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# Rate of Reaction

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## Chemical Kinetics

Chemical kinetics is the branch of physical chemistry that studies the rate of chemical reactions and the mechanisms by which they occur.

## Definition of Rate of Reaction

The rate of reaction is the change in concentration of a reactant or product per unit time. For a reaction  $A + B \rightarrow C$ , the rate can be expressed as:

$$\text{Rate of disappearance of A} = -\Delta[A] / \Delta t$$

$$\text{Rate of disappearance of B} = -\Delta[B] / \Delta t$$

$$\text{Rate of appearance of C} = \Delta[C] / \Delta t$$

Here, [A], [B], and [C] represent molar concentrations of the reactants and product respectively.

## Molar Concentration

Molar concentration is the amount of solute (in moles) dissolved in one litre of solution. It is the most convenient way to express concentration.

## Units of Rate

The unit of rate of reaction is  $\text{mol L}^{-1} \text{s}^{-1}$  or  $\text{mol L}^{-1} \text{min}^{-1}$  for reactions in liquid phase, and  $\text{atm s}^{-1}$  or  $\text{atm min}^{-1}$  for gaseous reactions.

## Instantaneous and Average Rate

Instantaneous rate is the rate at a particular moment and is given by the derivative of concentration with respect to time, e.g.,  $-d[A]/dt$ .

Average rate is the change in concentration over a finite time interval,  $\Delta x/\Delta t$ .

## Factors Affecting Rate

- **Concentration:** Rate increases with increase in reactant concentration.
- **Temperature:** Higher temperature increases kinetic energy, increasing rate.
- **Pressure:** Affects gaseous reactions by increasing concentration.
- **Catalyst:** Lowers activation energy, increasing rate without being consumed.
- **Nature of Reactants:** Simpler molecules react faster due to fewer bonds to break.
- **Surface Area:** Greater surface area increases rate in heterogeneous reactions.
- **Radiations:** Photochemical reactions initiated by light proceed faster.
- **Physical State:** Reactants in gaseous or aqueous state react faster than solids.

## Rate Law and Rate Constant

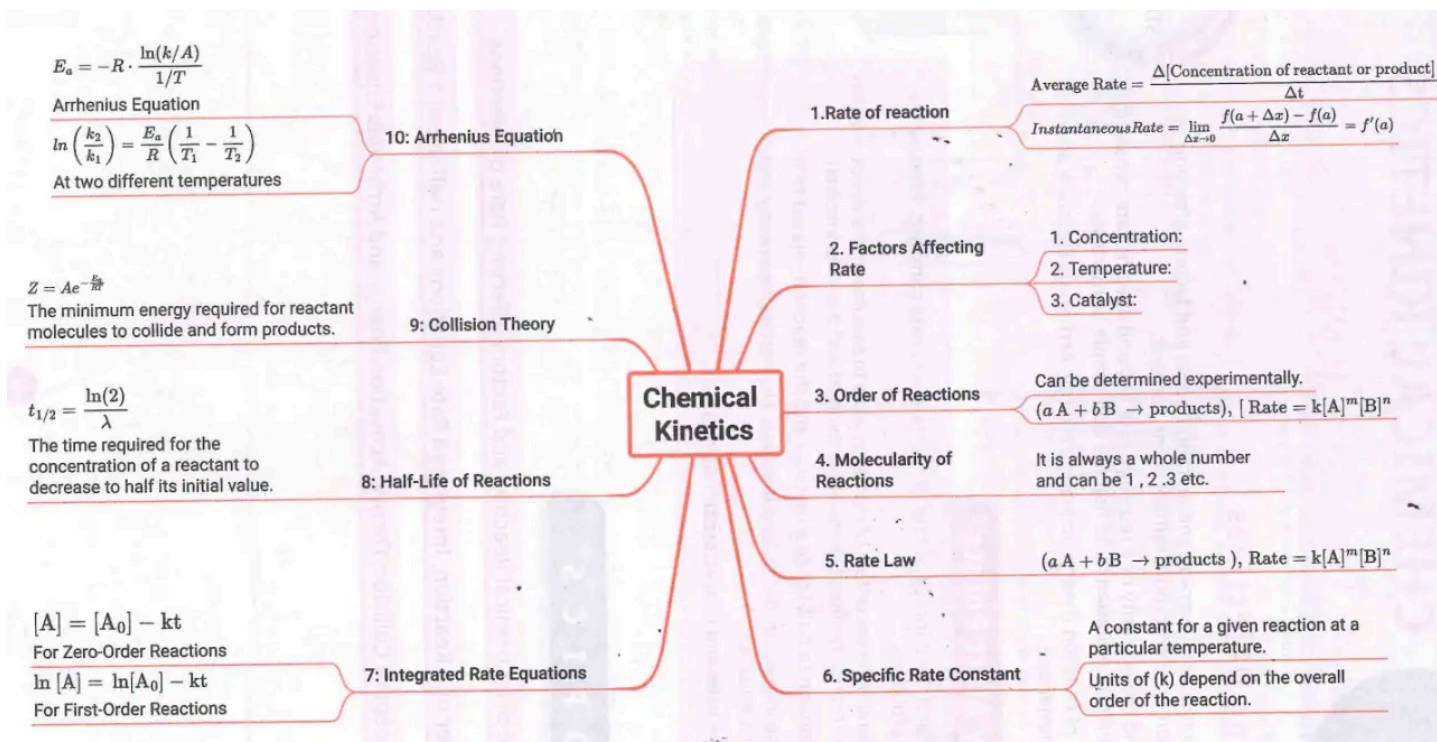
Rate law expresses the rate as a function of reactant concentrations:  $\text{Rate} = k[A]^m[B]^n$ , where  $k$  is the rate constant.

