

OUTLINE OF CHAPTER 13

REACTION THERMODYNAMICS

Starting Point (Chapter 8)

$$\sum_i \nu_i \bar{G}_i(T, P, \underline{z}) = 0$$

But

$$\bar{G}_i(T, P, \underline{z}) = \underline{G}_i(T, P) + RT \ln \frac{\bar{f}_i(T, P, \underline{z})}{f_i(T, P)}$$

Then

$$\sum_i \nu_i \bar{G}_i(T, P, \underline{z}) = \sum_i \nu_i \underline{G}_i(T, P) + RT \sum_i \nu_i \ln \left(\frac{\bar{f}_i(T, P, \underline{z})}{f_i(T, P)} \right) = 0$$

Or

$$\begin{aligned} \frac{-\sum_i \nu_i \underline{G}_i(T, P)}{RT} &= \sum_i \nu_i \ln \frac{\bar{f}_i(T, P, \underline{z})}{f_i(T, P)} \\ &= \ln \left[\prod_i \left(\frac{\bar{f}_i(T, P, \underline{z})}{f_i(T, P)} \right)^{\nu_i} \right] \end{aligned}$$

GAS MIXTURES

$$\bar{f}_i(T, P, \underline{y}) = y_i P \left(\frac{\bar{f}_i}{y_i P} \right) \quad \text{and} \quad f_i(T, P) = P \left(\frac{f}{P} \right)_i$$

Then

$$\frac{-\sum v_i G_i}{RT} = \ln \left[\prod_i \left(\frac{y_i (\bar{f}_i / y_i P)}{(f/P)_i} \right)^{v_i} \right]$$

Ideal gas (all fugacities equal to partial pressure)

$$\frac{-\sum v_i G_i}{RT} = \ln \left[\prod_i y_i^{v_i} \right]$$

Liquids

$$\bar{f}_i(T, P, \underline{x}) = x_i \gamma_i f_i(T, P)$$

$$\frac{-\sum v_i G_i}{RT} = \ln \left[\prod_i (x_i \gamma_i)^{v_i} \right]$$

Ideal liquid Phase

$$\frac{-\sum v_i G_i}{RT} = \ln \left(\prod_i x_i^{v_i} \right)$$

Thus, if

$$\prod_i x_i^{v_i} < \exp \left[-\frac{\sum_i v_i G_i(T, P)}{RT} \right]$$

The reaction proceeds as written and vice versa.

We now define standard state and activity as follows:

$$\begin{aligned} \bar{G}_i(T, P, \underline{z}) &= \bar{G}_i^\circ(T, P = 1 \text{ bar}, x_i^\circ) \\ &\quad + [\bar{G}_i(T, P, \underline{z}) - \bar{G}_i^\circ(T, P = 1 \text{ bar}, x_i^\circ)] \\ &= \bar{G}_i^\circ(T, P = 1 \text{ bar}, x_i^\circ) + RT \ln \left\{ \frac{\bar{f}_i(T, P, \underline{z})}{\bar{f}_i^\circ(T, P = 1 \text{ bar}, x_i^\circ)} \right\} \\ &= \bar{G}_i^\circ(T, P = 1 \text{ bar}, x_i^\circ) + RT \ln a_i \end{aligned}$$

That is,

$$a_i = \frac{\bar{f}_i(T, P, \underline{z})}{\bar{f}_i^\circ(T, P = 1 \text{ bar}, x_i^\circ)} = \exp \left(\frac{\bar{G}_i(T, P, \underline{z}) - \bar{G}_i^\circ(T, P = 1 \text{ bar}, x_i^\circ)}{RT} \right)$$

Then:

$$\begin{aligned} 0 &= \sum_{i=1}^c v_i \bar{G}_i = \sum_{i=1}^c v_i \bar{G}_i^\circ(T, P = 1 \text{ bar}, x_i^\circ) + RT \sum_{i=1}^c v_i \ln a_i \\ &= \Delta_{\text{rxn}} G^\circ + RT \sum_{i=1}^c v_i \ln a_i \end{aligned}$$

