

CHAPTER - 03

CHEMICAL KINETICS

Chemical kinetics

It is the branch of chemistry which deals with the rate of reaction and the factors affecting the rate.

Rate of reactions

It is the change in concentration of any one of the reactants or products in unit time.

$$\text{Rate} = \frac{\text{Change in concentration}}{\text{Time}}$$

Consider a reaction $A \rightarrow P$

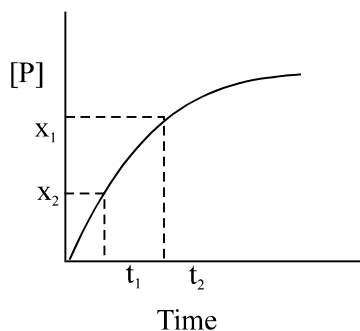
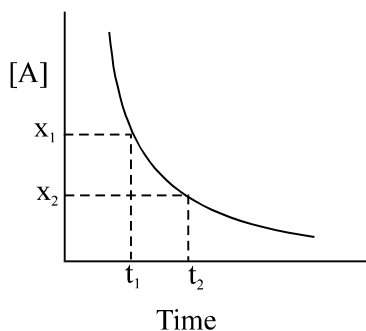
Rate of disappearance of A = $\frac{-d[A]}{dt}$. Since d[A] is -ve, it is multiplied with -1 to make rate positive.

Rate of appearance of P = $\frac{d[P]}{dt}$. Unit of rate - $\text{mol L}^{-1} \text{s}^{-1}$

TYPES OF RATE

1. Average rate

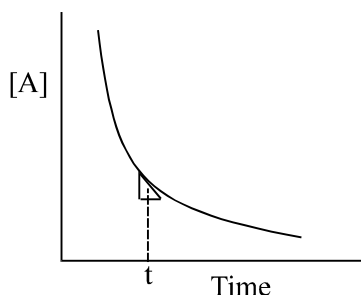
It is the rate of reaction determined for a particular interval of time.



$$\text{Average rate} = \frac{-(x_2 - x_1)}{t_2 - t_1} = \frac{-\Delta[A]}{\Delta t}; \quad \text{Average rate} = \frac{x_2 - x_1}{t_2 - t_1} = \frac{\Delta[P]}{\Delta t}$$

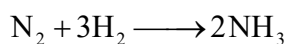
2. Instantaneous Rate

It is the ratio of reaction determined for a particular instant of time.



Slope of tangent gives inst.rate Here, $\text{rate} = \frac{\Delta A}{\Delta t}$; $\Delta t \rightarrow 0$

Rate of reaction in the form of stoichiometry



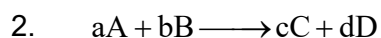
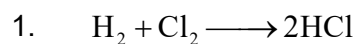
$$\text{Rate of disappearance of N}_2 = -\frac{d}{dt}[\text{N}_2]$$

$$\text{Rate of disappearance of H}_2 = -\frac{d}{dt}[\text{H}_2]$$

$$\text{Rate of appearance of NH}_3 = \frac{d}{dt}[\text{NH}_3]$$

$$\text{The rates can be equated as } -\frac{d}{dt}[\text{N}_2] = -\frac{1}{3} \frac{d}{dt}[\text{H}_2] = \frac{1}{2} \frac{d}{dt}[\text{NH}_3]$$

Write the same for



For gaseous reactions, rate is obtained from change in partial pressure.

RATE LAW/RATE EQUATION

It gives the dependance of rate on concentration of reactants.

For reaction $a\text{A} + b\text{B} \longrightarrow \text{Product}$

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

$$\text{Rate} = K[\text{A}]^x [\text{B}]^y$$

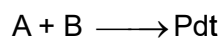
K = rate constant/velocity constant

When $[A] = [B] = 1$, then rate = K

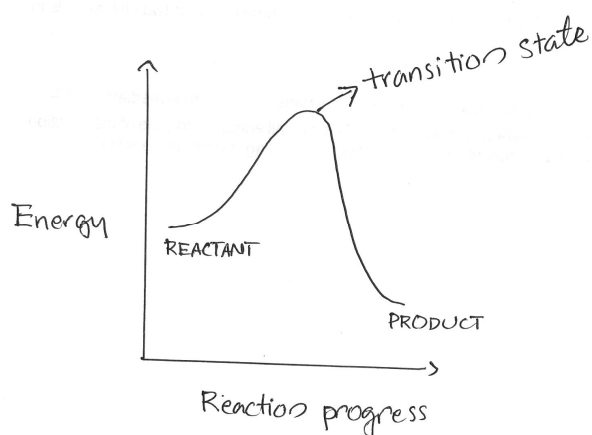
ie. rate constant is equal to the rate of reaction when concentration of reactants are unity.

