

Chapter-9

CHEMICAL KINETICS

“The branch of chemistry, which deals with the study of reaction rates, the factors affecting reaction rates and also mechanism of reactions, is called chemical kinetics”.

Rate of reaction:

Rate of reaction means speed of reaction.

It is defined as *“The change in concentration of reactant or product occurred per unit time.”*

or

“The amount of reactant consumed or amount of product produced in unit time” is called rate of reaction.

Consider a general reaction: $A + B \rightarrow C + D$

Rate of this reaction can be given in four ways:

$$\text{Rate} = -\frac{\Delta A}{\Delta t} \quad \text{or} \quad \text{Rate} = -\frac{\Delta B}{\Delta t} \quad \text{or} \quad \text{Rate} = \frac{\Delta C}{\Delta t} \quad \text{or} \quad \text{Rate} = \frac{\Delta D}{\Delta t}$$

Where as:

ΔA , ΔB , ΔC and ΔD are changes in concentration of A, B, C and D respectively.

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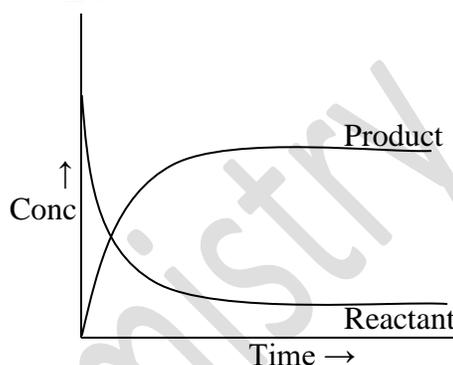
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A general reaction can also be written as: $R \rightarrow P$

$$\text{Then} \quad \text{Rate} = -\frac{\Delta R}{\Delta t} \quad \text{or} \quad \text{Rate} = \frac{\Delta P}{\Delta t}$$

Where R stands for reactant and P for product

The rate of a reaction at any moment is called instantaneous rate of reaction i.e. dx/dt .



The graph is showing changes in concentration with time. It is clear that with passage of time rate of reaction becomes slow and slow.

Consider a more general reaction

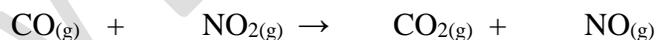


Rate of this reaction can be given as

$$\text{Rate} = -\frac{1}{a} \cdot \frac{d[A]}{dt} = -\frac{1}{b} \cdot \frac{d[B]}{dt} = \frac{1}{c} \cdot \frac{d[C]}{dt} = \frac{1}{d} \cdot \frac{d[D]}{dt}$$

Let apply the concept to some actual reaction

e.g.



$$\text{Rate} = -\frac{\Delta[\text{CO}]}{\Delta t} \quad \text{or} \quad \text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t} \quad \text{or} \quad \text{Rate} = \frac{\Delta[\text{CO}_2]}{\Delta t} \quad \text{or} \quad \text{Rate} = \frac{\Delta[\text{NO}]}{\Delta t}$$

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Units of reaction rate:

It has unit of concentration divided by unit of time i.e. conc per unit time e.g. $\text{mol.dm}^{-3}.\text{s}^{-1}$, M.s^{-1} ,

It is also expressed in amount per unit time e.g. g.s^{-1} , mol.s^{-1} , $\text{dm}^3.\text{s}^{-1}$, atm.s^{-1} etc.

Rate Law and Rate constant or velocity constant:

Rate law states “Rate of a reaction is directly proportional to the product of active masses of reactants raised to power of some numbers which are practically determined”.

Consider a general reaction $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$

$$\text{Rate or } dx/dt \propto [\text{A}]^m [\text{B}]^n$$

Or $\boxed{\text{Rate} = \frac{dx}{dt} = k [\text{A}]^m [\text{B}]^n}$This is rate equation.

Square brackets “[]” represent molar concentration. Molar concentrations are often taken as active masses in case of solutions.

k is rate constant.

Specific Rate Constant:

If molar concentrations of reactants are taken as unity then rate constant will be equal to rate of reaction and is known as specific rate constant or velocity constant.

$$\begin{aligned} dx/dt &= k (1)^m (1)^n \\ dx/dt &= k \end{aligned}$$

But this is not always true as

- (i) Some time concentration of some reactant cannot be made unity.
- (ii) During reaction, concentration changes and can't remain as unity.

So more precisely we can write $dx/dt = k.f(a.b.c.....)$ where f stands for function

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Let apply rate law to some actual reactions.



A series of reactions are performed and initial rates of reactions were noted as given in the table below. Rates are given in $\text{mol dm}^{-3} \text{sec}^{-1}$, and $k = 0.50 \text{ dm}^3 \text{mol}^{-1} \text{sec}^{-1}$.

Expt	Series 1			Expt	Series 2			Expt	Series 3		
	[CO]	[NO ₂]	Rate		[CO]	[NO ₂]	Rate		[CO]	[NO ₂]	Rate
1	0.10	0.10	0.005	1	0.10	0.20	0.010	1	0.10	0.30	0.015
2	0.20	0.10	0.010	2	0.20	0.20	0.020	2	0.20	0.30	0.030
3	0.30	0.10	0.015	3	0.30	0.20	0.030	3	0.30	0.30	0.045
4	0.40	0.10	0.020	4	0.40	0.20	0.040	4	0.40	0.30	0.060

For CO consider expt-1 and expt-2 in series 1

$$[C_2/C_1]^n = [R_2/R_1]$$

$$[0.20/0.10]^n = [0.010/0.005]$$

$$[2]^n = [2]$$

$$[2]^1 = [2]$$

So $n = 1$

For NO₂ consider expt-1 in series 1 & 2

$$[C_2/C_1]^n = [R_2/R_1]$$

$$[0.20/0.10]^n = [0.010/0.005]$$

$$[2]^n = [2]$$

$$[2]^1 = [2]$$

So $n = 1$

This means rate of reaction is directly proportional to molar concentration of CO.

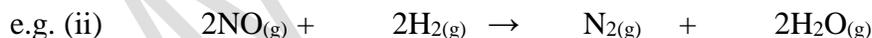
$$\text{Rate or } dx/dt \propto [\text{CO}]$$

Similarly it is evident from above data

$$\text{Rate or } dx/dt \propto [\text{NO}_2]$$

Thus overall reaction rate can be given as

$$\text{Rate or } dx/dt = k [\text{CO}] [\text{NO}_2]$$



A set of experiments were performed and results are given in table below.

