LECTURE-20

IDEAL & NON-IDEAL SOLUTIONS

Consider the vaporization of a component 'A' from a liquid solution at temp. T. if the vapor behaves as ideal gas, then the equilibrium constant is given as

$$K = {}^{P_A}\!/_{a_A} = P_A^0 \qquad (176)$$

The above process can be expressed as

$$A(liquid) \rightarrow A(solid)$$

Equilibrium constant can be calculated for above reaction as

$$K = \left[\frac{\text{Activity of product (vapour)}}{\text{Activity of reactant(Liquid)}}\right]_{\text{at eqlbm}} = \frac{P_A}{a_A} \qquad (177)$$

(Since ideal gas mixture case a=P)

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From above equation (176), we have

$$a_A = \frac{P_A}{P_A^0} \tag{177}$$

Now taking the temperature as T, Let us consider there are two closed containers out of which one contains a liquid solution, where A is the component & another contains pure A. So if in case of solution the vapour pressure is P_A & in case of pure A the vapour pressure is P_A^0. Then for solution case, we can expressed the mole fraction of component 'A' as

$$X_A = \text{mole fraction of A in the solution} = {}^{P_A}\!/_{P_A^0} \tag{178}$$

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Now, from equation (177) & (178), we have

$$a_A = x_A \tag{179}$$

If the solution obeys Raoult's law then it is called an ideal solution & if the solution does not obey Raoult's law then it is called non-ideal solution.

There is a term known as activity co-efficient (γ) & mathematically it represented as

$$\gamma_{\mathrm{i}} = \frac{\text{activity of the component}}{\text{Mole fraction of the component}} = \frac{\mathrm{a_i}}{\mathrm{x_i}} \tag{180}$$

$$\Rightarrow a_i = \gamma_{i.} x_i \tag{181}$$

[Where γ^i - Activity co-efficient of component in a solution]

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Now, if in a solution,

- $\gamma^i = 1$, solution is ideal.
- $\gamma^i > 1$, solution exhibits positive departure from Raoult's law.
- $\gamma^i < 1$, solution exhibits negative departure from Raoult's law.

In a solution, $a_i < 1$, in contrast to pure i where $a_i = 1$. This difference is due to the following two effects

- Dilution of component i in a solution due to the presence of other component (dilution effect).
- Interaction of component i with other components in a solution (interaction effect).

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Activity:

- It is measure of free concentration, i.e., concentration available for reaction.
- In an ideal solution, the entire concentration is available i.e. there is only dilution effect. In case of binary solution like A-B, interaction effect more easily followed. There is mainly three types of bonds between atoms (or molecules) of A & B such as A – A and B – B are like bonds & A –B is unlike bond.
    - If A – B bond stronger than the average of A – A & B – B bonds, i.e., A & B have the tendency to form a compound, then less number of A & B atoms remains free. In this case the solution exhibit negative departure from the Raoult's law i.e. $\gamma_A < 1$, $\gamma_B < 1$.
    - If A –A & B – B bonds average is greater than A – B bonds then atoms (or molecules) have the tendency more to form clusters. In this case the solution would exhibit's positive departure from Raoult's law.

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Examples:

- Ideal solution: Cu – Ag, Fe – Ni, Fe – Mn, FeO – MnO.
- Negative Departure from Raoult's Law: Silicates such as CaO – SiO_2 & MnO – SiO_2.
- Positive Departure from Raoult's Law: Cu – Fe.

<u>QUASI-CHEMICAL APPROACH TO SOLUTIONS:</u> Thermodynamics properties of solutions are consequence of interaction amongst atoms/molecules. Quasi-chemical theory is the simplest & able to explain the properties approximately from atomistic point of view. In a metallic solution, the components are assumed to be present as atoms & not molecules due to nature of metallic bonds. So there exit interaction energy between them.

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The quasi-chemical theory explained by considering some important assumptions.

a) Atoms have chemical bonds amongst them.
b) Bonds get associated with some enthalpy which alone contributes to enthalpy of solution.
c) Only bonds amongst nearest neighboring atoms are energetically significant.

- ☐ In, a binary A-B system, the bonds are A-A, B-B & A-B type. Assume that enthalpies associated with these bonds are H_{AA}, H_{BB} & H_{AB} respectively.
- ☐ Let us consider one gm-atom of the solution. Let it have P_{AA}, P_{BB} & P_{AB} numbers of A-A, B-B and A-B bonds respectively.
- ☐ Then enthalpy of formation of the solution for one gm-atom from gaseous state at temperature T is

$$H = P_{AA}H_{AA} + P_{BB}H_{BB} + P_{AB}H_{AB} \tag{182}$$

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If number of A atoms is N_A & B atomsN_B, Then

$$N_A = \frac{P_{AB}}{Z} + \frac{2P_{AA}}{Z} \qquad (183)$$

$$N_B = \frac{P_{AB}}{Z} + \frac{2P_{BB}}{Z} \qquad (184)$$

[Where Z – Coordination number]

Thus P_{AA} & P_{BB} can be expressed in terms of P_{AB},N_A, N_B and Z. Substituting these terms in the equation (182), we will get

$$H = \frac{1}{2} ZN_AH_{AA} + \frac{1}{2} ZN_BH_{BB} + P_{AB}[H_{AB} - \frac{1}{2} (H_{AA} + H_{BB})] \qquad (185)$$

Again enthalpy of mixture is

$$\Delta \mathrm{H}^{\mathrm{m}} = [\mathrm{H} - (\mathrm{Enthaply\ of\ N_A\ atoms\ in\ pure\ A + Enthaply\ of\ N_B\ atoms\ in\ pure\ B})]$$

(186)

$$\Delta H^m = P_{AB}[H_{AB} - \frac{1}{2} (H_{AA} + H_{BB}) \qquad (187)$$

Continued…

Application to Ideal & Regular Solutions:

Since $\Delta\mathrm{H}^{\mathrm{m}} = 0$ for ideal solution. So from equation (187), we will have

$$H_{AB} = \frac{1}{2}\,(H_{AA} + H_{BB}) \tag{188}$$

If N_0 is the total number of atoms in a solution. Then

$$x_A = \frac{N_A}{N_0}\ ,\ x_B = \frac{N_B}{N_0} \tag{189}$$

[Where $N_0$is the Avogadro's number]

Again total number of bonds is $\frac{1}{2}\ ZN_0$ in 1 mole. Hence we have

$$P_{AB} = 2\ x_A x_B\ \frac{1}{2}\ ZN_0 = Z\ N_0 x_A x_B \tag{190}$$

[Where x_A & x_B are respective atoms]

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Putting the equation (190) in equation (187), we have

$$\Delta \mathrm{H}^{\mathrm{m}} = Z\, N_0 x_A x_B \, [\, H_{AB} - \frac{1}{2}\, (H_{AA} + H_{BB}) \tag{191}$$

Again we know

$$\Delta \mathrm{H}^{\mathrm{m}} = \mathrm{x_A x_B} \Omega \tag{192}$$

Comparing above equation (191) and (192), we will have

$$\Omega = Z\, N_0 \, [\, H_{AB} - \frac{1}{2}\, (H_{AA} + H_{BB})] \tag{193}$$