

# श्री नाथ जी बुक डिपो

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मातृ छाया होस्टल शॉप नं. 2 ऐलन सत्यार्थ गेट नं. 2 के  
सामग्रे, जवाहर नगर, कोटा (राज.) मो. 7014774207

## Solution

### # Introduction:-

A homogenous mixture of 2 or more components  
is called as a solution.

$$\bullet \text{ Solution} = \text{Solute} + \text{Solvent}$$

↓      ↓

Lesser amount      Larger amount

\* 1 Solute + 1 Solvent  $\Rightarrow$  Binary solution.

$\Rightarrow$  Physical state of a solution can be solid, liquid and gas.

$\Rightarrow$  Physical state of solvent & solution is same.

\* On the basis of amount of solute:-

Dilute & Concentrated solution.

### # Concentration Term:-

(i) Normality (N):-

No. of equivalents (gram equivalents) of solute  
present in 1L of solution.

$$\boxed{\text{Normality} = \frac{\text{No. of equivalents of solute}}{\text{Vol}^n \text{ of sol}^n (\text{L})}}$$

$$= \frac{\text{Mass of solute (g)}}{\text{Eqwt of solute} \times \text{Vol}^n \text{ of sol}^n (\text{L})}$$

Unit = eqL<sup>-1</sup> or geqL<sup>-1</sup> or N

Eg:- 2N (normal) NaOH sol.

2 eq. of NaOH in 1L sol.

## ② Molarity (M) :-

No. of moles of solute present in 1L of solution.

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Vol. of soln (L)}} = \frac{\text{Mass of solute (g)}}{\text{Molar Mass of solute (g/mol)} \times \text{Vol. of soln (L)}}$$

Unit  $\Rightarrow \text{Mol L}^{-1}$  or M

Eg:- 2M (molar) NaOH soln  
 $\Rightarrow$  2 moles of NaOH in 1L soln

## ③ Molality (m) :-

(No. of moles of solute present in 1kg. of solvent.

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}}$$

Unit  $= \text{mol kg}^{-1}$  or m

Eg:- 2m (molal) NaOH soln  
 $\Rightarrow$  2 moles of NaOH in 1kg. solvent

## ④ Strength (s) :-

Mass of solute (ing) present in 1L of soln

$$\text{Strength (s)} = \frac{\text{Mass of solute (g)}}{\text{Vol. of soln (L)}}$$

Unit  $\Rightarrow \text{g L}^{-1}$

Eg:- 2g/L NaOH soln  
 $\Rightarrow$  2g NaOH in 1L soln

$$S = \frac{\text{Mass of solute}}{\text{Molar Mass} \times \text{Vol of soln}} \times \frac{\text{Molar mass of solute}}{\text{of solute}}$$

|   |
|---|
| $S = M \times \text{molar mass of solute}$      |
| $S = N \times \text{Equivalent mass of solute}$ |

⑤ Mole fraction ( $x$ ):—

Ratio of moles of component to the total no. of moles of all components present in a solution.

A = solvent; B = solute

$$x_A = \frac{n_A}{n_A + n_B}; \quad x_B = \frac{n_B}{n_A + n_B}$$

⇒ Sum of mole fraction of all components present in a solution is equal to 1.

$$\therefore x_A + x_B = 1$$

$$\Rightarrow 0 < x < 1$$

↓  
mole fraction of any component present in a solution.

⇒ Unitless quantity.

$$\Rightarrow \boxed{\frac{x_B}{x_A} = \frac{n_B}{n_A}}$$

⑥ In term of Percentage:—

(i) Mass percentage ( $\%_w$ ):—

Mass of solute (in g) present in 100g of solution.

$$\% \text{ w/w} = \frac{\text{Mass of solute (g)}}{\text{Mass of soln. (g)}} \times 100$$

Eg: - 10% w/w NaOH soln  
 $\Rightarrow$  10g NaOH in 100g soln.

### (B) Volume percentage ( $\text{V/V}$ ):—

Vol. of solute (in ml) present in 100ml of solution.

$$\% \text{ V/V} = \frac{\text{Vol. of solute (ml)}}{\text{Vol. of soln (ml)}} \times 100$$

Eg: - 10% V/V ethanol soln  
 $\Rightarrow$  10ml ethanol 100ml soln.

### (C) Mass by volume ( $\text{w/v}$ ):—

Mass of solute (in g) present in 100ml of solution.

$$\% \text{ w/v} = \frac{\text{Mass of Solute (g)}}{\text{Vol. of solution (ml)}} \times 100$$

Eg: - 10% w/v glucose soln.  
 $\Rightarrow$  10g glucose in 100ml soln.

### (D) Parts per million (PPM):—

$\Rightarrow$  It is used to express the conc. where solute is present in trace amounts.

Eg: - water & Air pollution.

$\Rightarrow$  No. of parts of solute present in  $10^6$  parts of solution.

$$\text{PPM} = \frac{\text{No. of parts of solute}}{\text{No. of parts of solution}} \times 10^6$$

Note:-

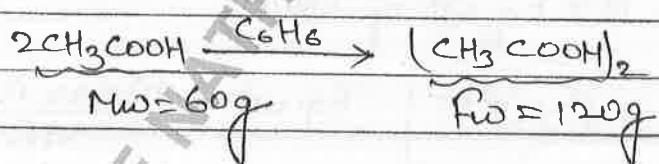
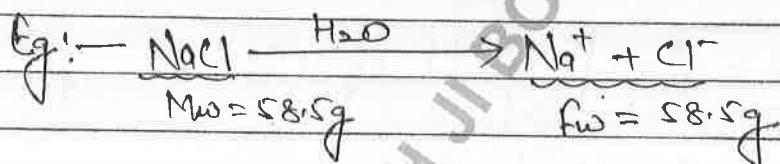
PPM can be expressed in terms of w/w, v/v & w/v.

### ⑧ Formality (F) :-

No. of gram formula mass unit of solute present in 1L of solution.

$$\text{Formality} = \frac{\text{No. of formula units of solute}}{\text{Vol. of Solution (L)}}$$

$$\text{Formality} = \frac{\text{Mass of solute (g)}}{\text{formula mass of solute} \times \text{Vol. of soln (L)}}$$



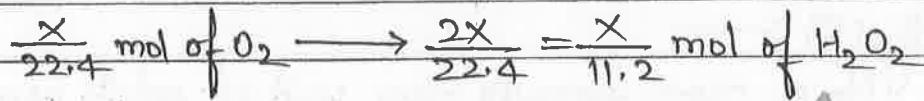
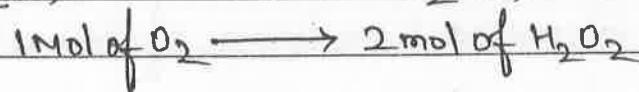
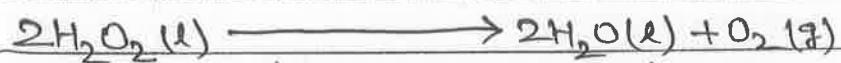
### ⑨ Volume Strength of solution :-

Volume of  $\text{O}_2$  (in L) produced at STP/NTP by the decomposition of 1L of  $\text{H}_2\text{O}_2$  soln is known as volume strength of  $\text{H}_2\text{O}_2$  solution.

# Relation b/w vol. strength of  $\text{H}_2\text{O}_2$  soln with M, N, S & %w/v:

Let, vol. strength of  $\text{H}_2\text{O}_2$  soln be: 'X' v

It means that 'X' L of  $\text{O}_2$  is produced at STP/NTP by the decomposition of 1L of  $\text{H}_2\text{O}_2$  soln?



① Molarity

$$M = \frac{\text{moles of solute}}{\text{Vol. of soln. (L)}} = \frac{x}{11.2 \times 1}$$

$$\therefore M = \frac{x}{11.2}$$

$$\text{② } N = M \times \text{v.f.} \Rightarrow \frac{x}{11.2} \times 2$$

$$\therefore N = \frac{x}{5.6} \quad \left. \begin{array}{l} \text{v.f. of H}_2\text{O}_2 = 2 \\ \end{array} \right\}$$

③ Strength =  $N \times \text{Eq. wt of solute}$

$$\therefore S = \frac{x}{5.6} \times 17 \quad \text{Eq. wt} = \frac{\text{Molar mass}}{\text{V.F.}}$$

$$= \frac{34}{2} = 17.$$

$$\text{④ Strength} = \frac{\text{Mass of solute (g)}}{\text{Vol. of soln. (m.l)}} \times 1000$$

$$\therefore S = \% \text{ w/v} \times 10$$

$$\therefore \% \text{ w/v} = \frac{x}{5.6} \times \frac{17}{10}$$



V.F. = Change in O.W.  $\times$  No. of atoms undergoing per atom the change in one molecule

$$\text{V.F.} = 1 \times 2 = 2$$

# Relation b/w various concentration terms:-

① Mole fraction ( $x$ ) & Molality ( $m$ ) :-

$$\frac{x_{\text{solute}}}{x_{\text{solvent}}} = \frac{n_{\text{solute}}}{n_{\text{solvent}}} = \frac{n_{\text{solute}} \times M_{\text{solvent}} \times 1000}{W_{\text{solvent}} \times 1000}$$

$$\frac{x_{\text{solute}}}{x_{\text{solvent}}} = \frac{m \times M_{\text{solvent}}}{100}$$

$M_{\text{solvent}}$   $\Rightarrow$  Molar Mass of solvent

② Molality ( $m$ ) & Molarity ( $M$ ) :-

'M' in molar soln.  $\Rightarrow$  M moles of solute present in 1000ml of soln?

Density of soln =  $\rho$  g ml<sup>-1</sup>

$$w_{\text{solvent}} = w_{\text{soln}} - w_{\text{solute}}$$

$$= (\rho \times V_d)_{\text{soln}} - (M \times M_{\text{solute}})_{\text{solute}}$$

$$\text{Molality} = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{\text{moles of solute}}{\text{mass of solvent (g)}} \times 1000$$

$$m = \frac{M \times 1000}{(d \times 1000) - (M \times M_{\text{solute}})}$$

$M_{\text{solute}}$  = Molar mass of solute

③ Molarity (M) & % w/w :-

$$M = \frac{10 \times d (\% \text{ w/w})}{\text{Molar mass of solute}}$$

④ Normality (N) & w/w

$$N = \frac{10 \times d \times (\% \text{ w/w})}{\text{Equivalent mass of solute}}$$

$d$  = density of soln in  $\text{g ml}^{-1}$

Note:- The conc. terms like molarity, Normality, % w/v are temp. dependent whereas the conc. terms like mole fraction, % w/w etc. are temp. independent because volume depends on temp. but may does not depends on temp.

# Law of Dilution:-

(Add<sup>n</sup> of solvent)

$$\downarrow C = \frac{n}{V_f} \rightarrow \text{Const}$$

Before dilution = After dilution

$$M_i V_i = M_f V_f$$

$$N_i V_i = N_f V_f$$

# Law of mixing:-

(A) Homogeneous mixture:

$$\underline{N_p} = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

Normality of resultant soln?

(B) Heterogeneous Mixture:

(i) complete Neutralisation:-

$$N_A V_A = N_B V_B$$

$$\underline{N_p} = \frac{N_A V_A}{V_A + V_B} = \frac{N_B V_B}{V_B + V_A}$$

Normality of resultant salt soln?

(ii) Incomplete Neutralisation:-

$$\underline{N_p} = \frac{N_A V_A - N_B V_B}{V_A + V_B}$$

Normality of  
resultant acidic soln

$$\underline{N_p} = \frac{N_B V_B - N_A V_A}{V_A + V_B}$$

Normality of resultant  
basic soln?

Ques. ① 20gm NaOH is present in 250ml aq. solution having a density of 1.2gm/ml then find out M, m, N & mole fraction of solute and strength of soln.

$$\textcircled{a} \quad M = \frac{20/40}{\frac{250}{1000}} \\ = 2M$$

$$\textcircled{b} \quad N = M \times v.f \\ = 2 \times 1 \\ = 2N$$

$$\textcircled{c} \quad w_{\text{solut}} = d \times \text{vol}$$

$$= 1.2 \text{ g mL}^{-1} \times 250$$

$$= 300 \text{ g}$$

$$w_{\text{solv}} = w_{\text{solut}} - \cancel{w_{\text{solute}}}$$

$$= 300 - 20$$

$$= 280 \text{ g}$$

$$m = \frac{\frac{20}{40}}{\frac{280}{1000}}$$

$$= 1.7 \text{ m}$$

$$\textcircled{d} \quad x_{\text{solute}} = \frac{20/40}{\frac{20}{40} + \frac{280}{18}}$$

$$= \frac{0.5}{0.5 + 15.5}$$

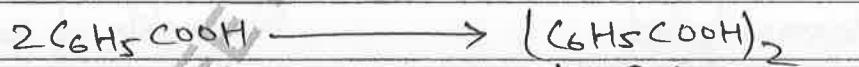
$$= 0.03$$

$$\textcircled{e} \quad \text{Strength} = \frac{20}{250/1000}$$

$$= 80 \text{ g L}^{-1}$$

Ques 2 24.4 g benzoic acid is dissolved in benzene to prepared 2 L soln if benzoic acid exist as a dimer in benzene then find out f and molarity of soln.  
(Benzoic acid MW = 122)

$$M = \frac{24.4/122}{2} = 0.1 \text{ M}$$



$$\text{MW} = 122 \text{ g}$$

$$\text{fw} = 244 \text{ g}$$

$$\text{formality} = \frac{24.4/244}{2}$$

$$= 0.05 \text{ F}$$

Ques 3 Calculate the molarity of 700 ml water.

$$\text{Mass of H}_2\text{O} = d \times \text{vol}$$

$$= 1 \text{ g mL}^{-1} \times 700 \text{ mL}$$

$$= 700 \text{ g}$$

$$M = \frac{700/18}{700/1000} \Rightarrow \frac{1000}{18} = \underline{55.5 \text{ M}}$$

Ques ① Calculate the mole fraction of a solute in 1 molal aq. soln.

Ques ② The mole fraction of solute in water 0.2 then find out the molality of soln.

Ans ① 1 molal aq. soln. = 1 mol solute in 1 kg solvent  
 $\frac{1}{1000g}$

$$\chi_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

$$= \frac{1}{1 + \frac{1000}{18}} = \frac{1}{56.5} = 0.017$$

Ans ②

OR

$$\frac{n_{\text{solute}}}{n_{\text{solvent}}} = \frac{m \times M_{\text{solvent}}}{1000}$$

$$\frac{\chi_{\text{solute}}}{1 - \chi_{\text{solute}}} = \frac{1 \times 18}{1000} = 0.017$$

Ques ③

$$\frac{0.2}{0.84} = \frac{m \times 18}{1000}$$

$$m = \frac{1000}{4 \times 18} = 13.8m$$

OR

$$\frac{n_{\text{solute}}}{n_{\text{solvent}}} = \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

$$m = \frac{1}{4 \times 18} \times 1000$$

$$\frac{0.2}{0.8} = \frac{1}{4} = \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

$$= \frac{1000}{72}$$

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

$$= 13.8m$$

Ques 5.

OR

$$\text{M}_\text{solute} = 0.2 = \frac{n_\text{solute}}{n_\text{solute} + n_\text{solvent}}$$

$$0.2 = \frac{1}{1 + \frac{n_\text{solvent}}{n_\text{solute}}}$$

$$1 + \frac{n_\text{solvent}}{n_\text{solute}} = \frac{1}{0.2} = 5$$

$$\frac{n_\text{solvent}}{n_\text{solute}} = 4$$

$$m = \frac{n_\text{solute}}{M_\text{solvent}(\text{g})} \times 1000$$

$$m = \frac{n_\text{solute}}{\left( \frac{n_\text{solute}}{M_\text{solvent}} \right) \times M_\text{solvent}} \times 1000$$

$$m = \frac{n_\text{solute} \times 1000}{n_\text{solute} \times M_\text{solvent}}$$

$$= \frac{1}{4} \times \frac{1000}{18}$$

$$= 13.8 \text{ m.}$$

Ques Calculate the wt. of ~~HNO<sub>3</sub>~~ (70% pure) that must be dissolved in 250ml soln. to prepare a 2M soln.

$$\text{moles of HNO}_3 = M \times \text{Vol. (L)}$$

$$= 2 \times \frac{250}{1000} = \frac{1}{2} \text{ mol.}$$

$$\text{Mol of HNO}_3 = \text{moles} \times \text{Molar mass}$$

$$= \frac{1}{2} \times 63 = 31.5 \text{ g}$$

~~HNO<sub>3</sub>~~ Sample is 70% pure

$$70 \text{ g HNO}_3 \rightarrow 100 \text{ g sample}$$

$$31.5 \text{ g} \rightarrow \frac{100}{70} \times 31.5$$

$$= 45 \text{ g}$$

Ques Calculate M and m of 30% w/w Urea soln having a density of 1.2 g / per mL.

$$\begin{aligned} M &= \frac{30}{60} \times 1000 \\ &= \frac{3}{6} \times 1000 = 500 \end{aligned}$$

$$m = \frac{30}{60} \times 1000 = 500$$

$$\text{Vol. of soln} = \frac{\text{mass}}{\text{density}} = \frac{1000}{1.2 \text{ g mL}^{-1}} = \frac{1000}{1.2}$$

$$\begin{aligned} M &= \frac{30/60}{1000/12} \times 1000 \\ &= 6M \end{aligned}$$

Ques. 40% w/v 150ml ammonium chloride soln is added to 25% w/v 300ml ammonium chloride then find out % w/v of mixture.

$$\% \frac{w}{v} = \frac{\text{Mass of solute}}{\text{Vol. of soln (mL)}} \times 100$$

$$40 = \frac{w_1}{150} \times 100 \Rightarrow w_1 = 60 \text{ g}$$

$$25 = \frac{w_2}{300} \times 100 \Rightarrow w_2 = 75 \text{ g}$$

$$\% \frac{w}{v} = \frac{(w_1 + w_2)}{(V_1 + V_2)} \times 100$$

$$= \frac{60 + 75}{150 + 300} \times 100$$

$$= 35\%$$

Ques 98% w/w  $\text{H}_2\text{SO}_4$  soln has a density of 1.2 gm/cm<sup>3</sup> then find out the required volume of this soln to prepare 4L of 3M  $\text{H}_2\text{SO}_4$  soln?

$$\rightarrow M = \frac{10 \times 98 \times 1.2 \times 10^{-3}}{98}$$

$$= 12 \text{ mol}$$

$$M_1 V_1 = M_F V_F$$

$$12 \times V_1 = 3 \times 4$$

$$V_1 = 1 \text{ L}$$

OR

$$\text{Moles of } H_2SO_4 = M \times \text{Vol. (L)}$$

$$= 3 \times 4 = 12 \text{ mol}$$

$$\text{Molar mass of } H_2SO_4 = 12 \times 98$$

$$= 1176 \text{ g}$$

$$98 \text{ g } H_2SO_4 \rightarrow 100 \text{ g soln}^n$$

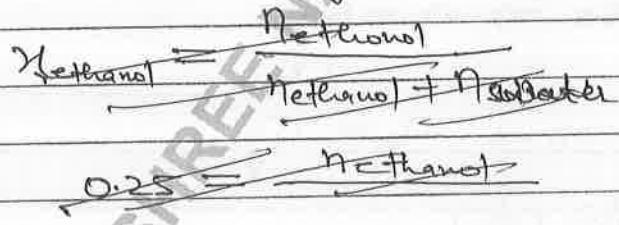
$$1176 \text{ g } H_2SO_4 \rightarrow \frac{100}{98} \times 1176$$

$$= 1200 \text{ g soln}^n$$

$$\text{Vol. of soln}^n = \frac{\text{mass}}{\text{density}} = \frac{1200 \text{ g}}{1.2 \text{ g cm}^{-3}} = 1000 \text{ cm}^3$$

$$= 1 \text{ L}$$

Ques The mole fraction of ethanol in water is 0.25 then determine the % by mass of ethanol in the soln.



$$\frac{x_{C_2H_5OH}}{x_{H_2O}} = \frac{0.25}{0.75} - \frac{1}{3} = \frac{n_{C_2H_5OH}}{n_{H_2O}}$$

$$\% \text{ by mass} = \frac{1 \times 46}{(1 \times 46) + (3 \times 18)} \times 100$$

$$= 46\%$$

Ques.: 4000g sample of hard water contains 12mg CaCO3 then determine the conc. of PPM

$$\text{PPM} = \frac{12 \times 10^3}{4000} \times 10^6 \\ = 3 \text{ ppm}$$

Ques.: Calculate the volume strength of H2O2 soln' If the strength of H2O2 is 3.4g/L

$$S = \frac{x}{5.6} \times 17$$

$$3.4 = \frac{x}{5.6} \times 17$$

$$x = \frac{3.4 \times 5.6}{17} =$$

$$x = 1.12N$$

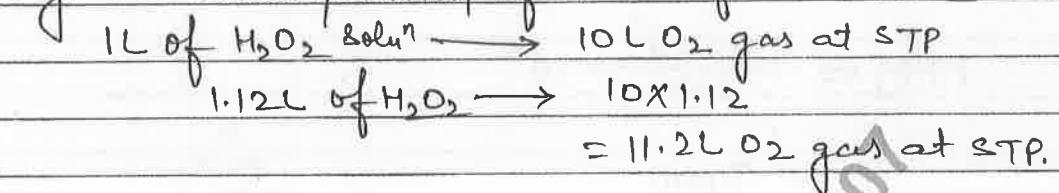
Ques.: Calculate M, N, % w/v and Strength of 10V H2O2 soln'.

$$\frac{0.89}{1.78} \quad M = \frac{100}{1112} \quad N = M \times V.F \\ = 0.89M \quad = 0.89 \times 2 \\ = 1.78N$$

$$\therefore \% w/v = \frac{x}{5.6} \times \frac{17}{10} \quad S = \frac{x}{5.6} \times 17$$

$$= 3.03\% \quad = 30.3 \text{ g L}^{-1}$$

Ques. Calculate the no. of moles and the O<sub>2</sub> gas at STP produced by the decomposition of 1.12L of 1/10V H<sub>2</sub>O<sub>2</sub>.



$$\text{Moles of O}_2 = \frac{11.2}{22.4} = 0.5 \text{ mol.}$$

$$\text{mass of O}_2 = 0.5 \times 32$$
$$= 16 \text{ g}$$

or

$$M = \frac{x}{11.2} = \frac{10}{11.2} M$$

$$\text{Moles of H}_2\text{O}_2 = M \times \text{Vol. (L)}$$
$$= \frac{10}{11.2} \times 1.12$$
$$= 1 \text{ mol}$$



Ques. Calculate the strength of H<sub>2</sub>SO<sub>4</sub> soln in gram/l if 12mL is completely neutralised by 15mL of 1/10 NaOH.

$$N_A V_A = N_B V_B$$

$$N_A \times 12 = \frac{1}{10} \times 15$$

$$N_A = \frac{1}{8} N$$

$$S = N \times \text{Eq. wt of solute}$$
$$= \frac{1}{8} \times \frac{98}{2}$$

$$= 6.125 \text{ g/l}$$

Ques ① Calculate the volume of water added to 200mL semi-molar HCl soln to convert it into demimolar soln.

