1 Stoichiometry

\[ H_2O + CO \rightleftharpoons CO_2 + H_2 \]
\[ H_2O + H \rightleftharpoons H_2 + OH \]
\[ OH + CO \rightleftharpoons CO_2 + H \]

\[ A_1 = H, A_2 = H_2, A_3 = OH, A_4 = H_2O, A_5 = CO, A_6 = CO_2. \]

\[ \sum_{j=1}^{n_s} v_{ij} A_j = 0, \quad i = 1, \ldots, n_r \]

\[ \nu > 0, \text{ for } A_j \text{ product; } \nu < 0, \text{ for } A_j \text{ reactant.} \]

\[ \nu A = 0, \quad \nu = \begin{bmatrix} 0 & 1 & 0 & -1 & -1 & 1 \\ -1 & 1 & 1 & -1 & 0 & 0 \\ 1 & 0 & -1 & 0 & -1 & 1 \end{bmatrix} \]

\[ r_i: \text{ reaction rate for reaction } i. \]
\[ R_j: \text{ production rate for species } j. \]

\[ R_j = \sum_{i=1}^{n_r} v_{ij} r_i, \quad j = 1, \ldots, n_s \]
\[ R = \nu^T r \]

Extent of reaction: \[ dn_j = \sum_{i=1}^{n_r} v_{ij} d\xi_i, \quad j = 1, \ldots, n_s. \]

2 Thermodynamics

At equilibrium, for a given \( T \) and \( P \), the Gibbs free energy is a minimum.

**Chemical Equilibrium**

\[ dG = -SdT + VdP + \sum_{j=1}^{n_s} \mu_j dn_j \]

\( \mu_j \): chemical potential for species \( j \).

\[ \left( \frac{\partial G}{\partial \xi_i} \right)_{T,P} = \sum_{j=1}^{n_r} v_{ij} \mu_j = 0, \quad i = 1, \ldots, n_r \]

\[ \mu_j = G_j^* + RT \ln a_j, \quad a_j = f_j/f_j^* \]

\[ K_i = \prod_{j=1}^{n_s} a_j^{v_{ij}} \quad \Delta G_i^* = -RT \ln K_i \]

Standard state: pure species \( j \) at 1 atm and system temperature.

**Phase Equilibrium**

\[ f_j^\alpha = f_j^\beta, \quad j = 1, \ldots, n_s, \quad \text{all phases } \alpha \text{ and } \beta \]

Know how to evaluate fugacities for ideal gases, ideal solutions, and Raoult and Henry law approximations.

**Temperature Dependence of \( K \)**

\[ \frac{\partial \ln K_i}{\partial T} = \frac{\Delta H_i^*/RT^2}{RT} \quad \text{(van ’t Hoff Equation)} \]

\[ \ln \left( \frac{K_{i2}}{K_{i1}} \right) = -\frac{\Delta H_i^*}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{(assumption?)} \]

How does raising temperature affect the equilibrium extent for exothermic and endothermic reactions?

3 Reaction-Rate Expressions

\[ r = k(T) f(c_j's) \]

Arrhenius expression for \( k \): \( k(T) = k_0 e^{-E_a/RT}, E_a \) is the activation energy, always positive. How does raising temperature affect reaction rate? What is \( f(c_j's) \) for a sequence of elementary steps. What is the difference between a mechanism and an overall stoichiometry. Quasi-steady-state assumption, equilibrium assumption and rate limiting step.
Langmuir Isotherms (chemisorption)

\[ A + X \rightleftharpoons A \cdot X \quad \Gamma_A = \frac{K_{AC}c_m}{1 + K_{AC}A} \]

Hougen-Watson rate expressions Deciding which mechanism best explains rate data.

4 Material and Energy Balances

\[ \frac{d}{dt} \int_V c_j dV = Q_0 c_{j0} - Q_1 c_{j1} + \int_V R_j dV, \quad j = 1, \ldots, n_s \]

\[ \frac{d}{dt} \int_V \rho \hat{V} dV = m_0 \hat{H}_0 - m_1 \hat{H}_1 + \hat{Q} + \hat{W}_s + \hat{W}_b \]