Rate constant  $k$  depends on temperature and catalyst presence.

## Molecularity and Elementary Reactions

Molecularity is the number of reactant particles involved in an elementary step; it is always a whole number (1, 2, or 3).

Elementary reactions occur in a single step with no intermediates.



## 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:**

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

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

## Practice Set

- **Level 1:** Define rate of reaction and state its units.
- **Level 2:** Explain how temperature affects the rate of a chemical reaction.

- **Level 3:** A reaction has a rate that becomes twenty-seven times when the concentration of a reactant is tripled. What is the order of the reaction with respect to that reactant?

## Answer Key

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- **Level 1:** Rate of reaction is the change in concentration of reactants or products per unit time. Units are  $\text{mol L}^{-1} \text{s}^{-1}$  or  $\text{mol L}^{-1} \text{min}^{-1}$ .
- **Level 2:** Increasing temperature increases kinetic energy of molecules, leading to more frequent and energetic collisions, thus increasing the reaction rate.
- **Level 3:** Since rate becomes twenty-seven times when concentration triples, the order with respect to that reactant is 3 (third order).

## Order of Reaction

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### Definition

Order of reaction is the sum of the powers of concentration terms in the experimentally determined rate law. It can be zero, whole number, or fractional.

### Zero Order Reaction

Rate is independent of reactant concentration:  $\text{Rate} = k$ .

Unit of  $k$  is  $\text{mol L}^{-1} \text{s}^{-1}$ .

Example: Thermal decomposition of HI on gold surface.

### First Order Reaction

Rate is directly proportional to the first power of reactant concentration:  $\text{Rate} = k[\text{A}]$ .

Unit of  $k$  is  $\text{s}^{-1}$ .

Example: Decomposition of  $\text{N}_2\text{O}_5$ .

## Pseudo First Order Reaction

A reaction that behaves like first order under certain conditions, e.g., acidic hydrolysis of ester.

## Second Order Reaction

Rate depends on the square of one reactant or product of two reactants:  $\text{Rate} = k[\text{A}][\text{B}]$ .

Unit of  $k$  is  $\text{mol}^{-1} \text{L s}^{-1}$ .

## Integrated Rate Equations

Used to calculate concentration changes over time for zero and first order reactions.

## Half-life

Time taken for concentration to reduce to half its initial value.

