Chemical Kinetics

Chemical
⇩
Chemical reaction

Substances with well defined properties are converted by chemical reactions into other substances with different properties

Kinetics
⇩
Greek word 'Kinesis' means movement

- The Branch of physical Chemistry which deals with the rate of reaction, factors affecting rate of reaction and correlate mechanism of the reaction with rate law is called chemical kinetics.
- Thermodynamics tells only about the feasibility of a reaction whereas chemical kinetics tells about the rate of a reaction.

for example, thermodynamic data indicate that diamond shall convert to graphite but in reality the conversion rate is too slow that the change is not perceptible at all. Therefore most people think that diamond is forever.

Rates of Reactions

The rate of a reaction mean the speed with which the reaction takes place. This is expressed either in terms of decrease in the concentration of a reactant per unit time or increase in the concentration of a product per unit time. Hence the rate of a reaction may be defined as follows :

The rate of reaction is the change in the concentration of any one of the reactants or products per unit time i.e.,

$$\text{Rate of reaction} = \frac{\text{Decrease in the concentration of a reactant}}{\text{Time interval}}$$

$$\text{or } = \frac{\text{Increase in the concentration of a product}}{\text{Time interval}}$$

Units of the Rate of Reaction

Since concentration is usually expressed in moles/litre and the time is taken in seconds or minutes, the unit of the rate of reaction is moles litre^{-1} sec^{-1} (mol L^{-1} s^{-1}) or moles litre^{-1} min^{-1} (mol L^{-1} min^{-1}).

In case of gaseous reactions, pressures are used in place of molar concentrations. As pressures are expressed in atmospheres, therefore the units of the rate of reaction are atm min^{-1} or atm s^{-1} etc. The relationship between partial pressure of a gas in reaction mixture and its molar concentration follows from the relationship $PV = nRT$

$$\text{i.e., } \frac{n}{V} = \frac{P}{RT}$$

Where partial pressure,

$$P = \frac{\text{No. of moles of the gas}}{\text{Total no. of moles}} \times \text{Total pressure}$$

Reaction Rates

Consider the reaction,

$$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$$

We can specify the rate of this reaction by telling the rate of change of the partial pressures of one the gases. However, it is convenient to convert these pressures into concentrations, so we will write our rates and rate equations in terms of concentrations, where square brackets, [ ], mean concentration in mol/L.

We might try to write the rate variously as,

$$\frac{d[NO_2]}{dt},$$

or as $-\frac{d[O_2]}{dt}$

But these are not the same because each molecule of O_2 gives two molecules of NO_2. To arrive at an unambiguous definition of reaction rate, we define the "reaction velocity," v, as

$$v = \frac{1}{2}\frac{d[NO_2]}{dt} = -\frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[NO]}{dt} \qquad \text{...(1)}$$

This is unambiguous. The negative sign tells us that species is being consumed and the fractions take care of the stoichiometry. Any one of the three derivatives can be used define the rate of the reaction.

For a general reaction,

$$aA + bB \rightarrow cC + dD \qquad \text{...(2)}$$

the reaction velocity can be written in a number of different but equivalent ways,

$$v = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt} \qquad \text{...(3)}$$

As in our previous example, the negative signs account for material that is being consumed in the reaction and the positive signs account for material that is being formed in the reaction. The stoichiometry is preserved by dividing the rate of change of concentration of each substance by its stoichiometric coefficient.

Rate of reaction is not uniform. It goes on decreasing from moment to moment due to decrease in the concentration(s) of reactant(s) with the progress of reaction i.e., with time as shown below by rate vs time curve. Thus, the rate defined above is actually the average rate of reaction during the time interval considered.

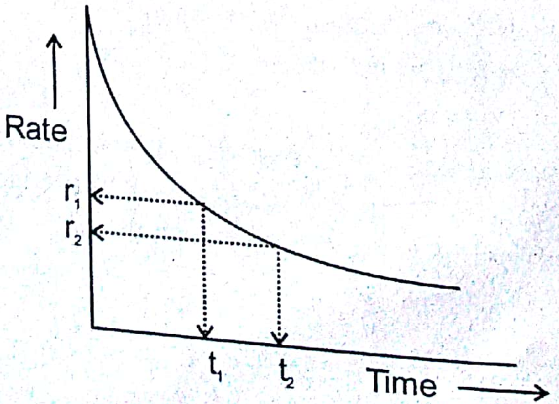


Fig.

The rate of reaction at any time t also called instantaneous rate is as defined below :

$$r_{inst} = \mp\frac{dc}{dt}$$

Where dc is the infinitesimal change in the concentration of the reactant or product during the infinitesimal small time interval dt after time t i.e., between t and t + dt.

dt being infinitesimal small, the rate of reaction may be assumed to be constant (uniform) during this time interval.

$$\text{Unit of rate of reaction} = \frac{\text{Unit of concetration}}{\text{Unit of time}}$$

$$\text{Unit of rate of reaction} = \text{mole litre}^{-1}\ \text{time}^{-1}$$

The rate of reaction at any time t may be determined by plotting concentration (of reactant or product) vs time and drawing a tangent at the point P of the curve corresponding to time t at which rate is to be determined. The slope of the tangent gives rate of reaction at the required time.

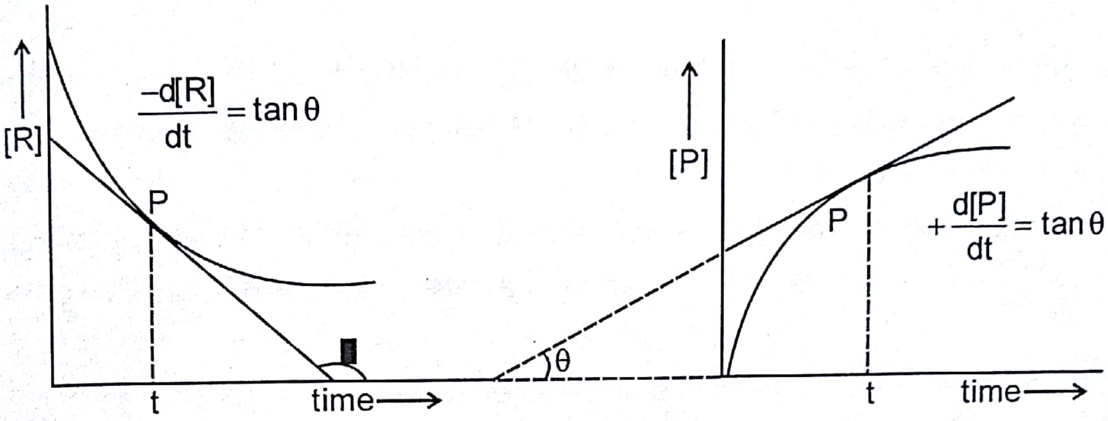


Fig.

([R] = concentration of reactant and [P] = concentration of product)

Rate at the time t = slope of tangent = tanθ

Illustration

In a reaction the concentration of a reactant (A) changes from 0.200 mol litre^{-1} to 0.150 mol litre^{-1} in 10 minutes. What is the average rate of reaction during this interval ?

Solution

$\Delta[A] = [A]_{\text{final}} - [A]_{\text{initial}}$

$= [0.150 - 0.200]$

$= -\ 0.050\ \text{mol litre}^{-1}$

$\Delta t = 10\ \text{minutes}$

Average rate of reaction

$$\frac{-\Delta[A]}{\Delta t} = \frac{0.050}{10} = 0.005\ \text{mol litre}^{-1}\ \text{min}^{-1}$$

Illustration

Decomposition of N_2O_5 is expressed by the equation,

$$N_2O_5 \longrightarrow 2NO_2 + \tfrac{1}{2}O_2$$

If in a certain time interval, rate of decomposition of N_2O_5 is 1.8 × 10^{-3} mol litre^{-1} min^{-1}, what will be the rates of formation of NO_2 and O_2 during the same interval ?

