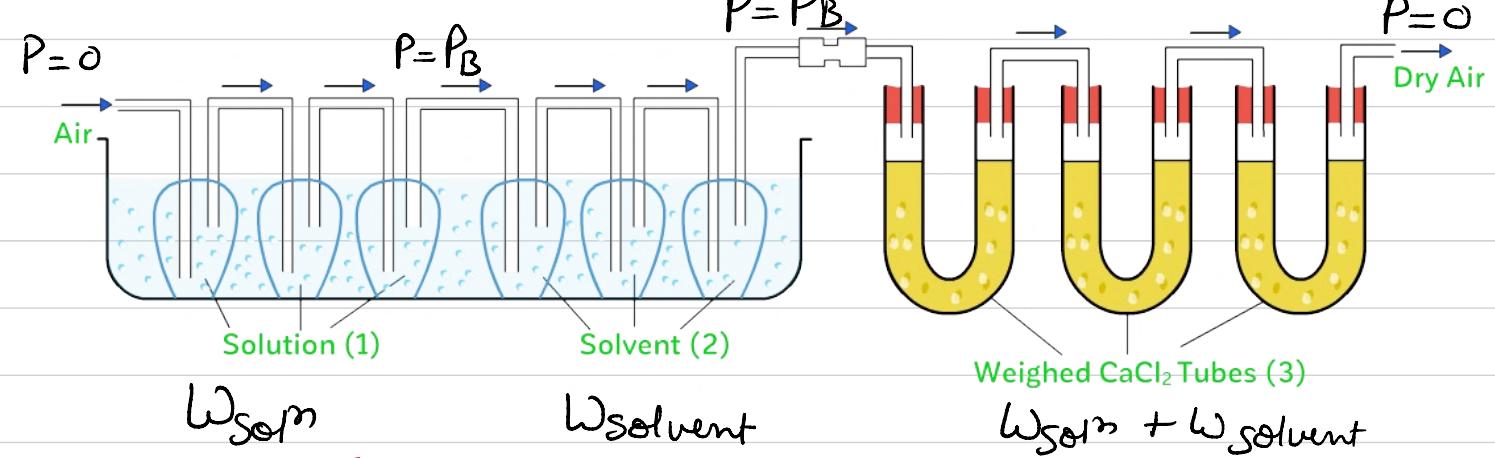


# Ostwald Walker method

Experimental method to calculate relative lowering.



$w_{\text{Soln}}$

$w_{\text{solvent}}$

$w_{\text{Soln}} + w_{\text{solvent}}$

$$w_{\text{Soln}} \propto (P_B^\circ - 0) \quad \text{--- I}$$

$$w_{\text{solvent}} \propto (P_B^\circ - P_B) \quad \text{--- II}$$

$$(w_{\text{Soln}} + w_{\text{solvent}}) \propto (P_B^\circ - 0) \quad \text{--- III}$$

Eqn I/II

$$\frac{w_{\text{solvent}}}{w_{\text{Soln}} + w_{\text{solvent}}} = \left( \frac{P_B^\circ - P_B}{P_B^\circ} \right) = X_A$$

$w_{\text{Soln}} = \text{wt loss of Solution}$

$w_{\text{solvent}} = \text{wt loss of Solvent}$

# Van't hoff factor (i)

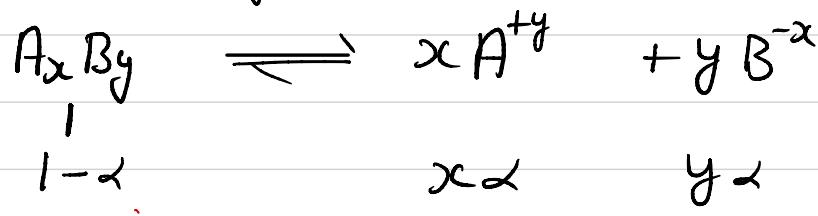
this is ratio of final No of solute particle in soln to initial no of solute particles added.

$$i = \frac{\text{Observed colligative property}}{\text{Normal or theoretical colligative property}} = \frac{(C_p)_f}{(C_p)_i}$$

$$i = \frac{\text{Normal Molar mass}}{\text{Observed molar mass}} = \left(\frac{M_i}{M_f}\right)$$

$$i = \frac{\text{Actual number of particles}}{\text{Expected number of particles}} = \left(\frac{N_f}{N_i}\right)$$

