

# Chemical Equilibrium - Ch. 16

Isolated system,  $\Pi$  phases,  $u$  components

$$d\underline{S} = \phi = \sum_{s=1}^{\Pi} S_u^{(s)} d\underline{u}^{(s)} + \sum_{s=1}^{\Pi} S_v^{(s)} d\underline{v}^{(s)} + \dots + \sum_{s=1}^{\Pi} \sum_{j=1}^u S_{N_j}^{(s)} dN_j^{(s)}$$

Must have: 
$$\sum_{s=1}^{\Pi} \sum_{j=1}^u S_{N_j}^{(s)} dN_j^{(s)} = 0 \Rightarrow$$

$$\Rightarrow \sum_{s=1}^{\Pi} \sum_{j=1}^u \mu_j^{(s)} dN_j^{(s)} = 0 \quad (16-2a)$$

If we had chosen a system @ constant  $T$  and/or  $P$ , we would still obtain (16-2a) as the condition of equilibrium, from minimization of appropriate function.

How many phases are there?

How many components/reactions?

} Thermodynamics cannot tell a priori

Better be conservative / overestimate: if a component/phase will not be present, minimization of  $\underline{G}$  (or other appropriate F.E.) will eliminate it.

For each reaction:  $v_1 C_1 + v_2 C_2 + \dots + v_i C_i = \phi$

( $r$  total reactions)

$$\sum_{j=1}^u v_j C_j = \phi$$

$n$  components,  $\Pi$  phases  
 $n' = u \cdot \Pi$

$$\frac{\delta N_1}{v_1} = \frac{\delta N_2}{v_2} = \dots = \frac{\delta N_i}{v_i} = \delta \beta \Rightarrow$$

$$d\underline{G} \Big|_{T, P, M} = \sum_{j=1}^{n'} \sum_{s=1}^{\Pi} (v_{j,s} \mu_j) \delta \beta_s = \phi \Rightarrow \sum_{s=1}^{\Pi} v_{j,s} \mu_j = \phi$$

for all reactions  
 $s=1$  to  $r$

Conservation of Atoms

Matrix  $\underline{D} =$

j components  $\rightarrow$

$$\begin{matrix} \downarrow \\ \text{i elements/atoms} \end{matrix} \left[ \begin{array}{cccc} d_{11} & \dots & & d_{1n'} \\ \vdots & \ddots & & \vdots \\ & & d_{ij} & \\ d_{e1} & \dots & & d_{en'} \end{array} \right]$$

Best to treat each component in each phase as a separate column - H<sub>2</sub>O(g) different from H<sub>2</sub>O(l) (u' = n, n')

Vector of Component moles  $\underline{N} = \begin{bmatrix} N_1 \\ N_2 \\ \vdots \\ N_{n'} \end{bmatrix}$ , init. moles  $\underline{b} = \begin{bmatrix} b_1 \\ \vdots \\ b_e \end{bmatrix}$

Must have  $\underline{D} \cdot \underline{N} = \underline{b}^T$  (mass balance)

Stoichiometric Formulation / Independent Reactions

Rank of  $\underline{D} = C$  (typically  $C = \min(\text{\# of rows}, \text{\# of columns})$ , but can be less)

Number of independent reactions =  $n' - C$

Example 16.1

mixture of  $\text{CO}_2, \text{H}_2, \text{H}_2\text{O}, \text{CO}$  in gas phase only  
 $C$  in solid phase only

$$n' = 5$$

$$D = \begin{matrix} & \text{CO}_2 & \text{H}_2 & \text{C} & \text{H}_2\text{O} & \text{CO} \\ \begin{matrix} C \\ H \\ O \end{matrix} & \begin{bmatrix} 1 & 0 & 1 & 0 & 1 \\ 0 & 2 & 0 & 2 & 0 \\ 2 & 0 & 0 & 1 & 1 \end{bmatrix} \end{matrix}$$

$$\text{rank}(D) = C = 3$$

$$\# \text{ of ind. reactions} \quad n' - C = 5 - 3 = 2$$

Example:  $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$  considered as a "reaction"

$$D = \begin{matrix} & \text{H}_2\text{O}(l) & \text{H}_2\text{O}(g) \\ \begin{matrix} H \\ O \end{matrix} & \begin{bmatrix} 2 & 2 \\ \phi & 1 \end{bmatrix} \end{matrix} \quad \text{rank}(D) = 1$$

$$\# \text{ of "reactions"} \quad 2 - 1 = 1 \Rightarrow \mu_l^{\text{H}_2\text{O}} = \mu_g^{\text{H}_2\text{O}}$$

(same as phase equil.)

