Chemical Reaction Engineering

Lecture 6: Complex Reactions

Jayant M. Modak
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Topic 3: Complex systems

- Analysis of "Simple complex" systems
- Kinetics of complex systems
  - Chain reaction
  - Catalysis
  - Polyermization
- Lumping analysis

Complex systems - Examples

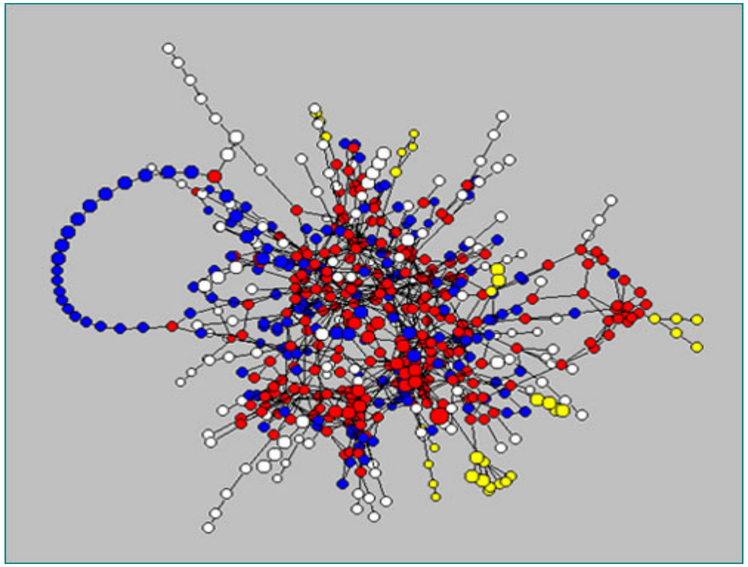
- Large number of reactions and reactants

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

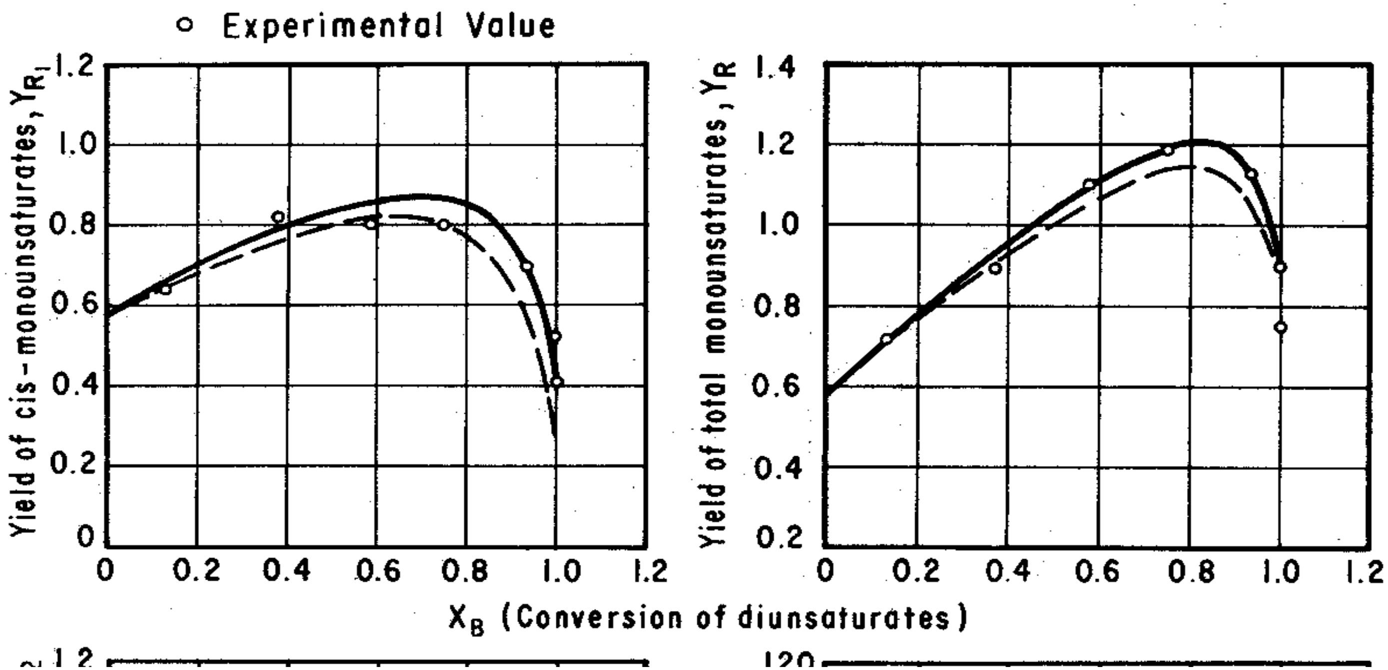
Thermal decomposition

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{acid} C_6H_{12}O_6 + C_6H_{12}O_6$$

Ammonia synthesis

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \xrightarrow{Fe} NH_3$$

Yield – conversion diagram



Polymer weight distribution

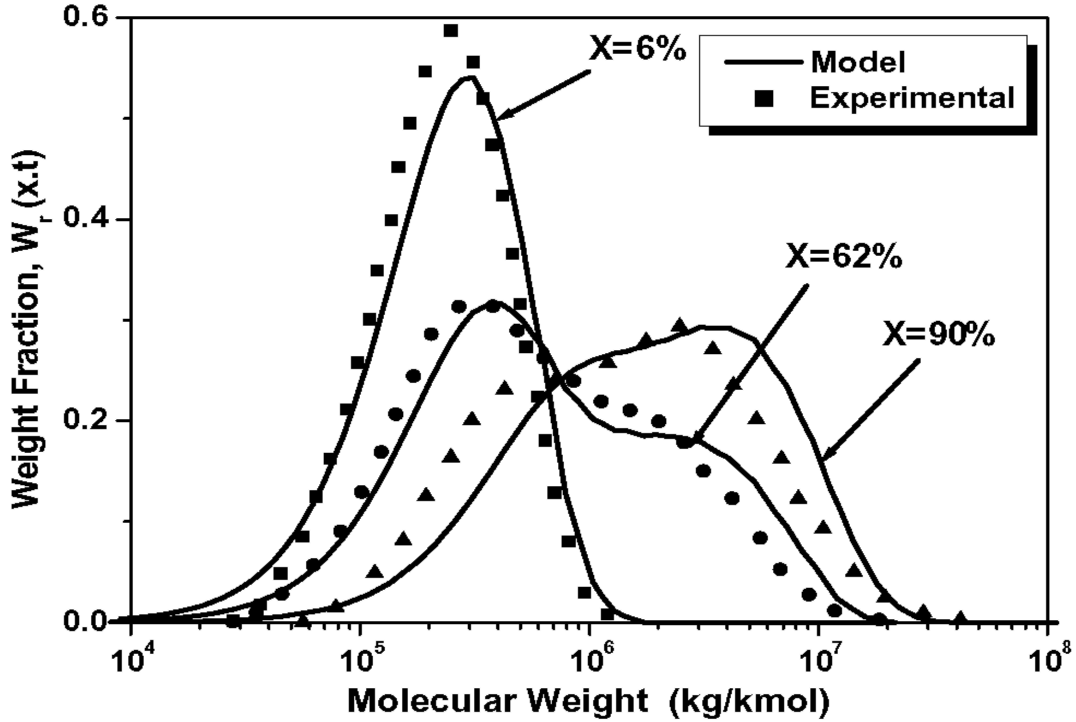
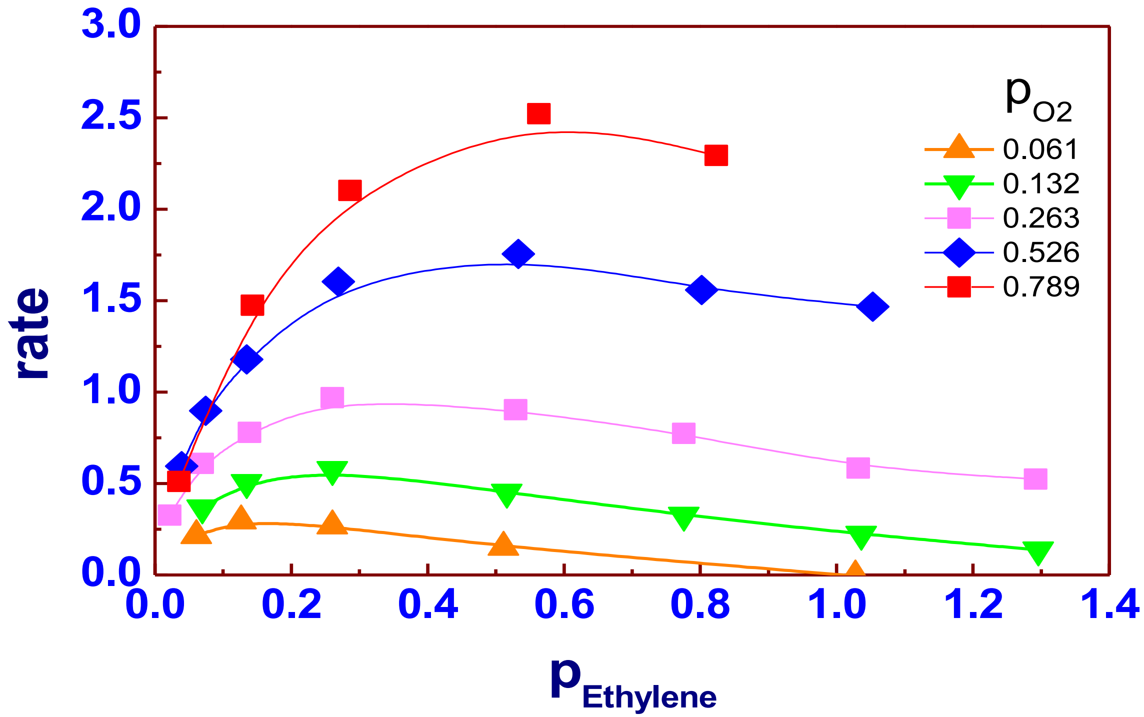


