

Molecular weight Determination

$$M_2 = \frac{w_2}{V} \frac{RT}{\Pi} = C_2' \frac{RT}{\Pi} \quad \text{--- } ①$$

①

This is equation to calculate M.wt. of solute in dil. soln.
But if solution is concentrated, then this equation will have an extra term

$$\Pi = \frac{RT}{M_2} C_2' + BC_2'^{1/2}$$

$$\frac{\Pi}{C_2'} = \frac{RT}{M_2} + BC_2' \quad \text{--- } ②$$

Value of 'B' depends on the solute-solute interaction

If a graph is plotted between $\frac{\Pi}{C_2'}$ vs C_2'

and line is extrapolated to zero concentration M_2 can be calculated from the intercept

If $\frac{\Pi}{C_2'} = \frac{RT}{M_2}$ for a particular solvent
 $C_2' \rightarrow 0$

and temp., $B = 0$

Since Π depends on the no. of molecules,
hence M.wt. determined in this way is
a number average molecular weight

Types of Molar Masses

Macromolecules like proteins are of not
of same size. In a solution of macromolecules

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②

of same size in a solution of macromolecules

(2) there is a mixture of different sizes. The molar mass of such a solute will be the average of the sum of the molar masses of all units of solute.

There are two types of molar masses

- (1) Number Average Molar Mass
- (2) wt. of mass average molar Mass

(1) Number Average Molar Mass (M_n) Let $x_1, x_2, x_3 \dots$ are mole fractions of different units of the macromolecule and $M_1, M_2, M_3 \dots$ are their molar masses

The Molar Mass of macromolecule

$$M_n = x_1 M_1 + x_2 M_2 + \dots = \sum x_i M_i$$

Mole fraction is $x_i = \frac{N_i}{\sum N_i}$

$$M_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{N_1 M_1 + N_2 M_2 + \dots}{\sum N_i}$$

R.H.S is the average of the sum of the molar mass of different units.

e.g if a macromolecule consists of 30% of molecules of molar mass 20,000 g/mole, 40% of molecules of " " 30,000 g/mole & 30% of " " " 60,000 g/mol. cal. are

No. average molar mass of macromolecule

$$M_n = \frac{30 \times 20,000 + 40 \times 30,000 + 30 \times 60,000}{100} = 36,000 \text{ g/mole}$$

It is calculated by $\frac{20+40+30}{3}$ any of the colligative properties

(2) Mean Average Molar Mass M_w : If $w_1, w_2, w_3 \dots$ are the masses of different units of macromolecules & M_1, M_2, \dots are their molar masses, then mean average molar mass

$$M_w = \frac{w_1 M_1 + w_2 M_2 + w_3 M_3 + \dots}{w_1 + w_2 + w_3}$$

$$= \frac{\sum w_i M_i}{\sum w_i} \quad \therefore w_i = n_i M_i$$

$$M_w = \frac{\sum n_i M_i \times M_i}{\sum n_i M_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

Same values is for M_n . substituted

$$M_w = \frac{30(20,000)^2 + 40(30,000)^2 + 30(60,000)^2}{30(20,000) + 40(30,000) + 30(60,000)} \\ = 43333 \text{ g/mole}$$

Molar Mass in this way is estimated by diffusion, sedimentation, light scattering

Q1 A mixture was prepared by dissolving 17.19 g of sucrose, 9g of glucose & 6g of urea in 300 ml of water. Calculate

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(1) No. average M_n & M_w of the solutes in the mixture.

$$M_2 = 342, M_3 = 180, M_4 = 60 \text{ g/mole}$$

(2) The osmotic pressure of solution at 27°C

(3) Molar Mass of solute from O.P. by assuming that entire mass ($17.1 + 9.0 + 6 = 32 \text{ g}$) was of only one hypothetical solute

$$\text{Ans } M_n = \sum x_i M_i$$

$$n_2 + n_3 + n_4 = \frac{17.1}{342} + \frac{9}{180} + \frac{6}{60} = 0.2$$

$$x_2 (\text{sucrose}) = \frac{0.05}{0.2} = 0.25$$

$$x_3 (\text{glucose}) = \frac{0.05}{0.2} = 0.25$$

$$x_4 (\text{urea}) = \frac{0.1}{0.2} = 0.5$$

$$\begin{aligned} \therefore M_n &= x_2 M_2 + x_3 M_3 + x_4 M_4 \\ &= 0.25 \times 342 + 0.25 \times 180 + 0.5 \times 60 \\ &= 160.5 \text{ g/mole} \end{aligned}$$