## ① Dissociation of Solute :-



$$i = \frac{1-\alpha + x\alpha + y\alpha}{1} \Rightarrow i = 1 - \alpha + x\alpha + y\alpha$$

$$\# i > 1$$

$$N_f > N_i$$

$$C_{pf} > C_{pi}$$

$$M_i > M_f$$

$$\text{eg: } \textcircled{a} \text{ NaCl} \Rightarrow i = 2$$

$$\textcircled{b} \text{ C}_6\text{H}_{12}\text{O}_6 \Rightarrow i = 1$$

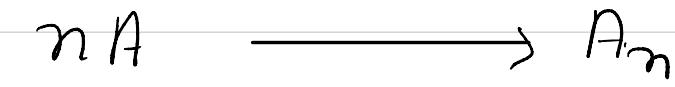
$$\textcircled{c} \text{ MgCl}_2 \Rightarrow i = 3$$

$$\textcircled{d} \text{ CH}_3\text{COOH} \quad (\alpha = 0.1)$$



$$\Rightarrow i = (1 + \alpha) = 1.1$$

## ② Association of Solute :-



$$\frac{1}{(1-\alpha)} \quad \left(\frac{\alpha}{n}\right)$$

$$j = \frac{1 - \alpha + \alpha/n}{1} \Rightarrow j = (1 - \alpha + \alpha/n) < 1$$

$$\Rightarrow j < 1$$

$$\left. \begin{array}{l} N_f < N_i \\ (C_p)_f < (C_p)_i \\ M_f > M_i \end{array} \right\}$$

e.g.  $\text{CH}_3\text{COOH}$  in Benzene

$$(\alpha = 0.2)$$



$$j = 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2} = \underline{\underline{0.9}}$$

# Colligative properties:-

Properties of solution which depend on no of Solute particles are called colligative properties.

Sol<sup>n</sup> = Non volatile solute + Volatile liquid.

No of Solute particle ↑ → Colligative Property ↑

following properties are colligative properties -

- ① Relative lowering in V.P.
- ② Elevation in B.P. ( $\Delta T_b$ )
- ③ Depression in F.P. ( $\Delta T_f$ )
- ④ Osmotic pressure ( $\Pi$ )

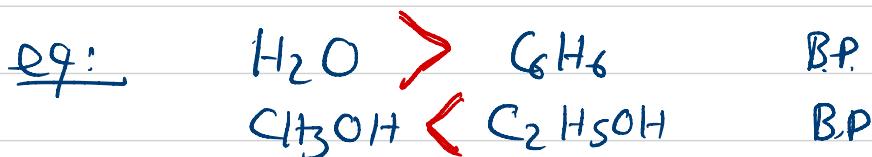
## ① Relative lowering in V.P. :-

$$\frac{P_B^o - P_B}{P_B^o} = X_A = \frac{i n_A}{i n_A + n_B}$$

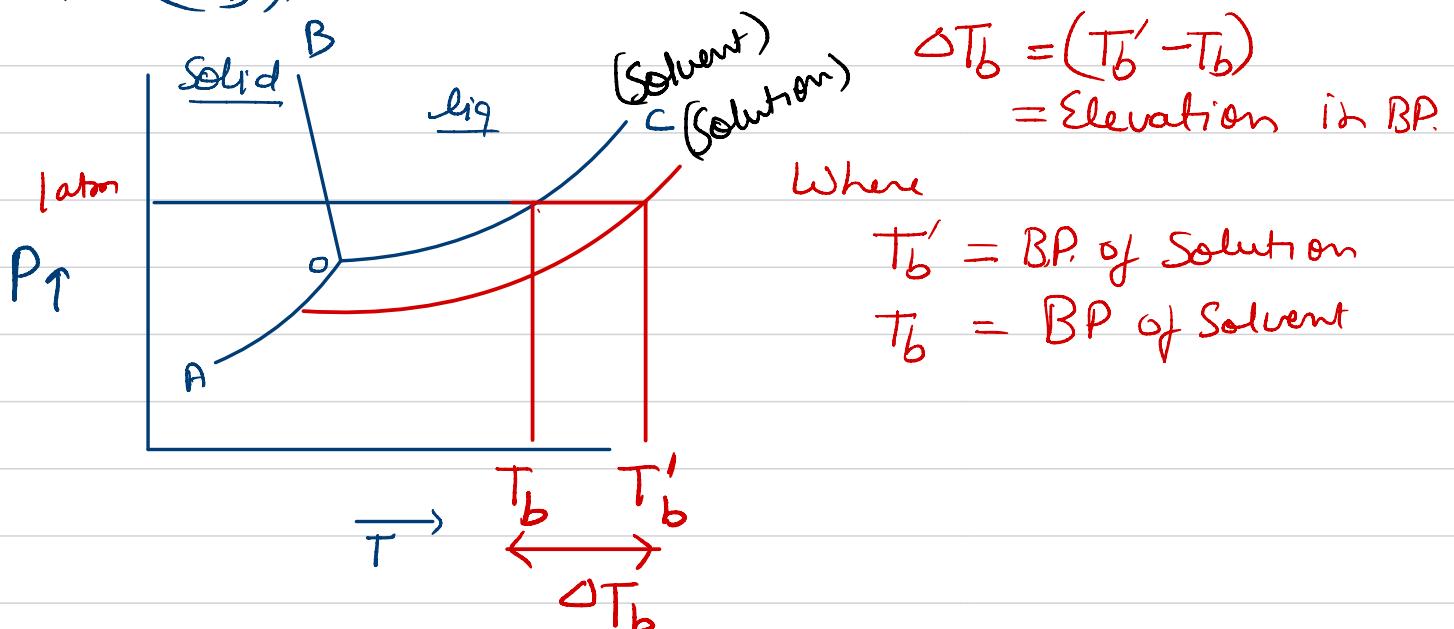
## ② Elevation in B.P ( $\Delta T_b$ ) :-

