Lecture 3

Uses of free energy

Effect of temperature on Gibbs energy

$$G = H - TS$$

We need to find out a relation where variation in G/T can be obtained as a function of H

Effect of temperature on Gibbs energy

$$G = H - TS$$

$$\frac{G}{T} = \frac{H}{T} - S$$

Differentiating partially with respect to T keeping P fixed

$$\left[\frac{\partial G/T}{\partial T}\right]_P = -\frac{H}{T^2} + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P$$

The last two terms get cancelled

$$H = -T^2\left(\frac{\partial G/T}{\partial T}\right)_P \qquad \Delta H = -T^2\left(\frac{\partial \Delta G/T}{\partial T}\right)_P$$

Gibbs-Helmholtz equation

Effect of pressure on Gibbs energy

$$V = \left(\frac{\partial G}{\partial P} \right)_{T, n_i}$$

Re arrange the equation and integrate it between Limits

Find out the effect of pressure on Gibbs energy of solids and gases

What difference do you observe?

Effect of pressure on Gibbs energy

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,n_i}$$

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} V dP \qquad G_2 = G_1 + \int_{P_1}^{P_2} V dP$$

If volume is independent of pressure $G_2 = G_1 + V(P_2 - P_1)$

For an ideal gas $G = G^0 + nRT\int_{P^0}^{P} d\ln P$

$$G = G^0 + nRT\ln\frac{P}{P^0}$$

$$\Delta G = nRT\ln\frac{P_2}{P_1}$$

The significance of chemical potential

Using, $$dG = -SdT + VdP + \sum_{i=1}^{N_s} \mu_i dn_i$$

Prove that,

$\mu_i(\alpha) = \mu_i(\beta)$ **<u>At equilibrium</u>**

$\mu_i(\alpha) > \mu_i(\beta)$ **<u>Spontaneous</u>**

$$\mu_i(\beta)$$

$$\mu_i(\alpha)$$

When dni is transferred from α to β phase

The significance of chemical potential

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,(n_{j=i})} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,(n_{j=i})} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,(n_{j=i})} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,(n_{j=i})}$$

$$dG = -SdT + VdP + \sum_{i=1}^{N_s} \mu_i dn_i$$

$$\mu_i(\beta)$$

$$\mu_i(\alpha)$$

Transfer of dn_i from α to β

$$(dG)_{T,P} = -\mu_i(\alpha)dn_i + \mu_i(\beta)dn_i = dn_i[\mu_i(\beta) - \mu_i(\alpha)]$$

$\mu_i(\alpha) = \mu_i(\beta)$ **At equilibrium**

$\mu_i(\alpha) > \mu_i(\beta)$ **Spontaneous**

Gibbs-Duhem equation

$$dG = -SdT + VdP + \sum_{i=1}^{N_s} \mu_i dn_i$$

For a binary system, at constant T, P

$$dG = \mu_1 dn_1 + \mu_2 dn_2$$

$$G(T, P, n_1, n_2) = \mu_1 n_1 + \mu_2 n_2$$

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + n_1 d\mu_1 + n_2 d\mu_2$$

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

What is the significance of Gibbs-Duhem equation?