Chemical kinetics

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Chemical Kinetics

Overall Weightage

- JEE Main: 6-10 marks (out of 100)
- JEE Advanced: 8-12 marks (out of 120)

Most Frequently Tested Concepts

- Rate Laws and Order of Reaction (35%)
- Temperature Dependence (25%)
- Reaction Mechanisms (22%)
- Catalysis (18%)

1. Basic Concepts

Rate of Reaction

- Rate of reaction is the change in concentration of reactants/products per unit time
- For a reaction A → B:
  - Rate = $-\Delta[A]/\Delta t = \Delta[B]/\Delta t$ (average rate)
  - Rate = $-d[A]/dt = d[B]/dt$ (instantaneous rate)
- Unit: mol L^{-1} s^{-1} ✓

Factors Affecting Rate of Reaction

1. Physical State
   - Rate: Gaseous > Liquid > Solid
   - Finely divided solids react faster due to increased surface area
2. Concentration ✓
   - Rate is directly proportional to concentration of reactants
   - Higher concentration means more frequent molecular collisions
3. Temperature
   - Rate increases significantly with temperature
   - Rule of thumb: Rate approximately doubles for every 10°C rise
4. Catalyst
   - Increases rate by providing alternate pathway with lower activation

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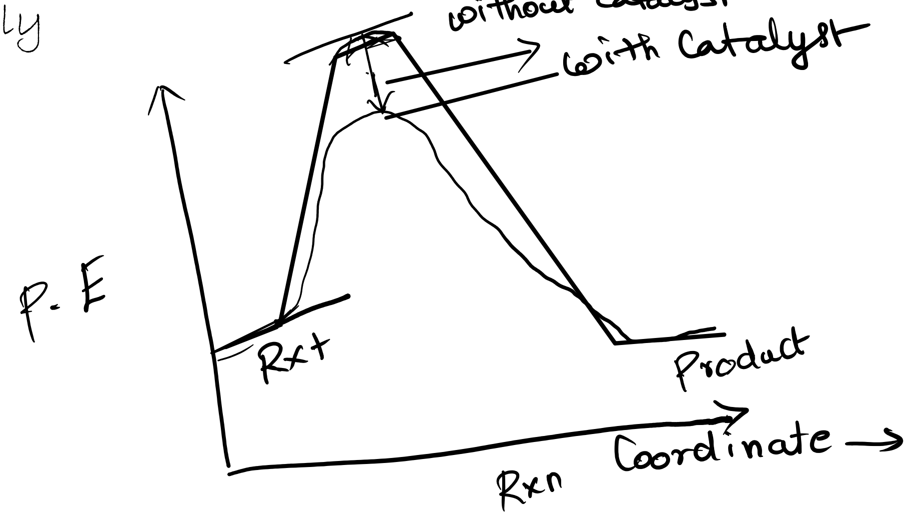
  - Increases rate by providing alternate pathway with lower activation energy
  - Does not affect equilibrium constant

5. Radiation
  - Certain frequencies of radiation can increase reaction rate considerably



2. Rate Law and Order of Reaction

Rate Law

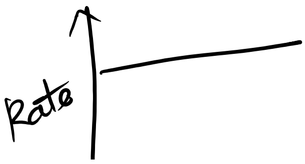
- Mathematical expression relating rate with concentration of reactants
- For reaction: $aA + bB \rightarrow$ Products
  - Rate $= k[A]^x[B]^y$
  - k = rate constant
  - x, y = order with respect to each reactant
  - Total order $= x + y$

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

Order of Reaction

1. Zero Order ($n=0$)
  - Rate $= k[A]^0 = k$
  - Rate independent of concentration
  - Half-life ∝ initial concentration

$$t_{1/2} = [A]_0 / 2K$$

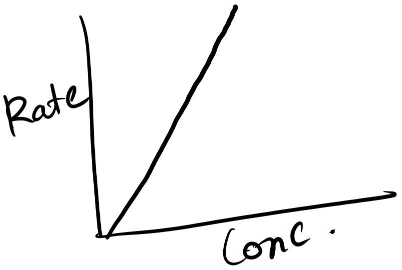


$t_{1/2} = [A]_0 / 2k$

First Order ($n=1$)

- Rate = $k[A]$
- Half-life = $0.693/k$ (independent of initial concentration)
- Examples: Radioactive decay, decomposition of N_2O_5

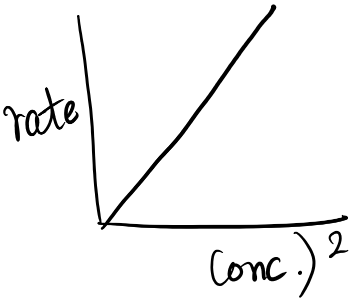
Unit s^{-1}



Second Order ($n=2$)