$$M_w = \frac{w_2 M_2 + w_3 M_3 + w_4 M_4}{w_2 + w_3 + w_4}$$

$$= \frac{n_2 M_2^2 + n_3 M_3^2 + n_4 M_4^2}{n_1 M_1 + n_2 M_2 + n_3 M_3}$$

$$= \frac{0.25 \times (342)^2 + 0.25 \times (180)^2 + 0.5 \times (60)^2}{0.25 \times 342 + 0.25 \times 180 + 0.5 \times 60}$$

$$= 243.8 \text{ g/mole}$$

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$$(2) \quad O.P = \frac{n_2 RT}{V} \quad \text{All molar of solute} \quad (3)$$

$$= n_2 + n_3 + n_4 = [0.2 \text{ mole} \times 0.082 \text{ atm dm}^3 \text{ mole}^{-1} \text{ K}^{-1} \times 300 \text{ K}] \times \frac{1}{3 \text{ dm}^3}$$

$$= 1.64 \text{ atm}$$

(3) If 32.1 g is mass of a single solute of unknown molar mass dissolved in 3 dm³ of H₂ O then

$$\Pi = \frac{w_2 RT}{M_2 V}$$

$$M_2 = \frac{w_2 RT}{\Pi V}$$

$$= \frac{32.1 \text{ g} \times 0.082 \text{ atm dm}^3 \text{ mole}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{1.64 \text{ atm} \times 3 \text{ dm}^3}$$

$$= 160.5 \text{ g/mole}$$

this is no. average molar mass calculated from O.P.

All the colligative properties studied share a common characteristic that each involving mole fraction of solute & each is independent of the individual prop. of solute

$$\text{POCO} = \frac{P_1^* - P_1}{P_1^*} = \frac{\Delta h_{vap}}{RT_{b2}} \quad \Delta T_b = \frac{\Delta h_f}{R T_{o2}} \quad \Delta T_f = \frac{\Pi V}{RT}$$

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This expression can be used to deduce

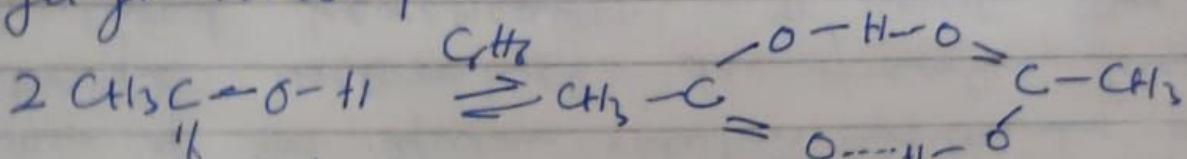
(1.)

any observed relationship betⁿ solute various colligative prop & hence it is possible to cal. other colligative props if any one is experimentally observed

Colligative Properties of chemically Reacting soluta.

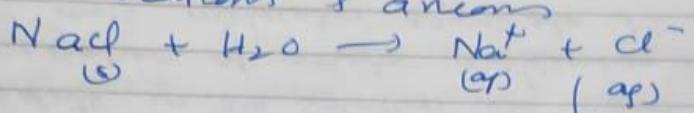
The observed colligative properties of a solution containing solute which can undergo association or dissociation are different than those calculated using ideal behavior. Difference is because the no. of particles (atoms, molecules or ions) of a solute in a solution is different than the no. of species before dissociation or association.

(1) Association - The experimentally measured colligative properties of solution of acetic acid in benzene is lower than calculated by using theoretical equations & it suggests that the number of molecules of the solute in the solution are reduced i.e. there is association of solute molecules in the solution. Two or more molecules aggregate to form a bigger molecule. e.g. $\text{C}_2\text{H}_5\text{COOH}$ forms a dimer via hydrogen bonding



solution ⁶ contains a mixture of monomer & dimer. e.g. $\text{C}_8\text{H}_8\text{COOH}$ also dimerize in C_6H_6

Dissociation → The experimentally measured colligative properties of an aqueous solution containing an electrolyte NaCl or KCl are greater than calculated theoretically. It suggests that solute undergoes dissociation in solutions & produces cations & anions.



