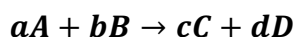


Lecture 10 “The rate of chemical reactions and the mechanisms of their occurrence”

Goal of the lecture: To study how fast chemical reactions occur, the factors that influence their rates, and the detailed steps by which reactants are converted into products. The lecture aims to explain the fundamental principles of **chemical kinetics**, including rate laws, reaction order, activation energy, and the effect of temperature and catalysts. Understanding these concepts allows chemists to control reaction conditions, predict reaction behavior, and design efficient chemical and industrial processes by analyzing the mechanisms through which reactions take place.

Brief lecture notes: Every chemical reaction occurs at a definite rate. Some reactions, such as explosions, take place almost instantaneously, while others, such as rusting of iron, proceed very slowly. **Chemical kinetics** is the branch of chemistry that deals with the **rate of reactions** and the **mechanisms** by which they occur.

The **rate of reaction** expresses how fast the concentration of a reactant or product changes with time. For a general reaction:



the rate is given by:

$$\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = -\frac{1}{c} \frac{d[C]}{dt} = -\frac{1}{d} \frac{d[D]}{dt}$$

The negative sign indicates the **decrease in reactant concentration** over time.

1. Rate Law and Rate Constant

Experimentally, the rate of a reaction often depends on the concentrations of reactants raised to certain powers:

$$\text{Rate} = k[A]^m[B]^n$$

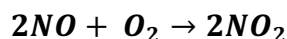
where:

- k is the **rate constant**,
- m and n are the **orders of reaction** with respect to each reactant,
- the **overall order** = m+n

The rate constant depends on **temperature** and the **nature of the reaction**, but not on concentrations.

Example:

For the reaction



the experimentally determined rate law is:

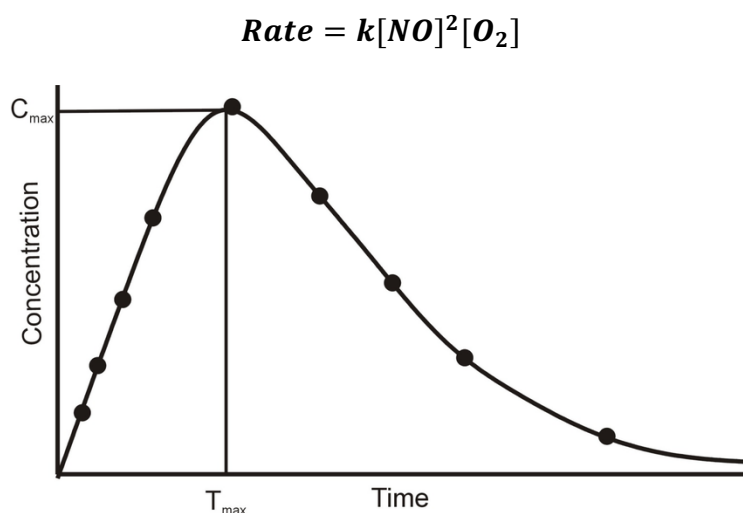


Figure 1 – Typical Concentration vs. Time Graph

The reactant concentration decreases with time, while the product concentration increases.

2. Integrated Rate Laws

For **first-order reactions**, where



the rate law is:

$$-\frac{d[A]}{dt} = k[A]$$

Integrating gives:

$$\ln[A] = \ln[A_0] - kt$$

or

$$[A] = [A_0]e^{-kt}$$

The **half-life** ($t_{1/2}$) for a first-order reaction is:

$$t_{1/2} = \frac{0.693}{k}$$

It is independent of the initial concentration.

For **second-order reactions**:

$$\frac{1}{[A]} = \frac{1}{[A_0]} + kt$$

3. Factors Affecting Reaction Rate

Several factors influence how fast a reaction proceeds:

Factor	Effect on Reaction Rate	Explanation
Concentration	Increases rate	More collisions between reactant particles
Temperature	Increases rate	Higher energy of particles → more effective collisions
Catalyst	Increases rate	Lowers activation energy
Surface area	Increases rate	More area available for collisions
Nature of reactants	Varies	Ionic reactions are faster than covalent ones

4. Collision Theory and Activation Energy

According to **collision theory**, molecules must collide with sufficient energy and proper orientation for a reaction to occur. Only a fraction of collisions, called **effective collisions**, lead to product formation.

The minimum energy required for a successful collision is the **activation energy (E_a)**.

The dependence of rate constant on temperature is expressed by the **Arrhenius equation**:

$$k = Ae^{-E_a/RT}$$

where

- A = frequency factor,
- E_a = activation energy,
- R = gas constant,
- T = temperature (K).

Taking logarithms:

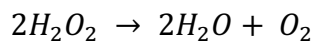
$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T}$$

A plot of $\ln k$ versus $1/T$ gives a straight line with slope $-E_a/R$.

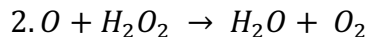
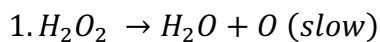
5. Reaction Mechanisms

A **reaction mechanism** is the sequence of elementary steps by which an overall chemical change occurs. Each elementary step involves a small number of molecules (unimolecular, bimolecular, or termolecular).

For example, the decomposition of hydrogen peroxide proceeds in two steps:



Mechanism:



The **rate-determining step** (the slowest step) controls the overall reaction rate.

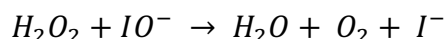
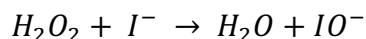
Catalysts often provide an **alternative mechanism** with a lower activation energy, increasing reaction speed without being consumed.

6. Catalysis in Reaction Mechanisms

In a catalyzed reaction, the catalyst forms temporary intermediates with reactants and lowers the activation energy barrier.

Example:

Decomposition of hydrogen peroxide catalyzed by iodide ion:



Here, iodide is regenerated at the end of the reaction.

The study of reaction rates, known as chemical kinetics, is extremely important because it helps scientists and engineers understand and control how quickly chemical processes occur. By analyzing reaction kinetics, it becomes possible to optimize the conditions used in **industrial processes**, such as ammonia synthesis in the Haber–Bosch process or polymerization reactions in plastics production. In **biochemistry**, kinetics explains how **enzymes** regulate the speed of metabolic reactions in living organisms. It is also crucial in **environmental chemistry**, where understanding the rates of reactions such as ozone depletion or pollutant degradation helps predict and manage ecological impacts. Furthermore, kinetic studies assist in the **design of catalysts**, which make reactions more energy-efficient and sustainable by lowering activation energy and increasing overall productivity.

Table 1 – Comparison of Reaction Orders

Order	Rate Law	Integrated Form	Half-life ($t_{1/2}$)	Example
Zero	Rate = k	$[A] = [A_0] - kt$	$t_{1/2} = [A_0]/2k$	Photochemical decomposition of HI
First	Rate = $k[A]$	$\ln[A] = \ln[A_0] - kt$	$t_{1/2} = 0.693/k$	Radioactive decay
Second	Rate = $k[A]^2$	$1/[A] = 1/[A_0] + kt$	$t_{1/2} = 1/(k[A_0])$	$2NO_2 \rightarrow 2NO + O_2$

Questions for self-control

1. Define the rate of a chemical reaction and write its general formula.
2. Explain the difference between rate law and rate constant.
3. State the Arrhenius equation and describe the significance of activation energy.
4. What is a reaction mechanism? How is the rate-determining step identified?
5. How do catalysts influence the rate and mechanism of reactions?

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