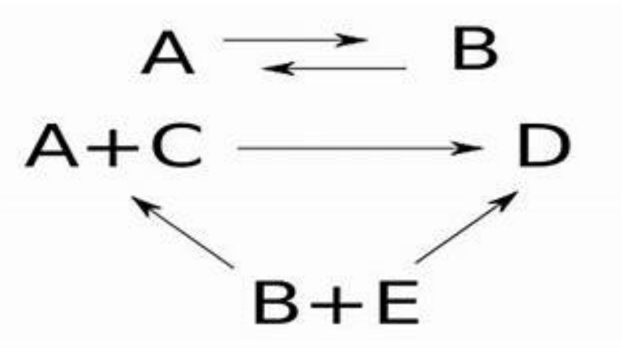
Reactor Design II



Week 5
Complex Reactions in Reactors

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Introduction

- Chemical Reaction Engineering (CRE) examines the principles governing reaction rates, mechanisms, and reactor design.

- This lecture focuses on complex reactions, their classification, and strategies for optimizing reactor performance in various scenarios.

Topics to be Addressed

- - Fundamentals of Complex Reactions
- - Types of Reactors: PFR, CSTR, Semibatch, and Membrane Reactors
- - Selectivity and Yield Analysis
- - Numerical Approaches for Reactor Optimization
- - Case Studies and Practical Applications

Objectives

- By the end of this lecture, students will be able to:

- - Understand the characteristics and challenges of complex reactions.
- - Apply mole balances, rate laws, and stoichiometry to complex systems.
- - Evaluate reactor performance for different configurations.
- - Develop strategies to enhance selectivity and yield in complex reactions.

Introduction

- Complex reactions involve multiple reactants and products, with intricate interdependencies.

- This session explores the theoretical concepts, practical applications, and numerical approaches to analyze and optimize complex reaction networks.

- Complex Reactions:

$$A + 2B \rightarrow C$$

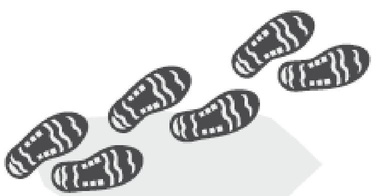
$$A + 3C \rightarrow D$$

  - Example A: Liquid Phase PFR
  - Example B: Liquid Phase CSTR
  - Example C: Gas Phase PFR
  - Example D: Gas Phase Membrane Reactors

    Sweep Gas Concentration Essentially Zero

    Sweep Gas Concentration Increases with Distance
- Example E: **Semibatch Reactor**

Gas Phase Multiple Reactions



Following the Algorithm

Number all reactions

Mole balances:

Mole balance on each and every species

PFR	$\frac{dF_j}{dV} = r_j$
CSTR	$F_{j0} - F_j = -r_j V$
Batch	$\frac{dN_j}{dt} = r_j V$
Membrane ("i" diffuses in)	$\frac{dF_i}{dV} = r_i + R_i$
Liquid-semibatch	$\frac{dC_j}{dt} = r_j + \frac{v_0(C_{j0} - C_j)}{V}$

Rates:

Laws	$r_{ij} = k_{ij} f_i(C_j, C_n)$
Relative rates	$\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i}$
Net rates	$r_j = \sum^{q} r_{ij}$

Stoichiometry:

Gas phase

$$C_j = C_{T0}\frac{F_j}{F_T}\frac{P}{P_0}\frac{T_0}{T} = C_{T0}\frac{F_j}{F_T}\frac{T_0}{T}y$$

$$p = \frac{P}{P_0}$$

$$F_T = \sum_{j=1}^{n} F_j$$

$$\frac{dp}{dW} = -\frac{\alpha}{2p}\left(\frac{F_T}{F_{T0}}\right)\frac{T}{T_0}$$

Liquid phase

$$v = v_0$$

$$C_A, C_B, \ldots$$

Combine:

Polymath will combine all the equations for you. Thank you,

New things for multiple reactions

1. **Number Every Reaction**
2. **Mole Balance on every species**
3. **Rate Laws**

(a) Net **Rates** of Reaction for every species

$$r_A = \sum_{i=1}^{N} r_{iA}$$

(b) **Rate** Laws for every reaction

$$r_{1A} = -k_{1A} C_A C_B^2$$

$$r_{2C} = -k_{2C} C_A^2 C_C^3$$

(c) Relative **Rates** of Reaction for every reaction

For a given reaction i: (i) $\mathbf{a_i}A + \mathbf{b_i}B \rightarrow \mathbf{c_i}C + \mathbf{d_i}D$:

$$\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i}$$

Reactor Mole Balance Summary

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Reactor Type	Gas Phase	Liquid Phase
Batch	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A$
Semibatch	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A - \frac{\upsilon_0 C_A}{V}$
	$\frac{dN_B}{dt} = r_B V + F_{B0}$	$\frac{dC_B}{dt} = r_B + \frac{\upsilon_0 [C_{B0} - C_B]}{V}$

Reactor Mole Balance Summary

Reactor Type	Gas Phase	Liquid Phase
CSTR	$V = \frac{F_{A0} - F_A}{-r_A}$	$V = \upsilon_0 \frac{(C_{A0} - C_A)}{-r_A}$
PFR	$\frac{dF_A}{dV} = r_A$	$\upsilon_0 \frac{dC_A}{dV} = r_A$
PBR	$\frac{dF_A}{dW} = r_A'$	$\upsilon_0 \frac{dC_A}{dW} = r_A'$

Note: The reaction **rates** in the above **mole balances** are net rates.

Batch

$$C_B = \frac{N_B}{V}$$

$$V = V_0 \frac{N_T}{N_{T0}} \frac{P_0}{P} \frac{T}{T_0}$$

$$C_B = \frac{N_B}{N_T} \frac{N_{T0}}{V_0} \frac{P}{P_0} \frac{T_0}{T}$$

$$C_B = C_{T0} \frac{N_B}{N_T} \frac{P}{P_0} \frac{T_0}{T}$$

Flow

$$C_B = \frac{F_B}{\upsilon}$$

$$\upsilon = \upsilon_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T}{T_0}$$

$$C_B = \frac{F_B}{F_T} \frac{F_{T0}}{\upsilon_0} \frac{P}{P_0} \frac{T_0}{T}$$

$$C_B = C_{T0} \frac{F_B}{F_T} \frac{P}{P_0} \frac{T_0}{T}$$

Concentration of Gas:

$$C_A = C_{T0}\left(\frac{F_A}{F_T}\right)p\left(\frac{T_0}{T}\right) \qquad F_T = F_A + F_B + F_C + F_D$$

Note: We could use the gas phase mole balances for **liquids** and then just express the concentration as:

Flow: $$C_A = \frac{F_A}{\upsilon_0}$$

Batch: $$C_A = \frac{N_A}{V_0}$$

Example A: Liquid Phase PFR

The complex liquid phase reactions follow elementary rate laws:

$$(1)\quad A + 2B \rightarrow C \qquad -r_{1A} = k_{1A} C_A C_B^2$$

NOTE: The specific reaction rate k_{1A} is defined with respect to species A.

$$(2)\quad 3C + 2A \rightarrow D \qquad -r_{2C} = k_{2C} C_C^3 C_A^2$$

NOTE: The specific reaction rate k_{2C} is defined with respect to species C.