Vant' Hoff factor → The ratio of experimentally measured colligative property & calculated colligative prop. is called Vant-Hoff factor & is denoted by i

$$i = \frac{\text{Measured colligative prop}}{\text{Calculated colligative Prop}}$$

$$i = \frac{(\Delta P)_o}{(\Delta P)_c} = \frac{(\Delta T_b)_o}{(\Delta T_b)_c} = \frac{(\Delta T_f)_o}{(\Delta T_f)_c} = \frac{(\Pi)_o}{(\Pi)_c}$$

'o' stands for observed, 'c' stands for calculated

$$(\Delta T_b)_o = i (\Delta T_b)_c = i K_b m$$

$$(\Pi)_o = i (\Pi)_c = i CRT = i mRT$$

Since colligative prop is directly proportional to the no. of moles & inversely proportional to M-wt. of solute.

$$i = \frac{\text{No. of moles after dissociation or Association}}{\text{No. of moles before dissociation or Association}}$$

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• Π = osmotic pressure

(?)

$$i = \frac{\text{Molecular weight Expected}}{\text{Molecular weight observed}}$$

(8)

- (1) For a "normal solute", $i = 1$, F.M.Wt and Measured Molecular weight are equal
- (2) For a solute which undergoes dissociation, $i > 1$, and formula Molecular weight is greater than Measured M.Wt
- (3) For a solute which undergoes association, $i < 1$, Formula Molecular weight is less than Measured Molecular weight. This is called abnormal Molecular weight.
e.g. CH_3COOH Normal Molecular Mass is 60 but in C_6H_6 solution it is 118. The increase in molecular mass is due to dimerization of CH_3COOH in C_6H_6

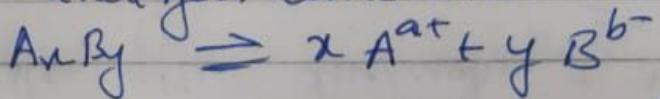
Colligative Property is degree of dissociation

Measured colligative prop of a solution containing an electrolyte is greater than calculated one. This property is used to calculate/evaluate the extent of ionization of the solute in solution.

e.g. Let there be of solute of general formula

AnBy (NaCl , CuSO_4 , Na_2SO_4 , MgCl_2 , FeCl_3 etc.)

that undergoes dissociation in solution



If $x=1$ & $y=2$ then $a=2$, $y=1$ like $\text{MgCl}_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{Cl}^-$

Let 'd' be degree of dissociation of the solute & 'n' is its initial moles

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After dissociation molar of $A_nB_y = n(1-\alpha)$ ①

Moles of $A^{a+} = x \alpha n$

Moles of $B^{b-} = y \alpha n$

Total molar after dissociation = $n[1 - \alpha + x \alpha + y \alpha] = n[1 + \alpha(n+y-1)]$

Experimentally observed colligative property like osmotic pressure $\Pi_0 \propto n[1 + \alpha(n+y-1)]$ & calculate $\Pi_0 \cdot P \propto n$

$$\frac{\Pi_0}{\Pi_C} = \frac{n[1 + \alpha(n+y-1)]}{n} = i$$

$$= \frac{[1 + \alpha(n+y-1)]}{1} = i$$

$$\frac{\Pi_0}{\Pi_C} = \alpha = \frac{i-1}{n+y-1}$$

$$\alpha = \frac{\left(\frac{\Pi_0}{\Pi_C}\right) - 1}{n+y-1}$$

Π_0 = experimentally measured & T_C is calculate from the relation $\Pi_C = mRT \approx C RT$

Similarly any colligative prop. can be used to calculate α .

Q1 The freezing point of a sample of abnormal blood was found to be -0.402°C . Estimate o.p. at 37°C . $K_{f, \text{H}_2\text{O}} = 1.86$

$$\Delta T_f = 0.402$$

$$(m-f)_C = K_f m = 1.86 m$$

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$$\frac{(\Delta T_f)_o}{(\Delta T_f)_c} = i = \frac{0.402}{1.86m} \longrightarrow ①$$

(10)

$$i = \frac{n_o}{n_c} = \frac{n_o}{CRT} = \frac{n_o}{mRT} \quad ②$$

From eq. ① & ②

$$\frac{(n)_o}{mRT} = \frac{0.402}{1.86m}$$

$$n_o = \frac{0.402 \times RT}{1.86} = \frac{0.402 \times 0.082 \times 310}{1.86}$$

$$= 5.5 \text{ atm.}$$

For the molar mass of a non volatile solute in terms of different colligative properties is given in the table

Colligative Properties	Definition	Molar Mass
(1) Lowering of vapour Pressure	$\Delta P = P_i^* n_2$	$M_2 = \frac{P_i^* M_1 w_2}{\Delta P w_1}$
(2) Elevation of Boiling Point	$\Delta T_b = K_b m$	$M_2 = \frac{1000 K_b w_2}{\Delta T_b w_1}$
(3) Depression Freezing Point	$\Delta T_f = K_f m$	$M_2 = \frac{1000 K_f w_2}{\Delta T_f w_1}$
(4) Osmotic Pressure	$\Pi = \frac{n_2 R T}{V}$	$M_2 = \frac{R T}{\Pi} \frac{w_2}{w_1}$

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