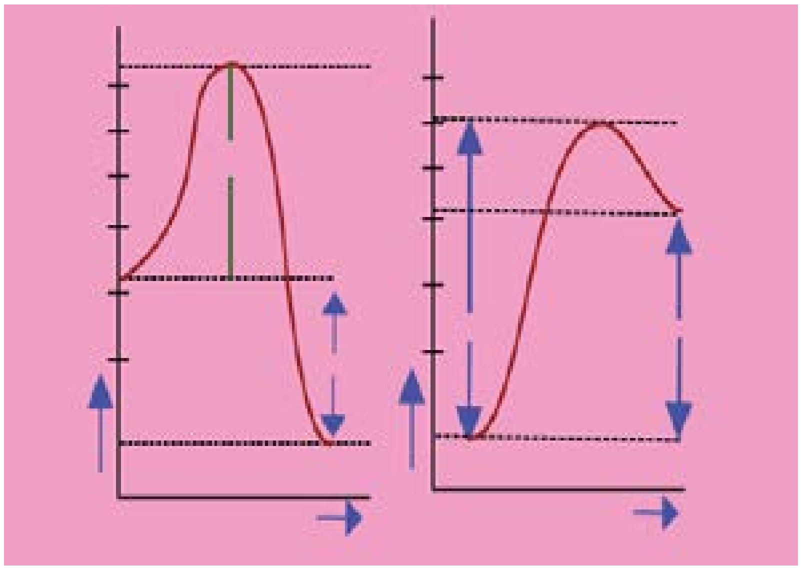
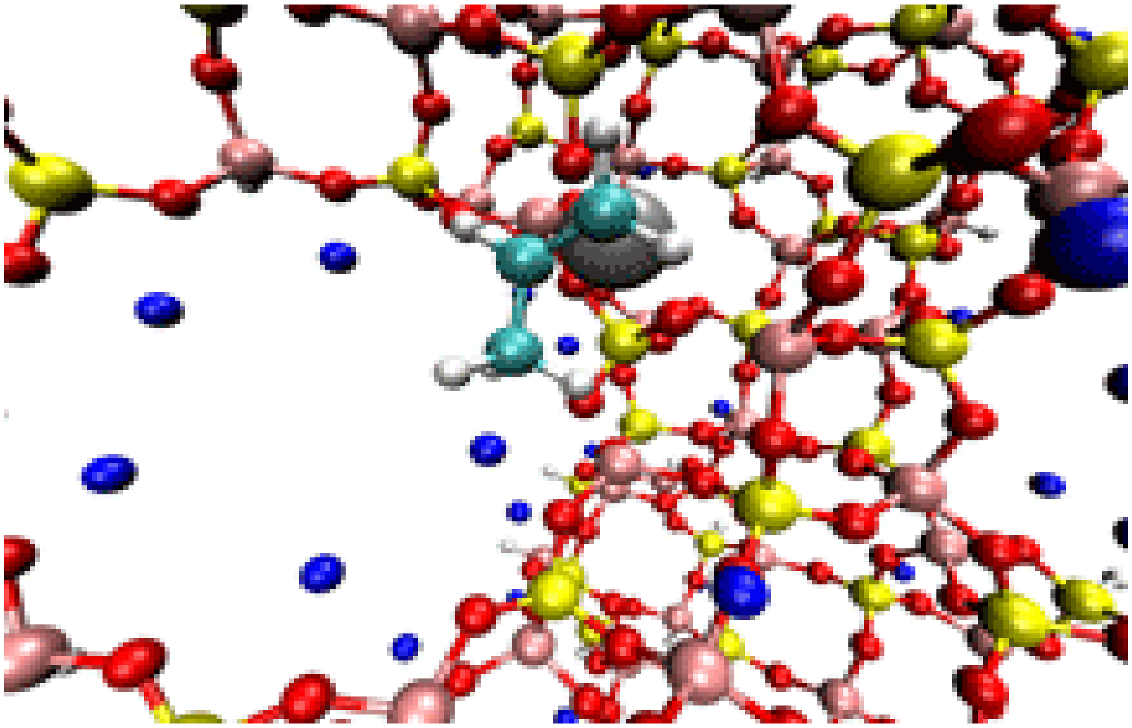


CHAPTER

11

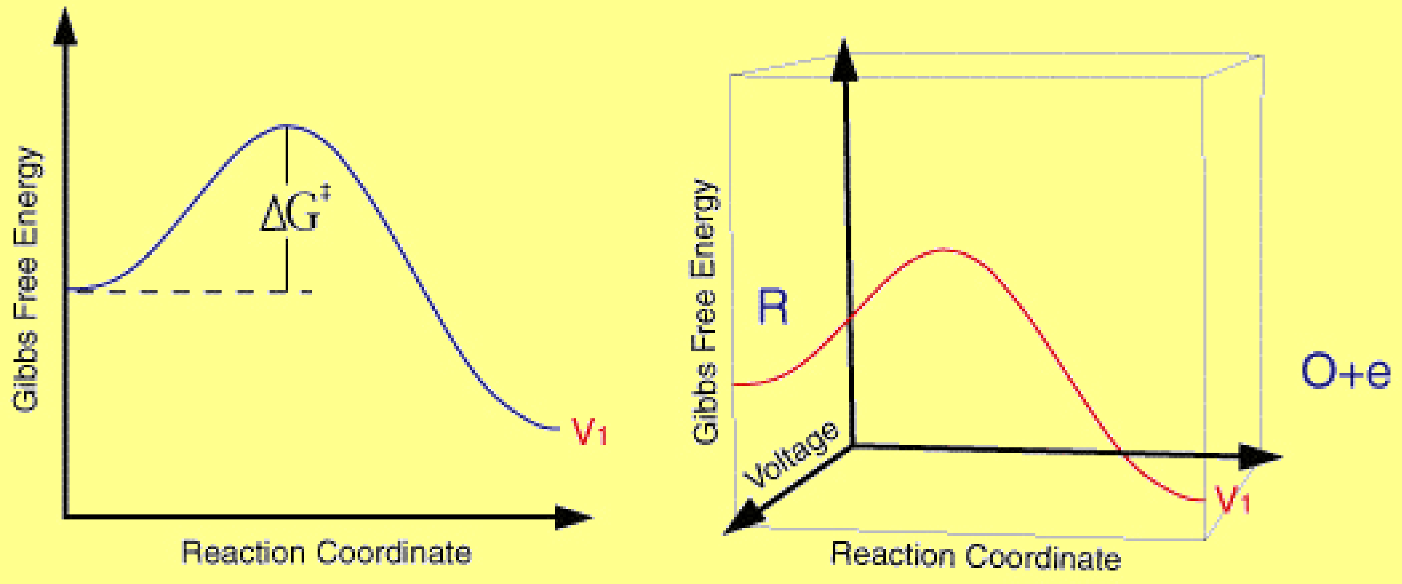
REACTION KINETICS



Animation 11.1: Spectrometer
Source & Credit: eLearn

11.0.0 INTRODUCTION

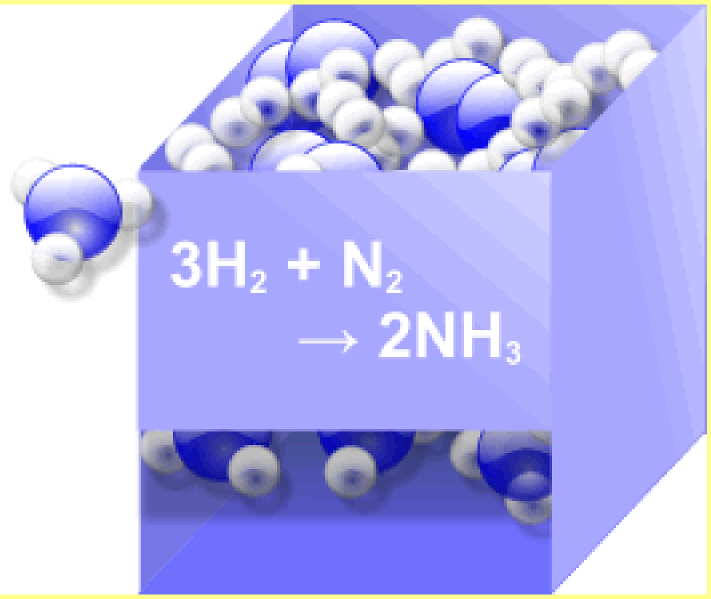
It is a common observation that rates of chemical reactions differ greatly. Many reactions, in aqueous solutions, are so rapid that they seem to occur instantaneously. For example, a white precipitate of silver chloride is formed immediately on addition of silver nitrate solution to sodium chloride solution. Some reactions proceed at a moderate rate e.g. hydrolysis of an ester. Still other reactions take a much longer time, for example,the rusting of iron, the chemical weathering of stone work of buildings by acidic gases in the atmosphere and the fermentation of sugars.
The studies concerned with rates of chemical reactions and the factors that affect the rates of chemical reactions constitute the subject matter of reaction kinetics. These studies also throw light on the mechanisms of reactions. All reactions occur in single or a series of steps. If a reaction consists of several steps, one of the steps will be the slowest than all other steps. The slowest step is called the rate determining step. The other steps will not affect the rate. The rates of reactions and their control are often important in industry. They might be the deciding factors that determine whether a certain chemical reaction may be used economically or not. Many factors influence the rate of a chemical reaction. It is important to discover the conditions under which the reaction will proceed most economically.



Animation 11.2: Kinetics
Source & Credit : ceb.cam

11.1.0 RATE OF REACTION

During a chemical reaction, reactants are converted into products. So the concentration of the products
increases with the corresponding decrease in the concentration of the reactants as they are being consumed.



Animation 11.3: RATE OF REACTION
Source & Credit : blobs

The situation is explained graphically in Fig.(11.1) for the reactant A which is changing irreversibly to the product B.

The slope of the graph for the reactant or the product is the steepest at the beginning. This shows a rapid decrease in the concentration of the reactant and consequently, a rapid increase in the concentration of the product. As the reaction proceeds, the slope becomes less steep indicating that the reaction is slowing down with time. It means that the rate of a reaction is changing every moment. The following curve for reactants should touch the time axis in the long run. This is the stage of completion of reaction. The rate of a reaction is defined as the change in concentration of a reactant or a product divided by the tim e taken for the change.

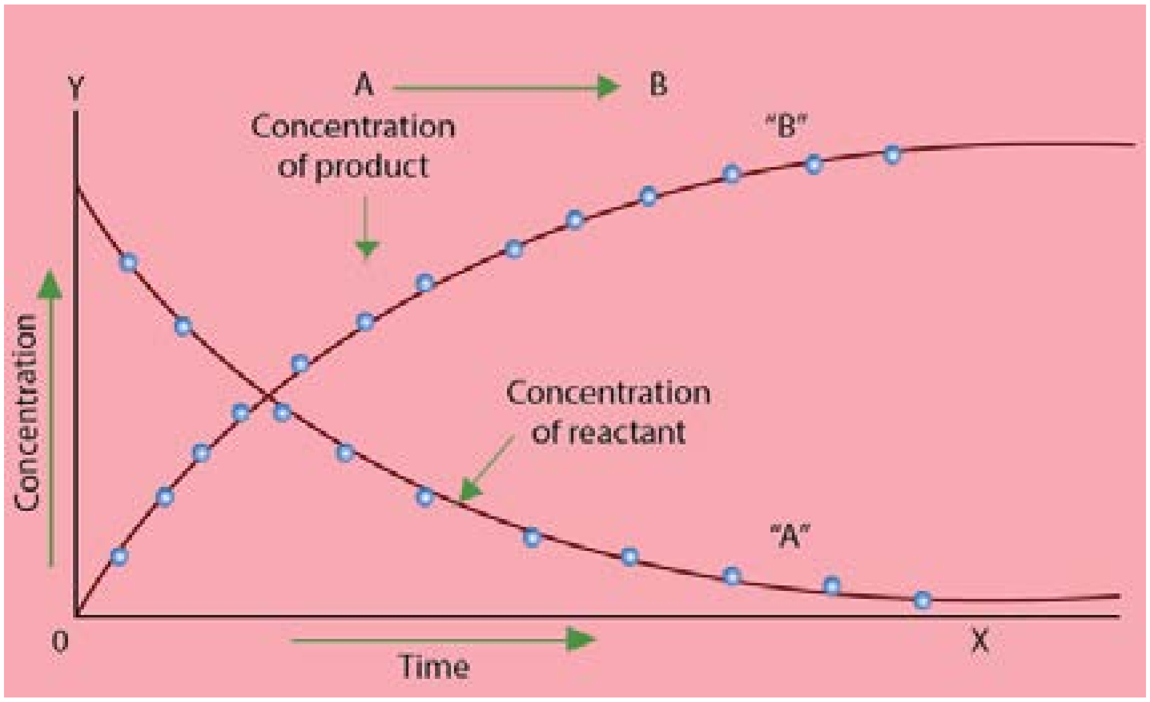


Fig. (11.1) Change in the concentration of reactants and products with time for the reaction $A \rightarrow B$

The rate of reaction has the units of concentration divided by time. Usually the concentration is expressed in mol dm^{-3} and the time in second, thus the units for the reaction rate are mol $dm^{-3}s^{-1}$.

$$\text{Rate of reaction} = \frac{\text{change in concentration of the substance}}{\text{time taken for the change}}$$

For a gas phase reaction, units of pressure are used in place of molar concentrations. It follows from the above graph that the change in concentration of the reactant A or the product B is much more at the start of reaction and then it decreases gradually.

So the reaction rate decreases with time. It never remains uniform during different time periods. It decreases continuously till the reaction ceases.

$$\text{Rate of reaction} = \frac{\text{mol dm}^{-3}}{\text{seconds}} = \text{mol dm}^{-3}\ \text{s}^{-1}$$

11.1.1 Instantaneous and Average Rate

The rate at any one instant during the interval is called the instantaneous rate. The rate of reaction between two specific time intervals is called the average rate of reaction.

The average rate and instantaneous rate are equal for only one instant in any time interval. At first, the instantaneous rate is higher than the average rate. At the end of the interval the instantaneous rate becomes lower than the average rate. As the time interval becomes smaller, the average rate becomes closer to the instantaneous rate.

The average rate will be equal to the instantaneous rate when the time interval approaches zero. Thus the rate of reaction is instantaneous change in the concentration of a reactant or a product at a given moment of time.