Expt No	Conc of NO	Conc of H ₂	Initial rate (atm/min)
1	0.006	0.001	0.025
2	0.006	0.002	0.050
3	0.006	0.003	0.075
4	0.001	0.009	0.0063
5	0.002	0.009	0.0252
6	0.003	0.009	0.0567

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To see the effect of change in concentration of NO on rate of reaction consider expt-4 and expt-5

$$\begin{aligned} [C_2/C_1]^n &= [R_2/R_1] \\ [0.002/0.001]^n &= [0.0252/0.0063] \\ [2]^n &= [4] \\ [2]^2 &= [4] \end{aligned}$$

So $n = 2$

This means rate of reaction is directly proportional to square of molar concentration of NO.

$$\text{Rate or } dx/dt \propto [\text{NO}]^2$$

To see the effect of change in concentration of H₂, on rate of reaction consider expt-1 and expt-2.

$$\begin{aligned} [C_2/C_1]^n &= [R_2/R_1] \\ [0.002/0.001]^n &= [0.050/0.025] \\ [2]^n &= [2] \\ [2]^1 &= [2] \end{aligned}$$

So $n = 1$

This means rate of reaction is directly proportional to molar concentration of H₂.

$$\text{Rate or } dx/dt \propto [\text{H}_2]$$

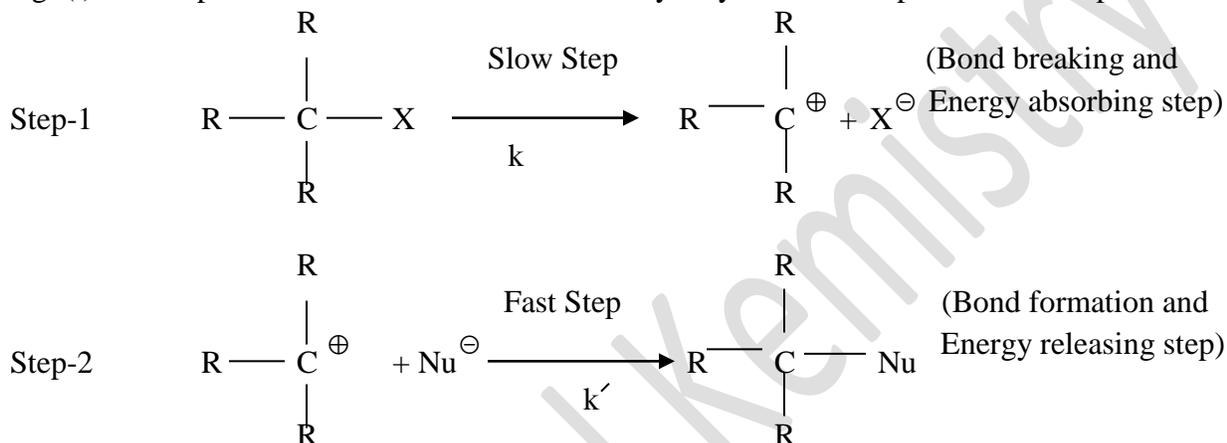
Thus overall reaction rate can be given as

$$\text{Rate or } dx/dt = k [\text{NO}]^2 [\text{H}_2]$$

Rate determining step:

If a reaction occurs in more than one steps then the slow step of the reaction will be rate determining step. This step is often energy absorbing step and is non-spontaneous process.

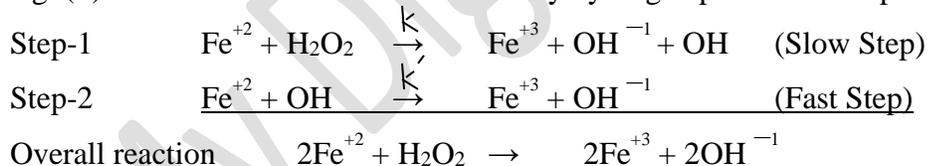
e.g. (i) Nucleophilic substitution reaction of tertiary alkyl halide take place in two steps.



As Step-1 is slow step so it is rate-determining step. Thus rate equation can be written as $k' < k$ which means that step-1 is slow while step-2 is fast.

$$\frac{dx}{dt} = k [\text{R}_3\text{C-X}]$$

e.g. (ii) Oxidation of ferrous to ferric ion by hydrogen peroxide take place in two steps.



Specific rate constant k' is thousand times greater than k so 2nd step is much fast then 1st step, therefore, 1st step is slow and rate-determining step. The free radical "OH" produced in 1st step is unstable and thus it rapidly reacts in 2nd step, so 2nd step is fast step. So rate of reaction will be determined from 1st step. The rate equation can be written as:

$$\frac{dx}{dt} = k [\text{Fe}^{+2}] [\text{H}_2\text{O}_2]$$

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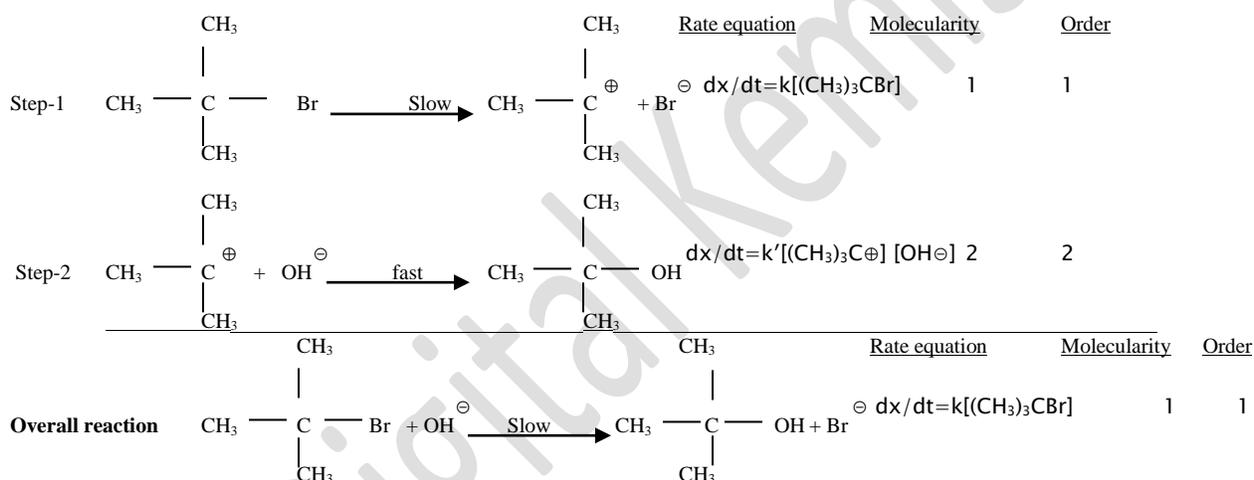
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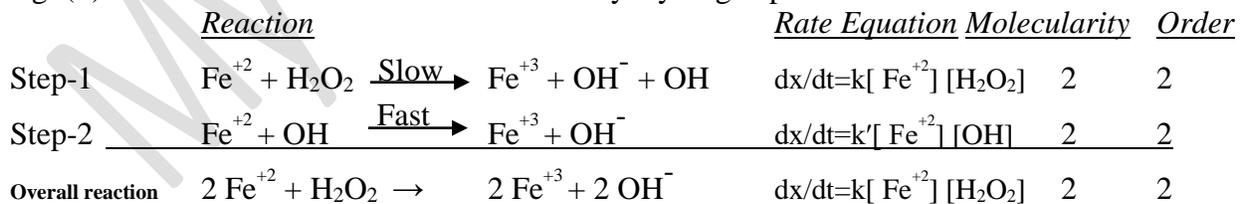
Order and Molecularity of a Reaction:

- “Sum of stoichiometric coefficients of reactants appearing in balanced chemical equation of rate determining step of a reaction” is called **molecularity of the reaction**.
- “Sum of exponents of concentration terms of reactant”s in the rate equation is called **order of reaction**.
- Although all steps of a reaction have their orders and molecularities but the order as well as molecularity of overall reaction is determined from rate determining step.

e.g. (i) Unimolecular Nucleophilic Substitution reaction of Tertiary Butyl Bromide



e.g. (ii) Oxidation of Ferrous ion to Ferric ion by Hydrogen peroxide



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e.g. (iii)	Reduction of Ferric Chloride by Potassium Iodide				
	<u>Reaction</u>	<u>Rate Equation</u>	<u>Molecularity</u>	<u>Order</u>	
Step-1	$2\text{FeCl}_3 + 4\text{KI} \xrightarrow{\text{Slow}} 2\text{FeI}_2 + 4\text{KCl} + 2\text{Cl}^-$	$\text{dx/dt} = k[\text{FeCl}_3][\text{KI}]^2$	6	3	
Step-2	$2\text{KI} + 2\text{Cl}^- \xrightarrow{\text{Fast}} 2\text{KCl} + \text{I}_2$	$\text{dx/dt} = k'[\text{KI}]^x[\text{Cl}^-]^y$	4	$x + y$	
Overall reaction	$2\text{FeCl}_3 + 6\text{KI} \longrightarrow 2\text{FeI}_2 + 6\text{KCl} + \text{I}_2$	$\text{dx/dt} = k[\text{FeCl}_3][\text{KI}]^2$	6	3	

- Order of an individual step can be obtained by summation of orders with respect to individual reactants
- e.g. in above case

Order of step-1 = order w.r.t. FeCl_3 + order w.r.t. $\text{KI} = 1 + 2 = 3$

Order of step-2 = order w.r.t. KI + order w.r.t. $\text{Cl}^- = x + y$

Examples of Various Orders of Reactions:

FIRST ORDER REACTIONS:

“The reaction, in which the rate of reaction is directly proportional to the first power of a single reactant, is called first order reaction” or “a reaction whose rate is directly proportional to the concentration of a single reactant” is called first order reaction.



$$\text{dx/dt} = k[\text{A}]$$

- Unit of its rate constant is s^{-1} .

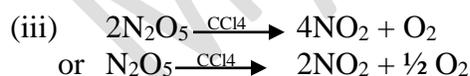
Examples:



$$\text{dx/dt} = k[\text{Br}_2]$$



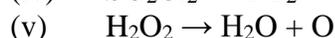
$$\text{dx/dt} = k[{}_{88}\text{Ra}^{226}]$$



$$\text{dx/dt} = k[\text{N}_2\text{O}_5]$$



$$\text{dx/dt} = k[\text{SO}_2\text{Cl}_2]$$



$$\text{dx/dt} = k[\text{H}_2\text{O}_2]$$



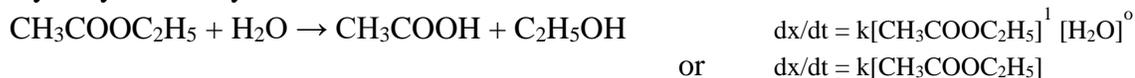
$$\text{dx/dt} = k[(\text{CH}_3)_3\text{CBr}]$$

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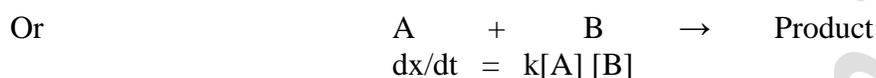
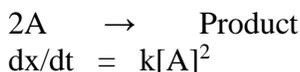
(vii) Hydrolysis of ethyl acetate



This last example is also called pseudo first order reaction.

SECOND ORDER REACTIONS:

“The reaction, in which exponents or sum of exponents of concentration terms appearing in the rate equation is 2, is called 2nd order reactions.” or “a reaction whose rate is directly proportional to the square of concentration of single reactant” is called second order reaction.



- Unit of its rate constant is $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$

Examples:

(i) Thermal decomposition of nitrous oxide



(ii) $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$

$$\frac{dx}{dt} = k[\text{HI}]^2$$

(iii) Formation of Urea



(iv) $\text{CH}_3\text{-CH}_2\text{-Br} + \text{OH}^- \rightarrow \text{CH}_3\text{-CH}_2\text{-OH} + \text{Br}^-$

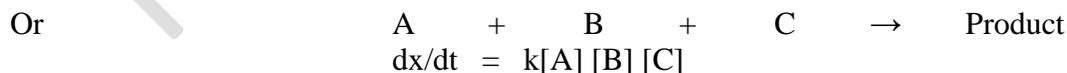
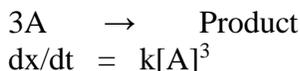
$$\frac{dx}{dt} = k[\text{C}_2\text{H}_5\text{OH}][\text{OH}^-]$$

(v) $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$

$$\frac{dx}{dt} = k[\text{NO}][\text{O}_3]$$

THIRD ORDER REACTIONS:

“The reaction, in which exponents or sum of exponents of concentration terms appearing in the rate equation is 3, is called 3rd order reactions.” or “a reaction whose rate is directly proportional to the cube of concentration of reactant” is called third order reaction.



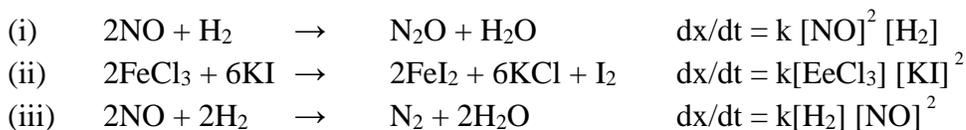
- Unit of its rate constant is $1/(\text{dm}^3)^2 \cdot \text{mol} \cdot \text{s}$

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Examples:

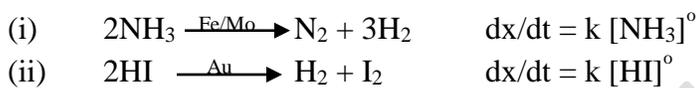


ZERO ORDER REACTIONS:

The reaction, whose rate of reaction is independent of concentration of reactant(s), is called Zero order reaction.