Temp at which V.P. of liquid become equal to external pressure is called as B.P. ( $T_b$ )

If external pressure is 1 atm then BP is called normal BP.



When we add a non volatile solute into volatile solvent then decrease in V.P. take place so B.P. increases. This increase in B.P. is called as elevation in B.P. ( $\Delta T_b$ ).



$$\Delta T_b \propto \text{No of Solute particle} \propto m$$

$$\Delta T_b \propto m$$

$$\Delta T_b = k_b m$$

Where  $m = \frac{n_A}{W_B (\text{kg})}$   
= molality.

If solute is dissociating /  
associating

$k_b$  = molal elevation cont

$\Theta_b$

molar ebullioscopic Cont

$$\Delta T_b = i k_b \cdot m$$

Note:

① No of Solute particle  $\uparrow \Rightarrow \Delta T_b \uparrow \Rightarrow T_b' \uparrow$

②

$$k_b = \frac{RT_b^2}{1000 \cdot \left( \frac{\Delta H_{\text{vap}}}{M} \right)}$$

depend on Solvent only

Where  $R$  = Gas cont

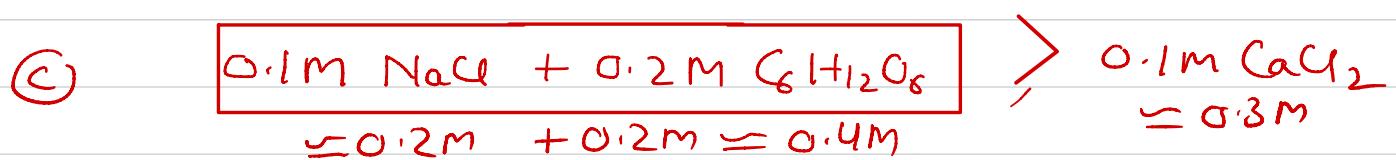
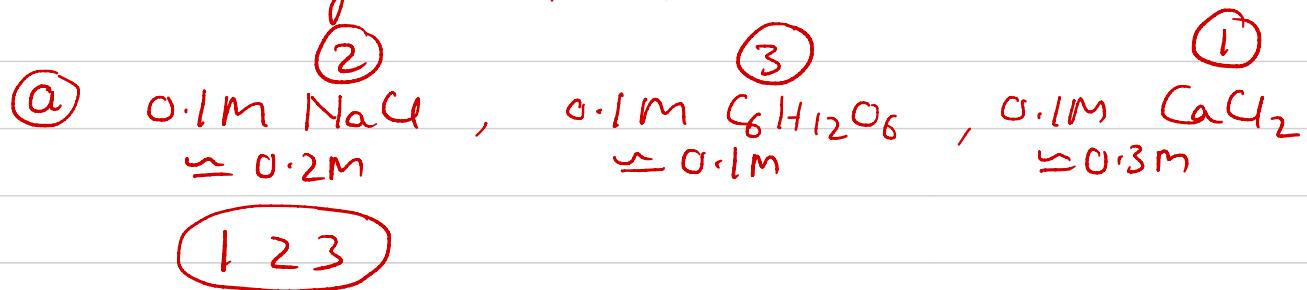
$T_b$  = BP of Solvent

$\Delta H_{\text{vap}}$  = Enthalpy of  
Vaporization of

Solvent

$M$  = Molar mass of  
Solvent

Eg. Write down the following sol<sup>n</sup> in decreasing order of their B.P.