Ques ② Calculate the volume of water which should be added to a mixture containing 750mL 2M HCl and 250mL 6M HCl to prepare a mixture having a molarity of 2.5M.

$$\text{Ques ①} \quad M_1 V_1 = M_F V_F$$

$$\frac{1}{2} \times 200 = \frac{1}{10} \times V_F$$

$$V_F = 1000 \text{ mL}$$

$$\therefore \text{Req. Vol.} = 1000 - 200$$

$$\text{H}_2\text{O} = 800 \text{ mL}$$

$$\text{Ques ②} \quad M_1 V_1 = M_F V_F$$

$$M_1 V_1 + M_2 V_2 = M_F V_F$$

$$(2)(750) + (6)(250) = (2.5)(V_F)$$

$$V_F = \frac{3200}{2.5} = 1200 \text{ mL}$$

$$\therefore \text{Req. Vol. of H}_2\text{O} = 1200 - 1000 \\ = 200 \text{ mL}$$

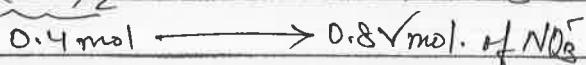
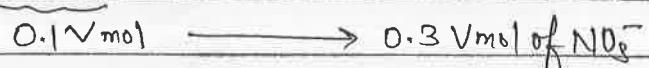
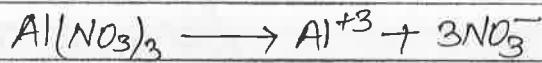
Ques Calculate the M of Nitrate ion when 0.1M  $\text{Al}(\text{NO}_3)_3$  and 0.2M  $\text{Pb}(\text{NO}_3)_2$  are mixed in the volume ratio 1:2.

$$V_1 = V_2$$

$$1 : 2$$

$$V_1 = 1 \text{ L}$$

$$V_2 = 2 \text{ L}$$



$$M \text{ of } \text{NO}_3^- = \frac{0.3V + 0.8V}{V + 2V}$$

$$= \frac{1.1V}{3V} = 0.366 \text{ M}$$

Ques. 1.575g of  $(\text{COOH})_2 \cdot n\text{H}_2\text{O}$  is dissolved in 250ml soln. On titration 16.6ml of this soln is completely neutralised by 25ml of  $\text{N}/15$   $\text{NaOH}$  solution. Then determine the value of water of crystallisation  $n$ .

$$N_A V_A = N_B V_B$$

$$N_A (16.6) = \left(\frac{1}{15}\right)(25)$$

$$N_A = 0.1\text{N}$$

$$\text{Normality} = \frac{\text{Mass of solute}}{\frac{\text{Eq. wt}}{\text{Eq. wt}} \times \text{Vol. of soln (L)}}$$

$$0.1 = \frac{1.575}{\left(\frac{90+18n}{2}\right) \times \left(\frac{250}{1000}\right)}$$

$$0.1 = \frac{1.575 \times 4 \times 2}{90+18n}$$

$$0.1 = \frac{12.6}{90+18n}$$

$$90+18n = \frac{12.6}{0.1} = 126$$

$$18n = 126 - 90$$

$$18n = 36$$

$\underbrace{n=2}_{\text{}} \quad \text{}}$

\* Note:-

If  $\text{d}_{\text{soln}} = 1 \text{ g mL}^{-1}$  or  $\text{d}_{\text{soln}} < 1 \text{ g mL}^{-1}$

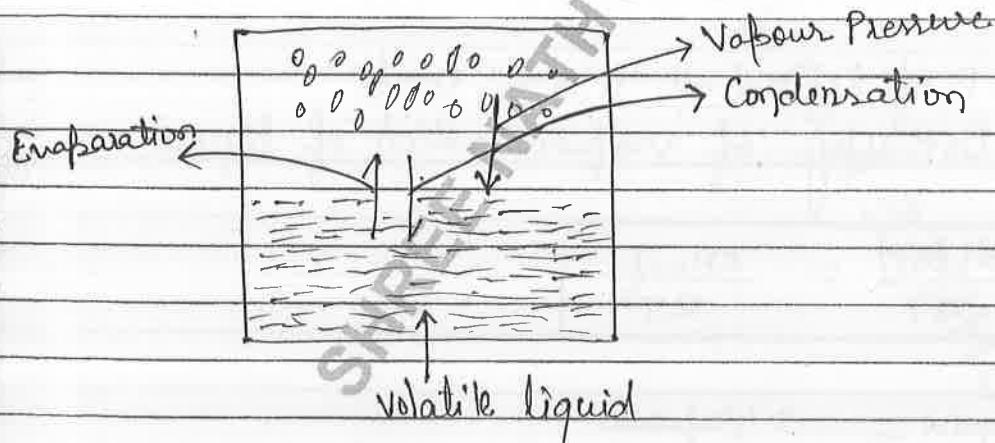
$m > M$  (for same soln)

When density is not given, then this only will be the answer because density is considered to be almost  $1 \text{ g mL}^{-1}$ .

$\Rightarrow$  If  $\text{d}_{\text{soln}} > 1 \text{ g mL}^{-1}$

$m > M ; m = M ; m < M$

# Vapour pressure in liquid :-



At eqm.  $\Rightarrow$  Rate of evaporation = Rate of condensation.  
 $\text{Liquid} \rightleftharpoons \text{Vapour}$

At const. temp, pressure exerted by the vapour of a volatile liquid on its own surface, when liquid & vapour are in eqm is known as vapour pressure of liquid.

⇒ Factors affecting V.P. of liquid :—

(i) Nature of liquid  $\Rightarrow$  IMF (weak)  $\downarrow =$  More vapours are formed  $\Rightarrow$  V.P.  $\uparrow$

(ii) Temperature  $\Rightarrow T \uparrow \Rightarrow$  K.E. of molecules  $\uparrow \Rightarrow$  IMF  $\downarrow \Rightarrow$  More vapours are formed  $\Rightarrow$  V.P.  $\uparrow$

# Clausius - Clapeyron Equation :—

The effect of temp on V.P. of liquid is given by Clausius - Clapeyron eqn as follow—

$$\log_{10}\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$P_1$  &  $P_2 \Rightarrow$  V.P. of liquid at  $T_1$  &  $T_2$  temp.

$\Delta H_{\text{vap.}}$   $\Rightarrow$  Enthalpy of vapourisation of liquid.

$$\frac{d(\ln P)}{dT} = \frac{\Delta H_{\text{vap.}}}{RT^2}$$

Liquid  $\rightleftharpoons$  Vapour

At  $T_1$  temp.

$$P_1 = kP_1$$

At  $T_2$  temp.

$$P_2 = kP_2$$

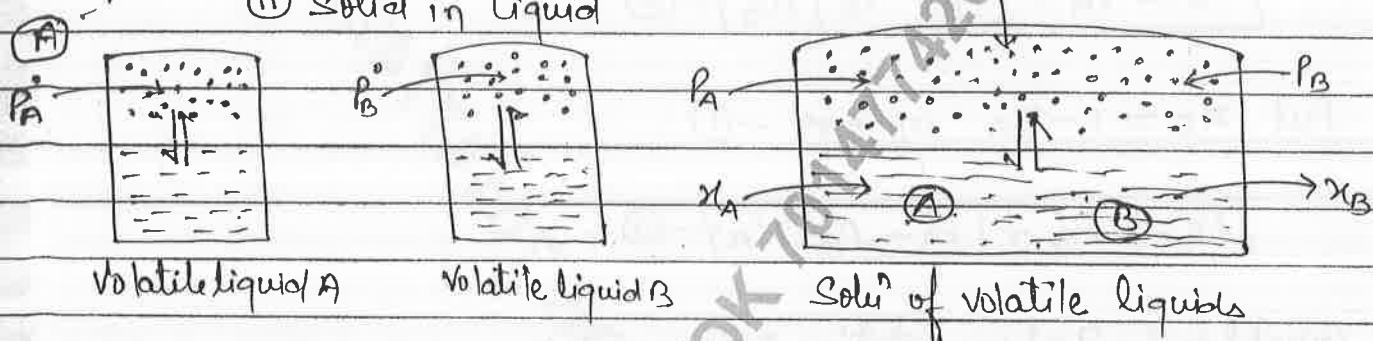
\* Note :— (1) More volatile liquid has higher V.P.

(2) V.P. of liquid  $\propto \frac{1}{\text{B.P. of liquid}}$

③ V.P. of pure liquid does not depends on amount of liquid and shape & size of vessel.

### # Raoult's law:

- ① Liquid in Liquid
- ② Solid in Liquid



Liq. A      Liq. B  
V.P. in liquid state  $\Rightarrow P_A^° \text{ & } P_B^°$

Mole fraction in soln  $\Rightarrow x_A \text{ & } x_B$

Partial V.P.

in soln  $\Rightarrow P_A \text{ & } P_B$

$\Rightarrow$  Acc. to Raoult's law, for a soln of volatile liquids, at const. temp. the partial v.p. of a component is directly proportional to the mole fraction of that component in solution.

$\therefore$  For liquid A

$$P_A \propto x_A$$

$$\boxed{P_A = P_A^° x_A}$$

for liquid B

$$P_B \propto x_B$$

$$\boxed{P_B = P_B^° x_B}$$

$\Rightarrow$  Acc. to Dalton's law

$$P_s \text{ or } P_{\text{Total}} = P_A + P_B$$

$$\boxed{P_s \text{ or } P_{\text{Total}} = P_A x_A + P_B x_B} \quad \text{--- (1)}$$

Put  $x_A = 1 - x_B$  in eqn ①

$$P_s = P_A^* (1 - x_B) + P_B^* x_B$$

$$P_s = P_A^* - P_A^* x_B + P_B^* x_B$$

$$\boxed{P_s = P_A^* + (P_B^* - P_A^*) x_B \quad \text{---} ②}$$

Put  $x_B = 1 - x_A$  in eqn - ①

$$\boxed{P_s = P_B^* + (P_A^* - P_B^*) x_A \quad \text{---} ③}$$

F Graphical Representation :—

From eqn ②

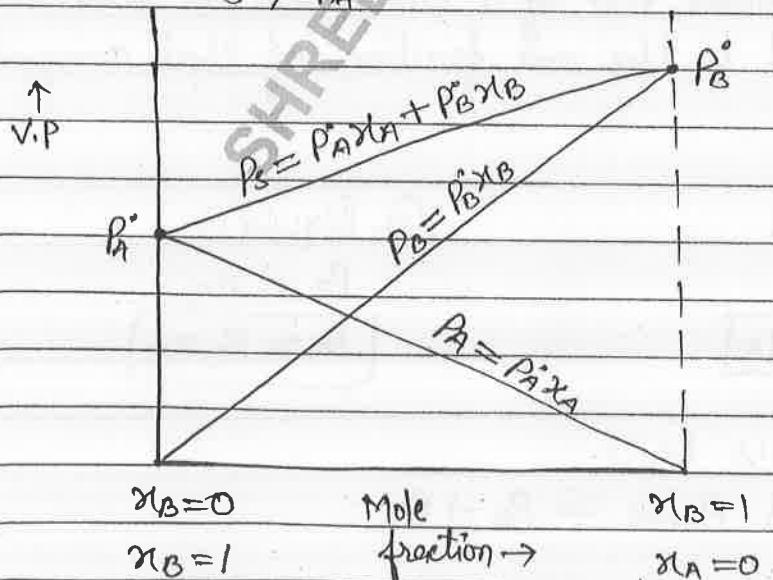
$$P_s = (P_B^* - P_A^*) x_B + P_A^*$$

$$y = m n + c$$

Slope can be  
Positive or Negative  
 $P_A^* > P_B^*$        $P_A^* < P_B^*$

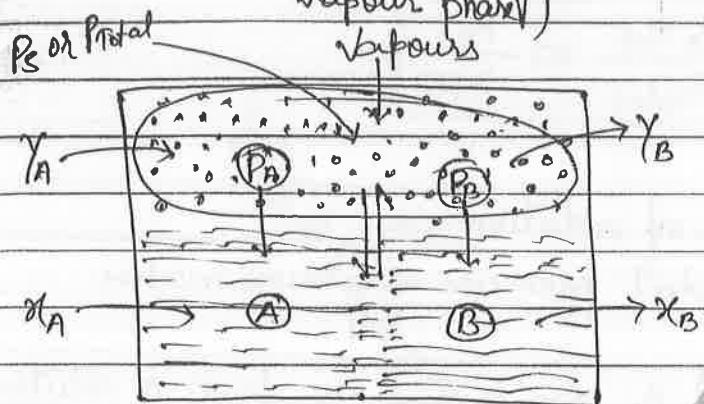
Assume B is more volatile than A.

$$\therefore P_B^* > P_A^*$$



# Relation b/w Raoult's law and Dalton's law :—

(Used for determining mole fraction of components in vapour phase)



$x_A \& x_B$  = Mole fraction of in liquid phase

$y_A \& y_B$  = Mole fraction in vapour phase

⇒ Acc. to Dalton's law (Only for gases)

Partial pressure of a gas = mole fraction of gas × Total Pressure

$$P_A = y_A \times P_{\text{Total}} \quad \text{--- (1)}$$

$$P_B = y_B \times P_{\text{Total}} \quad \text{--- (2)}$$

⇒ Acc. to Raoult's law (Only for solutions)

Partial V.P. of a component = V.P. of pure component × mole fraction of component in solution

$$P_A = P_A^{\circ} \times x_A \quad \text{--- (3)}$$

$$P_B = P_B^{\circ} \times x_B \quad \text{--- (4)}$$

$$\text{Eqn (1)} = \text{Eqn (3)}$$

$$y_A \times P_{\text{Total}} = P_A^{\circ} \times x_A$$

$$y_A = \frac{P_A^{\circ} x_A}{P_{\text{Total}}} = \frac{P_A}{P_{\text{Total}}}$$

$$\text{Eqn. ②} = \text{Eqn. ④}$$

$$Y_B \times P_{\text{total}} = P_B^{\circ} \times X_B$$

$$Y_B = \frac{P_B^{\circ} X_B}{P_{\text{total}}} = \frac{P_B}{\text{total}}$$

$P_{\text{total}}$  = V.P. of solution OR  
Total pressure of gaseous mixture.

Ques. 3 mole of A and 2 mole of B are mixed to form a solution if the V.P. of A & B are 60 & 80 mm of Hg respectively then find out the V.P. of solution and the mole fraction of A and B in V.P.

Solu. —

$$\begin{aligned} \text{① } P_s &= P_A^{\circ} X_A + P_B^{\circ} X_B \\ &= 60 \times \frac{3}{5} + 80 \times \frac{2}{5} \\ &= 36 + 32 \\ &= 68 \text{ mmHg} \end{aligned}$$

$$\begin{aligned} \text{② } Y_A &= \frac{P_A^{\circ} X_A}{P_{\text{total}}} \\ &= \frac{(60 \times \frac{3}{5})}{68} \\ &= \frac{36}{68} = \left(\frac{9}{17}\right) \end{aligned}$$

$$Y_B = \frac{P_B^{\circ} X_B}{P_{\text{total}}} = \frac{(80 \times \frac{2}{5})}{68} = \frac{32}{68} = \left(\frac{8}{17}\right)$$

Ques. The V.P. of a solution of two liquid A and B is 600 torr if the mole fraction of A in vapour phase is 0.4 and in liquid phase is 0.6 then find out the V.P. of A & B in pure state.

$$Y_A = 0.4 ; Y_B = 0.6$$

$$X_A = 0.6 ; X_B = 0.4$$

$$\gamma_A = \frac{P_A^* x_A}{P_{\text{total}}}$$

$$\gamma_B = \frac{P_B^* x_B}{P_{\text{total}}}$$

$$0.4 = \frac{P_A^*(0.6)}{600} = P_A^* = 400 \text{ torr} \quad 0.6 = \frac{P_B^*(0.4)}{600}$$

$$P_B^* = 900 \text{ torr}$$

Ques. The v.p. of a solution containing 1 mole of A and 1 mole of B is 500 mm Hg. When 2 mole of B are further added to a solution then its v.p. increased by 50 mm Hg then determine v.p. of A & B in pure state.

Solu<sup>n</sup>:

$$P_s = P_A^* x_A + P_B^* x_B$$

$$500 = P_A^* \left(\frac{1}{2}\right) + P_B^* \left(\frac{1}{2}\right)$$

$$1000 = P_A^* + P_B^* \quad \text{--- (1)}$$

B further added

$$550 = P_A^* \left(\frac{1}{4}\right) + P_B^* \left(\frac{3}{4}\right)$$

$$2200 = P_A^* + 3P_B^* \quad \text{--- (2)}$$

$$P_A^* = 400 \text{ mm Hg}$$

$$P_B^* = 600 \text{ mm Hg}$$

Ques. The v.p. of a solu<sup>n</sup> containing two volatile liquid A & B is represented by  $P_s (\text{torr}) = 254 - 119 x_A$  where  $x_A$  is mole fraction of A in solu<sup>n</sup> then find out value of  $P_A^*$  &  $P_B^*$ .

Solu<sup>n</sup>:

$$P_s (\text{torr}) = 254 - 119 x_A \quad \text{--- (1)}$$

$$P_s = P_B^* + (P_A^* - P_B^*) x_A \quad \text{--- (2)}$$

$$P_B^* = 254 \text{ torr}$$

$$P_A^* - P_B^* = -119 \text{ torr}$$

$$P_A^{\circ} - 254 = -119$$

$$P_A^{\circ} = 135 \text{ torr}$$

or

For Pure liquid A

$$\chi_A = 1; \chi_B = 0$$

$$P_s = P_A^{\circ} = 254 - 119 (1)$$

$$= 135 \text{ torr}$$

For Pure liquid B

$$\chi_B = 1; \chi_A = 0$$

$$P_s = P_B^{\circ} = 254 - 119 (0)$$

$$= 254 \text{ torr}$$

Ques. An aq. solution containing 28% w/w of liquid A ( $M_{\text{wt}} = 140$ ) has a V.P. of 160 mm Hg then find out V.P. of pure liq. A if the V.P. of water is 150 mm Hg.

28% w/w = 28 g of A in 100 g soln.

$$\text{Moles of A} = \frac{28}{140} = 0.2 \text{ mol}$$

$$\text{Moles of H}_2\text{O} = \frac{72}{18} = 4 \text{ mol}$$

$$P_s = P_A^{\circ} \chi_A + P_B^{\circ} \chi_B$$

$$160 = P_A^{\circ} \left( \frac{0.2}{4.2} \right) + (150) \left( \frac{4}{4.2} \right)$$

$$P_A^{\circ} = 360 \text{ mm Hg}$$

~~MCQ~~

Ques. The V.P. of A and B is 520 & 1000 mm Hg respectively if the mixture of A and B boils at 80°C temp. then determine mole % of A in mixture.