MECHANISM OF REACTION

1. Elementary reaction : These reactions complete in single step

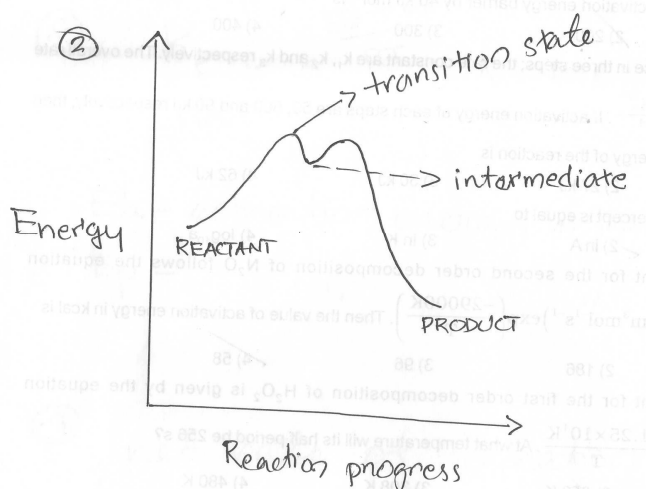
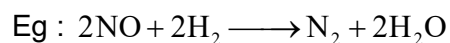


$$\text{Rate} = k[A][B]$$



2. Complex reactions

These reactions complete in multisteps. For such reactions, overall rate is determined from slowest step.



Mechanism

- $2\text{NO} \xrightleftharpoons[\text{K}_b]{\text{K}_f} \text{N}_2\text{O}_2 (\text{fast})$
- $\text{N}_2\text{O}_2 + \text{H}_2 \longrightarrow \text{N}_2\text{O} + \text{H}_2\text{O} (\text{slow})$
- $\text{N}_2\text{O} + \text{H}_2 \longrightarrow \text{N}_2 + \text{H}_2\text{O} (\text{fast})$

From slow step

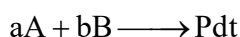
$$\text{Rate} = K [\text{N}_2\text{O}_2] [\text{H}_2]$$

$$\text{From eqn (1)} \quad K = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \quad \therefore [\text{N}_2\text{O}_2] = K [\text{NO}]^2$$

$$\text{So Rate} = K K [\text{NO}]^2 [\text{H}_2] = K' [\text{NO}]^2 [\text{H}_2]$$

ORDER OF REACTION

It is the sum of powers of concentration terms in the rate equation.



$$\text{Rate} = K [\text{A}]^x [\text{B}]^y; \text{ order} = x + y$$

Zero order reactions

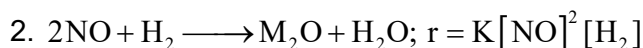
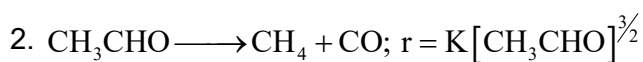
- $\text{H}_2 + \text{Cl}_2 \xrightarrow{h\nu} 2\text{HCl} \quad \text{Rate} = K$
- $2\text{NH}_3 \xrightarrow[\Delta]{\text{Pt}} \text{N}_2 + 3\text{H}_2 \quad \text{Rate} = K$
- $2\text{HI} \xrightarrow{\text{Au}} \text{H}_2 + \text{I}_2 \quad \text{Rate} = K$

First order reactions

- $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}; \quad r = K [\text{NH}_4\text{NO}_2]$
- $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2; \quad r = K [\text{H}_2\text{O}_2]$
- All radioactive decay

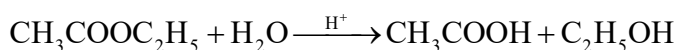
Second order reactions

- Saponification : $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}; \quad r = k [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{NaOH}]$
- $\text{H}_2 + \text{I}_2 \longrightarrow 2\text{HI}; \quad \text{Rate} = K [\text{H}_2] [\text{I}_2]$
- $2\text{Cl}_2\text{O} \longrightarrow 2\text{Cl}_2 + \text{O}_2; \quad \text{Rate} = K [\text{Cl}_2\text{O}]^2$

Third order reactions**Fractional order reactions****Pseudo order reactions**

Certain reactions have higher order, but they follow lower order kinetics. Such reactions are called pseudo order reactions.

