Lecture 8 Kinetics of Multiple Reactions: Parallel, Sequential, and Reversible Schemes

Goal of the lecture: To study the kinetic behavior and mathematical modeling of systems involving multiple chemical reactions — including parallel, sequential, and reversible reaction schemes — and their influence on selectivity and product yield.

Brief lecture notes: In this lecture, we examine how multiple reactions occur simultaneously or consecutively in chemical systems. We explore how reaction pathways compete or follow one another, how reversible reactions reach equilibrium, and how kinetic parameters determine product selectivity and conversion efficiency. The focus is on deriving rate equations for each reaction type, understanding the interplay between kinetic constants, and designing optimal conditions to maximize the desired product.

Main part

Real chemical processes rarely involve a single reaction; instead, they consist of networks of reactions that can proceed in parallel, in sequence, or in reversible directions. Understanding their kinetics allows chemical engineers and chemists to optimize yields, minimize undesired by-products, and control reactor conditions.

Multiple reactions are broadly categorized as:

1. Parallel (competitive) reactions – multiple reactions occur from the same reactant(s) simultaneously.
2. Sequential (consecutive) reactions – the product of one reaction acts as the reactant for the next.
3. Reversible reactions – reactions that can proceed in both forward and backward directions until equilibrium is established.

Parallel (Competitive) Reactions

In parallel reactions, a single reactant forms multiple products:

$$A \overset{k_1}{\rightarrow} B, A \overset{k_2}{\rightarrow} C$$

The rate of disappearance of A is:

$$-\frac{dC_A}{dt} = (k_1 + k_2)C_A$$

Selectivity, defined as the ratio of desired to undesired product formation rates, depends on rate constants and reaction order. For first-order reactions:

$$\text{Selectivity} = \frac{C_B}{C_C} = \frac{k_1}{k_2}$$

Thus, by changing temperature or catalyst type, one can alter selectivity toward the desired product.

Sequential (Consecutive) Reactions

In sequential reactions, one product is the reactant for the next:

$$A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$$

The concentration of the intermediate Bchanges dynamically. Initially, Bforms quickly, then depletes as it converts into C. The kinetic equations are:

$$\frac{dC_A}{dt} = -k_1 C_A, \frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$

The time-dependent profile of Bexhibits a maximum, representing the point where its formation and consumption rates are equal. This behavior is critical in reactor design for processes where intermediate recovery is desired (e.g., aldehyde formation from alcohol oxidation).

Reversible Reactions

Reversible reactions can reach a dynamic equilibrium:

$$A \rightleftharpoons \mathrm{k1k2}B$$

At equilibrium:

$$k_1 C_A^{eq} = k_2 C_B^{eq}$$

and the equilibrium constant is:

$$K_{eq} = \frac{k_1}{k_2} = \frac{C_B^{eq}}{C_A^{eq}}$$

Reversibility is significant in catalytic and biological systems, where controlling temperature and pressure shifts equilibrium positions (Le Châtelier's principle).

Industrial and Practical Importance

Understanding multi-reaction kinetics is crucial for:

- Selectivity control – e.g., in hydrocarbon cracking or oxidation processes.
- Catalyst design – tuning active sites to favor specific pathways.
- Reactor optimization – determining the best residence time and temperature profile to maximize yield.
- Environmental processes – managing pollutant formation and decomposition.

Figure 1.

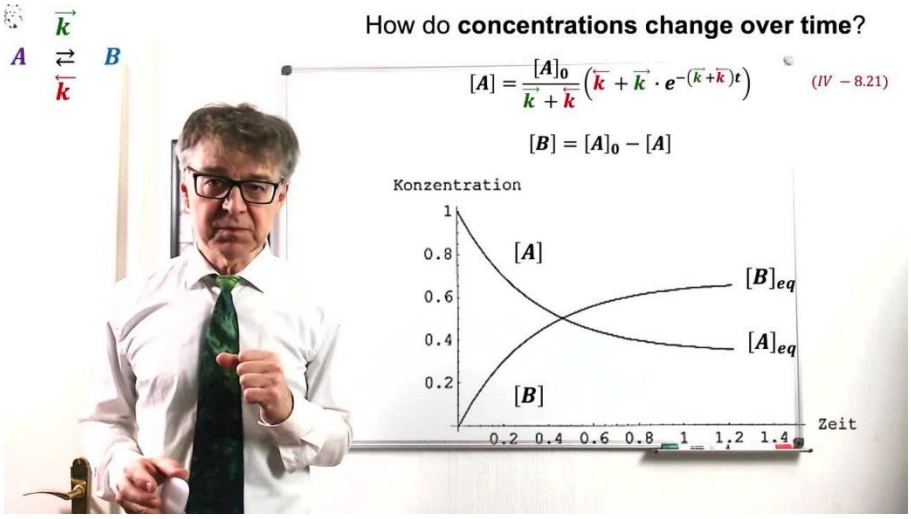

Table 1

Reaction Type	Typical Example	Rate Expression	Key Feature
Parallel	Ethanol oxidation to acetaldehyde and CO_2	$-r_A = (k_1 + k_2)C_A$	Competing pathways
Sequential	$NO \rightarrow NO_2 \rightarrow N_2O_4$	$r_B = k_1 C_A - k_2 C_B$	Intermediate formation
Reversible	$N_2 + 3H_2 \rightleftharpoons 2NH_3$	$r = k_1 C_{N_2} C_{H_2}^3 - k_2 C_{NH_3}^2$	Dynamic equilibrium

Questions for self-control

1. What are the main differences between parallel and sequential reactions?
2. How does temperature affect selectivity in parallel reactions?
3. Why does the intermediate concentration in sequential reactions exhibit a maximum?
4. How is equilibrium established in reversible reactions?
5. What strategies can be used to maximize desired product yield in systems with multiple reactions?

Literature

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