Lecture 1 Introduction to the Macrokinetics of Chemical Processes

Goal of the lecture: To study the fundamental concepts of macrokinetics, including reaction rates, mass and heat transfer, and the influence of external parameters on the overall rate of chemical processes.

Brief lecture notes: This lecture introduces the field of macrokinetics, which connects chemical reaction kinetics with transport phenomena such as diffusion, convection, and heat transfer. Students will learn how the overall rate of a chemical process depends not only on molecular reaction mechanisms but also on external factors—temperature, pressure, mixing, and reactor design. The lecture discusses the distinction between kinetic and diffusion control, the formulation of macrokinetic equations, and methods for analyzing heterogeneous and catalytic systems. Emphasis is placed on understanding how chemical and physical steps interact to determine the performance of reactors and industrial processes.

Main part

Macrokinetics is a branch of chemical kinetics that deals with the study of chemical reactions at the macroscopic scale, considering both chemical transformations and mass and heat transfer phenomena. While molecular kinetics examines the intrinsic rate constants and mechanisms at the molecular level, macrokinetics describes how these reactions proceed in real systems—such as reactors, catalysts, and industrial devices—where transport limitations and thermal gradients play a crucial role.

In general, the rate of a chemical process depends on:

- the rate of the chemical reaction itself,
- the rate of mass transfer of reactants and products,
- the rate of heat transfer associated with endothermic or exothermic reactions.

These processes occur simultaneously and influence one another, determining the overall behavior of a reactor or system.

Basic Kinetic Equations

At the core of macrokinetic analysis lies the rate equation, which expresses the change in concentration of reactants over time:

$$r = k\,C_A^n$$

where

r— rate of reaction,
k— rate constant (dependent on temperature),
C_A— concentration of reactant A,
n— reaction order.

The rate constant k follows the Arrhenius equation:

$$k = A\,e^{-E_a/(RT)}$$

where

A— frequency factor,
E_a— activation energy,
R— gas constant,
T— absolute temperature.

These relations describe the intrinsic kinetics of a chemical reaction, but in macrokinetics, additional steps—such as diffusion through a boundary layer or within a porous catalyst—can modify the observed rate.

Macrokinetic Model of a Heterogeneous Reaction

A typical heterogeneous process (e.g., gas–solid reaction or catalysis) involves multiple stages:

1. External diffusion of reactants from the bulk phase to the surface,
2. Internal diffusion within pores (if porous catalyst),
3. Adsorption of reactants onto the surface,
4. Surface chemical reaction,
5. Desorption and diffusion of products away from the surface.

The overall rate can be expressed as:

$$\frac{1}{r_{obs}} = \frac{1}{r_{chem}} + \frac{1}{r_{diff}}$$

where $r_{chem}$and $r_{diff}$are the rates of chemical and diffusion-controlled processes, respectively. This equation illustrates that the slowest stage controls the global kinetics.

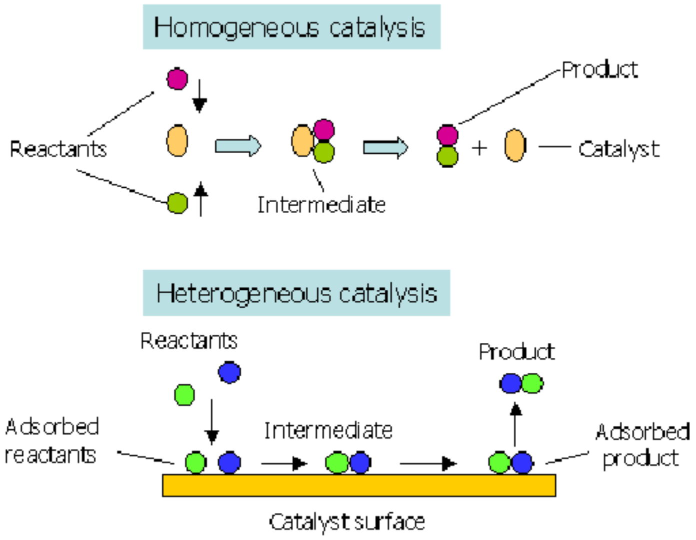

Figure 1. Schematic representation of macrokinetic stages in a catalytic chemical process

Macrokinetic Parameters and Reactor Design

Macrokinetic studies are essential for the design of reactors such as:

- Batch reactors (no flow, time-dependent concentration changes),
- Continuous stirred-tank reactors (CSTR) (well-mixed, steady-state conditions),
- Plug-flow reactors (PFR) (concentration gradient along the flow).

Each type has its own material and energy balance equations that incorporate reaction rate expressions.
Reactor design requires matching the kinetics with the flow regime and heat exchange characteristics.

Temperature and Pressure Effects

Temperature influences both the intrinsic rate constant and diffusion coefficients, usually increasing overall rates. Pressure affects mainly gaseous systems, altering reactant concentrations and sometimes equilibrium conversion. Macrokinetic modeling allows for quantitative prediction of these effects and optimization of industrial operating parameters.

Table: Factors Influencing the Overall Rate of Chemical Processes

Parameter	Influence Mechanism	Resulting Effect
Temperature	Changes rate constant (Arrhenius law)	Exponential increase of rate
Pressure	Alters reactant concentrations	Higher reaction rate in gases
Mixing intensity	Affects mass transfer	Reduced diffusion limitations
Catalyst structure	Determines surface area and pore diffusion	Enhanced effectiveness
Heat removal	Controls temperature gradients	Stabilizes reaction regime

Questions for Self-Control

1. What is the main difference between molecular kinetics and macrokinetics?
2. How do diffusion and heat transfer influence the overall rate of chemical processes?
3. What are the main regimes of kinetic, diffusion, and heat-transfer control?
4. How can macrokinetic models help in designing industrial reactors?
5. Why is it important to determine the rate-determining step in a complex process?

Literature

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