Solu. :-

B.P.  $\Rightarrow$  The temp at which the V.P. of liquid becomes equal to atmospheric pressure.

$$P_s = P_A x_A + P_B x_B$$

$$P_s = P_B + (P_A - P_B) x_A$$

$$760 = 1000 + (520 - 1000) x_A$$

$$(760 - 1000) = (-480) x_A$$

$$-240 = -480 x_A$$

$$x_A = \frac{-240}{-480}$$

$$= 0.5$$

$$\text{mole \%} = \text{mole fraction} \times 100$$

$$= 0.5 \times 100$$

$$= 50\%$$

Ques. The V.P. of liquid P and Q are 200 & 100 mm Hg respecti. then determine composition of P and Q in vapour phase which in contain with equimolar vol. of the two component.

$$\begin{aligned}
 P_s &= P_A x_A + P_B x_B \\
 &= 200 \times \frac{1}{2} + 100 + \frac{1}{2} \\
 &= 150 \text{ mm Hg}
 \end{aligned}$$

$$\gamma_A = \frac{P_A x_A}{P_{\text{Total}}}$$

$$= \frac{200 \times \frac{1}{2}}{150}$$

$$= \frac{2}{3} = 0.66$$

C.e. 66%

$$\gamma_B = \frac{P_B x_B}{P_{\text{Total}}}$$

$$= \frac{100 \times \frac{1}{2}}{150}$$

$$= \frac{1}{3} = 0.33$$

C.e. 33.3%

Ques. The ratio of V.P. of A and B in pure state is 1:2 and the ratio of moles A and B in solution is also 1:2 then find out the mole % of A in the vapour phase.

$$\frac{P_A}{P_B} = \frac{1}{2} ; \left( \frac{n_A}{n_B} \right)_{\text{solid}} = \frac{1}{2} \Rightarrow \frac{x_A}{x_B}$$

$$\frac{\gamma_A}{\gamma_B} = \frac{P_A x_A}{P_B x_B} = \frac{1}{2} \times \frac{1}{2} = \frac{1}{4} = \left( \frac{n_A}{n_B} \right)_{\text{vapour}}$$

$$\gamma_A = \frac{1}{1+4} = \underline{0.2}$$

### I) Solid in Liquid Solutions :

Solvent  $\Rightarrow$  A

(Volatile solid)

Solute  $\Rightarrow$  B

(Non-volatile solid)

$$P_A^o = P^o \Rightarrow \text{V.P. of pure solvent}$$

$$P_B^o = 0$$

$$P_s = P_A^o x_A + P_B^o x_B$$

0

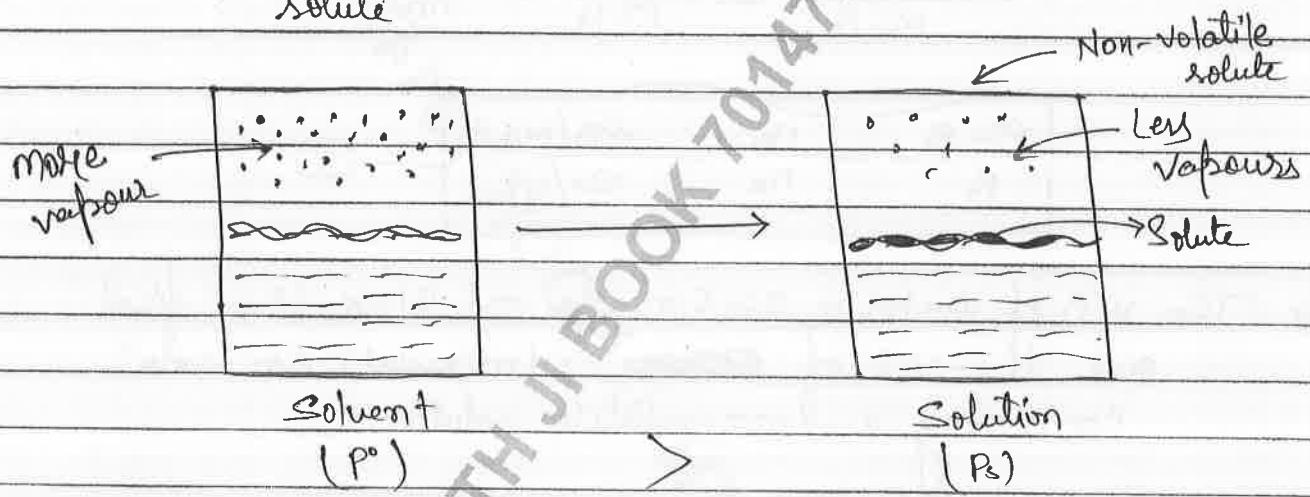
$$\therefore P_s = P_A^o x_A$$

$$P_s = P^\circ \times \chi_{\text{solvent}}$$

→ V.P. of solution of contain non-volatile solute

$P_s \propto \chi_{\text{solvent}}$

V.P. of soln<sup>n</sup> Mole fraction  
Containing of solvent  
non-volatile.  
solute



From eqn ① ⇒

$$\frac{P_s}{P^\circ} = \chi_{\text{solvent}} = 1 - \chi_{\text{solute}}$$

$$\chi_{\text{solute}} = 1 - \frac{P_s}{P^\circ} = \frac{P^\circ - P_s}{P^\circ}$$

$$\therefore \frac{P^\circ - P_s}{P^\circ} = \chi_{\text{solute}} = \frac{n_B}{n_A + n_B} \quad \boxed{\text{②}}$$

$P^\circ - P_s = \Delta P \Rightarrow$  Lowering in V.P.

$$\frac{P^\circ - P_s}{P^\circ} = \frac{\Delta P}{P^\circ} \Rightarrow \text{Relative lowering in V.P. (RLV)}$$

From eqn ②

$$\frac{P^*}{P^* - P_s} = \frac{n_A + n_B}{n_B} = \frac{n_A}{n_B} + 1$$

$$\frac{P^*}{P^* - P_s} - 1 = \frac{n_A}{n_B}$$

$$\frac{P^* - (P^* - P_s)}{P^* - P_s} = \frac{P_s}{P^* - P_s} = \frac{n_A}{n_B}$$

$$\boxed{\frac{P^* - P_s}{P_s} = \frac{n_B}{n_A} = \frac{w_B/M_B}{w_A/M_A}} \quad ③$$

Ques. The V.P. of water is 92.5 mm Hg. at 310K. Then find out the V.P. of ~~1 molal~~ (1m(molal)) aq. soln containing a non-volatile solution.

~~P<sub>s</sub> = P<sup>\*</sup> × Mole fraction~~

~~= 92.5~~

1 molal of aq. soln

1 mole solute in 1 kg. Solvent

1000g "H<sub>2</sub>O

$$P_s = P^* \times \text{Mole fraction}$$

$$= 92.5 \times \left( \frac{1000}{1000+18} \right)$$

$$= \left( 1 + \frac{1000}{1000+18} \right)$$

$$= 92.5 \times \frac{58.5}{58.5+18}$$

$$= 90.8 \text{ mm Hg}$$

Ques. The V.P. of aq. solution of glucose is 750 mm Hg. at 373K. Then determine

P.  
B.P. of  
 $H_2O$

① L.V.P.

② RLVP

③ m of solution.

④ mole fraction of glucose

①

$$\text{Solvent} = H_2O \Rightarrow 760 \text{ mm Hg}$$

$$L.V.P. = P^* - P_s$$

$$= 760 - 750$$

$$= 10 \text{ mm Hg}$$

$$② RLVP = \frac{P^* - P_s}{P^*}$$

$$= \frac{10}{760} = \frac{1}{76}$$

$$③ RLVP = \frac{\gamma_{\text{solute}}}{\gamma_{\text{glucose}}} = \frac{1}{76}$$

$$④ \frac{\gamma_{\text{solute}}}{\gamma_{\text{solvent}}} = \frac{\gamma_{\text{solute}}}{1 - \gamma_{\text{solute}}} \Rightarrow \frac{1/76}{1 - 1/76} = \frac{1/76}{75/76} = \frac{1}{75}$$

$$\frac{\gamma_{\text{solute}}}{\gamma_{\text{solvent}}} = \frac{1}{75} = \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

$$m = \frac{1}{75 \times 18} \times 1000$$

$$= 0.74m$$

Ques. The V.P. of pure Benzene is 0.850 bar if a solution is prepared by dissolving 0.5g of a non-volatile solute in 39g of benzene. Then the V.P. of soln is found to be 0.845 bar then determine the molar mass of non-volatile solute.

$$\frac{0.850 - 0.845}{0.845} = \frac{\omega_B}{M_B} \times \frac{M_A}{\omega_A}$$

$$\frac{0.850 - 0.845}{0.845} = \frac{0.5}{M_B} \times \frac{78}{39}$$

$$\frac{0.005}{0.845} = \frac{1}{M_B}$$

$$M_B = 169 \text{ g/mol}$$

Ques. How much mass of a non-volatile solute ( $M_w = 40$ ) needs to be dissolved in 114 g of Octane to reduce its V.P. to 80%.

Let:-  $P^o = 100$ ;  $P_s = 80$

$$\frac{P^o - P_s}{P_s} = \frac{\omega_B}{M_B} \times \frac{M_A}{\omega_A}$$

$$\frac{100 - 80}{80} = \frac{\omega_B}{40} \times \frac{114}{114}$$

$$\omega_B = 10 \text{ g}$$

Ques 18g glucose and 34.2g sugar are dissolved in 72g of  $H_2O$  in the V.P. of pure water is 30 mmHg then determine the V.P. of solution.

$$n_{\text{glucose}} = \frac{18}{360} = 0.1 \text{ mol}$$

$$n_{\text{sugar}} = \frac{34.2}{342} = 0.1 \text{ mol}$$

$$\eta_{\text{solute}} = 0.1 + 0.1 = 0.2 \text{ mol}$$

$$\eta_{\text{solvent}} = \eta_{\text{H}_2\text{O}} = \frac{72}{18} = 4 \text{ mol}$$

$$\begin{aligned} P_s &= P^\circ \times \eta_{\text{solvent}} \\ &= 30 \times \frac{4}{4.2} \\ &= 28.5 \text{ mm Hg} \end{aligned}$$

Ques A solution containing 30g Non-volatile solute in 90g water has a V.P. 21.85 mm Hg. If 18g of water is added to the solution then V.P. of solution becomes 22.15 mm Hg. Then find out the V.P. of water and molecular wt. of solute.

$$P_{\text{H}_2\text{O}} = P^\circ = x$$

$$\eta_{\text{solute}} = y$$

$$P_s = P^\circ \times \eta_{\text{solvent}}$$

$$21.85 = x \times \frac{5}{(5+y)}$$

$$x = \frac{30}{M}$$

$$M = \frac{30}{x}$$

$$\begin{array}{l} P = 24 \\ M = 67.8 \end{array}$$

$$21.85(s) + 21.85y = 5x \quad (i)$$

$$22.15 = x \times \frac{6}{6+y}$$

$$22.15(s) + 22.15y = 6x \quad (ii)$$

## F Colligative Properties of Dilute solutions :-

Colligative Properties depends on relative no. of solute particles present in solution.

→ Concentration of solution

→ Does not depends on nature of solute

Volatile solvent = A

Non-volatile solute = B

### ① Relative Lowering in v.p. :-

Acc. to Raoult's law,

$$\text{RLVP} \Rightarrow \frac{P^{\circ} - P_s}{P^{\circ}} = \chi_{\text{solute}} = \frac{n_B}{n_A + n_B} \Rightarrow \text{for concentrated solution}$$

for Dilute solution  $\Rightarrow n_A \ggg n_B$

$$\therefore (n_A + n_B) \approx n_A$$

$$\therefore \frac{\Delta P}{P^{\circ}} = \frac{P^{\circ} - P_s}{P^{\circ}} = \frac{n_B}{n_A} \Rightarrow \text{for dilute solution}$$

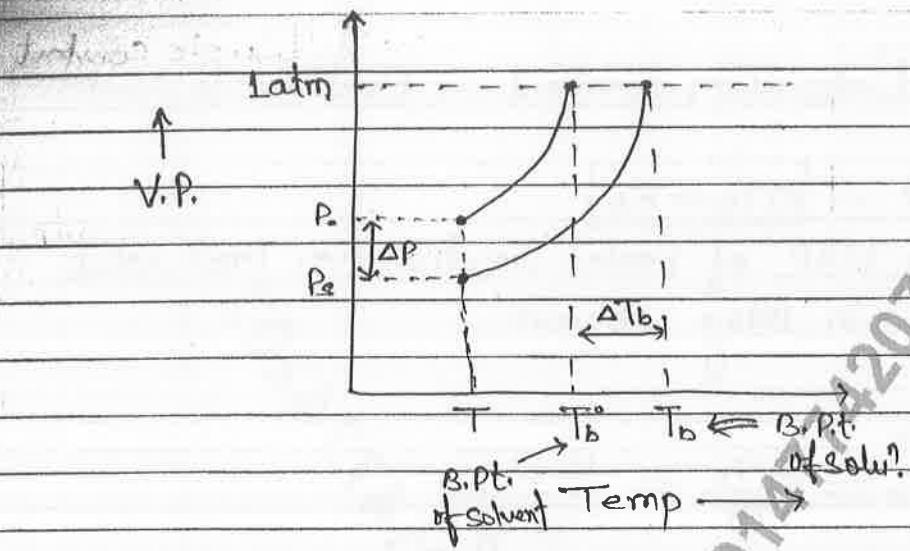
for dilute soln  
 $\Delta P \propto \frac{n_B}{n_A}$

### ② Elevation in Boiling point :-

→ Boiling point is the temp. at which —

v.p. of liquid  $\Rightarrow$  Atmospheric pressure

$\Rightarrow$  When atmospheric pressure is 1 atm then boiling point is known as Normal B.P.



$$\text{EIBP} \Rightarrow \Delta T_b = T_b - T_b^o = (B.P.t. \text{ of } \text{solution}) - (B.P.t. \text{ of pure solvent})$$

from graph,

$$\Delta T_b \propto \Delta P \quad \text{--- (1)}$$

$$\Delta P \propto \frac{n_B}{n_A} \quad \text{--- (2)}$$

From eqn (1) & (2)

$$\Delta T_b \propto \frac{n_B}{n_A}$$

$$\Delta T_b \propto \frac{n_B \times M_A}{w_A}$$

For a particular solvent

$$M_A = \text{constant}$$

$$\therefore \Delta T_b \propto \frac{n_B}{w_A}$$

$$\Delta T_b \propto m$$

$$\therefore \Delta T_b = k_b \cdot m = k_b \cdot \frac{w_B \times 1000}{m_B \times w_A(g)}$$

$K_b$  = Molal elevation constant or Ebullisopic constant

$$\Rightarrow \text{If } m=1 \Rightarrow \therefore [\Delta T_b = K_b]$$

$K_b$  is EBP of 1 molal solution i.e. 1 mol solute  
in 1000 g solvent.

$\Rightarrow$  Unit of  $K_b$

$$K_b = \frac{\Delta T_b}{m} = \frac{K \text{ or } ^\circ C}{\text{mol kg}^{-1}}$$

$$= [K \text{ Kg mol}^{-1} \text{ or } K \text{ m}^{-1}]$$

$$= [^\circ \text{C} \text{ Kg mol}^{-1} \text{ or } ^\circ \text{C m}^{-1}]$$

$K_b$  = depends only on nature of solvent

$$K_b = \frac{M \times R \times T_b^{\circ 2}}{1000 \times \Delta H_{\text{vap}}} = \frac{R \times T_b^{\circ 2}}{1000 \times L_{\text{vap.}}}$$

~~R~~ const.  $R$  = conc. constant.

$M$  = Molar mass of solvent

$T_b^{\circ}$  = Boiling point of pure solvent

$\Delta H_{\text{vap.}}$  = Enthalpy of vapourisation per mol.  
of solvent

$L_{\text{vap.}}$  = Latent heat of vapourisation  
per g of solvent.

\* 1 mol solvent =  $M$  g of solvent  $\rightarrow \Delta H_{\text{vap.}}$

1 g of solvent  $\rightarrow \frac{\Delta H_{\text{vap.}}}{M} = L_{\text{vap.}}$

$$\therefore \Delta H_{\text{vap.}} = L_{\text{vap.}} \times M$$

$$\begin{array}{c} \downarrow h \\ \text{kJ mol}^{-1} \end{array} \quad \begin{array}{c} \downarrow g \\ \text{kJ g}^{-1} \end{array} \quad \begin{array}{c} \downarrow g \\ \text{mol}^{-1} \end{array}$$

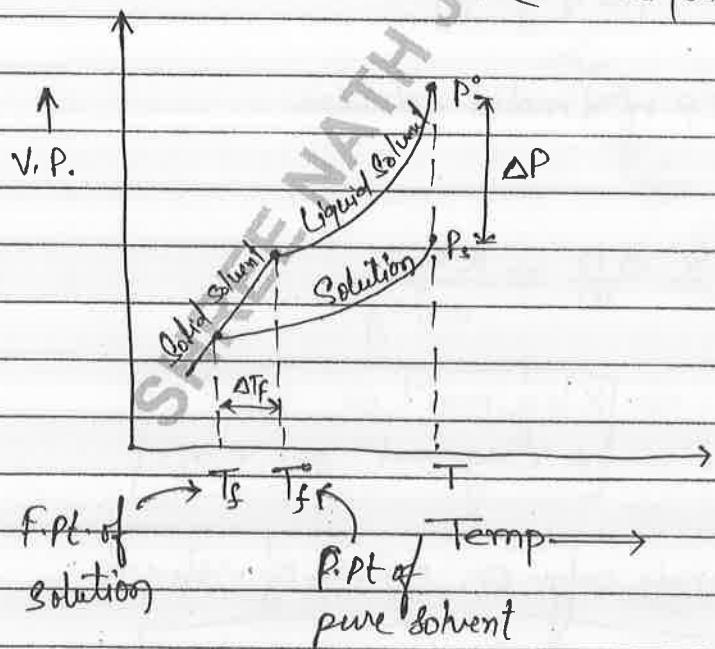
or      or

$$\begin{array}{c} \downarrow \text{kcal mol}^{-1} \\ \text{kcal g}^{-1} \end{array}$$

### ③ Depression in freezing point :—

⇒ Freezing is the temp. at which the solid phase, liquid phase of a substance are in dynamic equilibrium with each other i.e. the temp. at which —

$$\text{V.P. of solid phase} = \text{V.P. of liquid phase}$$



= A solution will freeze when the V.P. of solution will becomes equal to V.P. of pure solid Solvent.

$$\text{DIFP.} \Rightarrow \Delta T_f = T_f^{\circ} - T_f = \left( \text{f. pt. of pure solvent} \right) - \left( \text{f. pt. of solution} \right)$$

from graph :-

$$\Delta T_f \propto \Delta P \propto \frac{n_B}{n_A} \propto m$$

$$\therefore \Delta T_f = K_f \cdot m = K_f \cdot \frac{w_B \times 1000}{m_B \times w_A \text{ (g)}}$$

$m$  = molality of solution

$K_f$  = Molal depression constant  
or

Cryoscopic constant

$$\text{If } m=1 \Rightarrow \therefore \boxed{\Delta T_f = K_f}$$

$\Rightarrow K_f$  is DIFP of 1 molal solution

$\Rightarrow$  Unit of  $K_f$

$$K_f = \frac{\Delta T_f}{m} = \frac{\text{K or } ^\circ\text{C}}{\text{mol kg}^{-1}}$$

$$= \boxed{\text{K kg mol}^{-1} \text{ or } \text{K m}^{-1}}$$

$$= \boxed{0.01 \text{ K kg mol}^{-1} \text{ or } ^\circ\text{C m}^{-1}}$$

$\Rightarrow K_f$  depends only on nature of solvent

$$K_f = \frac{M \times R \times T_f^{*2}}{1000 \times \Delta H_{fus}} = \frac{R \times T_f^{*2}}{1000 \times L_{fus}}$$

$R$  = Gas constant

$M$  = Molar mass of solvent

$T_f^\circ$  = Freezing point of pure solvent

$\Delta H_{\text{fus}}$  = Enthalpy of fusion per mol of solvent

$L_{\text{fus}} = \text{Latent heat of fusion per g of solvent.}$

$$\Delta H_{\text{fus}} = L_{\text{fus}} \times M$$

Note:—

- ① Ostwald's Process is used for determining elevation in B.P.t.
- ② Beckmann's thermometer is used for determining depression in freezing point.
- ③ Camphor is the best solvent for determine the molar mass of solute using D.I.F.P. because of its high  $K_f$  value. ( $18.7 \text{ K m}^{-1}$ )

④ For  $\text{H}_2\text{O} \rightarrow K_f = 1.86 \text{ km}^{-1}$

$$K_b = 0.52 \text{ km}^{-1}$$

Ques. 6g Urea is dissolved in 100g of  $\text{H}_2\text{O}$  then determine the boiling point and freezing point. of the soln.

$$m = \frac{6/60}{100} = \frac{1}{1000}$$

$$T_b - T_b^\circ = 0.52$$

$$T_b = 0.52 + T_b^\circ$$

$$= 0.52 + 373 = 373.5 \text{ K}$$

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

$$= 0.52 \times 1$$

$$= 0.52 \text{ K}$$

$$\Delta T_f = K_f \cdot m = 1.86 \times 1 = 1.86 \text{ K}$$

$$T_f^{\circ} - T_f = 1.86$$

$$T_f = T_f^{\circ} - 1.86 = 273 - 1.86 \\ = 271.4 \text{ K}$$

Ques. The freezing point of an aqueous solution containing a non-volatile solute is  $-0.465^{\circ}\text{C}$  then find out boiling point of solution.

$$\begin{aligned}\Delta T_f &= T_f^{\circ} - T_f \\ &= 0 - (-0.465) \\ &= 0.465^{\circ}\text{C or K}\end{aligned}$$

$$\frac{\Delta T_b}{\Delta T_f} = \frac{K_b \cdot m}{K_f \cdot m}$$

$$\frac{\Delta T_b}{0.465} = \frac{0.52}{1.86}$$

$$\Delta T_b = 0.13$$

$$T_b - T_b^{\circ} = 0.13$$

$$\begin{aligned}T_b &= 0.13 + T_b^{\circ} \\ &= 0.13 + 373 \\ &= 373.13 \text{ K}\end{aligned}$$



Date \_\_\_\_\_ Page \_\_\_\_\_

Ques. In car radiator 8L water is mixed with 2L methanol ( $\rho = 0.8 \text{ g/mL}$ ) then determine the lowest temp at which the vehicle can be parked outdoor without freezing of the water of radiator.

