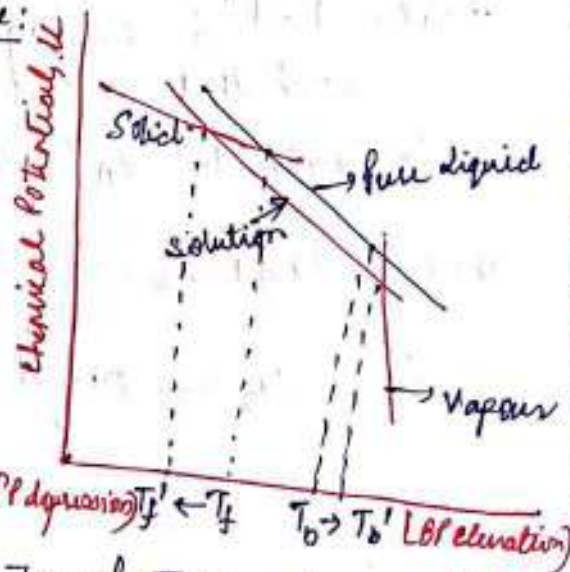


# Colligative Properties

\* Colligative properties are those which depend entirely upon the number of particles of the solute dissolved in known volume of a given solvent and not at all upon the nature (i.e. chemical composition or constitution) of the solute. These properties in fact depend upon the nature of the solvent

→ The various colligative properties are:

- (a) The elevation in boiling point
- (b) Osmotic pressure
- (c) Lowering of vapour pressure
- (d) Depression of freezing point.



(1) The elevation of Boiling point:-

→ The boiling is considered between two heterogeneous equilibria of interest that exist between solvent vapour and the solvent in solution. Where, we denote solvent as A and solute as B. Such that the chemical potential at equilibrium may be represented as:

$$\mu_A^*(g) = \mu_A^*(l) + RT \ln \chi_A$$

This can be rearranged as

$$\ln \chi_A = \frac{\mu_A^*(g) - \mu_A^*(l)}{RT} = \frac{\Delta_{vap}G}{RT}$$

where,  $\Delta_{vap}G$  is the Gibbs energy of vaporization of the pure solvent (A).

→ Now, differentiating both sides with respect to temperature such that according to Gibbs-Helmholtz equation

i.e.  $\left(\frac{\partial G}{\partial T}\right)_P = -\frac{H}{T^2}$ ; To express the terms on the right as;

$$\frac{d \ln \chi_A}{dT} = \frac{1}{R} \frac{d(\Delta_{\text{vap}} G/T)}{dT} = -\frac{\Delta_{\text{vap}} H}{RT^2}$$

Now integrating both sides as;

$$\Rightarrow \int_0^{\ln \chi_A} d \ln \chi_A = -\frac{1}{R} \int_{T^*}^T \frac{\Delta_{\text{vap}} H}{T^2} dT$$

$$\Rightarrow \ln(1 - \chi_B) = \frac{\Delta_{\text{vap}} H}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right)$$

here,  $T = T^*$ ;  $\Rightarrow$  boiling point of pure A

such that at this  $\ln \chi_A = 0$

where,

$$\ln \chi_A = \ln(1 - \chi_B)$$

to reach to  $\chi_A$  (when boiling point is  $T$ )

$$\text{Since, } \ln(1 - \chi_B) = -\frac{\Delta_{\text{vap}} H}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right)$$

$$\therefore \chi_B = -\frac{\Delta_{\text{vap}} H}{R} \left( \frac{1}{T^*} - \frac{1}{T} \right)$$

assuming;  $\ln(1 - \chi_B) \approx -\chi_B$   
when amount of solute 'B' is very small,  $\chi_B \ll 1$ .

As,  $T \approx T^*$ ; it follows

$$\frac{1}{T^*} - \frac{1}{T} = \frac{T - T^*}{T T^*} \approx \frac{\Delta T}{T^{*2}}$$

$$\Delta T = T - T^*$$

\* Thus, this shows that the presence of a solute at mole fraction  $\chi_B$  causes an increase in normal boiling point from  $T^*$  to  $T^* + \Delta T$ ,

$$\boxed{\Delta T = K \chi_B} \quad \text{Such that } K = \frac{RT^{*2}}{\Delta_{\text{vap}} H}$$

Since, the above equation makes the reference to just the mole fraction of solute ( $\chi_B$ ) and not to its nature, here, we conclude that elevation in boiling point is colligative property

The value of  $\Delta T$  does depend upon the properties of solv and the biggest changes are observed for solvents with high Boiling points. Thus, the above equation may also be written as;

$$\Delta T = K_b b$$

where, mole fraction of 'b';  $x_B$  is proportional to its molality,  $b$ , and here  $K_b$  is the empirical boiling point constant or ebullioscopic constant.