Solution

The rate expression for the decomposition of N_2O_5 is

$$-\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = 2 \times \frac{\Delta[O_2]}{\Delta t}$$

So $\dfrac{\Delta[NO_2]}{\Delta t} = 2\dfrac{\Delta[N_2O_5]}{\Delta t} = 2 \times 1.8 \times 10^{-3}$

$= 3.6 \times 10^{-3}$ mol litre^{-1} min^{-1}

and $\dfrac{\Delta[O_2]}{\Delta t} = \dfrac{1}{2}\dfrac{\Delta[N_2O_5]}{\Delta t} = \dfrac{1}{2} \times 1.8 \times 10^{-3}$

$= 0.9 \times 10^{-3}$ mol litre^{-1} min^{-1}

Rate is always positive and hence = $\dfrac{\Delta[N_2O_5]}{\Delta t}$ is taken positive.

Illustration

If the decomposition of nitrogen (V) oxide $2N_2O_5 \rightarrow 4NO_2 + O_2$, following a first order kinetics.

(i) Calculate the rate constant for a 0.04 M solution, if the instantaneous rate is 1.4×10^{-6} mol L^{-1} s^{-1}.

(ii) Also calculate the rate of reaction when the concentration of N_2O_5 is 1.20 M.

(iii) What concentration of N_2O_5 would give a rate of 2.45×10^{-5} mol L^{-1} s^{-1} ?

Solution

(i) As the given reaction is of first order, therefore,

Rate = $k[N_2O_5]$

or $k = \dfrac{\text{rate}}{[N_2O_5]} = \dfrac{1.4 \times 10^{-6}}{0.04}$ [M = conc. in mol L^{-1}]

$= 3.5 \times 10^{-5} s^{-1}$

(ii) Now if the concentration of N_2O_5 is 1.20 M, then

rate = $k[N_2O_5]$

$= 3.5 \times 10^{-5} \times 1.20 = 4.2 \times 10^{-5}$ mol L^{-1} s^{-1}

(iii) To obtain concentration of N_2O_5 when the rate is 2.45×10^{-5} mol^{-1} s^{-1}, we note that

$$[N_2O_5] = \frac{\text{Rate}}{k} = \frac{2.45 \times 10^{-5}}{3.5 \times 10^{-5}} = 0.7 \text{ mol L}^{-1} \text{ or } 0.7 \text{ M}$$

Factors Affecting the Reaction Rate

The rate of any particular reaction depends upon the following factors :

(i) **Concentration of The Reactants :** Greater the concentrations of the reactants, faster is the reaction. Conversely, as the concentrations of the reactants decrease, the rate of reactions also decreases.

(ii) **Temperature :** The rate of reaction increases with increase of temperature. In most of the cases, the rate of reaction becomes nearly double for 10 K rise of temperature. In some cases, reactions do not take place at room temperature but take place at higher temperature.

(iii) **Presence of Catalyst :** A catalyst generally increases the speed of a reaction without itself being consumed in the reaction. In case of reversible reactions, a catalyst helps to attain the equilibrium quickly without disturbing the state of equilibrium.

(iv) **Surface Area of The Reactants :** For a reaction involving a solid reactant or catalyst, the smaller is the particle size, i.e., greater is the surface area, the faster is the reaction.

(v) **Presence of Light :** Some reactions do not take place in the dark but take place in the presence of light e.g., $H_2 + Cl_2 \rightarrow 2HCl$. Such reactions are called "photochemical reactions".

Now we shall discuss the quantitative effect of concentration and temperature on the rate of reaction. The study of quantitative effect of concentration on the rate of reaction leads to the introduction of a number of new terms such as order of reaction, specific reaction rate (rate constant) and molecularity of reaction. It also leads to the study of mechanism of the reactions. These different aspects are discussed in the following sections.

Rate Law

The mathematical relationship between the rate of reaction and the concentration of the reactant is known as the rate equation or rate law.

According to this law the rate of the reaction is directly proportional to the active concentration of reactant.

For Example :

$$A \longrightarrow \text{Product}$$

$$\text{Rate} \propto [A]^n$$

$$\text{Rate} = k\,[A]^n$$

here : n = order of the reaction

k = Proportionality constant known as rate constant.

If concentration of A is unity i.e., [A] = 1M

then $\boxed{\text{rate} = k}$

this rate is called specific rate and the rate constant is called specific rate constant

The value of rate constant depends on :

(i) Nature of reactant

(ii) Temperature

(iii) Catalyst.

Rate constant for any reaction cannot be predicted by theoretically but must be determined experimentally

For Examples

	Reaction	Experimental rate expression
1.	$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$	Rate = $k[CHCl_3]\,[Cl_2]^{1/2}$
2.	$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$	Rate = $k[CH_3COOC_2H_5]$

Unit of Rate Constant

If $n_1A + n_2B \longrightarrow \text{product}$

according to rate law -

$$R = k[A]^{n_1}[B]^{n_2}$$

$$k = \frac{R}{[A]^{n_1}[B]^{n_2}} = \frac{dc/dt}{[A]^{n_1}[B]^{n_2}}$$

$$= \frac{\text{Concentration}}{\text{time}} \times \frac{1}{(\text{Concentration})^n}$$

where $n = n_1 + n_2$ = order of the reaction

$$= \frac{\text{mol litre}^{-1}\,\text{sec}^{-1}}{(\text{mol litre}^{-1})^n} = (\text{mol litre}^{-1})^{1-n}\,\text{sec}^{-1}$$

$$\boxed{\text{Unit of } k = (\text{mol litre}^{-1})^{1-n}\,\text{sec}^{-1}}$$

Molecularity and Order of a Reaction

(i) Molecularity of a Reaction : The total numbers of reactant molecules involved in the balanced stoichiometric chemical reaction is called molecularity of a reaction

or

The number of reactant species (atoms, ions, or molecules) taking part in an elementary reaction is called molecularity of reaction.

For Example :

$$H_2 + I_2 \longrightarrow 2HI$$

$$2H_2 + 2I_2 \longrightarrow 4HI$$

$$\frac{1}{2}H_2 + \frac{1}{2}I_2 \longrightarrow HI$$

that means molecularity of the reaction never changed with changing the balance equation of the reaction.

$PCl_5 \longrightarrow PCl_3 + Cl_2$	Unimolecular
$2HI \longrightarrow H_2 + I_2$	Bimolecular
$2CO + O_2 \longrightarrow 2CO_2$	Trimolecular

Note :

(i) It is a theoretical value.

(ii) It never be zero, fractional and negative.

(iii) It is always a whole numbers

(iv) Molecularity can be equal or more then order of reaction

(v) It cannot be greater than three because more than three molecular may not mutually collide with each other

(iv) for the complex reaction such as chain reaction, polymerization molecularity cannot be predictable because these are multistep reaction and for multistep reaction molecularity obtained very high.

(ii) Order of a Reaction : It is the sum of powers of concentration of reactants in the rate law expression is called the order of that chemical reaction.

for a reaction

$$A + B \longrightarrow P$$

$$\text{rate law} = k[A]^x[B]^y$$

$$\text{order (n)} = x + y$$

i.e, the order of the reaction is the total number of reactant molecules actively participate in the rate determining step (slow step of the reaction)

According to kinetic theory, molecularity is the number of molecules colliding simultaneously in one step of chemical reaction. Since it is very less probable that more than three molecules collide simultaneously in one step, molecularity rarely exceeds three.

A complicated reaction has no molecularity of its own but molecularity of each of the steps involved in its mechanism.

