CHAPTER 7

CHEMICAL KINETICS

SLOs: After completing this lesson, the student will be able to:

1. Explain the rate of reaction, and rate constant
2. Use experimental data to calculate the rate of a chemical reaction.
3. Explain the concept of activation energy and its role in chemical reactions.
4. Use the Boltzmann distribution curve to explain the effect of temperature on the rate of a reaction.
5. Explain the concept of catalyst and how they increase the rate of a reaction by lowering the activation energy.
6. Interpret reaction pathway diagrams, including in the presence and absence of catalysts.
7. Explain the relationship between Gibbs free energy change, ΔG° and the feasibility of a reaction.
8. Use rate equations, including orders of reaction and rate constant.
9. Suggest a reaction mechanism that is consistent with a given rate equation and rate-determining step.
10. Calculate the numerical value of a rate constant using the initial rates and half-life method.
11. Describe the effect of temperature change on the rate constant and rate of reaction.

Chemical reactions are dynamic processes in which matter and energy are constantly changing. Chemical reactions occur at different rates, from very fast to very slow. For example, fermentation is a slow reaction that can take several weeks to produce sufficient products. Is digestion a slow reaction? On the other hand, acid-base neutralization reactions complete in microseconds. Some reactions occur at a reasonable rate. For example, reactions that contract muscles and transmit impulses along nerves and record photographic images. In industry, it is important to know the conditions under which the reaction occurs most favorably. "The study of the rates, mechanisms and factors that affect the rate of chemical reactions is known as kinetics or chemical kinetics." Rate information is the most important information used to infer the mechanism of a chemical reaction. Mechanism refers to the sequence of all chemical steps leading from starting materials to products.

7.1 RATES OF REACTIONS

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

Mathematically,

$$\text{Rate} = \frac{\text{Change in concentration of a substance}}{\text{Time taken for change}}$$

The concentration of reactants decreases and concentration of products increases with the passage of time. Therefore, rate of a reaction can also be defined as **the decrease in concentration of reactants per unit time or the increase in concentration of products per unit time.** The unit of concentration is mole dm^{-3} and time is second, so unit of reaction rate is mole dm^{-3} s^{-1}.

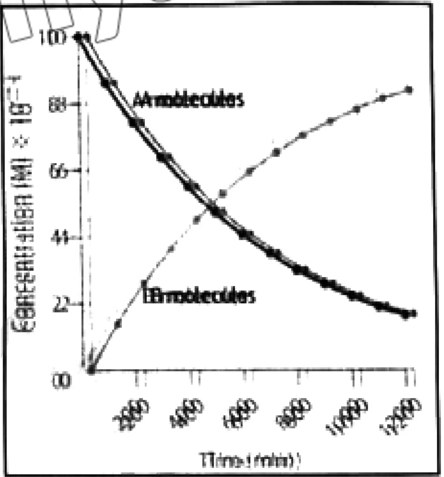


Figure 7.1: Change in concentration of reactants and products with passage of time. What does the slope of each graph show?

The change in concentration of reactants and products can be represented graphically (Fig. 9.1), for the general reaction

$$A \longrightarrow B.$$

The slope of the curve for both starting materials and products is steeper at the beginning than at later stages. This indicates a rapid decrease or increase in the concentration of reactant or product, respectively. As the reaction progresses, the slope becomes less steep, indicating a decrease in the reaction rate. Eventually the graph becomes horizontal and the reaction stops. So the reaction rate is never constant. The concentration of reactants continuously decreases while the concentration of products increases with time. Therefore, the reaction rate also decreases continuously.

Thus, the rate measured from a time interval is just the average reaction rate for that interval during any given interval, which can be determined by the difference in concentrations divided by the difference in measurement times.

If *dx* is very small change in concentration of a product in a very small time interval *dt*, the rate of reaction is expressed as

Rate of reaction = dx / dt

Consider a general reaction

$$A \longrightarrow B$$

The rate of reaction can be expressed in term of the rate of disappearance of reactant A or the rate of appearance of product B.

$$\frac{dx}{dt} = -\frac{d[A]}{dt}$$

$$\frac{dx}{dt} = +\frac{d[B]}{dt}$$

Where d [A] and d [B] represent changes in the concentration of A and B respectively. The negative sign indicates a decrease in the concentration of the reactant A. whereas the positive sign indicates the increase in the concentration of product B. Using these relationships, you can determine rate of reaction between any two-time intervals.

Example 7.1

Determine the rate of following reaction

$$A + B \longrightarrow C$$

Rate of a chemical reaction between any two-time intervals can be determined from the experimental data. For obtaining experimental data, you need to measure change in the concentration of reactants or products at different time intervals. From this data you can determine rate of reaction. Let suppose you measure the concentration of product C at different time intervals, following data is obtained.

Sr.No.	Time(s)	Concentration of C(mol/dm^3)
1	0.0	0.0
2	10	0.20
3	20	0.38
4	30	0.45
5	40	0.60

To calculate the rate of reaction, you need to follow change in the concentration of C between a specific time interval. Suppose you want to calculate the rate of reaction between time intervals 0.0 second and 20 seconds.

$$dt = \text{Change in time} = 20s - 0.0$$

$$= 20s$$

d[C]= Chage in the concentration of C= 0.38 − 0.0

$= 0.38\ mol/dm^3$

$dx/dt = + d[C]/dt$

$= 0.38/22$

$= 0.019 mol/dm^3/s$

Like this rate of reaction can be determined between any two time intervals. Note that you can determine only the average rate of reaction between the given time intervals.

