

### 5.31. VAN'T HOFF FACTOR

To account for abnormal cases, van't Hoff introduced a factor  $i$  known as the van't Hoff factor

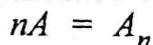
$$i = \frac{\text{Observed colligative property}}{\text{Calculated (normal) colligative property}}$$

Since colligative properties vary inversely as the molecular mass of the solute, it follows that

$$i = \frac{\text{Calculated (normal) molecular mass}}{\text{Observed molecular mass}}$$

#### Relation between degree of association and van't Hoff factor

Let us consider the association of  $n$  molecules of a solute  $A$  to give one molecule of  $A_n$



Let the degree of association be  $\alpha$ . If we start with 1 mole of  $A$ , the number of moles that associate is  $\alpha$  and the number of moles that remain unchanged is  $1 - \alpha$ .

$\alpha$  moles on association will give  $\alpha/n$  moles

$$\text{Total number of moles at equilibrium} = \frac{\alpha}{n} + (1 - \alpha)$$

van't Hoff factor is the ratio of observed colligative property to calculated colligative property. And colligative property is proportional to the number of moles of the solute. Hence

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

#### Relation between degree of dissociation and van't Hoff factor

Let us consider the dissociation of molecule to give  $n$  molecules or ions in solution



Let us start with 1 mole of  $A$  and let  $\alpha$  be the degree of dissociation.

At equilibrium

No. of moles of undissociated substance =  $1 - \alpha$

No. of moles of dissociated substance =  $n\alpha$

(one molecule dissociates to give  $n$  molecules)

Total number of moles of solute at equilibrium =  $1 - \alpha + n\alpha$

Hence van't Hoff factor ( $i$ ) =  $\frac{1 - \alpha + n\alpha}{1}$

## SOLVED PROBLEMS ON ABNORMAL MOLECULAR MASSES AND VAN'T HOFF FACTOR

**Example 1.** 0.1 M solution of  $KNO_3$  has an osmotic pressure of 4.5 atmosphere at 300 K. Calculate the apparent degree of dissociation of the salt.

**Solution.**  $\pi_{\text{obs}} = 4.5 \text{ atm}$   $C = 0.1 \text{ moles/litre}$

$n = 2$  because one  $KNO_3$  molecule dissociates to give two ions,  $K^+$  and  $NO_3^-$

$T = 300$

Substituting the values in the equation

$$\pi = C \cdot R \cdot T$$

$$\pi = 0.1 \times 0.082 \times 300$$

$$\pi = 2.6$$

$$i = \frac{\text{Observed osmotic pressure}}{\text{Calculated osmotic pressure}}$$

$$= \frac{4.5}{2.6} = 1.83 \quad \dots(1)$$

Also

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

or

$$i = 1 + \alpha(n - 1) \text{ or } \alpha(n - 1) = i - 1$$

or

$$\alpha = \frac{i - 1}{n - 1} \quad \dots(2)$$

Substitute the value of  $i$  from (1) in (2)

$$\alpha = \frac{1.83 - 1}{2 - 1} \quad \text{or } \alpha = 0.83$$

or

$$= 83\%$$

**Example 2.** Calculate the osmotic pressure of 20% anhydrous calcium chloride solution at 273 K, assuming that the solution is completely dissociated. ( $R = 0.082 \text{ lit. atm K}^{-1} \text{ mol}^{-1}$ ).

**Solution.** Molecular mass of  $CaCl_2 = 40 + 71 = 111$

Since solution is 20%

$\therefore$  Weight of  $CaCl_2$  per litre = 200 g

$$V = 1 \text{ litre}$$

$$T = 273 \text{ K}$$