Or (definition of equilibrium Constant)

$$K_a(T) = \exp \left(-\frac{\Delta_{\text{rxn}} G^\circ}{RT} \right)$$

Therefore

$$K_a(T) = \prod_{i=1}^c a_i^{\nu_i} = \frac{a_R^{\rho} \dots}{a_A^{\alpha} a_B^{\beta} \dots}$$

$$\Delta_{\text{rxn}} G^{\circ}(T = 25^{\circ}\text{C}) = \sum_i \nu_i \Delta_f G_i^{\circ}(T = 25^{\circ}\text{C})$$

For real gases (using Lewis and Randall), we have that
 $a_i = y_i P \phi$

$$K_a(T) = K_y K_P K_{\phi}$$

$$K_y = \prod_i y_i^{\nu_i} \quad K_P = \prod_i P_i^{\nu_i} \quad \boxed{K_{\phi} = \prod_i \left(\frac{f_i}{y_i P} \right)^{\nu_i} \quad \text{and} \quad K_{\gamma} = \prod_i \gamma_i^{\nu_i}}$$

Temperature dependence

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

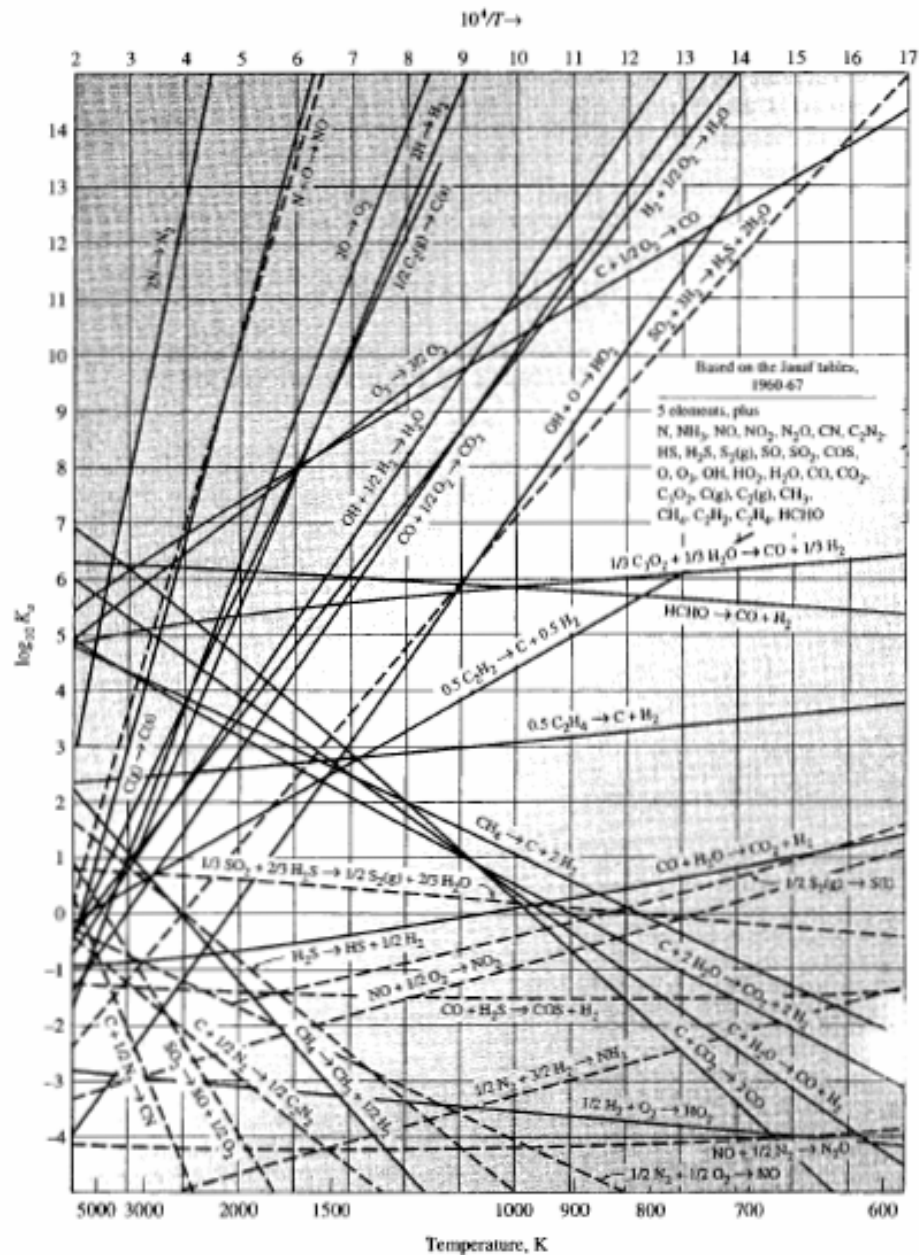
Now: $\ln K_a = -\sum \nu_i \Delta_f G_i^{\circ} / RT$. *Then (van't Hoff equation)*