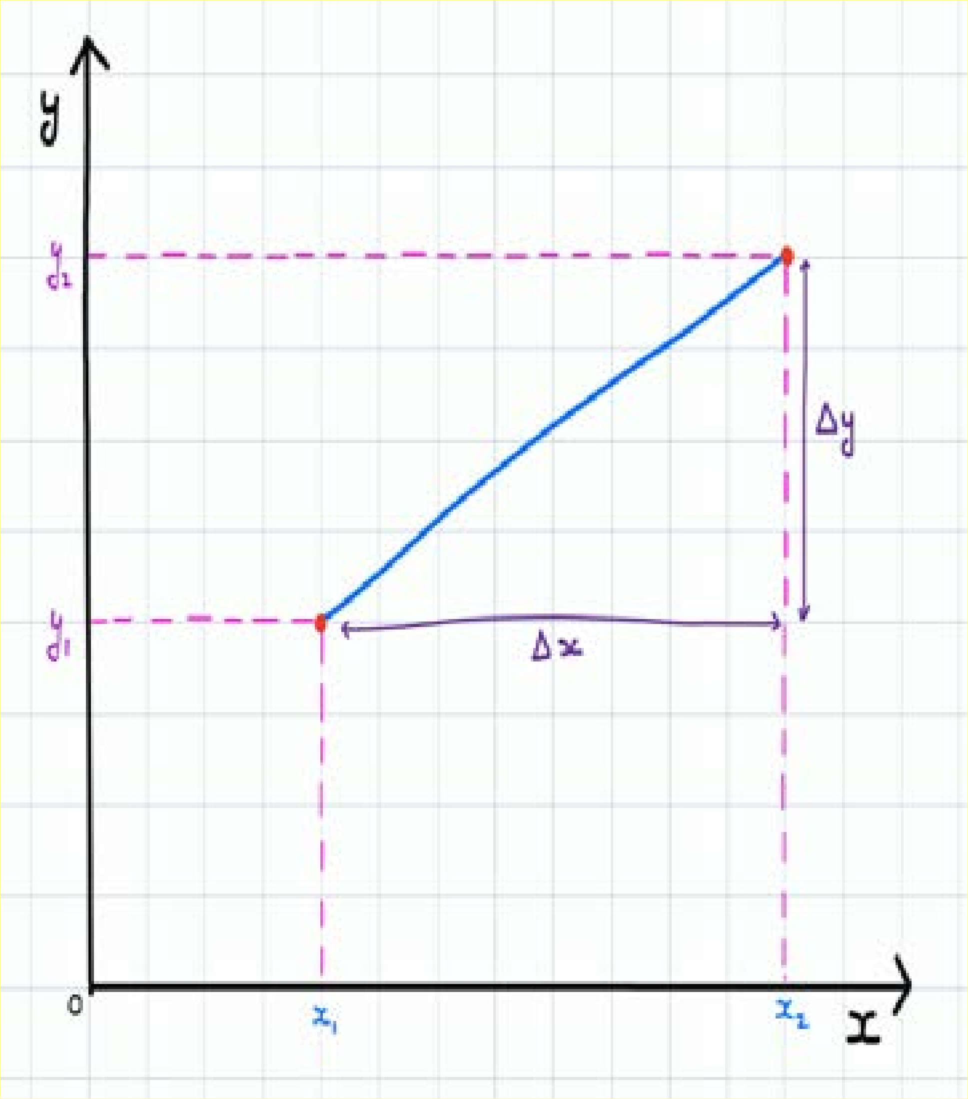
$$\text{Rate of reaction} = \frac{dx}{dt}$$

Where dx is a very small change in the concentration of a product in a very small time interval dt. Hence, dx/dt is also called rate of change of concentration with respect to time.

The rate of a general reaction, $A \rightarrow B$, can be expressed in terms of rate of disappearance of the reactant A or jthe rate of appearance of the product B. Mathematically,

$$\text{Rate of reaction} = \frac{-d[A]}{dt} = +\frac{d[B]}{dt}$$

Where d[A] and d[B] are the changes in the concentrations of A and B, respectively. The negative sign in the term indicates a decrease in the concentration of the reactant A. Since the concentration of product increases with time, the sign in rate expression involving the change of concentration of product is positive.



Animation 11.4: Average and Instantaneous Rate of Change
Source & Credit : brilliant

11.1.2 Specific Rate Constant or Velocity Constant

The relationship between the rate of a chemical reaction and the active masses, expressed as concentrations, of the reacting substances is summarized in the law of mass action. It states that the rate of reaction is proport ional to the active mass of the reactant or to the product of active masses if more than one reactants are involved in a chemical reaction.

For dilute solutions, active mass is considered as equal to concentration. By applying the law of mass action to a general reaction.

$$aA + bB \rightarrow cC + dD$$

Rate of reaction $= k\,[A]^a\ [B]^b$

This expression is called rate equation. The brackets [ ] represent the concentrations and the proportionality constant k is called rate constant or velocity constant for the reaction.

If $[A] = 1\ \text{mol dm}^{-3}$ and $[B] = 1\ \text{mol dm}^{-3}$

$$\text{Rate of reaction} = k \times 1^a \times 1^b = k$$

Hence the specific rate constant of a chemical reaction is the rate of reaction when the concentrations of the reactants are unity. Under the given conditions, k remains constant, but it changes with temperature.

Animation 11.5: Velocity Constant
Source & Credit : wikia

11.1.3 Order of Reaction

For a general reaction between A and B where ‘a’ moles of A and ‘b’ moles of B react to form ’c’ moles of C and ’d’ moles of D.

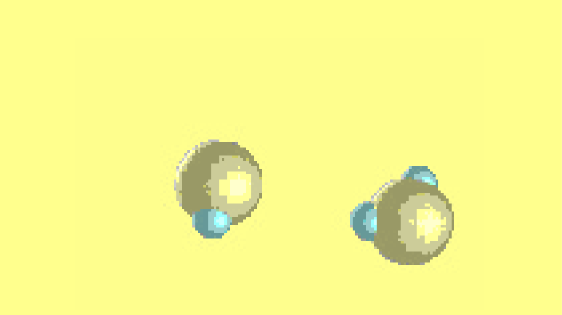
$$aA + bB \rightarrow cC + dD$$

We can write the rate equation as:

$$R = k\,[A]^a\,[B]^b$$

The exponent ’a’ or ‘b’ gives the order of reaction with respect to the individual reactant. Thus the reaction is of order ‘a’ with respect to A and of order b with respect to B. The overall order of reaction is (a+b). The order of reaction is given by the sum of all the exponents to which the concentrations in the rate equation are raised. The order of reaction may also be defined as the number of reacting molecules, whose concentrations alter as a result of the chemical change.

It is important to note that the order of a reaction is an experimentally determined quantity and can not be inferred simply by looking at the reaction equation. The sum of the exponents in the rate equation may or may not be the same as in a balanced chemical equation. The chemical reactions are classified as zero, first, second and third order reactions. The order of reaction provides valuable information about the mechanism of a reaction.



Animation 11.6: Rate and Order of Reaction
Source & Credit : science.uwaterloo

Examples of Reactions Showing Different Orders

1. Decomposition of nitrogen pentoxide involves the following equation.

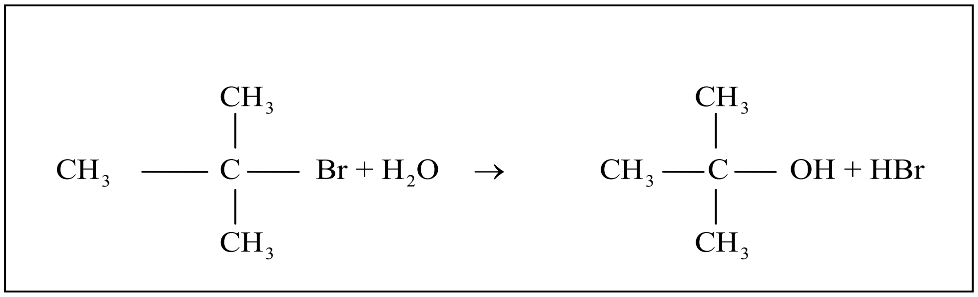
$$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$$

The experimentally determined rate equation for this reaction is as follows:

$$\text{Rate} = k[N_2O_5]$$

This equation suggests that the reaction is first order with respect to the concentration of N_2O_5.

2. Hydrolysis of tertiary butyl bromide



$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - Br + H_2O \rightarrow CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - OH + HBr$$

The rate equation determined experimentally for this reaction is

$$\text{Rate} = k[(CH_3)_3CBr]$$

The rate of reaction remains effectively independent of the concentration of water because, being a solvent, it is present in very large excess. Such type of reactions have been named as pseudo first order reactions.

3. Oxidation of nitric oxide with ozone has been shown to be first order with respect to NO and first order with respect to O_3. The sum of the individual orders gives the overall order of reaction as two.

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

$$\text{Rate} = k[NO][O_3]$$

4. Consider the following reaction

$$2FeCl_3(aq) + 6KI(aq) \rightarrow 2FeI_2(aq) + 6KCI(aq) + I_2$$

This reaction involves eight reactant molecules but experimentally it has been found to be a third order reaction.

$$\text{Rate} = k[FeCl_3][KI]^2$$

This rate equation suggests that the reaction is, in fact, taking place in more than one steps. The possible steps of the reaction are shown below.

$$FeCl_3(aq) + 2KI(aq) \xrightarrow{\text{slow}} FeI_2(aq) + 2KCl(aq) + Cl^-(aq)$$

$$2KI(aq) + 2Cl^-(aq) \xrightarrow{\text{fast}} 2KCl(aq) + I_2(s)$$

5. The order of a reaction is usually positive integer or a zero, but it can also be in fraction or can have a negative value. Consider the formation of carbon tetrachloride from chloroform.

$$CHCl_3(\ell) + Cl_2(g) \rightarrow CCl_4(\ell) + HCl(g)$$

$$\text{Rate} = k[CHCl_3][Cl_2]^{1/2}$$

The sum of exponents will be 1 + 1/2= 1.5, so the order of this reaction is 1.5.

From the above examples, it is clear that order of reaction is not necessarily depending upon the coeffients of balanced equation. The rate equation is an experimental expression. A reaction is said to be zero order if it is entirely independent of the concentration of reactant molecules. Photochemical reactions are usually zero order.

11.1.4 Half Life Period

Half life period of a reaction is the time required to convert 50% of the reactants into products. For example, the half life period for the decomposition of N_2O_5 at 45°C is 24 minutes.

It means that if we decompose 0.10 mole dm^{-3} of N_2O_5 at 45 °C, then after 24 minutes 0.05 mole dm^{-3} of N_2O_5 will be left behind. Similarly after 48 minutes 0.025(25%) mole dm^{-3} of N_2O_5 will remain unreacted and after 72 minutes (3 half times) 0.0125 (12.5%) mole dm^{-3} of N_2O_5, will remain unreacted.

Decomposition of N_2O_5 is a first order reaction and the above experiment proves that the half-life period of this reaction is independent of the initial concentration of N_2O_5. This is true for all first order reactions. The disintegration of radioactive ${}^{235}_{92}\mathrm{U}$ has a half-life of 7.1×10^8 or 710 million years. If one kilogram sample disintegrates, then 0.5 kg of it is converted to daughter elements in 710 million years. Out of 0.5 kg of ${}^{235}_{92}\mathrm{U}$, 0.25kg disintegrates in the next 710 million years. So, the half-life period for the disintegration of a radioactive substance is independent of the amount of that substance.

What is true for the half-life period of first order reactions does not remain true for the reactions having higher orders. In the case of second order reaction, the half-life period is inversely proportional to the initial concentration of the reactant. For a third order reaction, half life is inversely proportional to the square of initial concentration of reactants. Briefly we can say that

$$[t_{1/2}]_1 \propto \frac{1}{a^o},\ \text{scince}[t_{1/2}]_1 = \frac{0.693}{k}$$

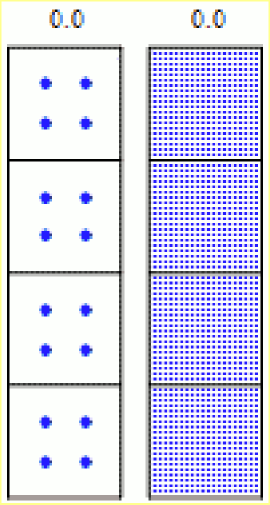
$$[t_{1/2}]_2 \propto \frac{1}{a^1},\ \text{scince}[t_{1/2}]_2 = \frac{1}{k_a}$$

$$[t_{1/2}]_3 \propto \frac{1}{a^2},\ \text{scince}[t_{1/2}]_3 = \frac{1.5}{ka^2}$$

Where $[t_{1/2}]_1$, $[t_{1/2}]_2$, and $[t_{1/2}]_3$ are the half-life periods for 1st, 2nd and 3rd order reactions respectively and 'a' is the initial concentration of reactants. In general for the reaction of nth order:

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

The half-life period of any order reaction is, thus, inversely proportional to the initial concentration raised to the power one less than the order of that reaction. So, if one knows the initial concentration and half-life period of a reaction, then order of that reaction can be determined.



Animation 11.7: Half Life
Source & Credit : askiitians

Example 1:

Calculate the half-life period of the following reaction when the initial concentration of HI is 0.05 M.

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

The value of rate constant k = 0.079 dm^3 mol^{-1} s^{-1} at 508 °C and rate expression is

$$\text{Rate} = k[HI]^2$$

Solution:

According to the rate expression it is a second order reaction. The half life paired of a second order reaction is

$$\left[t_{\frac{1}{2}}\right]_2 = \frac{1}{ka^{2-1}} = \frac{1}{ka}$$

Putting the values of k and a.

So,
$$\left[t_{\frac{1}{2}}\right]_2 = \frac{1}{k \times a} = \frac{1}{(0.079\,dm^3mol^{-1}s^{-1})(0.050\,mol\,dm^{-3})} = \frac{1}{0.079 \times 0.05}\,\text{sec.}$$

$$\left[t_{\frac{1}{2}}\right]_2 = \boxed{253\,\text{sec}}\,\text{Answer}$$

So, in 253 seconds, the half of HI i.e., 0.05/2=0.025 moles is decomposed.

11.1.5 Rate Determining Step

Finding out the rate equation of a reaction experimentally is very useful. Actually it gives us an opportunity to look into the details of reaction. Rate equation of example (4) in article 11.1.3 showed clearly that the reaction is taking place in more than one steps. There are many such reactions in chemistry which occur in a series of steps.

If a reaction occurs in several steps, one of the steps is the slowest. The rate of this step determines the overall rate of reaction. This slowest step is called the rate determining or rate limiting step. The total number of molecules of reacting species taking part in the rate determining step appear in the rate equation of the reaction.

Let us consider the following reaction

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

The rate equation of the reaction is found to be

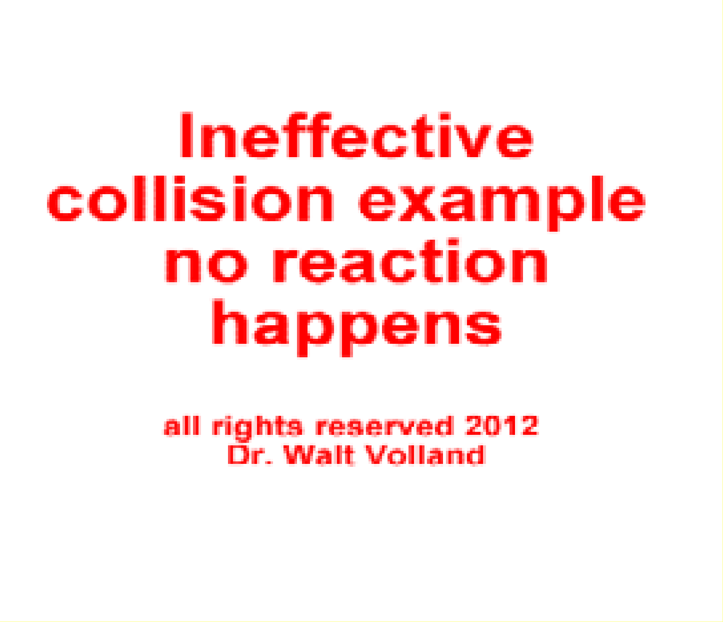
$$\text{Rate} = k[NO_2]^2$$

This equation shows that the rate of reaction is independent of the concentration of carbon monoxide. In other words the equation tells us that reaction involves more than one steps and two molecules of NO_2 are involved in the rate determining step. The proposed mechanism for this reaction is as follows.

$$NO_2(g) + NO_2(g) \xrightarrow{\text{slow}} NO_3(g) + NO(g) \quad \text{(rate determining step)}$$

$$NO_3(g) + CO(g) \xrightarrow{\text{fast}} NO_2(g) + CO_2(g)$$

The first step is the rate determining step and NO_3 which does not appear in the final balanced equation, is called the reaction intermediate. The reaction intermediate has a temporary existence and it is unstable relative to the reactants and the products. This is a species with normal bonds and may be stable enough to be isolated under special conditions. This reaction is a clear example of the fact that a balanced chemical equation may not give any information about the way the reaction actually takes place.



