Chapter # 09

Chemical Kinetics

Major Concepts

9.1 Chemical Kinetics
9.2 Rates of Reactions
9.3 Collision Theory, Transition State and Activation Energy
9.4 Catalysis

Learning Outcomes

The students will be able to:

- Define chemical kinetics. (Remembering)
- Explain and use the terms rate of reaction, rate equation, order of reaction, rate constant and rate determining step. (Understanding)
- Explain qualitatively factors affecting rate of reaction. (Applying)
- Given the order with respect to each reactant, write the rate law for the reaction. (Applying)
- Explain what is meant by the terms activation energy and activated complex. (Understanding)
- Relate the ideas of activation energy and the activated complex to the rate of a reaction. (Applying)
- Use the collision theory to explain how the rate of a chemical reaction is influenced by the temperature, concentration, size of molecules and. (Applying)
- Given a potential energy diagram for a reaction, discuss the reaction mechanism for the reaction. (Applying)
- Explain effects of concentration, temperature and surface area on reaction rates. (Applying)
- Explain the significance of the rate-determining step on the overall rate of a multi-step reaction. (Analyzing)
- Describe the role of the rate constant in the theoretical determination of reaction rate. (Applying)

- Describe that increase in collision energy by increasing the temperature can improve the collision frequency. (Applying)
- Define terms catalyst, catalysis, homogeneous catalysis and heterogeneous catalysis. (Understanding)
- Explain that a catalyst provides a reaction pathway that has low activation energy. (Applying)
- Describe enzymes as biological catalysts. (Understanding)
- Explain why powdered zinc reacts faster. (Analyzing)

9.1 Introduction to Chemical Kinetics

The different chemical reactions occur at very different rates. Some reactions occur very slowly and some occur very quickly. The reactions may take seconds, weeks or months to occur. The rusting of iron, the conversion of graphite into diamond, the setting of cement and the decay of plants into coal occur very slowly. Similarly the cooking of food, formation of yogurt, the fermentation of glucose to give ethanol and carbon dioxide; and the hydrolysis of an ester to give acid and ethanol are also the examples of slow reactions. On the other hand, the combustion of petrol, the explosion of gun powder, the neutralization of an acid (HCl) by a base (NaOH), and the reaction of hemoglobin with oxygen and CO occur very quickly and are called fast reactions. Chemical kinetics is the branch of chemistry which deals with the study of reaction rate (speed), reaction mechanism and factors that affect the reaction rate. The laws of thermodynamics support us to decide whether the reaction is feasible or not but chemical kinetics helps us to know:

i) How fast chemical reactions occur?
ii) How reactions speed can be controlled?
iii) What are the factors (variables) that affect reactions rate?

For example, when the food is stored in the refrigerator, the temperature of food is slowed down and the food is preserved. Here the reaction speed (decomposition of food) is controlled by decreasing the temperature. Chemical kinetics not only plays an important role in our daily life but it also plays a vital role in industries. For example, it helps to predict the expiry date of medicines. The medicines lose their effectiveness with the passage of time due to the decomposition of active ingredients. It also helps us to get the maximum yield during industrial process. It is the chemical kinetics that decides whether a certain chemical reaction is economical or not. For example, the economical synthesis of ammonia in the industry mainly depends on the speed of reaction at which reactants (N_2 and H_2) are converted into product (NH_3). In this chapter we mainly focus on the reaction rate, the mechanism and the variables that influence the reaction rate.

9.2 Rates of Reactions

The change in the concentration of reactants or products per unit time is called rate or speed of reaction.

$$\text{Rate of reaction} = \frac{\text{Change in concentration of reactants (or products)}}{\text{Change in time}} = \frac{\Delta C}{\Delta t}$$

The unit of rate of reaction depends on the concentration unit of reactants or products and the unit of time. The usual unit of rate of reaction is moles per decimeter cube per second (mol $dm^{-3}s^{-1}$). The usual unit for gaseous reaction is atm sec^{-1}.

Consider a general chemical reaction in which the reactant A is converted into product B.

$$A \longrightarrow B$$

When the reaction proceeds, then the concentration of reactant *A* decreases and that of product *B* increases with the passage of time. It can be best understand by the graph. When we plot a graph between concentration (of reactants and products) on y-axis and time on x-axis, then we will able to show the change in the concentration of reactants or products of a reaction with the passage of time. At the beginning, the slope of the graph for the molar concentration of reactants or products is the steepest which indicates that the reactants are converted into products at greater speed. After some times, the slope becomes less steep which shows that the change in concentration of reactants or products is slowing down. At the end of a reaction, the concentration of the reactant becomes zero and that of product becomes the maximum and the reaction stops. The change in the concentration of reactants or products with time gives us an idea about the rate of chemical reaction.

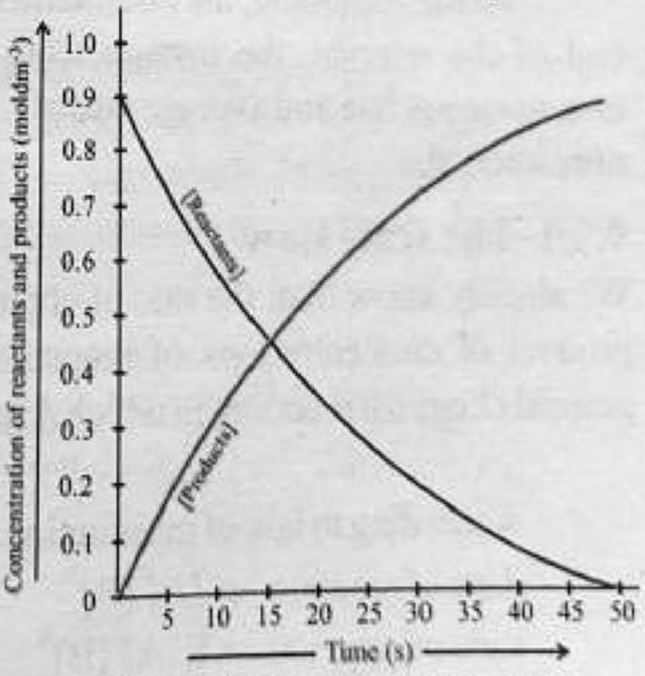


Figure 9.1: Change in the molar concentration of reactants and products with time for the reaction

There are two types of rates of reactions:

1) Instantaneous rate of reaction
2) Average rate of reaction.

i) Instantaneous Rate of Reaction

The rate of reaction at a particular instant during the time interval is called instantaneous rate of reaction. The instantaneous rate of reaction goes on changing every moment. It is very fast at the beginning and very slow at the end of reaction.

The instantaneous rate of reaction can be calculated from the following expressions:

$$\text{Instantaneous rate of reaction} = \frac{-d[A]}{dt} \qquad \text{or}$$

$$\text{Instantaneous rate of reaction} = \frac{d[B]}{dt}$$

Where d[A] and d[B] show a very small change in the concentration (of reactant A and product B) and dt shows a very small change in time. The d[A] has minus sign in the rate expression which shows the decrease in the concentration of reactant during the passage of time. The d[B] has no minus sign in the rate expression which shows that the concentration of product *B* increases during the passage of time.

ii) Average Rate of Reaction

The total change in concentration divided by total time is called average rate of reaction.

$$\text{Average rate of reaction} = \frac{\text{Total change in concentration}}{\text{Total change in time}}$$

At the beginning, the instantaneous rate is higher than the average rate. At the end of the interval, the instantaneous rate is lower than the average rate. The instantaneous rate and average rate of reactions are equal for only one instant in any time interval.