For example, the reaction : $2NO + 2H_2 \rightleftharpoons N_2 + 2H_2O$, takes place in the sequence of following three steps :

I. $NO + NO \rightleftharpoons N_2O_2$ (fast and reversible)

II. $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$ (slow)

III. $N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast)

The molecularity of each step involved in mechanism is 2 i.e., each step is bimolecular. So as regards the molecularity of the reaction under consideration we simply say that the reaction has mechanism and each step involved in it is bimolecular.

However, there is another view also-according to which molecularity of a complicated reaction is taken to be equal to the number of molecules, atoms or ions of reactant(s) and/or intermediates coming into contact and colliding simultaneously in the slowest step i.e., the rate-determining step of the reaction.

For example, the reaction $ROH + HCl \xrightarrow{ZnCl_2} RCl + H_2O$, which actually is a nucleophilic substitution reaction.

I. $R\ddot{\underset{\cdot\cdot}{O}}H + H^+ \rightleftharpoons R\overset{\oplus}{\ddot{O}}H_2$ (fast)

II. $R-\overset{+}{\ddot{O}}H_2 \rightleftharpoons R^+ + H_2\underset{\cdot\cdot}{\ddot{O}}$ (slow)

III. $R^+ + Cl^- \longrightarrow R-Cl$

Here the step II is the slowest step and hence the r.d.s. the molecularity of which is one.

Note :

(i) It is an experimental value.

(ii) It may be zero, fractional and negative.

(iii) Order is applicable to elementary as well as complex reaction whereas molecularity is applicable only for elementary reaction.

(iv) For complex reaction, order is given by the slowest step and generally molecularity of the slowest step is same as the order of the overall reaction.

(v) Order and molecularity is always same for elementary (simple reaction).

For Example :

(i) $2H_2O_2 \longrightarrow 2H_2O + O_2$

Mechanism -

Step - I $H_2O_2 \longrightarrow H_2O + [O]$ (slow)

Step - II $[O]\,[O] \longrightarrow O_2$ (fast)

$$-\frac{dx}{dt} = k[H_2O_2] \qquad \text{[First order]}$$

(ii) $2NO_2 + F_2 \longrightarrow 2NO_2F$

Mechanism -

Step - I $NO_2 + F_2 \longrightarrow NO_2F + F$ (slow)

Step - II $NO_2 + F \longrightarrow NO_2F$ (fast)

$$-\frac{dx}{dt} = k[NO_2][F_2] \qquad \text{[Second order]}$$

Reaction of Various Order

A reaction is said to be zero order is its rate is not affected by changes in concentrations of one or more reactants i.e., the rate is proportional to the zeroth power of the concentration of the reactants.

Mathematically,

for zero order reaction

	A $\longrightarrow$	P
at t = 0	a	0
at t	(a – x)	x

According to rate law :

$$\frac{dx}{dt} = k[A]^{0} = k \qquad \text{...(i)}$$

Integrate equation :

$$\int dx = \int k\,dt$$

$$x = kt + c \qquad \text{...(ii)}$$

when t = 0, then x = 0

Put this condition in equation (ii)

$$c = 0$$

then $x = kt$ ...(iii)

or $\boxed{k = \frac{x}{t}}$ ...(iv)

Half Life for Zero Order Reaction

when $t = t_{½}$

$x = a/2$

then $k = \frac{a/2}{t_{½}}$

or $\boxed{t_{½} = \frac{a}{2k}}$ ...(v)

At $t = t_{3/4}$ (which is the time required by the reactant to decompose 75%) $x = \frac{3}{4}a$

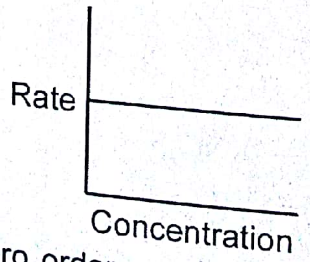
$$t_{3/4} = \frac{3a}{4k_0} = 1.5\ t_{1/2}$$

Thus, $t_{3/4}$ or $t_{1/2} \propto a$

Characteristics of Zero Order Reaction

1. Rate of zero order reaction is independent to the concentration of reactants

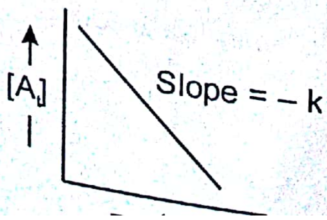
   Rate = k



2. The concentration of a zero order reaction linearly decreased with time

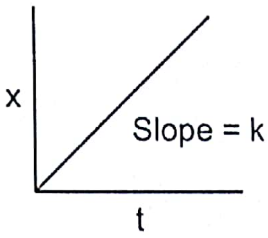
   $kt = x = [A_0] - [A_t]$

   or $[A_t] = [A_0] - kt$



3. The product concentration in zero order reaction linearly increased with time.

$$kt = x$$



4. The half life of a zero order reaction is directly proportional to the initial concentration of reactants.

5. Two half lives are required for 100% completion of a zero order reaction.

$$kt = x$$

$$t = \frac{x}{k} \qquad \text{...(i)}$$

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

$$k = \frac{a}{2t_{1/2}} \qquad \text{...(ii)}$$

putting the value of k in equation (i)

$$t = \frac{x}{a} \times 2t_{1/2}$$

we know that

$$x = 100$$

$$a = 100$$

$$t_{100\%} = \frac{100}{100} \times 2t_{1/2}$$

$$\boxed{t_{100\%} = 2t_{1/2}}$$

Examples :

(i) Photochemical reaction between hydrogen and chlorine

$$H_2(g) + Cl_2(g) \xrightarrow{hv} 2HCl(g)$$

(ii) Decomposition of N_2O on hot platinum surface

$$N_2O \longrightarrow N_2 + \frac{1}{2}O_2$$

(iii) Decomposition of HI on the gold surface

$$2HI \longrightarrow H_2 + I_2$$

(iv) Decomposition of NH_3 in presence of molybdenum or tungsten is a zero order reaction

$$2NH_3 \xrightarrow{[Mo]} N_2 + 3H_2$$

First Order Reaction

A reaction is said to be of first order if its rate is determined by the change of one concentration term only

	$A \longrightarrow$	Products
at t = 0	a	0
at t	(a-x)	x

according to rate law :

$$\frac{dx}{dt} = k[A] = k[a-x]$$

$$\frac{dx}{dt} = \frac{dx}{(a-x)} = k\,dt \qquad \text{...(i)}$$

Integrate equation :

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

$$-\ln (a-x) = kt + c \qquad \text{...(ii)}$$

when $t = 0$, then $x = 0$

then $c = -\ln a$ ...(iii)

Put the value of c in equation in (ii)

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

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

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

$$\boxed{k = \frac{2.303}{t} \log \frac{a}{a-x}} \qquad \text{...(iv)}$$

Also $\log_e(a-x) - \log_e a = -kt$

$$\log_e C - \log_e C_0 = -kt$$

$$\log_e\left(\frac{C}{C_0}\right) = -kt$$

$$C = C_0 e^{-kt}$$

$$N = N_0 e^{-kt}$$

Half Life :

when $t = t_{½}$

$$x = \frac{a}{2}$$

$$k = \frac{2.303}{t_{½}} \log 2$$

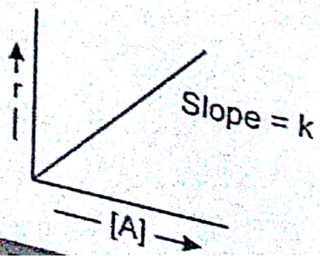
$$\boxed{t_{½} = \frac{.693}{k}} \qquad \text{...(v)}$$

Characteristics of First Order Reaction

1. The rate of a first order reaction is directly proportional to the concentration of reactant.

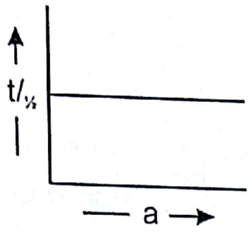
Rate ∝ [A]

Rate = k[A]



2. The half life of first order reaction independent to the initial concentration of reactant

$$t_{½} = \frac{0.693}{k}$$



3. The average life of a first order reaction is inversely proportional to k and is 1.44 times of the half life of the reaction.

