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Title: Chemical Kinetics

Chemical Kinetics

Reaction kinetics deals with the study of rates at which chemical processes occur and the factors influencing them. It helps in understanding reaction mechanisms, predicting product formation, and optimizing conditions in industries.

Rate of a Reaction

The rate of a reaction expresses how fast the concentration of a substance changes over time:

$$\text{Rate} = \frac{dx}{dt} = \frac{x_2 - x_1}{t_2 - t_1}$$

Where x is the concentration and t the time. The rate can be average (over an interval) or instantaneous.

Dependence of Rate on Concentration: Law of Mass Action

According to the law of mass action, the rate of a reaction is directly proportional to the product of the active masses (concentrations) of the reactants. For a general reaction:

$$aA + bB \to \text{products}, \quad \text{Rate} = k[A]^a[B]^b$$

Here, k is the rate constant, characteristic of the reaction.

Rate Constant and Its Unit:

$$[k] = (\text{mol L}^{-1})^{1-n}\,\text{s}^{-1}$$

Where n is the overall order of reaction.

Common Rate Laws and Examples

No.	Reaction	Rate Expression
1	$aA + bB \to$ product	$\frac{dx}{dt} = k[A]^a[B]^b$
2	$2H_2O_2 \to 2H_2O + O_2$	$k[H_2O_2]$
3	Ester hydrolysis	$k[CH_3COOC_2H_5]$
4	Sucrose hydrolysis	$k[C_{12}H_{22}O_{11}]$
5	SN1 hydrolysis of t-Butyl chloride	$k[(CH_3)_3CCl]$
6	SN2 hydrolysis of methyl chloride	$k[CH_3Cl][OH^-]$
7	Diazotization of aniline derivative	$k[C_6H_5N_2Cl]$
8	Photolysis of acetaldehyde	$k[CH_3CHO]^{3/2}$
9	Redox reaction of H_2O_2	$k[H_2O_2][I^-]$
10	Decomposition of ozone	$k[O_3]^2[O_2]^{-1}$

Kinetics of Reactions with Different Orders

Order	Rate Constant Expression	Unit	Half-life Expression
0	$k = \frac{x}{t}$	mol L^{-1} s^{-1}	$T_{1/2} = \frac{a}{2k}$
1	$k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$	s^{-1}	$T_{1/2} = \frac{0.693}{k}$
2	$k = \frac{1}{t}\left[\frac{1}{a-x} - \frac{1}{a}\right]$	L mol^{-1} s^{-1}	$T_{1/2} = \frac{1}{ka}$
3	$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$	L^2 mol^{-2} s^{-1}	$T_{1/2} = \frac{3}{2ka^2}$

Methods to Determine Reaction Order

1. Integration Approach

Compare experimental data with integrated rate laws. If the rate constant remains unchanged for a particular order's formula, that order is confirmed.

2. Half-life Approach

Useful when the rate depends on a single concentration.

$$t_{1/2} \propto a^{1-n}, \quad \text{thus} \quad n = 1 + \frac{\log t_{1/2,1} - \log t_{1/2,2}}{\log a_2 - \log a_1}$$

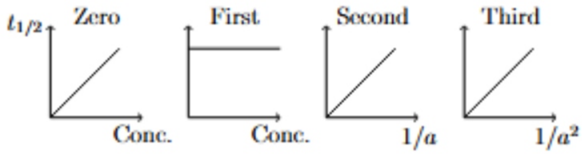
3. Graphical Approach

Based on plotting integrated forms:

- $[A]$ vs. t: Zero order
- $\log[A]$ vs. t: First order
- $\frac{1}{[A]}$ vs. t: Second order

- $\frac{1}{[A]^2}$ vs. t: Third order

Graphical Representations



Arrhenius Theory: Temperature Dependence of Rate

Arrhenius proposed a relationship between the rate constant k and temperature:

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

- A: Frequency factor (collision frequency)
- E_a: Activation energy
- R: Gas constant
- T: Temperature in Kelvin

Taking log:

$$\log k = \log A - \frac{E_a}{2.303RT}$$

Arrhenius Equation for Two Temperatures

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

This equation helps determine activation energy or predict k at different temperatures.