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Introduction

Chemical Kinetics Overview

- Chemical kinetics studies reaction rates and mechanisms.
- It helps determine how fast reactions occur and how conditions affect rates.

Solved Examples

- Ex 1: Identify the branch of chemistry studying reaction speed.
  Answer: Chemical kinetics.

Practice Set

- Q1: What does chemical kinetics study?
  A) Reaction equilibrium
  B) Reaction rates and mechanisms
  C) Atomic structure
  D) Molecular bonding
- Q2: Which factor is NOT studied in chemical kinetics?
  A) Reaction speed
  B) Reaction mechanism
  C) Reaction equilibrium constant
  D) Effect of temperature on rate
- Q3: Chemical kinetics helps to:
  A) Predict product stability
  B) Determine reaction speed and rate changes
  C) Calculate molecular mass
  D) Identify element types

Answer Key

- Q1: B - Chemical kinetics focuses on reaction rates and mechanisms.
- Q2: C - Equilibrium constant is studied in chemical equilibrium, not kinetics.

- Q3: B - Kinetics determines speed and how rates change with conditions.

Memory Aids

- "Kinetics = Speed + Path" (rate and mechanism)
- Focus on how fast and how reactions proceed.

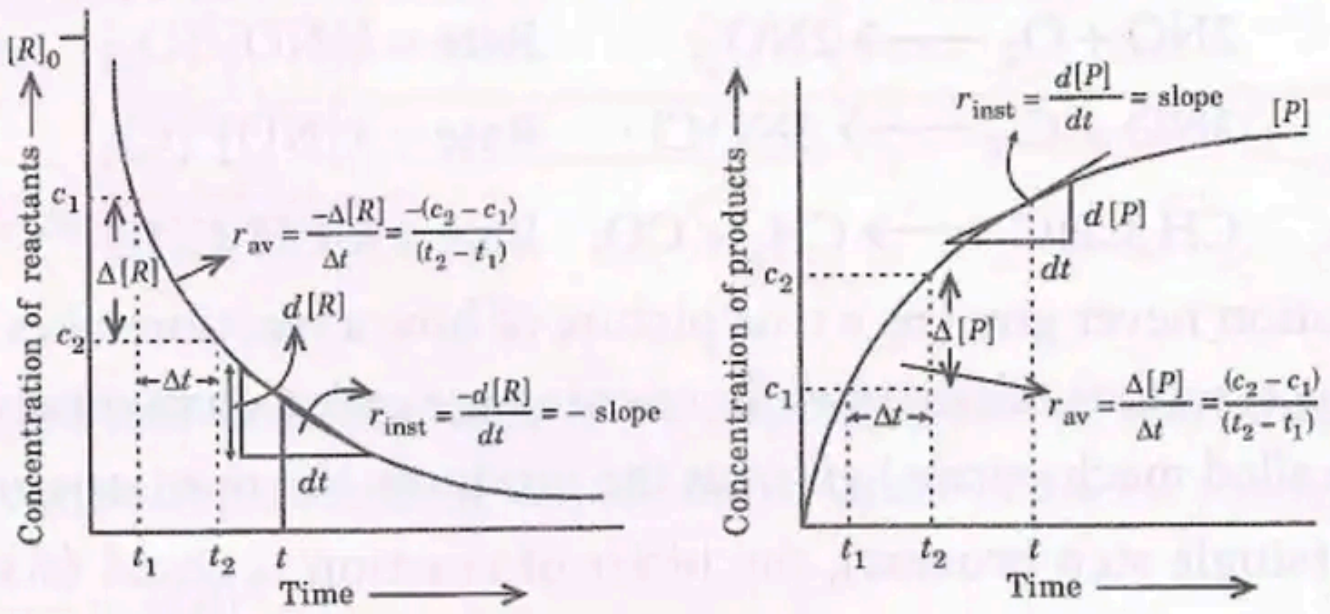
Rate of a Chemical Reaction

Definition and Units

- Rate = change in concentration of reactant or product per unit time.
- For reaction R → P, rate = $-\Delta[R]/\Delta t$ or $+\Delta[P]/\Delta t$.
- Units: mol L^{-1} s^{-1} or atm s^{-1} for gases.

Average and Instantaneous Rate

- Average rate: change over a large time interval, $r_{av} = -\Delta[R]/\Delta t$ or $+\Delta[P]/\Delta t$.
- Instantaneous rate: rate at a specific time, $r_{inst} = -d[R]/dt$ or $+d[P]/dt$.
- Δ indicates larger change (average), d indicates small change (instantaneous).



Average and instantaneous rate of reaction

Solved Examples

- Ex 1: Calculate average rate if [R] changes from 0.5 to 0.2 mol/L in 10 s.
  Rate = -(0.2 - 0.5)/10 = 0.03 mol L^{-1} s^{-1}.
- Ex 2: Find instantaneous rate at t = 5 s from slope of tangent on concentration-time graph.

