Chemical Reaction Engineering
Lecture 6: Complex Reactions

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Topic 3: Complex systems

- Analysis of “Simple complex” systems
- Kinetics of complex systems
  - Chain reaction
  - Catalysis
  - Polymerization
- Lumping analysis
Complex systems - Examples

- Large number of reactions and reactants

*Thermal cracking of alkanes*

\[ C_3H_8 \rightarrow C_3H_6 + H_2 \]

\[ C_3H_8 \rightarrow C_2H_4 + CH_4 \]

\[ C_3H_8 + C_2H_4 \rightarrow C_2H_6 + C_3H_6 \]

*Cracking of crude to petrol*

*Metabolic network inside cell*
Complex systems - Examples

- Chain reactions

  *Thermal decomposition*
  \[ CH_3CHO \rightarrow CH_4 + CO \]

  *Auto-oxidation*
  \[ R - H + O_2 \rightarrow ROOH \]

  *Polymerization*
  \[ styrene \rightarrow poly(styrene) \]
Complex systems - Examples

➢ Catalytic reactions

*Thermal decomposition*

\[
C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{acid}} C_6H_{12}O_6 + C_6H_{12}O_6
\]

*Ammonia synthesis*

\[
\frac{1}{2}N_2 + \frac{3}{2}H_2 \xrightarrow{\text{Fe}} NH_3
\]
Yield – conversion diagram
Polymer weight distribution

Fig. 2. Comparison of experimental and calculated by the OCFE MWDs at different monomer conversions (MMA free-radical polymerization. Initiator concentration = $3 \times 10^{-2}$ kg/kg of MMA; temperature = 70 °C) [23].
Catalytic reaction kinetics

![Graph showing the relationship between rate and pressure for different oxygen concentrations. The x-axis represents the pressure of ethylene, and the y-axis represents the rate. The graph includes data points for different oxygen pressures (0.061, 0.132, 0.263, 0.526, 0.789) depicted with various markers.](image-url)
Complex reactor behavior

Figure 10.4.1-4
Cracking of ethane to ethylene

New questions

- Are all products useful?
- How to monitor the reaction?
- Is conversion of ethane the only criteria for design?
Parallel reactions
Series reactions

\[ A_1 \rightarrow A_2 \rightarrow A_3 \]
Complex (Series-parallel) reactions

\[ A_2 + A_3 \rightarrow A_4 \]
Independent Reactions

\[ A_1 \rightarrow A_2 \]
\[ A_3 \rightarrow A_4 \]
Desired and Undesired Reactions

\[ A_1 \rightarrow A_2 \]

\[ A_1 \rightarrow A_3 \]

\[ A_1 \rightarrow A_2 \rightarrow A_3 \]
Yield

**Desired reaction** \( A_1 \rightarrow A_2 \quad r_1 \)

**Undesired reaction** \( A_1 \rightarrow A_3 \quad r_2 \)

**Overall Yield**

\[
Y_2 = \frac{\text{Exit molar flowrate of desired product}}{\text{Inlet molar flowrate of reactant}}
\]
Selectivity

Desired reaction \[ A_1 \rightarrow A_2 \quad r_1 \]

Undesired reaction \[ A_1 \rightarrow A_3 \quad r_2 \]

Instantaneous Selectivity \[ s_2 = \frac{r_1}{r_1 + r_2} \]

Overall Selectivity \[ \tilde{S}_2 = \frac{\text{Exit molar flowrate of desired product}}{\text{Exit molar flowrate of all products}} \]
Selection of reactor type and conditions

**Desired reaction** \[ A_1 \rightarrow A_2 \quad r_1 \]

**Undesired reaction** \[ A_1 \rightarrow A_3 \quad r_2 \]

**CSTR**
\[
\frac{C_2}{C_{10} - C_1} = \frac{r_1}{r_1 + r_2}
\]

**PFR**
\[
\frac{C_2}{C_{10} - C_1} = \frac{1}{C_{10} - C_1} \int_{C_1}^{C_{10}} \frac{r_1}{r_1 + r_2} dC_1
\]
Complex systems - selectivity

\[ C_{10} - C_1 \]

selectivity \((C_1)\)

\[ q_2 - q_1 \]