- Unit of its rate constant is $\text{mol. dm}^{-3} \cdot \text{s}^{-1}$

Examples:

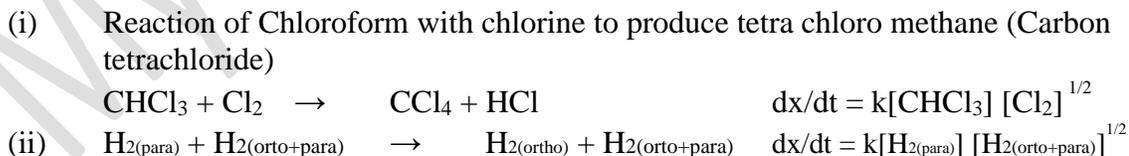


- Rate of reaction does not depend upon concentration of a reactant in following cases:
 - (a) If the reactant is solvent also e.g. in hydrolysis of ethyl acetate water is solvent as well as reactant, so rate does not depend upon its concentration.
 - (b) If reaction is photochemical reaction then rate does not depend upon concentrations of reactants and will depend upon intensity of light.
 - (c) If solid catalyst is used then rate does not depend upon concentrations of reactants and will depend upon the surface area of solid catalyst.

FRACTIONAL ORDER REACTIONS:

The reactions, in which exponents or sum of exponents of concentration terms appearing in the rate equation are fractional numbers, are called fractional order reactions.

Examples:



In the above two examples order of the reactions is $1\frac{1}{2}$.

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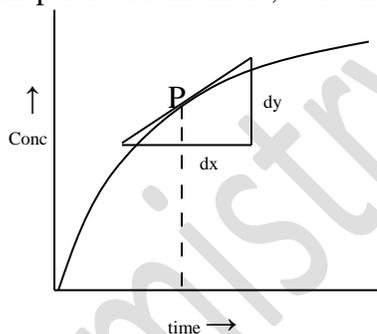
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Experimental determination of rate of reaction:

Rate of a reaction can be determined by noting decrease in concentration of any one reactant or increase in concentration of any one product in a given interval of time. But rate of a reaction does not remain constant through out. It goes on decreasing with passage of time, therefore, at any moment it is not equal to average rate.

To determine actual rate of a reaction at a certain particular moment, concentrations of any one reactant or product are determined after regular intervals of time by one of the methods given below. Concentrations are plotted versus time. The rate then at any moment is determined by calculating slope of tangent AC drawn on point P.



$$\text{Rate} = \text{Slope} = \frac{dy}{dx}$$

Methods for determining concentration:

Usually two types of methods are used to determine concentrations (a) physical methods and (b) chemical methods.

(a) Physical methods:

In these methods, concentration is measured by noting change in some physical property. Following physical methods can be applied to determine concentrations after regular intervals of times:

- (i) Colourimetry:
This method is used when some reactant or product is a coloured substance. The intensity of colour is measured and it determines the concentration.
- (ii) U.V or I.R. spectrophotometry:
This method is employed when some reactant or product absorbs U.V-rays or I.R-rays. The concentration is measured by measuring the amount of radiations absorbed.
- (iii) Conductometry:
This method is employed where ions are involved. The concentration is measured by measuring the current conducted. More is the number of ions more will be conductance of current.
- (iv) pH metry:
The concentration can be measured by noting the pH of solution. This method is used if some acid or base is involved in the reaction.

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(v) Dilatometry:

This method is useful for the reactions, which involve small volume changes in solutions. Change in volume is proportional to extent of reaction.

(vi) Polarimetry:

This method is used if some optically active substance is involved in reaction. The angle through which plane polarized light is rotated is measured by polarimeter.

The angle of rotation determines the concentration of optically active substance.

(vii) Refractometry:

This method is employed where there are changes in refractive indices of the substances taking part in the reaction. Changes in refractive indices determine the concentration.

(b) Chemical Method:

If some reactant or product is acid or base we can determine its concentration by titration. Concentration of acid could be found by titrating it against standard base solution and concentration of base could be found by titrating it against standard acid solution.

☞ It is to be noted that physical methods are preferred over chemical methods. In chemical methods samples are to be removed from reaction mixture after regular interval of times for titration which affects the reaction rate whereas in physical methods no samples are removed from reaction mixture. Hence physical methods are preferred over chemical method.

Half Life:

Time required to convert half (50%) of the reactant into product or the time taken for the concentration of a substance to reduce to half, is called half-life of the reaction.

e.g. Half life of decomposition of N_2O_5 is 24min at 45°C . If we decompose 0.10 mol/dm^3 at 45°C , then after 24 min 0.05 mol/dm^3 , after 48min 0.025 mol/dm^3 and after 72min 0.0125 mol/dm^3 of N_2O_5 will be left behind. So half life of this reaction is 24 min.

- Half-life is inversely proportional to initial concentration raised to a power of “n-1”.

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

Where

$t_{1/2}$ = half life

a = initial concentration

n = order of reaction

k = rate constant

$$t_{1/2} = \frac{1}{ka^{n-1}}$$

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For 1st order

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

$$t_{1/2} \propto 1/a^0 \quad \text{or} \quad 1 \quad \text{as } a^0 = 1$$

So half life of 1st order is independent of initial concentration.

For 2nd order

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

$$t_{1/2} \propto 1/a^1$$

So half life of 2nd order is inversely proportional to initial concentration.

For 3rd order

$$t_{1/2} \propto 1/a^{3-1}$$

$$t_{1/2} \propto 1/a^2$$

So half life of 3rd order is inversely proportional to square of initial concentration.

- Time taken by certain amount of a substance to react or disappear, can be related to half life as:

$$T = y \times t_{1/2} \quad \text{where}$$

T = Total time taken for the reactant to react

$t_{1/2}$ = Half life

y = Number of half lives

Number of half lives (y) is calculated as:

$$N = [1/2]^y N^0$$

where N^0 = Initial amount of reactant

$$\text{or} \quad N/N^0 = [1/2]^y$$

and N = Amount of reactant left behind

Taking log of both sides

$$\text{Log } N/N^0 = \text{log } [1/2]^y$$

Using log property we can write:

$$\boxed{\text{log } N/N^0 = y \text{ log } (1/2)}$$

By this expression we can determine number of half lives involved during consumption of a particular amount of reactant.

