

## Abnormal molecular masses.

Molecular masses can be calculated by measuring any of the colligative properties. The relation between colligative properties and molecular mass of the solute is based on following assumptions.

- (1) The solution is dilute, so that Raoult's law is obeyed.
- (2) The solute neither undergoes dissociation nor association in solution.

In case of solutions where above assumptions are not valid we find discrepancies between observed and calculated values of colligative properties. These anomalies are primarily due to

- (i) Association of solute molecules.
- (ii) Dissociation of solute molecules.

(i) **Association of solute molecules:** Certain solutes in solution are found to associate. This eventually leads to a decrease in the number of molecular particles in the solutions. Thus, it results in a decrease in the values of colligative properties. As already discussed, the colligative properties are inversely related to the molecular mass,

Colligative property  $\propto \frac{1}{\text{molecular mass of solute}}$ , therefore, higher values are obtained for molecular masses than normal values for unassociated molecules.

(ii) **Dissociation of solute molecules:** A number of electrolytes dissociate in solution to give two or more particles (ions). Therefore, the number of solute particles, in solutions of such substances, is more than the expected value. Accordingly, such solutions exhibit higher values of colligative properties. Since colligative properties are inversely proportional to molecular masses, therefore, molecular masses of such substances as calculated from colligative properties will be less than their normal values.

**Van't Hoff's factor (i):** In 1886, Van't Hoff introduced a factor 'i' called Van't Hoff's factor, to express the extent of association or dissociation of solutes in solution. It is ratio of the normal and observed molecular masses of the solute, i.e.

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

In case of association, observed molecular mass being more than the normal, the factor  $i$  has a value less than 1. But in case of dissociation, the Van't Hoff's factor is more than 1 because the observed molecular mass has a lesser value than the normal molecular mass. In case there is no dissociation the value of ' $i$ ' becomes equal to one.

Since colligative properties are inversely proportional to molecular masses, the Van't Hoff's factor may also be written as:

$$i = \frac{\text{Observed value of colligative property}}{\text{Calculated value of colligative property assuming no association or dissociation}}$$

$$i = \frac{\text{No. of particles after association or dissociation}}{\text{No. of particles before association or dissociation}}$$

Introduction of the Van't Hoff factor modifies the equations for the colligative properties as follows:

$$\text{Relative lowering of vapor pressure} = \frac{P_A^\circ - P_A}{P_A^\circ} = i X_B$$

$$\text{Elevation of boiling point, } \Delta T_b = i k_b m$$

$$\text{Depression in freezing point, } \Delta T_f = i k_f m$$

$$\text{Osmotic pressure, } \pi = \frac{i n R T}{V}; \pi = i C R T$$

From the value of " $i$ ", it is possible to calculate degree of dissociation or degree of association of substance.

**Degree of dissociation ( $\alpha$ ):** It is defined as the fraction of total molecules which dissociate into simpler molecules or ions.

$$\alpha = \frac{i-1}{m-1}; m = \text{number of particles in solution}$$

**Degree of association ( $\alpha$ ):** It is defined as the fraction of the total number of molecules which associate or combine together resulting in the formation of a bigger molecules.

$$\alpha = \frac{i-1}{1/m-1}; m = \text{number of particles in solution}$$

