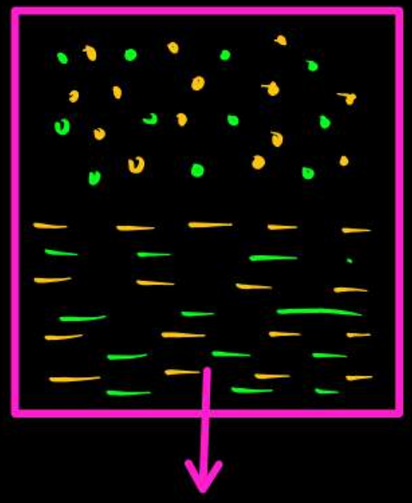
HF HCl HBr HI

B.P $HCl < HBr < HI < HF$

Intermolecular H-Bond

V.P $HCl > HBr > HI > HF$

2. Raoult's Law Case 1- For Two volatile liquids



A + B

Both Volatile

P_T or $P_S = P_A + P_B$

$$P_T = P_A^0 X_A + P_B^0 X_B$$

P_A^0 = V.P of pure A

P_B^0 = " " pure B

X_A = mole fraction of A

X_B = " " B

P_T or P_S = Total V.P

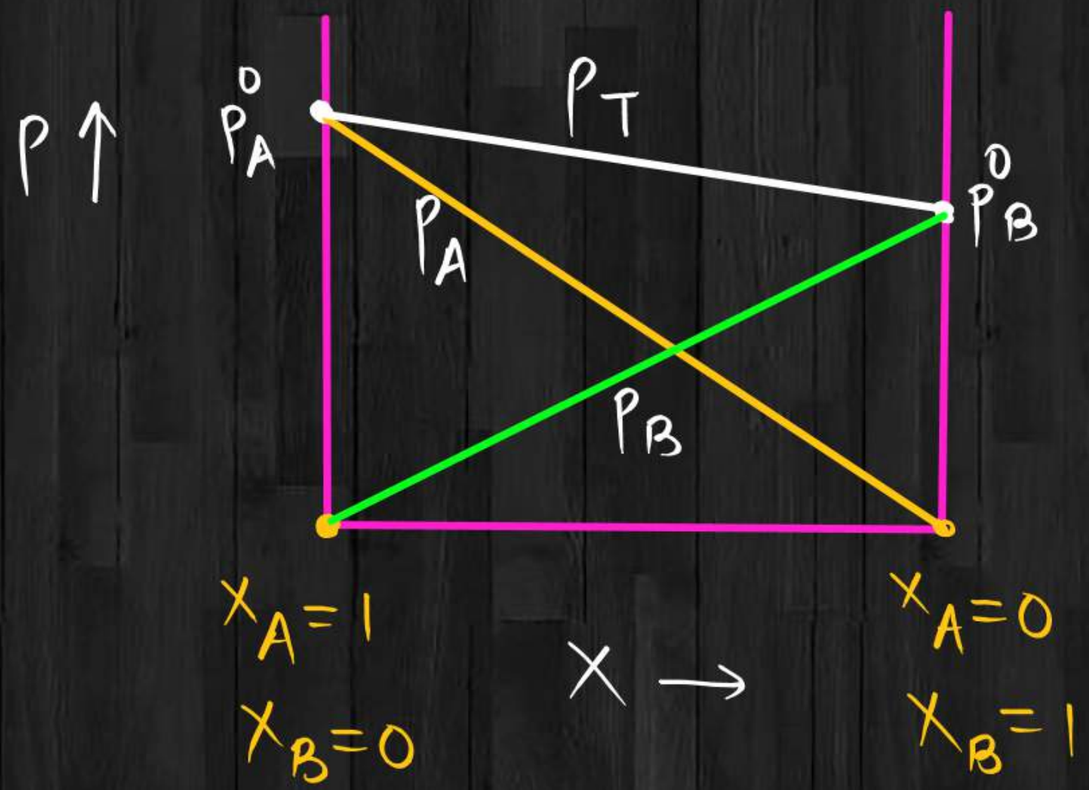
P_A = V.P of A in soln

P_B = " " B " "