Mass of methanol

$$\text{CH}_3\text{OH} = \rho \times \text{Vol.}$$

$$= 0.8 \text{ g/mL} \times 2000$$

$$= 1600 \text{ g}$$

$$\rho_{\text{H}_2\text{O}} = 1 \text{ g/mL}$$

mass of

$$\text{H}_2\text{O} = \rho \times \text{Vol.}$$

$$= 1 \text{ g/mL} \times 800 \text{ mL}$$

$$= 800 \text{ g.}$$

$$\Delta T_f = k_f \cdot m$$

$$= 1.86 \times \left( \frac{1600 \times 1000}{32 \times 8000} \right)$$

$$\Delta T_f = 11.625^\circ\text{C}$$

$$T_f^\circ - T_f = 11.625$$

$$T_f = T_f^\circ = -11.625$$

$$= 0 - 11.625$$

$$= -11.625^\circ\text{C}$$

Ques A solution containing 1.4g of acetone in 100gm benzene freez at ~~277.12K~~ another solution containing 2.8g. of solid A in 100g benzene freez at 277.76K then determine the molecular wt of solid A if the freezing point of benzene is 278.40K.

$$\Delta T_{f_1} = T_f^\circ - T_f$$

$$= 278.40 - 277.12$$

$$= 1.28 \text{ K}$$

$$\Delta T_{f_2} = T_f^\circ - T_f$$

$$= \cancel{278.40} 278.40 - 277.76$$

$$= 0.64 \text{ K}$$

$$\Delta T_f = k_f \times m_1$$

$$\Delta T_{f_2} = k_f \times m_2$$

$$\frac{1.4 \times 1000}{19.64} = \frac{1.4 \times 1000}{58 \times 100} \times \frac{2.8 \times 1000}{M \times 100}$$

$$2 = \frac{1.4 \times 4}{58} \times \frac{2.8}{2.8}$$

$$M = 58 \times 4 = 232 \text{ g mol}^{-1}$$

iii) The V.P. of water and the V.P. of an aqueous solution containing a non-volatile solute is 20 and 19.64 mm Hg respect. -tively. Then determining the Boiling point of solution.

$$\frac{P^{\circ} - P_s}{P_s} = \frac{n_B}{n_A} = \frac{\Delta T_b}{K_b \times M}$$

$$\frac{20 - 19.64}{20} = \frac{n_B \times n_A}{w_A}$$

$$\Delta T_b = K_b \times \frac{n_B}{w_A} \times 1000$$

$$\frac{0.36}{20 \times \Delta T_b} = \frac{18}{0.52 \times 1000}$$

$$\Delta T_b = 0.52$$

$$T_b - T_b^{\circ} = 0.52$$

$$T_b = 0.52 + T_b^{\circ}$$

$$= 0.52 + 100$$

$$= 100.52^{\circ}\text{C}$$

Ques. Calculate the freezing point of an aqueous solution containing 5% w/v and 10% glucose by mass. (PC).

$$\text{Moles of water} = \frac{5}{18} = \frac{1}{12} \text{ mol}; \text{Moles of glucose} = \frac{10}{180} = \frac{1}{18} \text{ mol}$$

$$\text{Moles of solute} = \frac{1}{12} + \frac{1}{18} = \frac{5}{36} \text{ mol}$$

$$\text{Weight of solvent} = 100 - (5 + 10) \\ = 85 \text{ g}$$

$$\Delta T_f = K_f \times m = 1.86 \times \frac{5 \times 1000}{85 \times 18}$$

$$\Delta T_f = 3.04^\circ\text{C}$$

$$T_f^{\circ} - T_f = 3.04$$

$$T_f^{\circ} = T_f = 3.04$$

$$= 0 - 3.04$$

$$T_f^{\circ} = \underline{-3.04^\circ\text{C}}$$

Ques. Calculate the mass of sucrose that should be dissolved in 100g of Water in order to prepare a solution having a difference of  $10^\circ\text{C}$  b/w its Boiling point and freezing point. (~~K\_f for H<sub>2</sub>O~~  $K_f = 1.8 \text{ K m}^{-1}$ ,  $K_b = 0.5 \text{ K m}^{-1}$ )

$$\Delta T_b = T_b - T_b^{\circ} \quad \text{--- (i)}$$

$$\Delta T_f = T_f^{\circ} - T_f$$

$$T_f^{\circ} = T_f - \Delta T_f \quad \text{--- (ii)}$$

$$T_b - T_f = 105$$

$$(\Delta T_b + T_b) - (T_f - \Delta T_f) = 105$$

$$(\Delta T_b + \Delta T_f) + (T_b - T_f) = 105$$

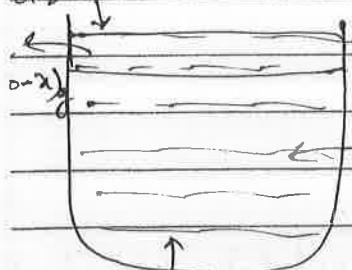
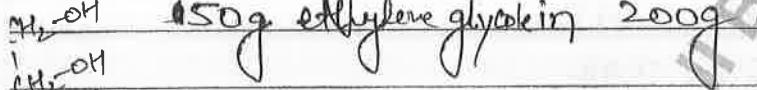
$$K_b \cdot m + K_f \cdot m + 100 = 105$$

$$(K_b + K_f)m = 5$$

~~$$(0.5 + 1.8) \frac{w \times 1000}{342 \times 100} = 5$$~~

$$w = 74.3 \text{ g}$$

Ques. Calculate the mass of ice that will be separated on cooling an solution upto  $-9.3^\circ\text{C}$  that contains  $150 \text{ g}$  ethylene glycol in  $200 \text{ g}$  water.



$$\Delta T_f = K_f \cdot m$$

$$T_f^* - T_f = K_f \cdot m$$

$$0 - (-9.3) = 1.86 \times \left( \frac{50 \times 1000}{62 \times x} \right)$$

$$9.3 = 1.86 \times \frac{50 \times 1000}{62 \times x}$$

$$x = 161.3 \text{ g}$$

Mass of ice

$$\begin{aligned} \text{separated out} &= 200 - x \Rightarrow 200 - 161.3 \\ &= 38.7 \text{ g} \end{aligned}$$

## Q#4 Osmotic Pressure:

Osmosis  $\rightarrow$  Osmosis is the process in which the spontaneous net flow of solvent occurs through semi-permeable membrane from solvent side (or lesser conc. soln.) towards solution

(more conc. soln) till equilibrium is attained. i.e. Net flow of solvent becomes zero.

\* SPM:— It appears to be a continuous sheet but consists of sub-microscopic hollow that allows the passage of smaller particle of solvent but passage of solute.

Eg:— Animal membrane  
Vegetable membrane  
Parchment

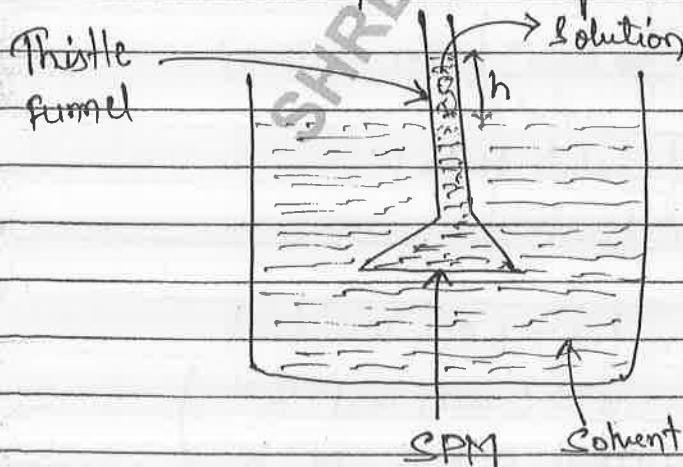
Cellophane, Copper ferrocyanide ( $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ )  
Cellulose Acetate

### \* Osmotic Pressure:—

The mini. external pressure that must be applied on the solution side to just stop the process of osmosis is known as osmotic pressure.

OR

It is the hydrostatic pressure developed in vertical column when solvent and solution are separated by SPM.



$$\text{Osmotic Pressure} = \text{Hydrostatic Pres}$$

$$\boxed{\pi = \rho gh}$$

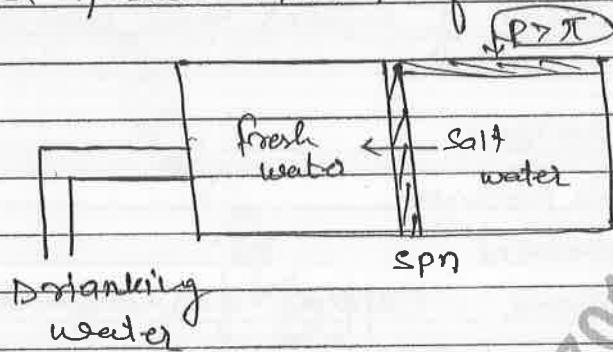
$\rho$  = density of soln

$g$  = Acc due to gravity

$h$  = Increase in the level of solution in Thistle funnel.

## Reverse Osmosis:-

When a pressure greater than osmotic pressure is applied on the soln then ~~normal~~ process of osmosis is reversed and is known as reverse osmosis.  
 ⇒ Used in desalination of sea water.



## # Vant Hoff law for Dilute solution.

Acc. to Raoult's law equation that is  $PV = nRT$  can be used for dilute solution when the pressure of gas is replaced by Osmotic pressure of solution.

$$\text{For gas} \Rightarrow PV = nRT$$

$$\text{for dilute soln} \Rightarrow PV = nRT$$

$\bar{\pi}$  = O.P. of soln (atm or bar)

$N$  = Vol. of soln (L)

$n$  = Moles of solute (mole)

$T$  = Temp. (kelvin).

$R$  (or  $S$ ) = Gas (or solution) constant

$$(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}) \\ (0.0831 \text{ L bar mol}^{-1} \text{ K}^{-1})$$

As,  $\pi V = nRT$

$$\pi = \left(\frac{n}{V}\right) RT$$

$$\pi = C RT$$

At const. T

$$\pi \propto C$$

$$\boxed{\frac{\pi_1}{\pi_2} = \frac{C_1}{C_2}}$$



# Isotonic solution :—

↪ Solutions having same osmotic pressure at a given temp.

Solu<sup>n</sup> ①

and Solu<sup>n</sup> ②

$$\pi_1 \propto C_1$$

$$\pi_2 \propto C_2$$

$$\therefore \boxed{\pi_1 = \pi_2}$$

$$C_1 RT = C_2 RT \text{ (at given temp)}$$

$$C_1 = C_2$$

$$\boxed{\frac{n_1}{V_1} = \frac{n_2}{V_2}}$$

# Hypertonic and Hypotonic Solutions :—

Solu<sup>n</sup> ① and Solu<sup>n</sup> ②

$$\pi_1 \propto C_1$$

$$\pi_2 \propto C_2$$

$$\text{If } \pi_1 > \pi_2 \Rightarrow C_1 > C_2$$

Solu<sup>n</sup> ①  $\Rightarrow$  Hypertonic (High O.P.)

Solu<sup>n</sup> ②  $\Rightarrow$  Hypotonic (Low O.P.)

Note →

- (i) Berkely-Hartley's Method & funnel experimental are used for determining osmotic pressure of soln.
- (ii) 0.9% w/v NaCl Solution is isotonic with blood.  
Ns → Normal Saline solution.
- (iii) Osmotic pressure is the best method for determining the molar mass of polymer, Protein and other macromolecules because its magnitude is large and it can be easily measured at room temp.

Ques Calculate the osmotic pressure of  $\text{5\%}$  w/v solution of cane sugar at  $27^\circ\text{C}$

$$\cancel{\pi} \Delta V = nRT$$

$$\pi \left( \frac{100}{1000} \right) = \frac{s}{342} (0.0821) (300)$$

$$\pi = \frac{50 \times 29.6}{342} = 3.6 \text{ atm}$$

Note:- In the question of osmotic pressure % solution is considered as "w/v soln" and in the question of all other colligative properties "% soln" is considered as "w/w soln".

Ques. At a certain temp. 1L solution containing 36g of glucose has an osmotic pressure of 6 atm. If the osmotic pressure of soln is found to be

1.5 bar at the same temp. then determine the conc. of solution.

$$\pi \propto c$$

$$\frac{\pi_1}{\pi_2} = \frac{c_1}{c_2}$$

$$\frac{6}{1.5} = \frac{36/180 \times 1}{c_2}$$

$$c_2 = \frac{0.2}{c_1}$$

$$c_2 = 0.05 M$$

Ques. Determine the osmotic pressure of 2m sucrose soln having a density of 1.4 g/ml at 27°C temp  
2 mol sucrose in 1 kg solvent

$$\cancel{\text{mass of soln}} = 1000 + (2 \times 342) \\ = 1684 \text{ g}$$

$$\text{Vol. of soln} = \frac{\text{mass}}{\text{density}} = \frac{1684 \text{ g}}{1.4 \text{ g/ml}} \\ = \frac{1684}{1.4} \text{ mL}$$

~~$$M = \frac{2 \times 1000}{1684} = \frac{2000}{1684} = 1.66 \text{ M}$$~~

$$\pi = CRT$$

$$= 1.66 \times 0.821 \times 300$$

$$= 40.8 \text{ atm}$$

Note :—

If density of solution is not given in the question,  
then assume,

$$M \approx m$$

Ans. The freezing point depression solution of urea is ~~0.62~~  
-0.62°C then find out O.P. of the soln at  
300K temp.

$$\begin{aligned}\Delta T_f &= T_f^{\circ} - T_f \\ &= 0 - (-0.62) \\ &= 0.62^{\circ}\text{C or K}\end{aligned}$$

$$\frac{\Delta T_f}{\pi} = \frac{k_f \cdot m}{MRT} \quad \left. \begin{array}{l} \text{As soln is not} \\ \text{given} \Rightarrow M \approx m \end{array} \right\}$$

$$\frac{0.62}{\pi} = \frac{1.86}{0.821 \times 300}$$

$$\pi = 8.2 \text{ atm.}$$

Ques. A 5% solution of urea is isotonic with 2% of solution of non-electrolyte at a given temp. then determine the molecular wt. of non-electrolyte.

$$\pi_1 = \pi_2$$

$$c_1 = c_2$$

$$\frac{n_1}{V_1} = \frac{n_2}{V_2}$$

$$\frac{\frac{s}{100}}{\frac{100}{1000}} = \frac{2/M}{\frac{100}{1000}} \Rightarrow M = 24 \text{ g/mol}$$

Ques. A straight line graph plotted b/w  $\pi$  and conc. ( $\text{g cc}^{-1}$ ) at  $27^\circ\text{C}$  has a slope of  $4.5 \times 10^{-3}$ . Then find out the molar mass of solute in the soln.

$$\pi V = nRT$$

$$\pi = \left( \frac{n}{MV} \right) RT$$

$$\pi = \left( \frac{RT}{M} \right) \cancel{\frac{W}{V}} \Rightarrow \cancel{L}$$

$$\pi = \left( \frac{1000RT}{M} \right) \cancel{\frac{W}{V}} \Rightarrow g \cancel{\text{cc}}$$

$$\gamma = M \cdot n$$

$$\text{Slope} = \frac{1000RT}{M} = 4.5 \times 10^{-3}$$

$$= \frac{1000 \times 0.821 \times 300}{4.5 \times 10^{-3}}$$

$$M = 5.4 \times 10^6 \text{ g mol}^{-1}$$

Ques O.P. of 100 mL soln at  $27^\circ\text{C}$  is 12 atm if  $x$  mL of water added and soln is heated upto  $327^\circ\text{C}$ . Then O.P. becomes 8 atm. Then find out  $x$ .

$$\frac{\pi_1 V_1}{\pi_2 V_2} = \frac{n_1 R T_1}{n_2 R T_2} \quad \left. \begin{array}{l} n_1 = n_2 \\ \text{becoz on adding H}_2\text{O} \end{array} \right\}$$

$$\frac{12 \times 100}{8 \times (100+x)} = \frac{300}{600}$$

$$x = 400 \text{ mL}$$

There is no effect on moley of solute.

Ques. A 10g mixture glucose of urea is present in 250mL of soln shown here O.P. of 7.4 atm at  $27^\circ\text{C}$ . Then determine the wt of glucose & urea in the mixture.

$$\pi V = n RT$$

$$\pi = \frac{nV}{RT} = (7.4) \left( \frac{250}{1000} \right) \\ (0.821) (300)$$

$$n = 0.075 \text{ mol}$$

$$\frac{x}{60} + \frac{10-x}{180} = 0.075$$

$$\frac{8x + 10 - x}{180} = 0.075$$

$$10 + 2x = 13.5$$

$$(x = 1.75 \text{ g})$$

$$\text{Mass of Urea} = x \text{ g} = 1.75 \text{ g}$$

$$\text{Mass of glucose} = (10 - x) \text{ g} = 8.25 \text{ g}$$

## # Abnormal Colligative properties:

1 mol Urea  $\xrightarrow{\text{in H}_2\text{O}}$  1 mol Urea in solution.

1 mol NaCl  $\xrightarrow{\text{in H}_2\text{O}}$  1 mol  $\text{Na}^+$  + 1 mol  $\text{Cl}^-$

$58.5 \text{ g} \xrightarrow{\text{2 mol ions in solution}}$

$58.5 \text{ g} \Rightarrow 1 \text{ mol} \rightarrow 29.5 \text{ g}$

1 mol  $\text{CH}_3\text{COOH} \xrightarrow{\text{in C}_2\text{H}_6} \frac{1}{2} (\text{CH}_3\text{COOH})_2$

$\frac{1}{2} \text{ mol dimer in solution.}$

$60 \text{ g} \Rightarrow 1 \text{ mol} \rightarrow 120 \text{ g}$

When a solute undergoes association or dissociation in solution it shows abnormal or observed or experimental colligative properties.

When a solute does not undergo ~~either~~ dissociation or association in solution then it shows normal or calculated or theoretical colligative properties.

### # Vant Hoff factor ( $i$ ):—

It gives a relative b/w normal & abnormal c.p.

$$i = \frac{\text{Abnormal (observed) C.P.}}{\text{Normal (calculated) C.P.}}$$

C.P.  $\propto n_{\text{solute}} \propto$  molar mass of solute

$$i = \frac{\text{Total no. of moles of solute after dissociation/Association}}{\text{Before}}$$

$$i = \frac{\text{Normal (calculated) Molar Mass}}{\text{Abnormal (observed) Molar mass}}$$

### # Modified formula of C.P. for dissociation/Association of solute in solution:

$$\text{Observed C.P.} = i \times \text{Calculated C.P.}$$

$$\frac{P - P_0}{P_0} = i \times \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

$$\Delta T_b = i \times K_b \cdot m$$

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

$$\pi = i \times CRT$$

# Possible values of 'i':—

$i=1 \Rightarrow$  Neither association nor dissociation of solute takes place.

