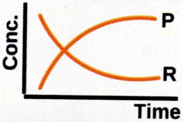
CHEMICAL KINETICS

Different Rates of a Reactions (mol L^{-1} s^{-1})

$$\text{Rate of a reaction} \propto \frac{\text{Change in concentration of species}}{\text{Time}}$$

For a reaction, $mA + nB \rightarrow pC + qD$

$$\frac{-1}{m}\frac{d[A]}{dt} = \frac{-1}{n}\frac{d[B]}{dt} = \frac{+1}{p}\frac{d[C]}{dt} = \frac{+1}{q}\frac{d[D]}{dt}$$

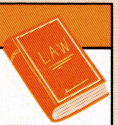


- Reactant R, Decreases with time
- Product P, Increases with time

Factors Influencing Rate of a Reaction

- Rate ∝ **Concentration** of the reacting species
- For every 10° rise in **Temperature**, rate becomes 2x
- **Catalyst** increases the rate without getting involved
- Greater **Surface Area** of reactant, faster the reaction
- **Light (*hv*)** increases the rate in some cases.

Rate Law and Rate Constant



For a reaction, $mA + nB \rightarrow pC + qD$

Rate $\propto [A]^x[B]^y \Rightarrow$ Rate $= k[A]^x[B]^y$

k depends on Temperature

k in independent of conc^n

k defines speed of the reaction, Large k - fast reaction

Order of the reaction = x + y = m + n (for elementary rxn)

- Order is calculated experimentally
- It can be Zero, Positive or Fraction.
- For a multistep reaction, order is not equal to sum of stoichiometry, it is calculated using slowest step of reaction. **Order = x + y**

Molecularity = No. of Particles participating in reaction

- Molecularity ranges between 1 to 3. NEVER 0.
- For a single step reaction, Molecularity = Order.

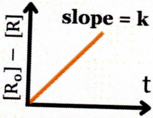
Integrated Rate laws & Graphs

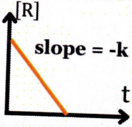
Zero Order Reaction, Units : mol L^{-1} s^{-1}

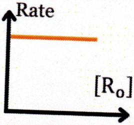
• **Differential Rate Law**	$-d[R]/dt = k$
• **Integrated Rate Law**	$kt = [R_0] - [R]$

Example : Adsorption of gases on metal surface at high P.

$[R_0]$ = a (initial conc.) ; **$[R]$ = a-x** (Conc. after t)





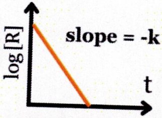


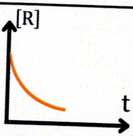
First Order Reaction, Units : s^{-1}

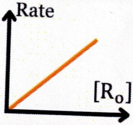
• **Differential Rate Law**	$-d[R]/dt = k[R]$
• **Integrated Rate Law**	$kt = 2.303 \log\left({}^{[R_0]}/_{[R]}\right)$

Examples

- Hydrolysis of aspirin.
- Reaction of *t*-butyl bromide with water





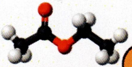


Pseudo First order reactions

Reactions which are second order but tend to behave as first order reactions. e.g. Hydrolysis of Ester in acid

$$CH_3COOC_2H_5(aq.) + H_2O(l) \xrightarrow{H^+} CH_3COOH\,(aq.) + C_2H_5OH\,(aq.)$$

$$\text{Rate} = k[CH_3COOC_2H_5][H_2O]$$
$$\text{Rate} = k'[CH_3COOC_2H_5]$$



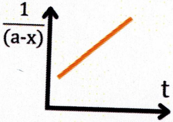
Second Order Reaction, Units : $mol^{-1}\ L\ s^{-1}$

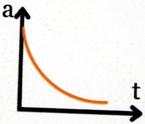
- **Differential Rate Law**	$-d[R]/dt = k[R]^2$

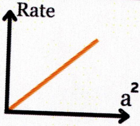
Integrated Rate Law (two cases)

Case I : One reactant or two reactants with same conc.

$A + B \longrightarrow$ Products $2A \longrightarrow$ Products	$kt = \frac{1}{(a-x)} - \frac{1}{a}$







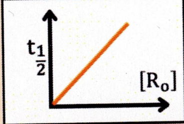
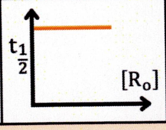
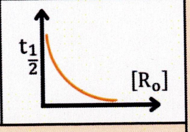
Case II : Two reactants with different conc.