Animation 11.8: Rate Determining Step
Source & Credit : 800mainstreet

11.2.0 DETERMINATION OF THE RATE OF A CHEMICAL REACTION

Determination of the rate of a chemical reaction involves the measurement of the concentration of reactants or products at regular time intervals as the reaction progresses. When the reaction goes on, the concentrations of reactants decrease and those of products increase. The rate of a reaction, therefore, is expressed in terms of the rates at which the concentrations change.

$$\text{Rate of reaction} = \frac{\Delta C}{\Delta t} = \frac{\text{mol dm}^{-3}}{\text{seconds}}$$

$$= \text{mol dm}^{-3}\text{s}^{-1}$$

Suppose, the concentration of a reactant of any chemical reaction changes by 0.01 mol dm^{-3} in one second, then rate of reaction is, 0 .01 mole dm^{-3} s^{-1}.

Rate of a chemical reaction always decreases with the passage of time during the progress of reaction. To determine the rate of reaction for a given length of time, a graph is plotted between time on x-axis and concentration of reactant on y-axis whereby a curve is obtained.

To illustrate it, let us investigate the decomposition of HI to H_2 and I_2 at 508°C. Table(11.1) tells us that the change in concentration of HI for first 50 seconds is 0.0284 mol dm^{-3} but between 300 to 350 sec, the decrease is 0.0031 mol dm^3. By using the data, a graph is plotted as shown in Fig (11.2). The graph is between time on x-axis and concentration of HI in mol dm^{-3} on y-axis. Since HI is a reactant, so it is a falling curve. The steepness of the concentration-time curve reflects the progress of reaction. Greater the slope of curve near the start of reaction, greater is the rate of reaction.

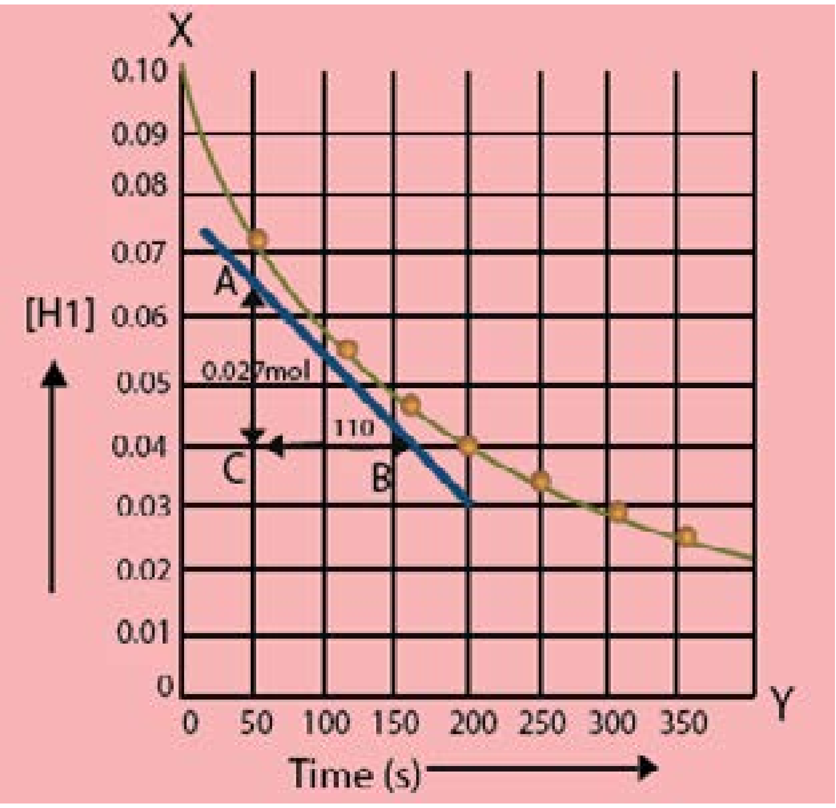


Fig.(11.2) T he change in the HI concentration with time for the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ at 508°C.

Table (11.1) Change in concentration of HI with regular intervals $2HI(g) \rightarrow H_2(g) + I_2(g)$

Concentrationof HI (mol dm^{-3})	Time (s)
0.100	0
0.0716	50
0.0558	100
0.0457	150
0.0387	200
0.0336	250
0.0296	300
0.0265	350

In order to measure the rate of reaction, draw a tangent say, at 100 seconds, on the curve and measure the slope of that tangent. The slope of the tangent is the rate of reaction at that point i.e., after 100 seconds. A right angled triangle ABC is completed with a tangent as hypotenuse. Fig. (11.2) shows that in 110 sec, the change in concentration is 0.027 mole dm^{-3}, and hence the

$$\text{Slope or rate} = \frac{0.027\text{mol dm}^{-3}}{110\text{ sec}}$$

$$=2.5\text{x}10^{-4}\ \text{mol dm}^{-3}\text{s}^{-1}$$

Animation 11.9: Chemical Reaction Rates
Source & Credit : crescentok

This value of rate means that in a period of one sec in 1 dm^3 solution, the concentration of HI disappears by 2.5 x 10^{-4} moles, changing into the products.

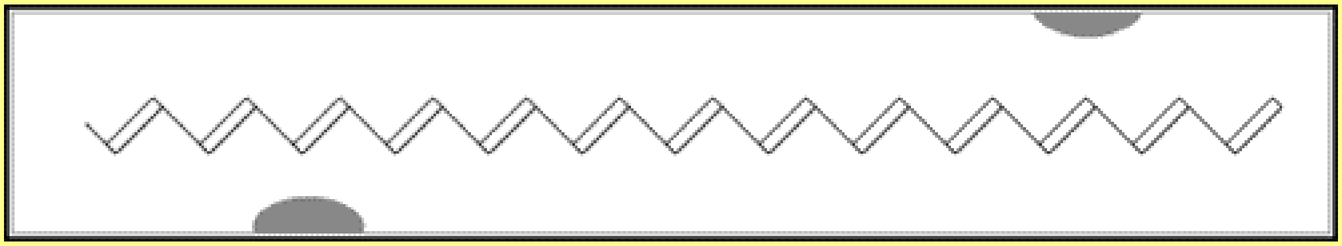
The right angled triangle ABC can be of any size, but the results for the rate of reaction will be the same.

If we plot a graph between time on x-axis and concentration of any of the products i.e H_2 or I_2, then a rising curve is obtained. The value of the tangent at 100 seconds will give the same value of rate of reaction as 2.5 x 10^{-4} mol $dm^{-3}S^{-1}$.

The change in concentrations of reactants or products can be determined by both physical and chemical methods depending upon the type of reactants or products involved.

11.2.1 Physical Methods

Some of the methods used for this purpose cure the following: In these methods, a curve has to be plotted as mentioned in 11.2.0. The nature of the curve may be rising for products and falling for reactants. Anyhow, the results will be same for the same reaction under the similiar conditions.



Animation 11.10: Electrical Conductivity of materials focused on polymer
Source & Credit : wikidot

(i) Spectrometry

This method is applicable if a reactant or a product absorbs ultraviolet, visible or infrared radiation. The rate of reaction can be measured by measuring the amount of radiation absorbed.

(ii) Electrical Conductivity Method

The rate of a reaction involving ions can be studied by electrical conductivity method. The conductivity of such a solution depends upon the rate of change of concentration of the reacting ions or the ions formed during the reaction. The conductivity will be proportional to the rate of change in the concentration of such ions.

(iii) Dilatometric Method

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

(iv) Refractrometric Method

This method is applicable to reactions in solutions, where there are changes in refractive indices of the substances taking part in the chemical reactions.

(v) Optical Rotation Method

In this method, the angle through which plane polarized light is rotated by the reacting mixture is measured by a polarimeter. The extent of rotation determ ines the concentration of optically active substance. If any of the species in the reaction mixture is optically active, then this method can be followed to find out the rate of reaction.

11.2.2 Chemical Method

This is particularly suitable for reactions in solution. In this method, we do the chemical analysis of a reactant or a product.

The acid hydrolysis of an ester (ethyl acetate) in the presence of a small amount of an acid is one of the best examples.

$$CH_3COOC_2H_5(\ell) + H_2O(\ell) \xrightarrow{H^+ \text{(catalyst)}} CH_3COOH(\ell) + C_2H_5OH(\ell)$$

In case of hydrolysis of an ester, the solution of ester in water and the acid acting as a catalyst are allowed to react. After some time, a sample of reaction mixture is withdrawn by a pipette and run into about four times its volume of ice cold water. The dilution and chilling stops the reaction. The acid formed is titrated against a standard alkali, say NaOH, using phenolphthalein as an indicator.

The analysis is repeated at various time intervals after the start of reaction. This would provide an information about the change in concentration of acetic acid formed during the reaction at different time intervals. The different concentrations of acetic acid are plotted against the time whereby a rising curve is obtained as shown in Fig (11.3).

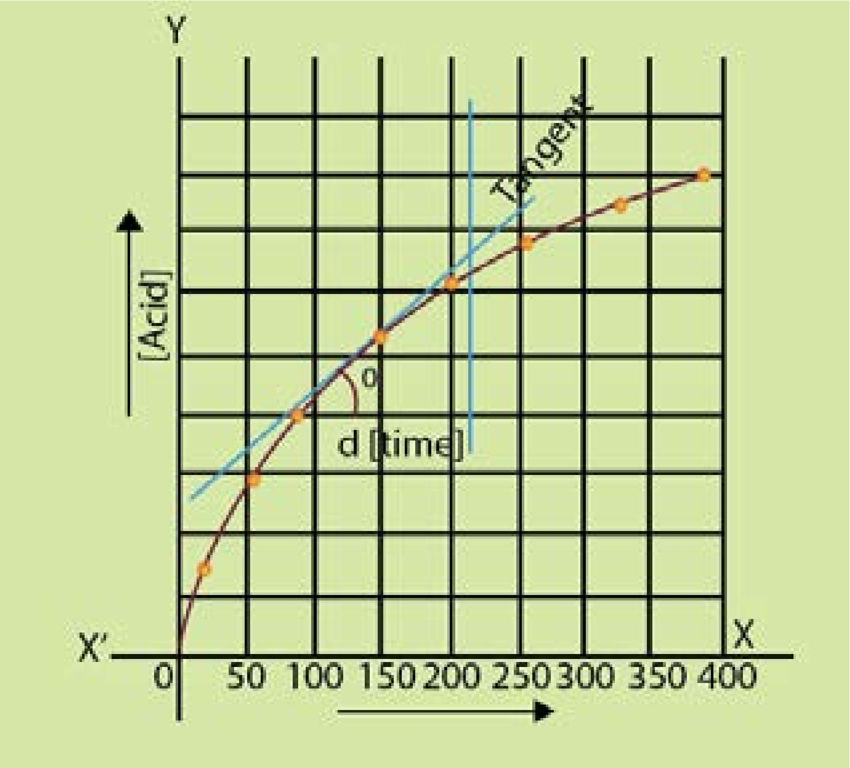
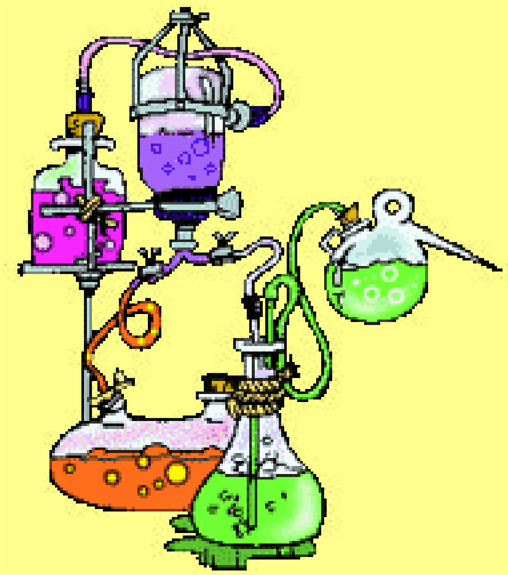


Fig. (11.3) Measurement of rate of ester hydrolysis

The slope of the curve at any point will give the rate of reaction. Initially, the rate of reaction is high but it decreases with the passage of time. When the curve becomes horizontal, the rate becomes zero.

If we plot the graph for decreasing concentrations of $CH_3COOC_2H_5$, then falling curves are obtained as shown in Fig.(11.2) If we have any laboratory technique to record the changing concentration of ester or alcohol, we can measure the rate of the reaction. This is a pseudo first order reaction. Actually water being in large excess in comparison to ester does not affect the rate and we think that water is not taking part in the reaction.



Animation 11.11: Chemical Method
Source & Credit : fg-a

11.3. ENERGY OF ACTIVATION

For a chemical reaction to take place, the particles atoms, ions or molecules of reactants must form a homogeneous mixture and collide with one another. These collisions may be effective or ineffective depending upon the energy of the colliding particles. When these collisions are effective they give rise to the products otherwise the colliding particles just bounce back. The effective collisions can take place only when the colliding particles will possess certain amount of energy and they approach each other with the proper orientation. The idea of proper orientation means that at the time of collision, the atoms which are required to make new bonds should collide with each other. The minimum amount of energy, required for an effective collision is called activation energy.

If all the collisions among the reacting species at a given temperature are effective in forming the products, the reaction is completed in a very short time. Most of the reactions, are, however, slow showing that all the collisions are not equally effective.