Eg:— Non-electrolytes like Urea, Sugar, glucose etc.

$i > 1 \Rightarrow$  For Dissociation of solute

Eg:— NaCl, KCl, in H<sub>2</sub>O

$i < 1 \Rightarrow$  For Association of solute

Eg:— C<sub>2</sub>H<sub>5</sub>COOH, C<sub>6</sub>H<sub>5</sub>COOH in C<sub>6</sub>H<sub>6</sub>

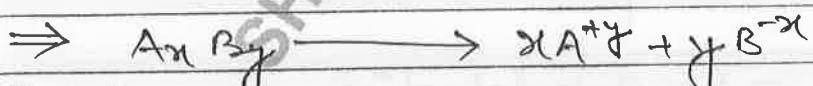
# Calculation of 'i'

Case I:— For Dissociation

$\Rightarrow i > 1$  because no. of moles of solute increases

$\Rightarrow$  Observed C.P. > Calculated C.P.

$\Rightarrow$  Observed  $\frac{\text{C.P.}}{\text{Molar mass}} <$  Calculated molar mass.



Initially 1 mol

After dissociation  $\rightarrow (1-\alpha) \quad x\alpha \quad y\alpha$

$$\begin{aligned} \Rightarrow \text{Total no. of moles after dissociation} &= 1 - \alpha + x\alpha + y\alpha \\ &= 1 - \alpha + (x + y)\alpha \\ &= 1 - \alpha + n\alpha \end{aligned}$$

$i = \frac{\text{Total moles of solute after dissociation}}{\text{Before}}$

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

$(x+y) = n \Rightarrow \text{Total no. of moles}$

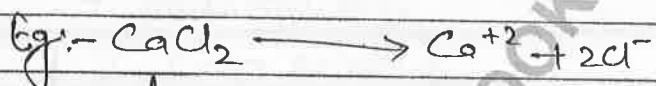
$$i = 1 + (n-1)\alpha$$

$\alpha = \text{Degree of dissociation}$

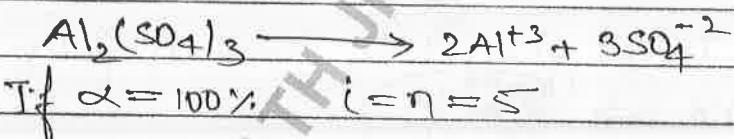
of ions given by  
1 mol of solute.

(i.e. electrolyte)

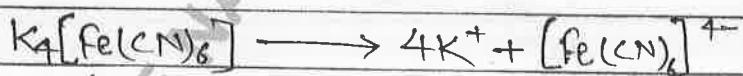
Note :— For strong electrolyte, if ' $\alpha$ ' is not given,  
then (consider  $\alpha=1$  i.e. 100%  $\Rightarrow i=n$ )



$$\text{If } \alpha = 100\% \Rightarrow i = n = 3$$



$$\text{If } \alpha = 100\% \Rightarrow i = n = 5$$



$$\text{If } \alpha = 100\% \Rightarrow i = n = 5$$

$$\text{If } \alpha = 50\% \Rightarrow i = 1 + (5-1)(0.5) \\ = 3$$

## # Case II Association

$\Rightarrow i < 1$  because no. of moles of solutes decreases.

$\Rightarrow$  Observed C.P.  $<$  Calculated C.P.

$\Rightarrow$  Observed molar mass  $>$  Calculated molar mass.



Initially 1 mol

After dissociation  $(1-\beta)$   $\frac{\beta}{n}$

$$\Rightarrow \text{Total no. of moles after dissociation} = 1 - \beta + \frac{\beta}{n}$$

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

$i = \frac{\text{Total no. of solute after dissociation}}{\text{Before}}$

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

$\beta$  = Degree of dissociation

$n$  = No. of mole of solute association.

$\left. \begin{array}{l} \text{Dimer } n=2 \\ \text{Trimer } n=3 \end{array} \right\}$

Note:— If ' $\beta$ ' is not given then consider  $\beta=1$  i.e.  
100%  $\Rightarrow i = \frac{1}{n}$

Q) Calculate the O.P. of 0.1 molar  $\text{Na}_2\text{SO}_4$  solution at 300 K temp If  $\text{Na}_2\text{SO}_4$  is 60% ionised.

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

$$i = 1 + (3-1)0.6$$

$$= 2.2$$

$$\pi = i \times CRT$$

$$= 2.2 \times 0.1 \times 0.0821 \times 300$$

$$= 5.4 \text{ atm.}$$

Ques. In  $500 \text{ cm}^3$  water 3g of acetic acid is added. If 25% of the acid is dissociated then find out the depression in freezing point.

Solu<sup>n</sup>:-

$$\begin{aligned} i &= 1 + (n-1)\alpha \\ &= 1 + (2-1)(0.25) \\ &= 1.25 \end{aligned}$$

$$\begin{aligned} d_{\text{H}_2\text{O}} &= 1 \text{ g mL}^{-1} \\ 1 \text{ cm}^3 &= 1 \text{ mL} = 1 \text{ g} \end{aligned}$$

$$\begin{aligned} \Delta T_f &= i \times K_f \cdot m \\ &= 1.25 \times 1.86 \times \left( \frac{3 \times 1000}{60 \times 500} \right) \\ &= 0.23^\circ\text{C or K} \end{aligned}$$

Ques. Calculate the B.P. of a solution prepared by dissolving 0.61g of benzoic acid in 50g carbon disulphide ( $\text{CS}_2$ ) (assuming that acid undergoes 80% dissociation).

Given: (B.P. of  $\text{CS}_2$  =  $46.2^\circ\text{C}$ ,  $K_b$  of  $\text{CS}_2$  =  $2.5^\circ\text{C m}^{-1}$ ) dimension

$$\begin{aligned} i &= 1 + \left( \frac{1}{n} - 1 \right) \beta \\ &= 1 + \left( \frac{1}{2} - 1 \right) (0.8) \\ &= 0.6 \end{aligned}$$

$$\begin{aligned} T_b - T_b^{\circ} &= 0.15 \\ T_b &= 0.15 + T_b^{\circ} \\ &= 0.15 + 46.2 \\ &= 46.35^\circ\text{C} \end{aligned}$$

$$\begin{aligned} \Delta T_b &= i \times K_b \cdot m \\ &= 0.6 \times 2.5 \times \left( \frac{0.61 \times 1000}{122 \times 50} \right) \\ &= 1.02 \\ &= 0.15^\circ\text{C or K} \end{aligned}$$

Ques. Calculate the O.P. of 0.1M weak monobasic acid solution having pH equal to 2 at 300K temp.

Solu<sup>n</sup>:—  $c = 0.1 \text{ M or N}$

$$\text{pH} = 2 \Rightarrow [\text{H}^+] = 10^{-2} \text{ N}$$

$$[\text{H}^+] = c\alpha$$

$$\alpha = \frac{[\text{H}^+]}{c} = \frac{10^{-2}}{10^{-1}} = 0.1$$

$$\begin{aligned} i &= 1 + (n-1)\alpha \\ &= 1 + (2-1)0.1 \\ &= 1.1 \end{aligned}$$

$$\begin{aligned} \pi &= i \times CRT \\ &= 1.1 \times 0.1 \times 0.0821 \times 300 \\ &= 2.7 \text{ atm.} \end{aligned}$$

Ques. 7.2% glucose solution is isotonic with 1.17% <sup>(w/v)</sup> sodium chloride solution at a given temp. Then find out the degree of dissociation NaCl.

$$\pi_1 = \pi_2$$

$$i_1 \times C_1 \times RT = i_2 \times C_2 \times RT$$

$$i_1 \times C_1 = i_2 \times C_2$$

$$1 \times \frac{7.2 \times 1000}{180 \times 100} = i_2 \times \frac{1.17 \times 1000}{58.5 \times 100}$$

$$i_2 = 2$$

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

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

$$\alpha = 1 \text{ i.e. } 100\%$$

Ques 11g Barium Nitrate is added to 100g water to prepared a soln that boils at 100.44°K + temp. then find out the degree of ionisation of Barium Nitrate.

(~~molar~~ molecular wt. of  $\text{Ba}(\text{NO}_3)_2 = 260$ )

$$\Delta T_b = i \times K_b \cdot m$$

$$T_b - T_b^{\circ} = i \times 0.52 \times 11 \times 1000$$

$$260 \times 100$$

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

$$100.44 - 100 = i \times \frac{0.52 \times 11}{26}$$

$$2 = 1 + (3-1)\alpha$$

$$0.44 = i \times \frac{0.52 \times 11}{26}$$

$$1 = 2\alpha$$

$$0.44 = i \times 0.22$$

$$\alpha = \frac{1}{2} = 0.5 \text{ i.e.}$$

$$i = \frac{0.44}{0.22} = 2$$

50%

Ques Arrange the following solution in increasing order of their B.P., f.pt, v.p,  $\Delta T_b$ ,  $\Delta T_f$ , RLVP, LVP and O.P. of solution.

$$(A) 0.05 \text{ molar } \text{NaNO}_3 \text{ (aq.)} = 2 \times 0.05 = 0.1$$

$$(B) 0.06 \text{ molar } (\text{NH}_4)_3 \text{PO}_4 = 4 \times 0.06 = 0.24$$

$$(C) 0.8 \text{ molar glucose (aq.)} = 1 \times 0.8 = 0.8$$

$$(D) 0.01 \text{ molar } \text{Al}_2(\text{SO}_4)_3 \text{ (aq.)} = 5 \times 0.01 = 0.05$$

$$\frac{1}{(V.P)_{\text{sol}}} \propto \frac{P^{\circ} - P_s}{P^{\circ}} = i \times \frac{n_{\text{solute}}}{n_{\text{solvent}}} \Rightarrow \Delta P = P^{\circ} - P_s \Rightarrow P_s = P^{\circ} - \Delta P \uparrow$$

$$(B.P.)_{\text{sol.}} \propto \Delta T_b = i \times K_b \cdot m \Rightarrow \Delta T_b \Rightarrow T_b - T_b^{\circ} \Rightarrow T_b = T_b^{\circ} + \Delta T_b$$

$$(\text{F.P.})_{\text{sol.}} \propto \Delta T_f = i \times K_f \cdot m \Rightarrow \Delta T_f \Rightarrow T_f - T_f^{\circ} \Rightarrow T_f = T_f^{\circ} - \Delta T_f \uparrow$$

$$\propto \pi = i \times CRT$$

$$c \cdot P \propto i \times C$$

$$(B.P.)_{\text{sol.}} \propto i \times C$$

$$(\text{F.P.})_{\text{sol.}} \propto \frac{1}{(V.P)_{\text{sol.}}} \propto \frac{1}{i \times C}$$

As  $\alpha$  is not given  $\Rightarrow \therefore \alpha = 1$

As  $d_{\text{sp.}}$  is not given  $\Rightarrow \therefore M \approx m$ .

\* RLVP, LVP,  $\Delta T_b$ ,  $\Delta T_f \Rightarrow d < a < b < c$

\*  $(B.P)_{\text{sol.}} \& (D.P)_{\text{sol.}} \Rightarrow d < a < b < c$

\*  $(F.P.)_{\text{soln.}} \& (V.P)_{\text{soln.}} \Rightarrow c < b < a < d$

Ques. 1g of monobasic acid 100g water lowers the freezing point by  $0.186^{\circ}\text{C}$  If 0.2g of same acid requires 16ml of  $\text{N}/10$  NaOH solution for complete neutralization then find out degree of dissociation of acid.

Soln:-

$$\text{Eq. of acid} = \text{Eq. of base}$$

$$\text{moles} \times \text{v.f.} = N \times \text{Vol. (L)}$$

$$\frac{0.2}{M} \times 1 = \frac{1}{10} \times \frac{16}{1000}$$

$$M = \frac{2000}{16} = \underline{125 \text{ g/mol}}$$

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

$$0.186 = i \times 1.86 \times \frac{1 \times 1000}{125 \times 100}$$

$$i = \frac{125}{100} = 1.25$$

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

$$1.25 = 1 + (2-1)\alpha$$

$$\alpha = 0.25$$

$$\therefore \text{c. } 25\%$$

### # Henry's law :-

This law states that at const. Temp. the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of the liquid or gas.

If the solubility of a gas is expressed in term of mole fraction then the Henry law can be stated as follows:-

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

$$P \propto X$$

$$P = K_H \cdot X$$

$P$  = partial pressure of gas in vapour phase

$X$  = mole fraction of gas in solution

$K_H$  = Henry's constant

Units of  $K_H$  = Unit of Pressure

$\Rightarrow K_H$  depends on nature of gas & temp.

$\Rightarrow$  On rising temp,  $K_H$  also rises  $\therefore$  solubility decreases

\* It is due to this reason that aquatic species are more comfortable in cold water as compare to warm water.

\* At constant temp. the mass of a gas dissolved in a given Vol. of solvent is directly proportional to the

pressure at which it is in equilibrium with the solution.

$$m \propto P$$

$$\frac{m_1}{m_2} = \frac{P_1}{P_2}$$

Note :—

- (i) Raoult's law is a special case of Henry's law.
- (ii) Henry's law is not applicable for when a gas undergoes any chemical reaction with a solvent.
- (iii) Henry law is not applicable when a gas associate or dissociate in solvent.

Ques. If  $N_2$  gas is bubbled through water at 293K then How many millimole of  $N_2$  gas would dissolve in 1L of water assuming that  $N_2$  exerts a partial pressure of 0.98 bar given that  $K_H$  of  $N_2$  at 293K is 76.48K bar.

$$P_{N_2} = K_H \cdot X_{N_2}$$

$$X_{N_2} = \frac{P_{N_2}}{K_H} = \frac{0.98}{76.48} \times 10^{-5}$$

$$= 1.3 \times 10^{-5}$$

$$\frac{n_{N_2}}{55.5} = 1.3 \times 10^{-5}$$

$$n_{N_2} = 55.5 \times 1.3 \times 10^{-5}$$

$$= 72.1 \times 10^{-5} \text{ mol}$$

$$= 72.1 \times 10^{-5} \times 10^3$$

$$= 0.72 \text{ mmol}$$

$$\frac{n_{N_2}}{n_{H_2O} + n_{N_2}} = 1.3 \times 10^{-5}$$

(As  $n_{N_2} \ll n_{H_2O}$ )

$$\frac{n_{N_2}}{n_{H_2O}} = 1.3 \times 10^{-5}$$

Ques. The value of  $K_H$  for the solubility of  $N_2$  in water at 298 K is  $1 \times 10^5$  atm. If the mole fraction of  $N_2$  in air is 0.8 then calculate the no. of mole of Nitrogen from air dissolved in 10 mole of water at 298 K and 5 atm pressure of air.

$$\text{Partial Pressure} = \text{Mole fraction} \times \text{Total Pressure}$$

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

$$P_{N_2} = K_H \cdot X_{N_2}$$

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

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

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

श्री नाथ जी बुक डिपो

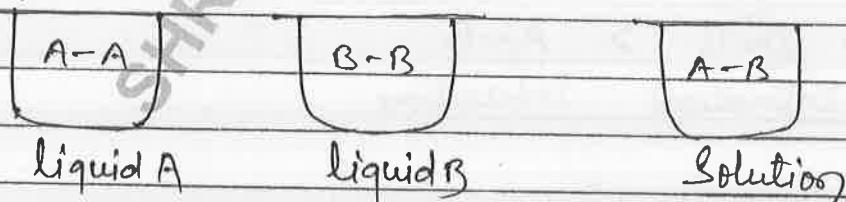
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Old Book Purchase & Sell,  
Study Material Purchase & Sell,  
Hand Writting Notes, Online Form

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## # Ideal & Non-ideal Solutions :

### ① Ideal Solution :

The solution that obey Raoult's law at all conc. and all temp. are known as ideal solution.



$$\Rightarrow A-A = B-B = A-B$$

Interaction Interaction Interaction

$$\Rightarrow \Delta H_{\text{mix.}} = 0 \quad (\text{No extra heat is absorbed or released})$$

$$\Rightarrow \Delta V_{\text{mix.}} = 0 \quad (V_{\text{sol}} = V_{\text{olute}} + V_{\text{solvent}})$$

Date \_\_\_\_\_ Page \_\_\_\_\_

$\Rightarrow$  Observed B.P. = Calculated B.P.

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

Eg:- Benzene + Toluene  
Bromoethane + Chloroethane  
n-Hexane + n-Heptane.

Note : \_\_\_\_\_

• Liquid having same molecular structure and same polarity form form ideal solution. Particularly No solution is ideal.

~~Raolt's law is only applicable for ideal solution.~~

## ⑪ Non-Ideal Solutions :-

(A) It shows Positive deviation from Raoult law:-

$$\Rightarrow A - A = B - B > A - B$$

Interactions      Interactions      Interactions

$$\Rightarrow \Delta H_{\text{mix}} > 0 \text{ (Endo)}$$

$$\Rightarrow \Delta V_{\text{mix}} > 0 \quad (\text{Vol.} > \text{Volute} + \text{Vsolvent})$$

$$\Rightarrow \text{Observed V.P.} > \text{Calculated V.P.} \quad \left[ \begin{array}{l} P_A > P_A^o x_A \\ P_B > P_B^o x_B \\ P_S > P_A^o x_A + P_B^o x_B \end{array} \right]$$

$\Rightarrow$  Observed B.P. < Calculated B.P.

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

Eg:— Ethanol & Acetone  
 $CS_2$  & Acetone

(B) Non-ideal Solution showing negative deviation from Raoult's law :—

$$\Rightarrow A-A = B-B < A-B$$

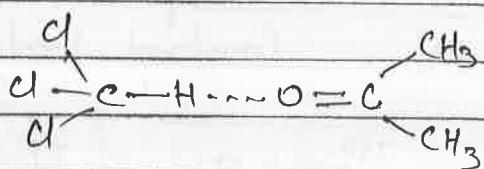
$$\Rightarrow \Delta H_{mix} < 0 \text{ (Exo)}$$

$$\Rightarrow \Delta V_{mix.} < 0 \text{ (Vol.} < \text{Volue + Voluent)}$$

$$\Rightarrow \text{Observed V.P.} < \text{Calculated V.P.} \quad \left[ \begin{array}{l} P_A < P_A^\circ \chi_A \\ P_B < P_B^\circ \chi_B \\ P_S < P_A^\circ \chi_A + P_B^\circ \chi_B \end{array} \right]$$

$\Rightarrow$  Observed B.P. > Calculated B.P.

Eg:— Phenol & Aniline  
 Chloroform & Acetone.

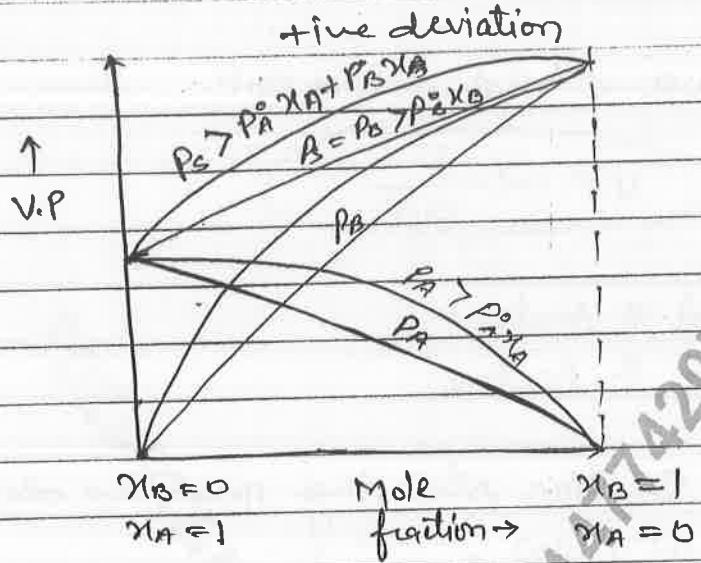


Note:—

For both ideal & Non-ideal Solu?

$$\boxed{\Delta S_{mix} > 0}$$

$$\boxed{\Delta G_{mix} < 0}$$



## # Azeotropes/Azeotropic mixtures:-

A binary mixture of two volatile liquids having same composition in vapour and liquid phase and boils at const. temp. are known as azeotropes.

The component of such mixture cannot be separated by fractional distillation because they boil at constant temp and hence they are also known as Constant boiling mixture.

There are of two types:-

### ① Mini boiling Azeotropes:-

The solution that shows large +ve deviation from Raoult's law forms mini-boiling azeotropes at a specific composition.

The boiling point of mixture is less than the B.P. of each component in pure state.

