

1. Introduction to Chemical Kinetics

Chemical Kinetics is the branch of chemistry that deals with the study of reaction rates, the factors affecting them, and the mechanisms by which reactions proceed.

Rate of a Chemical Reaction

The rate of a reaction is defined as the change in concentration of a reactant or product per unit time.

- **Units:** $\text{mol L}^{-1} \text{s}^{-1}$ (or atm s^{-1} for gaseous reactions).

For a general reaction: $R \rightarrow P$

A. Average Rate (r_{av})

The change in concentration over a macroscopic time interval (Δt).

$$r_{av} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

(The negative sign indicates a decrease in the concentration of reactants).

B. Instantaneous Rate (r_{inst})

The rate of reaction at a specific instant of time, obtained as $\Delta t \rightarrow 0$.

$$r_{inst} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

2. Factors Influencing Rate of Reaction

Several factors govern how fast or slow a reaction proceeds:

1. **Concentration of Reactants:** Generally, the rate increases with an increase in reactant concentration due to a higher frequency of collisions.

2. **Temperature:** For most reactions, a 10°C rise in temperature roughly doubles the reaction rate.
3. **Catalyst:** A catalyst increases the rate of reaction by providing an alternative pathway with a lower activation energy, without being consumed in the reaction.
4. **Surface Area:** For solid reactants, higher surface area (e.g., powdered form) increases the rate.
5. **Nature of Reactants:** The rate depends on the specific bonds being broken and formed.

3. Rate Law and Rate Constant

Rate Law (Rate Equation)

The mathematical expression that relates the rate of a reaction to the molar concentrations of the reactants, with each term raised to a specific power (determined experimentally).

For a reaction $aA + bB \rightarrow \text{Products}$:

$$\text{Rate} = k[A]^x[B]^y$$

- Where k is the **Rate Constant** (or specific reaction rate).
- x and y may or may not be equal to the stoichiometric coefficients a and b .

Order of a Reaction

The sum of the powers of the concentration of the reactants in the rate law expression.

$$\text{Order}(n) = x + y$$

- Order can be 0, 1, 2, 3, or even a fraction.
- It is a purely **experimental** quantity.

Molecularity of a Reaction

The number of reacting species (atoms, ions, or molecules) taking part in an elementary reaction, which must collide simultaneously to bring about a chemical reaction.

- Molecularity must be an integer (1, 2, 3). It cannot be zero or a fractional number.
- Reactions with molecularity ≥ 4 are very rare.

$$t_{1/2} = \frac{[R]_0}{2k}$$

(For a zero-order reaction, $t_{1/2}$ is directly proportional to initial concentration).



4. Integrated Rate Equations and Half-Life

Integrated rate laws give the direct relationship between the concentration of reactants and time.

A. Zero Order Reactions

The rate of the reaction is independent of the concentration of the reactants.

- **Differential Rate Law:**

$$Rate = -\frac{d[R]}{dt} = k[R]^0 = k$$

- **Integrated Rate Equation:**

$$[R] = -kt + [R]_0$$

(Where $[R]_0$ is the initial concentration and $[R]$ is the concentration at time t)

- **Half-Life ($t_{1/2}$):** The time required for the concentration of a reactant to reduce to half its initial value.

B. First Order Reactions

The rate of the reaction is proportional to the first power of the concentration of the reactant.

- **Differential Rate Law:**

$$Rate = -\frac{d[R]}{dt} = k[R]^1$$

- **Integrated Rate Equation:**

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

Or in exponential form:

$$[R] = [R]_0 e^{-kt}$$

- **Half-Life ($t_{1/2}$):**

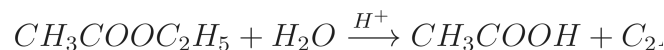
$$t_{1/2} = \frac{0.693}{k}$$

(For a first-order reaction, $t_{1/2}$ is independent of the initial concentration).

5. Pseudo First Order Reactions

Reactions that are not truly of the first order but behave as first-order reactions under certain conditions (usually when one reactant is present in a large excess).

- **Example:** Acid-catalyzed hydrolysis of ethyl acetate.



Because water is in vast excess, its concentration remains essentially constant.

$$Rate = k'[CH_3COOC_2H_5][H_2O]$$

$$Rate = k[CH_3COOC_2H_5]$$

(where $k = k'[H_2O]$)



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6. Temperature Dependence: Arrhenius Equation

The temperature dependence of the rate of a chemical reaction can be accurately explained by the **Arrhenius equation**.

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

- A = Arrhenius factor (Frequency factor or pre-exponential factor).
- R = Gas constant.
- E_a = Activation energy (in J mol^{-1}).
- T = Absolute temperature (in Kelvin).

Taking the natural logarithm of both sides:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

If k_1 and k_2 are the rate constants at temperatures T_1 and T_2 respectively, the equation becomes:

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

Activation Energy (E_a)

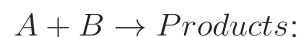
The minimum extra amount of energy required by the reacting molecules to get converted into products.

7. Collision Theory for Bimolecular Reactions

According to this theory, reactant molecules are assumed to be hard spheres, and a reaction occurs only when these molecules collide with each other.

- **Collision Frequency (Z):** The number of collisions per second per unit volume of the reaction mixture.

For a bimolecular elementary reaction



$$\text{Rate} = Z_{AB}e^{-E_a/RT}$$

Where Z_{AB} is the collision frequency of reactants A and B, and $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a .

Effective Collisions & The Steric Factor

Not all collisions lead to a reaction. For a collision to be effective, molecules must have:

1. Sufficient kinetic energy (Threshold energy).
2. Proper orientation during the collision.

To account for effective collisions, a probability or steric factor (P) is introduced:

$$\text{Rate} = PZ_{AB}e^{-E_a/RT}$$

Limitations of Collision Theory

- It considers atoms/molecules to be hard spheres and ignores their structural aspects.
- It does not account for the complex nature of breaking and forming specific bonds.