CHAPTER

4 Chemical Kinetics

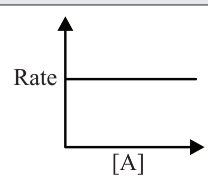
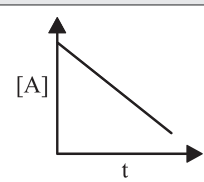
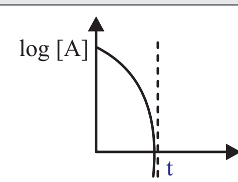
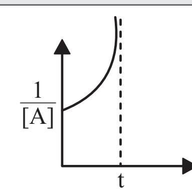
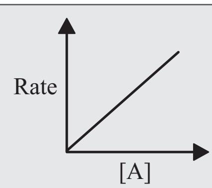
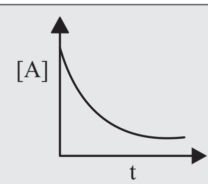
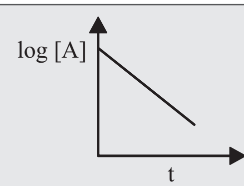
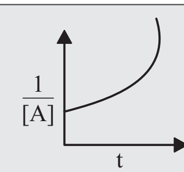
- **Rate of reaction (ROR)** = $\dfrac{\text{Rate of disappearance of reactant (appearance of products)}}{\text{Stoichiometric coefficient of reactant (products)}}$
- **For a reaction:** $aA + bB \rightarrow cC + dD$
- **Instantaneous rate:** $-\dfrac{1}{a}\left(\dfrac{d[A]}{dt}\right) = -\dfrac{1}{b}\left(\dfrac{d[B]}{dt}\right) = \dfrac{1}{c}\left(\dfrac{d[C]}{dt}\right) = \dfrac{1}{d}\left(\dfrac{d[D]}{dt}\right)$

  Relationship between rate of reaction and rate of disappearance of reactant (rate of appearance of product).
- **Average rate:** $-\dfrac{1}{a}\left(\dfrac{\Delta[A]}{\Delta t}\right) = -\dfrac{1}{b}\left(\dfrac{\Delta[B]}{\Delta t}\right) = \dfrac{1}{c}\left(\dfrac{\Delta[C]}{\Delta t}\right) = \dfrac{1}{d}\left(\dfrac{\Delta[D]}{d\Delta t}\right)$

Table: Important kinetic expression for reaction of type $A \rightarrow B$:

Order	Zero	1st	nth
Differential rate law	Rate = k	Rate = k[A]	Rate = $k[A]^n$
Integrated rate law	$[A_0]–[A] = kt$	$kt = \ln\dfrac{[A]_0}{[A]}$	$kt = \dfrac{1}{(n-1)}\left[\dfrac{1}{[A]^{n-1}} - \dfrac{1}{[A]_0^{n-1}}\right]$
Half life ($t_{1/2}$)	$t_{1/2} = \dfrac{[A]_0}{2k}$	$t_{1/2} = \dfrac{\ln 2}{k}$	$t_{1/2} = \dfrac{1}{k(n-1)}\left[\dfrac{2^{n-1}-1}{[A_0]^{n-1}}\right]$
$t_{3/4}$	$t_{3/4} = 1.5\ t_{1/2}$	$t_{3/4} = 2\ t_{1/2}$	$t_{3/4} = (2^{n-1}+1)t_{1/2}$

Table: Graphs of Zero and First Order Reactions

Order	Rate vs [A]	[A] vs t	log [A] vs t	$\dfrac{1}{[A]}$ vs t
Zero order				
First order				

Important Characteristics of First Order Reaction

- $t_{1/2}$ is independent of initial concentration.
- In equal time interval, reactions finishes by equal fraction.

	t = 0	t = t	t = 2t	t = 3t.....
Reactant conc.	a_0	a_0x	a_0x^2	a_0x^3.....

Zero Order

- $t_{1/2}$ of zero order is directly proportional to initial concentration.
- In equal time interval, reaction finishes by equal amount.

t = 0	t = t	t = 2t	t = 3t.....
C_0	$C_0 - x$	$C_0 - 2x$	$C_0 - 3x$....

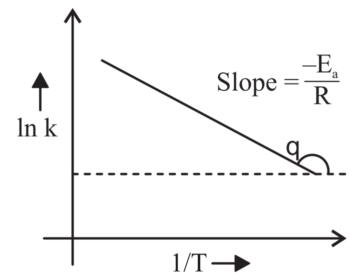
- Graph of [A] vs t is straight line.
  A zero order reaction finishes in $\boxed{t = \dfrac{[A]_0}{k}}$

Temperature Dependence

- Arrhenius equation : $k = Ae^{-E_a/RT}$
- A and E_a are constants i.e. do not vary with temperature

$$\ln k = \ln A - \frac{E_a}{RT}$$

Graph: Graphical determination of E_a.



Temperature coefficient = $\dfrac{k_{T+10}}{k_T}$

By default, T = 298K

Variation of rate constant with temperature

$$\Rightarrow \ln\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$