1. Acid hydrolysis of ester

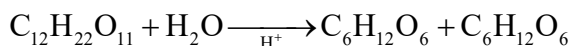


$$r = k[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]$$

Since water is taken in excess, its concentration remains almost constant

$$\therefore r = K'[\text{CH}_3\text{COOC}_2\text{H}_5], K' = K[\text{H}_2\text{O}]$$

2. Inversion of cane sugar



$$\text{Rate} = K'[\text{C}_{12}\text{H}_{22}\text{O}_{11}]; K' = K[\text{H}_2\text{O}]$$

Key points

- Order is an experimental quantity
- It can be zero, -ve, fractional also
- Applicable to elementary or complex reaction
- In complex reaction, order is obtained from solvent step

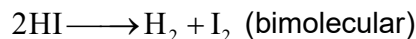
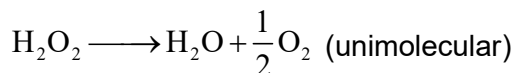
MOLECULARITY

It is the number of reactant molecules colliding simultaneously to bring about a chemical reaction.

It is a theoretical quantity.

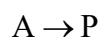
It can't be zero, -ve or fractional. Maximum value of molecularity is 3 because of the rare possibility of collision of more than 3 molecules at a time.

For complex reactions, molecularity no significance - each sep has molecularity.



INTEGRATED RATE EQUATIONS.

Zero order reaction



Initial concentration of A = $[\text{A}]_0$

Final concentration of A = $[\text{A}]$

In dt time, d[A] amount is reacted

$$\text{Rate} = \frac{-d[\text{A}]}{dt} = k[\text{A}]^0 = k; \quad -d[\text{A}] = kdt$$

$$\text{Integrating both sides } -\int d[\text{A}] = k \int dt$$

$$-[\text{A}] = k + C; \quad C = \text{Integration constant.}$$

To find C, $t = 0$, $[\text{A}] = [\text{A}]_0$

$$-[\text{A}]_0 = C$$

$$\therefore -[\text{A}] = kt - [\text{A}]_0$$

$$[\text{A}] = -kt + [\text{A}]_0$$

$$kt = [\text{A}]_0 - [\text{A}]$$

$$\therefore k = \frac{[\text{A}]_0 - [\text{A}]}{t}$$

Half life ($t_{1/2}$)

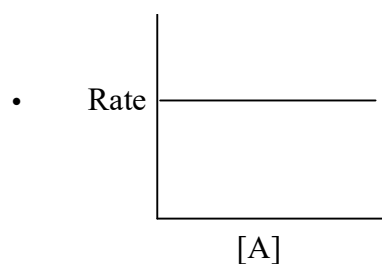
It is the time taken to complete half of the initial amount of the reactant. When $t = t_{1/2}$; $[\text{A}] = \frac{[\text{A}]_0}{2}$

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

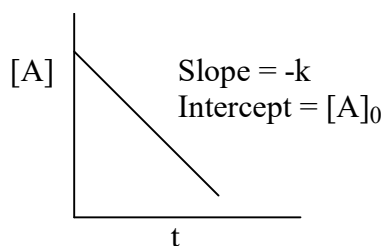
$$t_{1/2} = \frac{[\text{A}]_0}{2K}$$

For zero order reactions

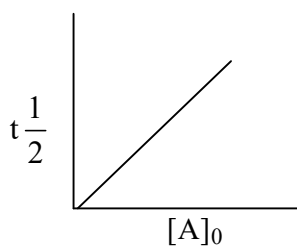
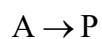
- Unit of rate = $\text{mol L}^{-1} \text{s}^{-1}$ (as that of K)
- Rate is constant
- $t \frac{1}{2} \propto [A]_0$