### Equilibrium Constants

$$\sum_{j=1}^{n'} \nu_j \mu_j = 0 \Rightarrow \sum_{j=1}^{n'} \nu_j \left( G_j^\phi + RT \ln \frac{f_j}{f_j^\phi} \right) = 0 \quad \text{for all independent reactions}$$

$$\Rightarrow - \frac{\sum_{j=1}^{n'} \nu_j G_j^\phi}{RT} = \ln \left[ \prod_{j=1}^{n'} \left( \frac{f_j}{f_j^\phi} \right)^{\nu_j} \right]$$

$$\Delta G_{\text{rxn}}^\phi = \sum_{j=1}^{n'} \nu_j G_j^\phi \quad \phi: \text{Standard state of Component}$$

Define Equilibrium "constant"

$$K_x = \prod_{j=1}^{n'} \left( \frac{\hat{p}_j}{p_j^\phi} \right)^{\nu_j} = \exp\left(-\frac{\Delta G_{rxn}^\phi}{RT}\right)$$

Temperature dependence  $\left(\frac{\partial \ln K_x}{\partial T}\right)_P =$

$$= \frac{\partial}{\partial T} \left[ -\frac{\Delta G_{rxn}^\phi}{RT} \right] = -\frac{1}{RT} \left( \frac{\partial \Delta G_{rxn}^\phi}{\partial T} \right)_P + \frac{\Delta G_{rxn}^\phi}{RT^2} =$$

$$= \frac{\Delta S_{rxn}^\phi}{RT} + \frac{\Delta G_{rxn}^\phi}{RT^2} = + \frac{\Delta H_{rxn}^\phi}{RT^2} \quad \left| \begin{array}{l} \text{cancel on} \\ \text{activation} \\ \text{of } \phi \text{ state} \\ \text{@ const } P! \end{array} \right.$$

$$\Delta H_{rxn}^\phi, T = \Delta H_{rxn}^\phi, T_0 + \int_{T_0}^T \Delta C_p^\phi dT$$

$$\Delta C_p^\phi = \sum_{j=1}^{n'} \nu_j C_{p,j}^\phi$$

Example: Problem 16.7

B graphite  $\rightarrow$  diamond?

$$\rho = 2.26 \frac{\text{g}}{\text{cm}^3}$$

$$\rho = 3.51 \frac{\text{g}}{\text{cm}^3}$$

$$\Delta G_{298}^\phi = +2870 \frac{\text{J}}{\text{g-atom}}$$

( $\phi$ :  $P=1$  bar)

Invention of process for conversion @ 37 Kbar

Check on validity of claim

Assume incompressible solids, no solid solutions

# Chem. Equilibrium (5)

Standard States: pure solids @ 1 bar

What is the equilibrium state @  $P = 1 \text{ bar}$ ?

Fugacity dependence on pressure?  $(dG = d\mu = -SdT + VdP$   
 $d\bar{G}_i = d\mu_i = -\bar{S}_i dT + \bar{V}_i dP + \dots$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \bar{V}_i = V_i \quad | \text{ pure solids}$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = RT \left(\frac{\partial \ln f_i}{\partial P}\right)_T = V_i \Rightarrow \ln f_i(P_2) - \ln f_i(P_1) = \frac{V_i \Delta P}{RT}$$

$$\Rightarrow f_i(P_2) / f_i(P_1) = \exp\left(\frac{V_i \Delta P}{RT}\right)$$

@  $P_2 = 37 \text{ kbar}$

$$V_{\text{graph}} = \frac{1 \text{ cm}^3}{2.26 \text{ g}} \cdot \frac{10^{-6} \text{ m}^3/\text{cm}^3}{\frac{1}{12} \frac{\text{mol}}{\text{g}}} = 5.31 \cdot 10^{-6} \frac{\text{m}^3}{\text{mol}}$$

$$V_{\text{diam}} = \frac{1}{3.51} \cdot \frac{10^{-6}}{1/12} = 3.42 \cdot 10^{-6} \frac{\text{m}^3}{\text{mol}}$$

$$f_{\text{graph}} \neq f_{\text{graph}}^\phi = \exp\left(\frac{5.31 \cdot 10^{-6} \text{ m}^3/\text{mol} \cdot 37 \cdot 10^8 \text{ Pa}}{8.314 \cdot 298 \text{ J/mol}}\right) = 2778$$

$$f_{\text{diam}} / f_{\text{diam}}^\phi = \exp\left(\frac{3.42 \cdot 10^{-6} \cdot 37 \cdot 10^8}{8.314 \cdot 298}\right) = 165$$

$$K = \exp\left(-\frac{2870 \text{ J/mol}}{8.314 \cdot 298}\right) = 0.31 > \frac{f_{\text{diam}}(37 \text{ kbar})}{f_{\text{graph}}(37 \text{ kbar})}$$

equilibrium favors diamond?

Easier approach:  $\Delta \mu_i = V_i \Delta P \Rightarrow \Delta(\Delta \mu) = \Delta V \cdot \Delta P$

$$\Delta P(\text{Equilibrium}) = \frac{\Delta G^\phi}{\Delta V} = \frac{2870 \text{ J/mol}}{(5.31 - 3.42) \cdot 10^{-6}} = 1,520 \text{ MPa} \quad (15.2 \text{ kbar})$$