Fig. 2. Comparison of experimental and calculated by the OCFE MWDs at different monomer conversions (MMA free-radical polymerization. Initiator concentration = 3×10^{-2} kg/kg of MMA; temperature = 70 °C) [23].

Catalytic reaction kinetics



Complex reactor behavior

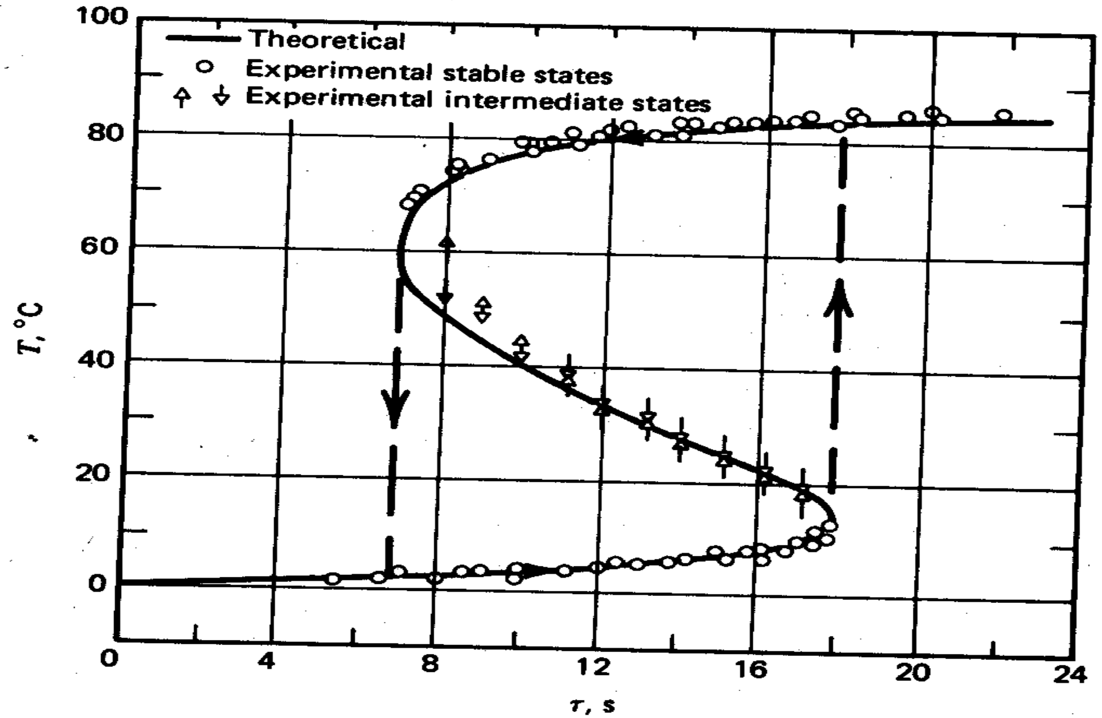


Figure 10.4.1-4
Steady-state hysteresis results. From Vejtassa and Schmitz (1970).

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

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$$2C_2H_6 \rightarrow C_3H_8 + CH_4$$

$$A_1 \nearrow A_2$$

$$A_1 \searrow A_3$$

Series reactions

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$$C_2H_4 \rightarrow 2C + 2H_2$$

$$A_1 \rightarrow A_2 \rightarrow A_3$$

Complex (Series-parallel) reactions

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$$2C_2H_6 \rightarrow C_3H_8 + CH_4$$

$$C_3H_8 + C_2H_4 \rightarrow C_4H_8 + CH_4$$

$$A_1 \rightarrow A_2$$

$$A_1 \rightarrow A_3$$

$$A_2 + A_3 \rightarrow A_4$$

Independent Reactions

$$C_2H_6 \rightarrow C_2H_4 + H_2 \qquad A_1 \rightarrow A_2$$

$$C_3H_8 \rightarrow C_3H_6 + H_2 \qquad A_3 \rightarrow A_4$$

Desired and Undesired Reactions

$$A_1 \to A_2$$

$$A_1 \to A_3$$

$$A_1 \to A_2 \to A_3$$

Yield

$$Desired\ reaction \qquad A_1 \rightarrow A_2 \qquad r_1$$

$$Undesired\ reaction \qquad A_1 \rightarrow A_3 \qquad r_2$$

Overall Yield

$$Y_2 = \frac{Exit\ molar\ flowrate\ of\ desired\ product}{Inlet\ molar\ flowrate\ of\ reactant}$$

Selectivity

$$\text{Desired reaction} \quad A_1 \rightarrow A_2 \quad r_1$$

$$\text{Undesired reaction} \quad A_1 \rightarrow A_3 \quad r_2$$

$$\text{Instantenous Selectivity} \quad s_2 = \frac{r_1}{r_1 + r_2}$$

$$\text{Overall Selectivity} \quad \tilde{S}_2 = \frac{\text{Exit molar flowrate of desired product}}{\text{Exit molar flowrate of all products}}$$

Selection of reactor type and conditions

$$\text{Desired reaction} \qquad A_1 \rightarrow A_2 \qquad r_1$$

$$\text{Undesired reaction} \qquad A_1 \rightarrow A_3 \qquad r_2$$

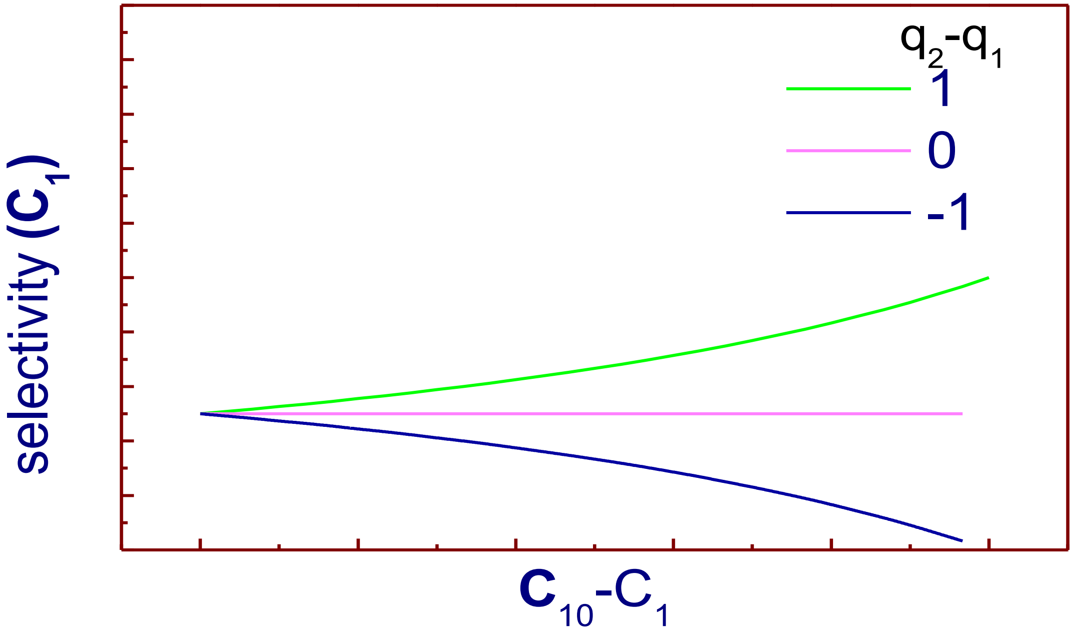
CSTR

$$\frac{C_2}{C_{10} - C_1} = \frac{r_1}{r_1 + r_2}$$

PFR

$$\frac{C_2}{C_{10} - C_1} = \frac{1}{C_{10} - C_1} \int_{C_1}^{C_{10}} \frac{r_1}{r_1 + r_2} dC_1$$