- Rate = $k[A]^2$ or $k[A][B]$
- Half-life = $1/k[A]_0$

Unit L/mol/s



Unit $(\text{mol L}^{-1})^{1-n} s^{-1} \Rightarrow (\text{mol L}^{-1})^{1-4} s^{-1} \Rightarrow (\text{mol/L})^{-3} s^{-1}$

Important Points

- Molecularity ≤ 3 (usually)
- Order can be zero, fractional, or integer
- Order can change with conditions, but molecularity remains constant

- For reversible reactions at equilibrium: (dx/dt)forward = (dx/dt) backward ✓

3. Integrated Rate Laws

Zero Order

- $[A]t = [A]_0 - kt$ ✓
- Linear plot of [A] vs t with slope = -k ✓

First Order

- $\ln[A]t = -kt + \ln[A]_0$
- Linear plot of ln[A] vs t with slope = -k

Second Order

- $1/[A]t = kt + 1/[A]_0$ ✓
- Linear plot of 1/[A] vs t with slope = k ✓

4. Temperature Dependence

Arrhenius Equation

- $k = Ae^{-Ea/RT}$ ⊗
- $\log k = \log A - Ea/2.303RT$ ⊗
- For rates at two temperatures: $\log(k_2/k_1) = (Ea/2.303R)[T_2 - T_1/T_1T_2]$

⊗

A - Exp. factor

T - Temp.

Ea - Ac. Energy

R - gas Const

$$\frac{Ea}{2.303\,R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

Collision Theory

Basic Principles

- Based on the assumption that for a reaction to occur, molecules must collide
- Not all collisions result in successful reactions

Two types of collisions:

- Effective collisions (lead to product formation)
- Ineffective collisions (no product formation)

Factors Determining Effective Collisions

<u>Energy Factor</u>

Colliding molecules must possess minimum threshold energy
Threshold energy = minimum energy required for effective collision
Only molecules with energy ≥ threshold energy can form products
Fraction of molecules with required energy = $e^{-Ea/RT}$

Orientation Factor (P)

Molecules must collide with proper spatial orientation
P = probability of correct orientation
Value between 0 and 1
Depends on complexity of molecules
For simple molecules, $P \approx 1$
For complex molecules, $P << 1$

Collision Frequency (Z)

Number of collisions per second per unit volume
Depends on:

- Concentration of reactants ✓
- Temperature (↑T = ↑molecular speed = ↑Z) ✓
- Size of molecules ✓
- Physical state of reactants ✓

Mathematical Expression

Rate constant $k = PZe^{-Ea/RT} \rightarrow$ Collision frequency.

P = orientation factor/steric factor
Z = collision frequency
$e^{-Ea/RT}$ = fraction of molecules with energy ≥ Ea

Q

Time to Practice:

Higher order (> 3) reactions are rare due to shifting of equilibrium towards reactants due to

elastic collisions
(a) loss of active species on collision
(b) molecules are involved
(c) low probability of simultaneous collision of all the reacting species
(d) increase in entropy and activation energy as more
(JEE Main)

For the non-stoichiometric reaction:
2A + B -> C + D, the following kinetic data were obtained in three separate experiments, all at 298 K.
The rate law for the formation of C is

Initial concentration [A]	Initial Concentration [B]	Initial rate of formation of C
0.1M	0.1 M	1.2X10-3
0.1M	0.2M	1.2X10-3 X
0.2M	0.1M	2.4X10-3

depend only A not B.

a) $\frac{dc}{dt} = K[A]$

b) $\frac{dc}{dt} = K[A][B]$

c) $\frac{dc}{dt} = k[A][B]$

d) $\frac{dc}{dt} = K[A]^2[B]$

Consider a reaction aG + bH -------> products. When concentration of both the reactants G and H is doubled, the rate increases eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is

(a) 0 (c) 2

(b) 1 [✓ (d) 3]

(IIT JEE)

doubling G ⇒ double the rate

Doubling G and H ⇒ ⑧

$2 \times 2^2 = 8$

$1+2=3.$

Decomposition of H_2O_2 follows a first order reaction. In fifty minutes the concentration of H_2O_2 decreases from 0.5 M to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be

(a) 6.93 X 10-2 mol min-1

(b) 6.93 x 10-4 mol L"1 min-1

(c) 2.66 L min-1 at STP

(d) 1.34 x 10 - mol min-1

(JEE Main)

$$K = \frac{\ln \frac{[\text{Initial}]}{[\text{Final}]}}{t}$$

$$= \ln 0.5 /$$

Cyclopropane rearranges to form propene (CH3-CH=CH2). This follows first order kinetics. The rate constant is 2.714 x 10^3 sec. The initial concentration of cyclopropane is 0.29 M. What will be the concentration of cyclopropane after 100 sec?

(a) 0.035 M	(c) 0.145 M
(b) 0.22 M	(d) 0.0018 M