Practice Set

- Q1: Rate of reaction is defined as:
  A) Change in temperature per time
  B) Change in concentration per time
  C) Change in pressure per time
  D) Change in volume per time
- Q2: Units of reaction rate for gases are:
  A) mol L^{-1} s^{-1}
  B) atm s^{-1}
  C) Both A and B
  D) mol s^{-1}
- Q3: Instantaneous rate differs from average rate because:
  A) It uses larger time intervals
  B) It is rate at a specific instant

C) It ignores concentration changes
D) It is always zero

Answer Key

- Q1: B - Rate measures concentration change per unit time.
- Q2: C - Both mol L^{-1} s^{-1} and atm s^{-1} are used.
- Q3: B - Instantaneous rate is at a specific moment, unlike average rate.

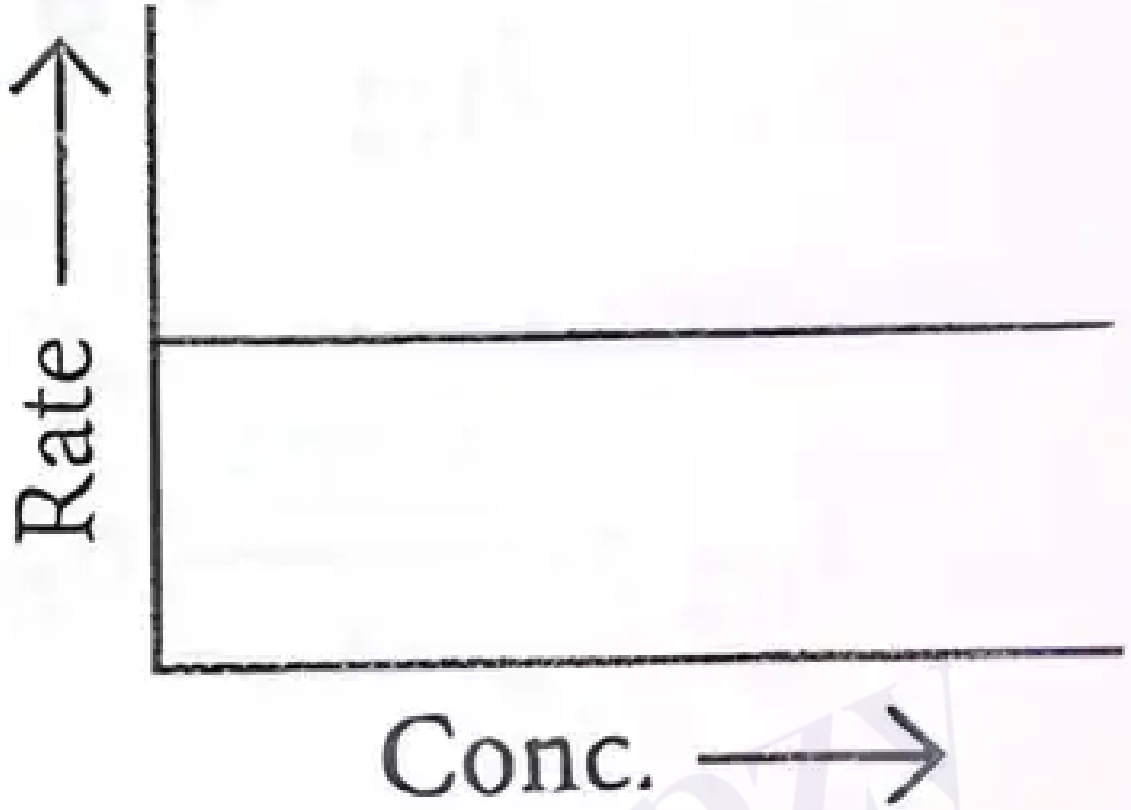
Memory Aids

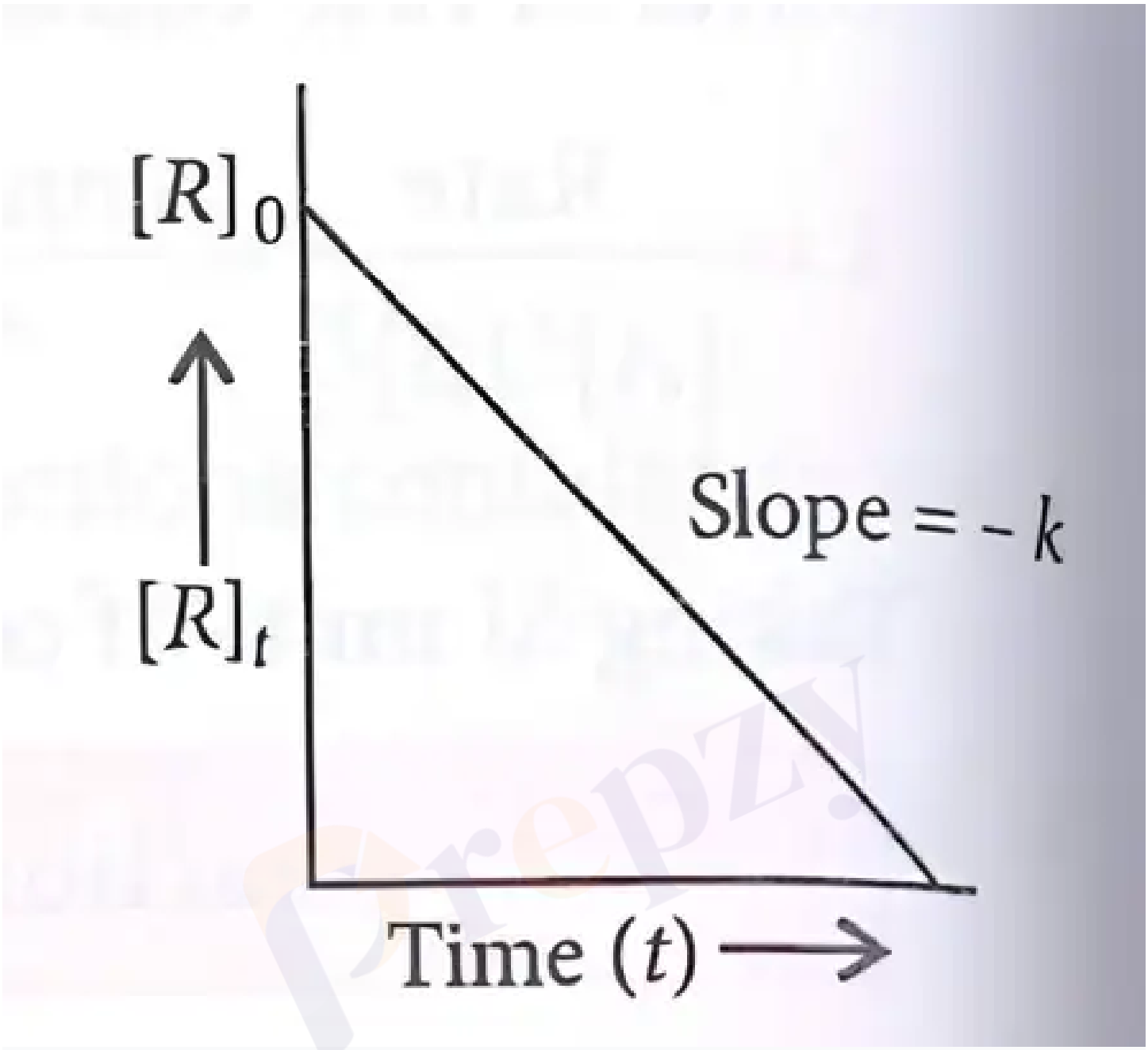
- Average rate uses Δ (big change), instantaneous uses d (small change).
- Rate = concentration change/time interval.