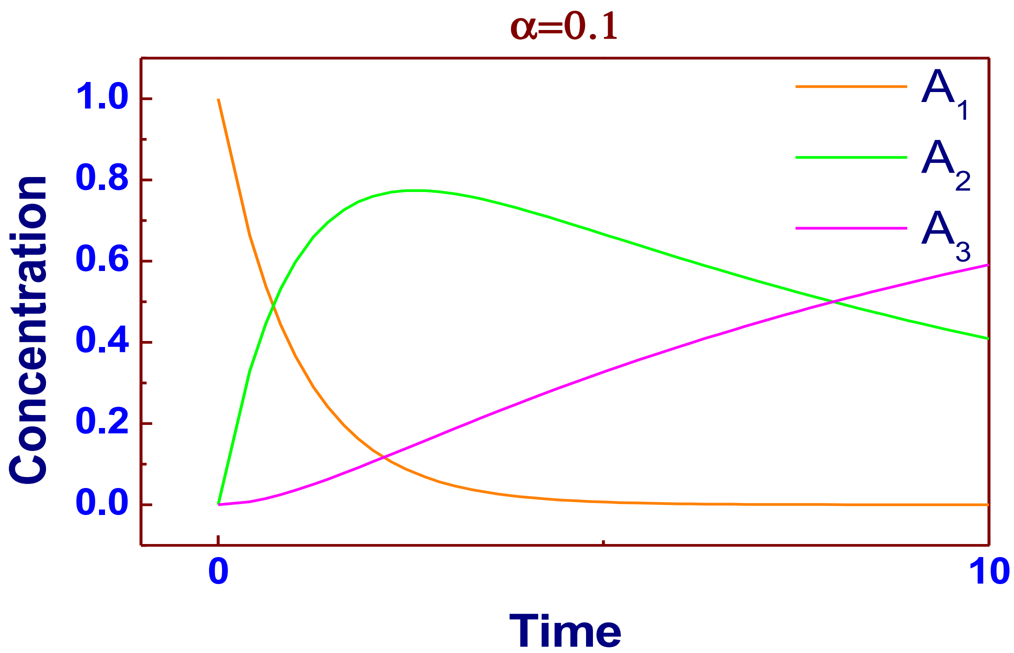
Complex systems - selectivity



Complex systems – series reactions

$$A_1 \rightarrow A_2 \qquad r_1 = k_1 C_1$$

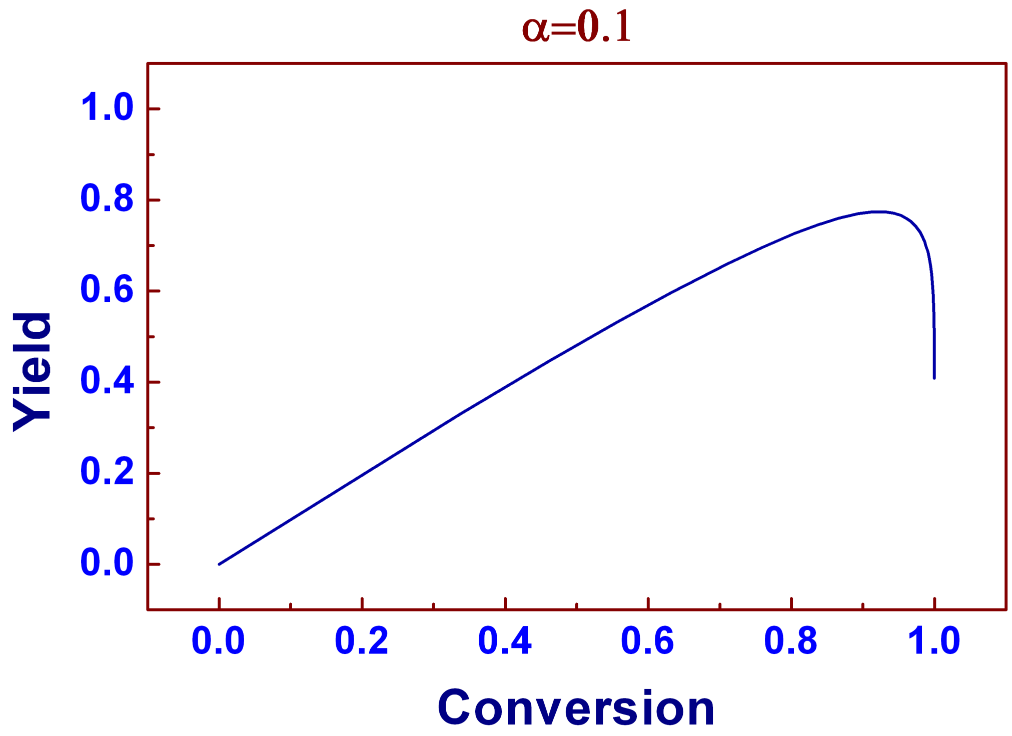
$$A_2 \rightarrow A_3 \qquad r_1 = k_2 C_2 \qquad \alpha = k_2 / k_1$$



Concept of yield-conversion diagram

$$A_1 \rightarrow A_2 \qquad r_1 = k_1 C_1$$

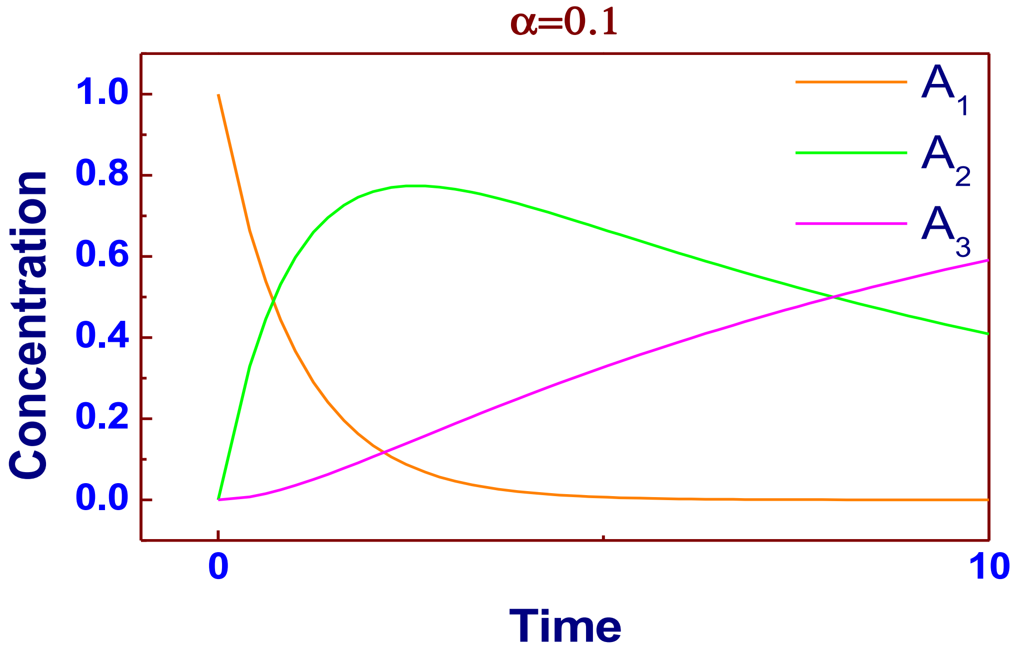
$$A_2 \rightarrow A_3 \qquad r_1 = k_2 C_2 \qquad \alpha = k_2 / k_1$$