Let us study a reaction between molecules A_2 and B_2 to form a new molecule AB. If these molecules will have energy equal to or more than the activation energy, then upon collisions their bonds will break and new bonds will be formed. The phenomenon is shown in Fig. (11.4)

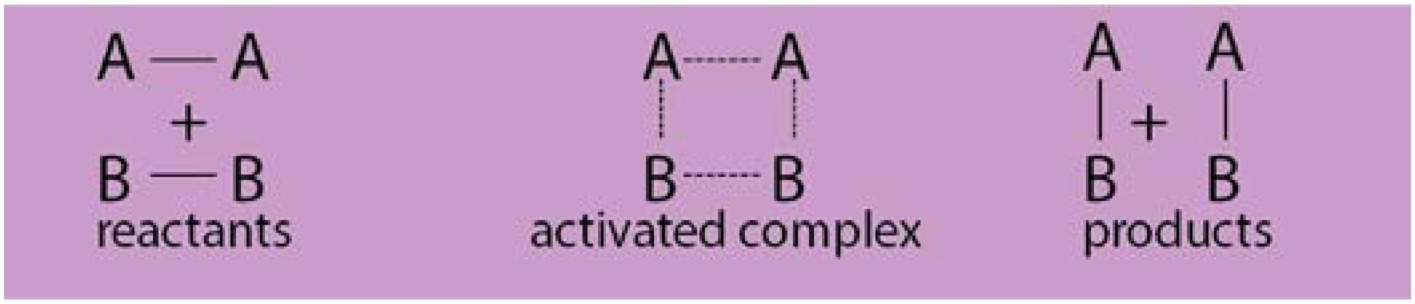


Fig. (11.4) Collisions of molecules, formation of activated complex and formation of products

Activated complex is an unstable combination of all the atoms involved in the reaction for which the energy is maximum. It is a short lived species and decomposes into the products immediately. It has a transient existence, that is why it is also called a transition state.

When the colliding molecules come close to each other at the time of collision, they slow down, collide and then fly apart. If the collision is effective then the molecules flying apart are chemically different otherwise the same molecules just bounce back.

When the molecules slow down just before the collision, their kinetic energy decreases and this results in the corresponding increase in their potential energy. The process can be understood with the help of a graph between the path of reaction and the potential energy of the reacting molecules. Fig. (11.5a,b)

The reactants reach the peak of the curve to form the activated complex. E_a is the energy of activation and it appears as a potential energy hill between the reactants and the products. Only, the colliding molecules with proper activation energy, will be able to climb up the hill and give the products. If the combined initial kinetic energy of the reactants is less than E_a, they will be unable to reach the top of the hill and fall back chemically unchanged.

This potential energy diagram can also be used to study the heat evolved or absorbed during the reaction. The heat of reaction is equal to the difference in potential energy of the reactants and the products. For exothermic reactions, the products are at a lower energy level than the reactants and the decrease in potential energy appears as increase in kinetic energy of the products Fig. (11.5a). For endothermic reactions, the products are at higher energy level than the reactants and for such reactions a continuous source of energy is needed to complete the reaction Fig. (11.5b).

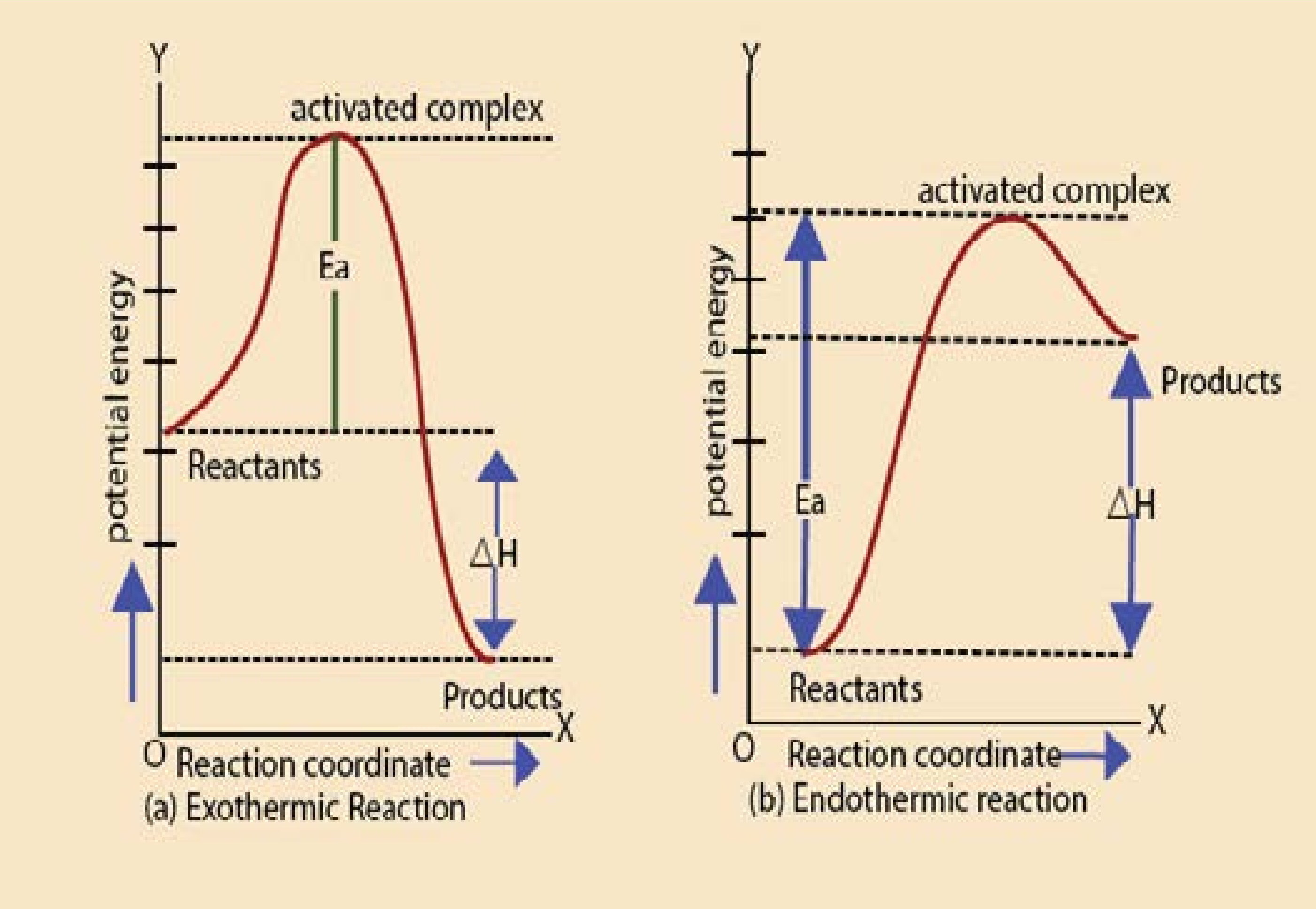
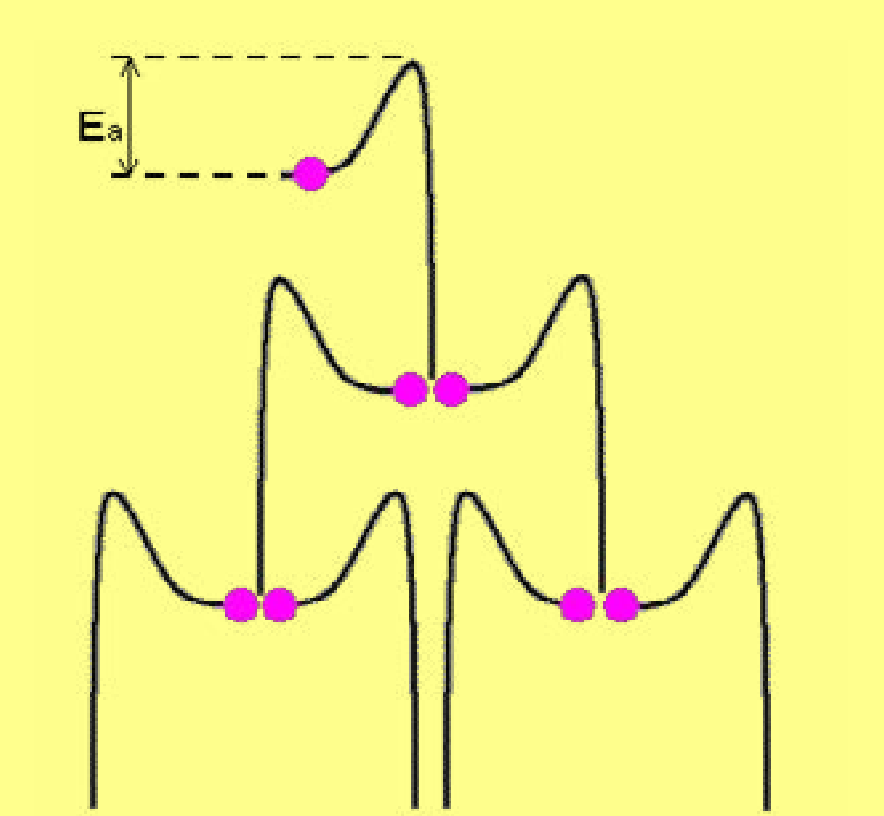


Fig. (11.5) A graph between path of reaction and the potential energy of the reaction

The energy of activation of forward and backward reactions are different for all the reactions. For exothermic reactions the energy of activation of forward reaction is less than that of backward reaction, while reverse is true for endothermic reactions. Energy of activation of a reaction provides a valuable information about the way a reaction takes place and thus helps to understand the reaction.



Animation 11.12: Activation Energy and Spontaneous reactions
Source & Credit : thompsona

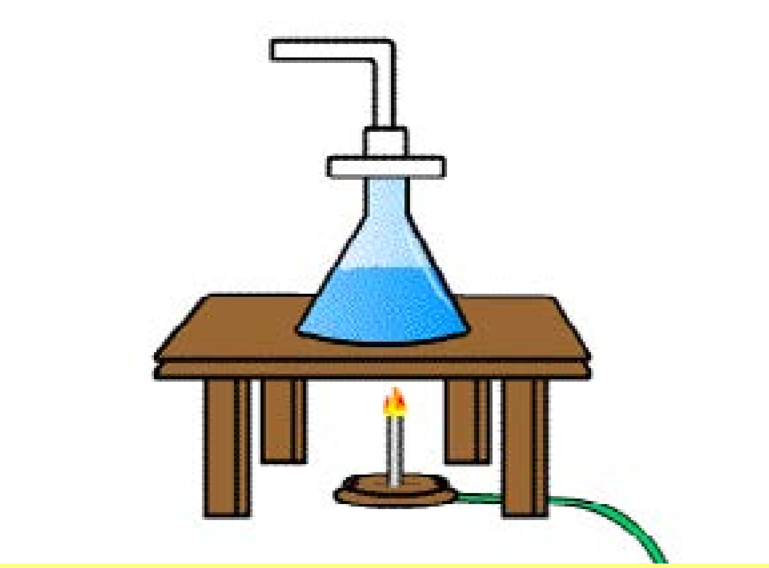
11.4 FINDING THE ORDER OF REACTION

The order of a reaction is the sum of exponents of the concentration terms in the rate expression of that reaction.

It can be determined by the following methods.

(i) Method of hit and trial
(ii) Graphical method
(iii) Differential method
(iv) Half life method
(v) Method of large excess

Here we will only discuss half-life method and the method of large excess.



Animation 11.13: Determination of Order of a Reaction
Source & Credit : askiitians

11.4.1 Half Life Method

As mentioned earlier, half life of a reaction is inversely proportional to the initial concentration of reactants raised to the power one less than the order of reaction.

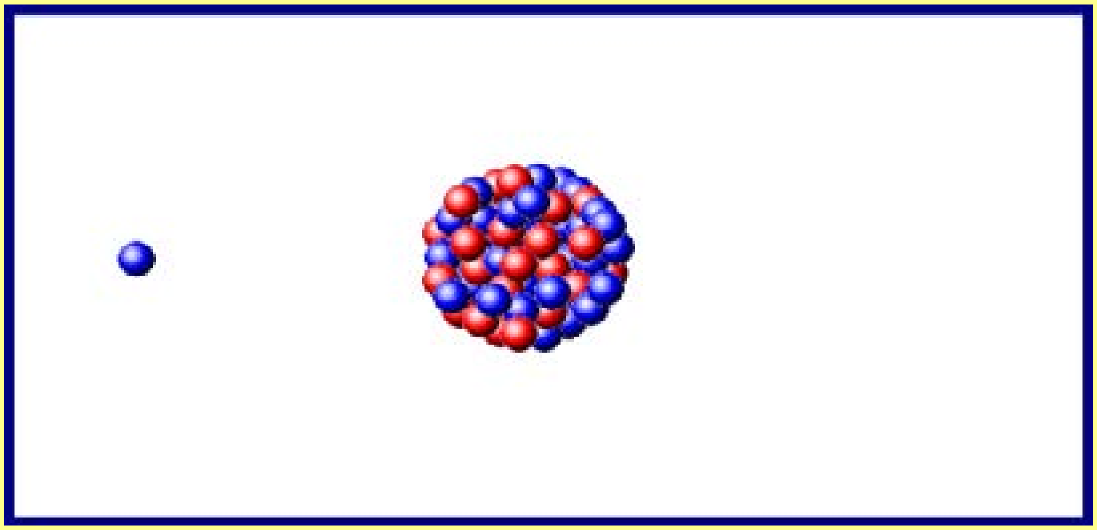
Therefore, $$(t_{1/2})_n \propto \frac{1}{a^{n-1}}$$

Let us perform a reaction twice by taking two different initial concentrations 'a_1' and 'a_2' and their half-life periods are found to be t_1 and t_2 respectively.

$$t_1 \propto \frac{1}{a_1^{\,n-1}} \qquad \text{and} \qquad t_2 \propto \frac{1}{a_2^{\,n-1}}$$

Dividing the two relations: $$\frac{t_1}{t_2} = \left[\frac{a_2}{a_1}\right]^{n-1}$$

Taking log on both sides: $$\log\frac{t_1}{t_2} = (n-1)\log\left[\frac{a_2}{a_1}\right]$$



Animation 11.14: Half Life
Source & Credit : wikipedia

$$n-1=\frac{\log\left[\frac{t_1}{t_2}\right]}{\log\left[\frac{a_2}{a_1}\right]}$$

Rearranging
$$n=1+\frac{\log\left[\frac{t_1}{t_2}\right]}{\log\left[\frac{a_2}{a_1}\right]}$$

So, if we know the two initial concentrations and two half life values we can calculate the order of reaction (n).

Example 2:

In the thermal decomposition of N_2O at 760 °C, the time required to decompose half of the reactant was 255 seconds at the initial pressure of 290 mm Hg and 212 seconds at the initial pressure of 360 mmHg. Find the order of this reaction.

Solution:

The initial pressures of $N_2O(g)$ are the initial concentrations.

Data $a_1 = 290\text{mm Hg}$ $t_1 = 255\text{ seconds}$

$a_2 = 360\text{mm Hg}$ $t_2 = 212\text{ seconds}$

Formula used

$$n = 1 + \frac{\log\left[\frac{t_1}{t_2}\right]}{\log\left[\frac{a_2}{a_1}\right]}$$

Putting the values in the above equation

$$n = 1 + \frac{\log\left[\frac{255}{212}\right]}{\log\left[\frac{360}{290}\right]}$$

$$n = 1 + \frac{0.0802}{0.0940}$$

$$n = 1 + 0.85 = 1.85 \approx 2$$

1.85 is close to 2, hence the reaction is of second order.

11.4.2 Method of Large Excess

In this method, one of the reactants is taken in a very small amount as compared to the rest of the reactants. The active masses of the substances in large excess remain constant throughout. That substance taken in small amount controls the rate and the order is noted with respect to that.

The reason is that a small change in concentration of a substance taken in very small amount affects the value of rate more appreciably. The hydrolysis of ethyl acetate as mentioned earlier shows that water being in large excess does not determine the order.