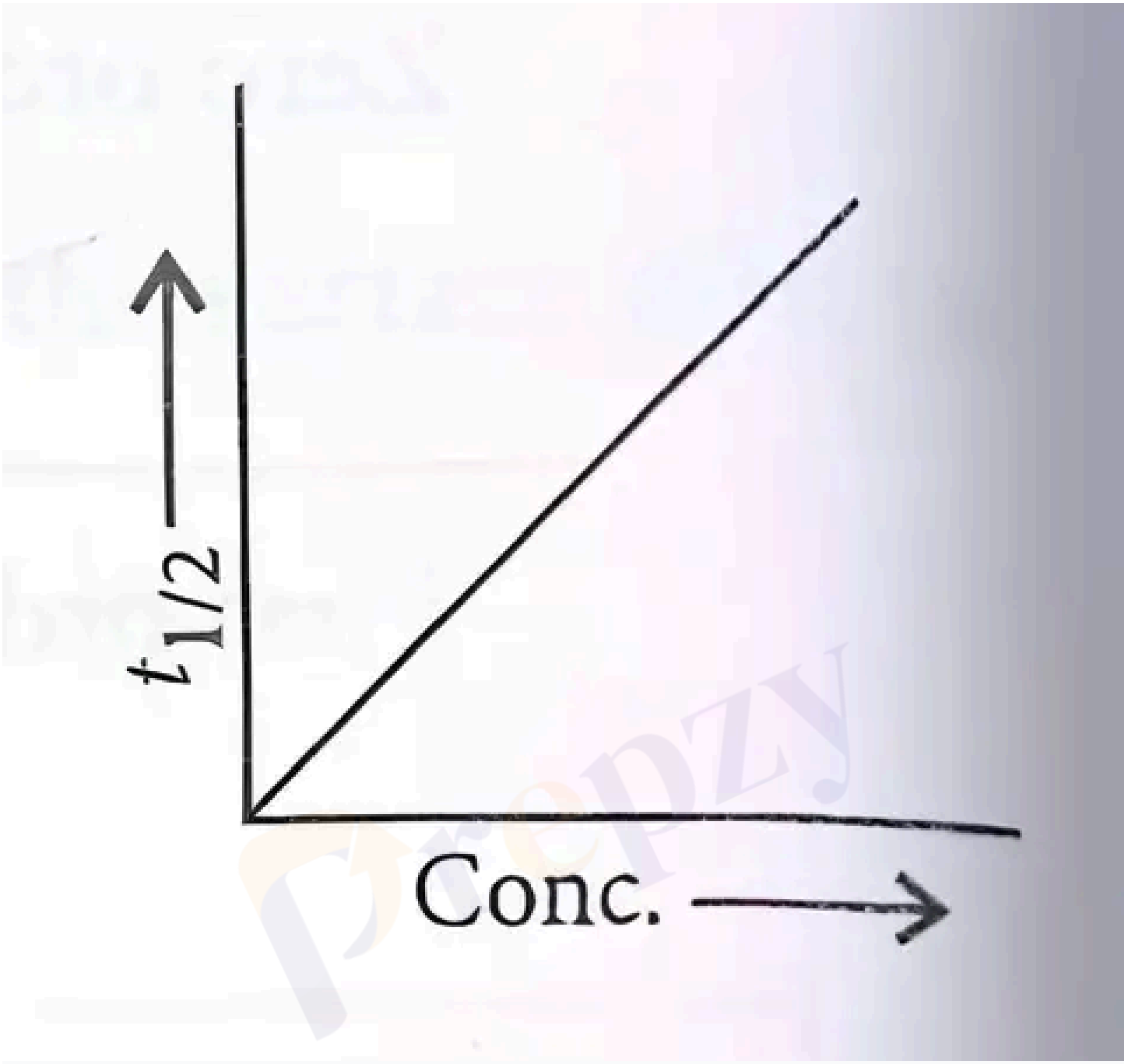
Integrated Rate Equations

Zero Order Reaction

- Rate is independent of reactant concentration.
- Rate remains constant: rate = k.
- Reaction: R → Products, rate = -d[R]/dt = $k[R]^0$ = k.
- Integrated rate equation: k = $\frac{1}{t}([R]_0 - [R]_t)$.
- Concentration-time relation: $[R]_t$ = -kt + $[R]_0$ (linear with slope -k).
- Half-life: $t_{1/2}$ = $\frac{[R]_0}{2k}$, directly proportional to initial concentration.


Rate
Conc.


$[R]_0$
$[R]_t$
Slope = – k
Time (t) ⟶



Solved Examples

- **Ex 1:** Calculate rate constant k if $[R]_0$ = 0.5 M, $[R]_t$ = 0.2 M after 10 s.
  Solution: k = (1/10)(0.5 - 0.2) = 0.03 M/s.

Practice Set

- Q1: For a zero order reaction, rate is:
  A. Proportional to [R]
  B. Independent of [R]

C. Proportional to $[R]^2$

D. Inversely proportional to [R]

- Q2: The half-life of a zero order reaction is:

  A. Constant

  B. Proportional to $[R]_0$

  C. Inversely proportional to $[R]_0$

  D. Independent of $[R]_0$

- Q3: If k = 0.04 M/s and $[R]_0$ = 0.8 M, time to reduce concentration to 0.4 M is:

  A. 10 s

  B. 20 s

  C. 5 s

  D. 15 s

Answer Key

- Q1: B - Rate is independent of concentration in zero order.
- Q2: B - Half-life is directly proportional to initial concentration.
- Q3: B - $t = ([R]_0 - [R]_t)/k = (0.8 - 0.4)/0.04 = 10$ s.

