

CHEMICAL KINETICS

Study of the rate of chemical reactions and the factors affecting the rate.

RATE OF REACTION

Change in concentration of reactants or products per unit time.



1. RATE OF A REACTION

A. AVERAGE RATE

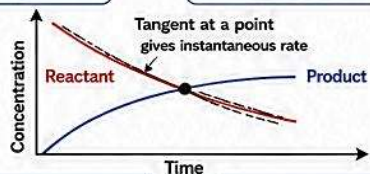
$$\text{Average rate} = -\frac{\Delta[A]}{\Delta t} \text{ (or) } \frac{\Delta[P]}{\Delta t}$$

(Over a time interval Δt)

B. INSTANTANEOUS RATE

$$\text{Instantaneous rate} = -\frac{d[A]}{dt} \text{ (or) } \frac{d[P]}{dt}$$

(At a particular moment)



RATE EXPRESSION (General)

For $aA + bB \rightarrow \text{Products}$

$$\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{d[P]}{dt}$$

2. FACTORS AFFECTING RATE OF REACTION

- Nature of reactants
- Concentration of reactants
- Temperature
- Presence of catalyst
- Surface area (in case of solids)
- Pressure (in case of gases)
- Light (in photochemical reactions)
- Solvent
- Presence of inhibitors / promoters

3. RATE LAW AND ORDER OF REACTION

Rate law gives the relationship between rate and concentration of reactants.

$$\text{Rate} = k[A]^m [B]^n$$

k = Rate constant
(Independent of concentration but depends on temperature & nature of reactants)

m, n = Order w.r.t. A and B

Overall order = $(m+n)$
(Sum of powers)

Order can be 0, fractional or integral but not negative.

4. DETERMINATION OF ORDER

- From Rate Law (if mechanism known)
- Initial Rate Method
- Half-Life Method
- Integrated Rate Equation Method
- Differential Method (Graphical)

5. IMPORTANT POINTS

- Rate is independent of stoichiometric coefficients.
- Order is determined experimentally.
- Overall order is the sum of powers.
- Unit of k depends on the order of reaction.

6. INTEGRATED RATE EQUATIONS

(i) ZERO ORDER REACTION ($aA \rightarrow \text{Products}$)

$$\text{Rate} = k[A]^0 = k$$

Integrated form:

$$[A]_t = [A]_0 - kt$$

Half-life:

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

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

Plot: $[A]$ vs $t \rightarrow$ Straight line
slope = $-k$

(ii) FIRST ORDER REACTION ($aA \rightarrow \text{Products}$)

$$\text{Rate} = k[A]$$

Integrated form:

$$\ln[A]_t = \ln[A]_0 - kt$$

$$[A]_t = [A]_0 e^{-kt}$$

Half-life:

$$t_{1/2} = \frac{0.693}{k} \text{ (Independent of } [A]_0)$$

Unit of k : s^{-1}

Plot: $\ln[A]$ vs $t \rightarrow$ Straight line
slope = $-k$

(iii) SECOND ORDER REACTION ($aA \rightarrow \text{Products}$)

$$\text{Rate} = k[A]^2$$

Integrated form:

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

Half-life:

$$t_{1/2} = \frac{1}{k[A]_0} \text{ (Depends on } [A]_0)$$

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

Plot: $\frac{1}{[A]}$ vs $t \rightarrow$ Straight line
slope = k

(iv) n^{th} ORDER REACTION ($n \neq 0, 1$)

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

Integrated form:

$$[A]_t^{1-n} = [A]_0^{1-n} + (n-1)kt$$

Half-life:

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$$

Unit of k : $\text{L}^{n-1} \text{mol}^{1-n} \text{s}^{-1}$

Plot: $[A]^{1-n}$ vs $t \rightarrow$ Straight line
slope = $(n-1)k$

7. INITIAL RATE METHOD

For $aA + bB \rightarrow \text{Products}$

Keep one reactant in large excess and vary the concentration of other.

$$\text{Rate} = k[A]^m [B]^n$$

By comparing initial rates:

Exp.	$[A]$ (mol L^{-1})	$[B]$ (mol L^{-1})	Initial Rate ($\text{mol L}^{-1} \text{s}^{-1}$)
1	a_1	b_1	r_1
2	a_2	b_1	r_2
3	a_1	b_2	r_3
4	a_2	b_2	r_4

$$m = \frac{\log(r_2/r_1)}{\log(a_2/a_1)} \text{ (Keeping } [B] \text{ constant)}$$

$$n = \frac{\log(r_3/r_1)}{\log(b_2/b_1)} \text{ (Keeping } [A] \text{ constant)}$$

8. HALF-LIFE METHOD

$t_{1/2}$ = Time taken for the concentration of a reactant to become half of its initial concentration.

