



CHEMICAL KINETICS

Chapter

9

Teaching Periods

8

Assessment

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Weightage

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Students will be able to:

- **Define** chemical kinetics.
- **Explain** the terms rate of reaction, rate equation, order of reaction, rate constant and rate determining step.
- **Determine** the order of reaction.
- **Calculate** units of rate constant.
- **Explain** effects of concentration, temperature and surface area on reaction rates.
- **Explain** why powdered zinc reacts faster.
- **Explain** what is meant by the terms activation energy and activated complex.
- **Relate** the ideas of activation energy and the activated complex to the rate of a reaction.
- **Illustrate** the collision theory to explain how the rate of a chemical reaction is influenced by the temperature, concentration, size of molecules.
- **Illustrate** a potential energy diagram for a reaction, discuss the reaction mechanism for the reaction.
- **Define** terms catalyst, catalysis, homogenous catalysis and heterogeneous catalysis.
- **Enlist** examples of catalyst in tabular form.
- **Explain** that a catalyst provides a reaction pathway that has low activation energy.
- **Describe** enzymes as biological catalysts.

reactants and products with time. Consider the chemical reaction involves in the hydrogenation of ethyne.



Now think, how is the rate of this reaction measured? What happens at molecular level when reactants change into product? What factors makes the process faster? How many steps involves in reaction completion? Answer of all these questions is associated with the study of chemical kinetics. **“The study of rate of chemical reaction, mechanism of reaction and the factors that influence on the rate of chemical reactions is known as chemical kinetics”.**

INTRODUCTION

The knowledge of stoichiometry, enthalpy change and speed of reaction seeks the attention of chemists whenever they are concerned about a chemical reaction for its commercial use. The profitability of chemical process can be measured by the speed at which reactants convert into products. Speed of reaction means how fast reactants are consumed and products are formed. In our routine life we see that different chemical reactions occur at different rates for example combustion of coal proceeds rapidly while rusting of iron slowly.

If you need to proceed a chemical reaction at a convenient rate, it is necessary to have knowledge about the factors which control the rate of this particular reaction. The subject which deals with this aspect of chemical reaction is called as Chemical Kinetics.

9.1 CHEMICAL KINETICS

Chemical kinetic is the specific area of chemistry that deals with the rate of a chemical reaction. The word kinetic refers to the rate in term of change in the concentration of



9.2 RATE OF REACTION

Chemical reactions are often carried out in solution the amount of reactants and products is conveniently taken in term of molar concentration. The reaction rate is therefore defined as **“Increase in the molar concentration of products or decrease in the molar concentration of reactants per unit time”**. It may express as the ratio of change in the concentration of product or reactant to the change in time.

$$\text{Rate of reaction} = \frac{\text{Change in concentration of product or reactant}}{\text{Change in time}}$$

$$\text{Rate} = \frac{\Delta x}{\Delta t}$$

Since in S.I system the concentration is taken in mol/dm³ and time in second, the unit of rate of reaction is mole/dm³.s.

Consider a simple hypothetical reaction.



Initially no product (B) is formed but as the time passes, the conc. of A decreases and concentration of B increases gradually. This trend of change in the concentration of reactant (A) and product (B) is illustrated in figure 9.1.

Reaction rate is expressed in the following two specific ways.

* The rate of appearance of products which indicates that concentration of product increases with time.

$$R = \frac{\Delta B}{\Delta t}$$

* The rate of disappearance of reactants which means concentration of reactants decreases with time.

$$R = \frac{-\Delta A}{\Delta t}$$

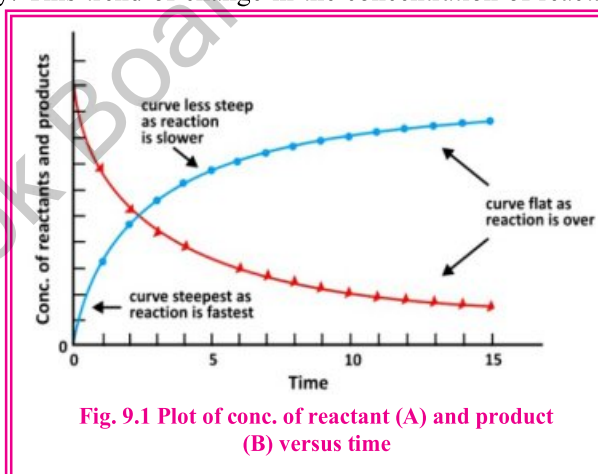


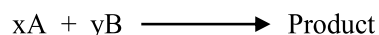
Fig. 9.1 Plot of conc. of reactant (A) and product (B) versus time

The negative sign indicates that reactant concentration decreases with time.

9.2.1 Rate law and Rate expression

Concentration of a substance represents the number of moles and molecules per unit volume. The higher the concentration of reactants, the more is the chances of molecular collision and hence the more is the rate of reaction. Rate law is a mathematical expression that explains the quantitative relationship of molar concentration of reacting species with the rate of reaction.