- 1

0

1
Complex systems – series reactions

\[ A_1 \rightarrow A_2 \quad r_1 = k_1 C_1 \]

\[ A_2 \rightarrow A_3 \quad r_1 = k_2 C_2 \quad \alpha = k_2 / k_1 \]
Concept of yield-conversion diagram

\[ A_1 \rightarrow A_2 \quad r_1 = k_1 C_1 \]
\[ A_2 \rightarrow A_3 \quad r_1 = k_2 C_2 \quad \alpha = \frac{k_2}{k_1} \]
Concept of rate determining step

\[ A_1 \rightarrow A_2 \quad r_1 = k_1 C_1 \]

\[ A_2 \rightarrow A_3 \quad r_1 = k_2 C_2 \quad \alpha = \frac{k_2}{k_1} \]
Concept of rate determining step

\[ A_1 \rightarrow A_2 \quad r_1 = k_1 C_1 \]

\[ A_2 \rightarrow A_3 \quad r_1 = k_2 C_2 \quad \alpha = \frac{k_2}{k_1} \]
Concept of quasi-equilibrium approximation

\[ A_1 \rightleftharpoons A_2 \quad r_1 = k_1 C_1 - k_{-1} C_2 \]
\[ A_2 \rightleftharpoons A_3 \quad r_1 = k_2 C_2 - k_{-2} C_3 \]

\[ k_1 = 1, \quad k_{-1} = 0.5, \quad k_2 = k_{-2} = 1 \]
Concept of quasi-equilibrium approximation

\[ A_1 \rightleftharpoons A_2 \quad r_1 = k_1 C_1 - k_{-1} C_2 \]
\[ A_2 \rightleftharpoons A_3 \quad r_1 = k_2 C_2 - k_{-2} C_3 \]

\[ k_1 = 1, \quad k_{-1} = 0.5, \quad k_2 = k_{-2} = 10 \]
Concept of quasi-equilibrium approximation

\[ A_1 \rightleftharpoons A_2 \quad r_1 = k_1 C_1 - k_{-1} C_2 \]
\[ A_2 \rightleftharpoons A_3 \quad r_1 = k_2 C_2 - k_{-2} C_3 \]

\( k_1 = 1, \ k_{-1} = 0.5, \ k_2 = k_{-2} = 10 \)
Concept of quasi-steady state approximation

\[ A_1 \rightarrow A_2 \quad r_1 = k_1 C_1 \]

\[ A_2 \rightarrow A_3 \quad r_1 = k_2 C_2 \quad \alpha = \frac{k_2}{k_1} \]

![Graph showing concentration over time with alpha = 5]
Concept of quasi-steady state approximation

\[ A_1 \rightarrow A_2 \quad r_1 = k_1 C_1 \]
\[ A_2 \rightarrow A_3 \quad r_1 = k_2 C_2 \quad \alpha = \frac{k_2}{k_1} \]
Chemical Reaction Engineering
Lecture 6: Complex Reactions

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Chain reactions

- Combustion reactions
- Decomposition reactions
- Autooxidation
- Polymerization
Chain reactions – decomposition of acetaldehyde

\[ CH_3CHO \rightarrow CH_4 + CO \]

\[ CH_3CHO \rightarrow CH_3^\cdot + CHO^\cdot \]

\[ CH_3^\cdot + CH_3CHO \rightarrow CH_3CO^\cdot + CH_4 \]

\[ CH_3CO^\cdot \rightarrow CH_3^\cdot + CO \]

\[ 2CH_3^\cdot \rightarrow C_2H_6 \]

\[ r = kC_{CH_3CHO}^{3/2} \]
Polymerization

- Chain polymerization of $\text{CH}_2 = \text{CHX}$ $(RX)$
  - Ethylene (X=H), vinyl chloride (X=Cl)
  - Styrene (X=C$_6$H$_5$) etc

- Initiator 1 (Φ-Φ)

  **Initiation**
  $$C_6H_5COO - OOCC_6H_5 \rightarrow 2C_6H_5COO \bullet$$
  $$\Phi \bullet + RX \rightarrow \Phi - RX \bullet$$

  **Propagation**
  $$\Phi - RX \bullet + RX \rightarrow \Phi - (R) - RX \bullet$$
  $$\Phi - (R)_{j-1} - RX \bullet + RX \rightarrow$$
  $$\Phi - (R)_{j} - RX \bullet$$

  **Termination**
  $$\Phi - (R)_{j-1} - RX \bullet + \bullet XR - (R)_{i-1} - \Phi \rightarrow$$
  $$\Phi - (R)_{j-1} - RX - XR - (R)_{i-1} - \Phi$$
Polymerization

Initiation  
\[ I \xrightarrow{k_0} 2\Phi \quad \text{and} \quad k_0 = 10^{-4} - 10^{-6} \]
\[ \Phi + M \xrightarrow{k_i} R_1 \]

Propagation  
\[ R_1 + M \xrightarrow{k_p} R_2 \quad k_p = 10^2 - 10^4 \]
\[ R_{j-1} + M \xrightarrow{k_p} R_j \]

Termination  
\[ R_j + R_i \xrightarrow{k_a} P_{i+j} \quad k_a = 10^6 - 10^8 \]
Polymerization