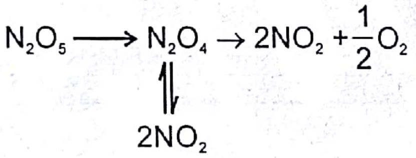
$$\boxed{T_{avg} = \frac{1}{k} = 1.44\ t_{½}}$$

4. Radioactivity is a first order reaction but its rate is independent to all the factors which effect first order kinetics because there is no chemical bonding in the nucleus.

5. The half life of a first order reaction decreased with increasing temperature but half life of radioactivity independent to temperature.

Example of the Reactions of First Order

1. **Decomposition of Nitrogen Pentoxide :** The compound, nitrogen pentoxide, is a volatile solid which decomposes in the gaseous state as well as in the form of its solution in an inert solvent like carbon tetrachloride, chloroform etc. according to the equation.



$$\begin{tikzcd} N_2O_5 \arrow[r] & N_2O_4 \arrow[r] \arrow[d, shift left] & 2NO_2 + \frac{1}{2}O_2 \\ & 2NO_2 \arrow[u, shift left] & \end{tikzcd}$$

(i) When the reaction is carried out in the solution, N_2O_4 and NO_2 remain in the solution and the volume of oxygen gas collected is noted at different intervals of time. It is obvious that Volume of oxygen gas collected at any time (V_t) left $\propto$ Amount of N_2O_5 decomposed (x) i.e.,

$$x \propto V_t$$

(ii) $\left.\begin{array}{l}\text{Volume of oxygen gas collected at} \\ \text{infinite time } (V_\infty) \text{ (which is done by} \\ \text{heating the reaction vessel)}\end{array}\right\} \propto$ Amount of N_2O_5 initially taken (a)

$$a \propto V_\infty$$

i.e., Substituting these value in the first order equation viz.

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

We get $k = \dfrac{2.303}{t}\log\dfrac{V_\infty}{V_\infty - V_t}$

The constancy in the value of k proves the reaction to be of the first order.

Decomposition of Hydrogen Peroxide

The decomposition of hydrogen peroxide in aqueous solution (catalyst by the presence of finely divided platinum) take place according to the equation

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

The kinetics of this reaction may be studied either by the same method as done earlier (i.e collecting the oxygen gas produced and noting its volume at different intervals of time) or by making use of the fast that H_2O_2 solution can be titrated against $KMnO_4$ solution. Thus by withdrawing equa amounts of the solution (usually 5 cc) at regular intervals of time rating against the same KMnO solution, the amount of H_2O_2 present can be found every time. It is obvious that for the same volume of the reaction solution withdrawn,

$$\left.\begin{array}{l}\text{Volume of } KMnO_4 \text{ solution used}\\ \text{before the commencement of the}\\ \text{reaction i.e. at zero time } (V_0)\end{array}\right\} \propto \left\{\begin{array}{l}\text{Initial concentration}\\ \text{of } H_2O_2 \text{ (a)}\end{array}\right.$$

i.e., $a \propto V_0$

$$\left.\begin{array}{l}\text{Volume of } KMnO_4 \text{ solution used}\\ \text{at any instant of time } (V_t)\end{array}\right\} \propto \left\{\begin{array}{l}\text{Amount of } H_2O_2\\ \text{present at that}\\ \text{instant i.e. } (a-x)\end{array}\right.$$

i.e., $(a-x) \propto V_t$

Substituting these values in the first order equation, we get

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

or $$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

The decomposition of hydrogen peroxide, as tested by this equation, is found to be of the first order.

Pseudo Unimolecular Reactions

Consider the following acid-catalysed reactions :

(i) Hydrolysis of ethyl acetate

$$\underset{\text{Ethylaccetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethylalcohol}}{C_2H_5OH}$$

(ii) Inversion of cane-sugar

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Both the above reactions are bimolecular but are found to be of the first order, as experimentally it is observed that

For the first reaction, Rate of reaction $\propto [CH_3COOC_2H_5]$ only

and for the second reaction, Rate of reaction $\propto [C_{12}H_{22}O_{11}]$ only.

The reason for such a behaviour is obvious from the fact that water is present in such a large excess that is concentration remains almost constant during the reaction.

Such reactions which are not truly of the first order but under certain conditions become reactions of the first order are called pseudo-unimolecular reactions.

The kinetics of the above reactions have been studied as follows :

(a) Hydrolysis of Ethyl Acetate

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH$$

In this reaction acetic acid is one of the product, the amount of which can be found by titration against standard NaOH solution. But being an acid-catalysed reaction, the acid present originally as catalyst, also reacts with NaOH solution. Hence a little careful though reveals that for the same volume of reaction mixture withdrawn at different times.

$$\left.\begin{array}{l}\text{Volume of NaOH solution used in}\\ \text{the beginning i.e. at zero time } (V_0)\end{array}\right\}\propto\left\{\begin{array}{l}\text{Amount of acid present only as catalyst}\\ \text{(as no } CH_3COOH \text{ is produced at } t=0\end{array}\right. \quad \text{...(i)}$$

$$\left.\begin{array}{l}\text{Volume of NaOH solution used}\\ \text{at any instant of time t } (V_t)\end{array}\right\}\propto\left\{\begin{array}{l}\text{Amount of acid present as catalyst}\\ +\text{ amount of } CH_3COOH \text{ produced}\end{array}\right. \quad \text{...(ii)}$$

Combining results (i) and (ii), we find that

$$\left.\begin{array}{l}\text{Amount of } CH_3COOH \text{ produced}\\ \text{at any instant of time}\end{array}\right\}\propto (V_t - V_0) \quad \text{...(iii)}$$

$$\left.\begin{array}{l}\text{But amount of } CH_3COOH \text{ produced}\\ \text{at any instant of time}\end{array}\right\}\propto\left\{\begin{array}{l}\text{Amount of } CH_3COOC_2H_5\\ \text{that has reacted (x)}\end{array}\right.$$

Hence $x \propto (V_t - V_0)$ ...(iv)

Further

$$\left.\begin{array}{l}\text{Volume of NaOH solution used after the reaction}\\ \text{has taken place for a long time, say 24 hours or so,}\\ \text{called infinite time } (V_\infty)\end{array}\right\}\propto\left\{\begin{array}{l}\text{Amount of acid present as}\\ \text{catalyst + Max. amount}\\ \text{of } CH_3COOH \text{ produced}\end{array}\right. \quad \text{...(v)}$$

Combining results (i) and (v), we find that

Max. amount of CH_3COOH produced $\propto (V_\infty - V_0)$

But Max. amount of CH_3COOH produced

$\propto$ Initial concentration of $CH_3COOC_2H_5$ ...(vi)

Hence, $a \propto (V_\infty - V_0)$

From equations (iv) and (vi), we have

$$(a - x) \propto (V_\infty - V_0) - (V_t - V_0)$$

or $$(a - x) \propto (V_\infty - V_t) \quad \text{...(vii)}$$

Substituting the values of a and (a – x) from equations (vi) and (vii) in the first order equation, we get

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

or $$k = \frac{2.303}{t}\log\frac{V_\infty - V_0}{V_\infty - V_t}$$

(b) Inversion of Cane Sugar (Sucrose)

Optical Rotation Method

$$\underset{\text{dextro – rotatory}}{\underset{((+);66.5°)}{C_{12}H_{22}O_{11}}} + H_2O \longrightarrow \underset{\text{laevo – rotatory}}{\underline{\underset{\underset{((+);52.5°)}{\text{glucose}}}{C_6H_{12}O_6} + \underset{\underset{((-);-92°)}{\text{fructose}}}{C_6H_{12}O_6}}}$$

In this reaction by the hydrolysis of dextro-rotatory sucrose produces a mixture of glucose (dextro-rotatory) and fructose (laevo rotatory). As laevo rotation of fructose is more therefore the resulting mixture is laevo rotatory.