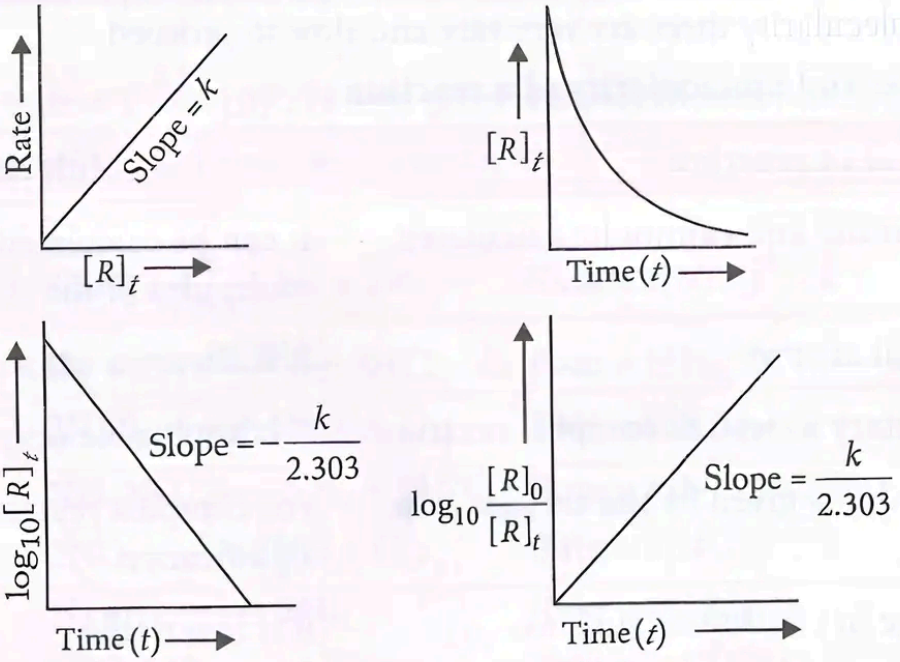
Memory Aids

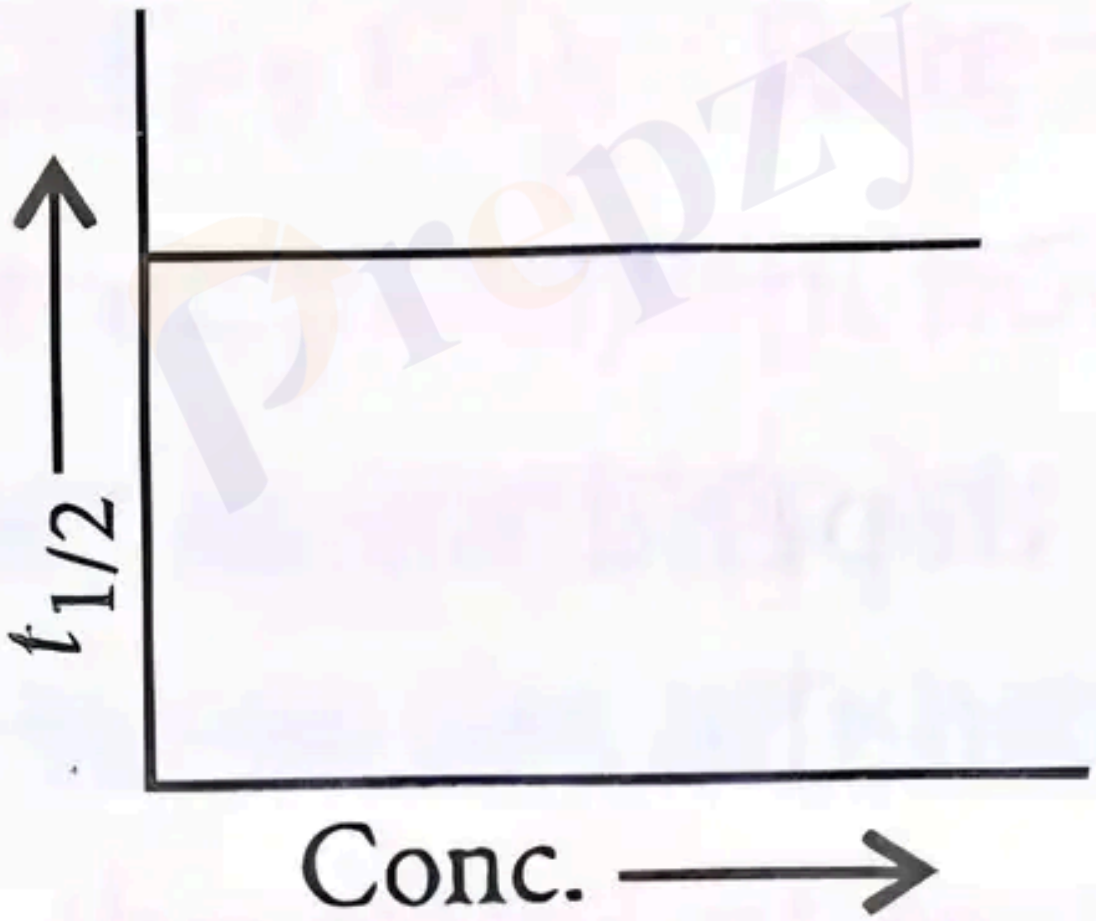
- Zero order: Rate constant, straight line [R] vs. t.
- Half-life ∝ initial concentration.
- Rate independent of [R].

First Order Reaction

- Rate depends on one reactant concentration: rate = k[R].
- Integrated rate equation: $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]_t}$.
- Half-life: $t_{1/2} = 0.693/k$, independent of concentration.
- Time for n^{th} fraction completion: $t_{1/n} = \frac{2.303}{k} \log \frac{n}{n-1}$.
- Time to reduce to n^{th} fraction: $t = \frac{2.303}{k} \log n$.

Graphical representation :





Solved Examples

- **Ex 1:** Calculate k if $[R]_0 = 0.5$ M, $[R]_t = 0.25$ M after 20 s.
  Solution: $k = (2.303/20) \log(0.5/0.25) = 0.115\ s^{-1}$.
- **Ex 2:** Find half-life if $k = 0.1\ s^{-1}$.
  Solution: $t_{1/2} = 0.693/0.1 = 6.93$ s.

Practice Set

- Q1: Half-life of first order reaction is:
  A. Proportional to $[R]_0$
  B. Independent of $[R]_0$
  C. Proportional to $1/[R]_0$
  D. Proportional to $[R]_0^2$
- Q2: For first order, integrated rate law is:
  A. $[R]_t = -kt + [R]_0$
  B. $k = (2.303/t) \log([R]_0/[R]_t)$
  C. $k = (1/t)([R]_0 - [R]_t)$
  D. $k = (1/t) \log([R]_0/[R]_t)$
- Q3: Time to reduce to half concentration for $k = 0.2\ s^{-1}$ is:
  A. 3.465 s
  B. 0.693 s
  C. 6.93 s
  D. 1.386 s

Answer Key

- Q1: B - Half-life is independent of initial concentration.
- Q2: B - Correct integrated rate law for first order.
- Q3: A - $t_{1/2} = 0.693/0.2 = 3.465$ s.

Memory Aids

- First order: Half-life constant, independent of concentration.

- Plot log[R] vs. time for straight line.
- Use $t_{1/2} = 0.693/k$ for calculations.

