Chemical Kinetics - Part 4

Objectives

After going through this lesson, the learners will be able to understand the following:

- Discuss the Effect of Temperature on the Rate of Reactions: Arrhenius Equation
- Discuss the Effect of Catalyst on the Rates of Reactions
- Describe the Collision Theory of Chemical Reactions

Contents Outline

- Temperature Dependence of the Rate of a Reaction
- Effect of Catalyst
- Collision Theory of Chemical Reactions
- Summary

Temperature Dependence of the Rate of a Reaction

Most of the chemical reactions are accelerated by increase in temperature, i.e., the rates of the reactions increase with increase in temperature. For example,

a) In decomposition of N_2O_5, the time taken for half of the original amount of material to decompose is 12 min at 50ºC, 5 h at 25ºC and 10 days at 0ºC.

b) Also, in a mixture of potassium permanganate ($KMnO_4$) and oxalic acid ($H_2C_2O_4$), potassium permanganate gets decolourised faster at a higher temperature than at a lower temperature.

It has been found that for most of the chemical reactions with rise in temperature by 10°, the rate constant is nearly doubled. It is also expressed in terms of temperature coefficient and given as

$$Temperature\ Coefficient = \frac{Rate\ constant\ T_1}{Rate\ constant\ T_2}$$

The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation (1). It was first proposed by Dutch chemist, J.H. van’t Hoff but Swedish chemist Arrhenius provided its physical justification and interpretation.

$$k = A\ exp\left(\frac{-E_a}{RT}\right) \qquad (1)$$

where A is the Arrhenius factor or the frequency factor. It is also called a pre-exponential factor. It is a constant specific to a particular reaction. R is gas constant and E_a is activation energy measured in Joules/ mole (J mol $^{-1}$).

A reaction can occur when the reactant molecules collide with each other and form an unstable intermediate (with higher energy) (Fig. 1). The life span of the unstable intermediate is very short and thus it leads to the formation of a stable product. The energy required to form this unstable intermediate (also known as activated complex) is known as the Activation energy (E_a).

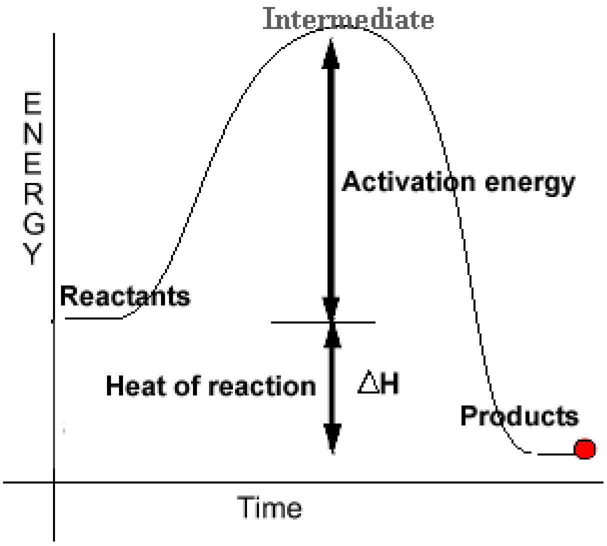

Fig. 1: Illustration of the Activation energy involved in a reaction.

(Source:http://www.dynamicscience.com.au/tester/solutions1/chemistry/rates/activationenerg1.gif)

It can be understood clearly using the following simple reaction

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

According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate (Fig. 2). It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.

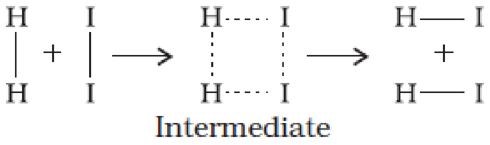

Fig. 2. Formation of HI through the intermediate

(Source: Fig 4.6, page no. 112, Chapter 4: Chemical Kinetics, NCERT Textbook)

As discussed earlier, the energy required to form this intermediate, called activated complex (C), is known as activation energy (E_a). Fig. 3 is obtained by plotting potential energy vs reaction coordinate for this reaction. Reaction coordinate represents the profile of energy change when reactants change into products. Initially, the energy of the reaction increases as the breaking of bonds of H–H predominates. After reaching maxima, due to dominance of the process of bond formation, energy is released resulting in the formation of products. So, the final enthalpy of the reaction depends upon the nature of reactants and products.