$X_A + X_B = 1$

A is more volatile than B

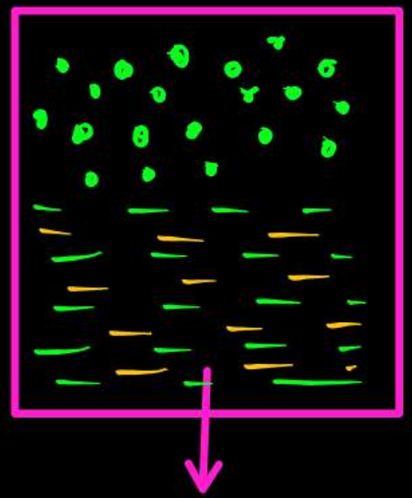
$P_A^0 > P_B^0$



$$P_T = P_A^0 X_A + P_B^0 X_B$$

2. Raoult's Law

Case 2- when solute is non volatile



A + B

Solvent Solute

(Volatile) (Non volatile)

P_T or $P_S = P_A + P_B^0$

$$P_T = P_A^0 X_A$$

P_T or P_S = Total V.P

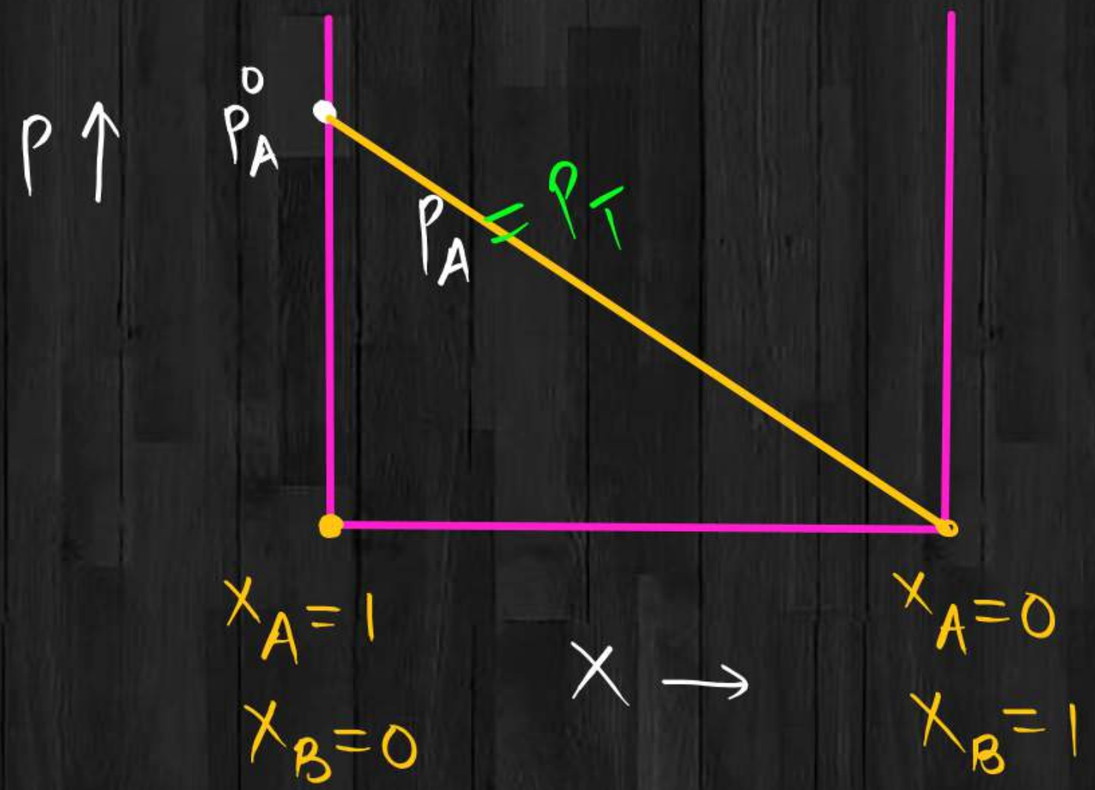
P_A = V.P of A in soln

P_A^0 = V.P of pure A

$X_A + X_B = 1$

X_A = mole fraction of A

X_B = " " " B



$$P_T = P_A$$

$$P_T = P_A^0 X_A$$

A ⟶ solvent , B ⟶ solute

Ideal

① obeys R·L ($P_A + P_B$)