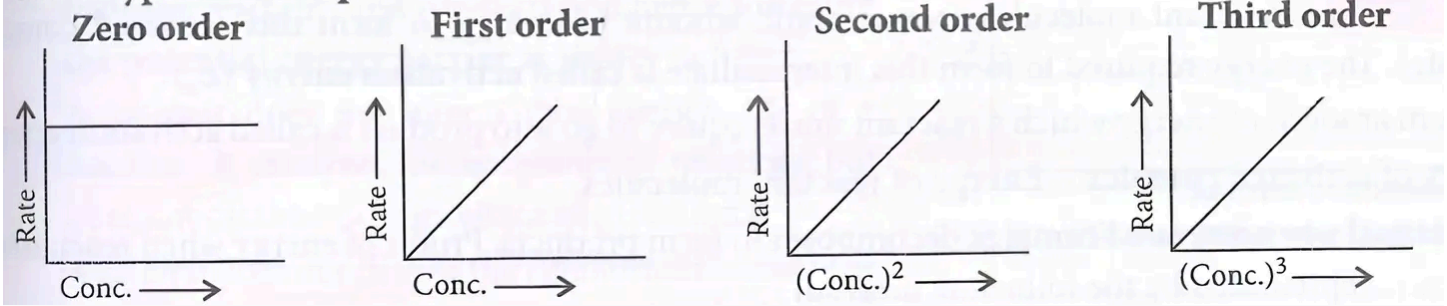
General Integrated Rate Equations and Graphs

- Zero order: Rate = k, $[R] = -kt + [R]_0$.
- First order: Rate = k[R], $\log[R] = -kt/2.303 + \log[R]_0$.
- Second order: Rate = $k[R]^2$, $1/[R] = kt + 1/[R]_0$.
- Third order: Rate = $k[R]^3$, $1/[R]^2 = 2kt + 1/[R]_0^2$.
- Half-life varies with order:
  - Zero order: $t_{1/2} \propto [R]_0$
  - First order: $t_{1/2}$ = constant
  - Second order: $t_{1/2} \propto 1/[R]_0$
  - Third order: $t_{1/2} \propto 1/[R]_0^2$

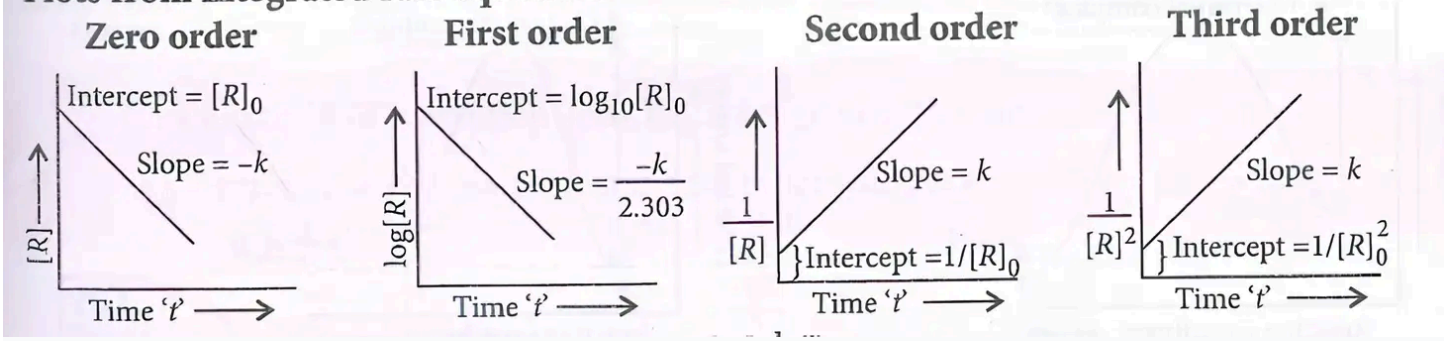
- **Integrated rate equations for reactions of different orders :**

Reaction	Order	Rate law	Rate constant
$R \longrightarrow$ Products	0	Rate $= k[R]^0$	$k = \frac{[R]_0 - [R]}{t}$
$R \longrightarrow$ Products	1	Rate $= k[R]$	$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$
$2R \longrightarrow$ Products	2	Rate $= k[R]^2$	$k = \frac{1}{t}\left(\frac{1}{[R]} - \frac{1}{[R]_0}\right)$
$A + B \longrightarrow$ Products	2	Rate $= k[A][B]$	$k = \frac{1}{t}\frac{2.303}{([A]_0 - [B]_0)} \log \frac{[B]_0[A]}{[A]_0[B]}$
$3R \longrightarrow$ Products	3	Rate $= k[R]^3$	$k = \frac{1}{2t}\left[\frac{1}{[R]^2} - \frac{1}{[R]_0^2}\right]$

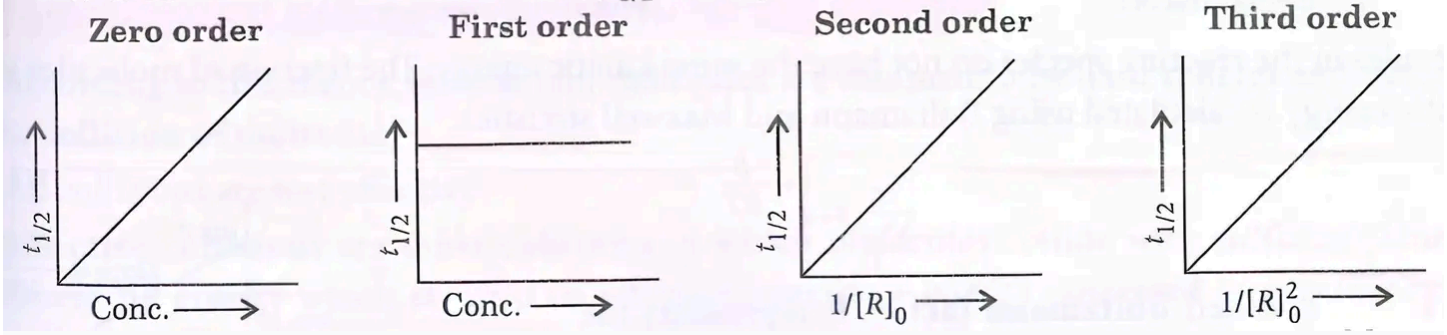
Some typical linear plots for reactions of different orders are given below :