<table>
<thead>
<tr>
<th>Species</th>
<th>Appearance</th>
<th>disappearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I$</td>
<td></td>
<td>$k_0 I$</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>$r_0 = 2 f k_0 I$</td>
<td>$r_i = k_i \Phi M$</td>
</tr>
<tr>
<td>$R_1$</td>
<td>$r_i$</td>
<td>$k_p M R_1 + k_a R_1 \sum R_j$</td>
</tr>
<tr>
<td>$R_j$</td>
<td>$k_p M R_j$</td>
<td>$k_p M R_j + k_a R_j \sum R_i$</td>
</tr>
<tr>
<td>$P_j$</td>
<td>$\frac{k_a}{2} \sum R_{j-i} R_i$</td>
<td></td>
</tr>
</tbody>
</table>
Polymerization

**Initiation rate** \( r_i = 2 f k_0 I \)

**Total radicals** \( \Sigma R_j = \Gamma_0 = \left( \frac{r_i}{k_a} \right)^{1/2} \)

**Monomer consumption** \( r_M = k_p M \Gamma_0 \)

**Radical concn** \( R_j = \left( \frac{r_i}{k_p M} \right) \left( \frac{1}{1 + r_i / r_M} \right)^j \)

**polymer generation** \( r_p = R_j (j - 1) \frac{k_a}{2} \left( \frac{r_i}{k_p M} \right) \)
Polymerization

- Time (min):
  - 360
  - 180
  - 60

- Initiator:
  - 0.04
  - 0.02
  - 0.08
Polymer weight distribution

Fig. 2. Comparison of experimental and calculated by the OCFE MWDs at different monomer conversions (MMA free-radical polymerization. Initiator concentration = $3 \times 10^{-2}$ kg/kg of MMA; temperature = 70 °C) [23].
Chemical Reaction Engineering
Catalytic reactions

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Catalytic reactions

Heterogeneous catalysis

- Gas
- Solid
- Liquid
- (2nd Liquid) Catalyst
Catalytic reactions

Example: Hydrogen peroxide decomposition

\[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \]

- \( \text{H}_2\text{O}_2 \) solution at 25°C stable over months
- Uncontrolled, thermal decomposition at >320°C in seconds
- Controlled, catalytic or enzymatic decomposition at 25°C in seconds
Catalytic reactions

Efficiency of Phthalic Acid Anhydride Production

Non-catalytic Oxidation of naphthalene in fluid phase with MnO₂+HCl (1872), Chromic acid (1881), Oleum (1891)

Yield: 5-15%

Catalytic Oxidation of o-Xylene in the gas phase on V₂O₅-catalyst

Yield: 75-87%
Catalytic reactions

Efficiency of nitrogen fixation

- Nitric Acid by Electric Arc (Birkeland & Eyde)
- Calcium Cyanide (Frank & Caro)
- Ammonia from coke (Haber & Bosch)
- Ammonia from electrolysis of water
- Ammonia from natural gas
- Partial oxidation
- Steam reforming

catalytic processes
Catalytic reactions

Product spectrum from partial oxidation of propene

Substrates: propene + oxygen

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi, Mo, P</td>
<td>acrolein, CH₂=CH-CHO</td>
</tr>
<tr>
<td>Mo, V, Fe</td>
<td>acrylic acid, CH₂=CH-COOH</td>
</tr>
<tr>
<td>Sn, Mo</td>
<td>acetone, CH₃-C-CH₂-CH₂</td>
</tr>
<tr>
<td>Ti, W</td>
<td>propylene oxide, CH₃-O-CH₂-CH₂</td>
</tr>
<tr>
<td>Ti, V</td>
<td>acetic acid, CH₃-COOH</td>
</tr>
<tr>
<td>Zn, Mo</td>
<td>1,5-hexadiene, CH₂=CH-CH₂-CH₂-CH=CH₂</td>
</tr>
<tr>
<td>Bi, Sb</td>
<td>benzene, C-CH₃-CH₂-CH₂-CH₂-CH₂</td>
</tr>
</tbody>
</table>

Propene + oxygen: CH₃-CH=CH₂ + O₂
Catalytic reactions

Steps during the course of the reaction
① External diffusion
② Internal diffusion
③ Adsorption on the active sites
④ Surface reaction
⑤ forming the products
⑥ Desorption of the products
⑦ Internal diffusion
External diffusion

reaction: substrate A → product P
Lumping analysis

\[ A_{10} = 1, \ A_{20} = 0, \ A_{30} = 0 \]

\[ A_{10} = 0.5, \ A_{20} = 0.5, \ A_{30} = 0 \]
Lumping analysis

\[ \hat{A}_1 = A_1 + A_3, \quad \hat{A}_2 = A_2 \]

Initial \( A_1, A_2, A_3 \)
- 1,0,0
- 0,0,1

Concentration vs. Time graph