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Determination of Order of Reaction:

There are several methods of determining order of a reaction. Some are following:

1) Half Life Method:

Half life of a reaction is inversely proportional to the initial concentration of reactants raised to a power which is one less than order of reaction

$$t_{1/2} = \frac{1}{ka^{n-1}} \quad \begin{array}{l} n = \text{order of reaction} \\ k = \text{rate constant} \end{array}$$

Let perform a reaction by starting with two different initial concentrations of reactants i.e. a_1 and a_2 , then two half lives can be given as

$$[t_{1/2}]_1 = \frac{1}{ka_1^{n-1}} \quad \dots\dots\dots (1)$$

$$[t_{1/2}]_2 = \frac{1}{ka_2^{n-1}} \quad \dots\dots\dots (2)$$

Divide eq-1 by eq-2

$$\begin{aligned} \frac{[t_{1/2}]_1}{[t_{1/2}]_2} &= \frac{\frac{1}{k a_1^{n-1}}}{\frac{1}{k a_2^{n-1}}} \\ \frac{[t_{1/2}]_1}{[t_{1/2}]_2} &= \frac{1}{\cancel{k} a_2^{n-1}} \times \frac{\cancel{k} a_2^{n-1}}{1} \\ \frac{[t_{1/2}]_1}{[t_{1/2}]_2} &= \frac{a_2^{n-1}}{a_1^{n-1}} \\ \frac{[t_{1/2}]_1}{[t_{1/2}]_2} &= \left[\frac{a_2}{a_1} \right]^{n-1} \end{aligned}$$

Taking log of both sides

$$\log \frac{[t_{1/2}]_1}{[t_{1/2}]_2} = \log \left[\frac{a_2}{a_1} \right]^{n-1}$$

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Using log property

$$\log \frac{[t_{1/2}]_1}{[t_{1/2}]_2} = (n-1) \log \left[\frac{a_2}{a_1} \right]$$

$$\frac{\log \left[\frac{[t_{1/2}]_1}{[t_{1/2}]_2} \right]}{\log \left[\frac{a_2}{a_1} \right]} = (n-1)$$

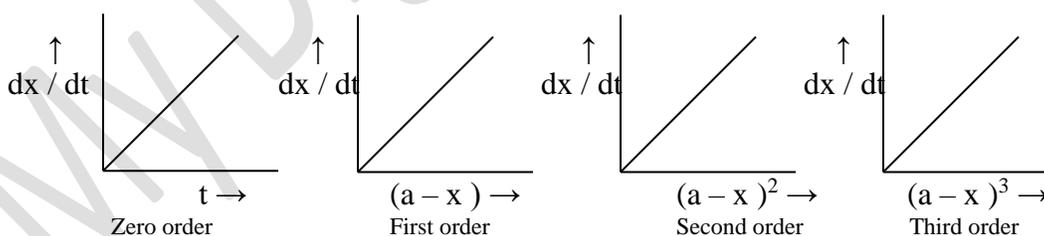
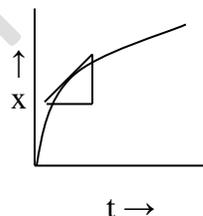
$$n = 1 + \frac{\log \left[\frac{[t_{1/2}]_1}{[t_{1/2}]_2} \right]}{\log \left[\frac{a_2}{a_1} \right]}$$

Thus knowing two half lives and also corresponding two initial concentrations we can calculate the order of reaction (n).

2) Graphic Method:

In this method x (the amount of reactant consumed) is plotted against t (time). Slopes (dx / dt) are determined for various values of x from the graph.

Then more graphs are plotted for dx/dt vs (a-x), (a-x)² and (a-x)³ respectively. By these Plots orders of reactions can be determined.



If plot of $\frac{dx}{dt}$ vs t is straight line then order of the reaction is Zero.

If plot of $\frac{dx}{dt}$ vs $a-x$ is straight line then order of the reaction is One.

If plot of $\frac{dx}{dt}$ vs $(a-x)^2$ is straight line then order of the reaction is Two.

If plot of $\frac{dx}{dt}$ vs $(a-x)^3$ is straight line then order of the reaction is Three.

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3) Ostwald Isolation Method:

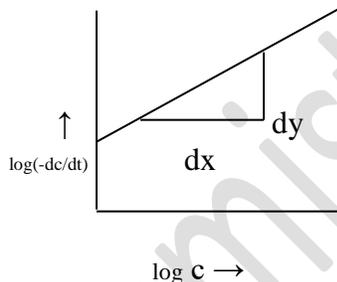
This method is also called method of large excess. In this method all the reactants except one are taken in large excess, so they will not affect the rate of reaction and only the reactant, which is not in excess, will affect the rate of reaction.

Order is determined with respect to this reactant "A". Same procedure is repeated for all other reactants one by one and orders are determined with respect to them. Overall order of reaction will be the sum of all these orders obtained for individual reactants.

4) Differential Method:

In this method $\log(-dc/dt)$ is plotted against $\log c$ and then slope is determined. order of reaction is equal to the slope.

Slope = $dy/dx = n$ where $n =$ order of reaction.



5) Integration Method:

This method is also called method of trial. In this method amount of reactant left (i.e. $a-x$) after various intervals of time are determined and then this data is inserted in the integrated rate equations of different order reactions. The equation giving the most constant value for specific rate constant (i.e. k) for different time intervals, determines the order of reaction e.g. If following equation gives constant values for k then order of reaction is 1.

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad (1^{\text{st}} \text{ order equation})$$

If values of k are not constant for first order equation then 2nd and 3rd order equations are tried.

Factors Affecting Rate of Reaction:

Following factors affect rate of a reaction.

I. Nature of Reactant:

Rate of a reaction depends upon nature of reactants e.g. elements of group I-A react rapidly than group II-A elements.

Highly electronegative or highly electropositive elements react rapidly. Acids and bases also react rapidly. Ionic compounds too react fast. However organic compounds and other covalent compounds react slowly.

II. Concentration of Reactants:

Generally speaking when concentration of reactants is high, molecules will be more crowded and thus effective collisions will be frequent so more will be the rate of reaction. But actual relation is only established experimentally.

Consider the reaction $2\text{H}_2 + 2\text{NO} \rightarrow 2\text{H}_2\text{O} + \text{N}_2$

The rate of this reaction can be determined in terms of change in pressure per unit time as reactants and products are gases. Rates for various concentrations of reactants are noted as given in the table below.

In first three experiments concentration of H_2 is increased keeping concentration of NO constant.

It is noted that by doubling the concentration of H_2 rate is doubled and by tripling the concentration of H_2 rate is tripled.