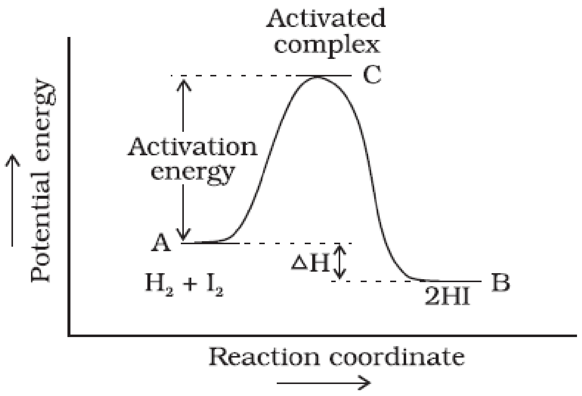

Fig. 3: Diagram showing plot of potential energy vs reaction coordinate.

(Source: Fig 4.7, page 112, Chapter 4: Chemical Kinetics, NCERT Textbook)

All the molecules in the reacting species do not have the same kinetic energy. Since it is difficult to predict the behaviour of any one molecule with precision, Ludwig Boltzmann and James Clark Maxwell used statistics to predict the behaviour of a large number of molecules. According to them, the distribution of kinetic energy may be described by plotting the fraction of molecules (N_E/ N_T) with a given kinetic energy (E) vs kinetic energy (Fig. 4). Here, $N/_E$ is the number of molecules with energy E and N_T is the total number of molecules.

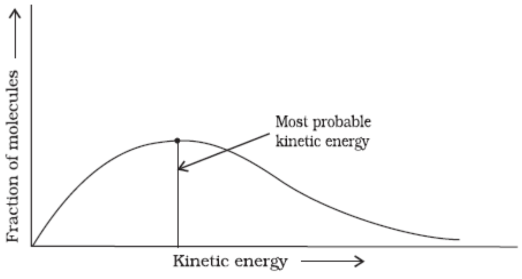

Fig. 4: Distribution curve showing energies among gaseous molecules

(Source: Fig 4.8, page no. 112, Chapter 4: Chemical Kinetics, NCERT Textbook)

The peak of the curve corresponds to the most probable kinetic energy, i.e., kinetic energy of the maximum fraction of molecules. There are decreasing numbers of molecules with energies higher or lower than this value.

Also, it has to be noted that only those collisions result in the formation of products whose energies are equal to or more than the threshold energy. Threshold energy is the certain minimum energy required for forming the products. Hence, the activation energy can be defined as the energy required to cross this barrier between reactants and products and is given by the kinetic energies of the molecules.

$Activation\ energy = (Threshold\ energy) - (Average\ energy\ of\ the\ reactants)$

$$E_a = E_T - E_R$$

The activation energy (E_a) depicts the fraction (f) of effective collisions and thus possesses a definite value for a particular reaction. For a given reaction, if activation energy is low, then the number of effective collisions is large resulting in a higher rate of reaction. On the other hand, for the reactions with higher activation energy, the number of effective collisions is low; hence, such reactions proceed with a lower rate.

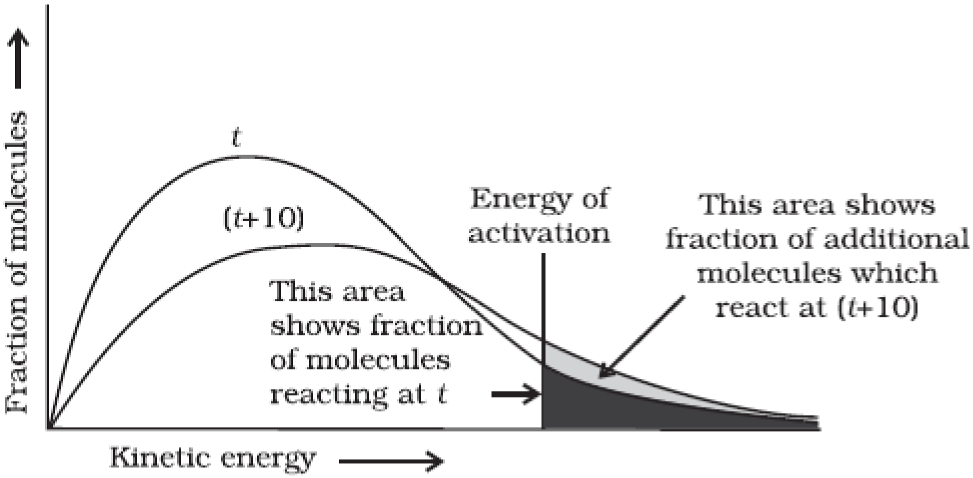

Fig. 5: Distribution curve showing temperature dependence of rate of a reaction

(Source: Fig. 4.9, page no. 112, Chapter 4: Chemical Kinetics, NCERT Textbook)

When the temperature is raised, the maximum of the curve moves to the higher energy value (Fig. 5) and the curve broadens out, i.e., spreads to the right such that there are a greater proportion of molecules with much higher energies. The area under the curve must be constant since total probability must be one at all times. We can mark the position of E_a on Maxwell Boltzmann distribution curve (Fig. 5).

Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than E_a. It is clear from the diagram that in the curve at (t + 10), the area showing the fraction of molecules having energy equal to or greater than activation energy gets doubled leading to doubling the rate of a reaction.

In the Arrhenius equation (1) the factor, $exp\left(\frac{-E_a}{RT}\right)$ corresponds to the fraction of molecules that have kinetic energy greater than E_a. Taking natural logarithm of both sides of equation (1), we get

$$lnk = \frac{-E_a}{RT} + lnA \qquad (2)$$

The plot of ln k vs $1/T$ gives a straight line according to the equation (2) as shown in Fig. 6.

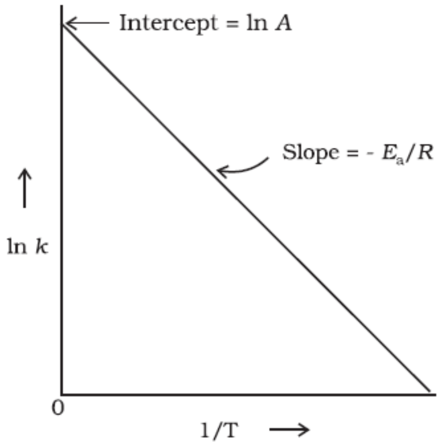

Fig. 6: A plot between ln k and 1/T

(Source: Fig. 4.10, page no. 113, Chapter 4: Chemical Kinetics, NCERT Textbook)

Thus, it has been found from Arrhenius equation (1) that increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in the rate constant.

In Fig. 6, $slope = \frac{-E_a}{R}$ and intercept = lnA. So we can calculate E_a and A using these values.

At temperature T_1, equation (2) will become

$$lnk_1 = \frac{-E_a}{RT_1} + lnA \qquad (3)$$

At temperature T_2, equation (2) will become

$$lnk_2 = \frac{-E_a}{RT_2} + lnA \tag{4}$$

(since A is constant for a given reaction)

where k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively.

Subtracting equation (3) from equation (4), we obtain

$$lnk_2 - lnk_1 = \frac{-E_a}{RT_2} - \left(\frac{-E_a}{RT_1}\right) = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

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

$$log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{5}$$

$$log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

Example 1: The rate constants of a reaction at 500 K and 700 K are 0.02 s^{-1} and 0.07 s^{-1} respectively. Calculate the values of E_a and A.

Solution: We know that

$$log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

Given:

$k_1 = 0.02\ s^{-1}$, $k_2 = 0.07\ s^{-1}$, $T_1 = 500$ K, $T_2 = 700$ K & R (gas constant) = 8.314 J K^{-1} mol^{-1}

$$log\frac{007}{0.02} = \left(\frac{E_a}{2.303\times8.314}\right)\left[\frac{700-500}{500\times700}\right]$$

$$0.544 = \frac{E_a\times5.714\times10^{-4}}{19.15}$$

$$E_a = 0.544 \times \frac{19.15}{5.714\times10^{-4}} = 18230.8\ \text{J}$$

Since $k = A\,exp\left(\frac{-E_a}{RT}\right)$

$$0.02 = A\,exp\left(\frac{-18230.8}{(8.314\times500)}\right)$$

$$A = \frac{0.02}{0..012} = 1.61$$

Example 2: The first order rate constant for the decomposition of ethyl iodide by the reaction

$$C_2H_5I\,(g) \rightarrow C_2H_4\,(g) + HI\,(g)$$

at 600 K is 1.60 × 10^{-5} s^{-1}. Its energy of activation is 209 kJ mol^{-1}. Calculate the rate constant of the reaction at 700 K.