- $kt = [A]_0 - [A]; \quad [A] = -kt + [A]_0$



- $t \frac{1}{2} \propto [A]_0$

**First order reaction**

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

$$\frac{-d[A]}{dt} = k[A]$$

$$\frac{-d[A]}{A} = k dt$$

On integration $-\int \frac{d(A)}{(A)} = K \int dt$

$$-\ln[A] = kt + C$$

To find C, $t = 0$, $(A) = (A)_0$

$$-\ln [A]_0 = C$$

$$\therefore -\ln(A) = kt - \ln[A]_0$$

$$\ln(A) = -kt + \ln[A]_0$$

$$kt = \ln(A)_0 - \ln(A)$$

$$kt = \ln \frac{(A)_0}{(A)}$$

$$k = \frac{1}{t} \ln \frac{(A)_0}{(A)}$$

$$k = \frac{1}{t} \ln \frac{(A)_0}{(A)}$$

$$k = \frac{2.303}{t} \log \frac{(A)_0}{(A)}$$

HALF LIFE ($t_{1/2}$)

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

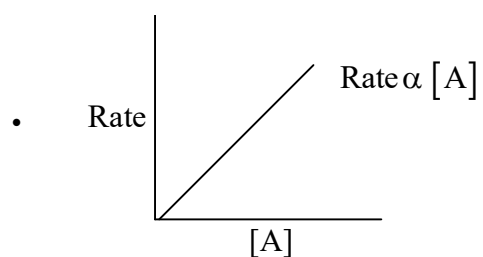
When $t = t_{1/2}$, $[A] = \frac{(A)_0}{2}$

$$t_{1/2} = \frac{2.303}{k} \log \frac{[A]_0}{[A]_0 / 2}$$

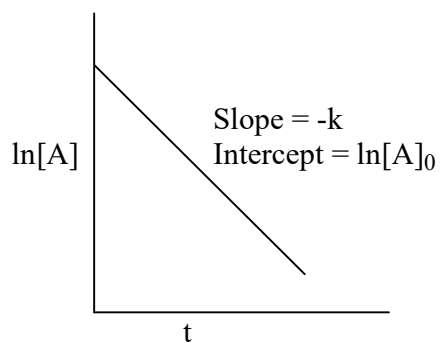
$$t_{1/2} = \frac{0.693}{k}$$

For first order reactions

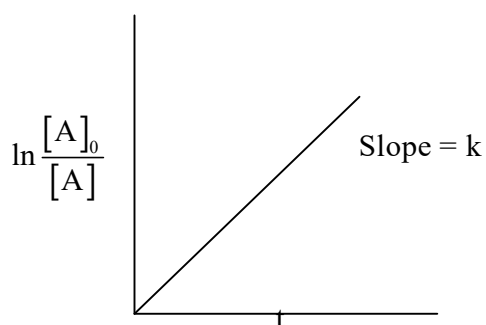
- Unit of $K = s^{-1}$
- $t \frac{1}{2}$ independent of $[A]_0$



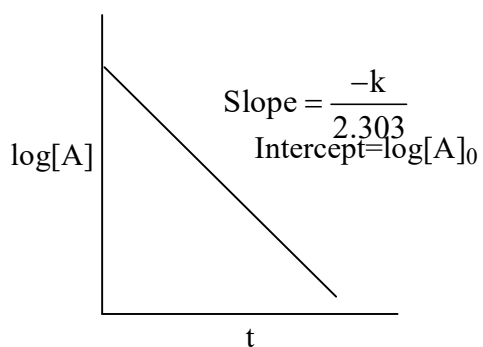
- $\ln[A] = -kt + \ln[A]_0$



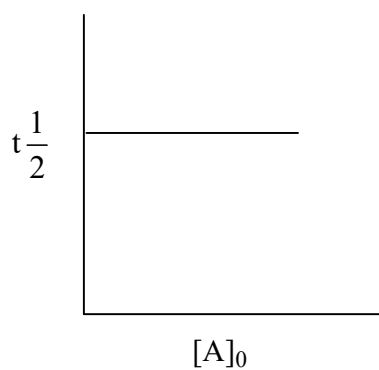
- $\ln \frac{[A]_0}{[A]} = kt$



- $\log A = \frac{-kt}{2.303} + \log[A]_0$



- $t_{\frac{1}{2}}$ and $[A]_0$



- t_{90} t_{99}
 $t = \frac{2.303}{k} \log \frac{100}{10};$ $t = \frac{2.303}{k} \log \frac{100}{1}$
 $t_{90} = \frac{2.303}{k};$ $t_{99} = \frac{2.303}{k} \times 2$