In this way, the reaction is repeated by taking rest of the substances in small amounts one by one and overall order is calculated. The method will be further elaborated in article 11.5.2.

11.5. FACTORS AFFECTING RATES OF REACTIONS

All those factors which change the number of effective collisions per second, affect the rate of a chemical reaction. Some of the important factors are as follows.

Animation 11.15: FACTORS AFFECTING RATES OF REACTIONS
Source & Credit : askiitians

11.5.1 Nature of Reactants

The rate of reaction depends upon the nature of reacting substances. The chemical reactivity of the substances is controlled by the electronic arrangements in their outermost orbitals. The elements of I-A group have one ejectron in their outermost s-orbital. They react with water more swiftly than those of II-A group elements having two electrons in their outermost s-orbital. Similarly, the neutralization and double decomposition reactions are very fast as compared to those reactions in which bonds are rearranged. Oxidation-reduction reactions involve the transfer of electrons and are slower than ionic reactions.

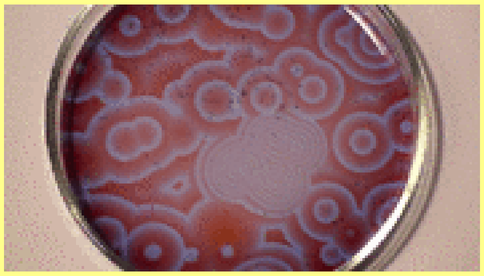
11.5.2 Concentration of Reactants

The reactions are due to collisions of reactant molecules. The frequency with which the molecules collide depends upon their concentrations. The more crowded the molecules are, the more likely they are to collide and react with one another. Thus, an increase in the concentrations of the reactants will result in the corresponding increase in the reaction rate, while a decrease in the concentrations will have a reverse effect. For example, combustion that occurs slowly in air (21 % oxygen) will occur more rapidly in pure oxygen.

Similarly, limestone reacts with different concentrations of hydrochloric acid at different rates. In the case of a gaseous reactant, its concentration can be increased by increasing its pressure. Therefore, a mixture of H_2 and Cl_2 will react twice as fast if the partial pressure of H_2 or Cl_2 is increased from 0.5 to 1.0 atmosphere in the presence of excess of the other component.

The effect of change in concentration on the rate of a chemical reaction can be nicely understood from the following gaseous reaction.

$$2NO(g) + 2H_2(g) \rightarrow 2H_2O(g) + N_2(g)$$



Animation 11.16: Reactants
Source & Credit : giphy

In this reaction, four moles of the reactants form three moles of the products, so the pressure drop takes place during the progress of reaction. The rates of reaction between NO and H_2 at 800°C are studied by noting the change in pressure. The following Table (11.2) has been obtained experimentally for the above reaction.

Table (11.2) Effect of change in concentrations of reactants on the rate of reaction

[NO] in (mol dm^{-3})	[H_2] in (mol dm^{-3})	Initial rate (atm min^{-1})
0.006	0.001	0.025
0.006	0.002	0.050
0.006	0.003	0.075
0.001	0.009	0.0063
0.002	0.009	0.025
0.003	0.009	0.056

Table (11.2)shows the results of six experiments. In the first three experiments the concentration of H_2 is increased by keeping the concentration of NO constant. By doubling the concentration of H_2, the rate is doubled and by tripling the concentration of H_2, the rate is tripled. So, the rate of reaction is directly proportional to the first power of concentration of H_2.

$$\text{Rate} \propto [H_2]$$

In the next three experiments, the concentration of H_2 is kept constant. By doubling the concentration of NO, the rate increases four times and by tripling the concentration of NO the rate is increased nine times. So, the rate is proportional to the square of concentration of NO.

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

The overall rate equation of reaction is,

$$\text{Rate} \propto [H_2][NO]^2$$

or $$\text{Rate} = k[H_2]^1[NO]^2$$

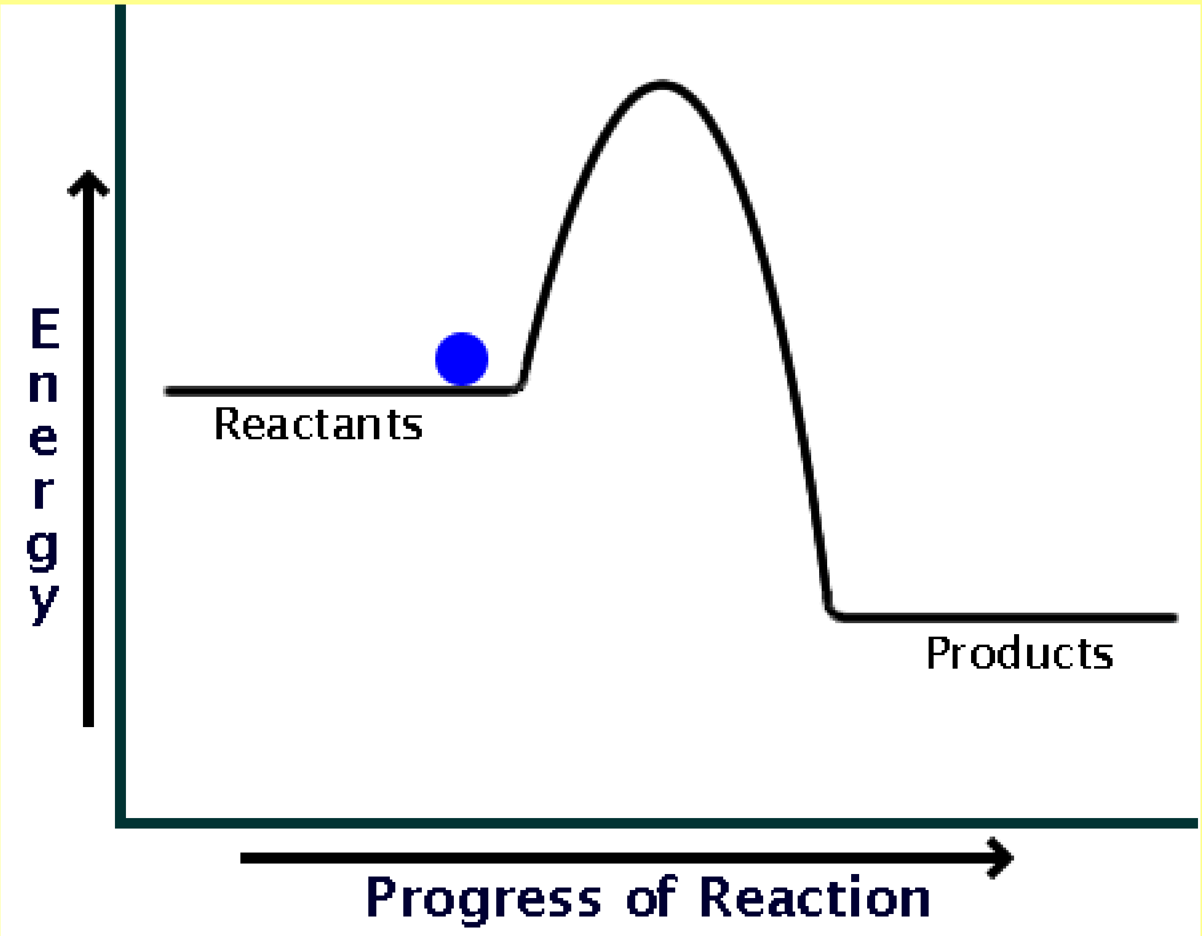
Hence, the reaction is a third order one. This final equation is the rate law for this reaction. It should be kept in mind that rate law cannot be predicted from the balanced chemical equation. This set of experiments helps us to determine the order of reaction as well.

The possible mechanism consisting of two steps for the reaction is as follows:

(i) $2NO(g) + H_2(g) \xrightarrow{slow} N_2(g) + H_2O_2(g)$ (rate determining)

(ii) $H_2O_2(g) + H_2(g) \xrightarrow{fast} 2H_2O(g)$

The step (i) is slow and rate determining.



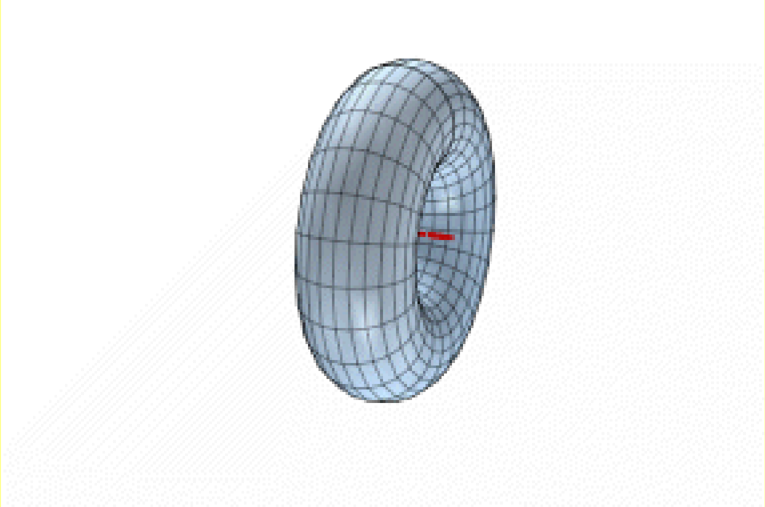
Animation 11.17: Concentration of Reactants
Source & Credit : socratic

11.5.3 Surface Area

The increased surface area of reactants, increases the possibilities of atoms and molecules of reactants to come in contact with each other and the rates enhance. For example, Al foil reacts with NaOH moderately when warmed, but powdered Al reacts rapidly with cold NaOH and H_2 is evolved with frothing.

$$2Al + 2NaOH + 6H_2O \rightarrow 2NaAl(OH)_4 + 3H_2$$

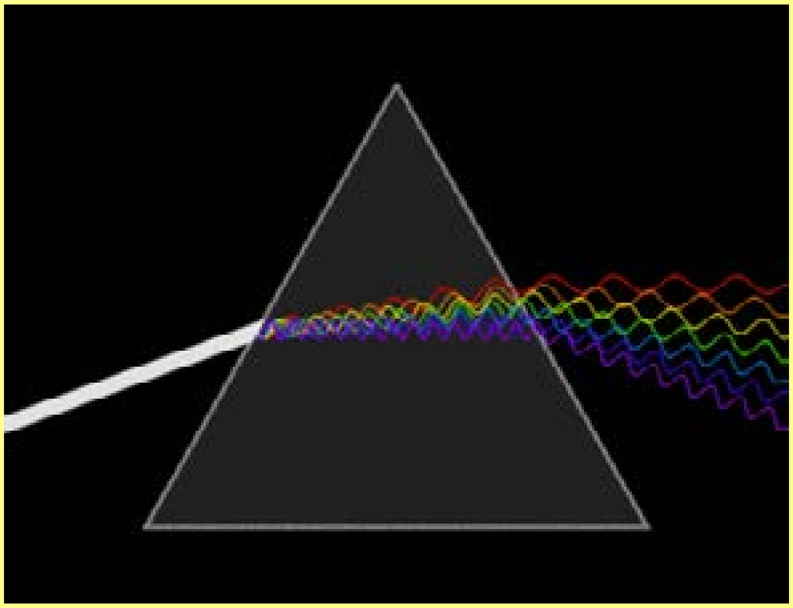
Similarly, $CaCO_3$ in the powder form reacts with dilute H_2SO_4 more efficiently than its big pieces.



Animation 11.18: Surface Area
Source & Credit : darelhardy

11.5.4 Light

Light consists of photons having definite amount of energies depending upon their frequencies. When the reactants are irradiated, this energy becomes available to them and rates of reactions are enhanced. The reaction of CH_4 and Cl_2 requires light. The reaction between H_2 and Cl_2 at ordinary pressure is negligible in darkness, slow in daylight, but explosive in sunlight. Similarly, light is vital in photosynthesis, and the rate is influenced by light.



Animation 11.19: Light
Source & Credit : wikipedia

11.5.5 Effect of Temperature on Rate of Reaction

The collision theory of reaction rates convinces us that the rate of a reaction is proportional to the number of collisions among the reactant molecules. Anything, that can increase the frequency of collisions should increase the rate. We also know, that every collision does not lead to a reaction. For a collision, to be effective the molecules must possess the activation energy and they must also be properly oriented. For nearly all chemical reactions, the activation energy is quite large and at ordinary temperature very few molecules are moving fast enough to have this minimum energy.

All the molecules of a reactant do not possess the same energy at a particular temperature. Most of the molecules will possess average energy. A fraction of total molecules will have energy more than the average energy. This fraction of molecules is indicated as shaded area in Fig.(11.6).

As the temperature increases, the number of molecules in this fraction also increases. There happens a wider distribution of velocities. The curve at higher temperature T_2 has flattened. It shows that molecules having higher energies have increased and those with less energies have deceased. So, the number of effective collisions increases and hence the rate increases. When the temperature of the reacting gases is raised by 10K, the fraction of molecule with energy more than E_a roughly doubles and so the reaction rate also doubles. Arrheinus has studied the quantitative relationship between temperature, energy of activation and rate constant of a reaction.