For zero order:  $t_{1/2} = [\text{A}]_0 / 2k$

For first order:  $t_{1/2} = 0.693 / k$

| Reaction           | Order | Unit of rate constant             | Example                                                                                                                                                       |
|--------------------|-------|-----------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Zero order         | 0     | $\text{mol L}^{-1} \text{s}^{-1}$ | $\text{H}_2 + \text{Cl}_2 \xrightarrow{\text{Sunlight}} 2\text{HCl}$                                                                                          |
| First order        | 1     | $\text{s}^{-1}$                   | $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$                                                                                                 |
| Pseudo first order | 1     | $\text{s}^{-1}$                   | $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$ |
| Second order       | 2     | $\text{mol}^{-1} \text{L s}^{-1}$ | $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$                                                                                                              |

## Solved Examples

### Example 2

If a first-order reaction is 20% complete in 40 minutes, find the time to complete 60% of the reaction.

**Solution:**

Using  $k = (2.303 / t) \log (a / (a - x))$ , calculate  $k$  for 20% completion, then use it to find time for 60% completion.

Time for 60% completion = 164.42 minutes.

## Practice Set

- **Level 1:** Define order of reaction and give an example of a zero order reaction.
- **Level 2:** Write the integrated rate law for a first order reaction.
- **Level 3:** Calculate the half-life of a zero order reaction with initial concentration  $0.1 \text{ mol L}^{-1}$  and rate constant  $0.02 \text{ mol L}^{-1} \text{s}^{-1}$ .

## Answer Key

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- **Level 1:** Order of reaction is the sum of powers of concentration in rate law. Example: Thermal decomposition of HI is zero order.
- **Level 2:** Integrated rate law for first order:  $\ln [A] = -kt + \ln [A]_0$ .
- **Level 3:** Half-life for zero order:  $t_{1/2} = [A]_0 / 2k = 0.1 / (2 \times 0.02) = 2.5$  seconds.

## Collision Theory

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### Concept

Collision theory states that chemical reactions occur when reactant molecules collide with sufficient energy and proper orientation.

### Activation Energy

Activation energy is the minimum energy required for reactants to form products during collision.

### Effective Collision

Only collisions with energy equal to or greater than activation energy and correct orientation lead to reaction.