② $(P_T)_{obs} = (P_T)_{cal}$

③ IMF b/w A-A & B-B are equal to A-B

④ $\Delta H_{mix} = 0$

$\Delta V_{mix} = 0$

$\Delta S_{mix} > 0$

$\Delta G_{mix} < 0$

Non Ideal

+ve deviation

① does not obey R·L

② $(P_T)_{obs} > (P_T)_{cal}$

③ IMF b/w A-A & B-B are greater than A-B

④ $\Delta H_{mix} > 0$

$\Delta V_{mix} > 0$

$\Delta S_{mix} > 0$

$\Delta G_{mix} < 0$

-ve deviation

① does not obey R·L

② $(P_T)_{obs} < (P_T)_{cal}$

③ IMF b/w A-A & B-B are lesser than A-B

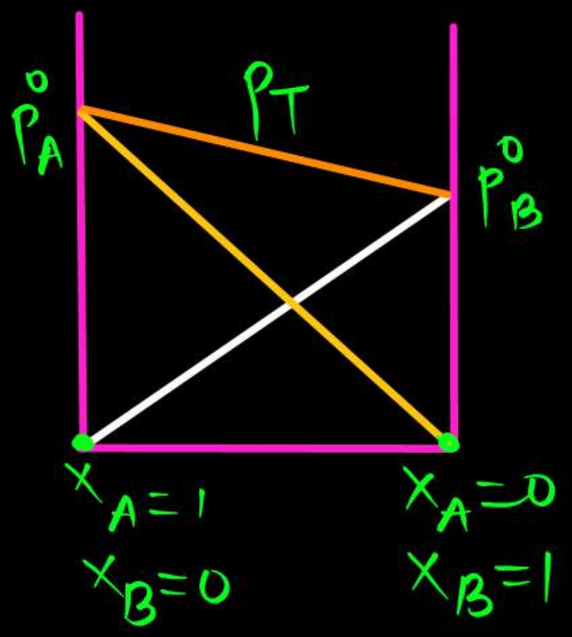
④ $\Delta H_{mix} < 0$

$\Delta V_{mix} < 0$

$\Delta S_{mix} > 0$

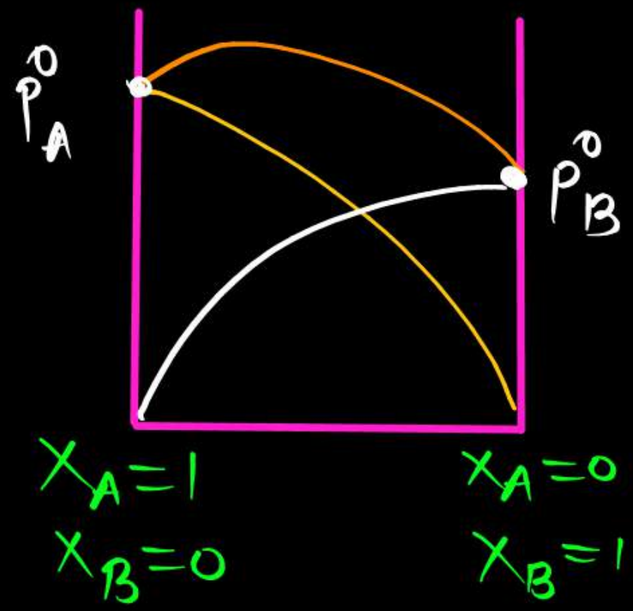
$\Delta G_{mix} < 0$

Ideal



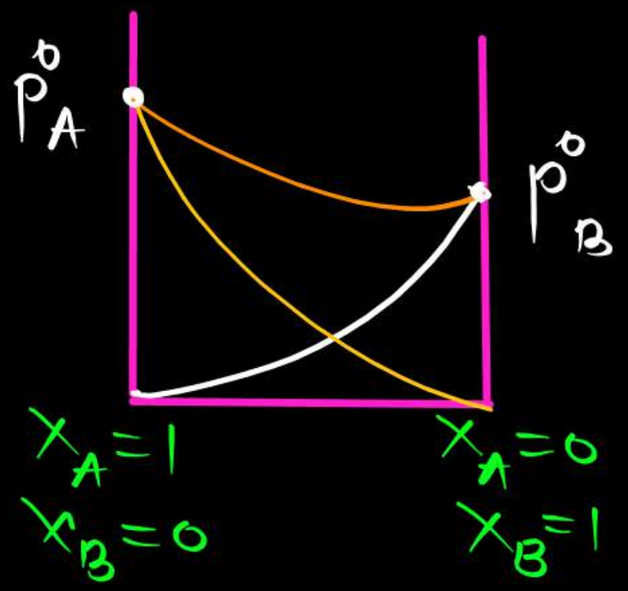
$(P_T)_{obs} > (P_T)_{cal}$

+ve deviation



Non Ideal

–ve deviation



Ideal

Examples

1. Bromo ethane + Chloro ethane
2. Benzene + Toluene

Non ideal

Min boiling azeo

+ve deviation

1. $CCl_4 + C_6H_6$
2. $CCl_4 + CH_3OH$
3. $CCl_4 + C_2H_5OH$
4. $C_2H_5OH + H_2O$

$>C=O \cdots H-CCl_3$ (H-B)

-ve deviation

Max boiling azeo

1. $HNO_3 + H_2O$
2. $>=O + CHCl_3$