Example A: Liquid Phase PFR

Complex Reactions

$$(1) \quad A + 2B \rightarrow C$$

$$(2) \quad A + 3C \rightarrow D$$

1) Mole Balance on each and every species

$$(1) \quad \frac{dF_A}{dV} = r_A \qquad (2) \quad \frac{dF_B}{dV} = r_B$$

$$(3) \quad \frac{dF_C}{dV} = r_C \qquad (4) \quad \frac{dF_D}{dV} = r_D$$

Example A: Liquid Phase PFR

2) Rate Laws:

Net Rates

$$(5)\ r_A = r_{1A} + r_{2A} \qquad (7)\ r_B = r_{1B} + r_{2B}$$

$$(6)\ r_C = r_{1C} + r_{2C} \qquad (8)\ r_D = 0 + r_{2D}$$

Rate Laws

$$(9)\ r_{1A} = -k_{1A} C_A C_B^2$$

$$(10)\ r_{2C} = -k_{2C} C_A^2 C_C^3$$

Relative Rates

Reaction 1

$$\frac{r_{1A}}{-1} = \frac{r_{1B}}{-2} = \frac{r_{1C}}{1}$$

$$(11)\ r_{1B} = 2 r_{1A}$$

$$(12)\ r_{1C} = -r_{1A}$$

Example A: Liquid Phase PFR

Relative Rates

Reaction 2

$$\frac{r_{2A}}{-2} = \frac{r_{2C}}{-3} = \frac{r_{2D}}{1}$$

$$(13)\ r_{2A} = \frac{2}{3} r_{2C}$$

$$(14)\ r_{2D} = -\frac{r_{2C}}{3}$$

$$r_A = -k_{1A} C_A C_B^2 - \frac{2}{3} k_{2C} C_A^2 C_C^3$$

$$r_B = -2k_{1A} C_A C_B^2$$

$$r_C = k_{1A} C_A C_B - k_{2C} C_A^2 C_C^3$$

$$r_D = \frac{k_{2C}}{3} C_A^2 C_C^3$$

Example A: Liquid Phase PFR

3) Stoichiometry

Liquid

$$(15)\ C_A = F_A/\upsilon_0$$

$$(16)\ C_B = F_B/\upsilon_0$$

$$(17)\ C_C = F_C/\upsilon_0$$

$$(18)\ C_D = F_D/\upsilon_0$$

$$(19)\ \tilde{S}_{C/D} = if\ (V > 0.00001)\ \text{then} \left(\frac{F_C}{F_D}\right) \text{else } 0$$

Example A: Liquid Phase PFR

Others

$$F_T = \text{Liquid} - \text{Not Needed}$$

$$(19)\ \alpha = \text{Liquid} - \text{Not Needed}$$

$$(20)\ C_{T0} = \text{Liquid} - \text{Not Needed}$$

4) Parameters

$$(21)\ k_{1A} = 10$$

$$(22)\ k_{2C} = 20$$

$$(23)\ \alpha = \text{Liquid}$$

$$(24)\ C_{T0} = \text{Liquid}$$

$$(25)\ V_f = 2500$$

$$(26)\ F_{A0} = 200$$

$$(28)\ F_{B0} = 200$$

$$(26)\ \upsilon_0 = 100$$

Example B: Liquid Phase CSTR

Same reactions, rate laws, and rate constants as Example A

$$(1)\quad A + 2B \rightarrow C \qquad\qquad -r_{1A} = k_{1A} C_A C_B^2$$

NOTE: The specific reaction rate k1A is defined with respect to species A.

$$(2)\quad 3C + 2A \rightarrow D \qquad\qquad -r_{2C} = k_{2C} C_C^3 C_A^2$$

NOTE: The specific reaction rate k_{2C} is defined with respect to species C.

Example B: Liquid Phase CSTR

The complex liquid phase reactions take place in a 2,500 dm^3 CSTR. The feed is equal molar in A and B with F_{A0}=200 mol/min, the volumetric flow rate is 100 dm^3/min and the reaction volume is 50 dm^3.

Find the concentrations of A, B, C and D existing in the reactor along with the existing selectivity.