$A + B \longrightarrow$ Products **a** **b** Initially	$kt = \frac{2.303}{(a-b)} \log \frac{b(a-x)}{a(b-x)}$

General nth order terms

- **Units**	$(mol\ L^{-1})^{1-n}(time)^{-1}$
- **Integrated Rate Law (1s~~t~~)**	$kt = \frac{1}{n-1}\left(\frac{1}{[R]^{n-1}} - \frac{1}{[R_o]^{n-1}}\right)$
- **Half Life**	$t_{1/2} = \frac{1}{k(n-1)}\left[\frac{2^{n-1} - 1}{a^{n-1}}\right]$

Half life and relations

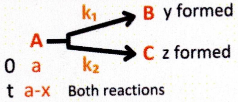
Zero Order	First Order	Second Order
$t_{\frac{1}{2}} = \frac{[R_o]}{2k}$	$t_{\frac{1}{2}} = \frac{0.693}{k}$	$t_{\frac{1}{2}} = \frac{1}{k[R_o]}$
		

Important Relations

$t_{75\%} = 2\, t_{1/2}$	$t_{99.9\%} = 10\, t_{1/2}$
Substance left after n half lives	$[R_o]/_{2^n}$

Types of Elementary reactions

Parallel/Side/Concurrent Reaction



Both reactions are 1st order

$$k_{overall} = k_1 + k_2$$

The ratio is used in a lot of questions $\frac{[B]_t}{[C]_t} = \frac{k_1}{k_2}$

$$[B]_t = A_o\left(1 - e^{-(k_1+k_2)t}\right)\frac{k_1}{k_1 + k_2}$$

$$[C]_t = A_o\left(1 - e^{-(k_1+k_2)t}\right)\frac{k_2}{k_1 + k_2}$$

$$A_t = A_o e^{-(k_1+k_2)t}$$

e.g. α or β-D-Glucose formed from D-Glucose aldehyde form

Opposed or Reversible reactions

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

	A	B
0	a	0
t	a-x	x

Both reactions are 1st order

At Eqm, R(f) = R(b)

$$R(f) = k_1\,(a-x)$$

$$R(b) = k_2\,x$$

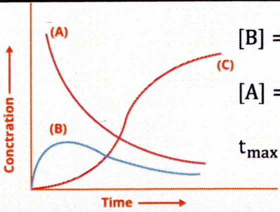
$$\text{net rate}: \; k_1(a-x) - k_2x$$

Consecutive or sequential reactions

$A \xrightarrow{k_1} B$ (Step 1)

$B \xrightarrow{k_2} C$ (Step 2)

- B is an intermediate.
- According to SSA, reactive intermediates are at constant conc.



$$[B] = A_0\left(e^{-k_1t} - e^{-k_2t}\right)\frac{k_1}{k_2-k_1}$$

$$[A] = A_0e^{-k_1t}$$

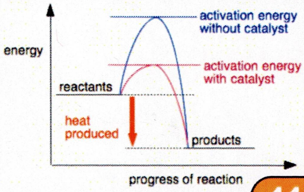
$$t_{max} = \frac{2.303}{k_2-k_1}\log\left(\frac{k_2}{k_1}\right)$$

when [B] is maximum

Effect of Catalyst on rate

A catalyst provides an alternative route for a reaction with a lower activation energy.

Thus, Speeds up reaction



Temperature Dependence of rate of reaction

Arrhenius eqn : Relates Temperature with rate constant.

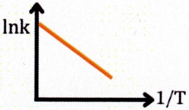
$$k = Ae^{-E_a/RT}$$

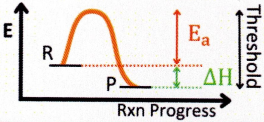
- E_a = Activation Energy
- A = Frequency factor

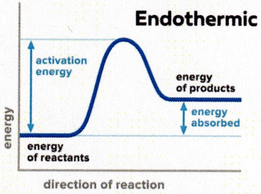
$$\ln k = \ln A - \frac{E_a}{RT}$$

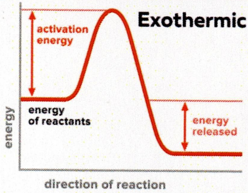
Plot vs lnk vs 1/T

Slope : **$-E_a/R$** Intercept : **lnA**









For a a reaction at two different temperatures

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

Temperature Coefficient

Rate constant doubles or triples with every 10° rise in temperature

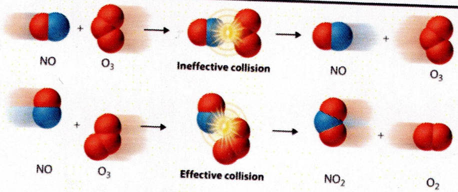
$$\frac{k_t + 10}{k_t} \approx 2$$

Some examples of first order rate constants

Gas phase reactions A (g) → B(g) + C (g)	
Partial pressure of A given Initially, P_o and at t, P_t	$k = 2.303 \log \frac{P_o}{P_t}$
Total pressure given Initially, P_o and at t, P_t	$k = 2.303 \log \frac{P_o}{2P_o - P_t}$

Collision theory

- The rate of a chemical reaction is proportional to the number of collisions between reactant molecules.
- Only Effective collision results in Products.



Steric/Probability Factor

$$\boxed{\text{Rate} : Z_{AB} \times P \times e^{-E_a/RT}}$$

Collision Frequency

Fraction of molecules having Energy>Activation