7.2 Rate Law

Rate of reaction is defined as **the instantaneous change in concentration of a reactant or product at a given time.** Experimental studies on reaction rates show that the rate of a chemical reaction is proportional to the molar concentration of reactants each raised to a power, the value of which is determined experimentally. Thus for a general reaction:

$A \rightarrow Product$

$Rate \propto [A]^x$

$Rate = k\,[A]^x$

Where k is proportionality constant and is known as **rate constant** and the expression as **rate law or rate equation.** The exponent *x* in the rate equation is called **order of reaction** with respect to reactant A.

When [A] = 1 M

Rate = k

Thus, the rate constant can be defined as the rate of reaction when the molar concentration of each reactant is unity. The rate constant gives the relationship between concentration and reaction rate. Each reaction has its own specific rate constant, independent of concentration and time. But the value of the rate constant changes with temperature. (See Section 7.2.2 for more information).

7.2.1 Order of Reaction and Rate Equation

Order of reaction may be defined as the number of molecules of reactants participating in the rate determining-step.

Consider a general reaction between *a* moles of A and *b* moles of B to give *c* moles C and *d* moles of D.

$aA + bB \rightarrow cC + dD$

The rate equation can be written as

$Rate \propto [A]^x\,[B]^y$

$Rate = k\,[A]^x\,[B]^y$

The exponent 'x' is the order of reaction with respect to species 'A' and the exponent 'y' is the order of reaction with respect to species 'B'. The order of the reaction expresses the effect of concentration on the rate of reaction. the sum 'x+y' is called the overall order of the reaction or simply the order of the reaction.

"Order of reaction may be defined as the sum of all the exponents to which the molar concentration terms in the rate equation are raised".

x and *y* may or may not be the same as *a* and *b* respectively. The order of a reaction for a particular species cannot be predicted by looking at the balanced chemical equation. It can be determined only by experiment.

For example for the reaction

$$2NO_2 + O_3 \longrightarrow N_2O_5 + O_2$$

Experimental studies show that the rate = $k\,[NO_2]\,[O_3]$

Notice that the order with respect to NO_2 is one, whereas its stoichiometric coefficient is two.

"An expression which shows how the reaction rate is related to the concentration of reactants is called the rate law or rate equation." Therefore, rate law or rate equation for the above reaction is,

$$\text{Rate} = k\,[NO_2]\,[O_3]$$

Order of reaction may be a whole number, zero or a fraction. It helps in determining the mechanism of a reaction.

Types of order of reactions

a) Zero order reaction

A reaction that is independent of the concentration of reactant molecules is called zero order reaction. An example is the decomposition of ammonia on heated tungsten.

$$2NH_{3(g)} \longrightarrow N_{2(g)} + 3H_{2(g)}$$

$$\text{Rate} = k\,[NH_3]^0$$

The concentration of ammonia decreases continuously until it reaches zero. The combination of H_2 and Cl_2 in presence of sunlight is also a zero-order reaction. Reactions catalyzed by enzymes also follow zero-order kinetics.

b) First order reactions.

A reaction whose rate of reaction is directly proportional to the first power of the concentration of single reactant molecule is called the first order reaction.

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

i Thermal decomposition of N_2O_5

$$2N_2O_{5\,(g)} \longrightarrow 2N_2O_{4(g)} + O_{2(g)}$$

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

ii) Decomposition of ammonium nitrite in aqueous solution.

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

$$\text{Rate} = k\,[NH_4NO_2]$$

c) Second order reactions

A reaction for which sum of exponents of rate equation is two is called the second order reaction.

$$\text{Rate} \propto [A]^2 \qquad \text{or} \qquad \text{Rate} \propto [A]^1[B]^1$$

i) Decomposition of nitrogen dioxide.

$$2NO_{2(g)} \longrightarrow 2NO_{(g)} + O_{2(g)}$$

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

ii) $NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2\,(g)}$

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

Order of reaction = 1 + 1 = 2

iii) $2NO_{2\,(g)} + O_{3\,(g)} \longrightarrow N_2O_{5\,(g)} + O_{2(g)}$

$$\text{Rate} = k\,[NO_2]\,[O_3]$$

d) Third order reactions

A reaction for which sum of exponents of rate equation is three is is called the third order reaction.

$$\text{Rate} \propto [A]^3 \text{ or Rate} \propto [A]^2[B]^1 \text{ or Rate} \propto [A]^1[B]^1[C]^1$$

i) The oxidation of NO by O_2 is an example of a third order reaction.

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

$$\text{Rate} = k\,[NO]^2\,[O_2]$$

ii) $2FeCl_{3(aq)} + 6KI_{(aq)} \longrightarrow 2FeI_{2(aq)} + 6KCl_{(aq)} + I_{2(s)}$

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

e) Fractional order reactions

A reaction for which the sum of exponents of rate equation is in fraction is called the fractional order reaction.

i) The reaction between H_2 and Br_2 to produce HBr is a half order in Br_2 and first order in H_2.

$$H_{2(g)} + Br_{2(g)} \longrightarrow 2HBr_{(g)}$$

Rate = $k\,[H_2]\,[Br_2]^{1/2}$

Order of reaction is 1 + 0.5 = 1.5

ii) $$CHCl_{3(l)} + Cl_{2(g)} \longrightarrow CCl_{4(l)} + HCl_{(g)}$$

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

f) Pseudo First order reaction

A bimolecular reaction for which solvent is in excess and its concentration remains constant and does not take part in rate determining step is called a Pseudo First order reaction.

$$(CH_3)_3C-Br_{(l)} + H_2O_{(Excess)} \longrightarrow (CH_3)_3C-OH_{(l)} + HBr_{(l)}$$

Rate = $k\left[(CH_3)_3C-Br\right]$

7.2.2 Determination of Reaction Order, Rate Law and Rate constant

The effect of a change in reactant concentration on reaction rates cannot be derived from a chemical equation. It can only be determined experimentally by determining the order of chemical reactions. For this purpose, the method of initial rates is a simpler way to find the value of the reaction order. In this method, an experiment is designed in which the concentration of one reactant is changed while keeping everything else constant. The concentration of one reactant is systematically varied and the initial reaction rate is determined for each change. This method can be understood by the following example:

Example 7.2

Jet engines release Nitrogen (II) oxide in the upper atmosphere. In the ozone layer of upper atmosphere Nitrogen (II) oxide reacts with ozone to form nitrogen (IV) oxide and oxygen.