For a general reaction



The rate law may be written as

$$\text{Rate} = K [A]^x [B]^y$$



“Rate law is an equation which specifies the rate in term of reactant concentration with each term raised to some power”. Here “K” is proportionality constant called as rate constant. It relates the reaction rate to the concentration of the reacting substances.

If we take the concentration of each reactants unity that is 1 mol/dm^3 , then rate law will be reduced to

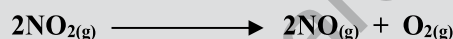
$$\text{Rate} = K$$

Hence specific rate constant at a given temperature may be defined as **“the rate of reaction when the molar concentration of each reactant is unity”.**

Each reaction has a fixed value of specific rate constant (K) at a particular temperature. Its value changes with the temperature, however independent upon change in concentrations of reactant.

Example 9.1

Nitrogen dioxide is an air pollutant gas. The rate of the decomposition of NO_2 is shown in the following equation.



In an experiment the initial concentration of NO_2 was found to be 0.35 mol/dm^3 . What was the initial rate of this reaction if the rate constant at experimental temperature was $1.8 \times 10^3 \text{ mol/dm}^3 \cdot \text{s}$.

Solution:

Since decomposition of NO_2 is of second order reaction, the rate law is written as

$$\text{Rate} = K [\text{NO}_2]^2$$

$$\text{Rate} = 1.8 \times 10^3 [0.35]^2$$

$$\text{Rate} = 2.2 \times 10^2 \text{ mol/dm}^3 \cdot \text{s}$$



Self Assessment

The reaction rate (R) for the reaction $2A + B \rightarrow A_2B$ was found experimentally is given by the expression. $R = K[A]^2 [B]$

(a) Will K increase, decrease or remain unchanged if the concentration of A is doubled?
If the concentration of B is doubled?

(b) Will R increase, decrease or remain unchanged, if the concentration of A is doubled?
If the concentration of B is doubled?

9.2.2 Order of Reaction and its Determination

From the study of rate law, it is clarified that the rate of reaction depends upon the concentration of reactant each raised to the power of some coefficients.

$$\text{Rate} = K [A]^x [B]^y$$

The exponent x and y are obtained experimentally. They may be a whole number or in fraction. The numerical value of x and y are not necessarily same as shown by stoichiometrical coefficient of equation. The exponents x and y specify the number of reacting molecules which



involves in chemical change as a result of their change in concentration and refers as order of reaction. The overall order of reaction defines as **“the sum of all the exponents of the concentration in terms of reactants involve in the rate law”**.

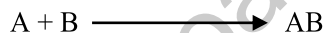
It is important to note that rate law, as well as order of reaction are experimental parameter and cannot be determined by looking at equation.

The order of reaction can be zero, a small whole number or even in a fraction depending upon the number of species whose concentration directly affects the rate of reaction.

By taking the algebraic sum of experimentally determined power of concentration of reactants in the rate equation, we may classify reactions into first order, second order, third order etc. However certain reactions are categorized into zero order. The rate of these reactions is entirely independent upon concentration of reactants. They most often occur on the surface of metals. Photochemical reactions are also zero order reactions because they proceed by absorbing light of certain wave length instead of collision of reactants molecules. Light provides necessary energy to the reactant molecules for their bond breaking process.

There are various methods to determine rate law and order of reaction. However, a simple and common method is “initial rate method”.

Consider a hypothetical reaction



Suppose we performed a series of three experiments with different initial concentrations of reactants A and B and estimate initial rate in each case. We then established a data of each experiment as given in the following table.

Experiment No.	Initial [A] (mol/dm ³)	Initial [B] (mol/dm ³)	Initial Rate (mol/dm ³ .s)
1	0.100	0.0050	1.25×10^{-4}
2	0.200	0.0050	2.50×10^{-4}
3	0.100	0.010	5.0×10^{-4}

A thorough look into above table gives the following conclusions.

In the first two experiments the concentration of B is held constant. The concentration of A is doubled from 0.100 mol/dm³ to 0.200 mol/dm³ which cause an increase in the initial rate by a factor of 2 from 1.25×10^{-4} mol/dm³.s to 2.50×10^{-4} mol/dm³.s. This indicates that the rate of reaction is directly proportional to concentration of A.

Rate \propto [A]

Comparing experiment 1 and 3, we noted that initial conc. of A is held constant. On the other hand conc. of B changes from 0.005M to 0.010M (two times). The effect of this change in conc. of B on its initial rate is found to be increase four times. This justifies that the reaction rate is directly proportion to the square of concentration of [B].

Rate \propto [B]²

Now the overall rate law of the reaction is written as

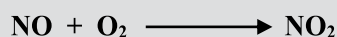
Rate = K [A]¹ [B]²

And thus the order of reaction is 1 + 2 = 3



Example 9.2

The initial rate data obtained in a series of experiments while working on the oxidation of nitric oxide to give nitrogen dioxide is given in the following table. Determine its rate law and find the order of reaction.