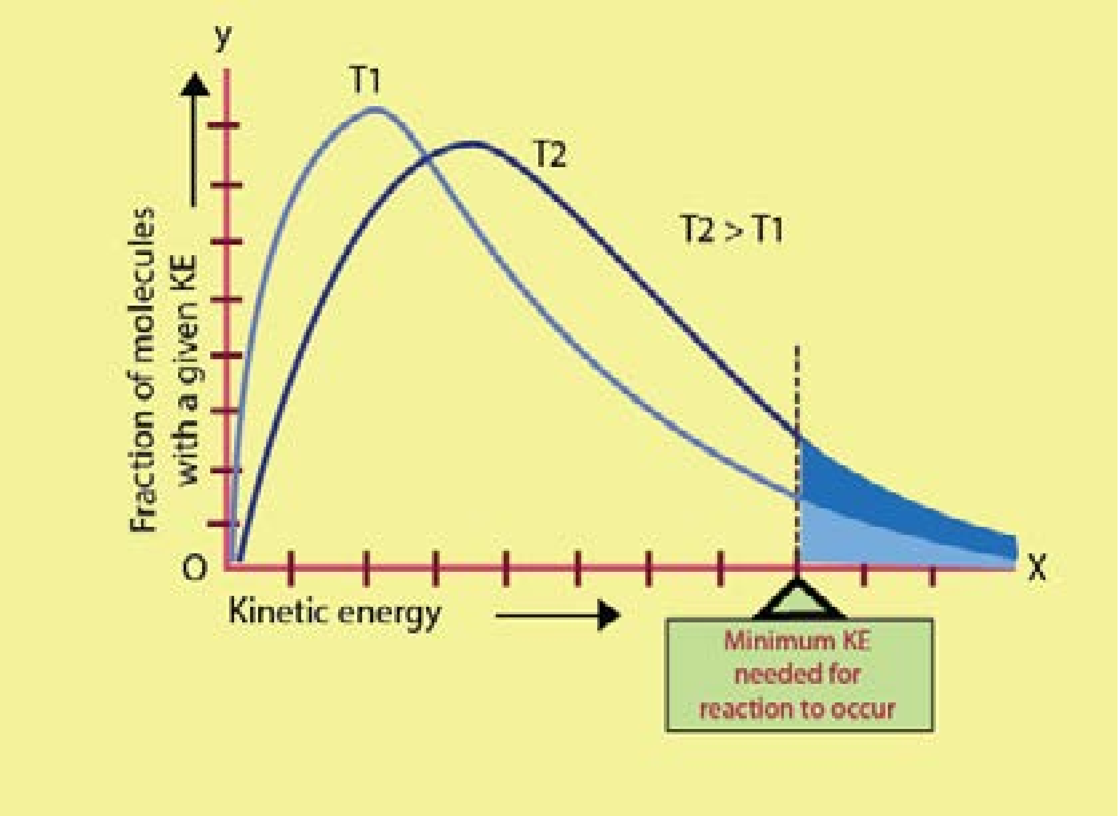
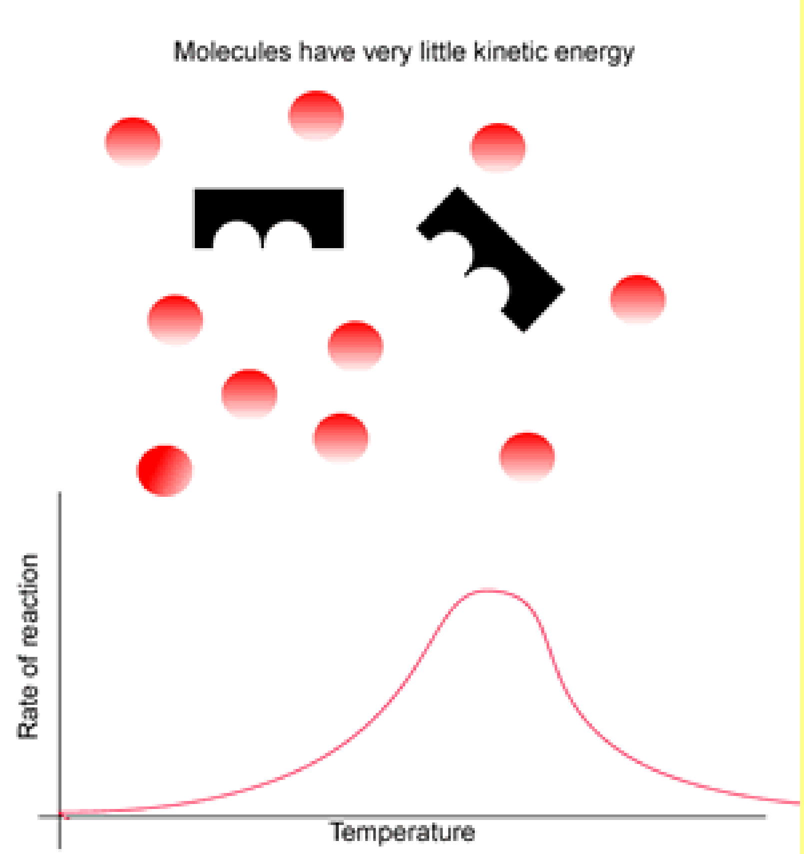


Fig. (11.6) Kinetic energy distributions for a reaction mixture at two different temperatures. The size of the shaded areas under the curves are proportional to the total fraction of the molecules that possess the minimum activation energy.



Animation 11.20: Effect of Temperature on Rate of Reaction
Source & Credit : dynamicscience

11.5.6 Arrhenius Equation

Arrhenius equation explains the effect of temperature on the rate constant of a reaction. The rate constant 'k' for many simple reactions is found to vary with temperature.
According to Arrhenius:

$$k=Ae^{-Ea/RT} \qquad \text{........ (1)}$$

So, 'k' is exponentially related to activation energy (E_a) and temperature (T). R is general gas constant and e is the base of natural logarithm. The equation shows that the increase in temperature, increases the rate constant and the reactions of high activation energy have low 'k' values.

The factor 'A' is called Arrhenius constant and it depends upon the collision frequency of the reacting substances. This equation helps us to determine the energy of activation of the reaction as well. For this purpose, we take natural log of Arrhenius equation, which is expressed as ℓn. The base of natural log is e and its value is 2.718281.

Now, take natural log on both sides

$$\ell nk = \ell n(Ae^{-Ea/RT})$$

or $$\ell nk = \ell nA + \ell ne^{-Ea/RT}$$

or $$\ell nk = \ell nA + \frac{-E}{RT}\ell ne$$

Since $\ell ne = 1$ (log of a quantity with same base is unity)

Therefore $$\ell nk = \frac{-E_a}{RT} + \ell nA \qquad \text{..........} \quad (2)$$

The equation (1) is the equation of straight line, and from the slope of straight line E_a can be calculated. In order to convert this natural log into common log of base 10, we multiply the ℓn term with 2.303.

$$2.303 \log k = \frac{-E_a}{RT} + 2.303 \log A$$ (The base of common log is 10)

Dividing the whole equation by 2.303

$$\log k = \frac{-E_a}{2.303RT} + \log A \qquad \text{..........} \quad (3)$$

This equation (3) is again the equation of straight line resembling.

y = -mx + c

Where 'm' is slope of straight line and 'c' is the intercept of straight line. Temperature is independent variable in this equation while rate constant k is dependent variable. The other factors like E_a, R and A are constants for a given reaction.

When a graph is plotted between $\frac{1}{T}$ on x-axis and log k on y-axis, a straight line is obtained with a negative slope. Actually, $\frac{E_a}{RT}$ has negative sign so the straight line has two ends in second and fourth quadrants, Fig. (11.7).

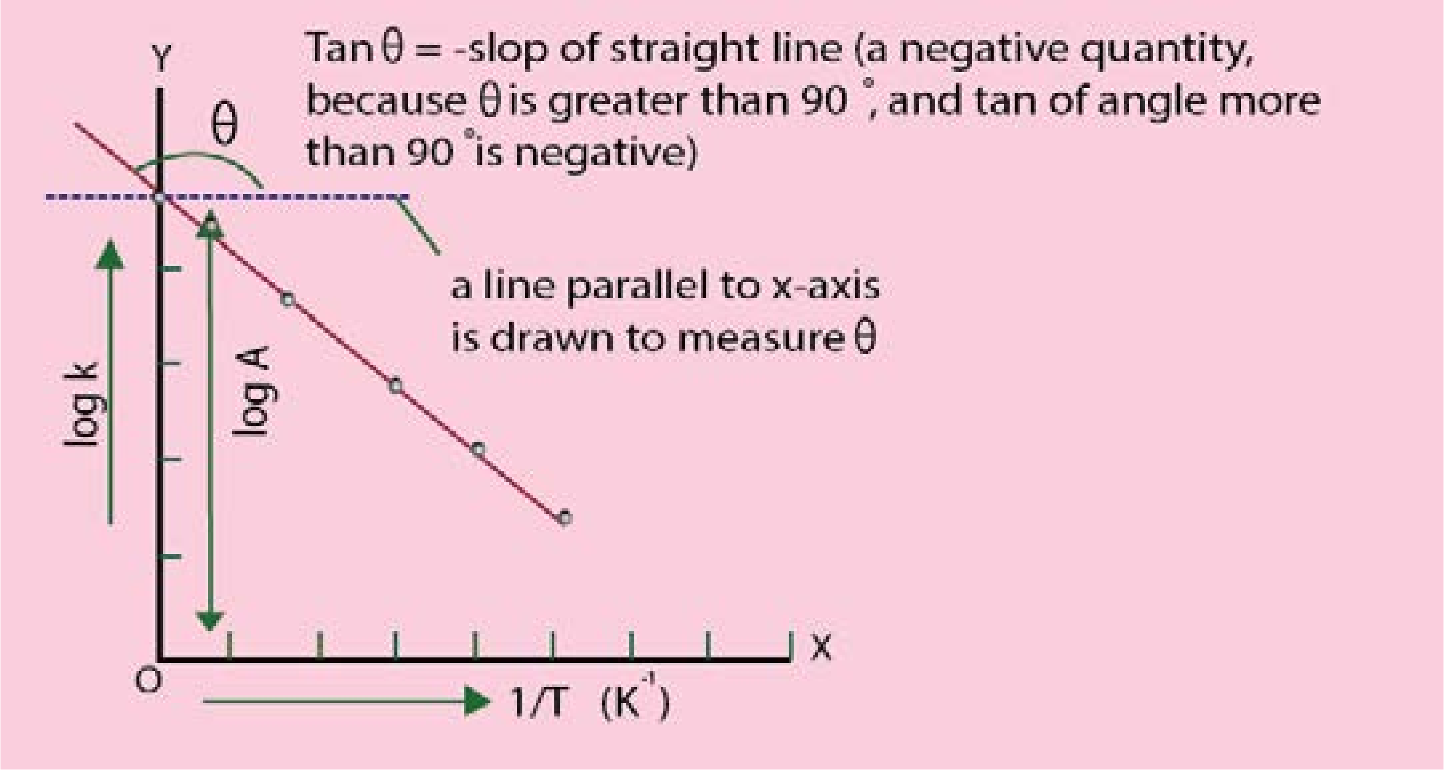


Fig. (11.7) Arrhenuis plot to calculate the energy of activation

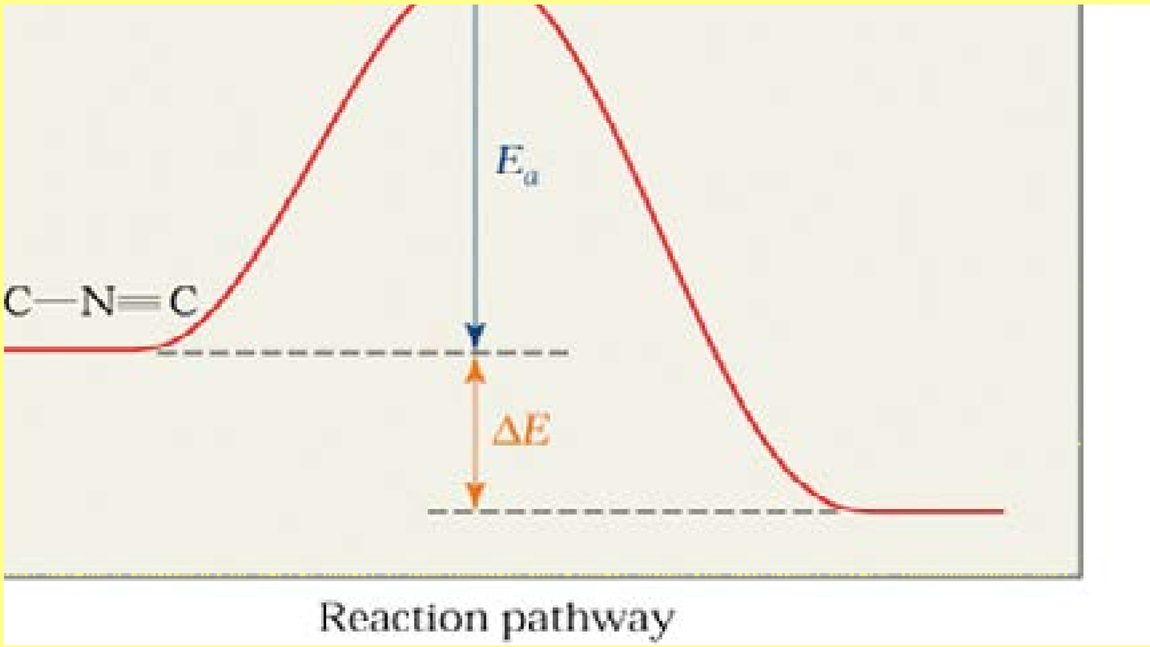
The slope of the straight line is measured by taking the tangent of that angle θ which this straight line makes with the x-axis. To measure the slope, draw a line parallel to x-axis and measure angle θ . Take tan θ which is slope. This slope is equal to $\frac{-E_a}{2.303R}$.

$$\text{Slop} = \frac{-E_a}{2.303\ R}$$

Therefore $E_a = -\text{Slop} \times 2.303\ R$ ....(4)

The straight lines of different reactions will have different slopes and different 'E_a' values. The units of slope are in kelvins (K).

Since $\text{Slop} = \frac{J\ mol^{-1}}{2.303\ JK^{-1}mol^{-1}} = K$



Animation 11.21: Arrhenius Equation
Source & Credit : wps

Example 3:

A plot of Arrhenius equation Fig (11.8) for the thermal decompositions of N_2O_5 is shown in the following figure. The slope is found to be -5400 K. Calculate the energy of activation of this reaction.

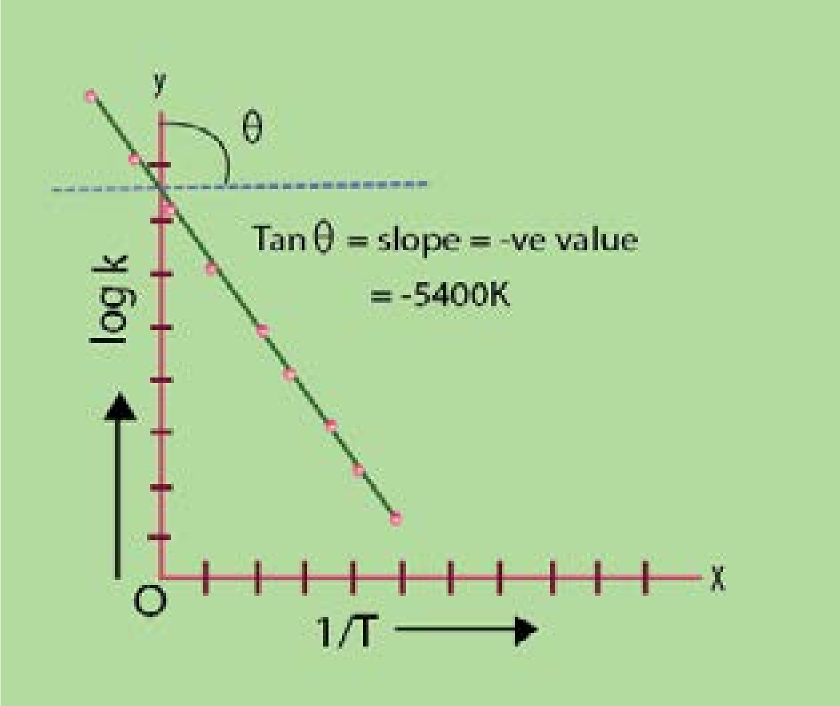


Fig. (11.8) Arrhenius plot for decomposition of N_2O_5

Solution:

(i) The reaction is

$$N_2O_5 \longrightarrow 2NO_2 + 1/2O_2$$

Slope of the straight line = -5400 K

Equation used, E_a = -slope x 2.303 R

R = 8.3143JK^{-1}mol^{-1}

Putting the values,

E_a =-(-5400K)x 2.303 x 8.3143JK^{-1}mol^{-1}

E_a= +103410 J mol^{-1}

E_a = 103.410 kJ mol^{-1}

Hence, the decomposition of N_2O needs 103.4kJmol^{-1} energy more than the average energy to cross the energy barrier Fig.(11.9)