The kinetics of above reaction is studied by noting the angle of rotation at different inter time using polarimeter.

Say angle of rotation at the start of experiment = r_0

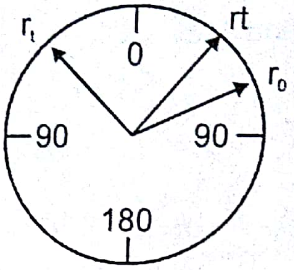
Angle of rotation at any time t = r_t

Angle of rotation at ∞ time = r_∞

Now, Angle of rotation at any instant of time = $(r_0 - r_t) \propto$ amount of sucrose hydrolysed

or $x \propto (r_0 - r_t)$

Similarly, angle of rotation at ∞ time



$= (r_0 - r_\infty) \propto$ initial conc. of sucrose (a)

or $a \propto (r_0 - r_\infty)$

Thus, $(a - x) \propto (r_0 - r_\infty) - (r_0 - r_t)$

$\propto (r_t - r_\infty)$

Hence, $k = 2.303 \log \frac{r_0 - r_\infty}{r_t - r_\infty}$

Second Order Reaction

A reaction is said to be second order if its reaction rate is determined by the variation of two concentration terms.

$$A + B \longrightarrow \text{Products}$$

or

$$2A \longrightarrow \text{Products}$$

Case-I : When A = B

		A	+	B	$\longrightarrow$	P
at	t = 0	a		a		0
at	t	(a–x)		(a–x)		x

According to rate law

$$\frac{dx}{dt} = k[A]\,[B]$$

$$= k(a - x)^2$$

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

Integrated equation :

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

$$\frac{1}{(a-x)} = kt + c \qquad \ldots(ii)$$

when t = 0,

then x = 0,

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

Put the value of c in equation (ii)

$$\frac{1}{(a-x)} = kt + \frac{1}{a} \quad \text{...(iv)}$$

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

$$\boxed{k = \frac{1}{t}\left(\frac{x}{a(a-x)}\right)} \quad \text{...(v)}$$

Half Life :

when $t = t_{½}$

then. $x = \frac{a}{2}$

Put the value in equation (v)

$$k = \frac{1}{t_{½}}\left[\frac{a/2}{a(a-a/2)}\right]$$

or $$t_{½} = \frac{1}{k}\left[\frac{1}{a-a/2} - \frac{1}{a}\right]$$

or $$t_{½} = \frac{1}{k}\left[\frac{2}{a} - \frac{1}{a}\right]$$

or $$\boxed{t_{½} = \frac{1}{ka}}$$

Case-II : When A ≠ B

		A	+	B	$\longrightarrow$	Products
at	t = 0	a		b		0
at	t	(a–x)		(b–x)		x

According to rate law :

$$\frac{dx}{dt} = k(a-x)(b-x)$$

$$\frac{dx}{(a-x)(b-x)} = k\,dt \quad \text{...(i)}$$

Integrated equation :

$$\int \frac{dx}{(a-x)(b-x)} = \int kdt$$

$$\frac{1}{(a-b)} \ln\frac{(a-x)}{(b-x)} = kt + c \quad \text{...(ii)}$$

when $t = 0$,

then $x = 0$

$$c = \frac{1}{(a-b)} \ln\frac{a}{b} \quad \text{...(iii}$$

$$\frac{1}{(a-b)} \ln\frac{(a-x)}{(b-x)} = kt + \frac{1}{(a-b)} \ln\frac{a}{b}$$

$$kt = \frac{1}{(a-b)}\ln\frac{(a-x)}{(b-x)} - \frac{1}{(a-b)}\ln\frac{a}{b}$$

$$\boxed{k = \frac{2.303}{(a-b)t}\log\frac{b(a-x)}{a(b-x)}}$$

Examples :

(i) Hydrolysis of ester by an alkali

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

(ii) The decomposition of NO_2 into NO and O_2

$$2NO_2 \longrightarrow 2NO + O_2$$

(iii) Conversion of ozone into oxygen at 100°c

$$2O_3 \longrightarrow 3O_2$$

nth Order Reaction

$$A \rightarrow \text{Product}$$

Rate law is

$$\frac{dx}{dt} = k[A]^n = k(a-x)^n$$

$$k_n = \frac{1}{(n-1)t}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right] \quad \text{where } n \geq 2$$

- k is expressed in the unit of conc.$^{(1-n)}$ time^{-1}.
- $t_{1/2}$ of nth order reaction is

$$= \frac{2^{n-1}-1}{(n-1)\,k_n\,(a)^{n-1}} \qquad \text{where } (n \geq 2)$$

- If concentration is changed to m times, new rate will be m^n times.

Order	Equation	Unit of the rate constant	Equation for half - life
0	$k = \frac{x}{t}$	mol dm^{-3} s^{-1}	$\frac{a}{2k}$
$\frac{1}{2}$	$k = \frac{2}{t}[a^{1/2} - (a-x)^{1/2}]$	$mol^{1/2}dm^{-3/2}s^{-1}$	–
1	$k = \frac{1}{t}\ln\left[\frac{a}{a-x}\right]$	s^{-1}	$\frac{0.693}{k}$
$\frac{3}{2}$	$k = \frac{2}{t}\left[\frac{1}{(a-x)^{1/2}} - \frac{1}{a^{1/2}}\right]$	$dm^{3/2}mol^{-1/2}s^{-1}$	–
2	$k = \frac{x}{ta(a-x)}$	dm^3 $mol^{-1}s^{-1}$	$\frac{1}{k \cdot a}$
3	$k = \frac{2ax - x^2}{2ta(a-x)^2}$	$dm^6mol^{-2}s^{-1}$	$\frac{3}{2ka^2}$
⋮	⋮	⋮	⋮
n	$k = \frac{1}{t(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]$	$dm^{3n-3}mol^{1-n}s^{-1}$	$2^{n-1}-1$

Methods for Determination the Order of a Reaction

The order of a reaction is never known before hand, thought majority of reactions are first order or second order.

The following methods are commonly used for determining the order of a reaction.

1. Method of Integration

for any reaction :

$$\text{rate}(r) \propto c^n$$

If r_1 and r_2 are the rates at two different reactant concentration c_1 and c_2

Then $\frac{r_2}{r_1} = \left(\frac{c_2}{c_1}\right)^n$ n = order of reaction

taking logs both the sides -

$$\ln\frac{r_2}{r_1} = n \ln\frac{c_2}{c_1}$$

$$\boxed{n = \frac{\ln(r_2/r_1)}{\ln(c_2/c_1)}}$$

2. Half Life Method

A general expression for the half life, ($t_{1/2}$), is given by :

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

If t_1 and t_2 are the half lives of a reaction at two different initial concentration a_1 and a_2

$$\frac{t_2}{t_1} = \left(\frac{a_1}{a_2}\right)^{n-1}$$

taking logs :

$$\ln\frac{t_2}{t_1} = (n-1) \ln\frac{a_1}{a_2}$$

or $\boxed{n = 1 + \frac{\ln t_2/t_1}{\ln a_1/a_2}}$

3. The use of Integral Rate Expression

We have already demonstrated this method in solving problems for reactions of various orders. If the plot of Inc versus t is a straight line, the reaction is first order.