Experiment No.	Initial [NO]	Initial [O ₂]	Initial Rate
1	0.10M	0.10M	$8 \times 10^{-4} \text{ Ms}^{-1}$
2	0.10M	0.20M	$16 \times 10^{-4} \text{ Ms}^{-1}$
3	0.20M	0.10M	$16 \times 10^{-4} \text{ Ms}^{-1}$

Solution:

(i) When the initial concentration of NO is doubled (experiment 1 and 3), the initial rate is also doubled. Thus rate law with respect to A is.

$$R \propto [\text{A}]^1$$

(ii) When the initial concentration of O₂ is doubled (experiment 1 and 2), the initial rate is also doubled. Thus rate law with respect to B is.

$$R \propto [\text{B}]^1$$

(iii) The overall rate law now written as

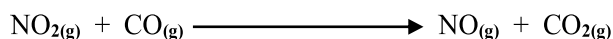
$$R = K [\text{A}]^1 [\text{B}]^1$$

(iv) Order of reaction is thus $1 + 1 = 2$

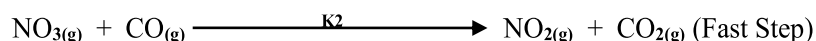
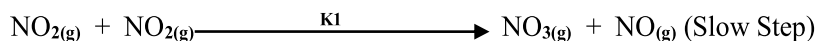
9.2.3 Elementary and Overall Rate Constant and its Units

Chemical reactions may occur in either a single step or in multiple steps. A single step reaction is known as elementary reaction while the reaction which completes in two or more steps is called complex reaction. A reaction mechanism consists of a set of elementary reactions and describes the feasible path followed by the reactant(s) in the formation of product(s). In the mechanism of a complex reaction, one of the steps is slowest; it determines the rate of overall reaction and known as rate determining step or rate controlling step.

Consider for example the reaction between Nitrogen dioxide and carbon monoxide



The mechanism of this reaction involves the following two elementary steps





Above mechanism provides us basic information that is kinetics and molecularity of reaction which may be summarized as.

- K_1 and K_2 are the rate constant of elementary reactions and NO_3 is reaction intermediate.
- Step-1 is slow therefore it must govern the kinetics of reaction and considered as rate determining step.
- Two molecules are involved in slow step therefore it is bimolecular reaction.
- In rate determining step only NO_2 is involved therefore the rate of this reaction is independent on concentration of CO .
- As far as kinetics concerned, this is second order reaction with respect to NO_2 and zero order reaction with respect to CO .
- The overall rate law is now written as

$$\text{Overall rate} = K_1 [\text{NO}_2]^2$$

Unit of Rate Constant

The unit of rate constant (k) of a particular reaction depends upon order of reaction and may be calculated by manipulating the rate law. For example the decomposition of NO_2 is of second order reaction and its rate law may be written as $R = K [\text{NO}_2]^2$.

$$\text{Thus } K = \frac{\text{Rate}}{[\text{NO}_2]^2}$$

Since the unit of rate of reaction is $\text{mol}/\text{dm}^3 \cdot \text{s}$ and unit of concentration is mol/dm^3 , the unit of K may be obtained as,

$$K = \frac{\text{mol}/\text{dm}^3 \cdot \text{s}}{[\text{mol}/\text{dm}^3]^2}$$

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

Because the molarity is specified in mol/dm^3 , we may express the unit of “ K ” in more simplified form as

$$K = \text{M}^{-1} \text{ s}^{-1}$$

The unit of rate constant (K) for the zero order, first order, second order and third order can be determine by inserting the units of concentration and rate of reaction in their rate laws. A summary of units of rate constant is given below.



Do You Know?

Order of reaction and molecularity are two different terms.

(i) Order of reaction is an experimental parameter where as molecularity is determined by looking at the balance chemical equation.

(ii) Order of reaction may be zero but molecularity may not be zero.



Do You Know?

When a wooden match stick is lighted in air, it will continue to glow for a periods of time. But if we insert this burning match stick into a cylinder of pure oxygen, it will glow five times faster. This is because air contains only 21% oxygen where as oxygen in the cylinder is five times more concentrated.



Table 9.1		Rate law and units of rate constant of various order of reactions	
Order of Reaction	Rate Law	Unit of K	Examples
Zero Order	Rate = K	Ms ⁻¹	$\text{H}_{2(g)} + \text{Cl}_{2(g)} \xrightarrow{h\nu} 2\text{HCl}_{(g)}$
1 st Order	Rate = K [A]	s ⁻¹	$\text{NH}_4\text{NO}_{2(aq)} \longrightarrow \text{N}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$
2 nd Order	Rate = K [A] [B] Rate = K [A] ²	M ⁻¹ s ⁻¹	$2\text{HI}_{(g)} \longrightarrow \text{H}_{2(g)} + \text{I}_{2(g)}$
3 rd Order	Rate = K [A] ² [B] or Rate = K [A] [B] ²	M ⁻² s ⁻¹	$2\text{NO} + \text{Cl}_2 \longrightarrow 2\text{NOCl}$

Example 9.3

Decomposition of SO_2Cl_2 is of first order reaction $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$ write its rate law and deduce the unit of rate constant.