9.2.1 The Rate Law

We already know that, the rate of chemical reaction is directly proportional to the product of concentrations of reactants each raised to some power. Consider general chemical reaction, in which A reacts with B to produce C and D.

$$aA + bB \longrightarrow cC + dD$$

According to law of mass action,

$$\text{Rate of reaction} \propto [A]^a[B]^b \qquad \text{or}$$

$$\text{Rate of reaction} = K[A]^a[B]^b$$

This equation is called rate equation or rate law. Here K is called constant.

The rate equation is generally written in the form:

Rate of reaction $= K[A]^m[B]^n$

Keep in Mind

The K is the proportionality constant of rate equation and is known as the rate constant or specific rate constant. We can determine its value, if we know the concentration of reactants and order of reaction. Its value is directly proportional to the rate of reaction, that is, the reactions with higher rate has higher value of K and the reactions which proceeds slowly have lower value of K. The value of K remains same for a specific reaction and is independent of reactants or products concentrations and does not change with time at constant temperature. The value of K increases by increase in temperature and decreases by decrease in temperature. The magnitude of K alters when a catalyst is added to the reaction mixture.

In the rate equation, it is not necessary that the powers (exponents m and n) are always equal to the co-efficient (a and b) of balanced chemical equations. Rate law can be defined as: An expression which shows how the reaction rate is related to concentration of reactants is called rate law or rate expression. It is determined experimentally. It is not predicted from a balanced chemical equation, because as we know that the sum of exponents in the rate equation may or may not be equal to the co-efficient of balanced chemical equation. The value of the exponents in the rate law shows the order of reaction with respect to each other. For example, consider the reaction of nitric oxide with hydrogen:

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O \qquad \text{Rate} = K[H_2][NO]^2$$

The exponent of 1 for hydrogen concentration shows that the reaction is first order with respect to hydrogen. The exponent of 2 for the nitric oxide (NO) concentration shows that the reaction is second order with respect to nitric oxide. The sum of the exponents of both the reactants shows the overall order of reaction, hence, this reaction is of third order $(1 + 2 = 3)$ overall.

Some examples of rate law are:

	Reactions	Rate Law
i)	$2NO_2 \longrightarrow 2NO + O_2$	Rate $= K[NO_2]^2$
ii)	$2N_2O_5 \longrightarrow 4NO_2 + O_2$	Rate $= K[N_2O_5]$
iii)	$H_2 + I_2 \longrightarrow 2\,HI$	Rate $= K[H_2][I_2]$

2.2 Elementary and Overall Reactions

Some reactions occur in single step but most of the reactions occur by a series of steps. The steps involved in a several step reaction are called mechanism of reaction or reaction pathway. A single step in a mechanism of reaction is called an elementary reaction or elementary step.

Keep in Mind

How do Chemists Determine the Mechanism of Chemical Reactions? It is not an easy work to determine the mechanism of chemical reaction, that is, it needs expertness. The chemists determine the rate law by experiments at first, and then they propose mechanism for chemical reactions. The elementary steps of the reaction are added up, if it gives the overall balanced chemical equation, then this mechanism is accepted, if not, then rejected. They also compare the proposed mechanism with experimentally determined rate law, if they do agree, then this mechanism is accepted, if do not agree, then this mechanism is rejected and work out for another mechanism.

To understand the chemical reaction, the chemists must know the step by step sequence of reactions by which the overall chemical change occurs. Consider the following reaction

$$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)} \qquad \text{Overall reaction}$$

According to law of mass action,

Rate of reaction $= K[NO_2][CO]$

But experimentally determined rate equation of the reaction is:

Rate of reaction $= K[NO_2]^2$

This equation shows that the rate of reaction depends upon the concentration of NO_2 and it does not depend upon the concentration of CO. The reaction is of second order. The proposed mechanism for this reaction is:

$$NO_{2(g)} + NO_{2(g)} \xrightarrow{\text{Slow}} NO_{3(g)} + NO_{(g)} \qquad \text{Elementary reaction}$$

$$NO_{3(g)} + CO_{(g)} \xrightarrow{\text{Fast}} NO_{2(g)} + CO_{2(g)} \qquad \text{Elementary reaction}$$

We get the overall reaction by taking the sum of the elementary reactions:

$$\cancel{NO}_{2(g)} + NO_{2(g)} \xrightarrow{\text{Slow}} \cancel{NO}_{3(g)} + NO_{(g)} \qquad \text{Elementary reaction}$$

$$\cancel{NO}_{3(g)} + CO_{(g)} \xrightarrow{\text{Fast}} \cancel{NO}_{2(g)} + CO_{2(g)} \qquad \text{Elementary reaction}$$

$$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)} \qquad \text{Overall reaction}$$

In the several steps reaction, all the elementary steps do not have the same rate, that is, one step is much slower than the others. The slowest step which determines the rate of chemical reaction in a several step reaction is called rate determining step or rate limiting step. Note that, the overall reaction cannot be faster than the rate of determining step (the slowest elementary reactions step). In the above reaction, the slowest step (first step) is the rate determining step and NO which does not appear in the balanced equation is called reaction intermediate. The reaction intermediate has temporary existence and is unstable. It is neither a reactant nor a product but it is produced during the path of reaction, that is, it is formed in one step and completely consumed in the later step. NO_2 has normal bonds and it can be isolated (separated) under special conditions.

9.2.3 Order of Reaction and its Determination

The number of atoms or molecules whose concentrations determines the rate of reaction is called order of reaction. It may also be defined as:

The sum of all the exponents of the concentration terms in a rate equation is called order of reaction. For example:

Rate of reaction $= K[A]^m[B]^n$
Order of reaction $= m+n$

Order of reaction is determined experimentally. Order of reaction is not predicted from a balanced chemical equation because the sum of exponents in the rate equation may or may not be the same as in a balanced chemical equation.

Important types of order of reaction are discussed below:

First Order Reaction

The reaction in which the rate of chemical reaction is directly proportional to the irst power of the concentration of one reacting substance is called first order eaction.

Rate of reaction $= K[A]^1$

The rate of first order reaction doubles by doubling the concentration of eactant.

For example:

$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$ Rate of reaction $= K[N_2O_5]$
) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$ Rate of reaction $= K[NH_4NO_2]$

econd Order Reaction

he reaction in which rate of a chemical reaction is directly proportional to the uare of the molar concentration of one reacting substance (or to the product of olar concentrations of two reacting substances) is called second order reaction.

Rate of reaction $= K[A]^2$ or Rate of reaction $= K[A][B]$

The rate of second order reaction quadruples by doubling the concentrations reactants.