It means rate is changing with same proportion as the concentration or in other words rate is proportional to the first power of conc of H_2 .

$$\text{Rate} \propto [\text{H}_2]$$

In last three experiments conc of H_2 is kept constant while that of NO is changed and it is noted that by doubling the conc of NO rate increases 4 times and by tripling the conc of NO rate increases 9 times, which means that rate is proportional to square of conc of NO.

$$\text{Rate} \propto [\text{NO}]^2$$

By combining we can write

$$\text{Rate} \propto [\text{H}_2] [\text{NO}]^2$$

$$\text{Rate} = dx/dt = k [\text{H}_2] [\text{NO}]^2$$

Expt.No	Conc of NO	Conc of H_2	Initial Rate (atm/min)
1.	0.006	0.001	0.025
2.	0.006	0.002	0.050
3.	0.006	0.003	0.075
4.	0.001	0.009	0.0063
5.	0.002	0.009	0.0252
6.	0.003	0.009	0.0567

The order of reaction is THREE while molecularity is also THREE as evident from rate determining step. This reaction takes place in two steps.

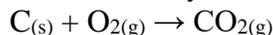
	Rate	Order	Molecularity
$2\text{NO} + \text{H}_2 \xrightarrow{\text{slow}} \text{N}_2 + \text{H}_2\text{O}_2$	$\text{dx/dt} = k[\text{NO}]^2[\text{H}_2]$	3	3
$\text{H}_2\text{O}_2 + \text{H}_2 \xrightarrow{\text{fast}} 2\text{H}_2\text{O}$	$\text{dx/dt} = k[\text{H}_2\text{O}_2][\text{H}_2]$	2	2
Overall reaction $2\text{NO} + 2\text{H}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$	$\text{dx/dt} = k[\text{NO}]^2[\text{H}_2]$	3	3

This shows that quantitative relationship between change in concentration and rate of reaction is only experimentally determined.

III. Surface area of solid reactant or Size of reactant:

As solid reactant reacts at surface so more is the surface area of solid reactant high will be rate of reaction.

e.g. (i) Lumps of coal do not burn readily in air but powdered coal burns explosively.



e.g. (ii) Marble chips react slowly with HCl but powdered marble reacts readily with HCl.

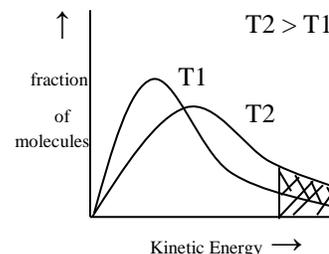


IV. Temperature:

At a given temperature all molecules do not possess equal energies. Majority of molecules possess average or intermediate energy and molecules possessing equal to or greater than activation energy are less.

When temperature is increased then energy of the molecules increases so more number of molecules will now possess activation energy.

Shaded area in graph represents fraction of activated molecules. As with rise in temperature number of activated molecules increases so rate of reaction increases.



It is a general fact that for every 10°C or 10K rise in temperature rate of reaction becomes doubled. But actual quantitative relation between rate constant and temperature is given by Arrhenius equation, which is

$$k = A e^{-E_a/RT} \dots\dots\dots (1)$$

This is exponential form of Arrhenius equation.

This equation shows that with rise in temperature, rate constant k increases.

Calculations with exponential form are comparatively difficult, so it should be converted to logarithmic form. taking natural log of both sides of equation-1

$$\ln k = \ln A e^{-E_a/RT}$$

where

k = Rate constant

A = Arrhenius constant

e = Base of natural log

E_a = Activation energy

R = Universal gas constant

T = Absolute temperature

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Subtracting equation-6 from equation-7

$$\log k_2 - \log k_1 = \left[\log A - \frac{E_a}{2.303RT_2} \right] - \left[\log A - \frac{E_a}{2.303RT_1} \right]$$

$$\log k_2 - \log k_1 = \cancel{\log A} - \frac{E_a}{2.303RT_2} - \cancel{\log A} + \frac{E_a}{2.303RT_1}$$

$$\log k_2 - \log k_1 = -\frac{E_a}{2.303RT_2} + \frac{E_a}{2.303RT_1}$$

On rearranging and using log property

$$\log \left[\frac{k_2}{k_1} \right] = \frac{E_a}{2.303RT_1} - \frac{E_a}{2.303RT_2}$$

Taking common

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

Taking LCM

$$\text{taking L.C.M} \quad \log \left[\frac{k_2}{k_1} \right] = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \dots\dots\dots (8)$$

Thus we can also calculate activation energy of a reaction by finding rate constant k_1 and k_2 at temperatures T_1 and T_2 respectively and then putting values in above equation-8.

V. Surface Area of Reactants:

With increase in surface area of reactants, the possibility of atoms or molecules of reactants to come into contact with each other increases and hence rate of reaction increases e.g. powdered substance can react more rapidly than a single big piece.

VI. Light:

Light provides energy, so energy of molecules increases and as a result rate of reaction increases e.g. a mixture of Methane and Chlorine placed in dark shows no reaction but in diffuse sunlight slow reaction occurs while in direct sunlight reaction occurs with explosive violence.

VII. Catalysis:

Berzlius first used the term catalyst in 1835. It is defined as the substance which changes or alters the rate of a reaction but itself remains chemically unchanged by the end of reaction. Such a substance is called catalyst while the process is called catalysis.

The process in which rate of a reaction changes due to catalyst is called catalysis.

Type of catalyst:

There are two types of catalyst, positive and negative catalysts.

(i) Positive catalysts: Positive catalysts are the one which increase the rate of a reaction e.g. MnO_2 used in decomposition of KClO_3 is a positive catalyst. Ni and Pt used in hydrogenation of alkenes are positive catalysts.

(ii) Negative catalysts: Negative catalysts are the one which decrease the rate of a reaction. Negative catalysts are also called inhibitors. e.g. Pyridine or Quinoline slow down rancidity in fats so they are negative catalysts or inhibitors. TEL and TML are also inhibitors.

Promoters or Activators:

The substances, which increase the activity of a catalyst, are called promoters or activators.

e.g. (i) Nickel is used as catalyst during hydrogenation of oil to make Vanaspati Ghee, if Copper or Tellurium are added they increase the activity of Nickel so they are promoters or activators.

e.g. (ii) During Haber's process of ammonia formation Iron (Fe) is used as catalyst while Mo, Al_2O_3 and Cr_2O_3 are used as promoters as they increase the efficiency of Iron.

Poisoning of catalyst:

To deactivate or to destroy or to decrease the catalytic ability of a catalyst due to impurity is called poisoning of catalyst.

Impurities make the active site of catalyst unavailable for reactant molecules so its catalytic ability decreases or destroys e.g. Dust and Arsenic impurities poisons Platinum. The substance that poisons a catalyst is called anti catalyst e.g. dust, water vapours, arsenic impurities, carbon monoxide etc are anti catalysts.

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Autocatalysis:

The phenomenon during which one of the product acts as catalyst, is called autocatalysis and the product, which act as catalyst is called auto catalyst.

e.g. (i) During hydrolysis of Ethyl acetate, acetic acid is produced which then act as catalyst so it is auto catalyst.

e.g. (ii) Reaction of Oxalic acid with acidified KMnO_4 produces MnSO_4 which then act as auto catalyst.

