Lecture #11

Temperature Dependence of G

Temperature dependence of G is shown by ***Gibbs-Helmholtz Equations.*** There are mainly 4 equations. The first one is obtained by using the fundamental equation giving dG.

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

The second equation is obtained by using the definition of G;

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

$$\left(\frac{\partial G}{\partial T}\right)_P = \frac{G-H}{T}$$

The third equation gives the change in G/T with respect to T;

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

The fourth equation is;

$$\frac{\partial (G/T)}{\partial (1/T)} = H$$

CHEMICAL EQUILIBRIUM

So far, we have studied systems composed of a pure substance or a mixture or a mixture with fixed composition. If there is a reaction proceeding in the system, then the composition of the system changes and the thermodynamic properties of the system change accordingly.

Chemical Potential

For a pure substance or for a mixture of fixed composition;

$dG = -SdT + VdP$

If the mole numbers of the substances present vary then G becomes the function of T, P and mole numbers;

$$G = G(T, P, n_1, n_2, \ldots\ldots\ldots)$$

The total differential of G is;
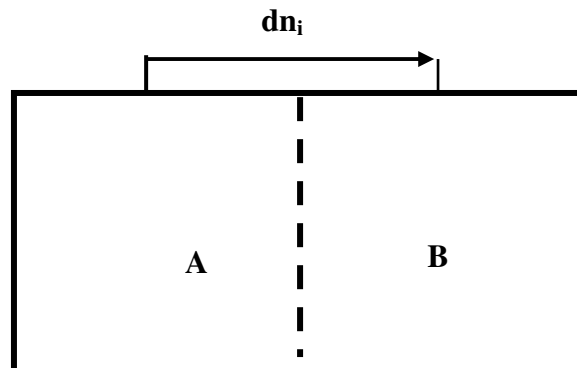
$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_j} dn_1 + \ldots\ldots$$

$$= -SdT + VdP + \mu_1 dn_1 + \ldots\ldots\ldots\ldots$$

The chemical potential of i, μ_i is the increase in free energy perm ole of the substance added;

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

Spontaneity

Suppose we are transferring dni moles from region A to region B. The total free energy change for the system is;

$$dG = dG(A) + dG(B) = -\mu_i(A)dn_i + \mu_i(B)dn_i = [\mu_i(A) - \mu_i(B)]dn_i$$

If $\mu_i(A) > \mu_i(B)$, dG is negative and the transfer occurs spontaneously. Substance i flows spontaneously from a region of high μ_i to a region of low μ_i.

Properties of Chemical Potential

Chemical potential is an ***intensive property.*** It has the same value at every point within a system at equilibrium.

Chemical potential obeys the ***additivity rule***

$$G = \sum n_i \mu_i$$

If the system contains only one substance;

$$G = n\mu \qquad\qquad \mu = \frac{G}{n}$$

The chemical potential of a pure substance is simply its molar free energy.

Chemical Potential of Gases

The chemical potential of a pure ideal gas is equal to its molar free energy;

$$\mu = \mu^{o}(T) + RT \ln P$$

At a given temperature, the pressure is a measure of the chemical potential of an ideal gas.

The chemical potential for a real gas is;

$$\mu = \mu^{o}(T) + RT \ln f$$

The function f is the fugacity of the gas. It is a function of temperature and pressure. Fugacity is a measure of the chemical potential of a real gas.

Chemical Potential in an Ideal Gas Mixture

Consider the system below. One side contains pure H_2 , the other side contains an ideal mixture of $N_2 + H_2$. When equilibrium is attained, the pressure of the pure H_2 is equal to the partial pressure of H_2 in the mixture. The equilibrium condition is;

$$\mu_{H2}(pure) = \mu_{H2}(mixture)$$

$$\mu_{H2}(mixture) = \mu^{o}_{H2}(T) + RT \ln p_{H2}$$

By using Dalton's Law;

$$\mu_{H2}(mixture) = \mu_{H2}(T) + RT \ln x_i P$$

$$\mu_{H2}(mixture) = \mu_{H2}(T,P) + RT \ln x_i$$

The chemical potential of any gas in a mixture is always less than the chemical potential of the pure gas under the same total pressure.