For example:

$H_2 + I_2 \longrightarrow 2HI$ Rate of reaction $= K[H_2][I_2]$
$2O_3 \longrightarrow 3O_2$ Rate of reaction $= K[O_3]^2$

Third Order Reaction

The reaction in which rate of a chemical reaction is directly proportional to the product of molar concentration of three reacting substances (or to the first power of molar concentration of one reacting substance and square of the other reacting substance) is called third order reaction.

Rate of reaction = $K[A][B][C]$ or Rate of reaction = $K[A]^2[B]$

The rate of third order reaction octuples by doubling the concentrations of reactants.

For example:

i) $2NO + O_2 \longrightarrow 2NO_2$ Rate of reaction = $K[NO]^2[O_2]$

ii) $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$ Rate of reaction = $K[NO]^2[H_2]$

Zeroth Order Reaction

The reaction whose rate does not depend upon the concentration of any reactant is called zeroth order reaction.

Rate of reaction = $K[A]^0$

The reactions catalyzed by enzymes and thermal decomposition reactions may be zero order.

For example:

i) Photosynthesis (Photochemical reactions).

ii) $2NH_3 \xrightarrow{\text{Tungsten}} N_2 + 3H_2$ Rate of reaction = $K[NH_3]^0$

Experimental Determination of Order of Reaction

We can calculate order of reaction, if we know the rate of reaction. The rate o reaction is the change in concentrations of the reactants or products. The rate o reaction is generally determined by physical and chemical methods. The physic methods include spectrometry, electrical conductivity, dilatometry, refractometr optical rotation method, pH metric method, and gas chromatography method The method used to monitor changes in the concentration of reactant or prod depends on the specific reaction. Suppose a series of experiments is conducted an observed the effect of concentration on the rate of reaction to predict the order reaction.

i) Suppose a reaction has only one reactant and its rate constant K value is 0.2

Table 9.1: Initial rate and concentration of reactants A and B

Experiments	Initial Concentration (mol dm^{-3})	Initial Rate (mol $dm^{-3}s^{-1}$)
	[A]	
1	0.01	0.0025
2	0.02	0.005
3	0.04	0.01

Experiments 1 and 2 show that when we double the initial concentration of A from 0.01 to 0.02, doubles the rate of reaction from 0.0025 to 0.005.

Experiments 1 and 3 shows that when we quadruples the initial concentration of A from 0.01 to 0.04, quadruples the rate of reaction from 0.0025 to 0.01. It means that the rate of reaction is directly proportional to the first power of concentration of reactant A.

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

A reaction whose rate of reaction depends on the concentration of a single eactant raised to the first power is known as first order reaction.

i) Consider the reaction between reactants A and B. the value of the rate onstant K is $1.20 mol^{-1}dm^3s^{-1}$.

Table 9.2: Initial rate and concentration of reactants A and B

Experiments	Initial Concentration (mol dm^{-3})		Initial Rate (mol $dm^{-3}s^{-1}$)
	[A]	[B]	
1	0.20	0.02	0.0048
2	0.20	0.08	0.0192
3	0.40	0.02	0.0096

Experiment 1 and 2 show that when we keep the concentration of reactant A stant and quadruples the initial concentration of B from 0.02 to 0.08, quadruples e rate of reaction from 0.0048 to 0.0192. It means that the rate of reaction is ectly proportional to the first power of the molar concentration of reactant B.

$\text{Rate} \propto [B]^1$ .... (i)

Experiments 1 and 3 show that when we keep the concentration of reactant B stant and double the initial concentration of A from 0.20 to 0.40, doubles the rate f reaction from 0.0048 to 0.0096. It means that the rate of reaction is directly proportional to the first power of concentration of reactant A.

Rate $\propto [A]^1$ .... (ii)

By comparing equation (i) and (ii), we have

Rate $\propto [A]^1[B]^1$ or

Rate = $K[A]^1[B]^1$

The sum of the exponents of both the reactants shows the overall order of reaction, hence this reaction is of second order $(1+1=2)$ overall.

iii) Consider the reaction between reactants *A* and *B*. the value of the rate constant *K* is $1.20 \text{mol}^{-2}\text{dm}^6\text{s}^{-1}$.

Table 9.3: Initial rate and concentration of reactants A and B

Experiments	**Initial Concentration (mol dm^{-3})**		**Initial Rate ($\text{mol dm}^{-3}\text{s}^{-1}$)**
	[A]	**[B]**	
1	0.20	0.02	0.0048
2	0.20	0.04	0.0192
3	0.40	0.02	0.0096

Experiments 1 and 2 show that when we keep the concentration of reactant *A* constant and double the initial concentration of *B* from 0.02 to 0.04, quadruples the rate of reaction from 0.0048 to 0.0192. It means that the rate of reaction is directly proportional to the square of the molar concentration of reactant *B*.

Rate $\propto [B]^2$ .... (i)

Experiments 1 and 3 show that when we keep the concentration of reactant *B* constant and double the initial concentration of *A* from 0.20 to 0.40, doubles the rate of reaction from 0.0048 to 0.0096. It means that the rate of reaction is directly proportional to the first power of concentration of reactant *A*.

Rate $\propto [A]^1$ .... (ii)

By comparing equation (i) and (ii), we have

Rate $\propto [A]^1[B]^2$ or

Rate = $K[A]^1[B]^2$

The sum of the exponents of both the reactants shows the overall order of reaction, hence this reaction is of third order $(1+2=3)$ overall.

Example 9.1

Consider the reaction between hydrogen and nitric oxide:

$$2NO + H_2 \longrightarrow 2H_2O + N_2$$

nitial rate data for the reaction between NO and H_2 is given below in the table:

Experiments	Initial Concentration (mol dm^{-3})		Initial Rate (mol $dm^{-3}s^{-1}$)
	$[H_2]$	$[NO]$	
1	0.025	0.050	2.5×10^{-3}
2	0.050	0.050	5.0×10^{-3}
3	0.025	0.100	1.0×10^{-2}

From the above data, determine (a) the rate equation for reaction, and the verall order of reaction and (b) the rate constant value at room temperature.

ı) Experiments 1 and 2 show that by doubling the concentration of H_2 from 0.025 to 0.050, doubles the rate from 2.5×10^{-3} to 5.0×10^{-3}, hence the rate of reaction is directly proportional to the first power of concentration of reactant H_2.

$$\text{Rate} \propto [H_2]^1 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(i)}$$

Experiments 1 and 3 show that by doubling the concentration of NO from 0.050 to 0.100, quadruples the rate from 2.5×10^{-3} to 1.0×10^{-2}, hence the rate of reaction is directly proportional to the square of concentration of NO.

$$\text{Rate} \propto [NO]^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(ii)}$$

By comparing equation (i) and (ii), we obtain the overall rate equation.

$$\text{Rate} \propto [H_2]^1[NO]^2 \qquad \text{or}$$

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

The sum of the exponents of both the reactants shows the overall order reaction, hence this reaction is of third order $(1 + 2 = 3)$ overall.