3. $CHCl_3 + CH_3COOH$
4. $HCl + H_2O$

$CCl_4 + \cdots \rightarrow +ve$

$CHCl_3 + \cdots \longrightarrow -ve$

$Acid + H_2O \longrightarrow -ve$

Azeotropic Mixture

Const boiling mix.

Minimum Boiling Azeotrope

B.P ↓ , V.P ↑ , +ve deviation

Maximum Boiling Azeotrope

B.P ↑ , V.P ↓ , −ve devi

Mole fraction in vapour phase

Dalton's Law

let y_A = mole fraction of A in vapour phase

y_B = " " " B " "

$y_A + y_B = 1$

$$p_A = y_A P_T$$

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

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

3. Colligative Prop

The Properties which depends on number of solute particles

1. RLVP (Relative Lowering in Vapour pressure)
2. EBP (Elevation in boiling point)
3. DFP (Depression in freezing point)
4. OP (Osmotic pressure)

1. R.L.V.P

$P_B = 0$

When non volatile solute is dissolve in volatile solvent its V.P decreases

$P_S = P_A$

$P_S = P_A^0 X_A$

$P_S = P_A^0 (1 - X_B)$

$P_S = P_A^0 - P_A^0 X_B$

$P_A^0 X_B = P_A^0 - P_S$

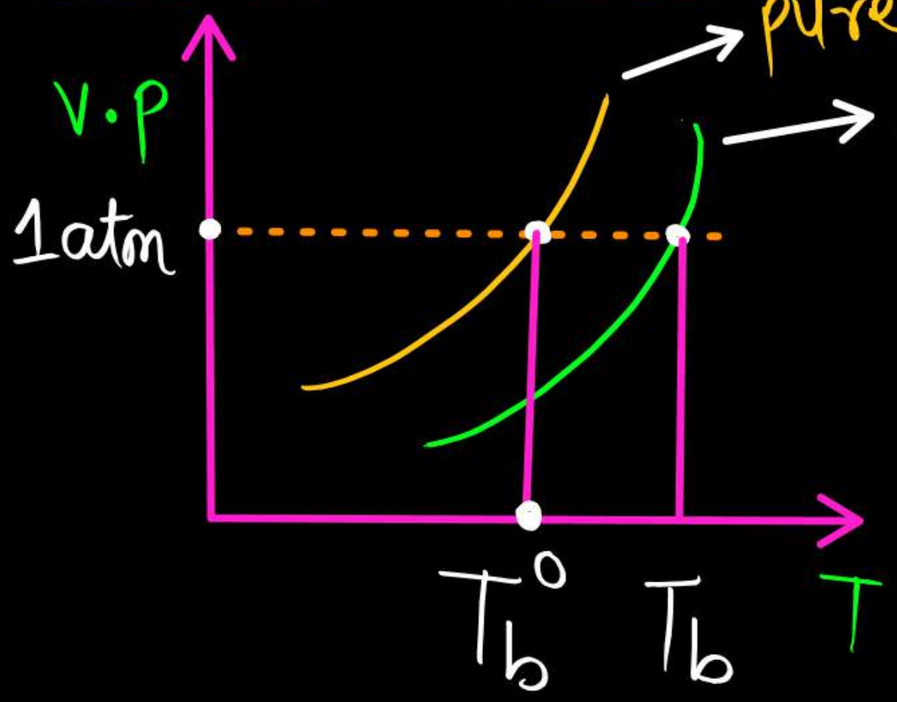
$X_B = \dfrac{P_A^0 - P_S}{P_A^0}$ → R·L·V·P