Concept of rate determining step

$$A_1 \rightarrow A_2 \qquad r_1 = k_1 C_1$$

$$A_2 \rightarrow A_3 \qquad r_1 = k_2 C_2 \qquad \alpha = k_2 / k_1$$



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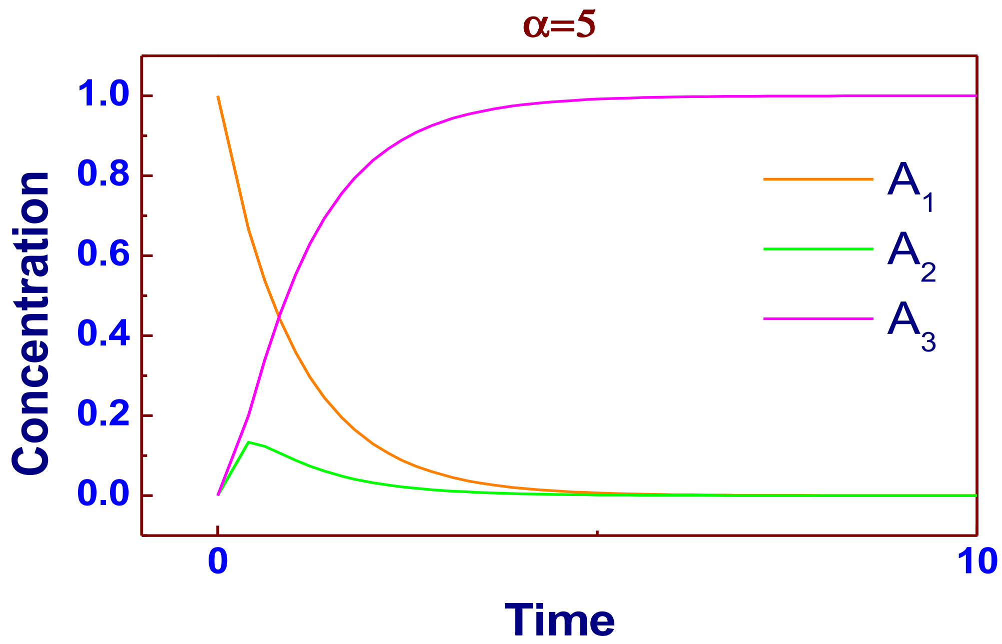
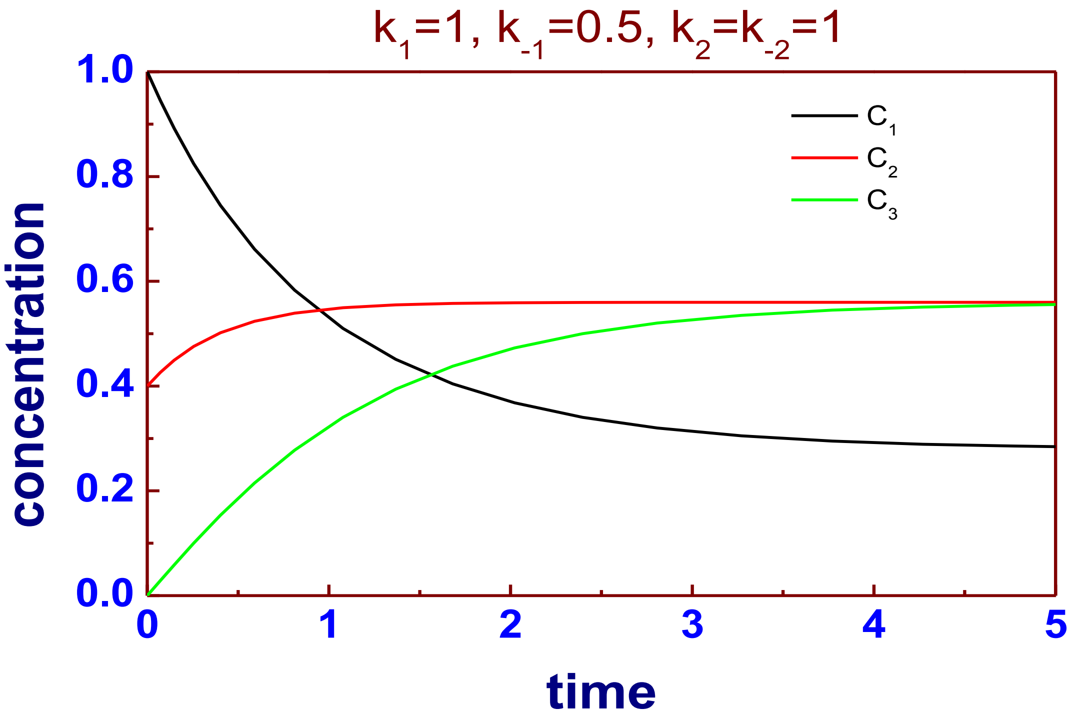


Concept of quasi-equilibrium approximation

$$A_1 \rightleftarrows A_2 \qquad r_1 = k_1 C_1 - k_{-1} C_2$$

$$A_2 \rightleftarrows A_3 \qquad r_1 = k_2 C_2 - k_{-2} C_3$$



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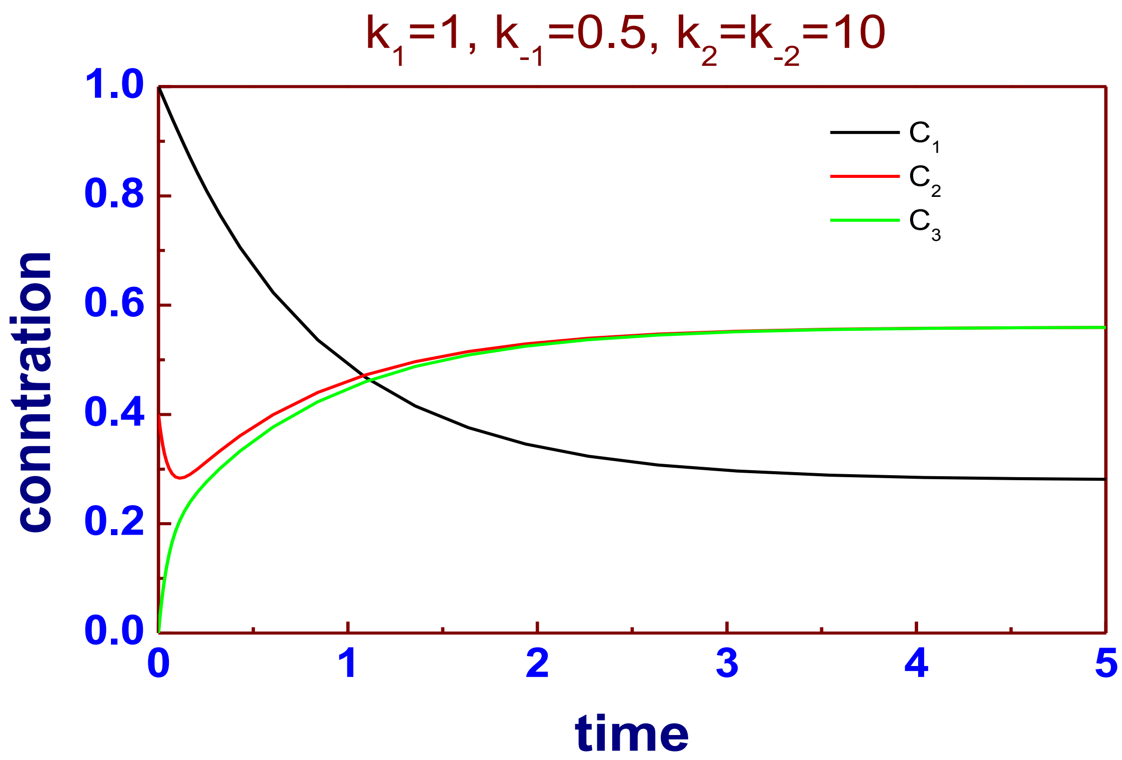

