

Chemical Kinetics

Introduction

Chemical Kinetics is the study of reaction rates, the factors that affect them, and the molecular mechanisms by which reactions occur. While thermodynamics tells us if a reaction is spontaneous ($\Delta G < 0$), kinetics tells us how fast that reaction will proceed. This field is essential for optimizing industrial processes and understanding biological systems.

This module focuses on quantifying reaction rates using the Rate Law, understanding reaction mechanisms, and exploring the temperature dependence of rate constants:

- We will apply integrated rate laws to determine the concentration of reactants over time for zero, first, and second-order reactions.
- We will use the Arrhenius equation to connect the rate constant to the activation energy.

Learning Objectives

By the end of this module, you will be able to:

- State and apply the rate law/equation for simple chemical reactions of different orders.
- Calculate the half-life for reactions of different orders.
- Discuss and apply the different methods for determining the order of a reaction.
- Apply the Arrhenius equation to calculate the activation energy and the reaction rate at different temperatures.
- Write the rate law for complex reactions.
- Apply the steady-state approximation to obtain the rate equations of complex reactions.

Key Concepts and Definitions

Term	Definition
Reaction Rate	The change in the concentration of a reactant or product per unit time (e.g., M/s).
Rate Law	An equation that expresses the reaction rate as a function of reactant concentrations, typically to the power of the reaction order.
Reaction Order	The exponent to which the concentration of a reactant is raised in the rate law; determined experimentally, not by stoichiometry.
Rate Constant (k)	The proportionality constant in the rate law. Its units depend on the overall reaction order.
Half-Life ($t_{1/2}$)	The time required for the concentration of a reactant to drop to one-half of its initial value.
Activation Energy (E_a)	The minimum energy required to initiate a chemical reaction (to reach the transition state).

Detailed Discussion

1. Integrated Rate Laws and Half-Life

The **Integrated Rate Law** is derived by integrating the differential rate law. It is crucial because it allows the prediction of reactant concentrations at any given time (t), or the time required for a reaction to reach a specific extent. The half-life ($t_{1/2}$) is a specific time period useful for characterizing a reaction's speed.

Order	Integrated Rate Law	$\frac{1}{2}$ Life
Zero	$[A]_t = kt + [A]_o$	$\frac{[A]_o}{2k} = t_{1/2}$
First	$\ln([A]_t) = -kt + \ln([A]_o)$	$t_{1/2} = \frac{0.693}{k}$
Second	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$	$\frac{1}{k[A]_o} = t_{1/2}$

Where: $[A]$ is concentration at time t , $[A]_0$ is the initial concentration, and k is the rate constant.

Key Difference: For zero-order and second-order reactions, the half-life depends on the initial concentration ($[A]_0$). For a **first-order reaction**, the half-life is **independent** of the initial concentration, meaning the time required to halve the concentration is constant throughout the reaction.

2. Methods for Determining Reaction Order

The overall reaction order (n) and the individual orders with respect to each reactant must be determined experimentally, as they cannot be deduced from the stoichiometry of the overall reaction.

A. Method of Initial Rates: This is the most common method. The initial rate of consumption of a reactant is measured at a set of constant conditions. In sequential experiments, the initial concentration of only *one* reactant is systematically changed. By comparing two experiments, the individual reaction order (x) for reactant A can be found:

$$\text{Rate2 / Rate1} = ([A]_2 / [A]_1)^x$$

Solving for x provides the reaction order with respect to A.

B. Isolation Method (or Flooding): In reactions involving multiple reactants (e.g., A and B), the initial concentration of all but one reactant (e.g., B) is held in large excess. This large excess ensures that the concentrations of these other reactants remain virtually constant throughout the measurement. The rate law is then simplified to a **pseudo-order** equation dependent only on the reactant not in excess (A). Once the pseudo-order rate constant is found, the true order can be determined.

C. Integrated Rate Law Method (Graphical): Experimental concentration data $[A]$ versus time (t) is plotted according to the linear forms of the zero, first, and second-order integrated rate laws (which all resemble $y = mx + b$):

- **Zero Order:** Plot $[A]$ vs. t . A straight line indicates zero order. The slope is $-k$.
- **First Order:** Plot $\ln[A]$ vs. t . A straight line indicates first order. The slope is $-k$.
- **Second Order:** Plot $1/[A]$ vs. t . A straight line indicates second order. The slope is $+k$.

The plot that yields the straightest line indicates the true reaction order.

3. Temperature Dependence: The Arrhenius Equation

The rate constant (k) increases exponentially with temperature (T). The **Arrhenius Equation** provides the quantitative description based on collision theory, which posits that molecules must collide with sufficient energy (greater than E_a) and the correct orientation to react.

Arrhenius Equation :

$$k = A \exp(-E_a / R T)$$

Where:

- A : The **Pre-exponential Factor** (or Frequency Factor). This term accounts for the frequency of collisions and the probability of correct orientation.
- $\exp(-E_a / R T)$: The **Boltzmann Factor**, which represents the fraction of molecules in a sample that possess kinetic energy greater than or equal to the Activation Energy (E_a).

Arrhenius Equation (Linear Form):

$$\ln k = - (E_a / R) (1/T) + \ln A$$

This linear form allows E_a to be determined graphically by plotting $\ln k$ versus $1/T$. The slope of the resulting straight line is equal to $-E_a / R$.

Two-Point Form :

If the rate constant (k) is known at two different temperatures (T_1 and T_2), the activation energy (E_a) can be calculated without needing the frequency factor A :

$$\ln (k_2 / k_1) = (E_a / R) * (1/T_1 - 1/T_2)$$

4. Rate Laws for Complex Reactions and Mechanisms

The overall rate law for a complex reaction is typically determined by the mechanism, which is a sequence of elementary steps. The overall rate is governed by the **Rate-Determining Step (RDS)**, the slowest step in the mechanism.

A. The Steady-State Approximation (SSA): For mechanisms involving highly reactive, short-lived intermediates (I) that are consumed almost as fast as they are produced, the SSA is used. This approximation simplifies the derivation of the overall rate law by assuming the concentration of the intermediate is constant over the course of the reaction:

Steady-State Assumption :

$$d[I]/dt \approx 0$$

This means the rate of formation of I equals the rate of consumption of I . Setting $d[I]/dt = 0$ allows the concentration of the unmeasurable intermediate $[I]$ to be mathematically expressed in terms of the measurable reactant concentrations, which is then substituted into the rate law for the RDS.

B. Pre-Equilibrium Approximation: This is used when a fast, reversible step precedes the slow, rate-determining step. In this case, the fast step is assumed to reach equilibrium rapidly. The equilibrium constant (K_{eq}) for the fast step is used to substitute the concentration of the intermediate into the rate law of the RDS.

$$\text{Rate} = k_2 [I] [B]$$

$$\text{From fast equilibrium: } K_{eq} = [I] / [A]$$

$$\text{Therefore: } [I] = K_{eq} [A]$$

$$\text{Final Rate Law: } \text{Rate} = k_2 K_{eq} [A] [B]$$

REFERENCES:

Laidler, K. J., Meiser, J. H., & Sanctuary, B. C. (2003). *Physical Chemistry* (4th ed.). Houghton Mifflin Company.

Silbey, R. J., Alberty, R. A., & Bawendi, M. G. (2005). *Physical Chemistry* (4th ed.). Wiley.

LibreTexts. (2024). *Physical and Theoretical Chemistry: Kinetics and Electrochemistry*.

Hunter, R. J. (2001). *Foundations of Colloid Science* (2nd ed.). Oxford University Press.