Such reactions are slow at start and then gradually they are speeded up.

Characteristic of Catalyst:

- 1) A catalyst remain unchanged by the end of reaction i.e. its chemical composition remain unchanged however physical state may change e.g. granules of MnO_2 (catalyst) change to powder by end of reaction.
- 2) Usually small amount of catalyst is required e.g. for reaction of 2.5 dm^3 of H_2 and 1.25 dm^3 of O_2 to produce water 1 mg of Pt catalyst is sufficient.
- 3) Catalyst is specific in function or action i.e. a particular catalyst catalyses only a particular reaction.

For example



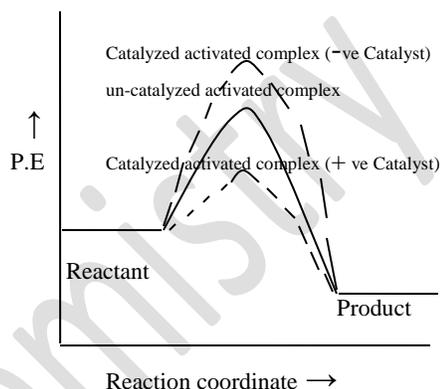
- Thus by changing catalyst reaction changes and hence product is changed.
- 4) A catalyst is more effective when powdered as it increases its surface area e.g. during hydrogenation of vegetable oils to form Vanaspati Ghee, finely divided Nickel is used.
 - 5) A catalyst does not change final position of equilibrium. It just increases rates of both forward as well as backward reactions so equilibrium is established rapidly.
 - 6) A catalyst cannot start a reaction that is thermodynamically not feasible.
 - 7) Temperature may affect catalytic ability of a catalyst by changing its composition.

Function of a Catalyst:

A catalyst actually changes the path of reaction by changing activated complex due to which activation energy changes.

Positive catalyst lowers the activation energy
So the number of molecules, which possess this energy will become larger i.e. number of activated molecules increases so rate of reaction increases.

Negative catalyst on the other hand increases the activation energy that is possessed by less number of molecules i.e. number of activated molecules be small, therefore rate of reaction will be slow.



Types of Catalysis:

Catalysis is of three types.

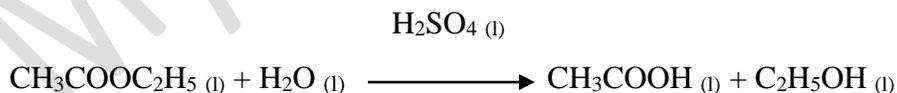
(a) Homogeneous Catalysis:

The catalysis, in which catalyst and reactants are in same phase, is called homogeneous catalysis.

e.g. (i) Lead chamber process of H_2SO_4 manufacturing

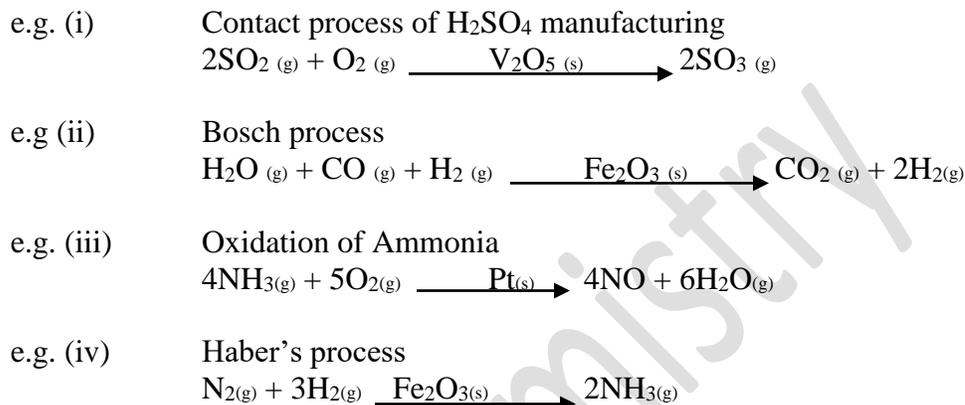


e.g. (ii) Hydrolysis of Ethyl acetate



(b) Heterogeneous catalysis:

The catalysis in which catalyst and reactants are in different phases, is called heterogeneous catalysis.



(c) Enzyme catalysis:

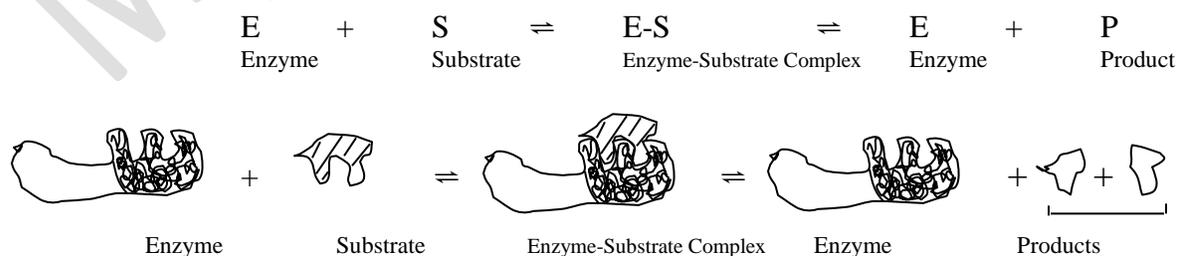
The catalysis, in which enzymes catalyze biochemical reactions, is called enzyme catalysis. Enzymes are complex protein molecules that catalyze the biochemical reactions taking place in living organisms.

Mode of Enzyme Action:

Enzyme molecules have an active site and a non-active site. The non-active site is called allosteric site.

In active site of enzyme there are cavities, which have active groups like -NH₂, -SH, -OH, -COOH etc. These groups are called active centers.

The substrate molecules fit into these cavities like key fits into lock and as a result enzyme-substrate complex is formed, which then converts to product.



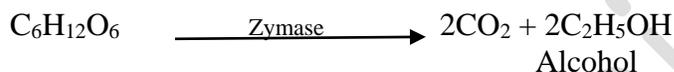
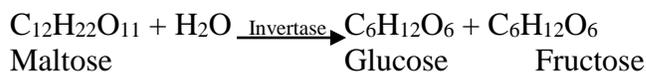
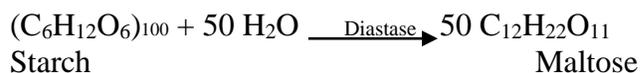
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Industrial Uses:

1. Alcohol is industrially prepared by fermentation of starches especially grape juice. In this process enzyme catalysts are used.



2. In presence of enzymes yogurt and cheese are prepared by fermentation of milk.

Theories of Reaction Rate:

There are two important theories of reaction rates. But before discussing these theories we will discuss activation energy.