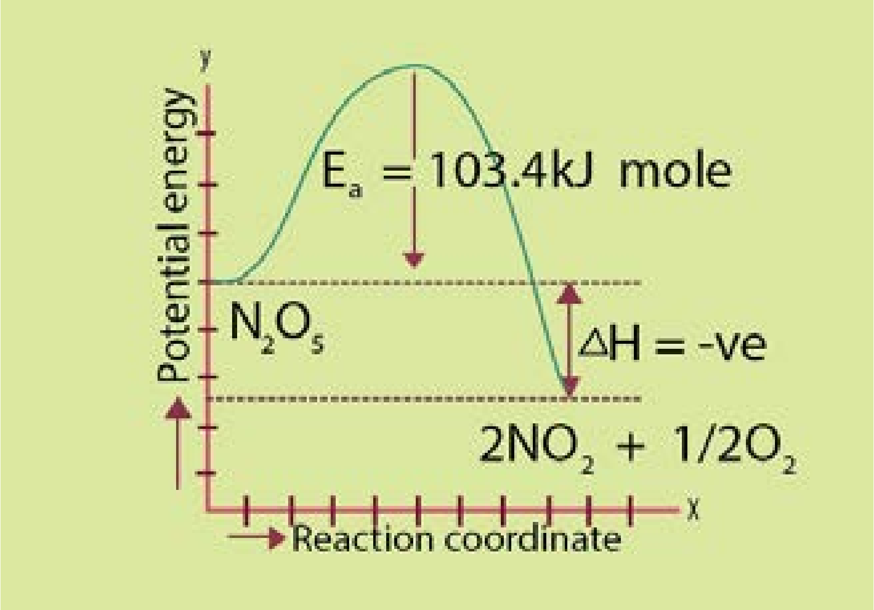


Fig. (11.9) Potential energy diagram of N_2O_5 decomposition

11.6 CATALYSIS

A catalyst is defined as a substance which alters the rate of a chemical reaction, but remains chemically unchanged at the end of the reaction. A catalyst is often present in a very small proportion. For example, the reaction between H_2 and O_2 to form water is very slow at ordinary temperature, but proceeds more rapidly in the presence of platinum. Platinum acts as a catalyst. Similarly, $KClO_3$ decomposes much more rapidly in the presence of a small amount of MnO_2. HCl is oxidised to Cl_2 in the presence of $CuCl_2$.

$$4HCl+O_2 \xrightarrow{CuCl_2} 2H_2O+2Cl_2$$

The process, which takes place in the presence of a catalyst, is called catalysis. A catalyst provides a new reaction path with a low activation energy barrier, Fig.(11.10). A greater number of molecules are now able to get over the new energy barrier and reaction rate increases.

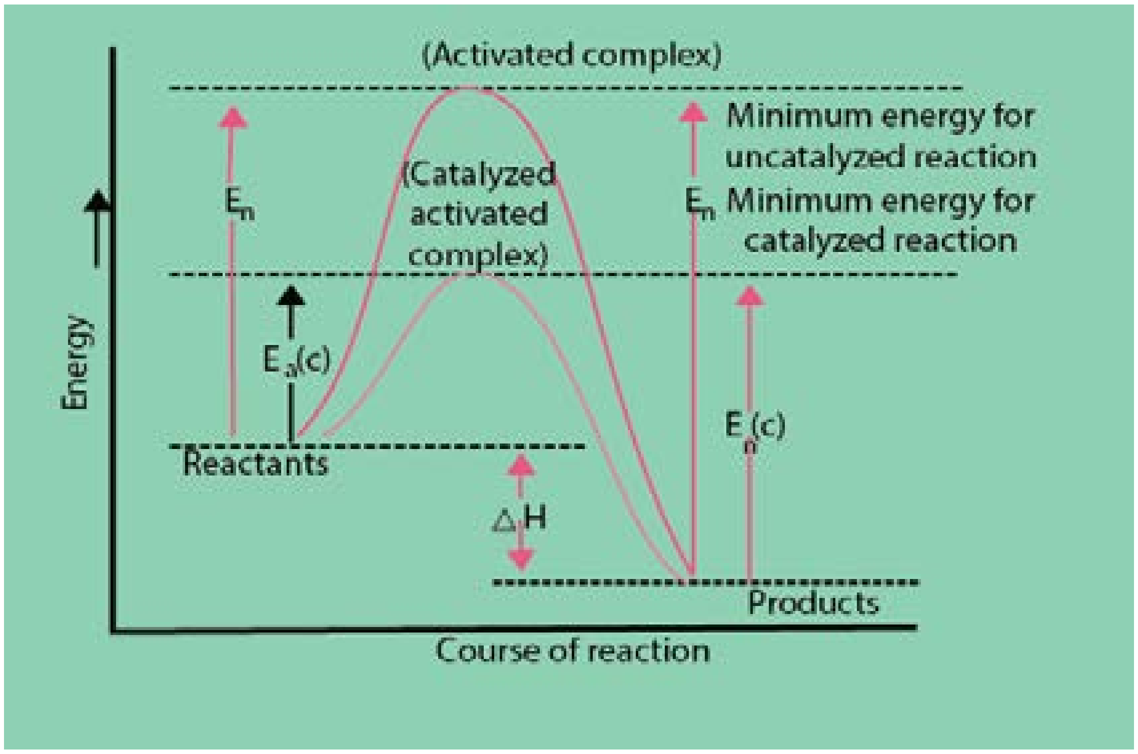
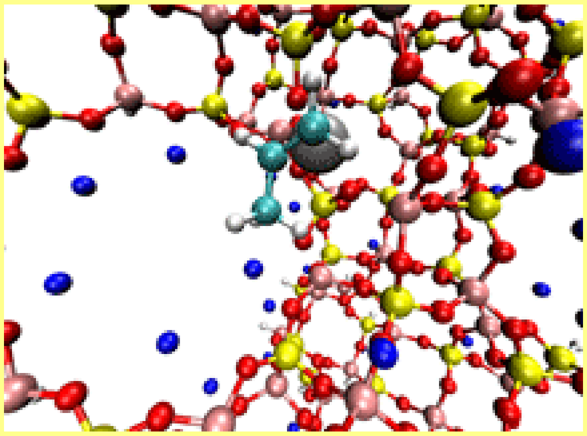


Fig. (11.10) Catalyzed and uncatalyzed reactions.



Animation 11.22: CATALYSIS
Source & Credit : lsa.umich

Types of Catalysis

(a) Homogeneous Catalysis
(b) Heterogeneous Catalysis

(a) Homogeneous Catalysis

In this process, the catalyst and the reactants are in the same phase and the reacting system is homogeneous throughout. The catalyst is distributed uniformly throughout the system. For example:

(i). The formation of SO_3 (g) from SO_2 (g) and O_2 (g) in the lead chamber process for the manufacture of sulphuric acid, needs NO (g) as a catalyst. Both the reactants and the catalyst are gases.

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

(ii). Esters are hydrolysed in the presence of H_2SO_4. Both the reactants and the catalyst are in the solution state.

$$CH_3COOC_2H_5(aq) + H_2O(\ell) \xrightarrow[H_2SO_4]{H_3O^+} CH_3COOH(aq) + C_2H_5OH(aq)$$

(b) Heterogeneous Catalysis

In such systems, the catalyst and the reactants are in different phases. Mostly, the catalysts are in the solid phase, while the reactants are in the gaseous or liquid phasse. For example:

(i). Oxidation of ammonia to NO in the presence of platinum gauze helps us to manufacture HNO_3.

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt(s)} 4NO(g) + 6H_2O(g)$$

(ii) Hydrogenation of unsaturated organic compounds are catalysed by finely divided Ni, Pd or Pt.

$$CH_2 = CH_2(g) + H_2(g) \xrightarrow{Ni(s)} CH_3 - CH_3(g)$$

11.6.1 Characteristics of a Catalyst

There are many types of catalysts with varying chemical compositions, but the following features are common to most of them.

1. A catalyst remains unchanged in mass and chemical composition at the end of reaction. It may not remain in the same physical state. MnO_2 is added as a catalyst for the decomposition of $KClO_3$ in the form of granules. It is converted to fine powder at the end of reaction. It has been found in many cases that the shining surfaces of the solid catalyst become dull.
2. Sometimes, we need a trace of a metal catalyst to affect very large amount of reactants. For example, 1 mg of fine platinum powder can convert 2.5 dm^3 of H_2 and 1.25 dm^3 of O_2 to water. Dry HCl and NH_3 don't combine, but in the presence of trace of moisture, they give dense white fumes of NH_4Cl. Thousands of dm^3 of H_2O_2, can be decomposed in the presence of 1 g of colloidal platinum.
3. A catalyst is more affective, when it is present in a finely divided form. For example, a lump of platinum will have much less catalytic activity than colloidal platinum. In the hydrogenation of vegetable oils finely divided nickel is used.
4. A catalyst cannot affect the equilibrium constant of a reaction but it helps the equilibrium to be established earlier. The rates of forward and backward steps are increased equally.
5. A catalyst cannot start a reaction, which is not thermodynamically feasible. It is now considered that a catalyst can initiate a reaction. The mechanism of a catalysed reaction is different from that of an uncatalysed reaction.

For example:

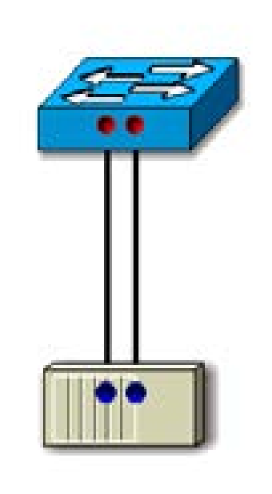
(i) The presence of CO as an impurity with hydrogen decreases the catalytic activity of catalyst in the Haber's process for the manufacture of NH_3.

(ii) The manufacture of H_2SO_4 in the contact process needs platinum as a catalyst. The traces of arsenic present as impurities in the reacting gases makes platinum ineffective. That's why arsenic purifier is employed in the contact process.

11.6.2 Activation of Catalyst

Such a substance which promotes the activity of a catalyst is called a promotor or activator. It is also called “catalyst for a catalyst”. For example :

(i) Hydrogenation of vegetable oils is accelerated by nickel. The catalytic activity of nickel can be increased by using copper and tellurium.



Animation 11.23: Characteristics of a Catalyst
Source & Credit : logilent

(ii) In Haber’s process for the manufacture of ammonia, iron is used as a catalyst. If small amounts of some high melting oxides like aluminum oxide, chromium oxide or rare earth oxides are added, they increase the efficiency of iron.

Negative Catalysis

When the rate of reaction is retarded by adding a substance, then it is said to be a negative catalyst or inhibitor. For example, tetraethyl lead is added to petrol, because it saves the petrol from pre-ignition.

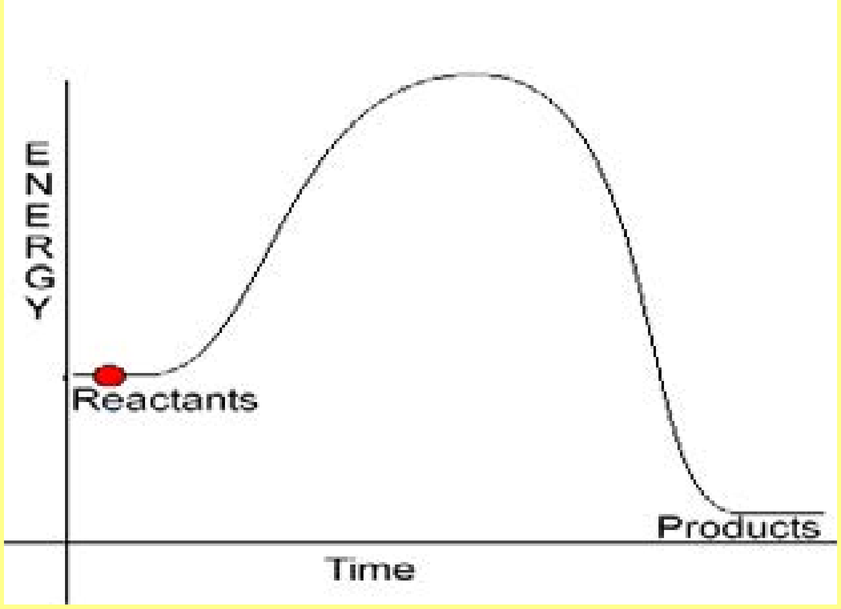
Autocatalyst

In some of the reactions, a product formed acts as a catalyst. This phenomenon is called auto-catalysis. For example:

(i) When copper is allowed to react with nitric acid, the reaction is slow in the beginning. It gains the speed gradually and finally becomes very fast. This is due to the formation of nitrous acid during the reaction, which accelerates the process.

(ii) The reaction of oxalic acid with acidified $KMnO_4$ is slow at the beginning, but after sometimes, $MnSO_4$ produced in the reaction makes it faster.

$$2KMnO_4 + 3H_2SO_4 + 5(COOH)_2 \xrightarrow{Mn^{2+}} K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

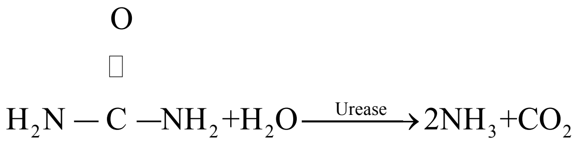


Animation 11.24: Activation of Catalyst
Source & Credit : dynamicscience

11.6.3. Enzyme catalysis

Enzymes are the complex protein molecules and catalyze the organic reactions in the living cells. Many enzymes have been identified and obtained in the pure crystalline state. However, the first enzyme was prepared in the laboratory in 1969. For example:

(i) Urea undergoes hydrolysis into NH_3 and CO_2 in the presence of enzyme urease present in soyabean.



$$H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2+H_2O\xrightarrow{\text{Urease}}2NH_3+CO_2$$

(ii) Concentrated sugar solution undergoes hydrolysis into glucose and fructose by an enzyme called invertase, present in the yeast.

$$C_{12}H_{22}O_{11}+H_2O\xrightarrow{\text{Inertase}}C_6H_{12}O_6+C_6H_{12}O_6$$

(iii) Glucose is converted into ethanol by the enzyme zymase present in the yeast.

$$C_6H_{12}O_6\xrightarrow{\text{Zymase}}2C_2H_5OH+2CO_2$$

Enzymes have active centres on their surfaces. The molecules of a substrate fit into-their cavities just as a key fits into a lock Fig. (11.11). The substrate molecules enter the cavities, form the complex, reactants and the products get out of the cavity immediately. Michaulis and Menter(1913) proposed the following mechanism for enzyme catalysis

$$E+S\rightleftharpoons ES\rightarrow P+E$$

Where

E = enzyme, S = substrate (reactant)