$P_A^0 - P_S$ = Lowering in V·P ~~(C·P)~~

$\dfrac{P_A^0 - P_S}{P_A^0}$ = R·L·V·P (C·P)

2. E.B.P

When non volatile solute is dissolve in volatile solvent its V.P decreases Thus boiling point increases.



$$T_b > T_b^0$$

$$\Delta T_b = T_b - T_b^0 \quad (E.B.P)$$

$\Delta T_b \propto m$

$$\boxed{\Delta T_b = K_b\, m}$$

$$m = \frac{n_B}{W_{A(kg)}}$$

K_b for $H_2O = 0.52$ K kg/mol

molal elevation constant

or

ebullioscopic Const

$$K_b = \frac{R T_b^{o\,2}}{1000 L_v}$$

R = gas const

T_b^o = standard B.P

L_v = Latent heat of vap $\left(\frac{\Delta H_{vap}}{MW}\right)$

Solid ⇌ liq T_f^0

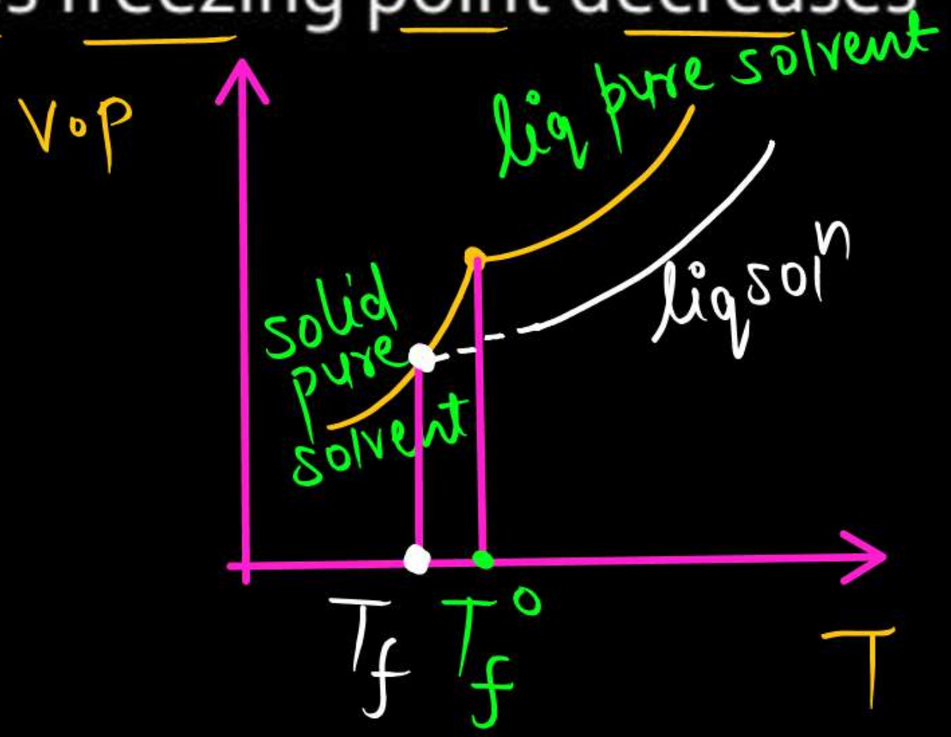
Solid pure ⇌ liq soln T_f

Solvent pure Solvent

3. D.F.P

When non volatile solute is dissolve in volatile solvent its V.P decreases

Thus freezing point decreases



$$T_f < T_f^0$$

$$\Delta T_f = T_f^0 - T_f$$

$\Delta T_f \propto m$

$$\boxed{\Delta T_f = K_f\, m}$$

$$m = \frac{n_B}{W_{A(Kg)}}$$

K_f for $H_2O = 1.86$ K Kg/mol

molal depression constant

or

cryoscopic Const

$$K_f = \frac{R\, T_f^{o\,2}}{1000\, L_f}$$

R = gas const