Order	Half-life ($t_{1/2}$)
Zero	$\frac{[A]_0}{2k}$
First	$\frac{0.693}{k}$
Second	$\frac{1}{k[A]_0}$
n^{th} ($n \neq 1$)	$\frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$

Use: To determine order and rate constant.

9. TEMPERATURE DEPENDENCE (ARRHENIUS EQUATION)

$$k = Ae^{-\frac{E_a}{RT}}$$

k = Rate constant

A = Frequency factor (pre-exponential factor)

E_a = Activation energy

R = Gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$)

T = Absolute temperature (K)

Two point form:

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

Higher $E_a \rightarrow$ Greater temperature sensitivity.

10. CATALYSIS

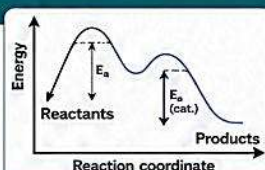
- Catalyst increases rate by providing an alternate pathway with lower activation energy.
- Does not change ΔG , equilibrium constant or the stoichiometry.
- Types:
 - Homogeneous catalysis (Reactant & catalyst in same phase)
 - Heterogeneous catalysis (Different phases)
 - Enzyme catalysis (Biocatalysis)
- Poisoning – Decrease in catalytic activity due to foreign substances.

11. MECHANISM OF A REACTION

A complex reaction occurs by a series of elementary steps.

Reactants $\xrightarrow{\text{Step 1}}$ Intermediate $\xrightarrow{\text{Step 2}}$ Intermediate $\xrightarrow{\text{Step 3}}$ Products

- The slowest step is called the rate determining step.
- Overall order is determined by the rate determining step.
- Sum of steps = Overall reaction.



12. COLLISION THEORY

- Reaction occurs by collision of reactant molecules.
- For effective collision:
 - Colliding molecules must have energy $\geq E_a$.
 - Proper orientation must exist.
- Rate $\propto$ Number of effective collisions.



KEY TAKEAWAY

The rate of a reaction depends on the concentration, nature of reactants, temperature, catalyst and other factors. Understanding rate laws, order, and mechanisms helps in controlling and predicting chemical reactions.

QUESTION BANK

Section – A (1 Mark)

Q.1: For the reaction $2P + Q \rightarrow P_2Q$, the order with respect to P and Q is 2 and 0 respectively. What will be the effect on the reaction rate if the concentration of reactant P is doubled and the concentration of reactant Q is decreased by half?"

- (a) increase 2 times (b) increase 4 times
(c) decrease 2 times (d) remain the same

Q.2: The value of rate constant for a reaction is $3.96 \times 10^{-30} \text{ Mol}^{-1}\text{Ls}^{-1}$. What is the order of the reaction?

- (a) 1 (b) 3 (c) 2 (d) Zero

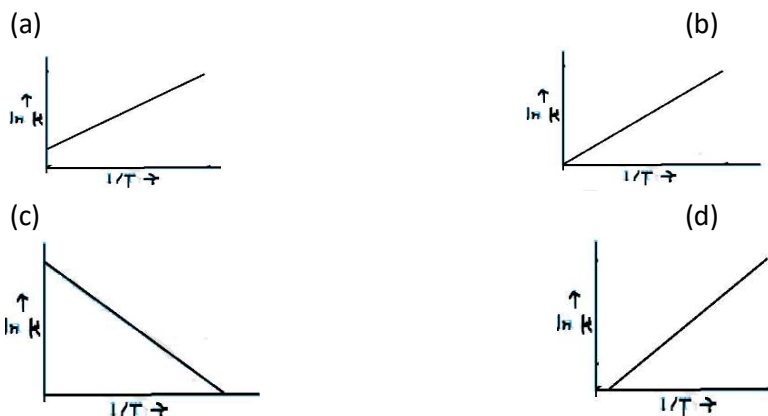
Q.3 The role of a catalyst is to change :

- (a) equilibrium constant (b) $\Delta_r G$ (c) $\Delta_r H$ (d) E_a

Q.4 "If the rate of the reaction $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$ is $r = k[\text{H}_2\text{O}_2]$, what is the reaction order?"