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

The following data was obtained for this reaction at 25 °C.

Experiment	Initial [NO]	Initial [O_3]	Initial rate (moles $dm^{-3}s^{-1}$)
1	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
2	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
3	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}

Use this data to determine the rate law for the reaction.

Solution:

To determine the order of reaction with respect to a reactant, examine the relationship between its initial concentration and the rate of reaction while holding the concentration of the other reactant constant.

In experiments 1 and 2 initial concentration of ozone is kept constant at

9.00×10^{-6} M while the concentration of NO is doubled from 1.00×10^{-6} M to 2.00×10^{-6} M, the initial rate increases from 1.98×10^{-4} to 3.96×10^{-4} moles $dm^{-3}s^{-1}$. The ratio between these two rates is

$$1.98\times10^{-4} : 3.96\times10^{-4}$$

$$\frac{1.98\times10^{-4}}{1.98\times10^{-4}} : \frac{3.96\times10^{-4}}{1.98\times10^{-4}}$$

$$1 : 2$$

Thus the initial rate doubles. This means the rate of reaction is directly proportional to the first power of concentration of NO.

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

In experiments 1 and 3 initial concentration of NO is kept constant at 1.00×10^{-6} and concentration of ozone is decreased to one third i.e. from 9.00×10^{-6} to 3.00×10^{-6}M, the initial rate decreases from 1.98×10^{-4} to 6.60×10^{-5} moles dm^{-3} s^{-1}, the ratio between these rates is

$$1.98\times10^{-4} : 6.60\times10^{-5}$$

$$\frac{1.98\times10^{-4}}{1.98\times10^{-4}} : \frac{6.60\times10^{-5}}{1.98\times10^{-4}}$$

$$1 : \frac{1}{3}$$

Thus, the rate of reaction also decreases one third. This means the rate of reaction is directly proportional to the first power of concentration of O_3.

$$\text{Rate} \propto [O_3]$$

Thus, the rate law for the reaction is

$$\text{Rate} \propto [NO]\,[O_3]$$

Hence this reaction is a second order reaction.

Once the rate law for a reaction is determined experimentally, the rate constant for the reaction can be determined from the same experimental data that has been used to calculate the order of the reaction. For this purpose, substitute the data for any of the above experiment into the rate law expression.

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

Let us use data of experiment 1:

$$1.98 \times 10^{-4} = k\,[1\times10^{-6}]\,[9\times10^{-6}]$$

$$1.98 \times 10^{-4} = k\,[9\times10^{-12}]$$

$$k = \frac{1.98\times10^{-4}}{9\times10^{-12}}$$

$$k = 2.2 \times 10^{7}\ mol.s.dm^{-3}$$

If you use the data of experiment of 2 or 3, same result will be obtained. Try yourself

Example 7.3

The following reaction is first order in H_2 and half order in Br_2 write rate law for the reaction

$$H_2 + Br_2 \longrightarrow 2HBr$$

Solution:

Given information indicates that

$$Rate \propto [H_2] \qquad \text{-----------------} (i)$$

$$Rate \propto [Br_2]^{1/2} \qquad \text{-----------------} (ii)$$

combining (i) and (ii) we get the rate law for the reaction

$$Rate \propto [H_2]\,[Br_2]^{1/2}$$

$$Rate = k\,[H_2]\,[Br_2]^{1/2}$$

Concept Assessment Exercise 7.1

1. Phosgene is a toxic gas. It has been used in World War II. This gas is prepared by the reaction of carbon monoxide with chlorine.

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

The following data were obtained for kinetic study of this reaction.

Experiments	Initial [CO]	Initial [Cl_2]	Initial rate (moles dm^{-3} s^{-1})
1	1.000	0.100	1.29×10^{-29}
2	0.100	0.100	1.30×10^{-30}
3	0.100	1.000	1.30×10^{-30}

Write rate law for this reaction.

2. The following reaction is second order in NO_2 and is independent of the concentration of CO. Write rate law for the reaction. What is the overall order of the reaction?

$$NO_2 + CO \longrightarrow NO + CO_2$$

7.2.3 Half-Life Method for Determining Rate constant

The half life ($t_{1/2}$) of a reaction is the time it takes for the concentration of a reactant is reduced to half. The relationship between half life and rate constant depend on the order of the reaction.