$$\left(\frac{d \ln K_a}{dT} \right)_P = -\frac{1}{R} \frac{d}{dT} \left[\frac{\sum_i \nu_i \Delta_f G_i^{\circ}}{T} \right] = \frac{1}{RT^2} \sum_i \nu_i \Delta_f H_i^{\circ} = \frac{\Delta_{\text{rxn}} H^{\circ}(T)}{RT^2}$$

Integrating assuming heat of reaction constant we get the simplified relation

$$\ln \frac{K_a(T_2)}{K_a(T_1)} = -\frac{\Delta_{rxn} H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Leading to



But is heat of reaction is a function of temperature,

$$\Delta_{\text{rxn}}H^\circ(T) = \sum v_i H_i^\circ(T) = \Delta_{\text{rxn}}H^\circ(T = 25^\circ\text{C}) + \int_{T=25^\circ\text{C}}^T \Delta_{\text{rxn}}C_p^\circ(T') dT'$$

(298.15 K)

$$\ln \frac{K_a(T_2)}{K_a(T_1)} = \int_{T_1}^{T_2} \frac{\Delta H_{\text{rxn}}^\circ(T)}{RT^2} dT$$

$$C_{p,i} = a_i + b_i T + c_i T^2 + d_i T^3 + e_i T^{-2}$$

$$\begin{aligned} \Delta_{\text{rxn}}H^\circ(T) &= \Delta_{\text{rxn}}H^\circ(T_1) + \Delta a(T - T_1) + \frac{\Delta b}{2}(T^2 - T_1^2) \\ &+ \frac{\Delta c}{3}(T^3 - T_1^3) + \frac{\Delta d}{4}(T^4 - T_1^4) - \Delta e(T^{-1} - T_1^{-1}) \end{aligned}$$

Then

$$\begin{aligned} \ln \frac{K_a(T_2)}{K_a(T_1)} &= \frac{\Delta a}{R} \ln \frac{T_2}{T_1} + \frac{\Delta b}{2R}(T_2 - T_1) + \frac{\Delta c}{6R}(T_2^2 - T_1^2) \\ &+ \frac{\Delta d}{12R}(T_2^3 - T_1^3) + \frac{\Delta e}{2R}(T_2^{-2} - T_1^{-2}) \\ &+ \frac{1}{R} \left[-\Delta_{\text{rxn}}H^\circ(T_1) + \Delta a T_1 + \frac{\Delta b}{2} T_1^2 + \frac{\Delta c}{3} T_1^3 \right. \\ &\left. + \frac{\Delta d}{4} T_1^4 - \frac{\Delta e}{T_1} \right] \times \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \end{aligned}$$

SOLIDS PRESENT

We use activity of a solid=1.

Thus solids do not decompose if gas products $K_y > K_a$

CONVERSION

Substitute x_i by $N_i/\text{Sum}_N N_i$ using

$$N_i = N_{i,0} + \nu_i X$$

Then

$$K_a(T) = K_y K_p$$

Becomes only a function of T and X (we assume $K_\phi=1$)

SEVERAL REACTIONS

$$N_i = N_{i,0} + \sum_{j=1}^{\mathcal{M}} \nu_{ij} X_j \quad i = 1, 2, \dots, \mathcal{C}$$

$$K_{a,j} = \prod_{i=1}^{\mathcal{C}} a_i^{\nu_{ij}} \quad j = 1, 2, \dots, \mathcal{M}$$