) We know that the rate equation for the reaction is:

$$\text{Rate} = K[H_2]^1[NO]^2 \quad \text{or} \quad K = \frac{\text{Rate}}{[H_2]^1[NO]^2}$$

By putting the values in the above equation, we get:

$$K_1 = \frac{2.5 \times 10^{-3} \text{mol dm}^{-3}\text{s}^{-1}}{(0.025 \text{ mol dm}^{-3})(0.050 \text{ mol dm}^{-3})^2} = 40 \text{ mol}^{-2}\text{dm}^6\text{s}^{-1}$$

$$K_2 = \frac{5.0\times10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}}{(0.050\ \text{mol dm}^{-3})(0.050\ \text{mol dm}^{-3})^2} = 40\ \text{mol}^{-2}\text{dm}^{6}\text{s}^{-1}$$

$$K_3 = \frac{1.0\times10^{-2}\ \text{mol dm}^{-3}\text{s}^{-1}}{(0.025\ \text{mol dm}^{-3})(0.100\ \text{mol dm}^{-3})^2} = 40\ \text{mol}^{-2}\text{dm}^{6}\text{s}^{-1}$$

As discussed earlier, the rate constant is independent of concentratio constant temperature. Note that the units of rate constant (K) depend on number of concentration terms in the rate equation and on the values exponents. Some of the common units of rate constant are given in the table:

Overall Order of Reaction	**Rate Equation**	**Units of *K***
First order	Rate = K[A]	s^{-1}
Second order	Rate = K[A][B]	$mol^{-1}dm^{3}s^{-1}$
Third order	Rate = $K[A]^2[B]$	$mol^{-2}dm^{6}s^{-1}$
Zeroth order	Rate = K	$mol\ dm^{-3}s^{-1}$

Practice Exercise 1:

Consider the reaction between oxygen and nitric oxide:

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

Initial rates data for the reaction between NO and O_2 is given below in t table:

Experiments	**Initial Concentration (mol dm^{-3})**		**Initial Rate (mol dm^{-3}s^{-1})**
	[NO]	**[O$_2$]**	
1	0.022	0.012	1.25×10^{-3}
2	0.022	0.024	2.50×10^{-3}
3	0.044	0.012	5.00×10^{-3}

(a) What is the rate law and overall order of reaction?

(b) What is the value of the rate constant at 25°C?

9.2.4 Factors Affecting Rate of Reaction

The rates of chemical reactions are influenced by five major factors:

i) The nature of the reactants.
ii) The concentration of the reactants.
iii) The surface area of the reactants.
iv) The temperature of the reactants.
v) The action of the catalysts.

In this topic we are going to discuss the first four and the action of the catalysts will be discussed in the forthcoming topic (9.4).

i) The Nature of the Reactants

The rate of chemical reactions depends upon the nature of the reactants. Some substances react swiftly while others react slowly. For example, the reaction of potassium with water is very fast than that of calcium.

$$2K + 2H_2O \xrightarrow{\text{Fast}} 2KOH + H_2$$

$$Ca + 2H_2O \xrightarrow{\text{Slow}} Ca(OH)_2 + H_2$$

The reactions between ionic compounds are fast. For example, the reaction between NaCl and $AgNO_3$ in the solution is very fast. In the solution, the silver ions and chloride ions have no bonds to break. In this case only new bonds are formed between silver ions and chloride ions to produce silver chloride.

$$NaCl_{(aq)} + AgNO_{3(aq)} \xrightarrow{\text{Fast}} AgCl_{(s)} + NaNO_{3(aq)}$$

On the other hand, the reactions between covalent compounds are usually slow. For example, the reaction between secondary propyl alcohol and HCl in the presence of $ZnCl_2$ is slow and takes five to ten minutes for completion because they have a lot bonds that have to be broken.

$$(CH_3)_2CH-OH + HCl \xrightarrow[\text{5–10 minutes}]{ZnCl_2} (CH_3)_2CH-Cl + H_2O$$

ii) The Concentration of the Reactants

The rate of chemical reactions increases by increasing the concentration of all or any one of the reactants. For example, wood burn much more rapidly in pure O_2 (100%) than in the air in which only 21% oxygen is present. Because the concentration of oxygen in pure oxygen is five times greater than air.

By increasing the concentration of reacting substances, the chances of collision between the molecules increases and the rate of reaction increases. This is because of the greater number of molecules per unit volume.

$$\text{Rate of reaction} \propto [A][B]$$

Quantitative effect of concentration on the rate of chemical reaction is given by order of reaction.

iii) The Surface Area of the Reactants

The actual reactions occur at the surface area between the reactants. The rate of reaction is directly proportional to the surface area of the reactants. The larger the surface area the higher is the reaction rate and the smaller the surface area the lower is the reaction rate. This is because, by increasing the surface area, more atoms or molecules come in contact with each other. The surface area can be increased by grinding the big crystals into smaller ones. For example, the reaction of zinc granules with hydrochloric acid is very slow and that of zinc dust (powder) is very fast.

$$Zn_{(s)}\text{(Granules)} + 2HCl_{(aq)} \xrightarrow{\text{Slow}} ZnCl_{2(aq)} + H_{2(g)}$$

$$Zn_{(s)}\text{(Dust)} + 2HCl_{(aq)} \xrightarrow{\text{Fast}} ZnCl_{2(aq)} + H_{2(g)}$$

Likewise, the reaction of marble chips (big pieces of $CaCO_3$) with sulphuric acid is slow and that of marble powder is fast. You know that it is difficult to ignite the big log. This is due to small surface area. If we break the log into smaller thin sticks (kindling), then the surface area increases and it will become easy to ignite the kindling.

iv) The Temperature of the Reactants

The kinetic energy of the particles of the substance is directly proportional to the temperature of the substance. By increasing temperature, the kinetic energy of a substance increases which in turn increase the rate of reaction of both the endothermic and exothermic reactions. Why we keep milk inside the refrigerator? We know that the rate of reaction decreases with decrease in temperature. When we keep milk at lower temperature inside the refrigerator, the chemical reactions that cause the milk to spoil are slow down and hence the milk remains fresh for a longer time. If we keep it in the kitchen at room temperature, the milk will spoil much more readily and becomes sour. On the other hand, food cooks more quickly in pressure cooker (airtight pot) than an open pot. The boiling point of water in pressure cooker is higher than its normal boiling point of 100°C. At higher temperature, the heat of decomposition of food (rate of reaction) is high and hence, the food cooks in short period of time.

At room temperature, the rates of many reactions roughly double with every 10°C rise in temperature. If the temperature is increased by 20°C, the rate of reaction will be increased four times. However, the actual rise in the rate of chemical reaction can be determined by experiments.

9.3 Collision Theory, Transition State and Activation Energy

9.3.1 Collision Theory

According to the collision theory of chemical kinetics, chemical reactions generally take place by collisions between the reacting substances (atoms, molecules or ions). By increasing the concentration of reacting substances, the chances of collision between particles increase due to greater number of particles per unit volume, and hence the rate of reaction increases. The rate of collision is directly proportional to the concentration of reactants *A* and *B*.

Rate of collision ∝ [A][B]

The rate of reaction is directly proportional to the number of collision between the reactant molecules per second.

Rate of reaction ∝ Number of collisions per second

We may say that by increasing the concentration of reacting substances, the rate of collision increases which in turn increase the rate of reaction and vice versa. Consider the formation of a product by the reaction of reactants *A* and *B*. If the concentration of reactant *A* is doubled, the rate at which *B* molecules collide with *A* molecules is also doubled. Likewise, if the concentration of reactant *B* is doubled, the rate at which *A* molecules collide with *B* molecules is also doubled. The reaction is second order overall. The rate of some reactions is directly proportional to the square of molar concentration of reactants.