Eg:- Ethanol (Ethanol) and water

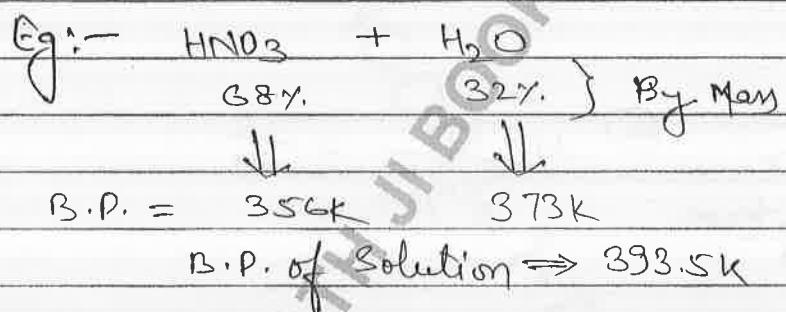
95.6%      4.4% } By mass

$$\begin{array}{ccc} \downarrow & & \downarrow \\ \text{B.P.} = 351.5\text{K} & & 373\text{K} \\ \text{B.P. of Solution} = 351\text{K} & & \end{array}$$

### # Maximum Boiling Azeotrope:—

Negative deviation.

The solutions that shows negative deviation from Raoult's law from max. boiling azeotrope at a specific composition.



Ques 10ml of liquid A (B.P. = 368K) and 10ml of liquid B (B.P. = 415K) are mixed to obtained 19.92mL of a constant boiling mixture then the B.P. of a solution will be.

- ① ~~<~~ 368K
- ② > 368K but < 415K
- ③ ~~>~~ 415K
- ④ Unpredictable

Vol.sol. < Volume + Vsolvent

$$19.92 < 10 + 10$$

-ive deviation  $\Rightarrow$  Maxn Boiling Azeotrope.

$\frac{\Delta T_b}{\Delta T_f} = \frac{k_b \cdot m}{k_f \cdot m}$

$\alpha = 59^\circ$   
 $T = 273.15K$

$\frac{0.15}{\Delta T_f} = \frac{0.512 \times m}{1.86 \times m/2}$

(103)

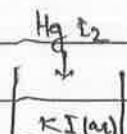
$KNO_3$  = strong electrolyte

$i=2$

$CH_3COOH$  = weak electrolyte

Ex#1

(114)



$2K^+ + 2I^-$   
4 molecules.

$2K^+ + (HgI_4)^{2-}$

3 mole ions.

$\uparrow$  solute ↓

$\Delta T_f \downarrow$

Ex#2

$\Delta T_f \uparrow$

Ex#2  
 $4 = 20$

Ex#2

(23)  $(\Delta T_b)_x > (\Delta T_b)_y$  (24)  $N = \frac{1/49}{1/00/000} = \frac{10}{49}$

$i_x \cdot k_b \cdot m > i_y \cdot k_b \cdot m$

# Solid State

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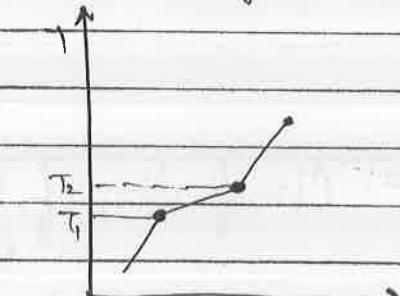
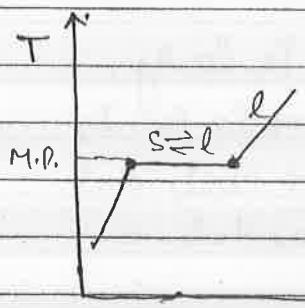
\* It is branch of chemistry that deals with various types of solids, arrangement of constituent particles resulting in vary structure / properties and defects in solid state.

\* Under the given condition of Pressure and Temp. the Characters properties are as follow:-

- (i) They have definite shape, mass and Volume
- (ii) Intermolecular distance are short.
- (iii) Intermolecular forces are strong.
- (iv) Their constituent particles i.e. atoms, molecules or ions have fixed positions and they can only oscillate their mean positions.
- (v) They are incompressible and rigid.

# Classification of Solids:-

| Property        | Crystalline                | Amorphous  |
|-----------------|----------------------------|--|
| ① Shape         | Definite geometrical shape | Irregular shape  |
| ② Melting point | Sharp M. pt.               | No sharp M. pt.<br>They gradually soften over a range of temp. |



③ Heat of fusion

Definite

Not definite

**(IV) Cleavage****Properties**

When cut into pieces with a sharp edged tool then newly generated surfaces are plain & smooth.

Newly generated Surface area irregular.

**(V) Anisotropy**

→ The value of some physical properties when measured along diff.

Anisotropic in Nature

Isotropic in Nature

dir<sup>n</sup> comes out to be diff. in the same crystal due to diff. arrangement of particles in diff. directions is known as Anisotropy.

**(VI) Nature**

True solids

Pseudosolids or Supercooled liquids.

**(VII) Order of arrangement of Constituents particles**

Large range Order

Short range Order

**(VIII) Examples**

Metal  $\Rightarrow$  Fe, Cu, Ag,

Glass, Plastic, Rubber

Non-metal  $\Rightarrow$  S<sub>8</sub>, P<sub>4</sub>, I<sub>2</sub>

Amorphous Si

Compd.  $\Rightarrow$  NaCl, ZnS

Photovoltaic

Naphthalene

Sunlight  $\rightarrow$  Electricity

**# Classification of Crystalline solids:**

On the basis of interactions b/w the particles

- Molecules, Metallic, covalent and Ionic

## # Some important Terminology :-

### ① Crystal Lattice / Space Lattice :-

A regular three dimensional arrangement of ~~infinite~~ <sup>indefinite</sup> constituent particles in space is known as crystal lattice.

- There are only 14 unique lattices which are known as BRAVAIS.

### ② Lattice point / Lattice site :-

The point at which a constituent particles i.e. atom, molecules and ions is present in space is known as lattice point.

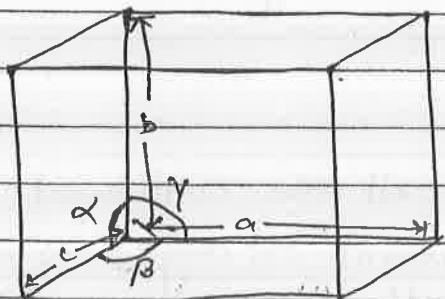
### ③ Unit Cell :-

The smallest portion of a crystal lattice which when repeated in all directions creates the entire lattice is known as unit cell.

- All unit cell are identical in crystal lattice.

⇒ Parameter of a unit cell

- ① Dimensions along the edges =  $a, b, c$  [Edge length or Axial length]
- ② Angle b/w the edges =  $\alpha, \beta, \gamma$  [Axial angle]



Unit cell

## Classification of Unit Cell :-

On the basis of position of particles in unit cell.

- These are of 2 types:-

### (A) Primitive / Simple Unit cell

When constituent particles are present only at corner position of a unit cell then it is known as primitive unit cell.

### (B) Centred Unit

When one or more constituent particles are present at any other position other than corner along with those present at corners are known as centred Unit.

#### (i) Body centred :-

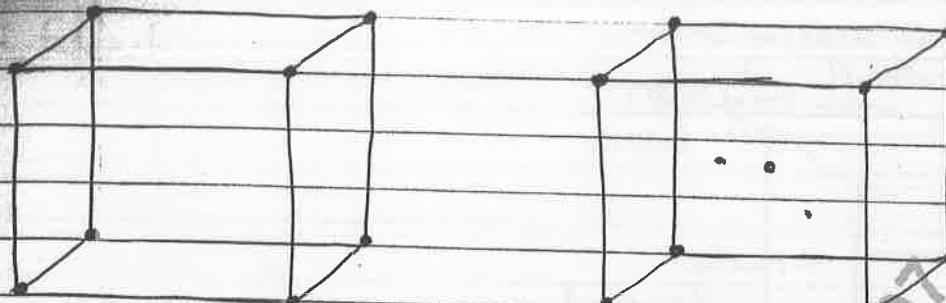
In such a unit cell constituent particles are present at the body centred along with those at corners.

#### (ii) Face centred :-

In such a unit cell the constituent particles are present at each face centred along with those present at corners.

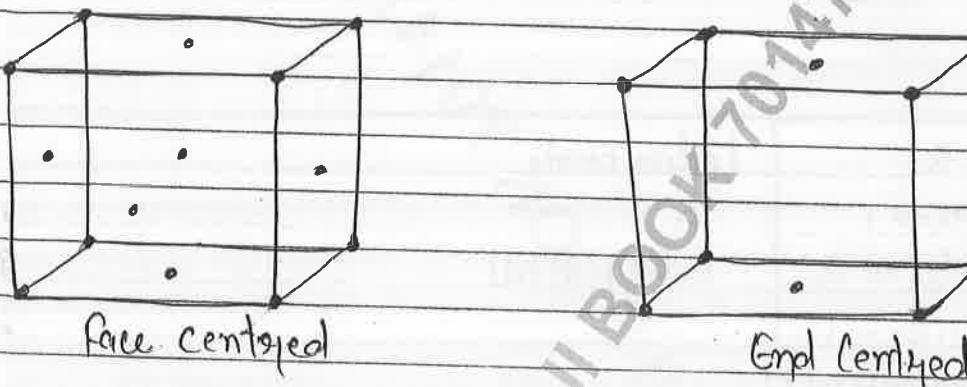
#### (iii) End centred :-

In such a unit cell the constituent particles are present at any two opposite face centres along with those present at their corners.



Primitive

Body Centred



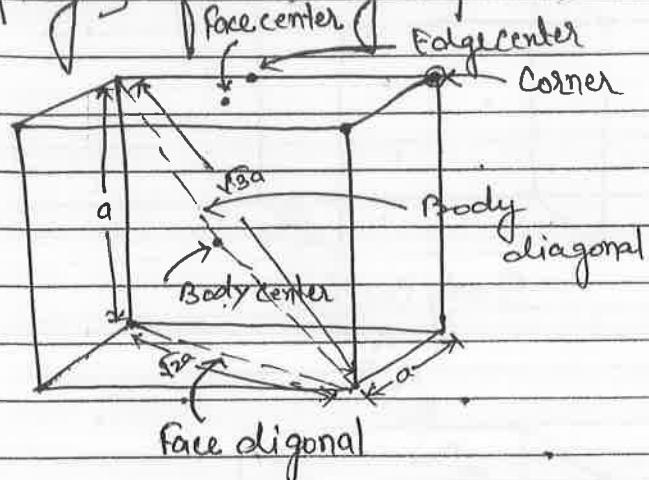
Face centred

End Centred

II On the basis of parameter of unit cell :—  
7 types :—

| Crystal System                 | Edge length<br><u>OR</u><br>Axial distances | Axial Angle.                                      |
|--------------------------------|---|---|
| (i) Cubic P, B, F              | $a = b = c$                                 | $\alpha = \beta = \gamma = 90^\circ$              |
| (ii) Tetragonal P, B           | $a = b \neq c$                              | $\alpha = \beta = \gamma = 90^\circ$              |
| (iii) Orthorhombic P, B, F, E  | $a \neq b \neq c$                           | $\alpha = \beta = \gamma = 90^\circ$              |
| (iv) Rhombohedral (Trigonal) P | $a = b = c$                                 | $\alpha = \beta \neq \gamma \neq 90^\circ$        |
| (v) Hexagonal P                | $a = b \neq c$                              | $\alpha = \beta = 90^\circ; \gamma = 120^\circ$   |
| (vi) Monoclinic P, E           | $a \neq b \neq c$                           | $\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$ |
| (vii) Triclinic P              | $a \neq b \neq c$                           | $\alpha \neq \beta \neq \gamma \neq 90^\circ$     |

## # Analysis of cubic system:-



No. of corners = 8

No. of body center = 1

No. of face center = 6

No. of edge center = 12

No. of face diagonals = 12

No. of body diagonals = 4

Length of face diagonal =  $\sqrt{2}a$

Length of body diagonal =  $\sqrt{3}a$

Volume of cubic unit cell =  $a^3$

where,  $a$  = edge length of cubic unit cell

Alternate corners = 4

Alternate faces = 2

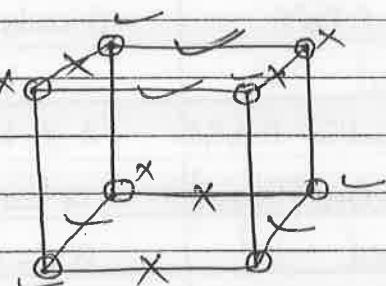
Alternate edges = 4

Distance b/w two

adjacent face center =  $\frac{a}{\sqrt{2}}$

Distance b/w two

adjacent edge center =  $\frac{a}{\sqrt{2}}$



### # Effective No. of atoms in a unit cell ( $Z$ ):—

For a unit cell,

$$Z = \sum z_i$$

where,  $z_i \Rightarrow$  effective no. of atoms at a particular lattice point in a unit cell.

For a particular lattice point,

$$z_i = \frac{\text{Total no. of atoms at that lattice point}}{\text{Effective contribution of one atom at that lattice point in a unit cell.}}$$

→ Effective contribution of an atom at various lattice points in a cubic unit cell.

$$\text{Corner} = \frac{1}{8}$$

$$\text{face centre} = \frac{1}{2}$$

$$\text{Body centre} = 1$$

$$\text{Edge centre} = \frac{1}{4}$$

### # Determination of formula of a compound:—

If a compound contains elements A, B, C & D then its formula will be —

$$A_{Z_A} B_{Z_B} C_{Z_C} D_{Z_D}$$

where,

$Z_A, Z_B, Z_C, Z_D$

effective no. of

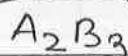
atoms in a unit

cell of that elements.

Ques. In solid cubic lattice A atoms are present at all corner and body center and 'B' atoms are present at all face centers then find out the simplest formula of the solid atom.

$$Z_A = 8 \times \frac{1}{8} + 1 \Rightarrow 2$$

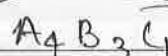
$$Z_B = 6 \times \frac{1}{2} \Rightarrow 3$$



Ques. In a cubic structure A atoms are arranged in FCC and B atoms are at every edge center and C atoms are at Body center Then find out the simplest formula of solid.

~~$$Z_A = 8 \times \frac{1}{8} = 1$$~~

$$Z_B = \left( 12 \times \frac{1}{4} \right) = 3$$



$$Z_C = 1 \times 1 = 1$$

Ques In solid cubic lattice A atoms are present at all corners B atoms at alternate face centers and C atoms at alternate Edge centres then find out simplest formula.

$$Z_A = 8 \times \frac{1}{8} = 1$$



$$Z_B = 2 \times \frac{1}{2} = 1$$

$$Z_C = 4 \times \frac{1}{4} = 1$$

Ques. In a solid cubic lattice A occupies corners B occupied 50%, face center and C occupied 25% edge center then find out formula of the solid.

$$Z_A = 8 \times \frac{1}{8} = 1$$

$$Z_B = 3 \times \frac{1}{2} = \frac{3}{2}$$

$$Z_C = 12 \times \frac{1}{4} = \frac{3}{4}$$

↑  
12 at 25%

$A_1 B_{\frac{3}{2}} C_{\frac{3}{4}}$  multiplied by 4,

$A_4 B_6 C_3$

Ques In a cubic structure A atoms are arranged in BCC and B atoms are ~~atoms~~ at <sup>every</sup> edge center and C atoms are at alternate face center then find out simplest formula if atoms are removed along any body diagonal.

$$Z_A = \left(8 \times \frac{1}{8}\right) + (1 \times 1) \Rightarrow 2 \Rightarrow 6 \times \frac{1}{8} = \frac{3}{4}$$

$$Z_B = 12 \times \frac{1}{4} = 3 \Rightarrow 3$$

$$Z_C = 2 \times \frac{1}{2} = 1 \Rightarrow 1$$

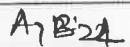
$A_3 B_3 C_1$

$A_3 B_{12} C_4$

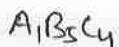
Ques for a ~~cubic~~ crystal the unit cell parameter are as follow:-  $a = 4.2 \text{ Å}$ ,  $b = 4.2 \text{ Å}$ ,  $c = 5 \text{ Å}$ . Then determine the crystal will be -

- ① Tetragonal
- ② Orthorhombic
- ③ Hexagonal
- ④ Either ① or ③

Ques. 1 In a solid cubic lattice A atoms are present at all corner, B atoms are at all face center. If one of the A atoms is removed from corner then the formula will be -

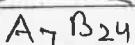


Ques. 2. In a cubic structure A atoms are present at every corner, B atom at every face center, and C atom at every edge center then find the simple of the solid if all atoms are removed from one face.



$$\text{Ques. 1} \quad Z_A = 8 \times \frac{1}{8} = 1 \quad 7 \times \frac{1}{8} = \frac{7}{8} \times 8 = 7$$

$$Z_B = \left( 6 \times \frac{1}{2} \right) = 3 \quad 3 \times 8 = 24$$



$$\text{Ques. 2.} \quad Z_A = \left( 8 \times \frac{1}{8} \right) = 1 ; \quad 4 \times \frac{1}{8} = \frac{1}{2} \times 2 = 1$$

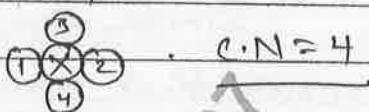
$$Z_B = 5 \times \frac{1}{2} = \frac{5}{2} ; \quad \frac{5}{2} \times 2 = 5$$

$$Z_C = 12 \times \frac{1}{4} = 3 ; \quad 8 \times \frac{1}{4} \times 2 \times 2 = 4$$



## # Co-ordination number :-

the number of nearest neighbours that are touching to a particle is known as co-ordination no.



## # Packing fraction or packing efficiency :-

It is define as the fraction of volume of a unit cell occupied by atom.

$$\text{Packing fraction} = \frac{\text{Vol. occupied atoms in a unit cell}}{\text{Vol. of unit cell}}$$

$$\boxed{\text{P.F.} = \frac{Z \times \frac{4}{3} \pi r^3}{\text{Vol. of unit cell}}}$$

$$\% \text{ Packing} = \text{P.F.} \times 100$$

$Z \Rightarrow$  effective no. of atoms in a unit cell

$r \Rightarrow$  Atomic radius

For a cubic unit cell,

$$\text{Vol. of cubic unit cell} = a^3$$

where,  $a \Rightarrow$  edge length of cubic unit cell

## # Void fraction:-

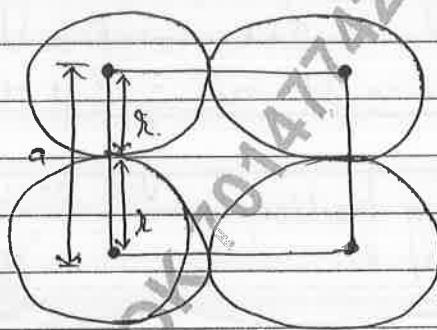
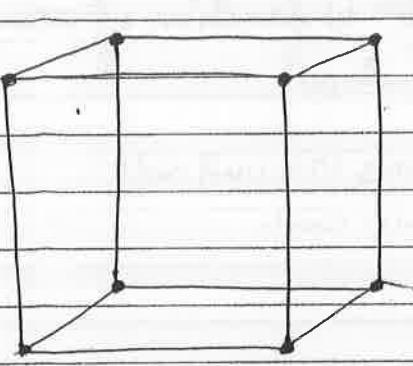
It is define as the fraction of vol. of a unit cell that is unoccupied.

$$\boxed{V.F. = 1 - P.F.}$$

## # Types of Cubic system :-

### ① Primitive / Simple Cubic (sc) :-

Similar atoms are present at all corner in such a manner that each corner atom is touching to its adjacent atom.