Concept of quasi-equilibrium approximation

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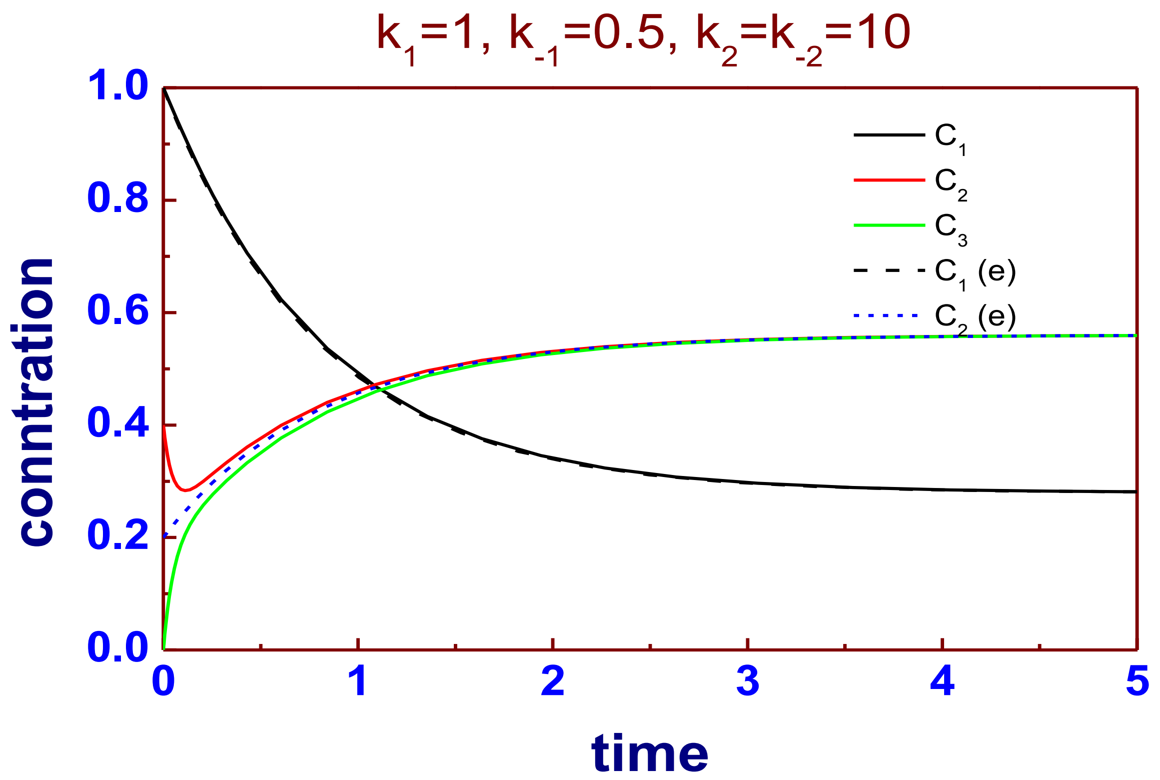
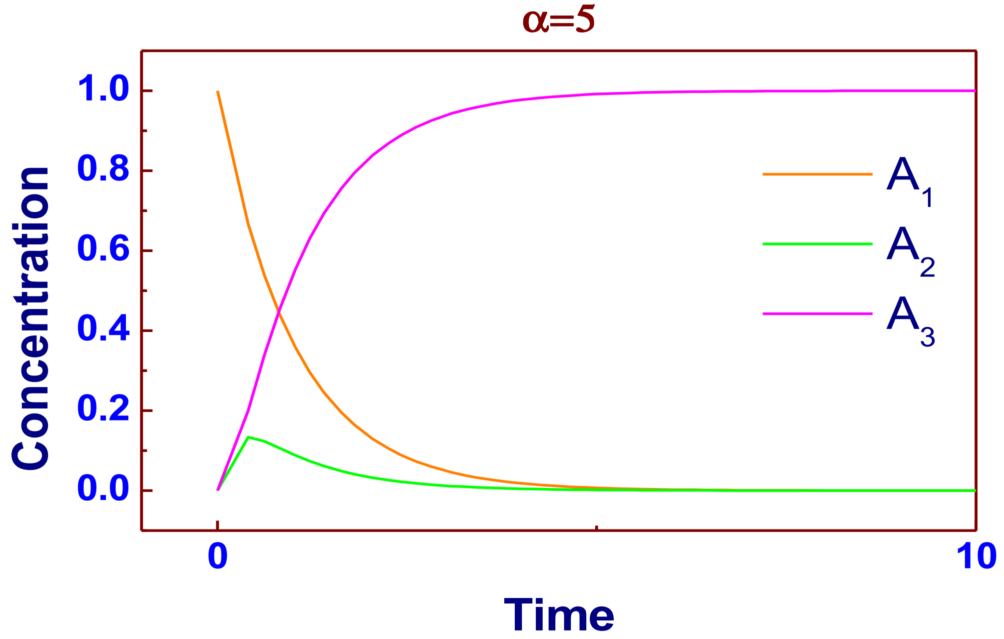


Concept of quasi-steady state approximation

$$A_1 \rightarrow A_2 \qquad r_1 = k_1 C_1$$

$$A_2 \rightarrow A_3 \qquad r_1 = k_2 C_2 \qquad \alpha = k_2 / k_1$$



Concept of quasi-steady state approximation

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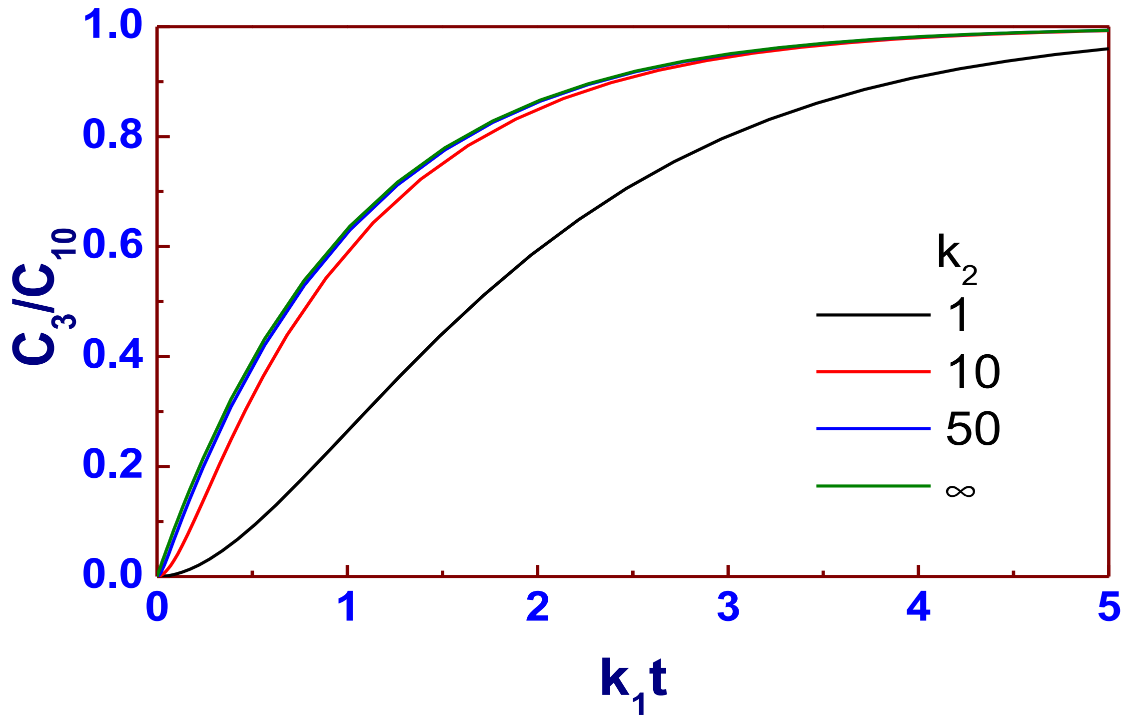


Chemical Reaction Engineering

Lecture 6: Complex Reactions

Jayant M. Modak
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Chain reactions

- Combustion reactions
- Decomposition reactions
- Autooxidation
- Polymerization

Chain reactions – decomposition of acetaldehyde

$$CH_3CHO \rightarrow CH_4 + CO$$

$$CH_3CHO \rightarrow CH_3^{\bullet} + CHO^{\bullet}$$

$$CH_3^{\bullet} + CH_3CHO \rightarrow CH_3CO^{\bullet} + CH_4$$

$$CH_3CO^{\bullet} \rightarrow CH_3^{\bullet} + CO$$

$$2CH_3^{\bullet} \rightarrow C_2H_6$$

$$r = kC_{CH_3CHO}^{3/2}$$

Polymerization

- Chain polymerization of $CH_2 = CHX \quad (RX)$
  - Ethylene (X=H), vinyl chloride (X=Cl)
  - Styrene (X=C_6H_5) etc
- Initiator I (Φ-Φ)

$$\textit{Initiation} \quad C_6H_5COO - OOCC_6H_5 \rightarrow 2C_6H_5COO\bullet$$

$$\Phi\bullet + RX \rightarrow \Phi - RX\bullet$$

$$\textit{Propogation} \quad \Phi - RX\bullet + RX \rightarrow \Phi - (R) - RX\bullet$$

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

$$\Phi - (R)_j - RX\bullet$$

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

$$\textit{Termination}$$

$$\Phi - (R)_{j-1} - RX - XR - (R)_{i-1} - \Phi$$

Polymerization

Initiation	$I \xrightarrow{k_0} 2\Phi$	$k_0 = 10^{-4} - 10^{-6}$
	$\Phi + M \xrightarrow{k_i} R_1$	
Propogation	$R_1 + M \xrightarrow{k_p} R_2$	$k_p = 10^2 - 10^4$
	$R_{j-1} + M \xrightarrow{k_p} R_j$	
Termination	$R_j + R_i \xrightarrow{k_a} P_{i+j}$	$k_a = 10^6 - 10^8$

