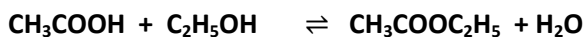


Chemical kinetics

Second order reaction

When the concentration of **two moles** of reactants alters in a reversible chemical reaction, it is called **second order reaction**.

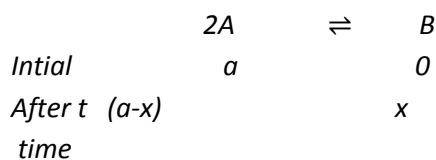
e.g.



Derivation of second order reaction

When the reactants are same :-

Let a substance A is dissociated into B by second order reaction.



The rate of reaction $\frac{dx}{dt} \propto (a-x)^2$

$$\text{or } \frac{dx}{dt} = K(a-x)^2$$

$$\text{or } \frac{dx}{(a-x)^2} = K dt \quad \text{---(i)}$$

equation (i) is on integration, we get.

$$\frac{1}{(a-x)} = Kt + I \quad \text{---(ii)}$$

where I is integration constt.

if $t = 0$, then $x = 0$. put this value in equation (ii).

$$\frac{1}{(a-0)} = K \times 0 + I$$

Or $\frac{1}{a} = I$, put this value of I in (ii), we get.

$$\frac{1}{(a-x)} = Kt + \frac{1}{a}$$

$$\frac{1}{(a-x)} - \frac{1}{a} = Kt$$

$$\frac{a-(a-x)}{a(a-x)} = Kt$$

$$\frac{1}{t} \frac{x}{a(a-x)} = K$$

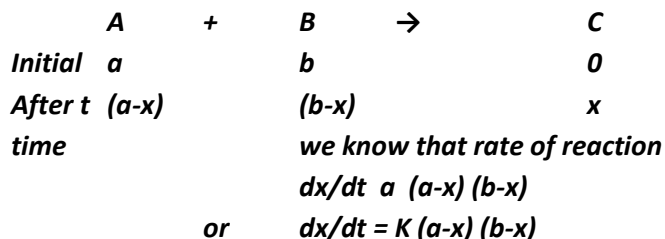
$$\text{Or} \quad K = \frac{x}{t \cdot a(a-x)}$$

Chemical kinetics

This is the characteristic equation of 2nd order

When reactants are different

Let two reactants A and B are converted into product by second order reaction.



where K – rate constt.

$$\text{or } \frac{dx}{(a-x)(b-x)} = K \cdot dt \text{---(i)}$$

equation (i) is on separation and integration

$$\frac{1}{(a-b)} \left(\frac{1}{(b-x)} - \frac{1}{(a-x)} \right) dx = K dt$$

$$\frac{1}{(a-b)} \left(-\log(b-x) + \log(a-x) \right) = Kt + I$$

where I – integration constant.

$$\frac{1}{(a-b)} \left(\frac{\log(a-x)}{(b-x)} \right) = Kt + I \text{---(ii)}$$

if t=0 then x=0

put these values in equation (ii), we get

$$\frac{1}{(a-b)} \left(\frac{\log(a-0)}{(b-0)} \right) = K \times 0 + I$$

$$\frac{1}{(a-b)} \frac{\log a}{b} = I$$

Put the value of I in equation (ii), we get

$$\frac{1}{(a-b)} \left(\frac{\log(a-x)}{(b-x)} \right) = Kt + \frac{1}{(a-b)} \left(\frac{\log a}{b} \right)$$

$$\frac{1}{(a-b)} \left(\frac{\log(a-x)}{(b-x)} - \frac{\log a}{b} \right) = Kt$$

$$\frac{1}{t(a-b)} \left(\frac{\log(a-x)}{(b-x)} - \frac{\log a}{b} \right) = K$$

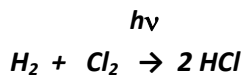
$$\frac{2.303}{t(a-b)} \left(\frac{\log \frac{b(a-x)}{a(b-x)}}{1} \right) = K$$

This is the equation of second order reaction.

Chemical kinetics

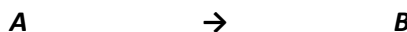
Zero order reaction

The reactions in which rate of reaction does not depend upon the initial concentration of the reactant are called zero order reactions.



Generally photochemical reactions are the zero order reactions

Let a substance A is converted into B by zero order reaction.



The rate of reaction

$$dx/dt \propto [A]^0$$

$$\text{Or } dx/dt = K \times 1$$

$$\text{Or } dx/dt = K$$

It means the rate of reaction of zero order reaction always remains constant.