Plot F_A, F_B, F_C, F_D and $S_{C/D}$ as a function of V

Example B: Liquid Phase CSTR

(1) A + 2B →C (2) 2A + 3C → D

$$r_{1A} = -k_{1A} C_A C_B^2$$

$$r_{2C} = -k_{2C} C_A^2 C_C^3$$

1) Mole Balance

$$(1) \quad A \qquad \upsilon_0 C_{A0} - \upsilon_0 C_A + r_A V = 0$$

$$(2) \quad B \qquad \upsilon_0 C_{B0} - \upsilon_0 C_B + r_B V = 0$$

$$(3) \quad C \qquad 0 - \upsilon_0 C_C + r_C V = 0$$

$$(4) \quad D \qquad 0 - \upsilon_0 C_D + r_D V = 0$$

Example B: Liquid Phase CSTR

2) Rate Laws: (5)-(14) same as PFR

3) Stoichiometry: (15)-(18)

same as Liquid Phase PFR

$$(19)\ S_{C/D} = \frac{F_C}{F_D + 0.0001} = \frac{\upsilon_0 C_C}{\upsilon_0 C_D + 0.0001}$$

4) Parameters:

$$k_{1A},\quad k_{2C},\quad C_{A0},\quad C_{B0},\quad V,\quad \upsilon_0$$

Example B: Liquid Phase CSTR

In terms of molar flow rates

(1) A + 2B →C   (2) 2A + 3C → D

$$r_{1A} = -k_{1A} C_A C_B^2$$

$$r_{2C} = -k_{2C} C_A^2 C_C^3$$

1) Mole Balance (1–4)

$$(1)\ f\left(F_A\right) = F_{A0} - F_A + r_A V \quad (=0)$$

$$(2)\ f\left(F_B\right) = F_{B0} - F_B + r_B V \quad (=0)$$

$$(3)\ f\left(F_C\right) = 0 - F_C + r_C V \quad (=0)$$

$$(4)\ f\left(F_D\right) = 0 - F_D + r_D V \quad (=0)$$

2) Rates (5–14)

Same as Example A

3) Stoichiometry: (15–19)

$$(15) \quad C_A = F_A / \upsilon_0$$

$$(16) \quad C_B = F_B / \upsilon_0$$

$$(17) \quad C_C = F_C / \upsilon_0$$

$$(18) \quad C_D = F_D / \upsilon_0$$

$$(19) \quad S_{C/D} = \frac{F_C}{F_D + 0.00001}$$

Example B: Liquid Phase CSTR

In terms of concentration

(1) A + 2B → C (2) 2A + 3C → D

$$r_{1A} = -k_{1A} C_A C_B^2$$

$$r_{2C} = -k_{2C} C_A^2 C_C^3$$

1) Mole Balance (1–4)

$$(1)\ f(C_A) = \upsilon_0 C_{A0} - \upsilon_0 C_A + r_A V \qquad (=0)$$

$$(2)\ f(C_B) = \upsilon_0 C_{B0} - \upsilon_0 C_B + r_B V \qquad (=0)$$

$$(3)\ f(C_C) = 0 - \upsilon_0 C_C + r_C V \qquad (=0)$$

$$(4)\ f(C_D) = 0 - \upsilon_0 C_D + r_D V \qquad (=0)$$

2) Rates (5–14)

Same as Example A

3) Stoichiometry: (15–19)

$$(15)\ S_{C/D} = \frac{F_C}{F_D + 0.00001}$$

No ΔP

Same reactions, rate laws, and rate constants as Example A:

$$(1)\quad A + 2B \rightarrow C \qquad\qquad -r_{1A} = k_{1A} C_A C_B^2$$

NOTE: The specific reaction rate k_{1A} is defined with respect to species A.

$$(2)\quad 3C + 2A \rightarrow D \qquad\qquad -r_{2C} = k_{2C} C_C^3 C_A^2$$

NOTE: The specific reaction rate k_{2C} is defined with respect to species C.