### Arrhenius Equation

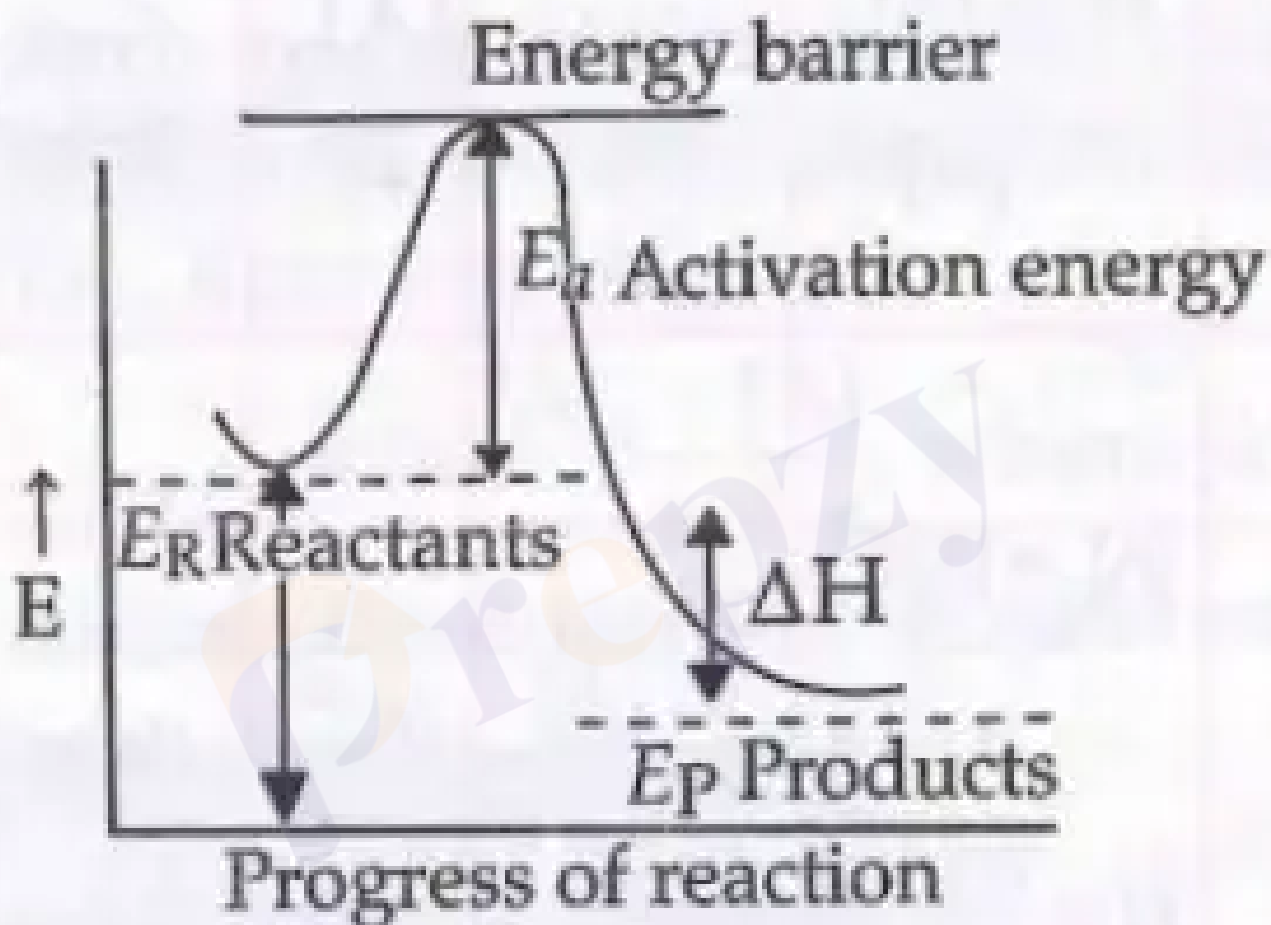
Relates rate constant  $k$  to temperature  $T$  and activation energy  $E_a$ :