→ The units of ' $K_b$ ' are  $\text{K kg mol}^{-1}$

# Determination of Molar Mass:- from boiling point elevation.

$$\text{As } \Delta T_b = K_b m$$

$$\text{then, } \Delta T_b = K_b \times \frac{w_2}{M_2 w_1}$$

$$M_2 = \frac{K_b w_2}{w_1 \Delta T_b}$$

where,  $w_2$  kg of solute of molar mass  $M_2$  is dissolved in  $w_1$  kg of solvent.

$$m \text{ (molality of solution)} = \frac{w_2}{M_2} \times \frac{1}{w_1} \text{ per kg of solvent.}$$

(2)

## Depression in Freezing Point

The heterogeneous equilibrium between pure solid solvent A and the solution with solute present at a mole fraction  $x_B$ . At, freezing point, the chemical potentials of A in the two phases are equal.

$$\mu_A^*(s) = \mu_A^*(l) + RT \ln x_A$$

Similar to the calculation of Boiling point just replace Solids chemical potential in place of vapours.

$$\Delta T = K' x_B \quad \text{;} \quad K' = \frac{RT^{*2}}{\Delta_{\text{fus}}H}$$

$\Delta T$  = freezing point depression,  $T^* - T$ ,  $\Delta_{\text{fus}}H$  enthalpy of fusion of the solvent.

→ for larger depressions; with low enthalpies of fusion and high melting points.

→ for dilute solutions the mole fraction is proportional to molality.

$$\Delta T = K_f b$$

$K_f$  is the empirical freezing point constant or cryoscopic constant.

units of  $K_f$   $\text{K kg mol}^{-1}$ .

## # Determination of Molar Mass from freezing point depression

$$\Delta T_{\text{fus}} = K_f m$$

$$\Delta T_{\text{fus}} = K_f \frac{w_2}{M_2 w_1}$$

$$M_2 = \frac{K_f w_2}{w_1 \times \Delta T_{\text{fus}}}$$

- if  $w_2$  kg of the solute of molar mass  $M_2$ , is dissolved in  $w_1$  kg of the solvent. The solute dissolved in 1 kg of solvent gives molality  $m = \left(\frac{w_2}{M_2}\right) \left(\frac{1}{w_1}\right)$

## # Abnormal results and Van't Hoff factor

Since colligative properties depend upon the number of particles of the solute, however in some cases where the solute associate or dissociate in the solution, may cause emergence of some abnormal results:

### (I) Association

There are many organic solutes which in non-aqueous solutions undergo association, that is two or more solutes associate to form a bigger molecule. Thus, the number of effective molecules decreases and consequently all the colligative properties have lesser values than that calculated on the basis of single molecules.

Example: Acetic acid in Benzene } chloroacetic acid in Naphalene.  
The molar mass of solute in such cases will be higher than the true molar mass of solute.

### (II) Dissociation

Inorganic acids, bases and salts in aqueous solutions undergo dissociation that is the molecules break down into positively and negatively charged ions. In such cases, the number of effective particles increases and therefore all the properties related to colligative properties are much higher than those calculated on the basis of undissociated molecules.

## # the Van't Hoff factor

In order to account for all abnormal cases, Van't Hoff introduced a factor 'i', known as Van't Hoff factor; may be given as

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

Colligative property includes, elevation in boiling point, lowering in freezing point, osmotic pressure

Since, these properties vary inversely as the molar masses of solutes, it follows.

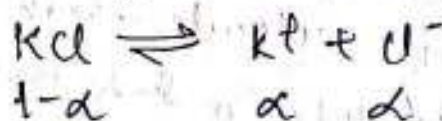
$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

### (a) Degree of Dissociation

The fraction of total molecules which dissociate, that is, break into simpler molecules or ions. Consider one mole of univalent electrolyte like KCl, dissolved in water.

Let  $\alpha$  be degree of dissociation.