When $n = 0$ $t_{1/2} = [A_0]/2k$. Where $[A_0]$ = initial concentration of reactant

$n = 1$ $t_{1/2} = 0.693/k$

$n = 2$ $t_{1/2} = 1/k[A_0]$

Consider the following reaction that follows 1st order kinetic, its half-life is 30s

$$A + 2B \rightarrow C$$

Rate constant for this reaction can be determined as follows.

$$t_{1/2} = 0.693/k$$

$$30 = 0.693/k$$

$$k = 0.0231\ s^{-1}$$

Therefore, the rate constant for the reaction is, $k = 0.0231\ s^{-1}$

7.3 EFFECT OF TEMPERATURE ON THE RATE OF REACTIONS

The reaction rate generally increases with increasing temperature. According to collision theory, the rate of a reaction is proportional to the number of collisions between the reacting molecules. An increase in temperature increases the average kinetic energy of the molecules. This increases the average speed of the reacting molecules. An increase in the kinetic energy of the reacting molecules increases the collision frequency, i.e., the number of effective collisions and thus the reaction speeds up. But only effective collisions produce a reaction. For the collision to be effective, the molecules must have activation energy and must be correctly oriented. At normal temperatures, very few molecules have this activation energy. Not all reactant molecules have the same energy at a given temperature. Most of them are of medium energy. Some molecules have a higher than average kinetic energy. The number of molecules with kinetic energy at least equal to Ea at temperature T is proportional to the shaded area under the Maxwell Boltzmann kinetic energy curve. The Maxwell-Boltzmann distribution curve shows how the available energy is distributed between the molecules of a gas at a constant temperature. (Figure 7.2 a)

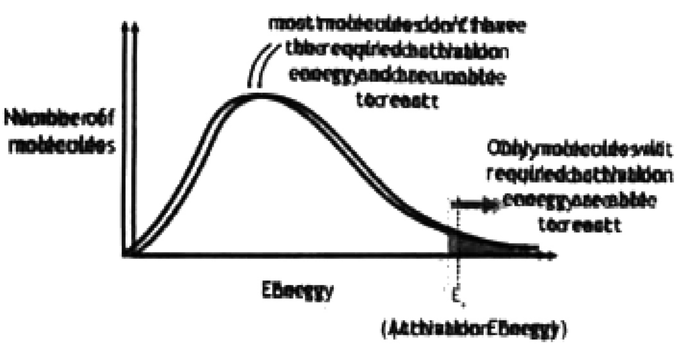


Figure 7.2a: Maxwell Boltzmann curve of kinetic energy

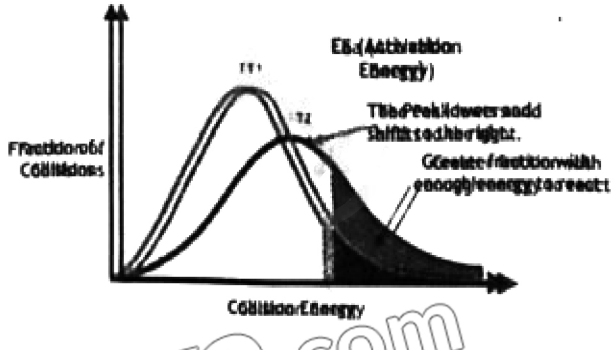


Figure 7.2b: Maxwell Boltzmann curve of kinetic energy at 2 temperature

The distribution curve shows that most molecules do not have the required activation energy at T_1 or lower temperature. Only some of the molecules that required the activation energy are able to react. When the temperature increases (from T_1 to T_2), the energy of the molecules also increases. Thus, the proportion of molecules with the required activation energy increases (Figure 7.2b). Thus, the reaction rate increases.

It was found that, in general, the reaction rate increases two to three times for every 10 K increase in temperature.

Arrhenius (1889) studied the effect of temperature on reaction rates. He found that the effect of temperature on rate of reaction is given by the following equation. This equation is known as **Arrhenius equation**.

$$\mathbf{k = Ae^{-Ea/RT}}$$

here k = rate constant, E_a is energy of activation, R is gas constant (R=8.3143 JK^{-1} $mole^{-1}$). A is constant known as **Arrhenius constant.** It is related with the frequency of collision and orientation of the reacting molecules. Therefore, rate constant k varies with the temperature. It increases with temperature which in turn increases rate of reaction.

7.4 THE MECHANISM OF A CHEMICAL REACTION

The path that reactants take to form products in a chemical reaction is called the mechanism. A reaction rate equation is very useful because it provides information about the reaction mechanism. The reaction can take place in one step or in several steps. If a reaction proceeds in two or more steps, one of the steps is the slowest. The rate of the slowest step determines the overall reaction rate. This is because it sets a limit to the rate at which the overall reaction can occur. No reaction can proceed more slowly than the rate-determining step. All other steps in the reaction mechanism are usually fast. **"The slowest step in the reaction mechanism, which determines the overall rate of the reaction, is called the rate-determining step."**

Example 7.4

For reaction

$$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$$

$$Rate = k[NO_2]^2$$

What information do you get from this about rate determining step?

Solution

The rate equation gives us following information.

i) The reaction is second order with respect to NO_2 and zero with respect to CO. Therefore it is independent of the concentration of CO.

ii) Two molecules of NO_2 are involved in the rate-determining step.

iii) Reaction must proceed in more than one step.

The proposed mechanism for the reaction is as follows.

Step I $$NO_{2(g)} + NO_{2(g)} \xrightarrow{Slow} NO_{3(g)} + N\dot{O}_{(g)}$$

Step II $$NO_{3(g)} + CO_{(g)} \xrightarrow{Fast} NO_{2(g)} + CO_{2(g)}$$

The first step is the rate determining step. Species NO_3 that does not appear in the overall reaction is called reaction intermediate. This example also proves that a balanced chemical equation may not give any information about the reaction mechanism.

Example 7.5

Hypochlorite ion ClO^- in aqueous solution decomposes to chlorate ion ClO_3^- and chloride ion.

$$3\,ClO^-_{(aq)} \longrightarrow ClO_3^- + 2Cl^-$$

The rate of the reaction is second order in ClO^- ion

Rate = k $[ClO^-]^2$

The following two-step mechanism is consistent with the rate law for the reaction.

