A First Course on Kinetics and Reaction Engineering

Class 3 on Unit 3

Where We've Been

- Part I - Chemical Reactions
  - 1. Stoichiometry and Reaction Progress
  - 2. Reaction Thermochemistry
  - 3. Reaction Equilibrium
- Part II - Chemical Reaction Kinetics
- Part III - Chemical Reaction Engineering
- Part IV - Non-Ideal Reactions and Reactors

Reaction Equilibrium

- Equilibrium constant

  - $K_j(298 \text{ K}) = \exp\left\{\dfrac{-\Delta G_j^0(298 \text{ K})}{R(298K)}\right\}$

  - $K_j(T) = K_j(298 \text{ K})\exp\left\{\displaystyle\int_{298 \text{ K}}^{T} \dfrac{\Delta H_j^0(T)}{RT^2}dT\right\}$

- Equilibrium expression

  - $K_j(T) = \displaystyle\prod_{\substack{i=\text{all} \\ \text{species}}} a_i^{\nu_{i,j}}$

- Relating thermodynamic activities to composition

  - Gases

    $a_i = \dfrac{y_i P}{1 \text{ atm}} \qquad a_i = \dfrac{y_i \varphi_i P}{1 \text{ atm}}$

  - Liquids

    $a_i = x_i \qquad a_i = h_i x_i \qquad a_i = \gamma_i x_i$

  - Solids

    $a_i = 1.0$

Questions?

Water-Gas Shift Equilibrium Analysis
$CO + H_2O \rightarrow CO_2 + H_2$

- If a system initially contains 3 moles of H_2O and 1 mole of CO at 1 atm and the isobaric water-gas shift reaction proceeds to equilibrium, what is the CO conversion if the temperature is (a) 150 °C, (b) 250 °C and (c) 350 °C?

  ‣ Noting that the water-gas shift reaction is exothermic; predict whether the equilibrium conversion will increase or decrease as the temperature increases before you perform the calculations

- The following expression for the heat of reaction (1) as a function of temperature and a value of -6810 cal mol^{-1} for ΔG^0(298 K) can be generated as described in Unit 2. They are being provided here so that you can focus on the analysis of the equilibrium composition. Expressions for the heat capacities of the reagents are provided in the Table below.

  ‣ $\Delta H_1^0(T) = -9437 - 3.863T + 0.01118T^2 - 9.620 \times 10^{-6}T^3 + 2.455 \times 10^{-9}T^4$

Species	$\hat{C}_p$ (cal/(mol K) with T in K)
CO	$7.373 - 3.07 \times 10^{-3}\,T + 6.662 \times 10^{-6}\,T^2 - 3.037 \times 10^{-9}\,T^3$
H_2O (g)	$7.701 + 4.595 \times 10^{-4}\,T + 5.521 \times 10^{-6}\,T^2 - 0.859 \times 10^{-9}\,T^3$
CO_2	$4.728 + 1.754 \times 10^{-2}\,T - 1.338 \times 10^{-5}\,T^2 + 4.097 \times 10^{-9}\,T^3$
H_2	$6.483 + 2.215 \times 10^{-3}\,T - 3.298 \times 10^{-6}\,T^2 + 1.826 \times 10^{-9}\,T^3$

Water-Gas Shift Equilibrium Analysis
$CO + H_2O \rightarrow CO_2 + H_2$

- If a system initially contains 3 moles of H_2O and 1 mole of CO at 1 atm and the isobaric water-gas shift reaction proceeds to equilibrium, what is the CO conversion if the temperature is (a) 150 °C, (b) 250 °C and (c) 350 °C?

- Show how to calculate the value of the equilibrium constant at 298 K

Water-Gas Shift Equilibrium Analysis
$CO + H_2O \rightarrow CO_2 + H_2$

- If a system initially contains 3 moles of H_2O and 1 mole of CO at 1 atm and the isobaric water-gas shift reaction proceeds to equilibrium, what is the CO conversion if the temperature is (a) 150 °C, (b) 250 °C and (c) 350 °C?