Similarly, the integrated expression for the second order reaction can be utilized graphically to as certain if the reaction is second-order, and so on.

4. Determination of order with respect to each reactants (Ostwald's isolation method)

In this method all the reactants except one are taken in large quantities so that concentrations remain constant through all this change.

Thus the order of the reaction is determined with respect to the isolated reactant which is not taken in large quantity.

for example,

$$aA + bB + cC \longrightarrow \text{Product}$$

So rate should be :

$$\text{rate} = kC_A^a \cdot C_B^b \cdot C_C^c$$

(i) If A and B are taken in large amount than C then reaction rate is given with respect to C

$$\text{rate} = kC_C^c \qquad ...(i)$$

(ii) If B and C are taken in large amount then A and order is determined with respect to A

$$\text{rate} = kC_A^a \qquad ...(ii)$$

(iii) If A and C are taken in large amount then B then reaction rate is given with respect to B

$$\text{rate} = kC_B^b \qquad ...(iii)$$

the total order of the reaction will be sum of orders obtained in each experiments.

$$\text{Order} = a + b + c$$

Temperature Coefficient

"Temperature coefficient of a chemical reaction is defined as the ratio of rate constants of a reaction at two temperatures differing by 10°C".

∴ Temperature coefficient = $\frac{k_{T+10}}{k_T}$ » 2 to 3

where k_T is the rate constant at temperature TK and k_{T+10} is the rate constant at temperature (T+10)K. This ratio generally falls between 2 and 3 which means for most of the chemical reactions, the rate becomes two or three folds for every 10°C rise in temperature.

Arrhenius Equation

Arrhenius proposed the following empirical equation for calculating the energy of activation of a reaction having the rate constant k at temperature T :

According to Arrhenius increasing temperature rate increases pre-exponentially -

$$\boxed{k = Ae^{-E_a/RT}} \qquad ...(i)$$

where E_a = Activation energy

A = Arrhenius parameter or Pre-exponentially factor

or frequency factor or Arrhenius coefficient

k = rate constant

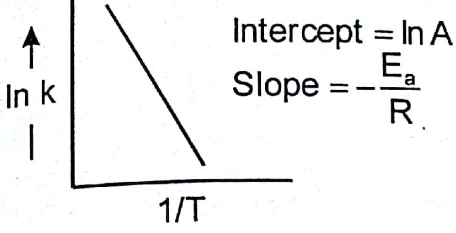
The unit of Arrhenius parameter is the unit of rate constant because $\frac{E_a}{RT}$ is a unit less quantity.

$$\boxed{k = A \text{ unit}}$$

Taking logs of equation (i)

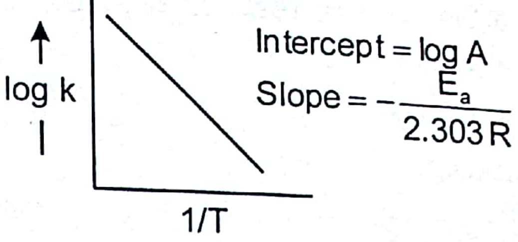
$$\ln k = \ln A - \frac{E_a}{RT} \qquad ...(ii)$$

$$\log k = \log A - \frac{E_a}{2.303\,RT} \qquad ...(iii)$$



Intercept = ln A

Slope = $-\frac{E_a}{R}$



Intercept = log A

Slope = $-\frac{E_a}{2.303\,R}$

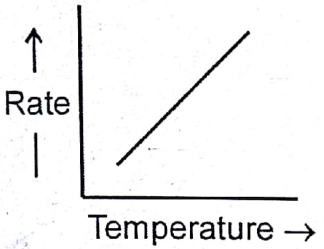
Integrated equation (iii) between temperature T_1 and T_2 when the corresponding rate constant are k_1 and k_2 respectively and assuming that E_a is constant over this temperature range, we obtain

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

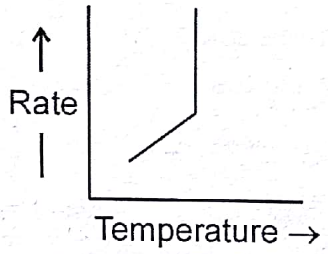
or

$$\boxed{\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]} \qquad \text{...(iv)}$$

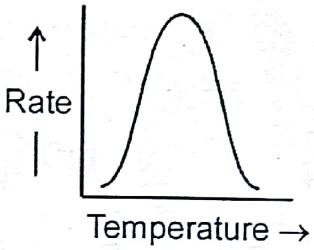
- This is the integrated Arrhenius equation thus, knowing the rate constant at two different temperature, the energy of activation E_a can be easily determined.
- Reactions on the basic of influence of temperature can be classified into give types-



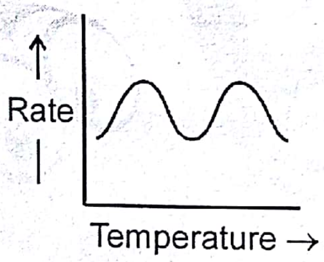
(Normal reaction)



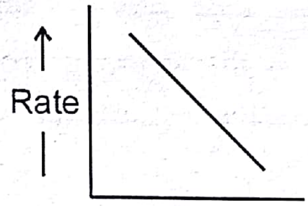
Explosive reaction



Biological reaction



Oxidation of carbon



$2NO + O_2 \rightarrow 2NO_2$

The only reaction with negative temperature coefficient

The Collision Theory of Reaction Rates

- According to collision theory, a chemical reaction can take place only by collision of molecule to each other.

  Rate ∝ numbers of colliding molecules per litre per second.
- More the concentration of reactant, more will be the possibilities of collision, hence more will be the rate of the reaction

  So, Rate ∝ product of concentration of reactant
- Every collision does not lead to product formation. A collision will be successful of colliding reactant molecules have minimum value of energy i.e., Activation energy.

However not every collision lead to reaction even if energy requirement is satisfied because the colliding reactant molecules must be a certain relative orientation.

Therefore the main three necessities for a reaction to proceed are :

(i) Collision between the reactant molecules

(ii) Activation energy

(iii) Orientation of molecules

Suppose a bimolecular reaction proceeds as :

$$A + A \rightarrow P$$

or $$A + B \rightarrow P$$

Rate of reaction

$$\frac{d[P]}{dt} = k[A]^2$$

$$\frac{d[P]}{dt} = k[A][B] \qquad \text{...(1)}$$

If the concentration of reactants are unity then rate of reaction is equal to the rate constant k

$$\frac{d[P]}{dt} = k \qquad \text{...(2)}$$

According to the collision theory this rate constant depends upon collision :

$$k = Zq \qquad \text{...(3)}$$

here Z = number of collision per mol per second

q = fraction of activated molecules

$$q = \frac{\text{number of activated molecules}}{\text{number of total molecules}}$$

$$q = \frac{n^*}{n} = e^{-E_a/RT} \qquad \text{...(4)}$$

here E_a = Energy of Activation

So $$\boxed{k = Z.e^{-E_a/RT}} \qquad \text{...(5)}$$

Collision number (Z) is calculated by the following process :

According to kinetic theory of gasses the total number of collision per second of all n-molecules that are contained in 1 cm^3 of gas is -

$$\boxed{Z_{AA} = \frac{1}{2}\sqrt{2}\pi d^2 n^2 \overline{c}} \qquad \text{...(6)}$$