Step I: $ClO^-_{(aq)} + ClO^-_{(aq)} \longrightarrow ClO_{2(aq)} + Cl^-_{(aq)}$

Step II: $ClO_{2(aq)} + ClO^-_{(aq)} \longrightarrow ClO^-_{3(aq)} + Cl^-_{(aq)}$

Overall reaction $3ClO^-_{(aq)} \longrightarrow ClO^-_{3(aq)} + 2Cl^-_{(aq)}$

Select the rate-determining step.

Solution:

Rate law for this reaction indicates that two ClO^- ions must participate in the rate-determining step. Therefore, Step I is the rate-determining step in this mechanism.

Example 7.6

Rate $= k[NO_2][O_3]$ for the following reaction indicates that one molecule of NO_2 and one molecule of O_3 participate in the determining step

$$2NO_{2(g)} + O_3 \longrightarrow N_2O_{5(g)} + O_{2(g)}$$

Thus rate law includes the concentration of each of the reactants raised to the power that equals the coefficient for the reactant in the equation for the rate-determining step.

Concept Assessment Exercise 7.2

For the following reaction,

$$2NO_{2(g)} + F_{2(g)} \longrightarrow 2NO_2F_{(g)}$$

Rate $= k[NO_2][F_2]$

Which of the following mechanism is consistent with the rate law?

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

(b) $NO_2 + F_2 \longrightarrow NO_2F + F$ (fast step)

$NO_2 + F \longrightarrow NO_2F$ (slow step)

(c) $NO_2 + F_2 \longrightarrow NO_2F + F$ (slow step)

$NO_2 + F \longrightarrow NO_2F$ (fast step)

(d) $F_2 \longrightarrow 2F$ (slow step)

$2NO_2 + 2F \longrightarrow 2NO_2F$ (fast step)

Example 7.7

NO reacts with H_2 according to the following equation:

$$2NO_{(g)} + 2H_{2(g)} \longrightarrow N_{2(g)} + 2H_2O_{(g)}$$

The mechanism for this reaction involves two steps

$$2NO + H_2 \longrightarrow N_2 + H_2O_2 \quad \text{(slow)}$$

$$H_2O_2 + H_2 \longrightarrow 2H_2O \quad \text{(fast)}$$

Write the experimental rate law for this reaction?

7.4.1 Potential Energy Diagram and Reaction Mechanism

Example 7.8

Potential energy diagram for the reaction between NO_2 and F_2 is shown in figure 7.3.

The experimental rate law for this reaction is given below:

Reaction:

$$2NO_{2(g)} + F_2 \longrightarrow 2NO_2F_{(g)} \quad \text{Rate} = k[NO_2][F_2]$$

Propose reaction mechanism.

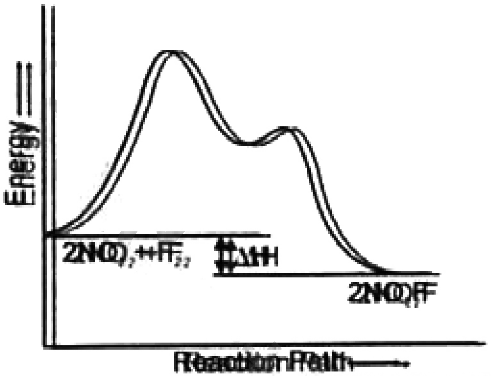


Figure 7.3: Potential energy diagram for the reaction between NO_2 and F_2

Solution:

Step 1: Determine the number of elementary steps.

As potential energy diagram shows two peaks, the reaction mechanism must involve two elementary steps.

Step 2: Determine the rate-setting step. Because the activation energy of step 1 is greater than the activation energy of step 2. Therefore, step 1 is a slow and rate-determining step.

Step 3: Use the rate law to determine the number of molecules involved in the rate-determining step. The given rate law indicates that one NO_2 and one F_2 molecule are involved in this step.

Step 4: Propose the two main steps of the mechanism. In the overall reaction, two NO_2 molecules and one F_2 molecule react to form two NO_2F molecules. However, in the rate-determining step, only one NO_2 molecule and one F_2 molecule need to react to form one NO_2F and a reaction intermediate. In the second initial step, the reaction intermediate must react with another NO_2 molecule to form another NO_2F molecule. (A species that is produced in one step of a chemical reaction and consumed in another step is called a reaction intermediate). Thus, proposed mechanism is,

$$NO_2 + F_2 \longrightarrow NO_2F + F \quad \text{(slow)}$$

$$NO_2 + F \longrightarrow NO_2F \quad \text{(fast)}$$

Step 5: Add the two steps to get the overall reaction which must be same as the reaction under consideration.

$$\begin{array}{l} NO_2 + F_2 \longrightarrow NO_2F + F \\ \underline{NO_2 + F \longrightarrow NO_2F} \\ 2NO_2 + F_2 \longrightarrow 2NO_2F \end{array}$$

Since sum of elementary steps give the reaction under consideration, the proposed mechanism may be acceptable.

Concept Assessment Exercise 7.3

1. The following data was collected for the reaction between H_2 and NO at 700°C.

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

Experiment	$[H_2]$	[NO]	Initial rate (moles $dm^{-3}s^{-1}$)
1	0.010	0.025	2.4×10^{-6}
2	0.0050	0.025	1.2×10^{-6}
3	0.010	0.0125	0.6×10^{-6}

Suggest a plausible mechanism that is consistent with the rate law. (Hint: assume the oxygen atom is reaction intermediate).