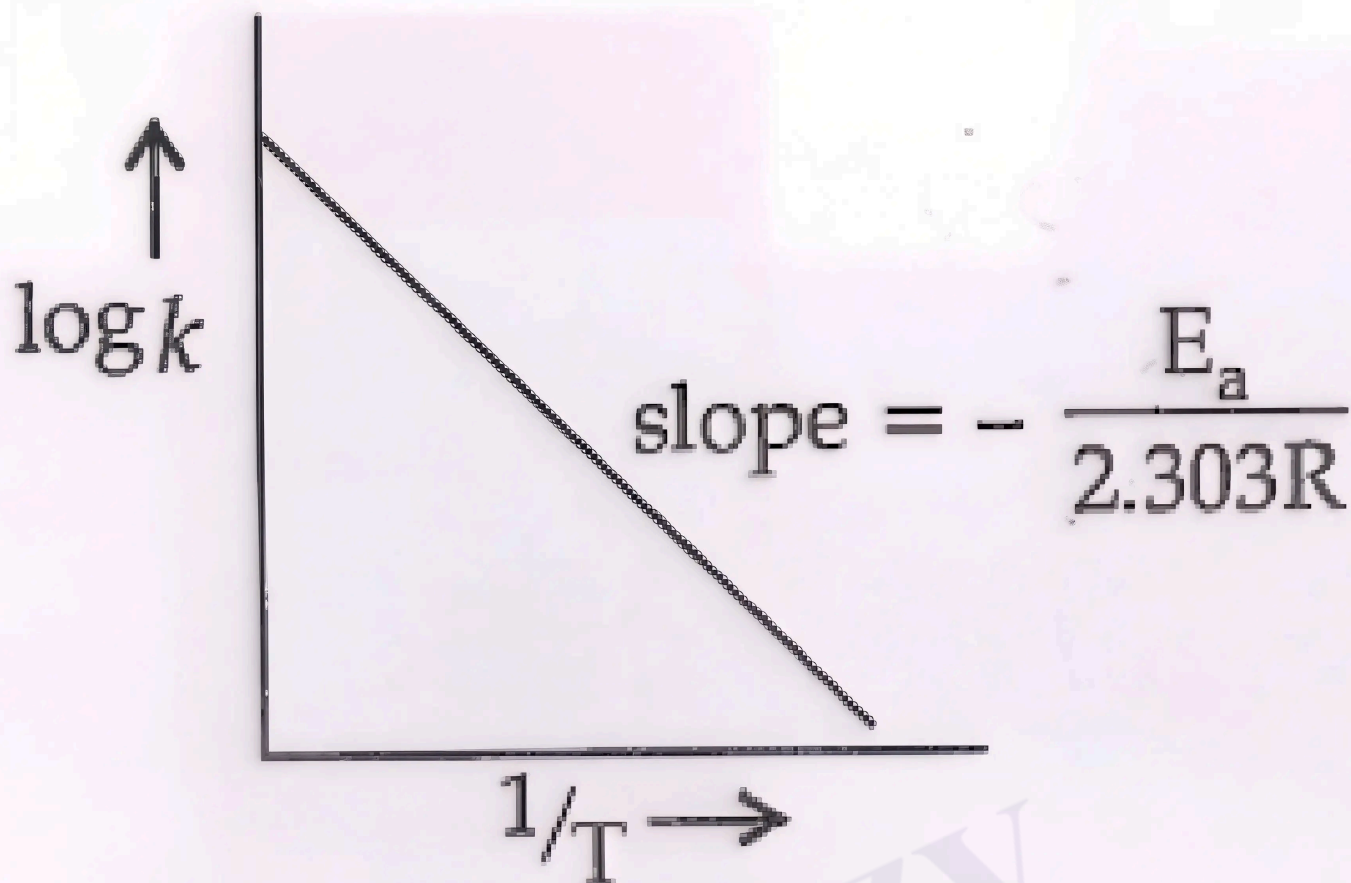
$$k = A e^{-E_a/RT}$$

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

## Graphical Representation

Plotting  $\log k$  vs  $1/T$  gives a straight line with slope  $-E_a / (2.303 R)$ .



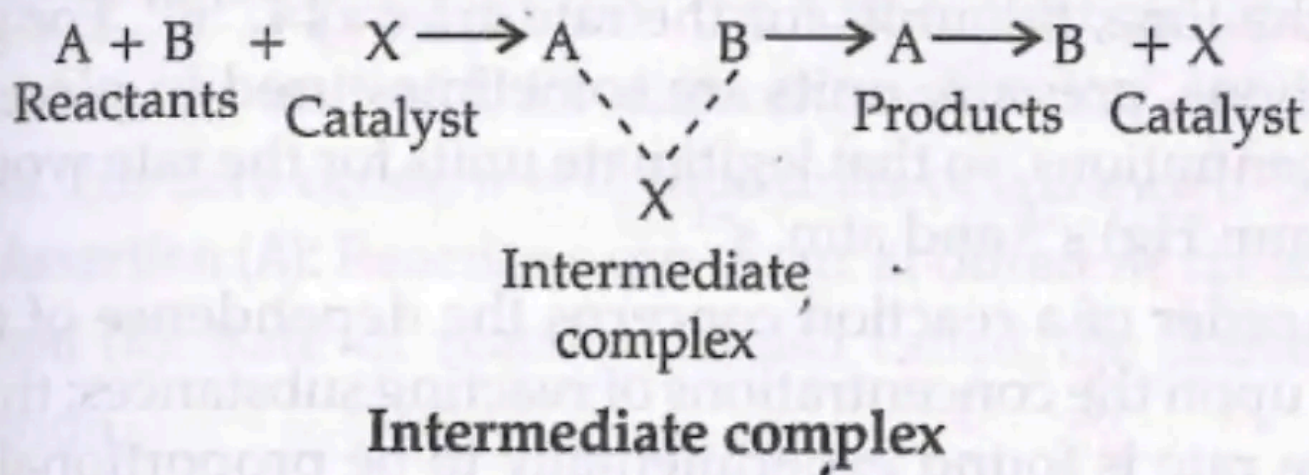


## Catalysts

A catalyst increases reaction rate by lowering activation energy without being consumed.