Plots from integrated rate equations :



Plots of half-lives *vs* concentration ($t_{1/2} \propto [R]_0^{1-n}$) :



Time Relationships in First Order Reactions

- Time for different completion fractions related to half-life:
- 75% completion ≈ 2 $t_{1/2}$, 87.5% ≈ 3 $t_{1/2}$, 93.75% ≈ 4 $t_{1/2}$, etc.
- Amount left after n half-lives: $[R]_0/2^n$.
- Pseudo first order reactions behave like first order under certain conditions.

$$t_{3/4} \text{ or } t_{75\%} = 2t_{1/2},\ t_{87.5\%} = 3t_{1/2},\ t_{93.75\%} = 4t_{1/2},\ t_{96.87\%} = 5t_{1/2},\ t_{99.9} = 10t_{1/2}$$

Examples of Pseudo First Order Reactions

- Acid hydrolysis of ethyl acetate: Rate = k[ethyl acetate].
- Acid-catalyzed inversion of cane sugar: Rate = k[cane sugar].

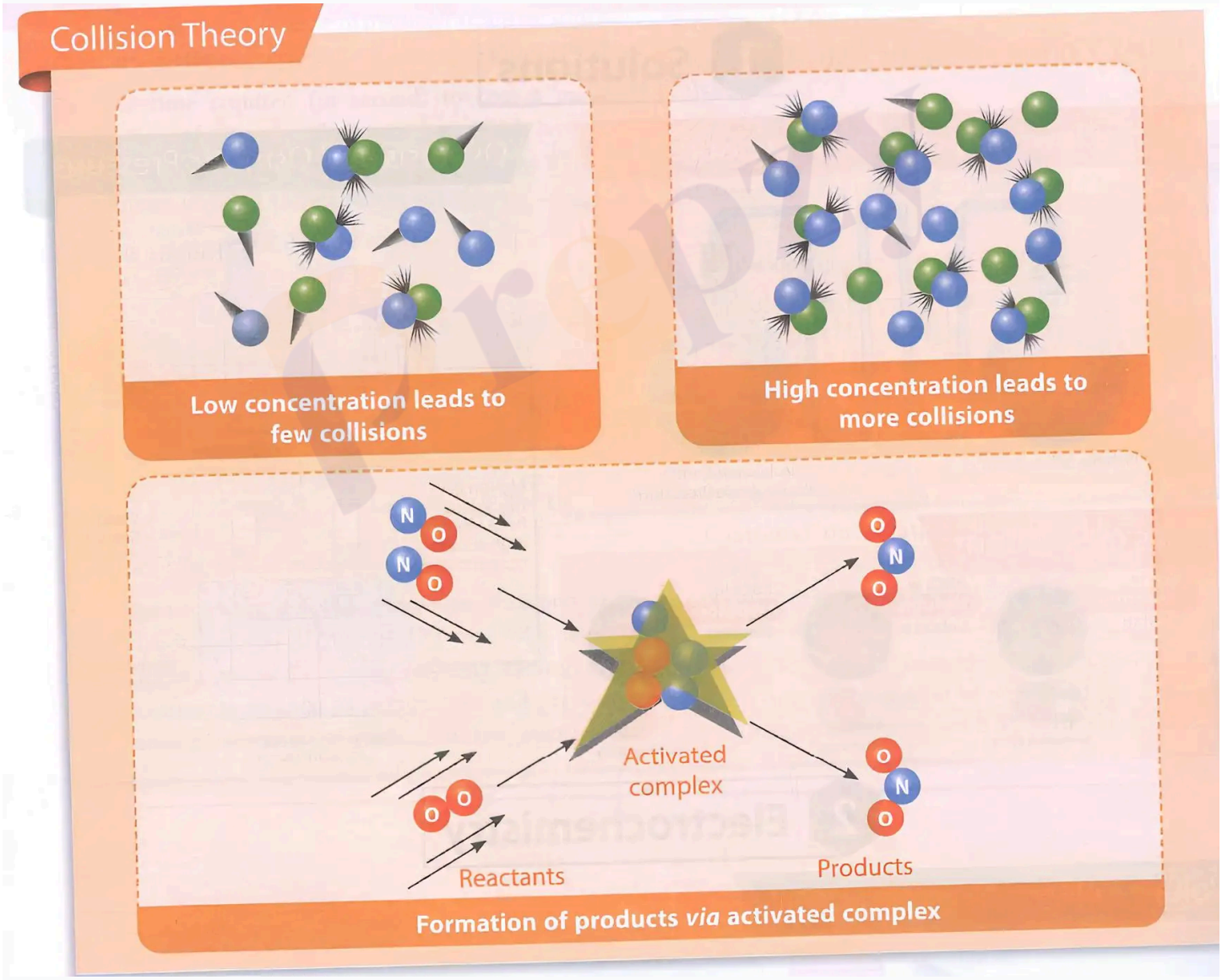
Examples :