Energy of Activation:

In a reaction old bonds are broken and new bonds are formed. Certain quantity of energy is required to bring the reactants to a state where they can rearrange to form products.

Molecules collide with one another but collision may not lead to reaction. Every molecule in motion possesses kinetic energy. When molecules collide, part of their kinetic energy is converted to potential energy (vibrational energy). If the initial kinetic energy is high, then the colliding molecules will vibrate so strongly as to break some of the chemical bonds. If the initial kinetic energy is low, the molecules will just touch each other with certain force without breaking bonds. Thus, there is some minimum collision energy below which no reaction occurs. This energy is called activation energy (E_a).

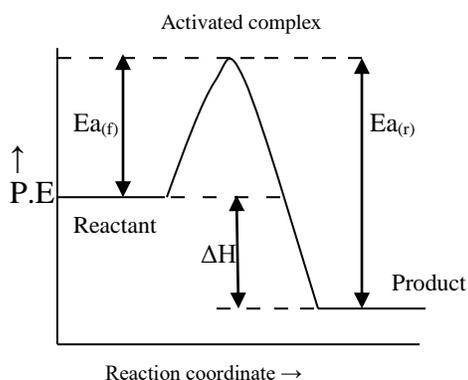
“Activation energy is a minimum amount of energy required to initiate a chemical reaction”.

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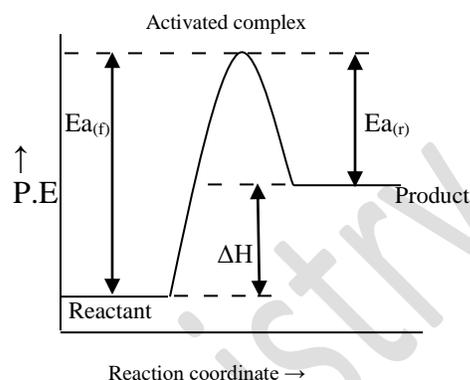
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The potential energy diagram can also be used to calculate heat of reaction (ΔH). It is equal to the difference of potential energy of reactants and products. It is also equal to the difference of activation energy of forward reaction and that of reverse reaction.



Exothermic Reaction



Endothermic Reaction

1. Collision Theory of Reaction Rate:

Collision theory has following postulates:

- (i) For a chemical reaction to occur, particle must collide.
- (ii) For the occurrence of reaction colliding particles must possess a certain minimum energy, known as activation energy.
- (iii) Not every collision between molecules having the required energy of activation leads to reaction. Only those collisions are effective which take place in proper orientation or arrangement of the colliding molecules.

Explanation:

Postulate (i):

When number of molecules is high then molecular collision will be more frequent and chances of reaction are high. With out collision of molecules no old bonds will be broken and thus no new bonds will be produced and thus no reaction will occur.

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Postulate (ii):

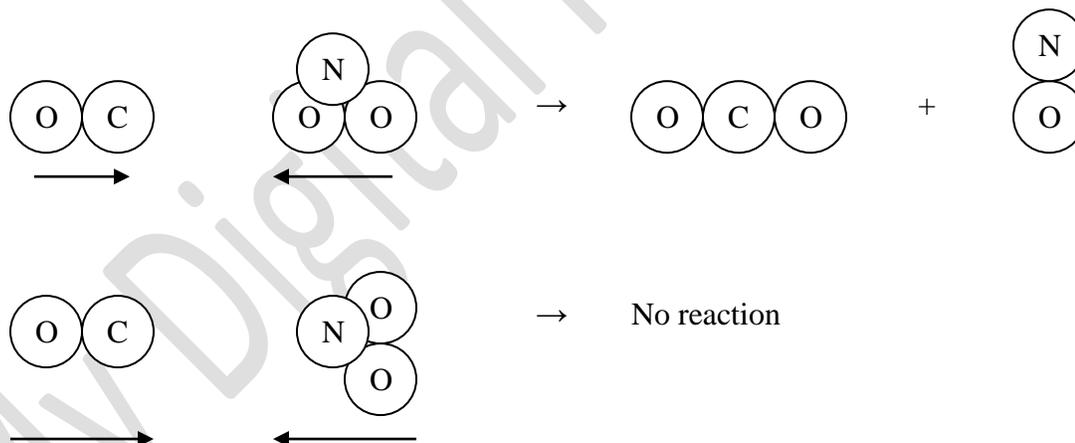
The number of colliding molecules of different gases calculated from kinetic theory of gases is of order of 10^{32} molecules per litre (dm^3) per second which is quite high number. If every collision lead to reaction then all gaseous reactions should occur with explosion. However it not happens as only effective collisions lead to reaction. Different gases show different reaction rates e.g. rate of decomposition of HI at STP is $4.4 \times 10^{-3} \text{ mol dm}^3 \text{ hour}^{-1}$, while rate of decomposition of N_2O_5 at STP is $9.4 \times 10^{-5} \text{ mol dm}^3 \text{ hour}^{-1}$. Thus number of collision is not only the factor controlling reaction rate. Actually it is number of effective collision which controls reaction. For effective collision it is necessary that molecules must possess energy equal to or more than activation energy (E_a). High energy molecules are able to cause atoms to vibrate violently on collision.

Postulate (iii):

This postulates shows that colliding molecules beside possessing activation energy, they also be properly oriented before collision and only then their collisions will be effective.



When CO and NO_2 molecules collide, then the probability of transfer of oxygen atom from NO_2 to CO molecule is high when carbon atom of CO collide with oxygen atom of NO_2 .

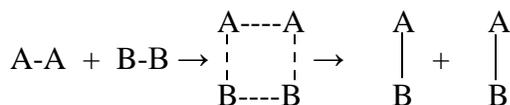


2. Transition State Theory (TST) of Reaction Rate:

This theory explains a transition state during conversion of reactants into products.

Actually reactant molecules are not directly converted to product. First they combine to form a transition state known as **activated complex**, which then converts to products. Activated complex is unstable and short lived species, so it immediately decomposes to products. It is assumed that activated complex possess properties common to real molecule, such as molecular weight, intermediate distances, a definite enthalpy, definite composition but loses structure, and ability to rotate and vibrate.

Let two molecules A_2 and B_2 react. They first convert to an activated complex, which then converts to product AB .



The energy required to make activated complex is called activation energy.

Activated complex is always higher in energy than reactant and products. When H_2 and O_2 are mixed in a vessel at room temperature, the reaction does not occur because molecules possess energy less than activation energy. But if spark is made in vessel or burning match stick is brought to the vessel, reaction will immediately occurs. Molecules absorb enough energy and become able to produce activated complex which then gives product, so reaction will occur. It means that collision between activated molecules (possessing energy equal to or more than activation energy) lead to reaction.

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