(One face of sc)

$$\Rightarrow \text{Effective no. of atoms in a unit cell } (z) = \left(8 \times \frac{1}{8}\right) = 1$$

$$\Rightarrow \text{Co-ordination No.} = 6$$

$\Rightarrow$  Relation b/w edge length ( $a$ ) & atomic radius ( $r$ )

$$2r = a \Rightarrow r = \frac{a}{2}$$

$\Rightarrow$  Packing fraction

$$PF = \frac{z \times \frac{4}{3} \pi r^3}{\text{Vol. of unit cell}} = \frac{1 \times \frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{a^3} = 0.524$$

$$\therefore PF = 52.4\%$$

$$\therefore VF = 47.6\%$$

(2) Body centred Cubic (BCC) :—

Similar atom are present at all corner along with body center in such a manner that all corner atoms are touching to the body center atom and Non of the corner atoms are touching each other.

$$\Rightarrow \text{Effective no. of atoms in a unit cell} = (z) = \left(8 \times \frac{1}{8}\right) + (1+1) = 2$$

$$\Rightarrow \text{Co-ordination No.} = 8$$

$$\Rightarrow \text{Relation b/w edge length (a) \& atomic radius (r)}$$

$$4r = \sqrt{3}a \therefore r = \frac{\sqrt{3}}{4}a$$

$\Rightarrow$  Packing fraction

$$PF = \frac{2 \times \frac{4}{3} \pi \left(\frac{\sqrt{3}a}{4}\right)^3}{a^3} = \frac{\sqrt{3} \pi}{8} = 0.68$$

$$\therefore PF = 68\%$$

$$\therefore V.F = 32\%$$

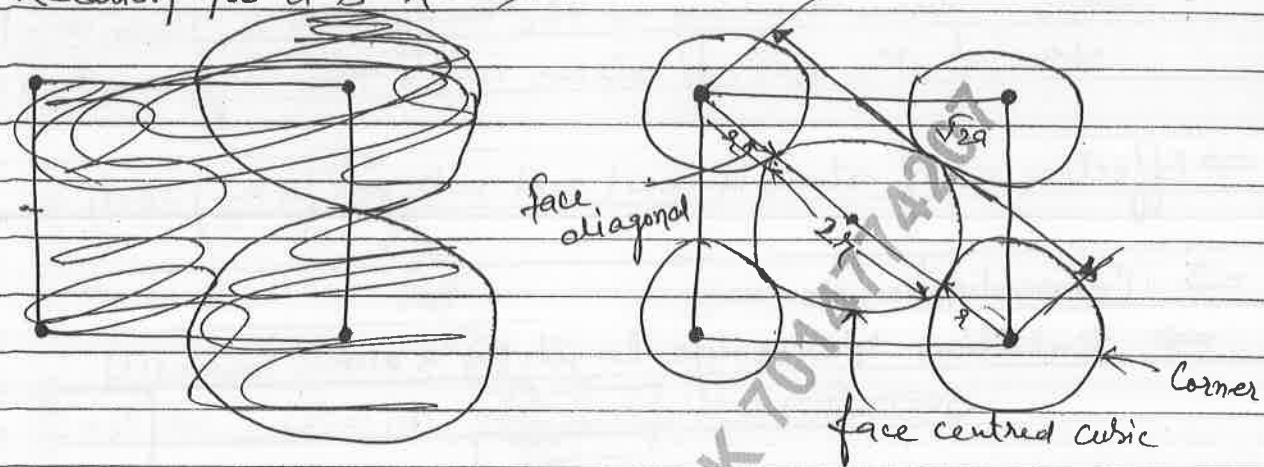
(3) Face centred Cubic (FCC) :—

Similar atom <sup>are</sup> present at all the corner and each face centred in such manner that each face centred atom is touching to all the corner atoms of its face and adjacent face centre atoms but it does not touches to the opp. face centre atom.  
(Non of the corner atoms are touching to each other)

$\Rightarrow$  Effective no. of atoms in a unit cell ( $z$ ) =  $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$

$\Rightarrow$  Co-ordination no. = 12

$\Rightarrow$  Relation b/w  $a$  &  $r$   $\Rightarrow$



$$4r = \sqrt{2}a \Rightarrow r = \frac{\sqrt{2}a}{4} \Rightarrow r = \frac{a}{2\sqrt{2}}$$

$\Rightarrow$  Packing fraction

$$PF = \frac{2 \times \frac{4}{3}\pi r^3}{\text{Vol. of unit cell}} = \frac{4 \times \frac{4}{3}\pi \left(\frac{a}{2\sqrt{2}}\right)^3}{a^3}$$

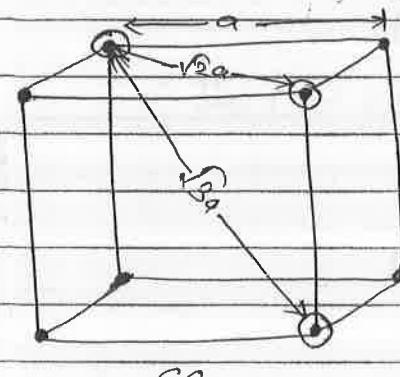
$$= \frac{\pi}{3\sqrt{2}} = 0.74.$$

$$\% PF = 74\%$$

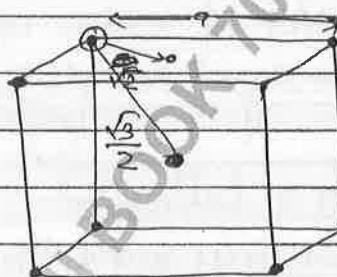
$$\therefore \sqrt{f} = 26\%$$

# Nearest Neighbours: —

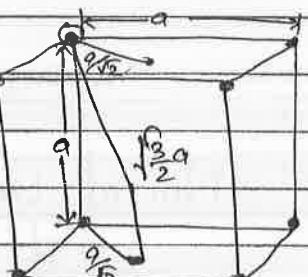
| Unit Cell | Nearest Distance      | Number | Next Nearest Distance | Number | Next to Next Nearest Distance | Number              |
|-----------|-----------------------|--------|-----------------------|--------|-------------------------------|---------------------|
| SC        | $a$                   | 6      | $\sqrt{2}a$           | 12     | $\sqrt{3}a$                   | 8                   |
| BCC       | $\frac{\sqrt{2}}{2}a$ | 8      | $a$                   | 6      | $\sqrt{2}a$                   | 12                  |
| FCC       | $\frac{a}{\sqrt{2}}$  | 12     | $a$                   | 6      | $\sqrt{\frac{3}{2}}a$         | 24 ( $3 \times 8$ ) |



SC



BCC



FCC

# Density of unit cell :—

$$\text{Density of unit cell} = \frac{\text{Density of crystal}}{\text{Volume of unit cell}}$$

$$\text{Density of Unit Cell} = \frac{\text{Mass of unit cell}}{\text{Vol. of unit cell}}$$

$\therefore$  Mass of unit cell = Effective no. of atoms  $\times$  Mass of one atom.

$$= Z \times m$$

$$= \sum z \times \frac{M}{N_A}$$

$$\therefore \boxed{\text{Density} = \frac{\sum z \times M}{N_A \times a^3}}$$

$M$  = Molar mass of substance ( $\text{g mol}^{-1}$ )

$N_A$  = Avogadro No.

$z$  = Effective no. of atoms in a unit cell.

$a^3$  = Vol. of cubic unit cell

where,  $a$  = edge length of cubic unit cell.

# No. of unit cells in a lattice:-

If, no. of particles in a lattice =  $N$   
then,

No. of SC unit cells =  $N$

No. of BCC unit cells =  $\frac{N}{2}$

No. of FCC unit cells =  $\frac{N}{4}$

- Q1. Ni metal crystallises in FCC lattice if the edge length of unit cell of Ni crystal is 350 pm  
then determine the atomic radius of Ni metal.

$$4r = \sqrt{2}a$$

$$r = \frac{a}{2\sqrt{2}} = \frac{350}{2(1.4)} = 121 \text{ pm}$$

Ques. Cs crystallise in bcc lattice with the nearest distance of  $1.73\text{ \AA}$  b/w the atom then find out the edge length of the unit cell in pm.

$$\frac{\sqrt{3}}{2}a = 1.73\text{ \AA}$$

$$a = 2\text{ \AA}$$

$$a = 2 \times 10^{-10}\text{ m} \times 10^{-12}$$

$$a = 200\text{ pm.}$$

Ques. K Crystallise in Bcc arrangement then find out the mass of K sample containing  $3.01 \times 10^{24}$  unit cell.

$$\text{No. of Bcc unit cell} = 3.01 \times 10^{24}$$

$$\text{No. of atoms} = 3.01 \times 10^{24} \times 2$$

$$= 6.02 \times 10^{24} \text{ atoms}$$

$$\text{moles of K-atoms} = \frac{6.02 \times 10^{24}}{6.02 \times 10^{23}}$$

$$= 10 \text{ mol}$$

mass of

$$\text{K-sample} = \text{moles} \times \text{molar mass}$$

$$= 10 \times 39$$

$$= 390 \text{ g}$$

Ques An element M (Molar mass 100g/mol) having fcc structure then calculate the No. of unit cells present in 10g of sample of element.

$$\text{mole} = \frac{10\text{ g}}{100\text{ g}} = 0.1 \text{ mole}$$

$$\text{No. of atoms} = 0.1 \times N_A$$

$$= 6 \times 10^{22} \text{ atoms}$$

$$\text{No. of FCC unit cells} = \frac{N}{4}$$

$$= \frac{6 \times 10^{22}}{4} = 1.5 \times 10^{22}$$

Ques A metal 'A' (Molar mass = 100g/mole) crystallise in BCC lattice if the edge length of a unit cell is 400 pm then determine the density of the unit cell in g/cm<sup>3</sup>

$$d = \frac{Z \times M}{N_A \times a^3}$$

$$a = 400 \text{ pm} = 400 \times 10^{-10} \text{ m}$$

$$4 \times 10^{-10} \text{ m} = 4 \times 10^{-8} \text{ m}$$

$$= \frac{2 \times 100}{6 \times 10^{23} \times (4 \times 10^{-8})^3}$$

$$= \frac{200}{6 \times 10^{23} \times 64 \times 10^{-24}}$$

$$= \frac{2000}{384} = 5.2 \text{ g cm}^{-3}$$

Ques 1. Na metal crystallise in BCC lattice if the radius of Na atom is found to be 160 pm then determine the edge length of a unit cell of Na-crystal.

Ques 2. An element (molar mass = 75g/mole) crystallise in cubic form with a density 2 g/cm<sup>3</sup> if the edge length of the unit cell is 5A° then find out the atomic radius of the element in A°.

$$\textcircled{1} \quad 4r = \sqrt{3}a$$

$$a = \frac{4r}{\sqrt{3}}$$

$$a = \frac{4(160)}{1.73}$$

$$a = 370 \text{ pm}$$

$$\textcircled{2} \quad d = \frac{Z \times M}{N_A \times a^3}$$

$$d = \frac{Z \times 75}{6 \times 10^{23} \times (5 \times 10^{-8})^3}$$

$$Z = 2 \Rightarrow \text{BCC}$$

$$4r = \sqrt{3}a$$

$$r = \frac{\sqrt{3}a}{4} = \frac{1.73 \times 5}{4}$$

$$r = 2.16 \text{ Å}$$

Ques. The density of an element (molar mass = 60 g/mol) having a fcc structure is 6.23 g/cm<sup>3</sup>. Then find out the edge length of unit cell. (in cm)

$$d = \frac{Z \times M}{N_A \times a^3}$$

$$6.23 = \frac{4 \times 60}{6 \times 10^{23} \times a^3}$$

$$6.23 = \frac{240}{6 \times 10^{23} \times a^3}$$

$$(a^3) = \frac{240}{6 \times 10^{23}} \times 6.23$$

$$\frac{(240)}{36 \times 10^{23}}$$

$$= \frac{40 \times 10^{-23}}{6.23}$$

$$a^3 = 6.4 \times 10^{-23}$$

$$a = (6.4 \times 10^{-24})^{1/3}$$

## श्री नाथ जी बुक डिपो

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सामने, जवाहर नगर, कोटा (राज.) मो. 7014774207

Ques. An element having fcc structure has the edge length of 200 pm. If 200 g of element have  $24 \times 10^{23}$  atom then find out its density.

$$d = \frac{Z \times m}{N_A} = \frac{4 \times 200}{24 \times 10^{23} \times (2 \times 10^{-8})^3}$$

$$= \frac{800}{24 \times 10^{23} \times 8 \times 10^{-24}}$$

$$= \frac{1000}{24} = 41.67 \text{ g cm}^{-3}$$

### # Closed Packed Structures:

Arrangement of particles is done to get max<sup>m</sup> packing fraction and mini. void fraction.

All Real structures are 3-D structure that can be build up in the following step:-

#### ① 1-D Closed packing (Single layer single row) :-

(This packing is formed by placing here spheres in a single row touching to each other.)



$$C.N = 2$$

#### ② 2-D closed packing (Single layer multiple rows) :-

\* It is 2 types:-

##### A) Square Closed packing :-

Type  $\rightarrow$  AAA... --

$$C.N = 4$$



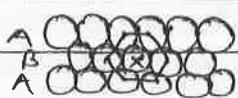
Void = Square (b/w 4 particles)

$$P.F. = 52.4\% ; Z = 1$$

→ This packing is formed by placing the square of second row in the same alignment with the sphere of 1st row both horizontally and vertically.

### (B) Hexagonal Closed Packing:

Type ABAB...



$$C.N. = 6$$

Void = Triangular (b/w 3 particles)

open up & apex down

$$P.F. = 60.4\% ; Z = 3$$

→ This packing is formed by placing the sphere of second row at the depression of second row.

### (C) 3-D Closed Packing (multiple layers multiple rows):—

| Types of Packing           | Types of arrng. of particles | Unit Cells   | Void                      | C.N. | Z | P.F.  |
|----------------------------|------------------------------|--------------|---------------------------|------|---|-------|
| 1.) Square Closed          | AAA--                        | Simple Cubic | Cubical                   | 6    | 6 | 52.4% |
| 2.) Hexagonal Closed (HCP) | ABAB---                      | Hexagonal    | Tetrahedral<br>Octahedral | 12   | 6 | 74%   |
| 3.) Cubic Closed (CCP)     | ABCABC--                     | FCC          | Tetrahedral<br>Octahedral | 12   | 4 | 74%   |

★ ↳ A 3-D closed packed structure is formed by a successive placing of 2-D closed packed over layer over one another.

### (A) Square Closed Packing:-

Type = AAA... .

$$C.N. = 4 + 1 + 1 = 6$$

Unit cell = Simple cubic

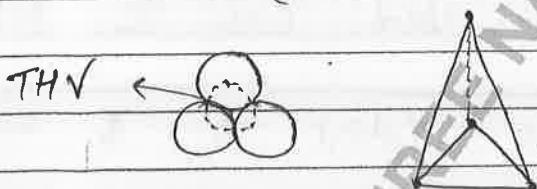
Void = Cubical (b/w 8 particles)

$$Z = 1; P.F. = 52.4\%$$

↳ This packing is formed by the successive placing of 2-D square closed packed layer in the same alignment both horizontally and vertically.

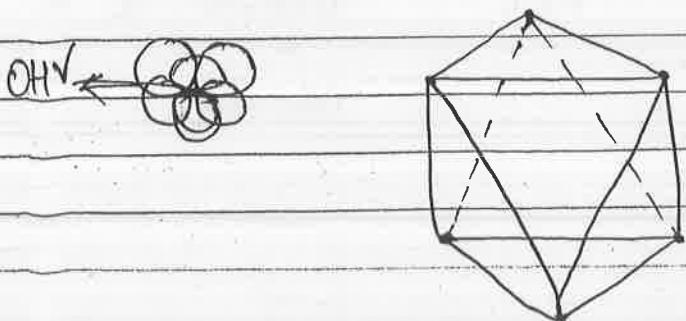
Note:-

① Tetrahedral void (b/w 4 particles)



When a triangular void is covered by a atom, it results in the formation of tetrahedral void.

② Octahedral void (b/w 6 particles)



When a triangular void is covered by another triangular void in opposite orientation then it result in the formation of Octahedral void.

Note \* No. of THV & OHV in a unit cell

$$\text{No. of THV} = 2Z \quad (2 \text{ voids per atom})$$

$$\text{No. of OHV} = Z \quad (1 \text{ voids per atom})$$

### (B) Hexagonal close Packing:-

Layer-I A. 2-D hexagonal closed packed layer  $\Rightarrow$  Layer A

Point a  $\Rightarrow$  Centre of atoms in 1st layer.

Point b  $\Rightarrow$  Triangular voids of 1st layer.  
(capped up or down)

Layer-II A similar 2-D hexagonal closed packed layer is placed at the depressions of 1st layer.

Different alignment from 1st layer  $\Rightarrow$  Layer B

Point b  $\Rightarrow$  THV of 1st layer;

Point a  $\Rightarrow$  THV of 2nd layer; Point c  $\Rightarrow$  OHV of 1st & 2nd layer.

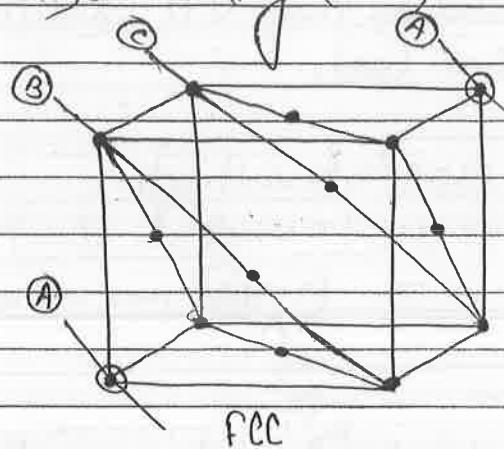
Layer-III A similar 2-D hexagonal closed layer can be placed in 2 ways:-

i) Covering THV  $\Rightarrow$  'a' voids  $\Rightarrow$  same alignment with 1st layer  $\Rightarrow$   
ABAB...  $\Rightarrow$  HCP.

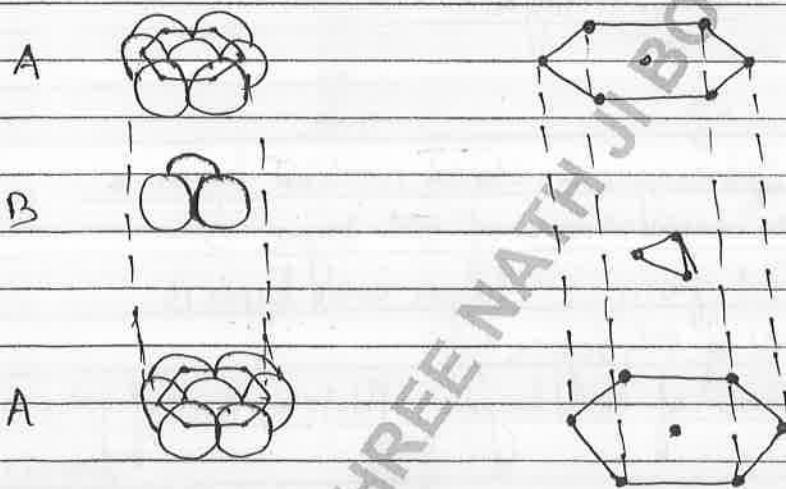
ii) Covering OHV  $\Rightarrow$  'c' voids  $\Rightarrow$  Diff alignment from  
1st and 2nd lay. ABCABC  $\Rightarrow$  CCP or

FCC Pack  
-1g

\* Cubic Closed Packing (CCP):—



# Hexagonal Closed Packing (HCP) : —



## Hexagonal Unit Cell

-12 Corners  $\Rightarrow$  each shared in 6 unit cells

→ 8 faces  $\Rightarrow$  ————— 11 ————— 2 ————— 11 —————

$\rightarrow$  18 edges

→ 12 edges → each ordered 4 in unit cell

6 side

edge  $\Rightarrow$   $\overrightarrow{e}$ ,  $\overleftarrow{e}$

In HCP

- 12 atom at all corners
- 2 atom at faces
- 3 atom ~~at~~ within the unit cell

$$Z(\text{HCP}) = \left(12 \times \frac{1}{6}\right) + \left(2 \times \frac{1}{2}\right) + (3 \times 1) = 6$$

$$\begin{array}{l} \text{No of THV} \\ \text{per unit cell} \end{array} = 12 ; \quad \begin{array}{l} \text{No. of OHV} \\ \text{per unit cell} \end{array} \rightarrow 6$$

$$C.N. = 12$$

$$\text{Volume of hexagonal unit cell} = \text{Bare Area} \times \text{Height}$$

$$\text{Height} = 2a \sqrt{\frac{2}{3}}$$

$$a = 2a$$

$$PF = 74\%$$

$$\text{Bare area} = \frac{6\sqrt{3}}{4} a^3$$

# Locations of voids in FCC:

$$\text{For FCC} \Rightarrow Z = 4$$

$$\therefore \text{No. of THV per unit cell} = 8$$

$$\therefore \text{No. of OHV per unit cell} = 4$$

THV

⇒ Each THV is present at a distance of  $\frac{\sqrt{3}}{4} a$  on the body diagonal from the corner.

⇒ ∴ Two THV are present on each body diagonal.

$$\text{So, Total no. of THV} = 2 \times 4$$

$$= (8)$$

OHV

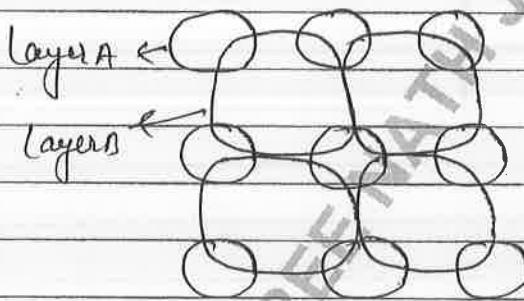
⇒ One at body centre

⇒ At all edge centre

$$\Sigma(\text{OHV}) = (1 \times 1) + (12 \times \frac{1}{2}) = 4$$

# Body Centred Cubic (Bcc Packing) :-

This packing is obtained when the spheres of first layer are slightly opened up & none of them are touching to each other. Now, the sphere of second layer are placed at the hollow surface spaces of 1<sup>st</sup> layer. Now when the 3<sup>rd</sup> layer is placed it is in same alignment with the 1<sup>st</sup> layer. This packing is not considered as closed packing due to its opened up structure.