- (a) second order (b) first order (c) third order (d) zero order

Q.5 According to Arrhenius equation rate constant k is equal to $A e^{-E_a/RT}$. Which of the following options represents the graph of $\ln k$ vs $1/T$?



Q.6 In the graph plotted between $\ln [R]$ and t for a first order reaction, the intercept on y-axis is

- (a) $-k$ (b) $[R]$ (c) $\ln [R]_0$ (d) $k/2.303$

Q.7 A reaction follows first-order kinetics and has a half-life of 69.3 seconds. What is the rate constant (k) for this reaction?

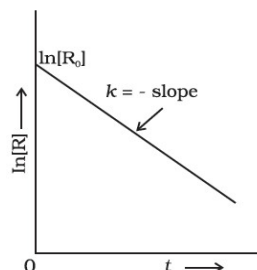
- (a) 1.0 s^{-1} (b) 0.01 s^{-1} (c) 0.1 s^{-1} (d) 0.001 s^{-1}

Q.8 If the rate of reaction is proportional to the concentration of A and the square of the concentration of B, what is the total order of the reaction?

- (a) 0 (b) 1 (c) 2 (d) 3

Q.9 To what order of a reaction does the following graph belong to?

- (a) Zero order reaction
(b) First order reaction
(c) Second order reaction
(d) Third order reaction



Q.10. In pseudo unimolecular reactions:

- (a) Both reactants are present in low concentrations,

- (b) Both reactants are present in the same concentrations,
- (c) One reactant is present in excess,
- (d) One reactant is non-reactive.

ASSERTION AND REASON TYPE QUESTIONS:

For the Questions given below, select the most appropriate answer from the options given below:

- A. Both A and R are true and R is the correct explanation of A
- B. Both A and R are true but R is not the correct explanation of A.
- C. A is true but R is false.
- D. A is false but R is true

Q.11 Assertion(A): Hydrolysis of methyl ethanoate is a pseudo-first-order reaction.

Reason(R): Water is present in large excess, and therefore its concentration remained constant throughout the reaction.

Q.12 Assertion (A): The presence of a catalyst increases the activation energy of a reaction.

Reason (R): Catalysts provide an alternative reaction pathway with a lower activation energy.

Q.13. Assertion(A): Increase in concentration of reactant will not change the rate for a zero-order reaction.

Reason(R): Rate constant for a zero-order reaction is a constant for a particular initial concentration.

Q.14. Assertion(A): Every collision between reacting molecules results in the formation of products.

Reason(R): Product formation occurs only when colliding molecules have the proper orientation and enough energy.

Q.15 Assertion(A): A bimolecular reaction becomes first order reaction when one of the reactants is in excess.

Reason(R): Rate is not significantly affected by change in concentration of the reactant present in small amount.

Answer Keys :

Q.1	Q.2.	Q.3	Q.4	Q.5	Q.6	Q.7	Q.8	Q.9	Q.10	Q.11	Q.12	Q.13	Q.14	Q.15
(b)	(c)	(d)	(b)	(c)	(c)	(b)	(d)	(b)	(c)	(a)	(d)	(a)	(d)	(c)

Section – B (Short answer Questions) 2 marks each

Q.1 A chemical reaction reduces the amount of a substance following first-order kinetics, with $k=60s^{-1}$. How long will it take for the substance to shrink to 1/16 of what it was?

(Hint: Put the values in formula $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$, Answer: 0.0460 Seconds)

Q.2. How order is different from Molecularity.

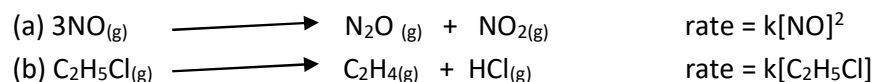
Q.3 Can the activation energy of a reaction be zero Justify your answer.

(Hint: Yes)

Q.4 The conversion of X to Y is a second- order reaction. Compare the rate of reaction when the concentration of X is increased from its initial value to three times that amount.

(Hint: rate will increase by nine times)

Q.5 From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants:



(Hint: (a) II order reaction and unit - $\text{Mol}^{-1} \text{L s}^{-1}$; (b) I order reaction and unit- s^{-1})

Section – C (3 marks)

Q.1 A chemical reaction has rate constants of 0.02 s^{-1} at 500 K and 0.07 s^{-1} at 700 K. Using this data, determine the activation energy and the frequency factor (A) using the Arrhenius equation.