Solution:

Since decomposition of SO_2Cl_2 is governed by first order kinetics the rate law is written as Rate = K [SO_2Cl_2]

Now the unit of rate constant (K) is obtained if we put the units of concentration and unit of rate of reaction in the rate law.

$$K = \frac{\text{mol/dm}^3 \cdot \text{s}}{\text{mol/dm}^3}$$

$$K = \text{s}^{-1}$$

9.2.4 Factors Affecting the Rate of reaction

A very useful aspect of chemical kinetic is to control the speed of chemical reactions. Often we ambitious to speed up a chemical reaction for economical or industrial point of view, but in many cases we deliberately slow down the reaction for a careful control of some potentially explosive process. Various factors influence on the rate of chemical reactions.

(i) Nature of Reactants

Different reactants undergo with different rates in the chemical change. It can be attributed to their structure, nature of bonding and physical state. For example when a piece of sodium and iron exposed to air, sodium oxidizes completely much faster than iron. Similarly when metal sodium and calcium are put into water, sodium reacts rapidly where as calcium moderately. The reason is that sodium is highly electropositive and it readily loses its valence electron.

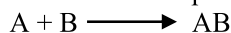
Generally substances having ionic bond reacts quickly as compared to the covalent substances.



(ii) Concentration of Reactants

According to rate law, the rate of reaction increases with increasing the concentration of one or more reactants. More crowding of reactant, molecules allow more collision to happen. Thus chances of successful collision increases resulting in increase rate of formation of products.

Consider a reaction in which A and B react to form a product AB.



Let suppose the reaction is obeyed by second order kinetics the rate law may be expressed as $R = K [A][B]$. If the concentration of A is doubled, the number of collision among particles of A and B per unit time would also be doubled. Consequently the rate of reaction increases by a factor of two fold. Now if we double the concentration of both A and B, the collision per unit time has therefore doubly doubled. It increases the rate of reaction four times.

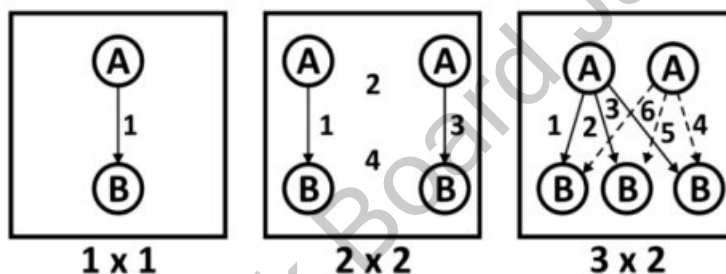


Fig 9.2: Effect of increase in concentration of A and B on the rate of reaction

Example 9.4

In the reaction $2SO_3 \rightarrow 2SO_2 + O_2$, the rate law of the decomposition of SO_3 is $R = K[SO_3]^2$. What will be the rate if concentration of SO_3 is (i) doubled (ii) halved

Solution:

By considering the rate law, the rate of reaction is determined as

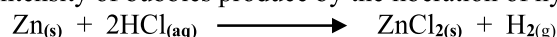
(i) When the concentration of SO_3 is doubled, the rate will increase by $[2]^2 = 4$ times

(ii) When the concentration of SO_3 is halved, the rate will decrease by $\left[\frac{1}{2}\right]^2 = \frac{1}{4}$ time.

(iii) Surface Area

The surface area of solid is an important factor to enhance the rate of reaction. The greater the surface area, the more is the possibility of reactant particles to collide with each other and increases the reaction rate.

Fine powdered substances have greater surface area as compared to chunk. For example powdered zinc reacts more vigorously with dilute hydrochloric acid as compared to its chips because powder zinc offer greater surface area for HCl to act upon. This can be demonstrated by the intensity of bubbles produce by the liberation of hydrogen gas.





(iv) Radiations

A specific class of chemical reactions occurs due to the absorption of light of certain wavelength; these are known as photo chemical reactions. The absorbed light provides appropriate energy for breaking the chemical bonds of reactant molecules and initiates the reaction. These reactions can be speed up by increasing the intensity of appropriate light. An increase in the intensity of light means more energy is provided to the reacting molecules which facilitate the bond breaking process.

The reaction of H_2 and Cl_2 is a zero order reaction in which light radiation (photon) provide necessary activation energy to the reactant molecules. Other examples are photo synthesis and photography etc.

(v) Temperature:

As a rule of thumb, reaction rate is approximately double with the rise of temperature by $10^\circ C$. A rise of temperature increases the kinetic energy of reacting molecules which enhances the frequency of collision. Although the reactant molecules collide with one another billions times per second but every collision does not lead to a reaction. Only those molecules would react to form products which have energy equal to or greater than certain critical energy known as activation energy.

The distribution of kinetic energies in a chemical system at two different temperatures as given in fig 9.4 tells us what happens when the temperature rises.

At temperature (T_1) large part of the molecules possess average kinetic energy however a small part of the total molecules found to possess kinetic energy equal or larger than activation energy. This small fraction of high energy molecules are illustrated in shaded area. As the temperature increases from T_1 to T_2 ($T_1 + 10^\circ C$), a change in energy distribution occur and more molecules have acquired high kinetic energy and cross the energy barrier. This is indicated by flattening the curve at temperature T_2 . Further, the shaded area which represents the molecules with energy equal or higher than activation becomes broader by roughly two folds.