By collision old bonds can be broken and new bonds can be formed. All the collisions of molecules do not give products. There are two types of collisions:

(a) Effective Collisions (b) Ineffective Collisions

The collisions which give products are called effective or fruitful collisions.

The collisions which do not give products are called ineffective collisions.

Three main conditions of this theory are:

i) The reacting substances must collide with one another to react.

ii) For effective collisions, the molecules must have sufficient amount of energy to start the reaction by breaking old bonds and forming new bonds during the process.

iii) The reactant molecules must collide with proper orientation that could enable them to react with one another.

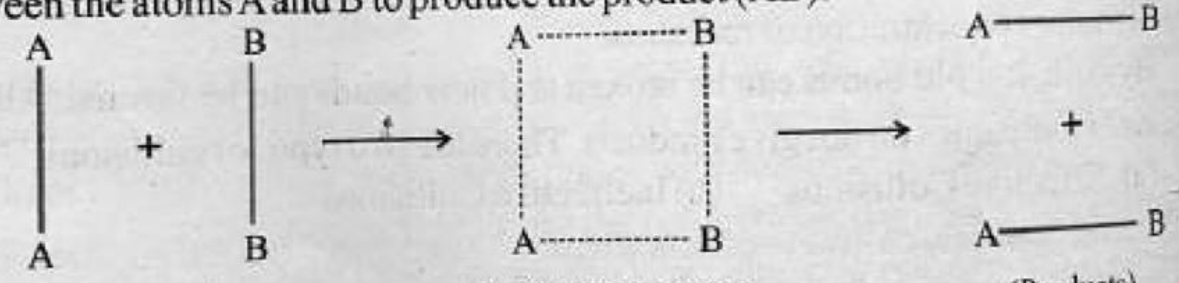
If all the collisions among the reactant molecules are effective, the reaction will be completed in a short time.

9.3.2 Transition State

The unstable high energy specie which is formed by collision of reactant molecules is called an activated complex. It is short-lived specie and decomposes into products immediately. It has a transient existence that is why; it is also called a transition state. The amount of energy needed to convert the reactants into the activated complex (Transition State) is called activation energy (E_a). When molecules collide, some of kinetic energy of colliding molecules is converted into potential energy and the molecules slow down. If this potential energy is equal to or more than activation energy, then the molecules may be activated and the activated complex is formed. If this potential energy is less than activation energy, then the molecules upon collision bounce back and do not form the activated complex and the reaction does not occur. The activated complex has partial bonding of both the reactants and products. When activated complex is formed, then there are two possibilities:

(a) It may reconstruct the original bonds and change back into the reactants;
(b) It may construct new bonds and change in to products.

Both forward and reverse reactions produce the same activated complex. For example, molecules A_2 react with B_2 to give product, AB. The activated complex is formed when molecules of A_2 collide with molecules of B_2. The activated complex has partially broken and partially formed bonds. In this process, old bonds are broken between the reactants atoms (A-A and B-B) and new bonds are formed between the atoms A and B to produce the product (AB).



(Reactants) (Activated Complex) (Products)

Figure 9.2: Activated Complex of Reactants A_2 and B_2

The transition state (activated complex) is always at higher energy state than the reactants and products.

9.3.3 Activation Energy

The minimum amount of energy required which the molecules must have to form an activated complex is called activation energy. It is represented by E_a. Its units are joules or kilojoules per mole (kJ mol^{-1}).

The reactants are not directly converted into products. They first gain energy to form an activated complex and then this activated complex decomposes into products. We can say that activation energy is an energy barrier (or energy hill) between the reactants and products. The reactant molecules must cross this energy barrier before they can form the products.

Crossing this barrier is similar to carrying a ball to the top of the hill and then rolling down the other side. But if the ball will not reach at the top of hill, it will ro back. Similarly, if activation energy is not provided, the reaction will not start and the reactants will not converted into products. It can be best understood by the energy diagram.

In case of exothermic reactions, the potential energy of reactants is higher than products. This difference is shown by ΔH. To start the reaction, we have to provide the energy E_a to reach at the top of the barrier.

In case of endothermic reactions, the potential energy of reactants is lower than products. This difference is shown by ΔH. To start the reaction, we have to provide the energy E_a to form an activated complex.

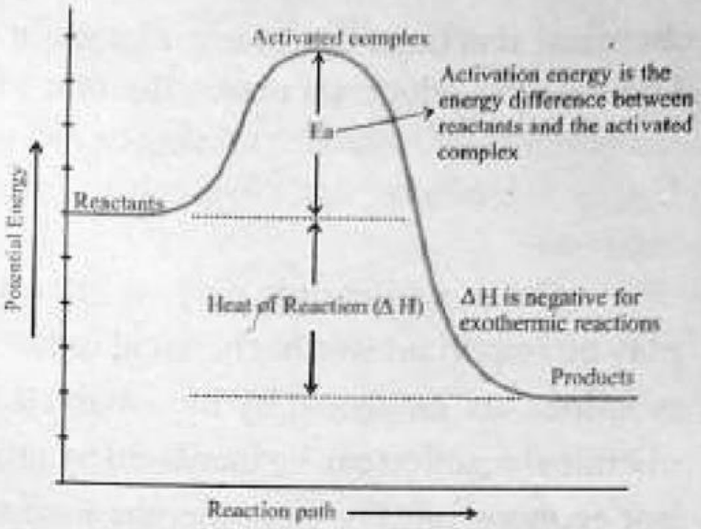


Figure 9.3: A graph between reaction path and potential energy for exothermic reaction

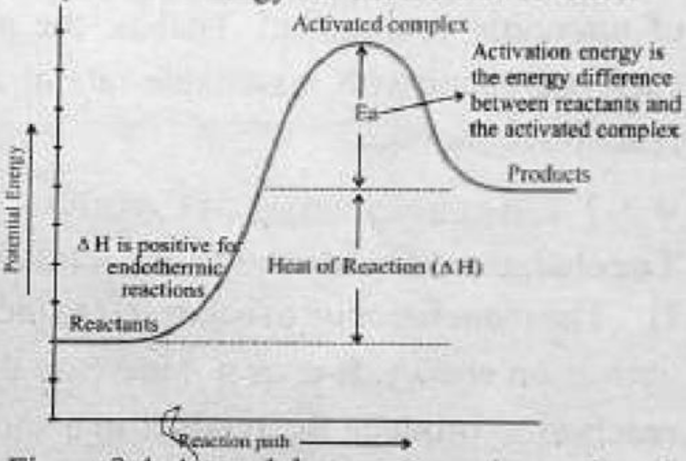


Figure 9.4: A graph between reaction path and potential energy for endothermic reaction

The activation energy for the orward and reverse reactions is not ame for all of the reactions. For xothermic reactions, the activation nergy for the forward reaction is less han that of reverse reaction because he reactants are at higher energy level than the products. On the other hand, the ctivation energy for the reverse reaction is higher than that of forward reaction ecause the products are at higher energy level than that of reactants. For ndothermic reactions, the activation energy for the forward reaction is higher than at of reverse reaction because the reactants are at lower energy level than that of roducts. On the other hand, the activation energy for the reverse reaction is lower an that of forward reaction because the products are at lower energy level than actants. Note that:

i) The reactions which are exothermic in forward direction will be ndothermic in the reverse direction,

) Fast reactions usually have low activation energies, and slow actions have high activation energies.