Types = A B A B ---

Pf = 68%

Z = 2

C.N. = 8

Only WOF option is correct regarding the cubic closed packing.

① 11<sup>th</sup> & 19<sup>th</sup> layer are identical

A B C

② 7<sup>th</sup> & 13<sup>th</sup> layer are "

1 2 3

③ 8<sup>th</sup> & 12<sup>th</sup> " " "

4 5 6

④ All

-7 8 9

10 11 12

-13 14 15

16 17 18

Ques. In a closed packed structure  $n$  atom are arranged in CCP  $\gamma$  atom in every tetrahedral void and  $z$  atom in every octahedral then determine the formula if all atoms are removed along one body diagonal.

CCP or FCC

$$Z(x) = \left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4 \Rightarrow \left(6 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = \frac{3}{4} + 3 = \frac{15}{4}$$

$$Z(\gamma) = (4 \times 2 \times 1) = 8 \Rightarrow (3 \times 2) = 6$$

$$Z(z) = (1 \times 1) (12 \times \frac{1}{4}) = 4 \Rightarrow 12 \times \frac{1}{4} = 3$$

$\frac{215}{4} \gamma_6 z_3$

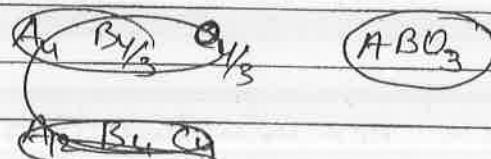
$\boxed{\gamma_5 \gamma_8 z_4}$

Ques. In solid oxide oxide ions are arranged in CCP then cation of A occupy  $\frac{1}{6}$ th of THV and cation of B occupy  $\frac{1}{3}$ th of OHV. find the formula of oxides.

$$Z(O) = \left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4$$

$$Z(A) = \left(8 \times \frac{1}{6}\right) = \frac{4}{3}$$

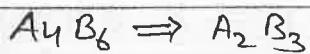
$$Z(B) = 4 \times \frac{1}{3} = \frac{4}{3}$$



Ques In a compound B atom are arranged in HCP packing and A atom are present in  $\frac{2}{3}$  th of OHV then determine the formula of compd.

$$Z(B) = 6$$

$$Z(A) = 6 \times \frac{2}{3} = 4$$



Ans: 1

Ques In a solid  $AB_2O_4$  oxides occupy <sup>one</sup> in CCP cations of A are in OHV and cations of B are equally distributed b/w THV and OHV then find out % age occupancy of both the voids.

$$Z(O) = 4 \Rightarrow CCP$$

$$Z(A) = 1 \Rightarrow OHV$$

$$Z(B) = 2 \rightarrow THV$$

$\rightarrow OHV$

Ans: 2

No. of OHV occupied per unit cell = 2

$\therefore$  THV —  $\therefore$  — = 1

$$\% OHV = \frac{2}{4} \times 100\% = 50\%$$

$$\% THV = \frac{1}{8} \times 100$$

$$= 12.5\%$$

Ques A metal crystallizes in HCP structure then determine the total No. of voids present in 0.5 mole of metal.

$$No. of atoms = 0.5 \times N_A$$

$$= 0.5 \times 6 \times 10^{23}$$

$$= 3 \times 10^{23} \text{ atoms}$$

As we know,

2 OHV are present per atom.

1 OHV is — — —

$$\therefore \text{Total OHV} = 2 \times 3 \times 10^{23} = 6 \times 10^{23}$$

$$\text{Total OHV} = 1 \times 3 \times 10^{23} = \underbrace{3 \times 10^{23}}_{9 \times 10^{23}}$$

## # Structure of Ionic Crystal :

- \* An ionic crystal is made by the packing of cations & anions.
- \* Larger ions (usually anions) form the closed packed structure that is lattice and the small ions (usually cations) occupy the void spaces.
- \* Co-ordination no. of anion = No. of nearest oppositely charged ions touching to that ions.
- \* The type of void occupied by the small ions depends upon the parameter known as limiting radius ratio which is given as follow.

\* L.R.R.  $\Rightarrow$   $x = \frac{r}{R}$

|                                      |
|--------------------------------------|
| $\rightarrow$ Radius of smaller ions |
| $\rightarrow$ Radius of larger ion   |

$x < 1 \Rightarrow$  Always

Usually,

$$x = \frac{r_+}{r_-}$$

# Limiting Radius Ratio ( $\kappa$ ) | C. No. $0.155 \leq \kappa < 0.225$ 

3

 $0.225 \leq \kappa < 0.414$ 

4

 $0.414 \leq \kappa < 0.732$ 

6

 $0.732 \leq \kappa < 1$ 

8

Types of void.

Triangular

Tetrahedral

Octahedral

Cubical.

# Rock Salt Type  
(NaCl Crystal)
 $\Rightarrow Cl^- \Rightarrow$  forms FCC } Vice-versa  
 $\Rightarrow Na^+ \Rightarrow$  All OHV }

$$\Rightarrow z(Cl^-) = 4$$

$$\Rightarrow z(Na^+) = 4$$

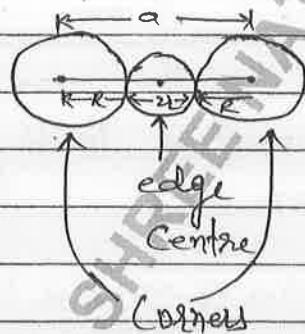
$$\Rightarrow z(NaCl) = 4Na^+ + 4Cl^-$$

$$= 4 NaCl$$

 $= 4$  formula units

$$C.N.O.(Cl^-) = 6$$

$$C.N.O.(Na^+) = 6$$

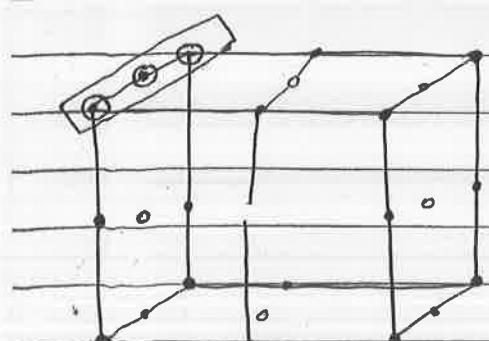


$$2r + 2R = a$$

$$\therefore r + R = \frac{a}{2}$$

 $(r + R) \Rightarrow$  Interionic distance
b/w  $\geq$  oppositely

charged ions



$$\circ = Cl^-$$

$$\bullet = Na^+$$

$$\frac{r}{R} = 0.414$$

for OHV

Example from Modules

### ② CsCl Crystal

$\Rightarrow \text{Cl}^- \rightarrow$  forms SC (at all corners) } vice  
 $\Rightarrow \text{Cs} \rightarrow$  At cubic void (at body centre) } versa

\* Note:-

It appears to be BCC

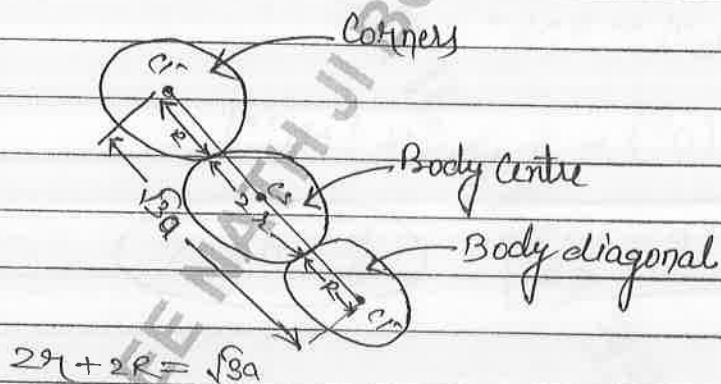
$$\Rightarrow Z(\text{Cl}^-) = \left(8 \times \frac{1}{8}\right) = 1$$

$$Z(\text{Cs}^+) = (1 \times 1) = 1$$

$$Z(\text{CsCl}) = 1\text{Cs}^+ + 1\text{Cl}^- = 1\text{CsCl} = 1$$

$$\Rightarrow \text{C.N.}(\text{Cl}^-) = 8$$

$$\text{C.N.}(\text{Cs}^+) = 8$$



$$\therefore R + R = \frac{\sqrt{3}}{2}a$$

$$\frac{R}{a} = 0.732$$

For Cubic Void

Example from module

### ③ CaF<sub>2</sub> Crystals (fluorite structure) :-

Ca<sup>+2</sup> = form fcc

F<sup>-</sup> = All BTHV

$$\Rightarrow Z(Ca^{+2}) = 4 ; Z(F^-) = 8$$

$$2(CaF_2) = 4Ca^{+2} + 8F^- \\ = 4CaF_2 = 4$$

$$\Rightarrow C.N.(Ca^{+2}) = 8 ; C.N.(F^-) = 4$$

$$\Rightarrow \boxed{r_{l+r} = \frac{\sqrt{3}}{4}a} \quad \boxed{\frac{r}{R} = 0.225}$$

for THV

④  $Na_2O$  Crystal (Anti-fluorite Structure) :-

$$\Rightarrow O^{2-} = \text{forming FCC}$$

$$Na^+ = \text{All THV}$$

$$\Rightarrow Z(O^{2-}) = 4 ; Z(Na^+) = 8$$

$$2(Na_2O) = 8Na^+ + 4O^{2-}$$

$$\Rightarrow C.N.(O^{2-}) = 8 ; C.N.(Na^{+*}) = 4$$

$$\Rightarrow \boxed{r_{l+r} = \frac{\sqrt{3}}{4}a} \quad \boxed{\frac{r}{R} = 0.225}$$

for THV

⑤  $ZnS$  Crystal (Zinc Blende Structure)  
Sphalerite

$S^{2-} \rightarrow \text{forms FCC}$

$Zn^{+2} = \text{Alternate THV (50% THV)}$

$$\Rightarrow Z(S^{2-}) = 4$$

$$Z(Zn^{+2}) = 8 \times \frac{1}{2} = 4$$

$$Z(ZnS) = 4Zn^{+2} + 4S^{2-}$$

$$= 4ZnS$$

$$= 4$$

$$C.N.(S^{2-}) = 4$$

$$C.N.(Zn^{+2}) = 4$$

$$2r + R = \frac{\sqrt{3}}{4}a$$

Example from module

Note:-

The structure of diamond is similar to ZnS crystal i.e. the carbon atom in diamond forms fcc lattice and also occupy alternate THV.

$$Z(\text{Diamond}) = \left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) + \left(8 \times \frac{1}{6}\right) = 8$$

$$\frac{\sqrt{3}}{4}a = 2r \quad (\text{C-atom})$$

$$PF = 34\%$$

$$CN(C) = 4$$

### ⑥ ZnS Crystal (Wurtzite structure):-

$S^{2-}$  form HEP

$Zn^{+2}$  = Alternate THV (50% THV)

$$Z(S^{2-}) = 6$$

$$Z(Zn^{+2}) = 12 \times \frac{1}{2} = 6$$

$$\begin{aligned} Z(ZnS) &= 6Zn^{+2} + 6S^{2-} \\ &= 6ZnS \\ &= 6 \end{aligned}$$

$$C.N.(S^{2-}) = 4$$

$$C.N.(Zn^{+2}) = 4$$

Note:-

For all ionic crystal

$$d = \frac{Z \times M}{N_A \times a^3}$$

$$PF = \frac{\text{Vol. of Cations} + \text{Vol. of Anions}}{\text{Vol. of unit cell}}$$

$$PF = \frac{Z \times \frac{4}{3} \pi (r^+)^3 + Z \times \frac{4}{3} \pi (r^-)^3}{\text{Vol. of unit cell}}$$

Note:-

Effect of Pressure and Temperature on C.N.

On Increasing P  $\Rightarrow$  C.N. increases

On Increasing T  $\Rightarrow$  C.N. decreases

Ques ① A solid crystal AB has ~~an~~ NaCl structure if radius of anion is 200pm then determine radius of cation.

Soln:-

$$\frac{r^+}{R} = 0.414 \Rightarrow \text{for OHN}$$

$$\frac{r^+}{r^-} = 0.414 \Rightarrow r^+ = 0.414 \times r^- \\ = 0.414 \times 200 \\ = 82.8 \text{ pm}$$

Ques.. The edge length of CsCl crystal is 390pm if the radius of cation is 150pm then determine the radius anion.

~~$$R = 235 \text{ pm}$$~~

$$R + r = \frac{\sqrt{3}}{2} a$$

$$r^+ + r^- = \frac{\sqrt{3}}{2} a$$

$$150 + r^- = \frac{\sqrt{3} \times 390}{2}$$

$$r^- = 187 \text{ pm}$$

Ques. Two ions  $A^+$  &  $B^-$  have a radius of 86 pm and 200 pm respectively in a closed packed crystal of  $AB$  Compd. Then determine the c.n. of cation.

$$\frac{R}{r} = \frac{86}{200} \Rightarrow 0.43 \Rightarrow \text{OHV}$$

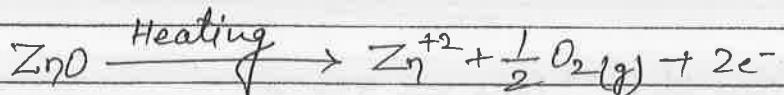
$$\text{C.N.} = 6$$

### # Defects or Imperfections in solids :—

The irregularity in the arrangement of constituent particles is known as defects or imperfections in solids.

for crystalline substance at absolute zero Kelvin temp. free enthalpy and defects are zero but with a increase in temp. both increases.

### # Due to presence of extra cations at interstitial site :-



$$\text{Zn}_{(1+x)}^0$$

Ques  $\text{NaCl}$  lattice is doped with  $10^{-5}$  mole $\text{y}$ .  $\text{SrCl}_2$  then  
 to find No. of vacancy that will be created  
 in  $58.5 \text{ g}$  of  $\text{NaCl}$

Soln:-

$$\text{Moles of NaCl} = \frac{58.5}{58.5} = 1 \text{ mol}$$

$$\text{Moles of } \text{SrCl}_2 = \frac{1 \times 10^{-5}}{100} = 10^{-7} \text{ mol}$$

$$\begin{aligned} \text{No. of } \text{Sr}^{+2} \text{ ions} &= 10^{-7} \times N_A = \text{No. of cationic} \\ &= 6.62 \times 10^{16} \text{ vacancies,} \end{aligned}$$

Ques An oxides of Fe has a formula  $\text{Fe}_{0.93}\text{O}$  then find  
 out the %age of Fe that exists in  $\text{Fe}^{+3}$  in  
 the compound.

Soln:-



→ 93% of Fe

→ 100% of ions of O

Let, No. of  $\text{Fe}^{+2}$  ions =  $x$

∴  $\text{Fe}^{+3}$  ions =  $(93-x)$

Oxidation of method :-

$$(2) x + (3)(93-x) + (-2)100 = 0$$

$$2x + 279 - 3x - 200 = 0$$

$$\underline{x = 79}$$

$$\text{No. of } \text{Fe}^{+3} \text{ ions} = 93 - x$$

$$= 93 - 79$$

$$= 14,$$

$$\% \text{ of } \text{Fe}^{+3} \text{ ions} = \frac{14}{93} \times 100$$

$$= 15\%$$

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## Atomic Structure

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\* Anode ray particle are +ively charged gaseous ion.

\* Proton was discovered when

$$\begin{array}{cccc} P & e^- & n \\ \text{e/m} & 9.6 \times 10^7 \text{ C/kg} & 1.76 \times 10^{11} \text{ C/kg} & 0 \end{array}$$

# Representation of an atom:

$$\begin{aligned} A &= \text{Mass No.} = (\text{No. of (Proton + neutron)}) = \text{No. of nucleons.} \\ Z &= \text{Atomic No.} = \text{No. of protons} \end{aligned}$$

- For a neutral atom = no. of  $e^-$  = no. of  $P = Z$ .
- For a ion = no. of  $e^- = Z -$  (charge on ion)
- No. of neutrons =  $A - Z$
- Mass no. is always a whole no. & it cannot be fractional.

\* Atomic mass of element can be fractional as it is the avg. of isotopic masses.

\* Atomic no. is a unique identity of every element and it is fixed & definite.

\* An atom & its ion differ in no. of  $e^-$ .



Ques. If  $A^{3-}$  no. of e<sup>-</sup> are 18 and mass no. of 31 then determine the atomic no., no. of neutrons and the no. of e<sup>-</sup> present in  $A^{+2}$ .

$$\text{No. of } e^- = z - (\text{charge on ion})$$

$$18 = z - (-3)$$

$$z = \underline{\underline{15}}$$

$$\text{No. of } n = A - z$$

$$= 31 - 15$$

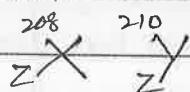
$$= \underline{\underline{16}}$$

$$\text{No. of } e^- \text{ in } A^{+2} = z - (\text{charge})$$

$$= 15 - (2)$$

$$= \underline{\underline{13}}$$

Ques The mass of X and Y having same atomic no. are 208 and 210 respectively. If X has 126 neutrons in its nucleus then find out the no. of neutrons in Y & its atomic no.



$$\text{no. of } n \text{ in } X = 126$$

$$A - z = 126$$

$$208 - z = 126$$

$$z = 82$$

$$\text{No. of } n \text{ in } Y = A - z$$

$$= 210 - 82$$

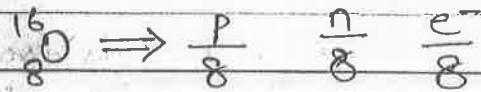
$$= 128$$

Ques If in  ${}^{18}_O$  atom mass of proton is doubled the mass neutrons made  $\gamma^{\text{th}}$  and mass of e<sup>-</sup> is tripled Calculate the % age of in atomic mass.

$$M_p \approx m_n \approx 1 \text{ amu}$$

$$m_e = 0.000559 \text{ amu}$$

$$m_e = \frac{1}{1837} \times m_p$$



Originally =  $8 \times 1 \quad 8 \times 1 - = 16 \text{ amu}$

final =  $8 \times 2 \quad 8 \times \frac{1}{4} - = 18 \text{ amu}$

$$\% \text{ Change} = \frac{\text{Change in value}}{\text{Initial value}} \times 100$$

$$= \frac{2}{16} \times 100 = 12.5\%$$

Ques. Assuming that the mass of  $^{12}\text{C}$  atom is 150 unit then under this assumption what will be the mass of 'N' atom.

$$^{12}\text{C atom} = 12 \text{ amu} = 150 \text{ unit}$$

$$1 \text{ amu} = \frac{150}{12} \text{ unit}$$

$$^{14}\text{N atom} = 14 \text{ amu} = 14 \times \frac{150}{12}$$

$$= 175 \text{ units}$$

Ques.  $X^+$ ,  $Y^{+2}$  and  $Z^-$  are isoelectronic of  $\text{CO}_2$  then pick out the correct sequence of proton in them.

(I)  $Y^{+2} < X^+ < Z^-$

$$\text{CO}_2 = 22 e^-$$

(II)  $Z^- < X^+ < Y^{+2}$

$$\text{No. of } e^- \text{ in } X^+ = 22$$

(III)  $X^+ < Y^{+2} < Z^-$

$$Z^- (\text{charge}) = 22$$

(IV)  $X^+ = Y^{+2} \neq Z^-$

$$Z^- (+) = 22$$

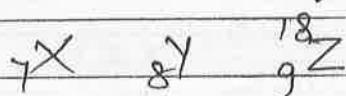
$$X^+ \Rightarrow Z = 23$$

$$Y^{+2} \Rightarrow Z = 24$$

$$Z^- \Rightarrow Z = 21$$

Ques Atom  $X_{18}Y_{18}^{18}Z_9$  are such that  $Y$  is isodiamonds, of  $X$  and  $Z$  is an isotope of  $Y$ . Then find out the  $A$  of  $X$  and  $Y$

Soln:-



$$\text{No. of 'n' in } Z = A - Z \\ = 18 - 9 = 9$$

$$\text{Mass No. of 'Y' } = n + p \\ = 9 + 8 \\ = 17$$

$$(n-p) \text{ value in } Y = 9 - 8 \\ = 1$$

$$(n-p) \text{ for } X = 1 \\ n - p = 1$$

$$n - 7 = 1$$

$$\underline{n = 8}$$

$$\text{mass no. of } X = n + 7 \\ = 8 + 7 \\ = \underline{\underline{15}}$$

Ques An element  $M$  has three isotope whose isotopic mass are  $11, 12, 13$  respectively. If there present ~~mass~~ occurrence in nature is  $85\%, 50\%, 5\%$  respectively then calculate the avg. atomic wt. of  $M$ .

Soln:-

$$\text{avg. atomic wt.} = \frac{(11 \times 85) + (12 \times 10) + (13 \times 5)}{100}$$

$$= \frac{935 + 120 + 65}{100}$$

$$= \frac{1120}{100} = \underline{\underline{11.2}}$$