

Zero Order Reactions

- [JEE Main 2018]** A zero-order reaction takes 20 minutes for 25% completion. Calculate the time required for 75% completion. *Solution:*
 - For zero order: $[A]_t = [A]_0 - kt$
 - 25% completion means $[A]_t = 0.75[A]_0$
 - If $t_1 = 20$ min, then: $0.75[A]_0 = [A]_0 - kt_1$
 - $k = 0.0125[A]_0/\text{min}$
 - For 75% completion: $0.25[A]_0 = [A]_0 - kt_2$
 - $t_2 = 60$ minutes
- [JEE Main 2015]** The half-life of a zero-order reaction is 50 min at $[A]_0 = 0.1$ M. Calculate the rate constant. *Solution:*
 - For zero order: $t_{1/2} = [A]_0/2k$
 - $50 = 0.1/(2k)$
 - $k = 0.001$ M/min

First Order Reactions

- [JEE Main 2019]** The rate constant for a first-order reaction is $1.54 \times 10^{-3} \text{ s}^{-1}$. Calculate its half-life. *Solution:*
 - $t_{1/2} = 0.693/k$
 - $t_{1/2} = 0.693/(1.54 \times 10^{-3})$
 - $t_{1/2} = 450$ s
- [JEE Main 2016]** A first-order reaction takes 40 min for 30% decomposition. Calculate the time for 60% decomposition. *Solution:*
 - Using: $\ln([A]_0/[A]_t) = kt$
 - For 30%: $\ln(100/70) = k \times 40$
 - $k = 0.0089 \text{ min}^{-1}$
 - For 60%: $\ln(100/40) = 0.0089 \times t$
 - $t = 102.5$ min

Temperature Dependence

- [JEE Main 2017]** The activation energy of a reaction is 75.2 kJ/mol. If the temperature increases from 27°C to 37°C, calculate the ratio of rate constants (k_2/k_1). *Solution:*
 - Using: $\ln(k_2/k_1) = -(E_a/R)(1/T_2 - 1/T_1)$
 - $T_1 = 300\text{K}$, $T_2 = 310\text{K}$
 - $k_2/k_1 = 2.03$
- [JEE Main 2020]** Rate constant doubles when temperature changes from 300K to 310K. Calculate activation energy. *Solution:*
 - $\ln(2) = (E_a/R)(1/300 - 1/310)$
 - $E_a = 52.8$ kJ/mol

Complex Reactions

7. **[JEE Main 2014]** For parallel reactions $A \rightarrow B$ ($k_1 = 0.3 \text{ s}^{-1}$) and $A \rightarrow C$ ($k_2 = 0.1 \text{ s}^{-1}$), calculate the ratio of products $[B]/[C]$ after completion. *Solution:*
- Rate of B formation = $k_1[A]$
 - Rate of C formation = $k_2[A]$
 - $[B]/[C] = k_1/k_2 = 3$
8. **[JEE Main 2013]** In consecutive reactions $A \rightarrow B \rightarrow C$, if $k_1 = 0.2 \text{ s}^{-1}$ and $k_2 = 0.1 \text{ s}^{-1}$, calculate maximum concentration of B relative to initial $[A]$. *Solution:*
- $[B]_{\text{max}}/[A]_0 = (k_1/(k_2-k_1))(e^{-k_1t} - e^{-k_2t})$
 - Maximum occurs at $t = \ln(k_2/k_1)/(k_2-k_1)$
 - $[B]_{\text{max}}/[A]_0 = 0.37$

Rate Laws and Order

9. **[JEE Main 2021]** Initial rates for reaction $2A + B \rightarrow C$ at different concentrations: $[A]_0$ (M) | $[B]_0$ (M) | Initial Rate (M/s) 0.1 | 0.1 | 0.001 0.2 | 0.1 | 0.004 0.1 | 0.2 | 0.002 Find the order with respect to A and B. *Solution:*
- Comparing rows 1&2: Rate $\propto [A]^2$
 - Comparing rows 1&3: Rate $\propto [B]$
 - Order w.r.t A = 2, B = 1
 - Total order = 3
10. **[JEE Main 2012]** For reaction $A + B \rightarrow C$, when $[A]$ doubles keeping $[B]$ constant, rate quadruples. When $[B]$ doubles keeping $[A]$ constant, rate doubles. Find the rate law. *Solution:*
- Rate $\propto [A]^2$ from first data
 - Rate $\propto [B]$ from second data
 - Rate = $k[A]^2[B]$