- Show how to calculate the value of the equilibrium constant at 298 K

  $$K_j(298\text{ K}) = \exp\left\{\frac{-\Delta G_j^0(298\text{ K})}{R(298K)}\right\}$$

- Show how to calculate the value of the equilibrium constant at any other temperature, T

Water-Gas Shift Equilibrium Analysis
$CO + H_2O \rightarrow CO_2 + H_2$

- If a system initially contains 3 moles of H_2O and 1 mole of CO at 1 atm and the isobaric water-gas shift reaction proceeds to equilibrium, what is the CO conversion if the temperature is (a) 150 °C, (b) 250 °C and (c) 350 °C?

- Show how to calculate the value of the equilibrium constant at 298 K

  ▸ $$K_j(298 \text{ K}) = \exp\left\{\frac{-\Delta G_j^0(298 \text{ K})}{R(298K)}\right\}$$

- Show how to calculate the value of the equilibrium constant at any other temperature, T

  ▸ $$K_j(T) = K_j(298 \text{ K})\exp\left\{\int_{298 \text{ K}}^{T} \frac{\Delta H_{j(T)}^0}{RT^2} dT\right\}$$

- Note, $K(T)$ could also be calculated from $\Delta G(T)$

  ▸ $$K_j(T) = \exp\left\{\frac{-\Delta G_j^0(T)}{RT}\right\} = \exp\left\{\frac{-\left(\Delta H_j^0(T) - T\Delta S_j^0(T)\right)}{RT}\right\} = \exp\left\{\frac{\Delta S_j^0}{R}\right\}\exp\left\{\frac{-\Delta H_j^0}{RT}\right\}$$

  ▸ Since $\Delta H < 0$, the second exponential will decrease as T increases, and so K will decrease

8

- Write the equilibrium expression in terms of thermodynamic activities. Then express the thermodynamic activities in terms of the mole fractions, assuming ideal gas behavior

- Write the equilibrium expression in terms of thermodynamic activities. Then express the thermodynamic activities in terms of moles, assuming ideal gas behavior

$$K_j(T) = \prod_{\substack{i=\text{all} \\ \text{species}}} a_i^{\nu_{i,j}}$$

$$a_i = \frac{y_i P}{1 \text{ atm}} = \frac{n_i P}{n_{total}(1 \text{ atm})}$$

$$K_1(T) = \frac{n_{CO_2} n_{H_2}}{n_{CO} n_{H_2O}}$$

- Express the moles in terms of the extent of reaction

- Write the equilibrium expression in terms of thermodynamic activities. Then express the thermodynamic activities in terms of moles, assuming ideal gas behavior

$$K_j(T) = \prod_{\substack{i=\text{all} \\ \text{species}}} a_i^{\nu_{i,j}}$$

$$a_i = \frac{y_i P}{1 \text{ atm}} = \frac{n_i P}{n_{total}(1 \text{ atm})}$$

$$K_1(T) = \frac{n_{CO_2} n_{H_2}}{n_{CO} n_{H_2O}}$$

- Express the moles in terms of the extent of reaction

$$K_1(T) = \frac{\xi_1^2}{\left(3 \text{ mol} - \xi_1\right)\left(1 \text{ mol} - \xi_1\right)}$$

- Solve for the equilibrium extent of reaction
- Calculate the equilibrium CO conversion

$$f_{CO} = \frac{n_{CO,0} - n_{CO}}{n_{CO,0}} = \frac{\xi}{n_{CO,0}}$$

Homework Assignment 3

Continuing from Activity 3.1, supposing that the reaction occurs at 260 °C and proceeds to thermodynamic equilibrium, what partial pressure of methanol would be produced if reaction (3) simultaneous occurs and reaches equilibrium, and what would the percent conversion of CO equal?

$$CO + 2\,H_2 \rightleftarrows CH_3OH \tag{3}$$

You may use the equations in Example 3.1 and Activity 3.1 to calculate the equilibrium constants for reactions (1) and (3); you do not need to derive them.

Where We're Going

- Part I - Chemical Reactions

- **Part II - Chemical Reaction Kinetics**
  - ▸ A. Rate Expressions
    - 4. Reaction Rates and Temperature Effects
    - 5. Empirical and Theoretical Rate Expressions
    - 6. Reaction Mechanisms
    - 7. The Steady State Approximation
    - 8. Rate Determining Step
    - 9. Homogeneous and Enzymatic Catalysis
    - 10. Heterogeneous Catalysis
  - ▸ B. Kinetics Experiments
  - ▸ C. Analysis of Kinetics Data

- **Part III - Chemical Reaction Engineering**
- **Part IV - Non-Ideal Reactions and Reactors**