5 Fixed-Bed Catalytic Reactors

Steps in a Catalytic Reactor
1. convection of reactant in the bulk fluid
2. mass transfer from bulk fluid to catalyst
3. diffusion of reactant in the pores (molecular and Knudsen diffusion)
4. adsorption of reactant on the active sites
5. reaction of adsorbed reactants to adsorbed products (surface reaction)
6. desorption of adsorbed products
7. diffusion out of pores
8. mass transfer from catalyst to bulk fluid
9. convection of product in the bulk fluid
Partial Differential Equations
\[ \frac{\partial c_j}{\partial t} = D_j \nabla^2 c_j + R_j \]

1st-order reaction, spherical pellet, steady state:
\[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) - \Phi^2 c = 0 \]
\[ c = 1, \quad r = 3 \]
\[ \frac{\partial c}{\partial r} = 0, \quad r = 0 \]

Solution:
\[ c(r) = \frac{3 \sinh \Phi r}{r \sinh 3\Phi} \]

Thiele modulus:
\[ \Phi = \left( \frac{n + 1}{2} \frac{k c_A n \cdot a^2}{D_A} \right)^{1/2} = \frac{V_p}{\rho \beta} \]

Effectiveness factor:
\[ \eta = \frac{\text{actual rate in pellet}}{\text{rate without diffusional limitations}} \]

**Simultaneous Reaction and Diffusion**

**Table 1:** Summary of Material and Energy Balances for Several Ideal Reactors.

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>Balance Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>BATCH</td>
<td>[ V_R \rho \hat{C}<em>p \frac{dT}{dt} = - \sum_i \Delta H</em>{Ri} V_R + \dot{Q} ]</td>
</tr>
<tr>
<td>CSTR (constant ( \hat{C}_p ))</td>
<td>[ V_R \hat{C}<em>p \frac{dT}{dt} = - \sum_i \Delta H</em>{Ri} V_R + \dot{Q} ] + ( Q_f \rho_f \hat{C}_p (T_f - T) )</td>
</tr>
<tr>
<td>PFR (steady state)</td>
<td>[ Q \rho \hat{C}<em>p \frac{dT}{dV} = - \sum_i \Delta H</em>{Ri} V_R + \dot{Q} ]</td>
</tr>
</tbody>
</table>

**Figure 4:** Expanded views of a fixed-bed reactor.

**Figure 5:** Effectiveness Factor Versus Thiele Modulus: Effect of Geometry and Reaction Order.

**Table 2:** Effectiveness factor versus Thiele modulus for the sphere, semi-infinite cylinder, and semi-infinite slab.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>( \eta ) Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>( \eta = \frac{1}{\Phi} \left[ \frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi} \right] ) (1)</td>
</tr>
<tr>
<td>Cylinder</td>
<td>( \eta = \frac{1}{\Phi} I_1(2\Phi) ) (2)</td>
</tr>
<tr>
<td>Slab</td>
<td>( \eta = \frac{\tanh \Phi}{\Phi} ) (3)</td>
</tr>
</tbody>
</table>

\( n \) typical reaction order, \( \Phi \) Thiele modulus, \( a \) mass transfer coefficient, \( V_p \) pellet volume, \( S_p \) pellet surface area, \( \rho \) material density, \( \dot{Q} \) heat generation, \( \Delta H_{Ri} \) reaction enthalpy change, \( T_f \) feed temperature, \( T \) reaction temperature.
6 Mixing in Chemical Reactors

Residence-time distribution

\[ p(\theta) d\theta, \quad \text{probability that a feed molecule spends time} \]
\[ \theta \text{ to } \theta + d\theta \text{ in the reactor} \]
\[ P(\theta), \quad \text{probability that a feed molecule spends time} \]
\[ \text{zero to } \theta \text{ in the reactor} \]

\[ c_e(t) = \int_0^t c_f(t') p(t - t') dt', \quad c_f(t) = 0, t \leq 0 \]

Step response, impulse response for CSTR, PFR, \( n \) CSTRs, PFR with dispersion. Effect of mixing on rates of convex and concave rate expressions. Simple mixing models.

7 Parameter Estimation

Probability review. Normal distribution, mean, variance.

\[ p(x) = \frac{1}{\sqrt{2\pi}\sigma^2} \exp \left( -\frac{1}{2} \frac{(x - m)^2}{\sigma^2} \right) \]
\[ p(x) = \frac{1}{(2\pi)^{n_p/2} |P|^{1/2}} \exp \left[ -\frac{1}{2} (x - m)^T P^{-1} (x - m) \right] \]

Least squares. Let \( y \) be measured as a function of \( x \)

\[ y_i = mx_i + b, \quad i = 1, \ldots n \]