# Chemical Kinetics

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Introduction: chemical kinetics may also be called reaction kinetics or simply kinetics. The rate of a chemical reaction usually has units of $sec^{-1}$.

⇒ In 1864 Peter waageand and cato Guldberg pioneered the development of chemical kinetics by formulating the law of mass ~~of unit~~ action. which states the speed of a chemical reaction is proportional to the quantity of the reacting substances.

⇒ Reaction rate is the rate at which the reactants of a chemical reaction from the product.

⇒ Reaction rates are expressed as concentration per unit time.

## Order and Molecularity:

**Order:** Order of reaction is the total power of concentration of reactants which is proportional to the experimental facts.

⇒ Order of reaction is an experimental fact which depends on experiment, observation and conclusion.

⇒ Order of reaction never be fraction.

Example: $2NH_3(g) \rightarrow 3H_2(g) + N_2(g)$

order – zero order reaction

**Molecularity:** Molecularity of a reaction is the number of atoms, ions or molecules taking part in a reaction as in chemical equation.

⇒ Molecularity is a theoritical concept which depends on chemical equation partly.

⇒ Molecularity can be fraction.

Example: $2NH_3(g) \rightarrow 3H_2(g) + N_2(g)$

Molecularity -2.

**Zero order reaction:** The reaction whose rate is independent of the concentration of a reactant, so that changing its concentration has no effect on the speed of the reaction is called zero order reaction.

Ex: $2NH_3(g) \rightarrow 3H_2(g) + N_2(g)$

**1st order reaction:** If a reaction rate depends on a single reactant and the value of the exponent is one, then the reaction is said to be 1st order.

The reaction whose rate is proportional to first power of concentration of one reactant is called the 1st order reaction.

According to ~~reaction:~~ def$^n$, rate of reaction:

$$R = \frac{-dc}{dt} = k \times c^1 = k \times c$$

Ex: $N_2O_5(g) \rightarrow N_2O_4(g) + \frac{1}{2}O_2(g)$

$H_2O_2(l) \rightarrow H_2O(l) + \frac{1}{2}O_2(g)$

**Second order reaction:** The reaction whose rates proportional to second power of concentration of one reactant or two reactants is called second order reaction.

According to def$^n$, rate of reaction, $r = \frac{-dc}{dt} = k \times c^2$

⇒ A reaction is said to be second order when the overall order is two. The rate of a second order reaction may be proportional to one concentration squared to the Product of two concentrations.

⇒ Two types: (i) $2A$ (reactant) $\rightarrow$ Products

(ii) $A + B \rightarrow$ Products

Ex: $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$

$2CH_3CHO(g) \xrightarrow{\Delta} 2CH_4(g) + 2CO(g)$

**Pseudo Unimolecular reaction:** It is a reaction which seems to be second degree but actually a first order reaction. One of the reactant is in excess which makes its importance negligible and to follow the 1st order rate is called, "Pseudo unimolecular Reaction."

Ex: (i) $C_{12}H_{22}O_{11} + H_2O_{(excess)} \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

$$Rate = K[C_{12}H_{22}O_{11}]$$

(ii) $CH_3COOC_2H_5 + H_2O_{(excess)} \rightarrow CH_3COOH + C_2H_5OH$

$$Rate = K[CH_3COOC_2H_5]$$

## Integrated rate equation for 1st order reaction:

$$A \text{ (reactant)} \longrightarrow B \text{ (Product)}$$

Intially $t=0$, $a$ mol$L^{-1}$ $\quad$ $0$

After $t=t$, $(a-x)$ mol$L^{-1}$ $\quad$ $x$

According to law of mass action, rate of 1st order reaction at that time will be:

$$\frac{dx}{dt} \propto (a-x)^1$$

$$\Rightarrow \frac{dx}{dt} = K(a-x) \quad [K \text{ is a constant}]$$

$$\Rightarrow \frac{dx}{(a-x)} = K\,dt$$

On integrating both sides we get

$$\int \frac{dx}{(a-x)} = \int K\,dt$$

$$\Rightarrow -\ln(a-x) = Kt + C \quad \text{--- ①} \quad [C = \text{Integration constant}]$$

when, $t=0$, $x=0$ from ①

$$-\ln(a-0) = k\times 0 + c$$

$$\Rightarrow -\ln a = c$$

$$\Rightarrow c = -\ln a$$

Putting the value of $c$ in eqⁿ ①

$$-\ln(a-x) = kt - \ln a$$

$$\Rightarrow kt - \ln a = -\ln(a-x)$$

$$\Rightarrow kt = \ln a - \ln(a-x)$$

$$\Rightarrow kt = \ln \frac{a}{a-x}$$

$$\Rightarrow k = \frac{1}{t}\ln \frac{a}{a-x}$$

$$\Rightarrow k = \frac{2.303}{t}\log \frac{a}{a-x}.$$

## Integrated equation for 2nd order reaction:

$$2A \rightarrow \text{Product (B)}$$

Initially, $t=0$    $a\ mol L^{-1}$    $0$

After, $t=t$    $(a-x)\ mol L^{-1}$    $x$

According to law of mass action at any time $t$ the rate of reaction will be,

$$\frac{dx}{dt} \propto (a-x)^2$$

$$\Rightarrow \frac{dx}{dt} = k(a-x)^2$$

$$\Rightarrow \frac{dx}{(a-x)^2} = k\,dt$$

On integrating both sides we get,

$$\int \frac{dx}{(a-x)^2} = \int k\,dt$$

$$\Rightarrow \frac{1}{a-x} = kt + c \quad \text{——①}$$

[ $c$ = Integration constant]