4 Catalysis (Effect of Catalysts)

ubstance which is not consumed in a reaction but alters the rate of chemical action is called Catalyst. In most of the cases, the catalyst increases the rate of chemical reactions but in some cases, it decreases the rate of chemical reactions. The catalyst which increases the rate of reaction is called positive catalyst. The catalyst which decreases the rate of reaction is called negative catalyst or inhibitor. The increase in the rate of chemical reaction by the addition of a catalyst is called catalysis.

Catalysts not only play an important role in living organisms but they also play an important role in chemical industries too. In living organisms, the chemical reactions are catalyzed by bio-catalysts called enzymes. In industries, the rate of chemical reaction can be increased by raising the temperature of the reaction but it is not economical. For example, the formation of ammonia by Haber process in the absence of catalyst is very expensive. The addition of catalyst makes the formation of ammonia economical. That is, the chemical reactions that are catalyzed by catalysts occur with reasonable rate at a much lower temperature and make the reaction economical.

9.4.1 Characteristics of Catalyst

The characteristics of catalyst are as follows:

I) The main function of catalyst is to increase the rate of reaction by decreasing the activation energy. It does not increase the amount of product but it speeds up the reaction to produce the product in a short time. In the presence of a catalyst, the reaction occurs at higher rate and at lower temperature. It changes path or mechanism of chemical reaction and a new reaction path is provided to the reaction. In this way, greater number of reactant molecules can cross the lower energy barrier. As a result of this, rate of reaction increases. For example, oxygen gas can be obtained by the thermal decomposition of potassium chlorate ($KClO_3$) in the laboratory:

$$2KClO_{3(s)} \xrightarrow{\quad} 2KCl_{(s)} + 3O_{2(g)}$$

The decomposition of $KClO_3$ at room temperature is very slow when heated in the absence of a catalyst.

$$2KClO_{3(s)} \xrightarrow[\text{Slow}]{\text{Heat}} 2KCl_{(s)} + 3O_{2(g)}$$

On industrial scale, the reaction must occur at an appreciable rate and it must have high yield of the product. Hence, the rate of decomposition can be increased when small amount of manganese dioxide (MnO_2), a black powder, is added to it.

$$2KClO_{3(s)} \xrightarrow[\text{Fast}]{\text{Heat+MnO}_2} 2KCl_{(s)} + 3O_{2(g)}$$

It is clear from the figure 9.5 that the catalyst lowers the activation energy and provides a new path to the reaction but ΔH remains same.

ii) The catalyst (MnO_2) is not consumed in the reaction as discussed earlier and can be recovered at the end of reaction. The catalysts recovered can be used again. Hence, catalyst is not written into the equation because it neither acts as a reactant nor as a product. It is usually written above the arrow.

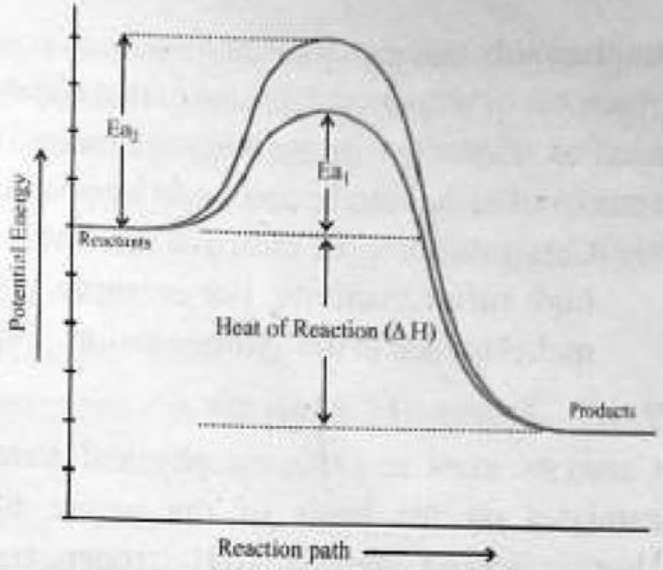


Figure 9.5: Effect of catalyst on activation energy of reaction

iii) A catalyst only reduce the time of equilibrium, it does not change the equilibrium position of reversible reactions.

iv) A catalyst has no effect on the total enthalpy (ΔH) of reaction. Hence, it can not start those reactions which are not thermodynamically feasible.

v) A particular catalyst works for a particular reaction. A catalyst can catalyzes only specific reaction and cannot be used for every reaction. Change of catalyst also changes the nature of the reaction. For example, in the presence of nickel (Ni), the carbon monoxide and oxygen gases of water gas ($CO+H_2$) react to produce CH_4 and H_2O while in the presence of ZnO catalyst, they react to produce CH_3OH.

$$CO_{(g)} + 3H_{2(g)} \xrightarrow{Ni} H_2O_{(l)} + CH_{4(g)}$$

$$CO_{(g)} + 2H_{2(g)} \xrightarrow{ZnO} CH_3OH_{(l)}$$

If iron coated alumina is used as a catalyst, then the mixture of carbon monoxide and hydrogen gases produce octane (gasoline).

$$8CO_{(g)} + 17H_{2(g)} \xrightarrow{Fe/Al_2O_3} C_8H_{18(l)} + 8H_2O_{(l)}$$

vi) Catalyst can be deactivated by small amount of impurity. Deactivation of a catalyst by small amount of impurity is called poisoning of a catalyst. A substance which deactivates the catalyst is called poison. For example, in contact process of H_2SO_4, the presence of small amount of As_2O_3 (impurity) in sulphur dioxide gas decreases the catalytic behaviour of V_2O_5 (vanadium pentaoxide). Here Arsenic oxide (As_2O_3) acts as a poison.

vii) The catalytic behavior of catalyst can be increased by the introduction of another substance. A substance which increases the activity of a catalyst is called promoter or activator. It is also called Catalyst for a catalyst. For example, nickel is used as a catalyst in the hydrogenation of vegetable oil to ghee. The catalytic activity of nickel can be increased by using copper and tellurium.

viii) Catalysts are more effective in a finely divided form (powder form) because of high surface activity. For example, a finely divided nickel also called Raney nickel is used in the hydrogenation of vegetable oil to form ghee.

9.4.2 Types of Catalysis

Catalysts exist in different physical states; therefore, there are three types of catalysis on the basis of the nature of the rate increasing substances: (a) Homogeneous Catalysis, (b) Heterogeneous Catalysis, and (c) Enzyme Catalysis.

a) Homogeneous Catalysis

In homogeneous catalysis, the reactants and catalysts are in same phase. Homogeneous catalysis occurs either in gaseous phase or in the liquid (solution) phase. Consider the example of the formation of sulphuric acid by lead chamber process. In lead chamber process, sulphuric acid is produced by dissolving SO_3 gas in water. The SO_3 gas is obtained by the oxidation of SO_2 gas. Such reaction is catalyzed by nitric oxide (NO).