The number of moles of KCl left undissociated will be  $1 - \alpha$



total no. of moles after dissociation =  $1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$\frac{\text{Observed colligative property}}{\text{Normal colligative property}} = \frac{1 + \alpha}{1}$$

Similarly, for molar masses

$$\frac{M_{\text{normal}}}{M_{\text{observed}}} = \frac{1 + \alpha}{1}$$

## (b) Degree of Association

The fraction of the total number of molecules which combine to form bigger molecules.

Let a given volume of solvent dissolves 1 mole of solute, such that 'n' simple molecules associate to form.



' $\alpha$ ' degree of association

$$\text{no. of associated moles} = \alpha/n$$

$$\text{no. of unassociated moles} = 1 - \alpha$$

$$\therefore \text{The number of effective moles} = 1 - \alpha + \alpha/n$$

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

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

## # Concept of Activity and Activity coefficients

→ Activity & Fugacity Concept

The concept of fugacity for representing the actual behavior of real gases which is distinctly different from behavior of ideal gases.

Variation of free energy with pressure at constant temperature

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$V$  = molar volume

equation is valid for ideal or non-ideal gases.

for ideal gas :-

$$\left(\frac{\partial G}{\partial P}\right)_T = RT/p \, dP$$

$$\therefore \left(\frac{\partial G}{\partial P}\right)_T = nRT \, dP/p = nRT \, d(\ln P)$$

on integration we get;  $G = G^* + nRT \ln P$

Free energy of ideal gas at temperature  $T$ , & pressure,  $P$

$$\Delta G = \int_{P_1}^{P_2} nRT \frac{dP}{P} = nRT \ln \frac{P_2}{P_1}$$

for 1 mole of gas;  $\Delta G = RT \ln(P_2/P_1)$

→ This is not valid for real gases.

(Thus) Lewis introduced a new function,  $f$  called fugacity function, which for real gases may be represented as;

$$(\partial G)_T = nRT d(\ln f)$$

$$G = G^* + nRT \ln f$$

$G = G^*$ ; when  $n$  moles of real gas has fugacity = 1

→ fugacity is a fictitious pressure.

which is used in order to retain for real gases.

Thus, for real gases

$$\Delta G = nRT \ln(f/H)$$

\* Fugacity of gas

→  $G = G^* + RT \ln f$ ; for 1 mole of gas.

differentiating with respect to constant temperature and constant number of moles of the various constituents, in closed system.

$$\left(\frac{\partial G}{\partial P}\right)_T = RT \left(\frac{d \ln f}{dP}\right)$$

and since,  $\left(\frac{\partial G}{\partial P}\right)_T = V$

$$\therefore \left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{V}{RT}$$

Thus at definite temperature;  $RT d(\ln f) = V dP$ .

# fugacity of gas in mixture

$$d\mu_i = RT d(\ln f_i) ; \mu_i = \mu_i^* + RT \ln f_i$$



## ⇒ Physical Significance of fugacity

⇒ Consider a system consisting of liquid water in contact with vapour. Water molecules have tendency to escape to vapour phase by evaporation while those in the vapour phase will have tendency to escape to liquid phase by condensation. At equilibrium, the two escaping tendencies will be equal. Thus, it has been concluded that each substance in a given state has a tendency to escape from that state. This escaping tendency was termed by Lewis as fugacity.

## II Concept of Activity

A quantity called 'fugacity' takes into account the effects of gas imperfections in a manner that result in form of equation having fugacity accounted. In case of activities we will see the same concept and encountered them to treat the system of ideal solutions.

### \* I) The solvent activity

The chemical potential of real or ideal solvent is given by;

$$\mu_A = \mu_A^\circ + RT \ln \left( \frac{P_A}{P_A^\circ} \right)$$

$P_A$  = Vapor pressure of A in solution

$P_A^\circ$  = Vapor pressure of A in pure state.

For, ideal solutions the solvent obey Raoult's law;

$$\mu_A = \mu_A^\circ + RT \ln X_A$$

But, If the solution does not obey the Raoult's law then the equation takes the form

$$\mu_A = \mu_A^\circ + RT \ln a_A$$

$a_A$  = Activity of A, a kind of effective mole fraction, just as the fugacity is an effective pressure.

\* Because all solvents obey Raoult's law ( $\lim_{x_A \rightarrow 1} p_A/p_A^* = x_A$ ) increasingly closely as the concentration of solute approaches zero, the activity of solvent reaches the mole fraction.

$$x_A \rightarrow 1$$

$$a_A \rightarrow x_A \text{ as } x_A \rightarrow 1$$

A convenient way, to express this convergence is to introduce the activity coefficient

$$a_A = \gamma_A x_A; \text{ as } x_A \rightarrow 1, \gamma_A \rightarrow 1$$

at all  $T$  &  $P$ .