When $t=0$, $x=0$ from ①

$$\frac{1}{a-0} = k \times 0 + c$$

$$\Rightarrow c = \frac{1}{a}$$

Putting the value of $c$ in eqn ①

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

$$\Rightarrow kt + \frac{1}{a} = \frac{1}{a-x}$$

$$\Rightarrow kt = \frac{1}{a-x} - \frac{1}{a}$$

$$\Rightarrow kt = \frac{a-a+x}{a(a-x)}$$

$$\Rightarrow kt = \frac{x}{a(a-x)}$$

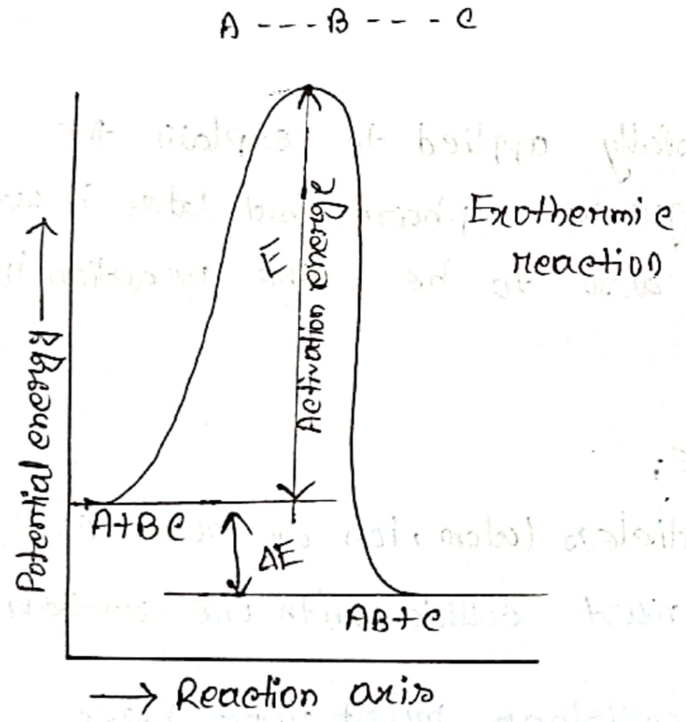
$$\Rightarrow k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

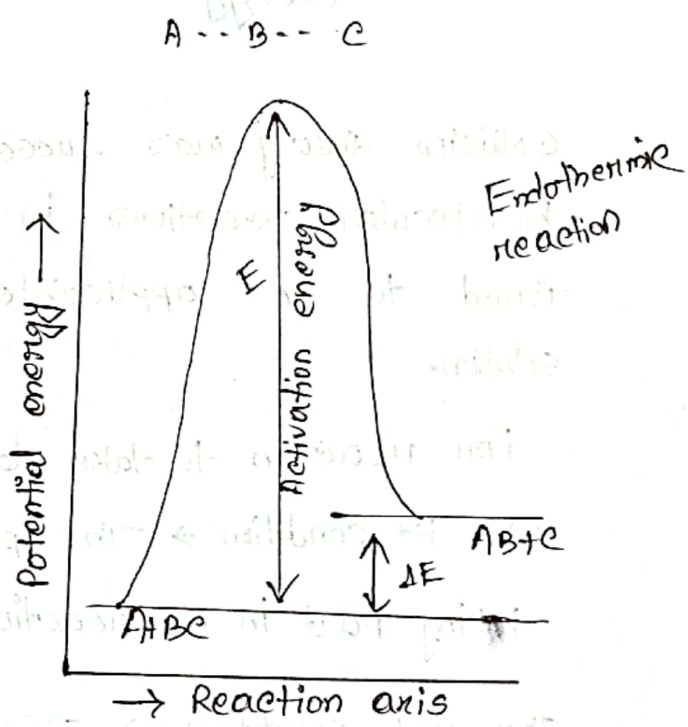
## Activation energy and activated complex:

$$A + BC \rightarrow AB + C$$

~~AB+~~ .

$$A + BC \leftrightarrow A - - - B - - - C \rightarrow AB + C$$



## Collision Theory:

$$k = PZ e^{-\frac{Ea}{RT}}$$

where, k = rate constant of reaction

P = static factor (condition no 3)

Z = collision rate (condition no 1)

$e^{-\frac{Ea}{RT}}$ = fraction of molecules with activation energy.

Collision theory was successfully applied to explain the biomolecular reactions in gaseous phase, but later it was found to be applicable also to be the reaction in solution.

For reaction to take place:

The 1st condition → The particles (atom, ion or molecules) taking part in a reaction must collide with one another.

The 2nd condition → The collisions must take place with a minimum amount of energy.

The 3rd condition → The collisions must take place with definite orientation. Arrhenius equation is in fact the mathematical expression of these conditions.

According to the 1st and 2nd conditions the reacting particles must collide with one another with minimum energy. Then some of the old chemical bonds will be broken down and new bonds will be formed.

$A \| B + C \rightarrow AB + C$ [insufficient bond energy]

$A \| B + C \rightarrow A + BC$ [sufficient energy]

$AC + B$

Example: $Cl_2$ or $Cl:Cl = 2Cl$

$Cl_3C-H + \cdot Cl = Cl_3C\cdot + HCl$

$Cl_3C\cdot + Cl\cdot = Cl_3C - Cl$ or $CCl_4$