LECTURE-23

Regular Binary Solutions:

For binary solution case, we have defined a function α that is given by

$$\alpha_i = \frac{\ln \gamma_i}{(1-x_{i)})^2} \tag{255}$$

So, for A-B solution

$$\alpha_B = \frac{\ln \gamma_B}{(1-x_{B)})^2} = \frac{\ln \gamma_B}{x_A^2} \tag{256}$$

$$\Rightarrow \ln \gamma_B = \alpha_B x_A^2 \tag{257}$$

Similarly,

$$lnx_A = \alpha_A x_B^2 \tag{258}$$

For binary regular solution

$$\alpha_A = \alpha_B = \alpha = \text{Constant} \tag{259}$$

Continued…

Since we know

$$\Delta H^m = G^{xs} = RT\,(x_A \ln \gamma_A + x_B \ln \gamma_B) \qquad (260)$$

$$\Rightarrow \quad \Delta H^m = RT(\,x_A \alpha_A x_B^2 + \, x_B \alpha_B \, x_A^2) \qquad (261)$$

$$\Rightarrow \quad \Delta H^m = RT\alpha\,(x_A x_B^2 + \, x_B \, x_A^2) \qquad (262)$$

(Using equation (258))

$$\Rightarrow \quad \Delta H^m = RT\alpha x_A x_B (x_A + \, x_B) \qquad (263)$$

$$\Rightarrow \quad \Delta H^m = RT\alpha X_A X_B \qquad (264)$$

$(Since\ x_A + \, x_B = 1)$

$$\Rightarrow \quad \Delta H^m = \Omega\, x_A x_B \quad \text{(Since } \Omega = RT\alpha) \qquad (265)$$

[Where Ω is a parameter related to interaction energies in the solution]

Continued…

Again, we have

$$\overline{H_A^m} = \overline{G_A^{xs}} = RT\ln\gamma_A = RT\alpha x_B^2 = \Omega x_B^2 \qquad (266)$$

$$\overline{H_B^m} = \overline{G_B^{xs}} = RT\ln\gamma_B = RT\alpha x_A^2 = \Omega x_A^2 \qquad (267)$$

ΔH^m, $\overline{H_i^m}$ of solutions mainly constant over a limited range approximately. So Ω assumed to be independent of temperature.

Therefore,

$$\alpha = \frac{\Omega}{RT} \Rightarrow \alpha \propto \frac{1}{T} \qquad (268)$$

Continued…

SIEVERT'S LAW: Statement of the law is "The atomic gases do not dissolve into the metal in their molecular form rather they dissolve by dissociation i.e. in atomic form."

So dissolution of a diatomic gas into metal (condensed phase)

$x_2 \rightarrow 2x$ (In solution)

[Where x_2 → diatomic gases]

Equilibrium constant of reaction

$$K_p = \left[\frac{h_x}{\left[P_{x_2}\right]^{\frac{1}{2}}}\right]_{eq} \qquad (269)$$

[Where, h_x → Henry activity of component x dissolve in condensed / solid phase.

P_{x_2} → Partial pressure of x_2.

K_p → Sievert's constant]

Continued…

As the solubility of gases in condensed phase under moderate condition of temperature and pressure is very small. So, the h_x for the above expression for gases are preferred to use in terms of wt. %. The above equation (269) changes to

$$K_p = \frac{f_x\,(wt.\%\,x)}{P_{x_2}^{1/2}} \tag{270}$$

[Where, $f_x \rightarrow$ Henry’s activity co-efficient]

In Henry’s law if the activity co-efficient $f_x \rightarrow 1$, then equation (270) becomes

$$K_p = \frac{(wt.\%\,x)}{P_{x_2}^{1/2}} \tag{271}$$

$$\Rightarrow wt.\%\,x = K_p\sqrt{P_{x_2}} \tag{272}$$

$$\Rightarrow \mathrm{wt.\%\,x} = (\mathrm{Sievert'slaw\ constant}) \times \sqrt{\mathrm{P_{x_2}}} \tag{273}$$

Continued…

From equation (272), Sievert's law can be expressed as, at constant temperature, the solubility of diatomic gases into the condensed phase is proportional to the square root of partial pressure.

<u>Limitation of Sievert's Law:</u> It is applicable only to the limiting type of solution where Henerian activity $h_x \rightarrow 1$ (when ($f_x \neq 1$)) in such case expression for Sievert's law take the form

$$\ln(\mathrm{wt.\%\ x}) = \ln \mathrm{K_p} + \frac{1}{2} \ln \mathrm{P_{x_2}} - \ln \mathrm{f_x} \qquad (274)$$

[Since, $f_x(wt.\%\,x) = (K_P)\left(P_{x_2}^{1/2}\right)$]

The function f_x can be expressed in terms of interaction co-efficient that means

$$\ln \mathrm{f_x} = \left(\epsilon_X^X.\,\mathrm{wt\%\ x}\right) + \left(\epsilon_X^1.\,\mathrm{wt\%\ of\ 1st\ component}\right) + \left(\epsilon_X^2.\,\mathrm{wt\%\ of\ 2nd\ component}\right) + \cdots + (\epsilon_X^n.\,\mathrm{wt\%\ of\ nth\ component}) \qquad (275)$$

[Where, ϵ_X^X −Self interaction parameter of the gas component "X"

$\epsilon_X^1, \epsilon_X^2, \ldots, \epsilon_X^n$ −Interaction parameter on component X of component 1, 2,..., n]

Continued…

Problem:- Calculate the solubility of N_2 gas under 1 atom pressure & 1600 ^{0}C in an iron-based alloyed having the composition C = 3.5%, Mn = 1%, Si = 1.2%, P = 0.5%. The interaction parameters for various components are

$$\epsilon_{\mathrm{N}}^{\mathrm{C}} = 0.25 \times 2.3 \text{ , } \epsilon_N^P = 0.51 \times 2.3, \epsilon_{\mathrm{N}}^{\mathrm{Mn}} 0.02 \times 2.3$$

$$\epsilon_{\mathrm{N}}^{\mathrm{N}} = 0, \epsilon_{\mathrm{N}}^{\mathrm{Si}} = 0.047 \times 2.3$$

Sievert's constant for N_2 (K_P) = 0.045

Solution:- As we from limiting condition of Sievert's law

$$\ln \mathrm{f_x} = \left(\epsilon_{\mathrm{N}}^{\mathrm{C}}.\,\mathrm{wt\%\ of\ C}\right) + \left(\epsilon_{\mathrm{N}}^{\mathrm{P}}.\,\mathrm{wt\%\ of\ P}\right) + \left(\epsilon_{\mathrm{N}}^{\mathrm{Mn}}.\,\mathrm{wt\%\ of\ Mn}\right) + \cdots + \left(\epsilon_{\mathrm{N}}^{\mathrm{N}}.\,\mathrm{wt\%\ of\ N}\right)$$

Continued…

$$= [(0.25 \times 3.5) + (0.51 \times 0.5) + (0.02 \times 1) + (0.047 \times 1.2)] \times 2.3$$

[Since, $\epsilon_N^N = 0$]

$$= [1.2064] \times 2.3 = 2.77472 \cong 2.775$$

Since, we know from Sievert’s law as

$$f_x \times (wt.\% \, N) = Sivert'sconstant \ (K_P) \times \sqrt{P_{N_2}}$$

$$\Rightarrow wt.\% \, N = \frac{0.045 \times \sqrt{1}}{16.04} = (2.8 \times 10^{-3})$$ (Ans)