Potential energy diagram for this reaction is given below.

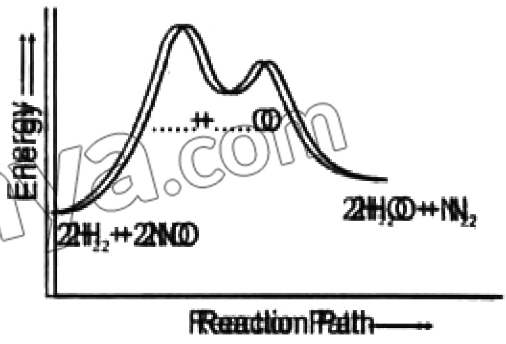


Figure 7.4: Potential energy diagram for the reaction between H_2 and NO

2. Following mechanism has been proposed for a reaction.

$$H_2O_{2(aq)} + I^-_{(aq)} \longrightarrow H_2O_{(l)} + OI^-_{(aq)}$$

$$OI^-_{(aq)} + H_2O_{2(aq)} \longrightarrow H_2O_{(l)} + O_{2(g)} + I^-_{(aq)}$$

Choose catalyst, reaction intermediate and rate determining step.

3. The rate law for the following reaction

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

is rate = $k[H_2][NO]^2$. Is the following mechanism is consistent with the rate law? Argue.

$H_2 + NO \longrightarrow H_2O + N$ (slow)

$N + NO \longrightarrow N_2 + O$ (fast)

$O + H_2 \longrightarrow H_2O$ (fast)

4. The rate law for the reaction,

$2N_2O \longrightarrow 2N_2 + O_2$

is rate = $k[N_2O]$. Reaction occurs in two elementary steps. Assume O atom as a reaction intermediate. Write mechanism for the reaction.

7.5 ACTIVATION ENERGY

Chemical reactions involve the breaking and making of chemical bonds. These changes are accompanied by changes in energies. Collision theory has been proposed to explain the observed kinetics of reactions. For a chemical reaction to occur, the combining atoms or molecules must collide with one another. These collisions may be effective or ineffective depending upon the energy and orientation of the colliding particles. The effective collision can take place only if the energy of the colliding particles is high enough to overcome the repulsion between electrons around the reacting particles. Proper orientation means that at the time of collision, the atoms which are required to make new bonds should collide with each other.

Do You Know?

Gas explosions in homes can be caused by switching on a light. If gas has been leaking, then a tiny spark from turning on a light can provide the activation energy to start the explosive reaction between the methane and the oxygen.

The minimum amount of energy, in addition to the average kinetic energy, which the particles must possess for effective collisions, is called activation energy.

No reaction occurs if the energy of the reacting particles is lower than the activation energy. Thus, the speed of a reaction depends on its activation energy. The higher the activation energy, the lower the reaction rate. This is because only a small fraction of the molecules have enough energy to react. On the other hand, if the activation energy is small, a large number of molecules can cause effective collisions. Therefore, the reaction rate is higher. Consider the reaction between A_2 and B_2 molecules and a new molecule AB. If the energy of these molecules is equal to or greater than the activation energy, the collision breaks their bonds and new bonds are formed. In an effective collision, the molecules form an unstable species called an activated complex. Being a high-energy species, it is short-lived and quickly breaks down into products. The activated complex is also called the transition state. (Figure 7.5)

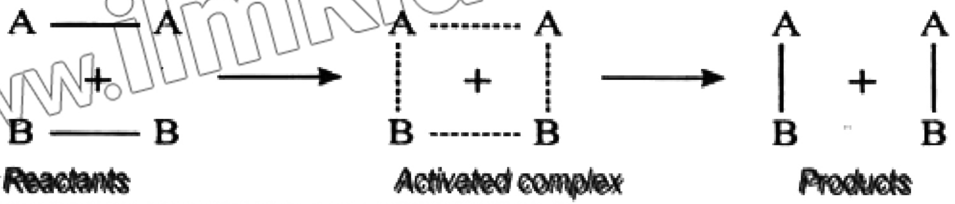
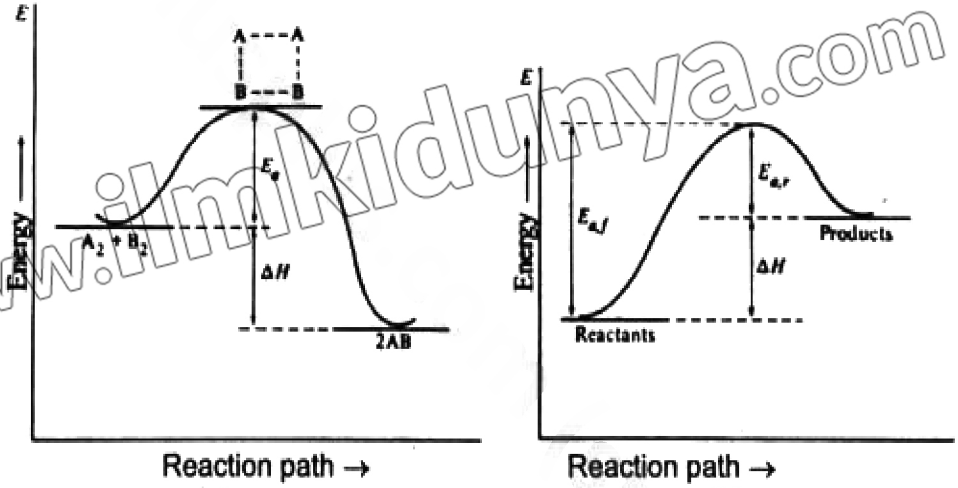


Figure 7.5: Effective collision of molecules.