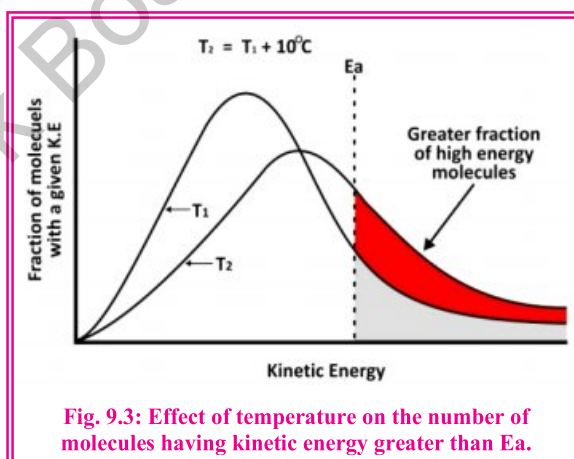


Fig. 9.3: Effect of temperature on the number of molecules having kinetic energy greater than E_a .



Self Assessment

A rise of $10^\circ C$, increases the rate of reaction twice, explain it by the help of energy diagram.



9.3 COLLISION THEORY, TRANSITION STATE AND ACTIVATION ENERGY

Chemical reaction initiate by bond breaking of reactants molecules and this happens only when they collide among each other. Collision theory postulated that the rate of chemical reaction increases with the increased number of collision per unit time. Many reactant molecules collide with each other under given set of conditions, however only a fraction of molecules undergo bond breaking process. The successful molecular collision depends not only upon their high kinetic energy but also the proper orientation of colliding molecules at the time of collision.

During movement when reactant molecules come closer together, they are repelled by their electron cloud and most of them bounce off without any chemical change but only those molecules which possess very high kinetic energy overcome this repulsive force and change into product since a part of their kinetic energy converts into vibrational energy. The vibration of colliding molecule results in bond breaking which is the first step towards product formation. Thus, in an energetic viewpoint, there is some minimum energy that must be needed by the reacting molecules and below which no effective collision occurs. This energy is known as threshold energy (E_t). In order to increase the energy content of reacting molecules up to the threshold level, energy is externally supplied (usually in the form of heat). This additional energy externally supplied is known as activation energy (E_a).

$$\text{Activation Energy} = \text{Threshold Energy} - \text{Average Internal Energy of Molecules}$$

If we have a look at fig 9.4(a) and 9.4(b), we can observe a potential energy hill. All those reactants molecules which possess energy equal to or greater than the energy barrier undergo effective collision.

Small value of activation energy indicates that a large number of reactant particles take part in effective collisions and the reaction is said to be fast. On the other hand, a large value of energy of activation illustrate that only a small fraction of reacting particles undergo effective collision, such reaction are identified as slow reactions.

The potential energy diagram depicted in fig. 9.4(a) of an exothermic reaction in which the reactants at the start of the reaction are at higher energy level then the products. Whereas the potential energy diagram depicted in fig 9.4(b) is of an endothermic reaction in which the reacts at the start of reaction are at lower energy level than the products.

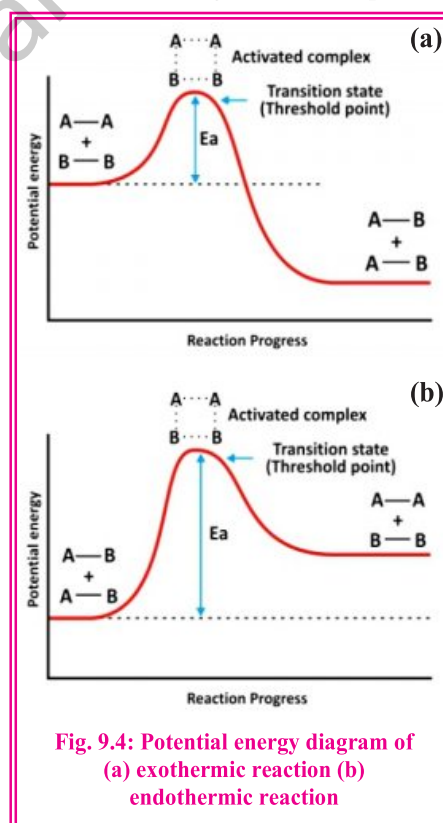


Fig. 9.4: Potential energy diagram of (a) exothermic reaction (b) endothermic reaction



In both the figures 9.4(a) and 9.4(b), the peak of potential energy curve represents a transition state of molecules that are neither reactants nor products having partial bonds and is highly unstable with very short life span. The chemical species undergoing this transition state is known as activated complex shown as dotted lines in fig. 9.4.