Polymerization

$Species$	$Appearance$	$disappearance$
I		$k_0 I$
Φ	$r_0 = 2 f k_0 I$	$r_i = k_i \Phi M$
R_1	r_i	$k_p M R_1 + k_a R_1 \sum R_j$
R_j	$k_P M R_j$	$k_p M R_j + k_a R_j \sum R_i$
P_j	$\frac{k_a}{2} \sum R_{j-i} R_i$	

Polymerization

$$Initiation\ rate \qquad r_i = 2fk_0 I$$

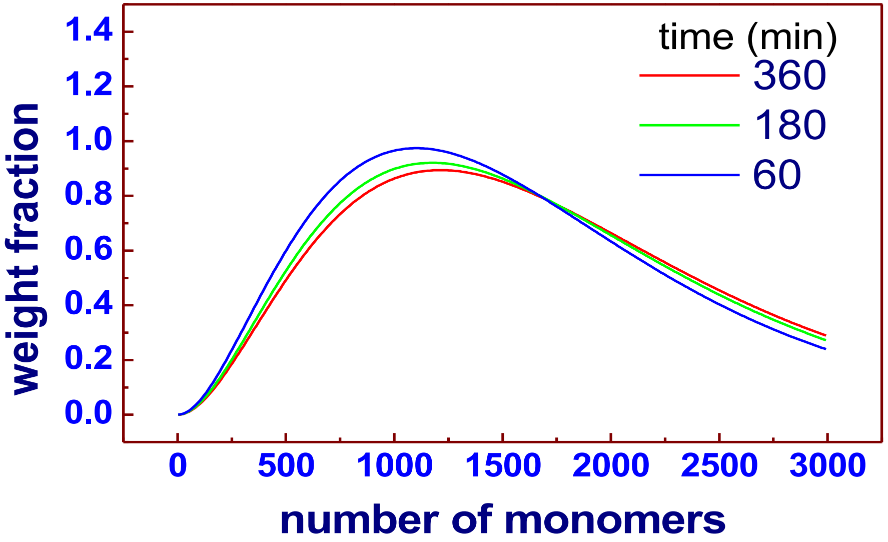
$$Total\ radicals \qquad \Sigma R_j = \Gamma_0 = \left(\frac{r_i}{k_a}\right)^{1/2}$$

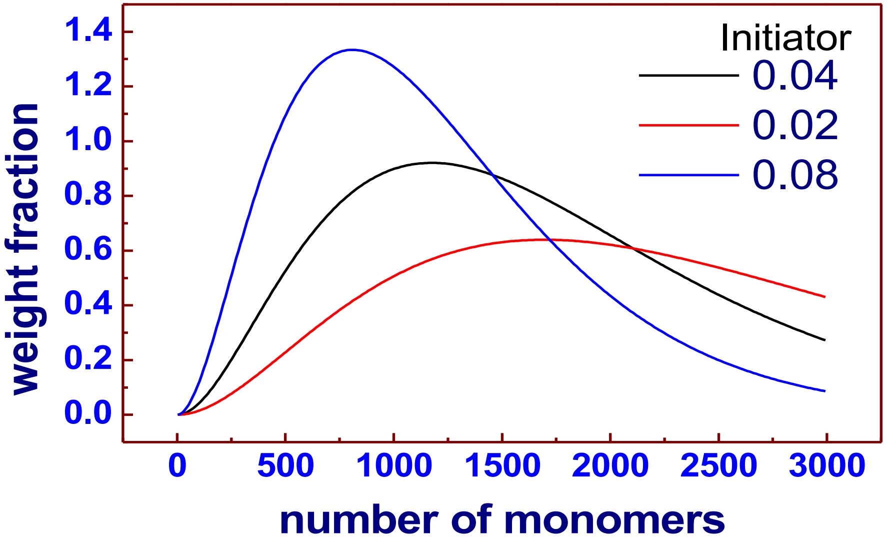
$$Monomer\ consumption \qquad r_M = k_p M \Gamma_0$$

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

$$polymer\ generation \qquad r_{P_j} = R_j\left(j-1\right)\frac{k_a}{2}\left(\frac{r_i}{k_P M}\right)$$

Polymerization





Polymer weight distribution

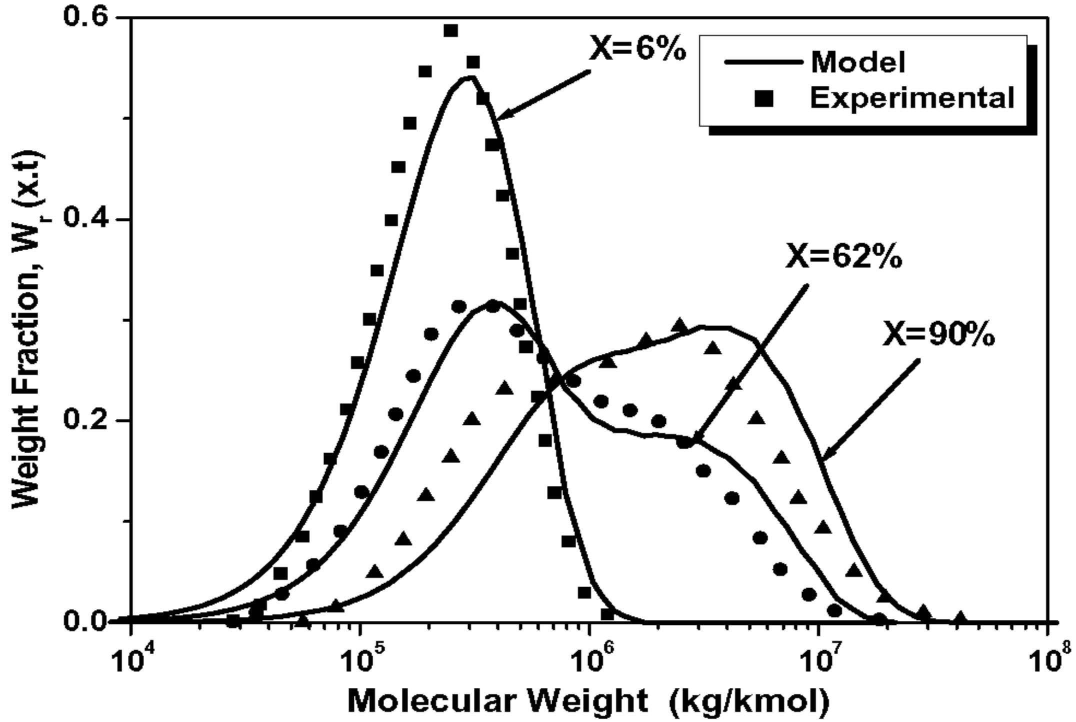


Fig. 2. Comparison of experimental and calculated by the OCFE MWDs at different monomer conversions (MMA free-radical polymerization. Initiator concentration = 3×10^{-2} kg/kg of MMA; temperature = 70 °C) [23].

Chemical Reaction Engineering
Catalytic reactions

Jayant M. Modak
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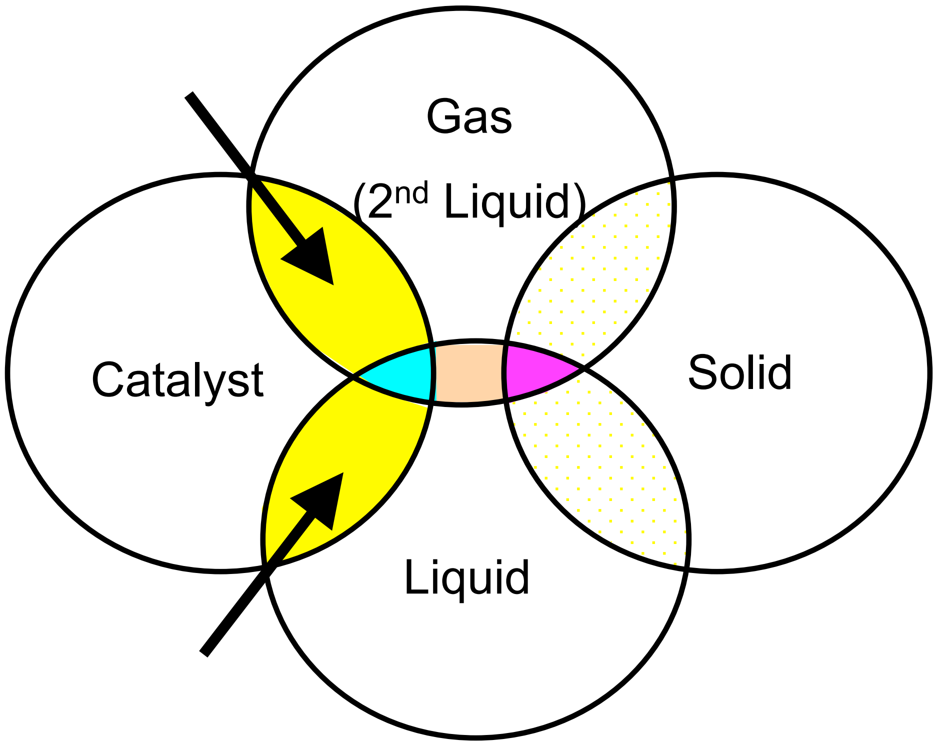
Catalytic reactions