Example C: Gas Phase PFR No ΔP

1) Mole Balance

$$(1) \quad \frac{dF_A}{dV} = r_A \qquad (3) \quad \frac{dF_C}{dV} = r_C$$

$$(2) \quad \frac{dF_B}{dV} = r_B \qquad (4) \quad \frac{dF_D}{dV} = r_D$$

2) Rate Laws: (5)-(14) same as CSTR

No ΔP

3) Stoichiometry:

Gas: Isothermal $T = T_0$

$$(15)\ C_A = C_{T0}\frac{F_A}{F_T}p \qquad (16)\ C_B = C_{T0}\frac{F_B}{F_T}p$$

$$(17)\ C_C = C_{T0}\frac{F_C}{F_T}p \qquad (18)\ C_D = C_{T0}\frac{F_D}{F_T}p$$

$$(19)\ F_T = F_A + F_B + F_C + F_D$$

Packed Bed with Pressure Drop

$$\frac{dp}{dW} = -\frac{\alpha}{2p}\left(\frac{F_T}{F_{T0}}\right)\left(\frac{T}{T_0}\right) = -\frac{\alpha}{2p}\frac{F_T}{F_{T0}}$$

Example C: Gas Phase PFR

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No ΔP

4) Selectivity

$$S = \frac{F_C}{F_D} = \text{if } (V > 0.00001) \text{ then } \left(\frac{F_C}{F_D} \right) \text{ else} (0) \quad (20)$$

$$p = 1 \quad (21)$$

Example D: Membrane Reactor

with ΔP

Same reactions, rate laws, and rate constants as Example A:

$$(1)\quad A + 2B \rightarrow C \qquad -r_{1A} = k_{1A}C_A C_B^2$$

NOTE: The specific reaction rate k_{1A} is defined with respect to species A.

$$(2)\quad 3C + 2A \rightarrow D \qquad -r_{2C} = k_{2C}C_C^3 C_A^2$$

NOTE: The specific reaction rate k_{2C} is defined with respect to species C.

Example D: Membrane Reactor with ΔP

Because the smallest molecule, and the one with the lowest molecular weight, is the one diffusing out, we will neglect the changes in the mass flow rate down the reactor and will take as first approximation: $\dot{m}_0 = \dot{m}$

1) Mole Balances

$$A \quad \frac{dF_A}{dV} = r_A \quad (1) \qquad C \quad \frac{dF_C}{dV} = r_C - R_C \quad (3)$$

$$B \quad \frac{dF_B}{dV} = r_B \quad (2) \qquad D \quad \frac{dF_D}{dV} = r_D \quad (4)$$

We also need to account for the molar rate of desired product C leaving in the sweep gas F_{Csg}

$$\frac{dF_{Csg}}{dV} = R_C$$

Example D: Membrane Reactor

with ΔP

We need to reconsider our pressure drop equation.

When mass diffuses out of a membrane reactor there will be a decrease in the superficial mass flow rate, G. To account for this decrease when calculating our pressure drop parameter, we will take the ratio of the superficial mass velocity at any point in the reactor to the superficial mass velocity at the entrance to the reactor.

$$\alpha = \alpha_0 \frac{G}{G_0} = \alpha_0 \left[\frac{\sum F_i \cdot MW_i}{\sum F_{i0} \cdot MW_i} \right]$$

Example D: Membrane Reactor with ΔP

The superficial mass flow rates can be obtained by multiplying the species molar flow rates, F_i, by their respective molecular weights, Mw_i, and then summing over all species:

$$\frac{G}{G_0} = \frac{m/A_{C_1}}{m_0/A_{C_1}} = \frac{\sum F_i \cdot (MW_i)/A_{C_1}}{\sum F_{i0} \cdot (MW_i)/A_{C_1}} = \frac{\sum F_i (MW_i)}{\sum F_{i0} (MW_i)}$$

Example D: Membrane Reactor with ΔP

2) Rate Laws: (5)-(14) same as Examples A, B, and C.