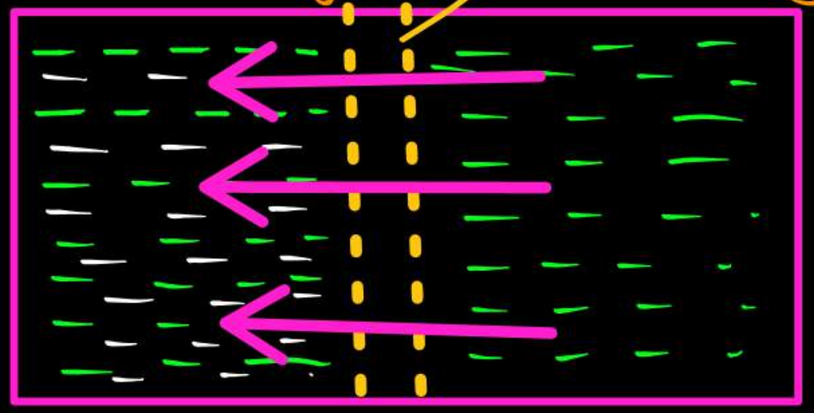
T_f^o = standard FP

L_f = Latent heat of fus $\left(\frac{\Delta H_{fus}}{MW}\right)$

4. O.P

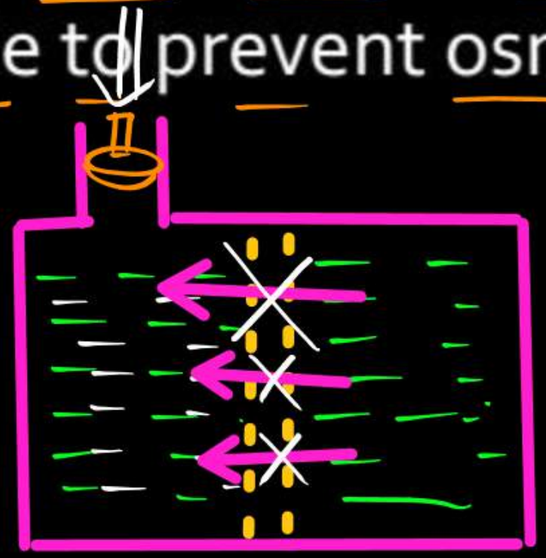
Osmosis- The flow of solvent molecules from lower conc. to higher conc.

Solute Solute



Pure solvent to Solution

Osmotic Pressure- The minimum pressure which must be applied to the solution side to prevent osmosis.



$\pi \propto c$, $\pi \propto T$

$\pi \propto cT$

$\boxed{\pi = cRT}$

c = Molarity

R = gas const

T = Temp (K)

$\left(\frac{1}{T_2}\right)$

Soln 1 π_1 Soln 2 π_2

Type of solutions

Isotonic $\pi_1 = \pi_2$

Hypertonic $\pi_1 > \pi_2$ 1 is Hypertonic, 2 is hypotonic

Hypotonic $\pi_1 < \pi_2$ 1 is Hypo, 2 is Hyper

4. Van't hoff factor and abnormal molecular mass

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mas}}$$

$$= \frac{\text{Observed colligative prop}}{\text{Calculated colligative prop}}$$

$$= \frac{\text{Total no. of moles after association / dissociation}}{\text{Total no. of moles before association / dissociation}}$$

Calculation of i

Case① for diss.