In an efficient collision, the colliding molecules move closer to each other and slow down just before the collision. Their kinetic energy decreases and this leads to a corresponding increase in their potential energy. Activation energy appears in the form of hills between reactants and products. Molecules must first climb over an energy barrier before they can roll down the hill to form products. Only molecular collisions with the right activation energy and orientation can do this. On the other hand, if they lack the right activation energy, they will not reach the top of the mountain and will fall back chemically unchanged.



(a)

(b)

Figure 7.6: (a) Exothermic reaction (b) Endothermic reaction

A potential energy diagram can also be used to understand enthalpy changes in chemical reactions. **The reaction enthalpy is equal to the difference between the energies of the reactants and the products.** In an exothermic reaction, the products are at a lower energy level than the reactants. Instead, in an endothermic process, the products have a higher energy level than the reactants. In both reactions, the activation energy (Ea) is an energy barrier that must be overcome before products can be formed. If the activation energy is not available to the reacting particles, the reaction will not start. Endothermic reactions require a constant source of energy to complete the reaction. Figure 7.6 shows the energy profile of exothermic and endothermic reactions.

7.6 CATALYSIS

Many industrial reactions are carried out at high temperature to maximize the amount of product that can be synthesized in a given time. High temperature reactions introduce safety concerns and many chemical species are not stable at high temperature. Thus a different method for increasing the rates of chemical reactions would be useful.

Another way to increase reaction rate is to change its mechanism in a way that lowers the activation energy of the rate determining step. This can be done by introducing a catalyst.

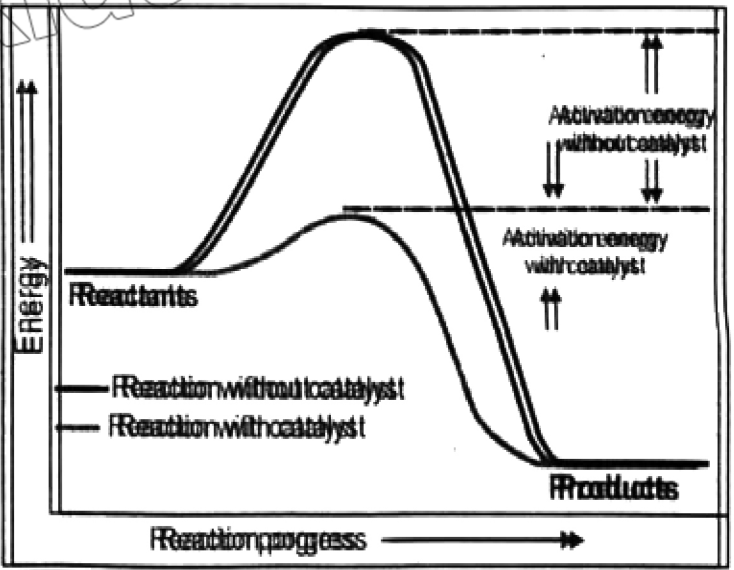


Figure 7.7: Effect of Catalyst on energy of activation

A substance which accelerates a chemical reaction but remains chemically unchanged at the end of a reaction is called as catalyst and the phenomenon is called catalysis. A catalyst provides a new mechanism for the reaction with low energy of activation (Fig 7.7). Thus catalyst increases the rate of reaction by decreasing its energy of activation. A catalyst has no effect on the total thermodynamic or enthalpy of the reaction. For this reason a catalyst cannot be used to bring about a chemical reaction, which is not favoured thermodynamically.

For example, in the stratosphere, conversion of an ozone molecule by an oxygen atom into two O_2 molecules occurs. This reaction has higher energy of activation.

$$O_3 + O \longrightarrow 2O_2 \qquad E_a = 17.1\,\text{kJ mole}^{-1}$$

Chlorofluorocarbon compounds diffuse up into the stratosphere. These compounds absorb short wave length ultraviolet light from the sun, that breaks carbon-chlorine bonds and produce chlorine atoms. Cl atom catalyze the mechanism requiring less energy of activation.

$$O_3 + Cl \longrightarrow O_2 + ClO \qquad E_a = 2.1\,\text{kJmole}^{-1}$$

$$O + ClO \longrightarrow O_2 + Cl \qquad E_a = 0.4\,\text{kJmole}^{-1}$$

$$\text{Net reaction:} \quad O_3 + O \longrightarrow 2O_2 \qquad E_a = 2.5\,\text{kJmole}^{-1}$$

It shows that the direct reaction between O_3 and O has a substantially higher activation energy than the chlorine catalyzed reaction .

7.7 GIBBES FREE ENERGY CHANGE AND FEASIBILITY OF A REACTION

Free energy change, ΔG^0 is a measure to predict whether a reaction is feasible. A feasible reaction is one which once started will go to completion, without any energy being supplied to it.

- If ΔG^0 is negative or equal to zero, then the reaction is feasible.

- **If ΔG^0 is positive, then the reaction is not feasible.**

For more information see section 6.7.

Key Points

- The rate of a chemical reaction is a change in the concentration of reactant or infinitesimally small change in concentration that occurs over an infinite product in the given time. The instantaneous rate of reaction is the infinitesimally small period of time.
- The rate law is an expression that relates the rate of a reaction to the rate constant and the concentration of reactants raise to an appropriate powers. It can only be determined experimentally.
- Overall reaction order is sum of the powers to which reactants concentration are raised in the rate law.
- A reaction mechanism is the sequence of elementary steps that describe the reaction. The rate of reaction is determined by the slowest elementary step called the rate determining step in the reaction mechanism.
- The rate of a chemical reaction depends upon the activation energy for the reaction. The rate constant and activation energy are related by the Arrhenius equation: $k = Ae^{-\frac{Ea}{RT}}$
- Reaction rates are influence by the catalyst, which change mechanism of the reaction by decreasing energy of activation.
- In homogenous catalysis, the catalyst and the reactant are in the same phase whereas in heterogeneous catalysis the catalyst and reactants are in different phases.
- Enzymes are catalysts in living organism.