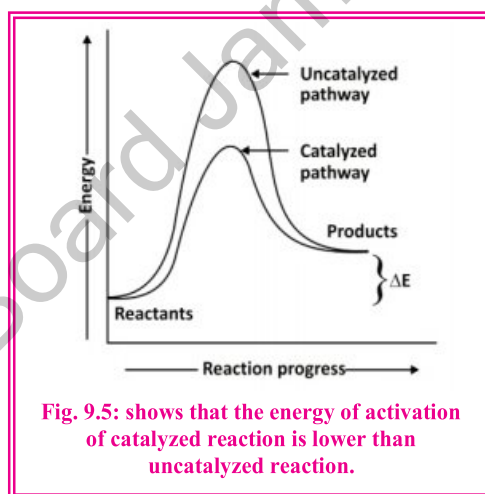


Self Assessment

In term of collision theory how can you explain that all molecular collisions do not lead to formation of product.

9.4 CATALYSIS

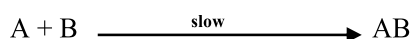
In many synthetic processes, our concern is to get maximum yield of product in minimum period of time. We often avoid accelerating the reaction by elevating the temperature because of energy cost and also due to heat sensitivity of reacting chemicals. Alternatively we use catalyst, “**A substance which alters the rate of a chemical reaction without undergoing permanent changes in its chemical nature is called catalyst and the process involving the use of catalyst is referred as catalysis**”. Catalyst can be separated after the completion of reaction and hence use over and over again.



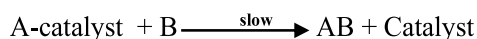
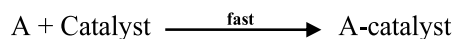
9.4.1 Characteristics of Catalyst

Now we shift towards how does a catalyst works? How can we speed up the reaction without raising the temperature? Catalyst provides a new and more efficient pathway with a lower energy of activation so a relatively large fraction of reactant molecules cross the energy barrier and undergo effective collision. It must involves in early step of the reaction and then reproduce in equal amount in the later step that is why it not appeared as reactant in the equation of chemical reaction.

Consider an uncatalyzed bimolecular reaction.



When catalyst is added, the reaction involves two step pathway during which catalyst first used and then reproduced.





A positive catalyst increases the rate of reaction by lowering the energy of activation where as negative catalyst retard the reaction rate by placing itself in between reacting molecules to decrease the number of effective collision. In many chemical processes our concern is to fasten the reaction therefore positive catalyst are simply called as catalyst on the other hand negative catalyst are known as retarding catalyst or inhibitors.

Table 9.2 List of positive and negative catalyst of some industrially significant process		
Chemical Process	Catalyst	Nature
Synthesis of NH ₃ by Haber Process $N_2 + 3H_2 \longrightarrow 2NH_3$	Iron Powder	Positive
Synthesis of H ₂ SO ₄ by contact process $2SO_2 + O_2 \longrightarrow 2SO_3$	V ₂ O ₅	Positive
Decomposition of Potassium Chlorate $2KClO_3 \longrightarrow 2KCl + 3O_2$	MnO ₂	Positive
Oxidation of Chloroform $CHCl_3 + \frac{1}{2}O_2 \longrightarrow COCl_2 + HCl$	2% ethyl alcohol	Negative
Decomposition of H ₂ O ₂ $H_2O_2 \longrightarrow H_2 + O_2$	Glycerin	Negative

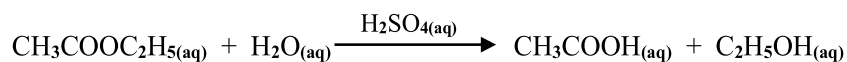
Catalytic reactions are generally categorized into two groups depending upon catalyst physical state and its mode of action. These are named as homogenous catalysis and heterogeneous catalysis.

9.4.2 Homogenous Catalysis

All those catalytic reactions in which both catalyst and reactants are in the same phase refer as homogenous catalysis. Homogenous catalytic reactions are segregated into two classes.

(i) Acid Base Catalysis

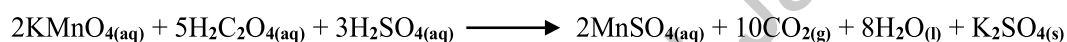
A number of organic reactions proceed catalytically in the presence of H⁺ or OH⁻ ions. In these reactions both catalyst and reactants are present in the same aqueous phase. For example hydrolysis of ethyl acetate can be speed up if strong mineral acid is added.



In this reaction both ethyl acetate (reactant) as well as H_2SO_4 (catalyst) exist in aqueous state.

(ii) Auto Catalysis

In some chemical reactions one of the products itself serves as catalyst, these are known as auto catalyzed reactions. Initial rate of this reaction is slow but as soon as the product formed, the rate of reaction increases. For example in redox titration between KMnO_4 and oxalic acid Mn^{+2} ion of MnSO_4 catalyzed the reaction.



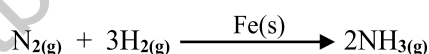
9.4.3 Heterogeneous Catalysis

In most of the catalytic process catalyst exist in different physical state than reactants. These are identified under the category of heterogeneous catalysis. For example

(i) In the manufacturing of sulphuric acid by contact process a solid catalyst vanadium penta oxide (V_2O_5) is used to convert gaseous sulphur dioxide to sulphur trioxide.