The chemical potential of the solvent is then

$$\mu_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A$$

thus, the standard state of solvent, the pure liquid solvent at 1 bar, is established when  $x_A = 1$ .

## (II) The Solute activity

The problem with defining activity coefficients and standard states for solutes is that they approach ideal-dilute (Henry's Law) behavior as  $x_B \rightarrow 0$ , not as  $x_B \rightarrow 1$  (corresponding to pure solute).

### (a) Ideal-dilute solutions

A solute 'B' satisfies Henry's law as;  $p_B = k_B x_B$ ,  $k_B$  = empirical constant.

$$\mu_B = \mu_B^* + RT \ln \frac{p_B}{p_B^*} = \mu_B^* + RT \ln \frac{k_B}{p_B^*} + RT \ln x_B$$

Both  $k_B$  and  $p_B^*$  are characteristic of solute, so the 2<sup>nd</sup> term may be combined with the 1<sup>st</sup> to give new standard chemical potential

$$\mu_B^{\circ} = \mu_B^* + RT \ln k_B/p_B^*$$

Chemical potential of solute in an ideal solution is

$$\mu_B = \mu_B^\circ + RT \ln x_B$$

And if the solution is ideal,  $k_B = P_B^\circ$ ; reduces to  $\mu_B^\circ - \mu_B^\circ$

### (b) Real Solutes

If the system deviates from ideal-dilute, Henry's law behavior. For the solute we introduce  $a_B$  in place of  $x_B$ , then

$$\mu_B = \mu_B^\circ + RT \ln a_B$$

All the deviations from ideality are captured in activity  $a_B$

$$a_B = \frac{P_B}{k_B}$$

As, for solvent, it is sensible to introduce an activity coefficient through

$$a_B = \gamma_B x_B$$

All the deviations from ideality are captured in  $\gamma_B$ .

Because, the solute obeys Henry's law, so its  $\ln \gamma_B$  goes to zero.  $a_B \rightarrow x_B$  and  $\gamma_B \rightarrow 1$  as  $x_B \rightarrow 0$ .

### (iii) Activity of ions in solution

Interactions between ions are so strong that the approximation of replacing activities by molalities is valid only for very dilute solutions, especially in preparation for the discussion of electrochemical phenomenon.

### (iv) Mean Activity Coefficients

Chemical potential of univalent cation  $M^+$ , and anion  $X^-$  is denoted by  $\mu^+$  and  $\mu^-$  respectively.

The total molar Gibbs energy of an ideal solution is

$$G_m^{\text{ideal}} = \mu^{\text{ideal}} + \mu_-^{\text{ideal}}$$

For real solutions of  $M^+$  and  $X^-$  of the same molality.

$$G_m = \mu^+ + \mu^- = \mu^{\text{ideal}} + RT \ln \gamma^+ + RT \ln \gamma^- = G_m^{\text{ideal}} + RT \ln \gamma^+ \gamma^-$$

All deviations from ideality are contained in the last term ( $\gamma_{\pm}$ )  
 → For a 1,1- electrolyte type, the mean activity coefficient is given as the geometric mean of the individual coefficients.

$$\gamma_{\pm} = (\gamma_{+}\gamma_{-})^{1/2}$$

with individual chemical potentials of ions as;

$$\mu_{\pm} = \mu_{\pm}^{\text{ideal}} + RT \ln \gamma_{\pm}$$

### # Generalized formula:-

In case of an compound of type  $M_pX_q$  that dissolves in solution to give  $p$  cations and  $q$  anions from each formula unit. Thus, the molar Gibbs energy of the ions given as the sum of their partial molar Gibbs energies as:-

$$G_m = p\mu_{+} + q\mu_{-} = G_m^{\text{ideal}} + pRT \ln \gamma_{+} + qRT \ln \gamma_{-}$$

Thus, the mean activity coefficients may be represented as;

$$\gamma_{\pm} = (\gamma_{+}^p \gamma_{-}^q)^{1/s} ; \quad s = p + q$$

To write the chemical potential of each ion as;

$$\mu_i = \mu_i^{\text{ideal}} + RT \ln \gamma_{\pm}$$

Such that,

$$G = p\mu_{+} + q\mu_{-}$$

Here, both types of ion now share equal responsibility for the non-ideality.