	A_n	$\rightleftharpoons$	nA
n_i	1		0
n_t	$1-x$		nx

$$i = \frac{1-x+nx}{1+0}$$

$x = D.O.D$

$$\boxed{i = 1+(n-1)x}$$

Signi of 'n' ⇒ no. of moles of products

$AlCl_3 \longrightarrow Al^{3+} + 3Cl^-$

$n = 4$

Case② for associ

$$nA \rightleftharpoons A_n$$

	A	$\rightleftharpoons$	$\frac{1}{n}A_n$
n_i	1		0
n_t	$1-x$		$\frac{x}{n}$

$x = D.O.A$

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

$$\boxed{i = 1+\left(\frac{1}{n}-1\right)x}$$

Signi of n n = no. of moles of reactant

$2\,CH_3COOH \rightleftharpoons (CH_3COOH)_2$

$n = 2$

Q. Calculate DOD for $Ba(NO_3)_2$ (given i= 2.74)

$n = 3$

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

$$2.74 = 1 + (3-1)\alpha$$

$$1.74 = 2\alpha$$

$$\alpha = \frac{1.74}{2}$$

Q. Find i for $Ca_3(PO_4)_2$ if D.O.D is 100%

$3 + 2 = 5$

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

$$i = n = 5$$

Colligative prop formula - imp for exam

① $\frac{P_A^\circ - P_s}{P_s} = \frac{i\, n_B}{n_A}$

② $\Delta T_b = i\, K_b\, m$

③ $\Delta T_f = i\, K_f\, m$

④ $\pi = i\, C\, R\, T$

Q. which is not equal to zero for an ideal sol^{n} ?

(A) ΔH_{mix}

(B) ΔS_{mix}

(C) ΔV_{mix}

(D) NOT

Q. If 3 moles of A is mixed with 2 moles of B find

P_A, P_B and P_T ?

Given $P_B^o = 100$ mm of Hg

$P_A^o = 200$ mm of Hg

$P_T = 160$

$x_A = \frac{3}{5}$

$x_B = \frac{2}{5}$

$P_A = P_A^o X_A$

$= 200 \times \frac{3}{5}$

$= 120$

$P_B = P_B^o X_B$

$= 100 \times \frac{2}{5}$

$= 40$

Q. Which show negative deviation ?

(A) $CCl_4 + C_6H_6$

(B) $C_2H_5OH + H_2O$

(C) Acetone + $CHCl_3$

(D) $CCl_4 + CH_3OH$

Q. Compare freezing point

(A) K_2SO_4 $n=3$

(B) NaCl $n=2$

(C) Urea $n=1$

(D) $AlCl_3$ $n=4$

$x=1$

$i \uparrow$, $C.P \uparrow$, $\Delta T_f \uparrow$ $T_f \downarrow$

$i = n$

$D < A < B < C$

Q. Compare BP

(A) 0.1 M K^+Cl^- $n=2$

(B) 0.1 M $BaCl_2$ $n=3$

(C) 0.1 M $FeCl_3$ $n=4$

(D) 0.1 M $Fe_2(SO_4)_3$ $n=5$

$\alpha=1$ $\quad i=n$ $\quad i\uparrow \quad C.P\uparrow \quad \Delta T_b\uparrow \quad T_b\uparrow$

$A<B<C<D$

Q. which salt would have same i as that of $K_3^{+}[Fe(CN)_6]^{3-}$ $n=4$

(A) NaCl $n=2$

(B) Na_2SO_4 $n=3$

(C) $Al_2(SO_4)_3$ $n=5$

(D) $Al(NO_3)_3$ $n=4$

Q. 0.5 M sol^n of urea is isotonic with

(A) 0.5 M NaCl

(B) 0.5 M sugar

(C) 0.5 M $BaCl_2$

(D) 0.5 M Benzoic acid in benzene

$\pi_1 = \pi_2$

$i_1 C_1 = i_2 C_2$

$i_1 = i_2$

Q. 0.2 molal acid HA is 20% Ionized aq. sol^n (k_f = 1.86 K Kg/mol) find F.P of sol^n ?

$n = 2$

$$\Delta T_f = i\, k_f\, m$$

$$T_f^\circ - T_f = 1.2 \times 1.86 \times 0.2$$

T_f° → $0^\circ C$

$$i = 1 + (n-1)x$$

$$= 1 + (2-1)x$$

$$= 1 + x$$

$$= 1 + 0.2 = 1.2$$

Q. 2×10^{-3} m aq sol^{n} of an Ionic comp $Co(NH_3)_5NO_2Cl$ freezes at – 0.00732°C

Find i ?

$$\Delta T_f = i^{\circ} K_f m$$

$$0 - (-0.00732) = i^{\circ} \times 1.86 \times 2 \times 10^{-3}$$

Q. The V P of pure CH_3OH(A) is 0.15 bar at 25°C. The V.P of this liq in sol^n is 0.09 bar calculate mole fraction of B?

$$RLVP = X_B$$

$$\frac{P_A^0 - P_S}{P_A^0} = X_B$$

$$\frac{0.15 - 0.09}{0.15} = X_B$$

Henry's Law

At constant temperature , the solubility of gas in liquid is directly proportional to the pressure

$[S \propto P]$

If solubility is expressed in terms of mole fraction

Partial pressure of gas in liquid is directly proportional to the mole fraction of gas in liq .