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{NO_{(g)}} 2SO_{3(g)}$$

In this reaction both the reactants and catalyst are gases.

Consider another example of the hydrolysis of an ester (ethyl acetate) in the presence of an acid (sulphuric acid) or a base (KOH).

$$CH_3COOC_2H_{5(aq)} + H_2O_{(l)} \xrightleftharpoons{H_3O^+ \text{ or } OH^-} CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$$

Here both the reactants and catalyst are in solution.

b) Heterogeneous Catalysis

In heterogeneous catalysis, the reactants and catalysts are in different phases. In heterogeneous catalysis, the reactants are mostly in gaseous or in liquid states while catalysts are in solid states. Heterogeneous catalysis most often involves gaseous reactants which are being on the surface of the solid catalyst. The atoms and ions of the surface of catalyst are very reactive and provide a site for the reaction. The adsorption may either be physical or chemical. In physical adsorption, the reactants are attached to catalysts surface by weak intermolecular forces while in chemical adsorption, the reactants are attached to the surface of the reactants by chemical bonding. The bonds in the reactant species during chemical adsorption may either be broken or weakened. The adsorption of reactants on the surfaces of solid catalyst increases the concentration of reactants which in turn increases the rate of reaction. Consider the manufacture of sulphuric acid by contact process. In contact process, sulphuric acid is produced by dissolving SO_3 gas in water. The SO_3 gas is obtained by the oxidation of SO_2 gas in the presence of vanadium pentaoxide (V_2O_5) catalyst.

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{V_2O_{5(s)}} 2SO_{3(g)}$$

Here reactants are gases and catalyst is solid.

Consider another example of the hydrogenation of ethene to ethane in the presence of nickel catalyst.

$$CH_2=CH_{2(g)} + H_{2(g)} \xrightarrow{Ni_{(s)}} CH_3-CH_{3(g)}$$

Here reactants are gases and catalyst is solid. Most of the catalysts used in industrial chemical processes are heterogeneous, because such catalysts can be easily separated from the reaction products to some extent.

Table 9.4: The Uses of Some Heterogeneous Catalysts

Catalysts	Uses	Reactions
V_2O_5 or Pt	Contact process (in the manufacture of sulphuric acid)	$2SO_2 + O_2 \rightleftharpoons 2SO_3$
Ni, Pd, or Pt	Hydrogenation of alkenes	$CH_2=CH_2 + H_2 \longrightarrow CH_3-CH_3$
Fe, Al_2O_3, and K_2O	Haber process (in the manufacture of NH_3)	$N_2 + 3H_2 \rightleftharpoons 2NH_3$
Cr_2O_3 and ZnO	Formation of methanol from water gas ($CO + H_2$)	$CO + 2H_2 \longrightarrow CH_3OH$
Pt and Rh	In the formation of NO gas which is further used in the manufacture of nitric acid by Ostwald process	$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$
Cu	Oxidation of alcohols to aldehydes.	$CH_3CH_2OH + [O] \longrightarrow CH_3-CHO + H_2O$

c) Enzyme Catalysis

The complex protein molecules which catalyze the chemical reactions in the living cells are called enzymes. The chemical reaction which is catalyzed by enzymes is called enzyme catalysis. Each enzyme is produced in a particular living cell to catalyze a reaction taking place in that cell. Many enzymes have been identified and obtained in pure crystalline state from the cells to which they belong. However, the first enzyme was prepared in the laboratory in 1960. Some common examples of enzyme catalysis are:

i) The starch is hydrolyzed into maltose by diastase enzyme present in the yeast.

$$\underset{\text{(Starch)}}{2(C_6H_{10}O_5)_n} + n\,H_2O \xrightarrow[\text{Yeast}]{\text{Diastase}} \underset{\text{(Maltose)}}{n\,C_{12}H_{22}O_{11}}$$

ii) The maltose can be converted into glucose and fructose by maltase enzyme present in the yeast.

$$\underset{\text{(Maltose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Yeast}]{\text{Maltase}} \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

iii) The cane sugar juice can also be converted into glucose and fructose by invertase enzyme present in the yeast.

$$\underset{\text{(Sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Yeast}]{\text{Invertase}} \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

iv) Glucose can be converted into ethyl alcohol by the zymase enzyme present in the yeast.

$$C_6H_{12}O_6 \xrightarrow[\text{Yeast}]{\text{Zymase}} 2\,C_2H_5OH + 2\,CO_2$$

v) The urea is hydrolyzed into ammonia and carbon dioxide by urease enzyme present in the soya bean.

$$\underset{\text{Urea}}{(NH_2)_2CO} + H_2O \xrightarrow[\text{Soya bean}]{\text{Urease}} \underset{\text{Ammonia}}{2\,NH_3} + CO_2$$

Society, Technology and Science

Enzymes can be Effective in Removing Stains From Fabrics:
Some laundry detergents have added enzymes that break down proteins, helping to remove them from the cloth fibers, and thus remove stains. The enzymes such as proteases, amylases, lipases and cellulases are some of the active ingredients in the laundry detergents. The enzyme amylase catalyzes the breakdown of starch based stains to smaller segments. Amylases remove starch-based soils that contain eggs, sugars, sauces, ice cream and gravy. The action of proteases is similar to that of amylase, except that a large protein molecule is hydrolyzed. Proteases remove soils and protein-based stains that contain blood, foods, urine, feces, wines, and other beverages. Lipases are effective in removing oily body and food stains. Cellulases remove dust and mud and are used to soften fabric and restore colour of fibers.

Summary of Facts and Concepts

- Chemical kinetics concern with the study of reaction rate, reaction mechanism, and factors that affect the reaction rate.
- Reaction rate is the change in the concentration of reactants or products per unit time. The rate of reaction is not constant. The rate of reaction is influenced by concentration of reactants, surface area, temperature, nature of reactants, and the action of catalysts.
- The rate of reaction between two specific time intervals is called average rate of reaction while the rate of reaction at any one instant during the interval is called instantaneous rate of reaction.
- Rate law or rate equation is an equation that shows the relationship between the rate of a chemical reaction and the molar concentrations of the reactants each raised to some power.

  $\text{Rate of reaction} \propto [A]^m[B]^n$ or

  $\text{Rate of reaction} = K[A]^m[B]^n$
- The rate constant (K) is a proportionality constant that relates the rate of chemical reaction to the molar concentrations of reactants. The exponents *m* and *n* are called reaction orders for the reactants.
- The overall order of reaction is the sum of all the exponents of the concentration terms in the rate equation. It is determined experimentally. The sum of the exponents in the rate equation may or may not be equal to the coefficients of balance chemical equation. Order of reaction may be whole number, zero, or fractional.
- Reaction mechanismis the step-by-step process by which reactants are converted into products. A single step in a reaction mechanism is called an elementary reaction or elementary step.
- The slowest step which controls the rate of reaction in a multistep reaction is called rate determining step.
- Activation energy is the amount of energy required for molecules to form an activated complex so that a reaction can occur.
- Activated complex (or transition state) is unstable intermediate complex with very high energy and is formed by the collision of reactant molecules.
- According to collision theory, the reactant molecules must collide effectively for reaction to occur.
- The collision that results in the formation of an activated complex and produce

product is called effective collision.