Half-Life Problems

11. **[JEE Main 2016]** A second-order reaction has $t_{1/2} = 100\text{s}$ when $[A]_0 = 0.1\text{M}$. Calculate $t_{1/2}$ when $[A]_0 = 0.2\text{M}$. *Solution:*
- For second order: $t_{1/2} \propto 1/[A]_0$
 - New $t_{1/2} = 50\text{s}$
12. **[JEE Main 2019]** If three successive half-lives of a first-order reaction are 10, 10, and 10 minutes respectively, what fraction of reactant remains? *Solution:*
- After each $t_{1/2}$, concentration halves
 - After 3 half-lives: $[A]/[A]_0 = (1/2)^3$
 - Remaining fraction = 0.125

Pseudo First Order

13. **[JEE Main 2017]** Hydrolysis of ester with excess water follows pseudo first-order kinetics. If $k' = 2.0 \times 10^{-2} \text{ s}^{-1}$, calculate $t_{99\%}$ (time for 99% completion). *Solution:*

- Using $\ln([A]_0/[A]_t) = k't$
- $\ln(100/1) = 0.02t$
- $t = 230s$

Catalyst Effects

14. [JEE Main 2015] A reaction has $E_a = 100$ kJ/mol. A catalyst reduces it to 60 kJ/mol. Calculate ratio of rate constants at 300K. *Solution:*
- $k_2/k_1 = e^{[(E_{a1}-E_{a2})/RT]}$
 - $k_2/k_1 = e^{[40000/(8.314 \times 300)]}$
 - $k_2/k_1 = 3.2 \times 10^7$

Integrated Rate Laws

15. [JEE Main 2020] Plot of $1/[A]$ vs time is linear with slope $0.5 \text{ M}^{-1}\text{s}^{-1}$. If $[A]_0 = 0.1\text{M}$, calculate time for 80% completion. *Solution:*
- Second order reaction
 - $1/[A]_t = 1/[A]_0 + kt$
 - $1/(0.2 \times 0.1) = 1/0.1 + 0.5t$
 - $t = 32s$

Mixed Concepts

16. [JEE Main 2014] A first-order reaction at 300K has $k = 2.0 \times 10^{-2} \text{ s}^{-1}$. Calculate E_a if k doubles at 310K. *Solution:*
- Using $\ln(k_2/k_1) = -(E_a/R)(1/T_2 - 1/T_1)$
 - $\ln(2) = (E_a/8.314)(1/300 - 1/310)$
 - $E_a = 52.8$ kJ/mol
17. [JEE Main 2018] For reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$, initial rates at different concentrations: [NO] (M) | [O₂] (M) | Rate (M/s) 0.1 | 0.1 | 0.001 0.1 | 0.2 | 0.002 0.2 | 0.1 | 0.004 Find rate law and k . *Solution:*
- Rate $\propto [\text{NO}]^2$ from rows 1&3
 - Rate $\propto [\text{O}_2]$ from rows 1&2
 - Rate = $k[\text{NO}]^2[\text{O}_2]$
 - $k = 1.0 \text{ M}^{-2}\text{s}^{-1}$
18. [JEE Main 2016] A reaction has $t_{90\%} = 230s$ at 300K and 115s at 310K. Calculate E_a . *Solution:*
- $t_{90\%} \propto 1/k$
 - $k_2/k_1 = 230/115 = 2$
 - Using Arrhenius equation
 - $E_a = 52.8$ kJ/mol
19. [JEE Main 2019] For parallel decomposition $\text{A} \rightarrow \text{B}$ and $\text{A} \rightarrow \text{C}$, if 60% of A forms B and 40% forms C, calculate k_1/k_2 . *Solution:*
- $[\text{B}]/[\text{C}] = k_1/k_2$
 - $60/40 = k_1/k_2$
 - $k_1/k_2 = 1.5$

20. [JEE Main 2017] A reaction follows first order kinetics. Calculate concentration of reactant at time equal to mean life (τ). *Solution:*

- Mean life $\tau = 1/k$
- $[A] = [A]_0 e^{-t/\tau}$
- At $t = \tau$, $[A] = [A]_0/e$
- $[A] = 0.368[A]_0$

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