

Lecture 1B. Thermodynamics:

Brief Review of Chemical Equilibria

System: Single Phase;
Single Reaction $\sum_{j=1}^S \nu_j A_j = 0$

Equilibrium state is defined by:

- i) $\sum_{j=1}^S \nu_j \tilde{G}_j = 0$
- ii) $N_j = N_{j0} + \nu_j X_e$ for all j
- iii) appropriate equation of state

$\tilde{G}_j(T, P, X_i)$ is the partial molal Gibbs free energy of j and is the function of temperature, pressure and composition.

In general

$$\tilde{G}_j = \tilde{G}_j^{ex} + \underset{\sim j}{G} + RT \ln x_j$$

\tilde{G}_j^{ex} is the excess mixing Gibbs free energy to be evaluated from an appropriate mixture model;

x_j is mole fraction of j ;

N_j is moles of j ;

N_{j0} is initial moles of j ;

ν_j is stoichiometric coefficient of j (positive for products, negative for reactants);

$\underset{\sim j}{G}$ is the Gibbs free energy of species j (function of T only);

T is temperature of the system;

X_e is the equilibrium reaction molar extent;

If we define the standard Gibbs free energy of reaction at temperature T by

$$\Delta G_r = \sum_{j=1}^S \nu_j \underset{\sim j}{G} \quad (1)$$

with $\underset{\sim j}{G}$ being evaluated at temperature T of interest.

Then the thermodynamic equilibrium constant, K , which is a function of temperature only, is given by:

$$K = \prod_{j=1}^S a_j^{\nu_j} = e^{-\frac{\Delta G_r}{RT}} \quad (2)$$

where a_j is the activity of species j .

In order to calculate the equilibrium reaction extent and equilibrium composition we need to:

- Calculate K at the temperature of interest,
- Relate the activity of each species, j , a_j , to a measure of composition (e.g. mole fraction) by an appropriate model for the mixture,
- Relate measure of composition to reaction extent using stoichiometric relations indicated above by relation ii).

Van Hoff's equation establishes the rate of change of the equilibrium constant K with temperature:

$$\frac{d \ln K}{dT} = \frac{\Delta H_r}{RT^2} \quad (3)$$

$$T = T_o (= 298 \text{ K}); K = K_{298} = e^{-\frac{\Delta Gr_{T_o}}{RT_o}} \quad (3a)$$

where ΔH_r is the standard heat of reaction at temperature T , K_{298} is the equilibrium constant at the standard state temperature of T_o (most likely 298 K) and ΔGr_{T_o} is the standard Gibbs free energy of reaction at T_o which is obtained from tabulated Gibbs free energies of formation ΔG_{f_j}

$$\Delta Gr_{T_o} = \sum_{j=1}^S \nu_j \Delta G_{f_j} \quad (4a)$$

The heat of reaction at temperature T is also obtained from the tabulated heats of formation, ΔH_{f_j} , and specific heats, C_{p_j} .

$$\Delta H_r = \sum_{j=1}^S \nu_j \Delta H_{f_j} + \sum_{j=1}^S \nu_j \int_{T_o}^T C_{p_j} dT$$

For gases (standard state pure gas at 1 atm) we use y_j for mole fraction of j and:

$$a_j = y_j P \left(\frac{\tilde{f}_j}{y_j P} \right) / 1 \text{ atm} = p_j \left(\frac{\tilde{f}_j}{y_j P} \right) / 1 \text{ atm}$$

$$a_j = y_j P \phi_j / 1 \text{ atm} = p_j \phi_j / 1 \text{ atm}$$

$$K = \prod_{j=1}^s a_j^{\nu_j} = \left(\frac{P}{1 \text{ atm}} \right)^{\sum \nu_j} \prod_{j=1}^s y_j^{\nu_j} \prod_{j=1}^s \phi_j^{\nu_j}$$

$$K = \left(\frac{P}{1 \text{ atm}} \right)^{\sum \nu_j} K_y K_\phi$$

or

$$K = \prod_{j=1}^S a_j \nu_j = \prod_{j=1}^S p_j \nu_j \prod_{j=1}^S \phi_j \nu_j / (1 \text{ atm})^{\sum \nu_j}$$

$$K = \prod_{j=1}^S a_j \nu_j = K_p K_\phi / (1 \text{ atm})^{\sum \nu_j}$$

The generalized fugacity coefficients $\phi_j, \phi_j = \left(\frac{\tilde{f}_j}{y_j P} \right)$, would have to be evaluated from an

appropriate equation of state. If Lewis-Randall rule is used $\phi_j = \left(\frac{f_j}{P} \right)$

For gases at low pressure $K_\phi \approx 1$

$$K_a = \left(\frac{P}{1 \text{ atm}} \right)^{\sum \nu_j} K_y = K_p / (1 \text{ atm})^{\sum \nu_j}$$

For liquids (assuming standard state of unit activity i.e. the standard state of each component is the pure component state)

$$a_j = x_j \gamma_j$$

where γ_j is the activity coefficient

$$K = \prod_{j=1}^S a_j \nu_j = \prod_{j=1}^S (x_j \gamma_j)^{\nu_j} = K_x K_\gamma$$

Since $x_j = C_j / C$

$$K = C^{-\sum \nu_j} K_c K_\gamma$$

For an ideal mixture $K_\gamma \approx 1$

Above C_j is the molar concentration of species j and C is the total molar concentration.