(ii) In the manufacturing of ammonia by Haber process solid iron powder is used to enhance the reaction rate between nitrogen and hydrogen gases.



In heterogeneous catalysis, solid catalyst adsorbs reactant molecules on its surface by lowering the energy of activation and enhances the reaction rate.

9.4.4 Enzyme Catalysis

Enzymes are special kind of the proteins which serve as biochemical catalysts in living system. They not only catalyze the reaction thousand time faster but also highly specific as compared to inorganic catalyst. Each enzyme acts only upon a specific substrate. The specificity of enzymes can be attributed to presumption that each enzyme has a specific shaped active site on its surface where molecule of substrate can attached when come in close contact through proper orientation in the same way as key fit into particular lock.

Enzymes kinetics for catalyzing biochemical process is quite complex, however a simple scheme is shown below.





Where A and B are reactants and E is enzyme while ABE represent substrate-enzyme intermediate in the transition state. The ABE complex provides a new pathway to product (AB) with a lower energy of activation.

Many biochemical processes occurring in living system are catalyzed by enzymes. For example digestion of food is catalyzed by various enzymes such as protease, amylase, lipase etc. They breakdown the bigger size carbohydrate, proteins and lipid molecules into smaller one which then easily be absorbed by cellular membrane of intestine.

Enzymes are also use to catalyze several industrial processes. For example in the fermentation of sugarcane into commercial alcohol two enzymes (zymase and invertase) are used which are found in yeast.

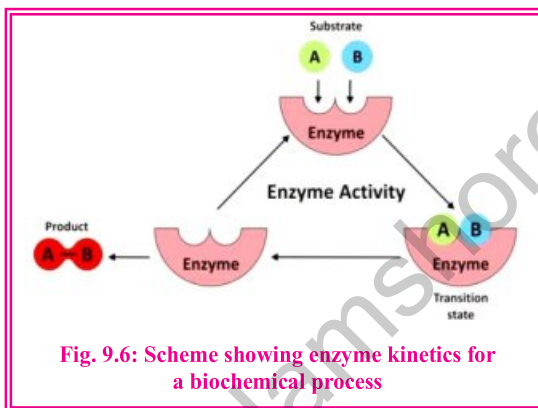


Fig. 9.6: Scheme showing enzyme kinetics for a biochemical process



Society, Technology and Science

Use of enzyme in removing stain from fabric

Certain hydrolyses enzymes such as protease, amylase and lipase are used in modern laundry detergents for the removal of stains from fabric. Their presence increases the rate of cleaning action of detergent without damage of fabric thread.

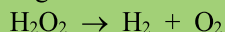
Since stains on the fabric are of different types such as sweat, gravy, oil etc, a range of enzymes is added into detergents. For example: Protease removes egg or gravy stain, amylase eliminate starch stains, lipase take out oil and fat spots.

Enzymes break down protein, fats and starch molecules of stain to form water soluble substances which then washed away.



Activity

This activity enables you to understand how catalyst alters the rate of chemical reaction. Hydrogen per oxide decomposes as give in the following reaction.



Take equal volume of hydrogen peroxide in two different conical flask. Now put some black powder of manganese dioxide into first flask only.

Observe what happens in both flasks. You will see that oxygen gas evolves with effervescence in the first flask quickly. This indicates that rate of decomposition of H_2O_2 is faster in the presence of catalyst.



SUMMARY with Key Terms

- ◆ **Chemical Kinetics** is the branch of chemistry which deals with the rate of chemical reaction, mechanism of reaction and the factors that influence the rate of chemical reaction.
- ◆ **Rate of reaction** is the increase in concentration of product or decrease in the concentration of reactants per unit time during a chemical reaction.
- ◆ **Average rate** is the change in concentration of reactants or products in a specified time period. It can be determined by dividing the difference in concentration with difference in measured time.
- ◆ **Rate law** is an equation which specifies the rate in term of reactant concentration with each term raised to some power.
- ◆ **Specific rate constant** is the rate of reaction when the molar concentration of each reactant is unity.
- ◆ **Order of reaction** is the sum of power of concentration of reactants as expressed in rate law. It may be a whole number, a fractional value or even zero.
- ◆ **Molecularity** is the total number of molecules taking part in a chemical reaction.
- ◆ **Reaction mechanism** is a set of elementary reactions which describes the feasible path followed by reactants to convert into products.
- ◆ **Rate determining step** is the slowest step in a complex reaction.
- ◆ **Factors that affect on the rate of chemical reactions** are nature of reactants, concentration of reactants, surface area of reactants, molecular size of reactants, temperature, radiations and catalysts.
- ◆ **Collision theory** tells that chemical reaction occur due to the effective collision among reacting molecules.
- ◆ **Activation energy** is the additional energy which the reacting molecules must achieve above their average kinetic energy for their effective collision.
- ◆ **Activated complex** is a high energy, unstable and short live time state exists during the transformation of reactants into products.
- ◆ **Catalyst** is substance that alters the rate of chemical reaction without itself being permanently changed.
- ◆ **Homogenous catalyst** is one which exist in the same phase as that of reactant species.
- ◆ **Heterogenous catalyst** is those which exist in different phase from reacting species.
- ◆ **Enzymes** are biochemical catalyst. They enhance the rate of chemical reactions in much biochemical process.