- **Acid hydrolysis of ethyl acetate :** $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$
  Rate = $k[CH_3COOC_2H_5]$
- **Acid catalysed inversion of cane sugar :**
  $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$; Rate = $k[C_{12}H_{22}O_{11}]$
  Cane sugar — Glucose — Fructose

Collision Theory

Explanation

- Reaction occurs due to collision between reactant molecules (assumed as hard spheres).
- Not all collisions lead to reaction; only effective collisions do.
- Effective collisions require sufficient kinetic energy (threshold energy = activation energy + energy of reactants) and proper molecular orientation.
- Rate equation: Rate = $PZ_{AB}e^{\u2212E_a/RT}$, where P = steric factor, Z_{AB} = collision frequency.
- Activation energy and orientation determine reaction rate.
- Drawback: Ignores molecular structure, treats molecules as hard spheres.



Solved Examples

- **Ex 1:** Calculate rate if P = 0.5, $Z_{AB} = 10^{10}$ collisions/s, E_a = 50 kJ/mol, T = 300 K, R = 8.314 J/mol·K.

  Solution: Rate = $0.5 \times 10^{10} \times e^{\u2212(50000)/(8.314\times300)} = 0.5 \times 10^{10} \times e^{\u221220.04} \approx$ negligible (very slow reaction).

Practice Set

- Q1: What is required for an effective collision?
  - A. Any collision
  - B. Collision with sufficient energy and proper orientation
  - C. Collision with low energy
  - D. Collision without orientation
- Q2: Which factor does NOT affect collision frequency?
  - A. Concentration of reactants
  - B. Temperature
  - C. Molecular orientation
  - D. Volume of reaction mixture
- Q3: Rate equation in collision theory includes:
  - A. Activation energy and steric factor
  - B. Only activation energy
  - C. Only collision frequency
  - D. None of these

Answer Key

- Q1: B - Effective collisions need sufficient energy and proper orientation.
- Q2: C - Molecular orientation affects effectiveness, not frequency.
- Q3: A - Rate = $PZ_{AB}e^{\u2212E_a/RT}$ includes activation energy and steric factor.

Memory Aids

- "Collision + Energy + Orientation = Reaction"

- Only collisions with energy ≥ activation energy and correct orientation produce products.
- Hard sphere model ignores molecular shape.

Reaction Order and Rate Constants

Explanation

- Zero order: $k = ([A]_0 - [A]) / t$; half-life $t_{1/2} = [A]_0 / 2k$.
- First order: $k = (2.303 / t) \log ([A]_0 / [A]) = (2.303 / t) \log (a / (a - x))$.
- In terms of pressure: $k = (2.303 / t) \log (P_i / (2P_i - P_t))$.
- Half-life for first order: $t_{1/2} = 0.693 / k$.
- Other times: $t_{60\%} = 0.9166 / k$, $t_{75\%} = 1.386 / k$, $t_{90\%} = 2.303 / k$, $t_{99.9\%} = 6.93 / k$.
- Time to reduce to n^{th} fraction: $t = (2.303 / k) \log (a / (a / n)) = (2.303 / k) \log n$.
- Concentration after n half-lives: $[A] = [A]_0 / 2^n$.
- Order determination by half-life method: $n = 1 + (\log t_{1/2^1} - \log t_{1/2^2}) / (\log a_2 - \log a_1)$.

Solved Examples

- **Ex 1:** For a zero order reaction with $[A]_0 = 0.1$ M, $k = 0.02$ M/s, find $t_{1/2}$.
  Solution: $t_{1/2} = [A]_0 / 2k = 0.1 / (2 \times 0.02) = 2.5$ s.
- **Ex 2:** For a first order reaction, if $k = 0.1\ s^{-1}$, find $t_{1/2}$.
  Solution: $t_{1/2} = 0.693 / k = 0.693 / 0.1 = 6.93$ s.

Practice Set

- Q1: For a zero order reaction, half-life is:
  - A. Independent of initial concentration
  - B. Directly proportional to initial concentration
  - C. Inversely proportional to initial concentration
  - D. Equal to 0.693/k
- Q2: For a first order reaction, rate constant k is given by:
  - A. $k = (2.303 / t) \log (a / (a - x))$
  - B. $k = (a - x) / t$
  - C. $k = (a + x) / t$

    - D. $k = (2.303 / t) \log (a + x)$
- Q3: The half-life of a first order reaction is 10 min. What is the rate constant?
    - A. 0.0693 min^{-1}
    - B. 0.693 min^{-1}
    - C. 6.93 min^{-1}
    - D. 0.00693 min^{-1}

Answer Key

- Q1: B - Half-life for zero order is proportional to initial concentration.
- Q2: A - $k = (2.303 / t) \log (a / (a - x))$ for first order.
- Q3: A - $k = 0.693 / t_{1/2} = 0.693 / 10 = 0.0693\ min^{-1}$.

Memory Aids

- Zero order: $t_{1/2}$ □ $[A]_0$, First order: $t_{1/2}$ constant.
- First order k from log formula: $k = (2.303 / t) \log (a / (a - x))$.
- Half-life formula: $t_{1/2} = 0.693 / k$ for first order.