[Hint: Put the $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$ value of E_a by this formula
And A by this formula $\log k = \log A - \frac{E_a}{2.303RT}$]

Q.2. In a graph $\ln[\text{reactant}]$ was plotted vs. time, it gave a straight line, predict the order of the reaction also give the expression of its half life and rate constant.

[Hint: 1st order, $t_{1/2} = 0.693/k$, rate constant $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$]

Q3 . For the reaction $A + B \rightarrow C$, you find that the rate $= k[A]^2$. What does this imply about the mechanism of the reaction?

[Hint: 2nd order w.r.t. A, B do not participate in rate determining step (large excess)]

Q4. Account for the following:

- Reactions with higher molecularity are rare.
- A zero-order reaction show a linear concentration vs. time graph
- Adsorption of gases becomes faster on powdered charcoal

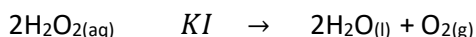
[Hint: (a)- Chances of effective collision decreases, (b)- Rate is independent of initial concentration, (c)- Large surface area]

Q5 .If half life period of A in a first order reaction reaction is 2 minutes , How long will it take [A] to reach 25% of its initial concentration.

[Hint: Use formula of $t_{1/2} = 0.693/K$ for 1st order, Ans- $t_{75} = 4 \text{ min.}$]

Section – D (CBQ) 04 marks

A group of Class 12 students performed an experiment to study the rate of decomposition of hydrogen peroxide (H_2O_2) in the presence of a potassium iodide (KI) catalyst. They observed that the reaction was faster at higher temperatures. The balanced reaction is:



They measured the time taken to collect a certain volume of oxygen at different temperatures and found that the reaction rate increased with temperature. Their teacher explained that the reaction follows first-order kinetics and the rate constant k can be calculated using the integrated rate equation:

The class was also introduced to the Arrhenius equation: $k = Ae^{-E_a/RT}$ which shows how the rate constant changes with temperature and activation energy.

- What role does potassium iodide (KI) play in the reaction?
- Predict the order and unit of rate constant for the above reaction
- How does temperature affect the rate of a chemical reaction? If the rate constant at two temperatures is known, how can you calculate the activation energy?

Hint: (a) Catalyst

(b) Definition ,first order

(c) As the temperature increases rate of reaction increases.

[Hint $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$]

LONG ANSWER TYPE QUESTIONS [5 MARKS]

Q 1(a). Radioactive decay follows first order kinetics. The rate constant for the decomposition of a hydrocarbon is $2.418 \times 10^{-5} \text{ s}^{-1}$ at 546 K. If the energy of activation is $179.9 \text{ kJ mol}^{-1}$, what will be the value of pre-exponential factor.

[Hint:

According to Arrhenius equation,

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

so value of pre-exponential $A = \text{Antilog } 12.5916 = 3.9 \times 10^{12} \text{ s}^{-1}$.

(b). The initial rate of a reaction $A+B \rightarrow C$ is studied at various initial concentrations.

The data obtained is:

[A] (mol/L)	[B] (mol/L)	Initial Rate (mol L ⁻¹ s ⁻¹)
0.1	0.1	0.02
0.2	0.1	0.04
0.2	0.2	0.08

Determine the order of the reaction with respect to A and B. Write the rate law and the value of rate constant (k).

Hint: (b). order: w.r.t. A = 1, w.r.t. B = 1; rate law $R = k[A][B]$; $K = 2 \text{ lit/mol s}$

Q 2. (a). Describe the concept of pseudo first order reaction and support your explanation with an example.

(b). For a zero order reaction, the rate constant k is 0.005 mol/L sec . If the initial concentration of the reactant is 0.2 mol/L then calculate:

(i) The time required for the reactant to be reduced to 0.05 mol/L .

(ii). The half-life of the reaction.

[Hint: (a) Refer summary]

(b) (i) $t = \{ [A]_0 - [A] \} / k$; $t = 30 \text{ sec}$

(ii) $t_{1/2} = [A] / 2k = 20 \text{ sec}$

Q.3a) A reaction is first order in A and second order in B.

(i) Write the differential rate equation.

(ii) How is the rate affected when the concentrations of both A and B are doubled?

b) The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

Hint- a. i) $\text{Rate} = k[A][B]^2$ (ii) Use formula, $\text{Rate} = k[A][B]^2$

b) use first order integrated rate equation to solve the problem.