Colligative Properties

ABNORMAL COLLIGATIVE PROPERTIES OF SOLUTIONS

In the derivation of colligative properties, it has been assumed that the molecular form of the solute remains unchanged in solution. Furthermore the solutions are dilute and behave ideally. In such cases, experimental value of the colligative property is in agreement with the theoretically calculated value. However, there are certain substances like solutions of salts, acids or bases in water or acetic acid in benzene where the experimental value differs considerably from the calculated value. Such solutions are said to be abnormal solutions. The abnormalities observed in such solutions are of two types: (i) dissociation of solute molecules, and (ii) association of the solute molecules.

Association leads to a decrease in the number of solute particles and hence the colligative proper-ties will show lower values. In case of dissociation, the number of solute particles increases and consequently, the colligative properties will show abnormally enhanced values.

In order to account for the abnormal behaviour of such solutions, van't Hoff introduced a factor 'i' which is called the van't Hoff factor and is defined as the ratio of the experimental value of a colligative property to the calculated value of that property, i.e.,

$$i = \frac{\text{Experimental value of the colligative property}}{\text{Calculated value of the property when the solution behaves ideally}}$$

Since the colligative property is proportional to number of solute particles in solution,

Hence,
$$i = \frac{\text{Actual number of solute particles present in solution}}{\text{Number of solute particles in solution if it behaves ideally}}$$

or, we may write

$$i = \frac{(\Delta T_b)_{\text{obs}}}{(\Delta T_b)_{\text{cal}}} = \frac{(\Delta T_f)_{\text{obs}}}{(\Delta T_f)_{\text{cal}}} = \frac{(\Delta P/P^0)_{\text{obs}}}{(\Delta P/P^0)_{\text{cal}}} = \frac{\pi_{\text{obs}}}{\pi_{\text{cal}}} = \frac{M_{\text{cal}}}{M_{\text{obs}}} \qquad \text{.............................(41)}$$

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where M is the molar mass of the solute and ΔT_b, ΔT_f, $\Delta P/P^0$ and π are the boiling point elevation, freezing point depression, relative lowering of vapour pressure and the osmotic pressure of the solution respectively. The subscripts 'obs' and 'cal' refer to the experimental and calculated values of the colligative properties.

(i) Dissociation of Solute: Consider an electrolyte A_xB_y which partly dissociates in solution yielding x ions of A^{y+} and y ions of B^{x-} and if a is the degree dissociation, i.e., the fraction of the total number of molecules which dissociates and C the initial concentration of the solute, then the dissociation equilibrium in solution can be represented as

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

Initial concentration $\qquad$ C $\qquad$ 0 $\qquad$ 0

Concentration at equilibrium $\qquad$ $C(1-\alpha)$ $\quad$ $Cx\alpha$ $\quad$ $Cy\alpha$
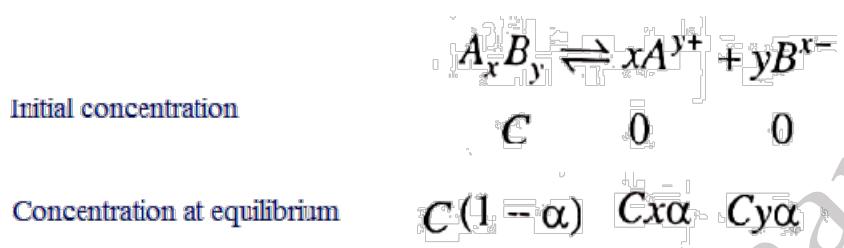
The total number of moles at equilibrium $= Cx\alpha + Cy\alpha + C(1-\alpha)$

$$= C[1 - \alpha + x\alpha + y\alpha] = C[1 + \alpha(x + y - 1)]$$

Hence, $\qquad$ $$i = \frac{C[1 + \alpha(x + y - 1)]}{C}$$ ....(42)

and the degree of dissociation α is given by

$$\alpha = \frac{i - 1}{(x + y - 1)}$$ ....(43)

Equation (43) is applicable to any colligative property and provides an important method for calculating the degree of dissociation of a solute. If alpha = 1 i.e., the dissociation is complete, i = x + y the observed colligative property will be (x + y) times the calculated value. On the other hand, when no dissociation occurs, alpha = 0 and i = 1 the calculated and observed values will be equal.

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(ii) Association of Solute: Consider the association of a solute A into its associated form $(A)_n$ according to the reaction

$$nA \rightleftharpoons (A)_n$$
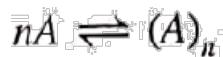
where n is the number of molecules of solute which combine to form an associated species. If C is the initial concentration and α the degree of association of the solute, at equilibrium the number of moles of the undissociated solute is $C(1 - \alpha)$ and that of associated form is $C\alpha/n$.

The total number of moles in solution is given by

$$C(1 - \alpha) + \frac{C\alpha}{n}$$

or

$$C\left(1 - \alpha + \frac{\alpha}{n}\right)$$
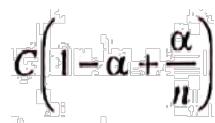
Hence the Van't Hoff factor,

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

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

$$= \left[1 + \left(\frac{1}{n} - 1\right)\alpha\right]$$

or,

$$\alpha = \frac{i - 1}{\frac{1}{n} - 1} \qquad\qquad ....(43)$$

If association is complete, i.e., $\alpha = 1$, $i = 1/n$, the observed value of a colligative property is $1/n$ times the calculated value and if $\alpha = 0$, no association occurs in solution, i.e., $i = 1$ and the observed and calculated values will be equal.

Problem A solution of 1×10^{-2} kg of sodium chloride in 1000 g of water freezes at -0.604^0 C. The molal depression constant K_f of water is $(1.85$ K kg mol$^{-1})$. Calculate the degree of dissociation of sodium chloride.

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Solution:

$$\left(\Delta T_f\right)_{cal} = K_f \frac{W_2 \times 1000}{W_1 M_2}$$

$$= \frac{\left(1.85 \text{ deg kg mol}^{-1}\right)\left(1 \times 10^{-2} \text{ kg}\right)\left(1000 \text{ g kg}^{-1}\right)}{\left(1.00 \text{ kg}\right)\left(58.5 \text{ g mol}^{-1}\right)}$$

$$= 0.316°C$$

$$\left(\Delta T_f\right)_{obs} = 0.0 - (-0.604) = 0.604°C$$

van't Hoff factor, $$i = \frac{\left(\Delta T_f\right)_{obs}}{\left(\Delta T_f\right)_{cal}}$$

$$= \frac{0.604}{0.316} = 1.91$$

Sodium chloride dissociates as $\quad$ NaCl $\rightleftharpoons$ Na$^+$ + Cl$^-$

Number of moles initially $\qquad\qquad$ 1 $\qquad$ 0 $\quad$ 0

Number of moles after dissociation $\quad$ 1 $-$ α $\qquad$ α $\quad$ α

Total number of moles after dissociation = $1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$i = \frac{\text{Number of moles after dissociation}}{\text{Number of moles initially present}} = \frac{1 - \alpha}{1}$$

Therefore, $\quad \dfrac{1 - \alpha}{1} = 1.91$

or, $\qquad \alpha = 0.91$ or 91%

The degree of dissociation = 91%