ES = activated complex, P = product

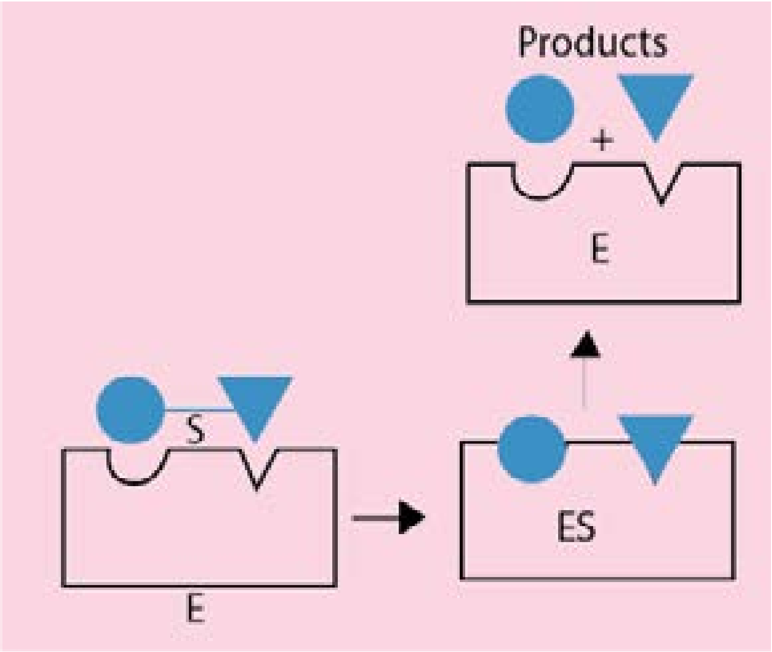
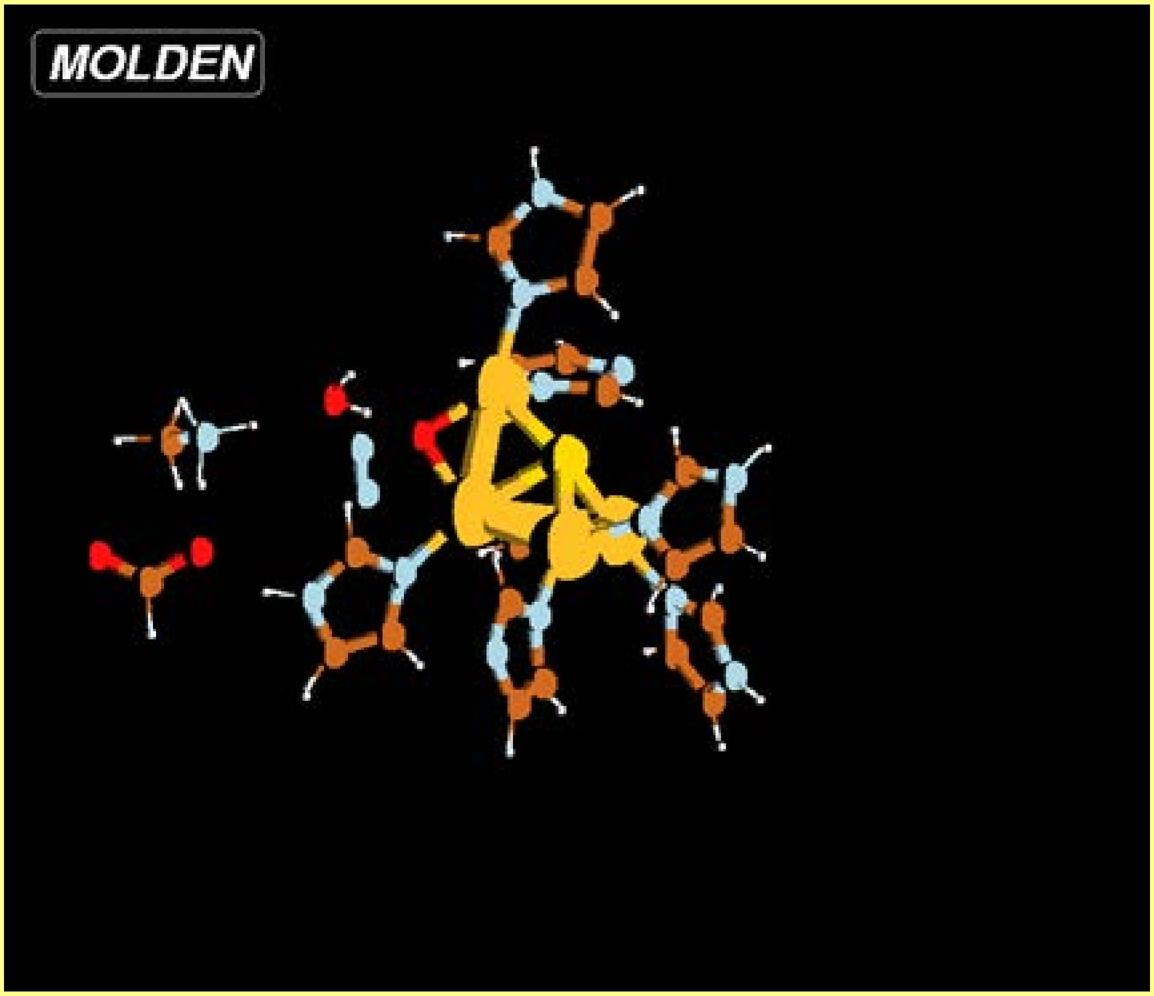


Fig. (11.11) Lock and key model of enzyme catalysis



Animation 11.25: Enzyme catalysis
Source & Credit : kth

11.6.4 Characteristics of Enzyme Catalysis

The role of enzyme as catalysts is like inorganic heterogeneous catalysts. They are unique in their efficiency and have a high degree of specificity. For example:

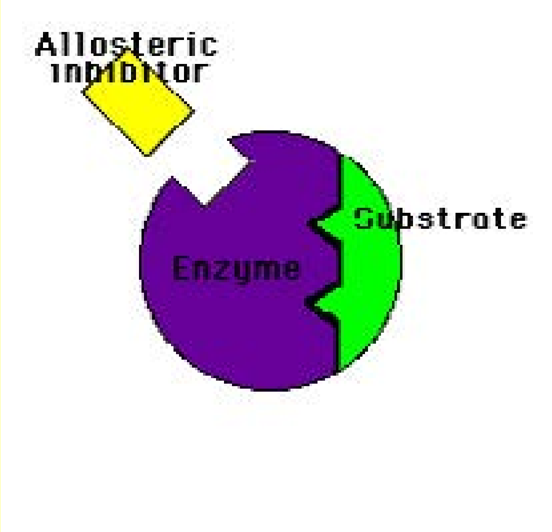
(i) Enzymes are the most efficient catalysts known and they lower the energy of activation of a reaction.

(ii) Enzymes catalysis is highly specific, for example, urease catalyses the hydrolysis of urea only and it cannot hydrolyse any other amide even methyl urea.

(iii) Enzyme catalytic reactions have the maximum rates at an optimum temperature.

(iv) The pH of the system also controls the rates of the enzyme catalysed reaction and the rate passes through a maximum at a particular pH, known as an optimum pH. The activity of enzyme catalyst is inhibited by a poison.

(v) The catalytic activity of enzymes is greatly enhanced by the presence of a co-enzyme or activator.



Animation 11.26: Characteristic of Enzyme
Source & Credit : tdmu

KEY POINTS

1. The studies concerned with rates of chemical reactions and factors that affect the rates of chemical reactions and the mechanism of reactions constitute the subject matter of reaction kinetics.
2. The rate of a reaction is the change in the concentration of a reactant or a product divided by the time taken for the reaction. The rate of reaction between two specific time intervals is called the average rate of reaction. While the rate at any one instant during the interval is called the instantaneous rate. Rate constant of a chemical reaction is rate of reaction when the concentrations of reactants are unity.
3. Order of reaction is the sum of exponents of the concentation terms in the rate expression of a chemical reaction.The exponents in the expression may or may not be different from the coefficients of the chemical equation. Order of a reaction may be zero, whole number or fractional.
4. Half life period of a reaction is the time required to convert 50% of the reactants into products. Half-life period of any reaction is inversely proportional to the initial concentration raised to the power one less than the order of that reaction.
5. The step which limits how fast the overall reaction can proceed, is known as the rate determining step.
6. Determination of the rate of a chemical reaction involves the measurement of the concentration of reactants or products at regular time intervals during the progress of reaction. The change in concentration of reactants and products can be determined by both physical and chemical methods.
7. The effective collisions between the colliding species will take place only when the reactant molecules possess minimum amount of energy, which is called the energy of activation. Moreover, proper orientation is also necessary.
8. All those factors, which change the number of effective collisions per second, affect the rate of chemical reaction. Some of the important factors are, nature and concentration of reactants, surface area, light, and temperature and catalyst.
9. A catalyst is a substance, which alters the rate of a chemical reaction, but itself remains chemically unchanged at the end of reaction. The process when the catalyst and the reactants are in the same phase is said to be a homogenous catalysis. In case of heterogeneous catalysis, the catalyst and the reactants are in different phases. A substance, which promotes the activity of a catalyst, is called promoter or activator. In certain reactions, a product formed acts as a catalyst, the phenomenon is called auto-catalysis.
10. Enzymes are the complex protein molecules, which catalyze the reactions in the living cells.

EXERCISE

Q.1 Multiple choice questions.

(i) In zero order reaction, the rate is independent of

a) temperature of reaction. (b) concentration of reactants,

c) concentration of products (d) none of these

(ii) If the rate equation of a reaction $2A + B \rightarrow$ products is, rate =k$[A]^2$ [B], and A is present in large excess, then order of reaction is

a) 1 (b) 2 (c) 3 (d) none of these

(iii) The rate of reaction

a) increases as the reaction proceeds.
b) decreases as the reaction proceeds.
c) remains the same as the reaction proceeds.
d) may decrease or increase as the reaction proceeds.

(iv) With increase of 10°C temperature the rate of reaction doubles. This increase in ate of reaction is due to:

a) decrease in activation energy of reaction.
b) decrease in the number of collisions between reactant molecules.
c) increase in activation energy of reactants.
d) increase in number of effective collisions.

(v) The unit of the rate constant is the same as that of the rate of reaction in

(a) first order reaction. (b) second order reaction.

(c) zero order reaction. (d) third order reaction.

Q.2 Fill in the blanks with suitable words.

(i) The rate of an endothermic reaction_______ with the increase in temperature.
(ii) All radioactive disintegration nuclear reactions are of________ order
(iii) For a fast reaction the rate constant is relatively and half - life is ______ .
(iv) The second order reaction becomes______ if one of the reactants is in large excess.
(v) Arrhenius equation can be used to find out________of a reaction.

Q.3 Indicate true or false as the case may be.

(i) The half life of a first order reaction increases with temperature.
(ii) The reactions having zero activation energies are instantaneous.
(iii) A catalyst makes a reaction more exothermic.
(iv) There is difference between rate law and the law of mass action.
(v) The order of reaction is strictly determined by the stoichiometry of the bdanced equation.

Q4. What is chemical kinetics? How do you compare chemical kinetics with clemical equilibrium and thermodynamics.

Q5. The rate of a chemical reaction with respect to products is written with positive sign, but with respect to reactants is written with a negative sign. Explain it with reference to the following hypothetical reaction.

$$aA + bB \rightarrow cC + dD$$

Q6 . What are instantaneous and average rates? Is it true that the instantaneousrate of a reaction at the beginning of the reaction is greater than average rate and beomes far less than the average rate near the completion of reaction?

Q7. Differentiate between

(i) Rate and rate constant of a reaction
(ii) Homogeneous and heterogeneous catalyses
(iii) Fast step and the rate determining step
(iv) Enthalpy change of reaction and energy of activation of reaction

Q8. Justify the following statements

(i) Rate of chemical reaction is an ever changing parameter uner the given conditions.
(ii) The reaction rate decreases every moment but rate constant 'k' of the reation is a constant quantity, under the given conditions.
(iii) 50% of a hypothetical first order reaction completes in one hour. The renaming 50% needs more than one hour to complete.
(v) The radioactive decay is always a first order reaction.

(iv) The unit of rate constant of a second order reaction is dm^3 $mol^{-1}s^{-1}$, but the uit of rate of reaction is mol $dm^{-3}s^{-1S}$.

(vi) The sum of the coefficients of a balanced chemical equation is not neessarily important to give the order of a reaction.

(vii) The order of a reaction is obtained from the rate expression of a reaction anthe rate expression is obtained from the experiment.

Q9. Explain that half life method for measurement of the order of a reaction can help us to measure the order of even those reactions which have a fractional order.

Q10. A curve is obtained when a graph is plotted between time on x-axis and concentration on y-axis. The measurement of the slopes of various points give us the instantaneous rates of reaction. Explain with suitable examples.

Q11. The rate determining step of a reaction is found out from the mechanism of that reaction. Explain it with few examples.

Q12. Discuss the factors which influence the rates of chemical reactions.

Q.13. Explain the following facts about the reaction.

$$2NO(g) + 2H_2(g) \rightarrow 2H_2O(g) + N_2(g)$$

(i) The changing concentrations of reactants, change the rates of this reaction.

(ii) Individual orders with respect to NO and H_2 can be measured.

(iii) The overall order can be evaluated by keeping the concentration of one of the substances constant.

Q14. The collision frequency and the orientation of molecules are necessary conditions for determining the proper rate of reaction. Justify the statement.

Q.15. How does Arrhenius equation help us to calculate the energy of activation of a reaction?

Q16. Define the following terms and give examples

(i)	Homogeneous catalysis	(ii)	Heterogeneous catalysis
(iii)	Activation of a catalyst	(iv)	Auto-catalysis
(v)	Catalytic poisoning	(vi)	Enzyme catalysis

Q17. Briefly describe the following with examples

(i) Change of physical state of a catalyst at the end of reaction.

(ii) A very small amount of a catalyst may prove sufficient to carry out a reaction.

(iii) A finely divided catalyst may prove more effective.

(iv) Equilibrium constant of a reversible reaction is not changed in the presence of a catalyst.

(v) A catalyst is specific in its action.

Q18. What are enzymes? Give examples in which they act as catalyst. Mention the characteristics of enzyme catalysis.

Q19. In the reaction of NO and H_2, it was observed that equimolecular mixture of gases at 340.5 mm Hg pressure was half changed in 102 seconds. In another experiment with an initial pressure of 288 mm of Hg, the reaction was half completed in 140 seconds. Calculate the order of reaction.

(Ans:2.88)

Q20. A study of chemical kinetics of a reaction

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

gave the following data at 25 °C. Calculate the rate law.

[A]	[B]	Rate
1.00	0.15	4.2×10^{-6}
2.00	0.15	8.4×10^{-6}
1.00	0.2	5.6×10^{-6}

(Ans: second order)

Q21. Some reactions taking place around room temperature have activation energies around 50kJ mol^{-1}.

(i) What is the value of the factor $e^{\frac{-E}{RT}}$ at 25°C ?

(Ans: 1.72×10^{-9})

(ii) Calculate this factor at 35 °C anat 45 ^{0}C and note1 the increase in this factor for every 10 ^{0}C rise in temperature.

(Ans:3.31×10^{-9})

(iii) Prove that for every 10°C rise in of temperature, the factor doubles and so rate constant also doubles.

(Ans:6.12×10^{-9})

Q22. H_2 and I_2 react to produce HI. Following data for rate constant at various temperatures (K) have been collected.

(i) Plot a graph between $\frac{1}{T}$ on x-axis and log k on the y-axis.

(ii) Measure the slope of this straight line and calculate the energy for activation of this reaction.

Temp. (K)	Rate constant ($cm^3\ mol^{-1}\ s^{-1}$) (K)
500	6.814×10^{-4}
550	2.64×10^{-2}
600	0.56×10^{0}
650	7.31×10^{0}
700	66.67×10^{0}

(Ans: 8326.32,160.6kJmol^{-1})