Here : d is the distance between the centre of the spheres when the collision occur, also called mean collision diameter

n = number of molecules per cc of gas

$\overline{c}$ = average velocity of each molecule

$$= \sqrt{\frac{8kT}{\pi m}} \qquad \text{...(7)}$$

Here k = boltzmann constant

m = mass of each molecule

from equation (6) and (7)

$$Z_{AA} = \frac{1}{2}\sqrt{2}\pi d^2 \sqrt{\frac{8kT}{\pi m}} \cdot n^2$$

$$Z_{AA} = 2n^2 d^2 \sqrt{\frac{\pi kT}{m}} \qquad \text{...(8)}$$

or if $n^2 = 1$

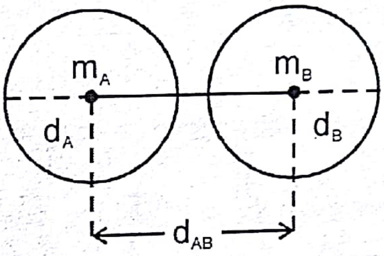
$$\boxed{Z_{AA} = d_{AA}^2\sqrt{\frac{4\pi kT}{m}}}$$

The corresponding expression for the frequency Z_{AB} between unlike molecule. A & B of mass m_A and m_B respectively n_A and n_B are unity then

$$\boxed{Z_{AB} = d_{AB}^2\sqrt{\frac{8\pi kT}{\mu}}} \quad \text{...(9)}$$

where μ is reduced mass $= \dfrac{m_A m_B}{m_A + m_B}$ ...(10)

d_{AB} is known as collision cross reaction



$$d_{AB} = \frac{d_A + d_B}{2} \quad \text{...(11)}$$

from eq.(9) and (10)

$$Z_{AB} = d^2{}_{AB}\sqrt{8\pi kT\left[\frac{m_A + m_B}{m_A m_B}\right]} \quad \text{...(12)}$$

So rate of reaction

[Collision between like molecules]

$$\frac{d[P]}{dt} = k = Z_{AA} \cdot e^{-E_a/RT} = d^2{}_{AA}\sqrt{\frac{4\pi kT}{m}}\, e^{-E_a/RT} \quad \text{...(13)}$$

[Collision between unlike molecules]

$$\frac{d[P]}{dt} = k = Z_{AB} \cdot e^{-E_a/RT} = d^2{}_{AB}\sqrt{8\pi kT\left[\frac{m_A + m_B}{m_A m_B}\right]}\, e^{-E_a/RT} \quad \text{...(14)}$$

Comparing the theoretical equation of collision theory with Arrhenius equation

According to collision theory

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

In generally the Arrhenius equation.

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

So if z = A then both equation are same.

Steric Factor

Collision must occur in order for a chemical reaction to proceed but they do not guarantee that a reaction will occur. If colliding molecules have improper orientations, they do not react even though they may possess sufficient energy. To account for effective collisions, another factor P, called steric factor is introduced. The fraction of collisions having proper orientation for conversions of reactants to products is called steric factor, P.

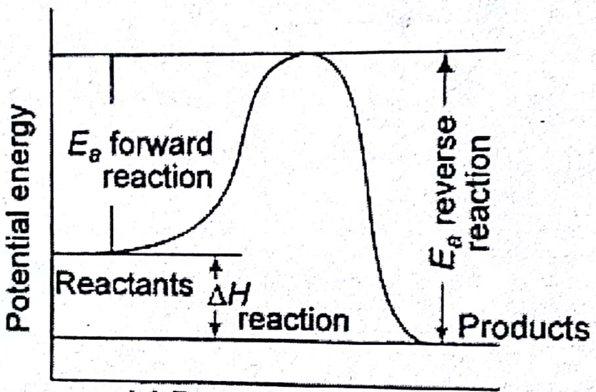
$$k = PZ_{AB} \cdot e^{-E_a/RT}$$

Absolute Reaction Rate Theory or Transition State Theory or Activated Complex Theory

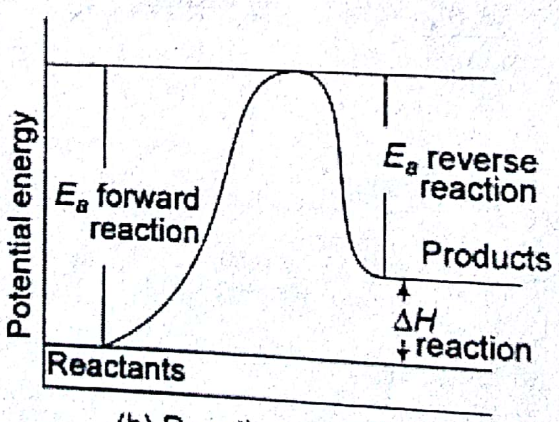
It is developed by Eyring, Polanyi and Evans in 1935. According to this theory bimolecular reaction between two molecules takes place through the formation of the activated complex.

$$\underset{\text{Reactions}}{A+B} \rightleftharpoons \underset{\substack{\text{Transition state} \\ \text{(Activated complex)}}}{[AB]^{\bullet}} \longrightarrow \text{Products}$$

The activation energy, E_a is the additional energy that must be absorbed by the reactants in their ground states to allow them to reach the transition state. If they do possess sufficient energy to reach the transition state, the reaction can proceed.



(a) Reaction coordinate



(b) Reaction coordinate

Fig. : Potential energy diagram (a) for exothermic reaction, (b) endothermic reaction

Rate of reaction = frequency of crossing energy barrier
× concentration of activated complexes at the top of energy barrier
× probability of crossing the barrier

Rate of reaction

$$= \frac{1}{\delta} \times \left(\frac{kT}{2\pi m}\right)^{1/2} \times C^{\bullet} \times \frac{(2\pi mkT)^{1/2}\,\delta}{h}$$

$$= C^{\bullet}\,\frac{kT}{h} \qquad \ldots(1)$$

$\frac{kT}{h}$ = Universal frequency with dimension of time^{-1}. Its value depends only on temperature.

Rate of formation of activated complex = Rate of decomposition of activated complex

$$k_S C_A C_B = C^{\bullet} \frac{kT}{h}$$

(k_S = Specific reaction rate, C_A and C_B are the concentration of A and B respectively)

$$k_S = \frac{C^{\bullet}}{C_A C_B} \cdot \frac{kT}{h} \qquad \text{...(2)}$$

On applying law of mass action to the following equilibrium

$$A + B \rightleftharpoons [AB]^{\bullet}$$

$$K^{\bullet} = \frac{C^{\bullet}}{C_A C_B} \quad (K^{\bullet} = \text{equilibrium constant})$$

On substituting the value of $C^{\bullet}$ in equation (2), we get

$$k_S = \frac{kT}{h} \cdot K^{\bullet} \qquad \text{...(3)}$$

From statistical mechanics, the value of equilibrium constant can be written in terms of partition function as

$$K^{\bullet} = \frac{q^{\bullet}}{q_A q_B} \cdot e^{-\Delta E_0/RT} \qquad \text{...(4)}$$

where, $q^{\bullet}$, q_A and q_B are partition functions of the activated complex and reactants A and B respectively, ΔE_0 = heat of activation.

On substituting the value of $K^{\bullet}$ in equation (3), we get

$$k_S = \frac{kT}{h} \cdot \frac{q^{\bullet}}{q_A q_B} \cdot e^{-\Delta E_0/RT} \qquad \text{...(5)}$$

Eyring's Equation

The equation of the theory of absolute reaction rate can be expressed in terms of thermodynamical functions instead of partition functions.

$$k_S = \frac{kT}{h} \cdot e^{-\Delta H^{\bullet}/RT} \cdot e^{\Delta S^{\bullet}/R}$$

The above equation is known as Eyring's equation.

Transmission Coefficient

It is not necessary that every activated complex is converted into the products. To allow for this possibility, it is convenient to introduce a transmission coefficient K in equation (5)

$$k_s = K \frac{kT}{h} \frac{q^{\bullet}}{q_A q_B} e^{-\Delta E_0/RT}$$

For many reactions the value of transmission coefficient is unity. It means that every activated complex becomes a product. However, the value of K is less than unity in the following types of reactions.