3) Stoichiometry: (15)-(20) same as Examples A and B

($T=T_0$)

$$\frac{dp}{dW} = -\frac{\alpha}{2p}\frac{F_T}{F_{T0}} \qquad \frac{dp}{dV} = -\frac{\rho\alpha}{2p}\frac{F_T}{F_{T0}} \quad (21)$$

$$R_C = k_C\left(C_C - C_{CSweep}\right)$$

4) Sweep Gas Balance:

$$F_{Csg}\Big|_V - F_{Csg}\Big|_{V+\Delta V} + R_C \Delta V = 0$$

$$\frac{dF_{Csg}}{dV} = R_C$$

Example E: Liquid Phase Semibatch

Same reactions, rate laws, and rate constants as Example A:

$$(1)\quad A+2B\rightarrow C \qquad -r_{1A}=k_{1A}C_AC_B^2$$

NOTE: The specific reaction rate k_{1A} is defined with respect to species A.

$$(2)\quad 3C+2A\rightarrow D \qquad -r_{2C}=k_{2C}C_C^3C_A^2$$

NOTE: The specific reaction rate k_{2C} is defined with respect to species C.

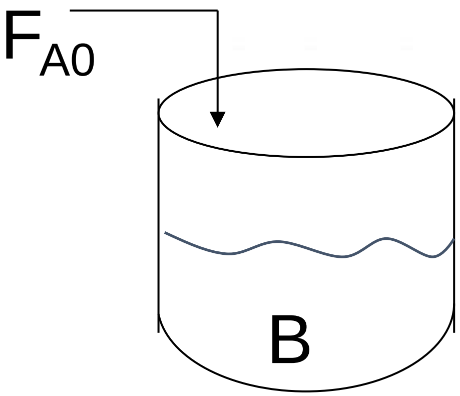
Example E: Liquid Phase Semibatch

The complex liquid phase reactions take place in a **semibatch reactor** where A is fed to B with F_{A0}= 3 mol/min. The volumetric flow rate is 10 dm^3/min and the initial reactor volume is 1,000 dm^3.

The maximum volume is 2,000 dm^3 and C_{A0}=0.3 mol/dm^3 and C_{B0}=0.2 mol/dm^3. Plot C_A, C_B, C_C, C_D and $S_{S/D}$ as a function of time.

Example E: Liquid Phase Semibatch

(1) A + 2B → C   (2) 2A + 3C → D



1) Mole Balances:

$$\frac{dN_A}{dt} = r_A V + F_{A0} \qquad N_{A0} = 0$$

$$\frac{dN_B}{dt} = r_B V \qquad N_{B0} = C_{B0} V_0 = 2.000$$

$$\frac{dN_C}{dt} = r_C V \qquad N_{C0} = 0$$

$$\frac{dN_D}{dt} = r_D V \qquad N_{D0} = 0$$

Example E: Liquid Phase Semibatch

2) Rate Laws: (5)-(14)

Net Rate, Rate Laws and relative rate – are the same as Liquid and Gas Phase PFR and Liquid Phase CSTR

$$V = V_0 + v_0 t \quad (15)$$

$$C_A = \frac{N_A}{V} \quad (16) \qquad C_B = \frac{N_B}{V} \quad (17)$$

$$C_C = \frac{N_C}{V} \quad (18) \qquad C_D = \frac{N_D}{V} \quad (19)$$

3) Selectivity and Parameters:

$$S_{C/D} = \text{if } (t > 0.0001) \text{ then} \left(\frac{N_C}{N_D}\right) \text{else}(0) \quad (20)$$

$$\upsilon_0 = 10\,\text{dm}^3/\text{min} \qquad V_0 = 100\,\text{dm}^3 \qquad F_{A0} = 3\,\text{mol/min}$$

Are you ready?

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Summary

- In this lecture, we covered:

- - The principles and analysis of complex reactions.
- - Key reactor types: PFR, CSTR, semibatch, and membrane reactors.
- - Selectivity and yield optimization strategies.
- - Practical examples and numerical methods for reactor analysis.

- Complex reactions are essential for advancing chemical process efficiency and innovation.