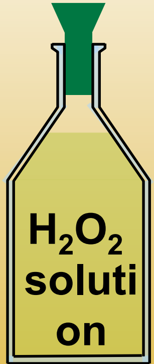
Heterogeneous catalysis



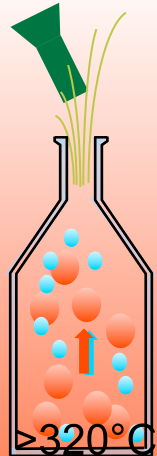
Catalytic reactions

Example: Hydrogen peroxide decomposition

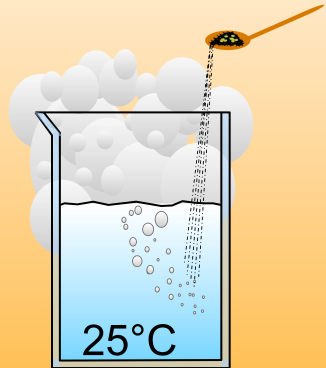
$$2H_2O_2 \rightarrow 2H_2O + O_2$$



25°C
stable over months



uncontrolled, thermal decomposition in seconds

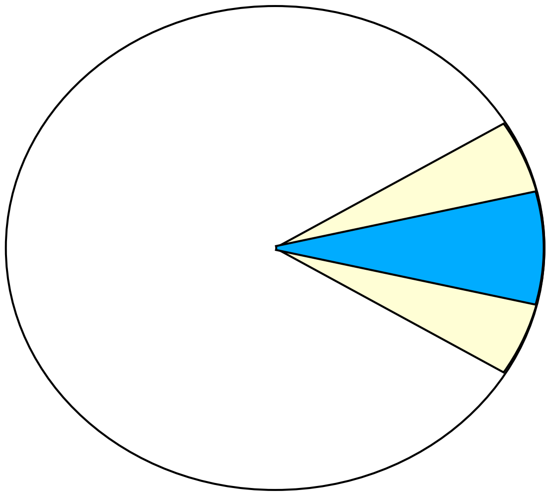


controlled, catalytic or enzymatic decomposition in seconds

Catalytic reactions

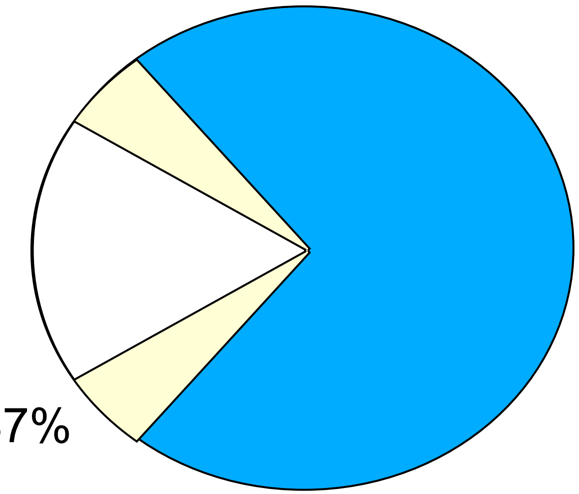
Efficiency of Phthalic Acid Anhydride Production

Non-catalytic Oxidation of naphthalene in fluid phase with MnO_2+HCl (1872), Chromic acid (1881), Oleum (1891)



Yield: 5-15%

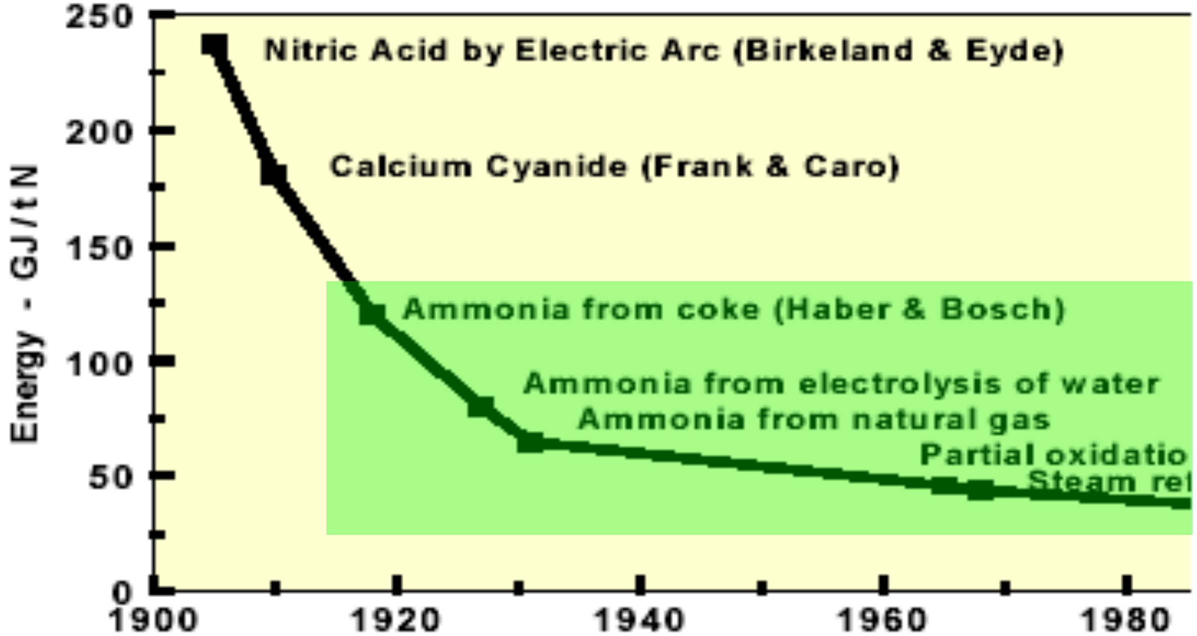
Catalytic Oxidation of o-Xylene in the gas phase on V_2O_5-catalyst