1. Reactions in which there is a change from one type of electronic state to another.
2. Bimolecular atom recombination in the gas phase.
3. The reverse decomposition of atomic molecules.

In certain cases the value of K is greater than unity due to quantum mechanical tunnelling.

Comparison of Absolute Reaction Rate Theory With Arrhenius Equation

Arrhenius equation is given as

$$k_S = Ae^{-E_a/RT} \qquad ...(6)$$

where, 'A', the pre exponential factor is known as the "frequency factor'. However the physical significance of the frequency could not be explained. But the physical significance of 'A' can be explained using Absolute Reaction Rate (ARR) theory.

Consider equation (5)

$$k_S = \frac{kT}{h} \cdot \frac{q^*}{q_A q_B} e^{-\Delta E_0/RT}$$

Replacing ΔE_0 by E_a, energy of activation, we get

$$k_S = \frac{kT}{h} \cdot \frac{q^*}{q_A q_B} e^{-E_a/RT}$$

On comparing the above equation with equation (6), the value of 'A' can be obtained as

$$A = \frac{kT}{h} \frac{q^*}{q_A q_B} \qquad ...(7)$$

From thermodynamics,

$$q_A = \frac{(2\pi m_A kT)^{3/2}}{h^3} \qquad ...(8)$$

$$q_B = \frac{(2\pi m_B kT)^{3/2}}{h^3} \qquad ...(9)$$

$$q^* = \left[\frac{(2\pi(m_A + m_B)kT)^{3/2}}{h^3}\right]\left[\frac{8\pi^2\ IkT}{h^2}\right] \qquad ...(10)$$

where, I is the moment of inertia and its value is given as

$$I = \sigma^2 \left[\frac{m_A m_B}{m_A + m_B}\right]$$

where, σ is the mean diameter of the activated complex. Substituting the values of q_A, q_B, q^* and I in equation (7) we get

$$A = \frac{kT \times \dfrac{(2\pi(m_A + m_B)kT)^{3/2} \cdot \dfrac{8\pi^2 m_A m_B \sigma^2 kT}{(m_A + m_B)h^2}}{h^3}}{h \times \dfrac{(2\pi m_A kT)^{3/2}}{h^3} \cdot \dfrac{(2\pi m_B kT)^{3/2}}{h^3}}$$

$$A = \left[\frac{8\pi(m_A + m_B)}{m_A m_B} kT\right]^{1/2} \sigma^2$$

$$A = \left[\frac{8\pi(Nm_A + Nm_B) \cdot kTN}{Nm_A \cdot Nm_B}\right]^{1/2} \sigma^2$$

$$A = \left(8\pi \frac{M_A + M_B}{M_A \cdot M_B} RT\right)^{1/2} \sigma^2 \qquad ...(11)$$

where, Nm = M and R = Nk

This equation for A indicates its physical significance.

Enzyme Kinetics

Enzyme

Enzymes are the homogenous biological catalyst, Basically the enzymes are all proteins but they are associated with non-protein substances known as co-enzyme or prosthetic group.

A catalyst is defined as a substances which increases the rate of reaction without undergoing any change and can be recovered as such at the completion of the reaction.

The phenomenon of increase in the rate of a reaction with the help of a catalyst is known as catalysis.

Kinetics of Enzyme Catalyzed Reactions

In 1913, biochemist Michaelis and menton proposed a mechanism for the kinetics of enzyme - catalyzed reaction.

According to this mechanism an enzyme substrate complex is formed in the first step and product is formed in the second step.

Step-1 :

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES \text{ Complex} \qquad \text{(Fast)}$$

Step-2 :

$$ES \xrightarrow{k_3} P + S \qquad \text{(Slow)}$$

where E = Enzyme ;
S = Substrate
ES = Enzyme substrate complex
P = Product

The rate of product formation according to this mechanism is -

$$\text{Rate} = k_3 [ES] \qquad \text{...(1)}$$

Applying steady state approximation :

$$\frac{d[ES]}{dt} = k_1[E][S] - k_2[ES] - k_3[ES] = 0 \qquad \text{...(2)}$$

[E] cannot be measured experimentally. The equation between the free and the bound enzyme is given by the enzyme conservation equation :

$$[E_0] = [E] + [ES]$$

$$[E] = [E_0] - [ES] \qquad \text{...(3)}$$

where $[E_0]$ = Total enzyme concentration putting the value of [E] in equation - (2)

$$\frac{d[ES]}{dt} = k_1\{[E_0] - [ES]\}[S] - k_2[ES] - k_3[ES] = 0$$

$$= k_1[E_0][S] - k_1[ES][S] - k_2[ES] - k_3[ES] = 0$$

$$k_1[E_0][S] = k_1[ES][S] + k_2[ES] + k_3[ES]$$

$$[ES] = \frac{k_1[E_0][S]}{k_1[S] + k_2 + k_3} \qquad \text{...(4)}$$

Putting the value of [ES] in equation (i)

$$\text{Rate} = \frac{k_1 k_3 [E_0][S]}{k_1[S] + k_2 + k_3} \qquad \text{...(5)}$$

Cont

Dividing numerator and denominator by k_1

$$\text{Rate} = \frac{k_3[E_0][S]}{[S] + \frac{k_2 + k_3}{k_1}}$$

$$\boxed{\text{Rate} = \frac{k_3[E_0][S]}{[S] + K_m}} \qquad \text{...(6)}$$

where $K_m = \frac{k_2 + k_3}{k_1}$ = constant = Michaelis constant

Note that k_m is not an equilibrium constant.

Equation (6) is known as the Michaelis - menton equation when all the enzyme has reacted with substrate at high concentration, the reaction will be going at maximum rate. No free enzyme will remain so that

$$[E_0] = [ES]$$

Hence from equation (1)

$$R_{max} = V_{max} = K_3\,[E_0] \qquad \text{...(7)}$$

The Michaelis-menton equation can now be written as

$$\text{Rate} = \frac{V_{max}[S]}{K_m + [S]} \qquad \text{...(8)}$$

Two cases arrises :

(a) if $K_m << [S]$, then

$$\text{Rate} = \frac{V_{max}[S]}{[S]}$$

$$\text{Rate} = V_{max} = \text{constant} \qquad \text{(zero order reaction)} \qquad \text{...(9)}$$

(b) if $K_m >> [S]$, then

$$\text{Rate} = \frac{V_{max}[S]}{K_m} \qquad \text{(first order reaction)} \qquad \text{...(10)}$$

(c) if $K_m = [S]$, then

$$\text{Rate} = \frac{1}{2}\,V_{max} \qquad \text{...(11)}$$

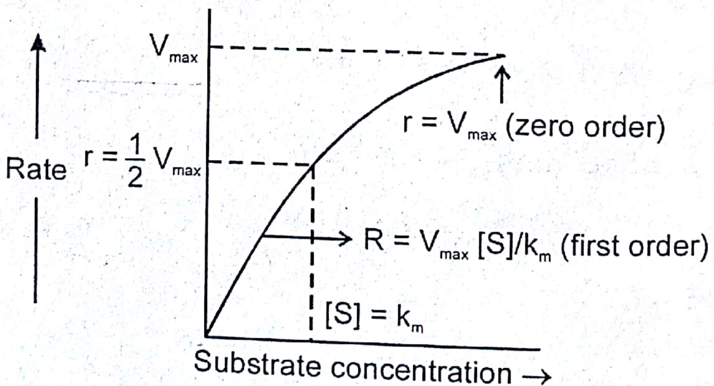


Fig. : Kinetics of An Enzyme - Catalysed Reaction

The constant k_3 is called the turnover number of the enzyme. The turnover number is the number of molecules converted in unit time by one molecule of enzyme.