Characteristics include not changing equilibrium constant or free energy change, and catalysing both forward and backward reactions.

### Intermediate complex theory:



## Solved Examples

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### Example 3

- (i) For reaction  $A \rightarrow B$ , if rate increases 27 times when concentration triples, find the order.
- (ii) Activation energy decreases from  $75.2 \text{ kJ mol}^{-1}$  to  $50.14 \text{ kJ mol}^{-1}$  with catalyst at  $25^\circ\text{C}$ . Calculate rate increase.

#### Solution:

- (i) Rate  $r = k[R]^n$ . Given  $r' = 27r$  when  $[R]' = 3[R]$ , so  $27 = 3^n$  implies  $n=3$ .
- (ii) Using Arrhenius equation, rate increases by  $2.46 \times 10^4$  times with catalyst.

## Practice Set

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- **Level 1:** Define activation energy and explain its significance.
- **Level 2:** State the Arrhenius equation and explain each term.
- **Level 3:** Explain how a catalyst affects the activation energy and rate of reaction.

## Answer Key

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- **Level 1:** Activation energy is the minimum energy required for reactants to form products during collision.
- **Level 2:** Arrhenius equation:  $k = A e^{-E_a/RT}$ , where  $k$  is rate constant,  $A$  frequency factor,  $E_a$  activation energy,  $R$  gas constant,  $T$  temperature.
- **Level 3:** A catalyst lowers activation energy, increasing the fraction of effective collisions, thus increasing the reaction rate.

## Quick Reference Table

| Concept                         | Formula                                                                | Key Point                                                    |
|---------------------------------|------------------------------------------------------------------------|--------------------------------------------------------------|
| Average rate                    | $\text{Rate} = \pm \Delta[\text{conc.}] / \Delta t$                    | Measured over a finite time interval                         |
| Instantaneous rate              | $\text{Rate} = \pm d[\text{conc.}] / dt$                               | Rate at a specific moment; slope of concentration-time curve |
| Rate law                        | $\text{Rate} = k[A]^m[B]^n$                                            | m, n are experimentally determined, not from stoichiometry   |
| Order of reaction               | Sum of exponents (m + n) in rate law                                   | Can be zero, whole number, or fractional                     |
| Molecularity                    | Number of reacting species in an elementary step                       | Always a whole number (1, 2, or 3); never zero or fractional |
| Zero order rate law             | $\text{Rate} = k$ , unit of k: $\text{mol L}^{-1} \text{s}^{-1}$       | Rate independent of concentration                            |
| Zero order integrated equation  | $[A] = [A]_0 - kt$                                                     | Straight line plot of [A] vs t                               |
| Zero order half-life            | $t_{1/2} = [A]_0 / 2k$                                                 | Half-life depends on initial concentration                   |
| First order rate law            | $\text{Rate} = k[A]$ , unit of k: $\text{s}^{-1}$                      | Rate proportional to concentration                           |
| First order integrated equation | $\ln [A] = -kt + \ln [A]_0$ , or $k = (2.303/t) \log([A]_0/[A])$       | Straight line plot of $\log [A]$ vs t                        |
| First order half-life           | $t_{1/2} = 0.693 / k$                                                  | Independent of initial concentration                         |
| Second order rate law           | $\text{Rate} = k[A][B]$ , unit of k: $\text{mol}^{-1} \text{L s}^{-1}$ | Depends on two reactant concentrations or square of one      |
| Arrhenius equation              | $k = A e^{-E_a/RT}$                                                    | Relates rate constant to temperature and activation          |

|                    |                                                |                                                    |
|--------------------|------------------------------------------------|----------------------------------------------------|
|                    |                                                | energy                                             |
| Arrhenius plot     | $\log k$ vs $1/T$ , slope = $-E_a / (2.303 R)$ | Used to determine activation energy graphically    |
| Effect of catalyst | Lowers $E_a$ , increases $k$                   | Does not change $\Delta G$ or equilibrium constant |