$P_{gas} \propto x_{gas}$

Henry's Law

$P_{gas} \propto x_{gas}$

$P_{gas} = k_H x_{gas}$

k_H = Henry's law const
(depends on temp)

$T \uparrow \; k_H \uparrow$

$S \propto \frac{P}{T}$

$P \uparrow \; S \uparrow$ $\quad$ $T \uparrow \; S \downarrow$

Q. At 40°C the vap. pressure of CH_3OH (A) and EtOH(B) Sol^n is represented by $P = 120\,X_A + 138$ where X_A is mole fraction of MeOH find values of

$\left(\frac{P_B^0}{X_B}\right)_{x_A \to 0}$ and $\left(\frac{P_A^0}{X_A}\right)_{x_B \to 0}$

$x_A \to 0$

$X_B \to 1$

P_B^0

$X_A = 0 \;,\; X_B = 1$

$P_B^0 = 138$

$X_A = 1 \;,\; X_B = 0$

$P_A^0 = 120 + 138 =$

Q. Which one of the following statements regarding Henry's law is not correct? **(2019 Main, 8 Jan I)**

(a) Different gases have different K_H (Henry's law constant) values at the same temperature

(b) Higher the value of K_H at a given pressure, higher is the solubility of the gas in the liquids

$T \uparrow K_H \uparrow S \downarrow$

(c) The value of K_H increases with increase of temperature and K_H is function of the nature of the gas

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

Solution:

Q. 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution is **(2016 Main)**

$P^\circ_A = 760$

(a) 76.0 (b) 752.4 (c) 759.0 (d) 7.6

Solution:

$$\frac{P^\circ_A - P_S}{P^\circ_A} = x_B$$

$$\frac{P^\circ_A - P_S}{P_S} = \frac{n_B}{n_A}$$

$$n_B = \frac{18}{180} \qquad n_A = \frac{178.2}{18}$$

$$\frac{760 - P_S}{P_S} = \frac{0.1}{178.2} \times 18$$

Q. The Henry's law constant for the solubility of N_2 gas in water at 298 K is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water of 298 K and 5 atm pressure is **(2009)**

(a) 4.0×10^{-4}

(b) 4.0×10^{-5}

(c) 5.0×10^{-4}

(d) 4.0×10^{-6}

Solution: $K_H = 10^5$ atm

$P_{N_2} = 0.8 \times 5 = 4$ atm

$P_{gas} = K_H \, x_{gas \text{ in liq}}$

$$4 = 10^5 \times \frac{n_{N_2}}{n_{N_2} + n_{H_2O}}$$

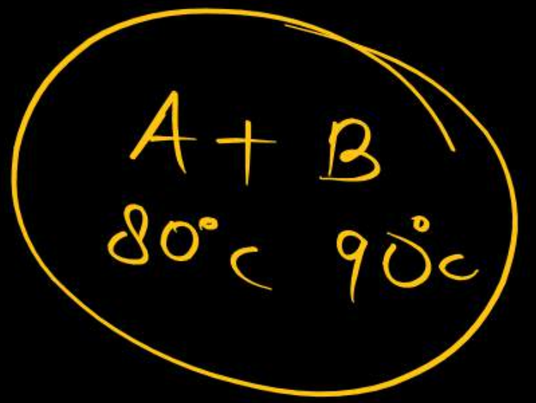
$n_{N_2} \to 0$

$$4 = 10^5 \times \frac{n_{N_2}}{10}$$

$$n_{N_2} = 4 \times 10^{-4}$$

Q. An azeotropic solution of two liquids has boiling point lower than either of them when it **(1981, 1M)**

(a) shows negative deviation from Raoult's law
(b) shows no deviation from Raoult's law
(c) shows positive deviation from Raoult's law
(d) is saturated



Solution:

$$\left(\frac{P^{\circ}_A - P_S}{P^{\circ}_A} = \frac{i n_B}{i n_B + n_A} \right) \qquad \left(\frac{P^{\circ}_A - P_S}{P_S} = \frac{i n_B}{n_A} \right)$$

Thank you!!