Prob: Calculate B.P of 0.1 molal NaCl aq sol<sup>n</sup>  
 $K_b$  for  $\text{H}_2\text{O} = 0.5$

$$\Delta T_b = i K_b m = 2 \times 0.5 \times 0.1 = 0.1$$

$$T_b' - T_b = 0.1 \Rightarrow T_b' = 100.1^\circ\text{C} \text{ or } \underline{373.1\text{K}}$$

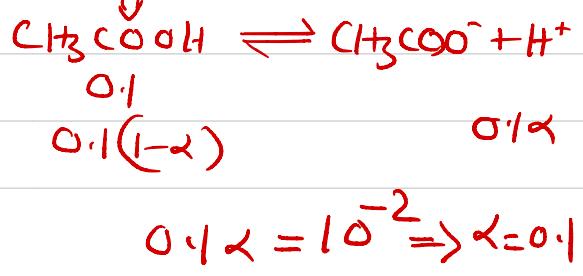
Prob: Calculate B.P of 0.1 M  $\text{CH}_3\text{COOH}$  sol<sup>n</sup>, having pH = 2. Given  $K_b(\text{H}_2\text{O}) = 0.5$  and assume molality and molarity to be same.

$$(T_b' - T_b) = i K_b \cdot m$$

$$= (1.1) \times 0.5 \times 0.1 = 0.055$$

$$T_b' = 100.055^\circ\text{C}$$

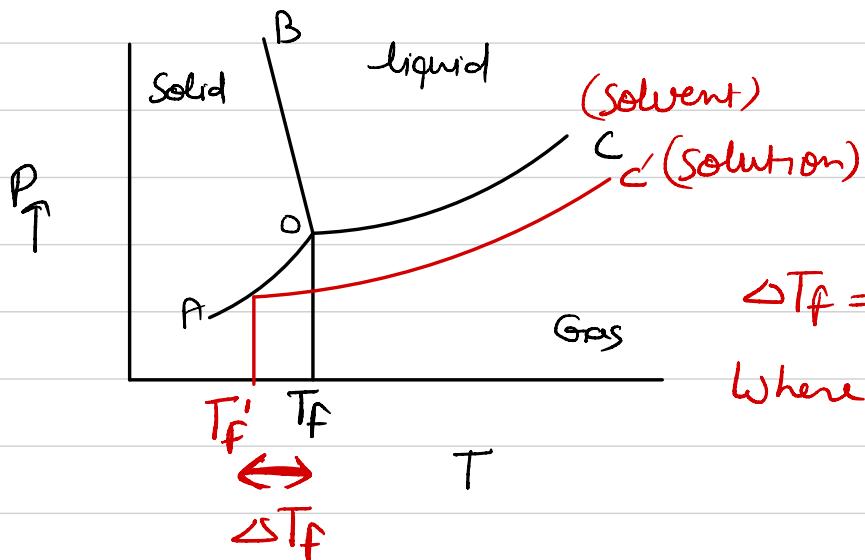
or  $373.055\text{K}$



## ② Depression in F.P. ( $\Delta T_f$ ):

Temp. at which solid and liquid are in equib is called as F.P. ( $T_f$ ).

Or Temp at which V.P. of solid and liq. become equal is called F.P.



$$\Delta T_f = (T_f - T_f') = \text{Depression in F.P.}$$

Where

$T_f$  = F.P. of Solvent

$T_f'$  = F.P. of Solution

$\Delta T_f \propto$  No. of Solute particle  $\propto m$

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

for dissociation / association of solute

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

Where  $k_f$  = Molal depression const  
or Cryoscopic const

$$m = \text{molality} = \frac{\text{m}_A}{W_B(\text{kg})}$$

Note:

① No of solute particle  $\uparrow$  =  $\Delta T_f \uparrow \Rightarrow T_f \downarrow$

$$② K_f = \frac{RT_f^2}{1000 \frac{\Delta H_{\text{fusion}}}{M}}$$

Depend on solvent

Where  $R$  = Gas cont

$T_f$  = F.P. of Solvent

$\Delta H_{\text{fusion}}$  = Enthalpy of fusion

$M$  = Molar mass of Solvent.

43. How many grams of sucrose (molecular weight = 342) should be dissolved in 100 g water in order to produce a solution with a  $104.76^\circ\text{C}$  difference between the freezing point and the boiling point temperature? ( $K_f = 1.86$ ,  $K_b = 0.52$ )

- (a) 34.2 g      (b) 68.4 g  
 (c) 684 g      (d) 313.06 g

$$T_b' - T_b = K_b \times m$$

$$T_f - T_f' = K_f \times m$$

$$(T_b' - T_f') - (T_b - T_f) = (K_f + K_b) \times m$$

$$104.76 - 100 = 4.76 = 2.38 \text{ m}$$

$$m = 2 = \frac{n_A}{0.1} \Rightarrow n_A = 0.2$$

$$n_A = 68.4$$



$$i \rightarrow \alpha/2$$

$$\gamma = (1 - \alpha/2)$$

$$1.96 = (1 - \frac{\gamma}{2}) \times 4.9 \times \frac{2/122}{25/1000}$$

$$\alpha = 0.78$$