Yield: 75-87%

Catalytic reactions

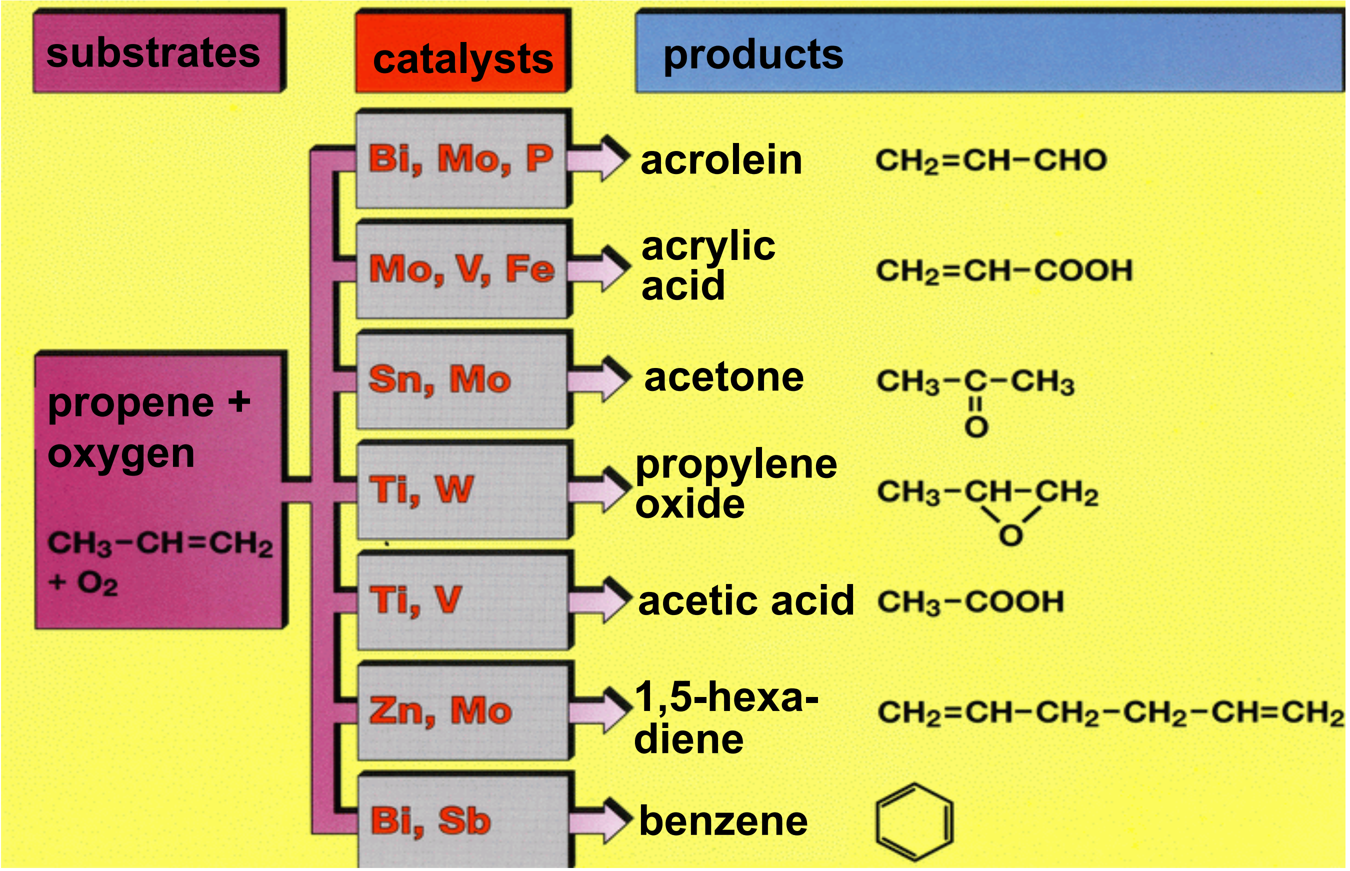
Efficiency of nitrogen fixation



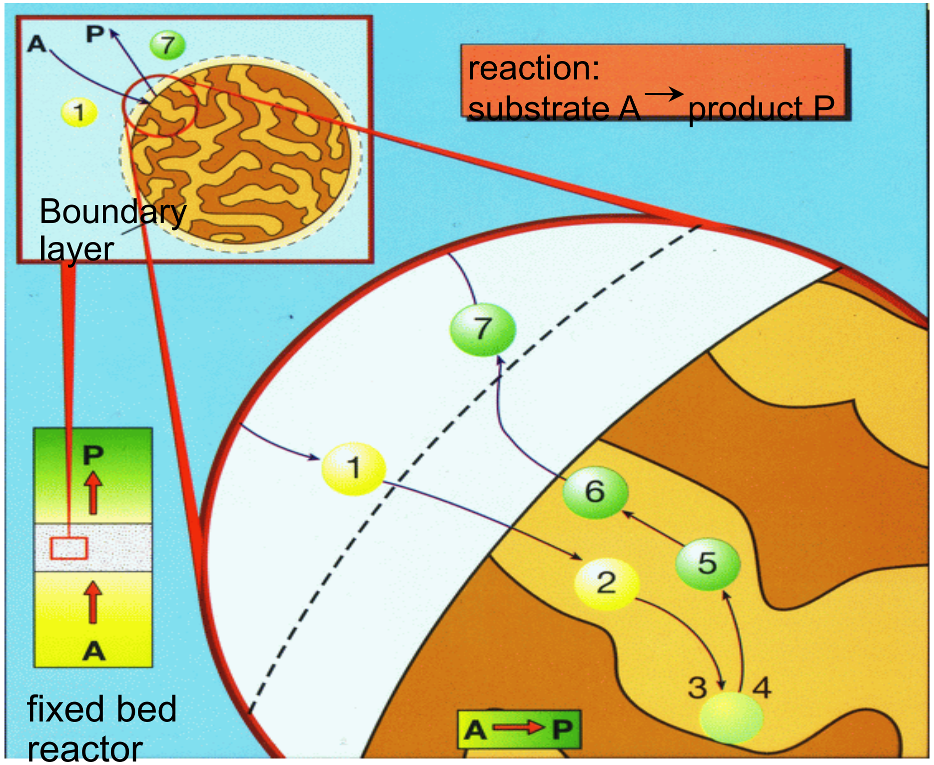
catalytic processes

Catalytic reactions

Product spectrum from partial oxidation of propene



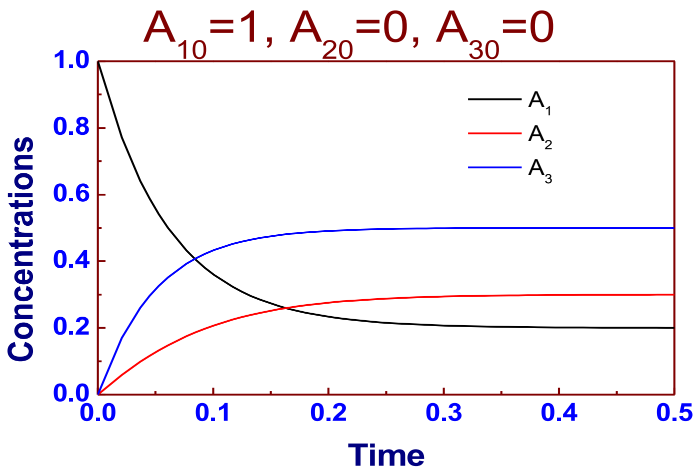
Catalytic reactions

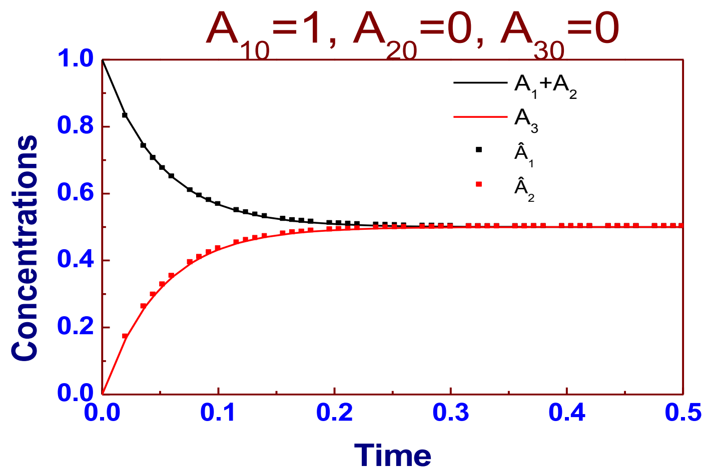


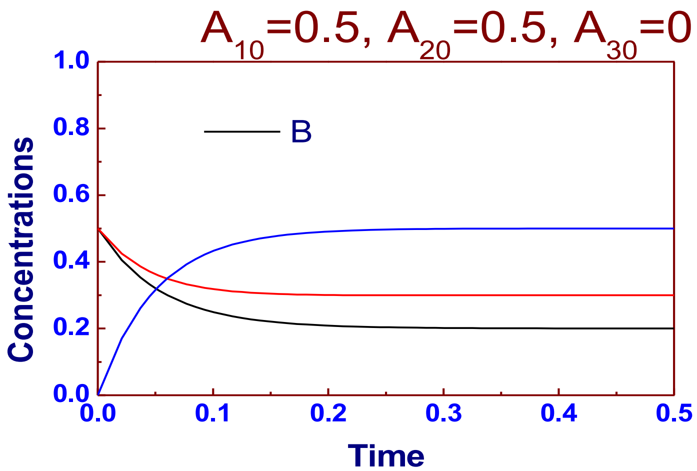
Steps during the course of the reaction

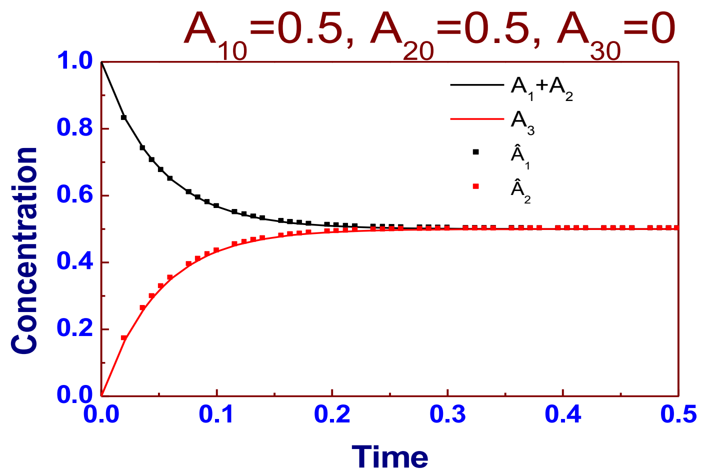
① External diffusion
② Internal diffusion
③ Adsorption on the active sites
④ Surface reaction
⑤ forming the products
⑥ Desorption of the products
⑦ Internal diffusion
External diffusion

Lumping analysis









Lumping analysis