## Common Mistakes and Misconceptions

- **Confusing order of reaction with molecularity:** Order is determined experimentally and can be zero, fractional, or a whole number; molecularity is a theoretical concept for elementary steps and must always be a whole number (1, 2, or 3).
- **Assuming order matches stoichiometric coefficients:** Unlike molecularity, the order of reaction with respect to a species is not necessarily equal to its stoichiometric coefficient — it must be found from experimental rate data, not written directly from the balanced equation.
- **Mixing up average rate and instantaneous rate:** Average rate is calculated over a finite time interval ( $\Delta$ ), while instantaneous rate is the rate at one specific moment, found using derivatives ( $d/dt$ ) or the slope of the tangent on a concentration-time graph.
- **Forgetting the negative sign for reactants:** Since reactant concentration decreases with time, the rate of disappearance is written as  $-\Delta[A]/\Delta t$  (with a negative sign) so that the overall rate remains a positive quantity.
- **Misremembering half-life dependence:** A common error is assuming half-life is always independent of initial concentration. This is true only for first order reactions ( $t_{1/2} = 0.693/k$ ); for zero order reactions, half-life does depend on initial concentration ( $t_{1/2} = [A]_0/2k$ ).
- **Believing a catalyst changes the reaction's thermodynamics:** A catalyst only lowers the activation energy and speeds up the reaction (both forward and backward); it does not alter the equilibrium constant, the equilibrium position, or the free energy change of the reaction.
- **Assuming higher temperature always means higher activation energy:** Temperature and activation energy are independent quantities — increasing temperature increases the fraction of molecules with energy  $\geq E_a$ , but does not change the value of  $E_a$  itself.
- **Ignoring orientation in collision theory:** Students often think any collision with enough energy will lead to a reaction; proper molecular orientation during collision is equally necessary for an effective collision.

# Glossary

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- **Chemical kinetics:** The branch of chemistry that studies the rate and mechanism of chemical reactions.
- **Rate of reaction:** The change in concentration of a reactant or product per unit time.
- **Average rate:** The rate of reaction measured over a finite time interval.
- **Instantaneous rate:** The rate of reaction at a particular instant, given by the derivative of concentration with respect to time.
- **Rate law:** An expression relating the rate of reaction to the concentrations of reactants, each raised to an experimentally determined power.
- **Rate constant (k):** The proportionality constant in the rate law, dependent on temperature and the presence of a catalyst.
- **Order of reaction:** The sum of the powers of the concentration terms in the experimentally determined rate law.
- **Molecularity:** The number of reacting species (atoms, ions, or molecules) that collide simultaneously in an elementary reaction step.
- **Elementary reaction:** A reaction that occurs in a single step without the formation of any intermediate.
- **Zero order reaction:** A reaction whose rate is independent of the concentration of the reactant(s).
- **First order reaction:** A reaction whose rate is directly proportional to the concentration of one reactant.
- **Pseudo first order reaction:** A reaction that is not truly first order but behaves as one under specific conditions, usually because one reactant is present in large excess.
- **Second order reaction:** A reaction whose rate depends on the concentration of two reactants, or the square of one reactant's concentration.
- **Integrated rate equation:** An equation obtained by integrating the rate law, expressing concentration as a function of time.
- **Half-life ( $t_{1/2}$ ):** The time required for the concentration of a reactant to reduce to half of its initial value.
- **Collision theory:** A theory stating that a chemical reaction occurs when reactant molecules collide with sufficient energy and correct orientation.
- **Activation energy ( $E_a$ ):** The minimum energy that colliding reactant molecules must possess for a reaction to occur.
- **Effective collision:** A collision between reactant molecules that has both sufficient energy and proper orientation to result in a reaction.
- **Arrhenius equation:** An equation expressing the temperature dependence of the rate constant in terms of activation energy and a frequency factor.

- **Frequency factor (A):** A constant in the Arrhenius equation representing the frequency of collisions with proper orientation.
- **Catalyst:** A substance that increases the rate of a reaction by lowering its activation energy, without being consumed in the process.

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