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Rate of Chemical Reaction

Definition and Measurement

Chemical kinetics is the branch of chemistry that studies the speed or rate of chemical reactions and the mechanisms by which they occur. The rate of a chemical reaction is defined as the change in concentration of a reactant or product per unit time.

Rate Expressions

For a reaction $A + B \rightarrow C$, the rate of disappearance of reactant A is given by $\text{Rate} = -\frac{\Delta [A]}{\Delta t}$. Similarly, the rate of appearance of product C is $\text{Rate} = \frac{\Delta [C]}{\Delta t}$. Concentrations are expressed in molarity (mol L⁻¹).

Units and Types of Rates

The unit of rate of reaction is mol L⁻¹ s⁻¹ or mol L⁻¹ min⁻¹ for reactions in solution, and atm s⁻¹ or atm min⁻¹ for gaseous reactions. Instantaneous rate refers to the rate at a

specific moment, while average rate is measured over a time interval.

Factors Affecting Rate

- **Concentration:** Increasing reactant concentration generally increases the reaction rate.
- **Temperature:** Higher temperatures increase molecular kinetic energy, increasing reaction rates.
- **Pressure:** For gases, increased pressure increases concentration and rate.
- **Catalysts:** Substances that lower activation energy and increase reaction rate without being consumed.
- **Nature of Reactants:** Simpler molecules react faster due to fewer bonds to break.
- **Surface Area:** Greater surface area of solids increases reaction rate.
- **Radiation:** Photochemical reactions are initiated by light and often proceed faster.
- **Physical State:** Reactivity depends on whether substances are solid, liquid, or gas.

Solved Examples

Example 1

For the reaction $R \rightarrow P$, the concentration of R changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction in $\text{mol L}^{-1} \text{min}^{-1}$ and $\text{mol L}^{-1} \text{s}^{-1}$.

Solution:

$$\text{Average rate} = -\frac{\Delta [R]}{\Delta t} = -\frac{0.02 - 0.03}{25} = 4 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$$

$$\text{Converting to seconds: } 4 \times 10^{-4} / 60 = 6.67 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$$

Practice Set

- **Level 1:** Define the rate of a chemical reaction and state its units.
- **Level 2:** Explain how temperature affects the rate of a chemical reaction.
- **Level 3:** A reaction has a rate of disappearance of reactant A as $0.005 \text{ mol LB9 sB9}$. Calculate the rate of appearance of product if the reaction is $A + B \rightarrow 12 \rightarrow 12 \rightarrow 12 \rightarrow 12 C$.

Answer Key

- **Level 1:** Rate of reaction is the change in concentration of reactants or products per unit time. Units are mol LB9 sB9 or mol LB9 minB9 .
- **Level 2:** Increasing temperature increases molecular kinetic energy, leading to more frequent and energetic collisions, thus increasing reaction rate.
- **Level 3:** Rate of appearance of product C = rate of disappearance of A = $0.005 \text{ mol LB9 sB9}$.

Order of Reaction

Definition and Determination

The order of a reaction is the sum of the powers of the concentration terms in the experimentally determined rate law. It indicates how the rate depends on reactant concentrations and can be zero, whole number, or fractional.

Types of Reaction Orders

- **Zero Order:** Rate is independent of reactant concentration. $\text{Rate} = k$.
- **First Order:** Rate is directly proportional to concentration. $\text{Rate} = k[A]$.
- **Pseudo First Order:** Reaction behaves like first order under certain conditions.
- **Second Order:** Rate depends on the square of one reactant or product of two reactants. $\text{Rate} = k[A][B]$ or $k[A]^2$.

Rate Constant and Units

The rate constant k varies with temperature and has units depending on the order: $\text{mol L}^{-1} \text{s}^{-1}$ for zero order, s^{-1} for first order, and $\text{mol}^{-1} \text{L s}^{-1}$ for second order.

Half-life

Half-life is the time required for the concentration of a reactant to reduce to half its initial value. For first order reactions, half-life is independent of concentration and given by $t_{1/2} = 0.693/k$.

Solved Examples

Example 2

A first-order reaction is 20% complete in 40 minutes. Calculate the time required for 60% completion.

Solution:

Using $k = (2.303 / t) \log (a / (a - x))$

For 20% completion: $40 = (2.303 / k) \log (100 / 80)$

Calculate k , then for 60% completion:

$$t = (2.303 / k) \log (100 / 40) = 164.42 \text{ minutes}$$

Practice Set

- **Level 1:** Define the order of a reaction.
- **Level 2:** Write the rate law for a second-order reaction involving two reactants.
- **Level 3:** Calculate the half-life of a first-order reaction with rate constant $k = 0.02 \text{ s}^{-1}$.

Answer Key

- **Level 1:** Order is the sum of powers of concentration terms in the rate law.
- **Level 2:** Rate = $k[A][B]$
- **Level 3:** $t_{1/2} = 0.693 / 0.02 = 34.65 \text{ seconds}$

Collision Theory

Concept and Activation Energy

Collision theory states that chemical reactions occur when reactant molecules collide with sufficient energy and proper orientation. The minimum energy required for a collision to be effective is called activation energy (E_a).

Effective Collisions and Rate

Only collisions with energy equal to or greater than E_a and correct orientation lead to product formation. The rate of reaction depends on collision frequency (Z) and the fraction of effective collisions (f): Rate = $f \cdot Z$.

Arrhenius Equation

The Arrhenius equation relates the rate constant k to temperature T and activation energy E_a :

$$k = A e^{\{-E_a / RT\}}$$

where A is the frequency factor, R is the gas constant, and T is temperature in kelvin.

Solved Examples

Example 3

(i) For the reaction $A \rightarrow B$, the rate increases 27 times when concentration of A is tripled. Find the order of the reaction.

Solution:

$$\text{Rate} = k[R]^n$$

$$27 = 3^n \quad n = 3$$

(ii) Activation energy decreases from 75.2 kJ mol^{-1} to $50.14 \text{ kJ mol}^{-1}$ with catalyst at 25°C . Calculate rate increase.

Using Arrhenius equation, rate increases by 2.46×10^4 times.

Practice Set

- **Level 1:** Define activation energy.
- **Level 2:** Explain the role of a catalyst in a chemical reaction.
- **Level 3:** Calculate the factor by which rate increases if activation energy decreases from 80 kJ mol⁻¹ to 60 kJ mol⁻¹ at 298 K.

Answer Key

- **Level 1:** Activation energy is the minimum energy required for reactant molecules to undergo a reaction.
- **Level 2:** A catalyst lowers activation energy, increasing the rate without being consumed.
- **Level 3:** Use Arrhenius equation to calculate rate increase factor.

Quick Reference Table

Common Mistakes and Misconceptions

Glossary