References for Further information:

- Silberberg, Chemistry the Molecular Nature of Matter and Energy
- Bonderand Pardue, Chemistry and Experimental Science 2/e
- Uno Kask and J. David Rawn, General Chemistry
- Graham Hill and John Holman, Chemistry in Context
- John M. Deman, Principles of food Chemistry

Exercise

1: Choose thecorrect answer

(i) The rate of a reaction ___________ as the reaction proceeds.

(a) Increases (b) Decreases

(c) Remains the same (d) May increase or decrease.

(ii) The unit of the rate constant in the same as that of the rate of reaction in __________ order reaction.

(a) First (b) Second

(b) (c) Third (d) Zero.

(iii) For the reaction;

$2A + B \xrightarrow{\text{slow}} C$, the rate law for the reaction is

(a) rate = $k[A]^2[B]$ (b) rate = $k[A][B]$

(c) rate = $k[C]$ (d) None of these

(iv) For the reaction;

$2A + B \rightarrow C + D$

The expression for the rate law is, rate = $k[A]^2$, the order of reaction in B is;

(a) First (b) Second

(b) (c) Third (d) zero

(v) The activation energy for a reaction can be;

(a) Increased by increasing temperature

(b) Increased by decreasing temperature

(c) Decreased by increasing concentration of reactants

(d) None of these

(vi) Rate law for the reaction;

$R\text{-}X + H_2O \rightarrow R\text{-}OH + HX$ is, rate = $k[R\text{-}X]$. The rate of reaction will be doubled when;

(a) Concentration of H_2O is doubled

(b) Concentration of R-X is reduced to half

(c) Concentration of R-X is doubled

(d) None of these

(vii) The rate of an enzyme catalyzed reaction is independent of;

(a) Concentration of Substrate (b) Concentration of Product

(c) Enzyme (d) Temperature

(viii) If a reaction proceeds in such a way that order of reaction is independent of the reactants concentration, the overall order of reaction would be;

(a) First (b) Second

(c) Third (d) Zero

(ix) Reactions with high activation energy are usually;

(a) Fast (b) Slow (c) Exothermic (d) Reversible

(x) In a reversible reaction catalyst lowers the activation energy of the;

(a) Forward reaction

(b) Reverse reaction

(c) Forward as well as reverse reaction

(d) Forward reaction but increases for the reverse reaction

2. What is chemical kinetics? How do you differentiate chemical kinetics from chemical equilibrium?

3. Explain effects of concentration, temperature and surface area on reaction rates.

4. Evaluate that increase in collision energy by increasing the temperature can improve the collision frequency.

5. Draw energy diagrams that represent the activation energy and show the effect of a catalyst.

6. What is the effect of a catalyst on the following?

The rate of reaction

The energy of activation

7. The reaction of an alkyl halide, R-X with water is as follows

$$R\text{-}X + H_2O \longrightarrow R\text{-}OH + HX$$

If the reaction were a single step process, what would you predict the rate law to be?

8. The reaction of a compound A and B to give C and D was found to be second order in A and second order overall. Write rate expression for the reaction.

9. Defend the following statements?

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

(b) The reaction rate decreases every moment.

(c) The unit of rate constant of a second order reaction is $dm^3 mole^{-1} s^{-1}$

10. For the reaction $A + B \longrightarrow AB$

The following data were obtained for the reaction

Experiment	Initial conc. (mole dm^{-3})	Initial rate (mole dm^{-3} s^{-1})	Experiment
	[A]	[B]	
1	0.10	0.01	1.00×10^{-5}
2	0.10	0.02	2.00×10^{-5}
3	0.20	0.01	2.00×10^{-5}
4	0.30	0.02	6.00×10^{-5}

Illustrate the rate equation for the reaction? (Ans: Rate $\propto$ [A] [B])

11. Explain why powdered Zn reacts faster with an acid than a piece of Zn.

12. Explore the impact of catalysts on the energetics of chemical reactions.

13. How does the concept of activation energy relate to speed of a chemical reaction.

14. Calculate the free energy change for the following reaction at 298K.

$MgCO_{3(s)} \longrightarrow MgO_{(s)} + CO_{2(g)}$

$\Delta H^0 = +117kJ\ mol^{-1}$

$\Delta S^0 = +0.175kJK^{-1}mol^{-1}$

a. Is this reaction feasible at this temperature.
b. Define Gibbs free energy
c. Define enthalpy

15. Consider the following reaction

$2H_{2(g)} + 2NO_{(g)} \longrightarrow 2H_2O_{(g)} + N_{2(g)}$

This reaction is first order with respect to H_2 and second order with respect to NO.

a. Write the rate expression for this reaction.
b. Predict the overall order of this reaction.
c. How would you expect the rate of this reaction would change if the concentration of NO is doubled.
d. At a certain temperature, k was found to be 220 mol^{-2} $dm^6 s^{-1}$.

when [H_2] = [NO] = 1.54 x 10^3 mol dm^{-3}. Calculate the rate of reaction at this temperature.

Project:

Develop a hypothetical chemical reaction and propose a mechanism for it. Predict its overall rate expression.