- $t_{99.9} = \frac{2.303}{k} \times 3$ $t_{99.99} = \frac{2.303}{k} \times 4$

- $100 \xrightarrow{t_{1/2}} 50 \xrightarrow{t_{1/2}} 25 \xrightarrow{t_{1/2}} 12.5 \xrightarrow{t_{1/2}} 6.25$

$$t_{75} = 2 \times t_{\frac{1}{2}}$$

$$t_{87.5} = 3 \times t_{\frac{1}{2}}$$

$$t_{93.75} = 4 \times t_{\frac{1}{2}}$$

Amount of reactant left reactant in 'n' half lives $[A] = \frac{[A]_0}{2^n}$

In general

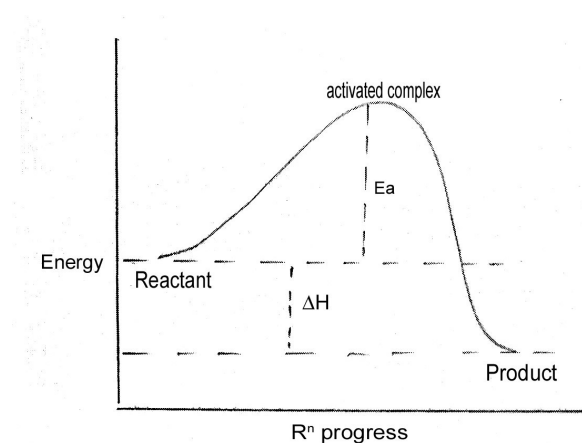
- Unit of $k = (\text{mol/L})^{1-n} \text{s}^{-1}$
- $t \frac{1}{2} \propto [A]_0^{1-n}$

COLLISION THEORY OF CHEMICAL REACTIONS

According to the theory, chemical reactions occur by the collision of reactant molecules. But all the collisions are not effective. To make effective collisions.

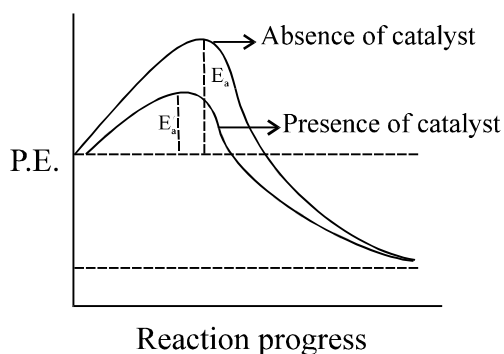
1. Colliding molecules should possess a minimum amount of energy called threshold energy.
2. They should collide in proper orientation

Energy profile



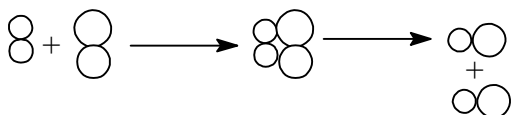
The extra amount of energy required by reactant molecules to make effective collision is called activation energy (E_a). It depends on

1. Nature of reactant
2. Presence of catalysis

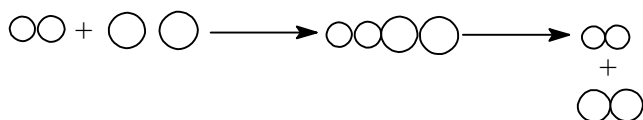


Orientation factor

Proper orientation



Improper orientation



According to the theory $\text{Rate} = Z e^{\frac{-E_a}{RT}}$

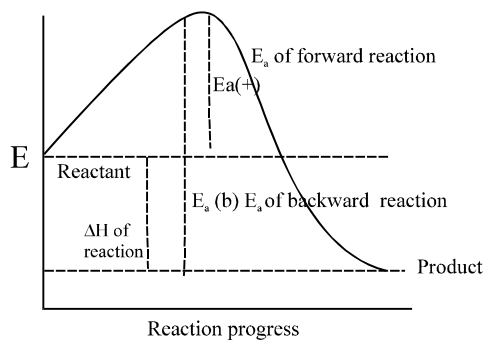
Z = Collision frequency (no collisions per second per unit volume of the reaction factor)

$e^{\frac{-E_a}{RT}}$ = fraction of molecules with energies equal to or greater than E_a (Boltzman factor)

Another factor P called steric factor or probability factor is introduced

$$\text{Rate} = PZ e^{\frac{-E_a}{RT}}$$

Energy profile of reversible reaction



$$\frac{K_p}{K_a} = e^{\frac{(E_a - E_p)}{RT}}; E_a - \text{activation energy in the absence of catalyst}$$

E_p - activation energy in the presence of catalyst.