- Catalyst is a substance that usually speeds up a chemical reaction by lowerin activation energy. The catalyst is not used up by the reaction and can recovered at the end of reaction.
- The process by which a catalyst increases the rate of chemical reaction is call catalysis. Catalysis may either be homogeneous or heterogeneous. homogeneous catalysis, the catalyst and reacting substances exist in the sa phase while in heterogeneous catalysis, the catalyst and reacting substanc exist in different substances.
- Enzymes are usually the complex protein molecules and are present in living cells. They are also known as biological catalysts because they cataly the reactions in the living cells.

Questions and Problems

Q.1. Four answers are given for each question. Select the correct one:

i) Chemical kinetics deals with the study of:

(a) Reaction rate (b) reaction mechanism

(c) factors that affect the reaction rate (d) all of them

ii) The energy of activated complex is:

(a) Lower than the energy of reactants and higher than the energy products

(b) lower than the energy of products and higher than the energy reactants

(c) lower than the energy of both the reactants and products

(d) higher than the energy of both the reactants and products

iii) A substance that alters the rate of chemical reaction without bei consumed in the reaction is called:

(a) Catalyst (b) reactant

(c) product (d) activated complex

iv) The slowest step in a step-by-step reaction is called

(a) Rate determining step (b) rate limiting step

(c) rate controlling step (d) all of them

v) The rate of which reaction increases four times by doubling th concentration(s) of reactant(s)?

(a) First order (b) second order

(c) third order (d) zero order

vi) Decomposition of N_2O_5 is an example of:

(a) First order (b) second order

(c) third order (d) zero order

vii) The collision that results in the formation of product is called:

(a) Fruit full collision (b) effective collision

(c) both a and b (d) ineffective collision

viii) Which one of the following does **NOT** influence rate of reaction?

(a) Concentration (b) temperature

(c) catalyst (d) activation energy

ix) The unit of rate constant for third order reaction is:

(a) s^{-1} (b) $mol^{-1}dm^{3}s^{-1}$

(c) $mol^{-2}dm^{6}s^{-1}$ (d) $mol\,dm^{-3}s^{-1}$

x) Which one of the following reactions is **NOT** the example of heterogeneous catalysis?

a) $2SO_2 + O_2 \overset{Pt}{\rightleftharpoons} 2SO_3$

b) $CH_2 = CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_3$

c) $CO + 2H_2 \xrightarrow{Cr_2O_3 + ZnO} CH_3OH$

d) $2SO_2 + O_2 \overset{NO}{\rightleftharpoons} 2SO_3$

Q.2. Fill in the blanks with suitable words given in the brackets:

i) The change in the concentration of reactants or products over time is called_________. (reaction rate/reaction mechanism)

ii) At the beginning the instantaneous rate is _________ than the average rate. (lower/higher)

iii) A catalyst that increases the rate of chemical reaction is called _________catalyst. (positive/negative)

iv) The rate of reaction _________ by increasing temperature. decreases/increases)

v) A catalyst _________ the activation energy of the chemical reaction. (decreases/increases)

vi) he amount of energy needed for molecules to undergo reaction is _________. (internal energy/activation energy)

vii) The smaller the surface area of the reacting substances, the _________is the reaction rate. (higher/lower)

viii) Alkali metals (group IA elements) react with water swiftly than alkaline earth metals (group IIA elements) due to _________ atomic sizes. (smaller/larger)

ix) At room temperature, the rates of many reactions roughly double with every 10°C rise in temperature due to ________ in the number of effective collisions. (decrease/increase)

x) A substance which increases the activity of a catalyst is called ________. (activator/inhibitor)

Q.3. Label the following statements as True or False:

i) The neutralization of acids by bases is the example of slow reactions.

ii) Order of reaction is predicted from a balanced chemical equation because the sum of exponents in the rate equation is equal to the coefficient of balanced chemical equation.

iii) For exothermic reactions, the potential energy of reactants is higher than the potential energy of products.

iv) The activation energy is the minimum when all the collisions among the molecules of reactants are effective.

v) The rate of both forward and reverse reaction increases by increasing temperature.

vi) It is easy to ignite the match stich than a big log.

vii) The reaction intermediate has temporary existence and is unstable.

viii) The activation energy for the forward and reverse reactions is same for all of the reactions.

ix) A substance which slows down a reaction is called inhibitor.

x) A particular catalyst works for a particular reaction.

Q.4: What is chemical kinetics? What information it gives for the chemical reactions?

Q.5: What is meant by the reaction rate? What are the usual units of reaction rate?

Q.6: How can you differentiate between average rate and instantaneous rate of chemical reaction?

Q.7: Name the factors that affect the reaction rate. Discuss the effects of the concentration, temperature, and surface area on reaction rates.

Q.8: What is reaction mechanism? Discuss the reaction mechanism for the reaction.

Q.9: What is order of reaction? What do you know about first order, second order, third order and zero order chemical reactions? Give an example for each.

Q.10: Consider the formation of phosgene gas from CO and Cl_2:

$$CO_{(g)} + Cl_{2(g)} \longrightarrow COCl_{2(g)}$$

The initial rates obtained from three experiments at a given temperature are given in the table.

Experiments	Initial Concentration (mol dm^{-3})		Initial Rate (mol dm^{-3}s^{-1})
	[CO]	[Cl_2]	
1	0.015	0.0068	1.7×10^{-10}
2	0.030	0.0068	3.40×10^{-10}
3	0.015	0.0204	5.10×10^{-10}

By using the data, determine (a) the reaction orders for both the reactants, the overall order of reaction and the rate law, and (b) the value of the rate constant at a given temperature.

Q.11: Define rate determining step, elementary step, and reaction intermediate.

Q.12: Explain the significance of the rate determining step on the overall rate of a multistep reaction.

Q.13: Explain collision theory and give main conditions of this theory.

Q.14: Explain the following:

(a) Rate law (b) Transition state (c) Activation energy

Q.15: Explain how activation energy influences the rate of chemical reaction?

Q.16: What is catalysis? Explain the difference between homogeneous and heterogeneous catalysis. Give an example of each.

Q.17: What is catalyst? What are the characteristics of catalyst? What is the effect of a catalyst on the activation energy?

Q.18: Describe some of the important industrial processes that are dependent on catalysts.

Q.19: Explain the following statements:

a) The reaction of thick copper wire with hot concentrated sulphuric acid is slow and that of thin copper wire is fast.

b) All collisions of reactant molecules do not result in the formation of product. Give reasons.

c) The rate expression for a reaction is determined from experiment and not from the balanced chemical equation.

d) The rate of reaction can be increased without changing the temperature.

e) The order of reaction is not necessarily equal to the sum of the coefficients in the balanced chemical equation.

f) Catalyst is neither a reactant nor a product.

g) The radioactive decay is the example of first order reaction.

h) The second order and third order reactions have different units.

i) Which sugar dissolves the fastest, the granular sugar or the powder sugar? Give reason.