EXERCISE

Multiple Choice Questions

1. Choose the correct answer

- (i) For a hypothetical reaction $x + y \rightarrow z$, if the conc. of x is double, the rate increases by square and if the conc. of y is doubled the rate increases by twice. The experimental rate law of this reaction is:
- (a) $R = K [x]^1 [y]^1$ (b) $R = K [x]^1 [y]^2$
(c) $R = K [x]^2 [y]^1$ (d) $R = K [x]^2 [y]^2$
- (ii) The unit of rate constant (K) for the first order reaction is:
- (a) s^{-1} (b) conc. s^{-1}
(c) $\text{conc}^{-1} \cdot s$ (d) $\text{conc.}^{-1} s^{-1}$
- (iii) Rate constant of a reaction is affected by:
- (a) Conc. of reactants (b) Conc. of products
(c) Temperature (d) Reaction time
- (iv) The purpose of using of catalyst in a chemical reaction is to change:
- (a) Equilibrium constant (b) Enthalpy of reaction
(c) Activation energy (d) Nature of reaction
- (v) The overall order of reaction to which the rate law is $R = K$:
- (a) Zero order (b) First order
(c) Second order (d) Third order
- (vi) Ionic reactions are classified into:
- (a) Slow reaction (b) Moderate reactions
(c) Fast reactions (d) Reversible reaction
- (vii) The decomposition of H_2O_2 is inhibited by:
- (a) 2% ethanol (b) Glycerin
(c) MnO_2 (d) V_2O_5
- (viii) The best alternative term for the velocity of reaction is:
- (a) Rate of appearance (b) Rate of disappearance
(c) Average rate (d) Instantaneous rate
- (ix) Order of reaction is the power to which concentration of reactant is:
- (a) Lowered (b) Raised
(c) Stopped (d) Constant
- (x) In the reaction $A \rightarrow B$, the rate of disappearance is written as:
- (a) $\frac{dA}{dt}$ (b) $\frac{-dA}{dt}$
(c) $\frac{dB}{dt}$ (d) $\frac{-dB}{dt}$

Short Questions

1. Define the following:
- (a) Rate of reaction (b) Velocity of reaction
(c) Order of reaction (d) Rate constant



2. The rate law of the reaction $2\text{NO} + \text{Br}_2 \rightarrow 2\text{NOBr}$ is given as $\text{Rate} = k[\text{NO}]^2 [\text{Br}_2]$, What is the order of reaction?
 - (i) With respect to each reactant
 - (ii) Overall reaction
3. How can you define order of reaction? What are the units for the rate constants of zero order, first order and second order reactions?
4. Explains the following:
 - (i) Powdered marble (CaCO_3) reacts quickly with hydrochloric acid than solid lump of marble.
 - (ii) Milk sour more rapidly in summer than in winter.
 - (iii) Reactants in solution reacts faster at high concentration.
 - (iv) Raising the temperature causes an increase in the rate of reaction.
5. Differentiate between the following:
 - (i) Rate of reaction and rate constant
 - (ii) Homogenous and Heterogeneous catalyst
 - (iii) Positive catalyst and inhibitor
 - (iv) Elementary and overall reaction

Descriptive Questions

1. Enlist various factors which influence on the rate of chemical reactions and describe the effect of concentration and surface area of reactants on the reaction rate.
2. Explain in terms of collision theory how the reaction rate increases with the rise of temperature.
3. What is meant by energy of activation and activated complex? Explain with the help of potential energy diagram.

Numerical Questions

1. Decomposition of NO_2 into NO and O_2 is of second order reaction.

$$2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$$
 If the rate constant at certain temperature is $3.8 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and the initial concentration of NO_2 is 0.38M , calculate the initial rate of the reaction.

[Ans: $5.48 \times 10^{-5} \text{ mol/dm}^3.\text{s}$]
2. The overall rate law for the reaction

$$\text{A} + \text{B} \longrightarrow \text{C} \text{ is } R = k [\text{A}] [\text{B}]$$
 If in an experiment the initial concentration of A and B was found to be 0.43M and 0.78M respectively while the initial rate was $3.8 \times 10^{-3} \text{ Ms}^{-1}$. Determine rate constant and mention its unit.

[Ans: $1.13 \times 10^{-2} \text{ dm}^3/\text{mol.s}$]
3. The reaction $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$ was studied at 25°C . the following results were obtained

Experiment No.	Initial concentration (mol/dm^3)		Initial rate ($\text{mol/dm}^3.\text{s}$)
	NO	Cl_2	
1	0.1	0.1	2.52×10^{-3}
2	0.1	0.2	5.04×10^{-3}
3	0.2	0.1	10.05×10^{-3}

Illustrate the rate law and find the order of reaction.

[Ans: Order of reaction = 3]