Unit of K of first order reaction

We know that in first order reaction

$$K = 2.303/t \cdot \log a/(a-x)$$

$$K = 1/\text{sec}.$$

$$\text{Or } K = \text{sec}^{-1}$$

Unit of K for 2nd order reaction

we know from 2nd order reaction

the characteristic equation of second order is

$$K = 1/t \cdot x / a \cdot (a-x)$$

$$K = \text{sec}^{-1} \text{ mole}^{-1} \cdot \text{litre}$$

Unit of k for zero order reaction

we know from zero order reaction

$$K = dx/dt.$$

$$K = \frac{\text{mole}}{\text{litre} \cdot \text{second}}$$

$$K = \text{mole} \cdot \text{litre}^{-1} \cdot \text{second}^{-1}.$$

Energy of activation

The minimum energy which is required to activate a molecule for participating in a chemical reaction is called energy of activation.

It is represented by E.

Arrhenius gave an equation for energy of activation, which may be given as

Chemical kinetics

$$K = A e^{-E/RT}$$

Where

K- Rate constant.

A- Arrhenius constant.

E- Energy of activation.

R- Rydberg constant.

T- Temperature.

On differentiating and integrating the equation with respect to rate constant K_1 and K_2 and temperature T_1 and T_2 .

$$\log K = \log A \cdot e^{-E/RT}$$

$$\log K = \log A + \log e^{-E/RT}$$

$$\log K = \log A - E/RT \log e$$

Or $\log K = \log A - E/RT$

Or $d(\log K) = +E/R [dt/T^2]$

$$\int_{K_1}^{K_2} d(\log K) = E/R \int_{T_1}^{T_2} \frac{1}{T^2}$$

$$\log \frac{K_2}{K_1} = -\frac{E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\log \frac{K_2}{K_1} = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

or $\log \frac{K_2}{K_1} = \frac{E}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

or $\log \frac{K_2}{K_1} = \frac{E}{2.303 R} \left(\frac{T_2 - T_1}{T_1 \cdot T_2} \right)$

or $\log \frac{K_2}{K_1} = \frac{E}{2.303 R} \left(\frac{\Delta T}{T_1 \cdot T_2} \right)$

Collision Theory Energy & orientation barriers to reaction

we know that for a reaction the reacting species like atom, molecule or ion must collide with one another.

The no. of collision that takes place per second per unit volume of the reaction mixture is known as collision frequency z . The value of collision frequency is normally very high. The binary collision is the order of 10^{25} to 10^{28} .

If all the collisions are effective in forming the products, the reactions must be completed in very short time.

The collisions which actually produce the products are called effective collisions.

There are two important barriers for a reaction.

(i). Energy barrier

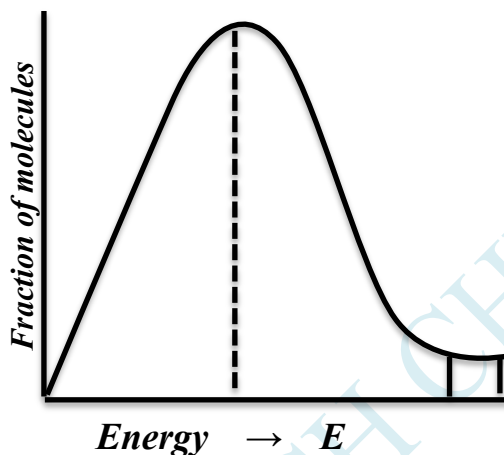
Chemical kinetics

(ii). Orientation barrier.

Energy barrier

The minimum energy which is required to split the bond after collision is called threshold energy. It means only those collisions are effective in which the molecule has the energy more than threshold energy.

Therefore the molecule having the energy more than threshold energy can pass energy barrier and converted into the products.



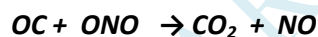
Orientation barrier

The colliding molecules should also have proper orientation, so the old bonds break and new bonds are formed.

When the molecules do not have proper orientation at the time of collision, it becomes ineffective collision and no products are formed.

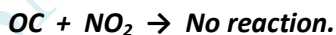
e.g.

When CO and NO₂ are collided in proper orientation as the oxygen atom of NO₂ should be in the direction of C of CO. The collision is perfect and the products obtained will be CO₂ and NO.



When CO and NO₂ do not collide in proper orientation as the oxygen atom of NO₂ should not be in the direction of C of CO. The collision is ineffective and the products are not obtained.

e.g.



Therefore it follows that only a small fraction is effective.

So the theory is postulated as-

(i). There must be collisions between the reacting species for a chemical reaction.

(ii). Only a certain fraction of the total number of collisions are effective in forming the products.

(iii). For effective collisions, the molecules should possess sufficient energy as well as orientation.

Chemical kinetics

Therefore the rate of reaction is directly proportional to the product of -

(a). The no. of collision per unit volume per second between the reacting molecules.

(b). The fraction of effective collisions, f .

$$\text{Rate} = \frac{dx}{dt} = f \times z$$

SMARK HITECH CHEMISTRY