Limitations

This theory is mainly applicable for gaseous reactions and also for solutions in which reacting species are molecules.

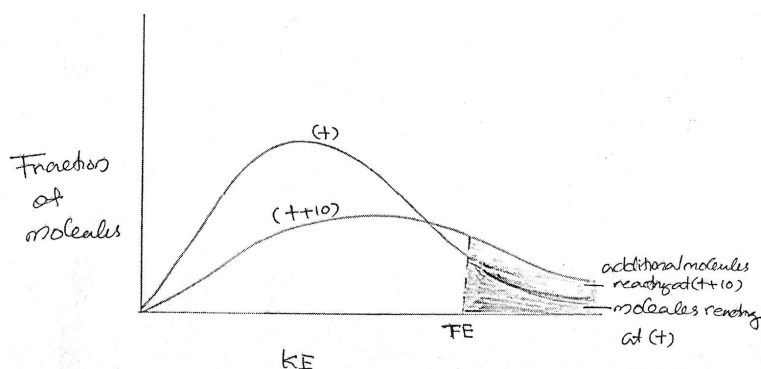
It is applicable to simple biomolecular reactions but fails for complex.

It considers molecules to be hard sphere and ignore structural aspect of molecules.

RATE OF REACTION AND TEMPERATURE

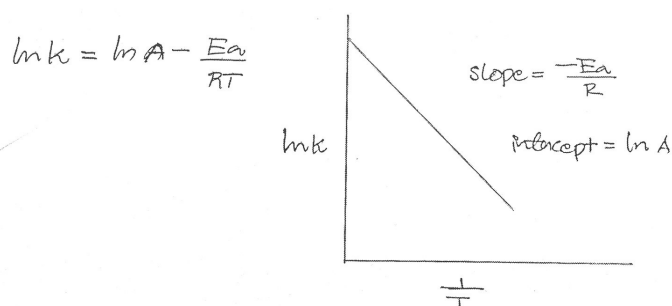
As temperature increases, rate of reaction also increases. It is found that rate of reaction doubles for each 10° rise in temperature.

$$\text{Temperature coefficient} = \frac{K(t+10)}{K(t)} \approx 2$$

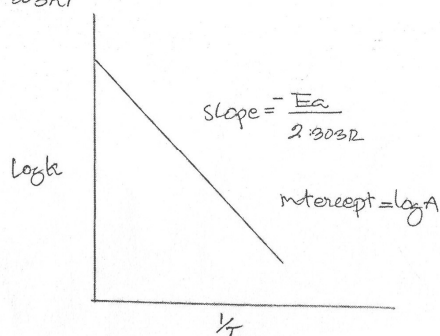


The dependence of rate on temperature is given by Arrhenius equation $k = Ae^{\frac{-E_a}{RT}}$

A = Arrhenius factor/frequency factor/pre exponential factor



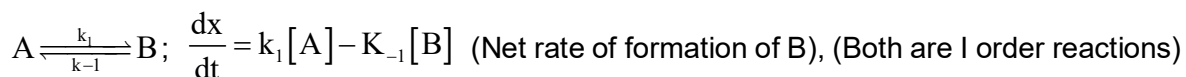
$$\log k = \log A - \frac{E_a}{2.303RT}$$



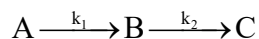
$$\text{Also } \log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

K_1 and K_2 are rate constants of a reaction at temperature T_1 and T_2 respectively.

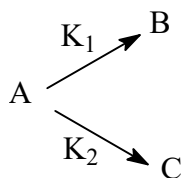
Reversible reactions



Consecutive reactions



Parallel reaction



$$\% \text{ B in the mixture} = \frac{K_1}{K_1 + K_2} \times 100$$

$$\% \text{ C in the mixture} = \frac{K_2}{K_1 + K_2} \times 100$$