

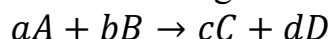
Lecture 3 Kinetic Equations: Reaction Order and the Law of Mass Action

Goal of the lecture: To study the mathematical description of chemical reaction rates based on the law of mass action and to understand the effect of reaction order on kinetics and process design.

Brief lecture notes: This lecture introduces the fundamental relationships between chemical reaction rates, reactant concentrations, and reaction mechanisms. Students will explore the law of mass action, the concept of rate constant, and the determination of reaction order through differential and integral methods. The lecture will also cover examples of first-order, second-order, and complex reactions, with emphasis on their kinetic equations and graphical interpretations. Practical applications in chemical reactor design and rate data analysis will also be discussed.

Main part

The law of mass action, proposed by Guldberg and Waage, states that the rate of a chemical reaction is directly proportional to the product of the concentrations of the reactants, each raised to a power corresponding to its stoichiometric coefficient in the reaction mechanism. For a general reaction:



the rate equation can be expressed as:

$$r = k[A]^m[B]^n$$

where:

- r — rate of reaction,
- k — rate constant (depends on temperature and catalyst presence),
- $[A]$ and $[B]$ — molar concentrations of reactants,
- m and n — reaction orders with respect to A and B, respectively.

The overall order of the reaction is given by $m + n$, which may or may not coincide with the stoichiometric coefficients depending on the reaction mechanism. Reaction order determines how sensitive the rate is to changes in reactant concentration. For example, in a first-order reaction, the rate is directly proportional to one reactant's concentration, while a second-order reaction depends on the square of one concentration or the product of two.

The rate constant (k) follows the Arrhenius equation, which describes its temperature dependence:

$$k = Ae^{-\frac{E_a}{RT}}$$

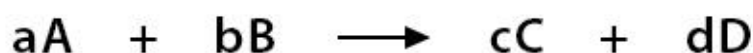
where A is the pre-exponential factor, E_a — activation energy, R — universal gas constant, and T — temperature in Kelvin. The exponential relationship explains why even small increases in temperature can significantly accelerate chemical reactions. Graphical methods help determine reaction order experimentally. For instance, for a first-order reaction, plotting $\ln[A]$ versus time yields a straight line, while a second-order reaction gives linearity for $1/[A]$ versus time.

Typical Kinetic Behavior Table

Reaction Order	Rate Equation	Integrated Form	Example
Zero-order	$r = k$	$[A] = [A_0] - kt$	Catalytic surface reaction
First-order	$r = k[A]$	$\ln([A_0]/[A]) = kt$	Radioactive decay, isomerization
Second-order	$r = k[A]^2$	$\frac{1}{[A]} - \frac{1}{[A_0]} = kt$	Dimerization reactions
Mixed-order	$r = k[A]^m[B]^n$	Complex	Multi-step or chain reactions

Figure 1 — Law of mass action

Law of Mass Action



Equilibrium Constant:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

[A], [B], [C], and [D] are concentrations of A, B, C, and D respectively

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The understanding of reaction order and mass action law is fundamental for reactor modeling, optimization of industrial processes, and kinetic parameter estimation, as they form the basis for both steady-state and transient reactor design equations.

Questions for self-control

1. What is the main statement of the law of mass action?
2. How does reaction order influence the rate of reaction?
3. Explain how temperature affects the rate constant.
4. What graphical methods are used to determine reaction order experimentally?
5. How does the overall order of reaction differ from the stoichiometric coefficients?

Literature

1. Smith, J. M., Chemical Engineering Kinetics, McGraw-Hill, 1981.
2. Levenspiel, O., Chemical Reaction Engineering, 3rd ed., Wiley, 1999.
3. Fogler, H. S., Elements of Chemical Reaction Engineering, 5th ed., Pearson, 2016.
4. Laidler, K. J., Chemical Kinetics, Harper & Row, 1987.
5. Atkins, P. and de Paula, J., Atkins' Physical Chemistry, 11th ed., Oxford University Press, 2018.