Solution: We know that

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

$$\log k_2 = \log k_1 + \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Given: k_1= 1.60 × 10^{-5} s^{-1}, E_a = 209 kJ mol^{-1} = 209000 J mol^{-1}, T_1 = 600 K, T_2 = 700 K

$$\log k_2 = \log\left(1.60 \times 10^{-5}\right) + \frac{209 \times 10^3}{2.303 \times 8.314}\left(\frac{1}{600} - \frac{1}{700}\right)$$

$$\log k_2 = (-\ 4.796\ +\ 2.599) =-\ 2.197$$

$$k_2 = 6.36 \times 10^{-3} s^{-1}$$

Example 3: The decomposition of hydrocarbon follows the equation

$$k = \left(4.5 \times 10^{11} s^{-1}\right) e^{\frac{-28000K}{T}}$$

Calculate E_a.

Solution: According to Arrhenius equation, we have

$$k = A.e^{\frac{-E_a}{T}}$$

On comparing this equation to the given equation, we get

$$\frac{-E_a}{RT} = \frac{-28000K}{T} \qquad \text{or} \qquad \frac{E_a}{R} = 28000K$$

Hence, E_a = (28000 K) × R = 28000 K × 8.314 J K^{-1} mol^{-1}

= 232792 J mol^{-1} = 232.79 kJ mol^{-1}

Example 4: The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the value of A is 4 × 10^{10} s^{-1}, calculate k at 308 K and E_a.

Solution: At T = 298 K and time = t,

concentration of the reactant, i.e. [A] = 90 % of $[A]_0$

or $\frac{[A]_0}{[A]} = \frac{100}{90}$

therefore $k_{298} = \frac{2.303}{t} log\left(\frac{[A]_0}{[A]}\right) = \frac{2.303}{t} log\left(\frac{100}{90}\right)$ (i)

Similarly, at T = 308 K and time = *t*,

given that $\frac{[A]_0}{[A]} = \frac{100}{75}$

therefore $k_{308} = \frac{2.303}{t} log\left(\frac{[A]_0}{[A]}\right) = \frac{2.303}{t} log\left(\frac{100}{75}\right)$ (ii)

Taking the ratio of (i) and (ii), we have

$$\frac{k_{308}}{k_{298}} = \frac{\frac{2.303}{t} log\left(\frac{100}{75}\right)}{\frac{2.303}{t} log\left(\frac{100}{90}\right)} = \frac{log\left(\frac{100}{75}\right)}{log\left(\frac{100}{90}\right)} = \frac{0.1249}{0.0457} = 2.733$$

According to Arrhenius equation

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

Therefore, we get

$$log(2.733) = \frac{E_a}{2.303 \times 8.314}\left[\frac{308-298}{298\times308}\right]$$

$$E_a = 0.436 \times \frac{2.303 \times 8.314}{1.809 \times 10^{-4}} = \frac{8.36}{1.809 \times 10^{-4}} = 76658\, J\, mol^{-1}$$

Now $k_{308} = A.e^{\frac{-E_a}{RT}}$

$$logk_{308} = logA - \frac{E_a}{2.303\times RT} = log\left(4 \times 10^{10}\right) - \frac{76658}{2.303\times8.314\times308}$$

$$logk_{308} = 10.602 - 12.998 =- 2.396$$

$$k_{308} = antilog(-2.396) = 4.02 \times 10^{-3} s^{-1}$$

Example 5: The activation energy for the reaction

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

is 209.5 kJ mol^{-1} at 581 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy.

Solution: In the dissociation reaction of HI, given is:

E_a = 209.5 kJ mol^{-1} = 209500 J mol^{-1}, T = 581 K, R = 8.314 J K^{-1} mol^{-1}

Let the fraction of the molecules of reactants having energy equal to or greater than activation energy (E_a) be x, then we have

$$x = e^{\frac{-E_a}{RT}}$$

$$lnx = \frac{-E_a}{RT} \quad \text{or}$$

$$log\, x = \frac{-E_a}{2.303RT}$$

$$log\, x = \frac{-209500}{2.303\times8.314\times581} =- 18.8323$$

$$x = antilog(- 18.8323) = 1.47 \times 10^{-19}$$

Effect of Catalyst

A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent chemical change. In other words, a catalyst is one which provides an alternate pathway or mechanism of lower activation energy to form an activated complex readily. It gets involved in the reaction chemically but temporarily, and continually changes as reaction proceeds. For example, MnO_2 catalyses the following reaction so as to increase its rate considerably.

$$2\ KClO_3 \xrightarrow{MnO_2} 2\ KCl + 3\ O_2$$

The word catalyst should not be used when the added substance reduces the rate of reaction. The substance is then called inhibitor. The action of the catalyst can be explained by intermediate complex theory. According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.

As mentioned above, it is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier as shown in Fig. 7.

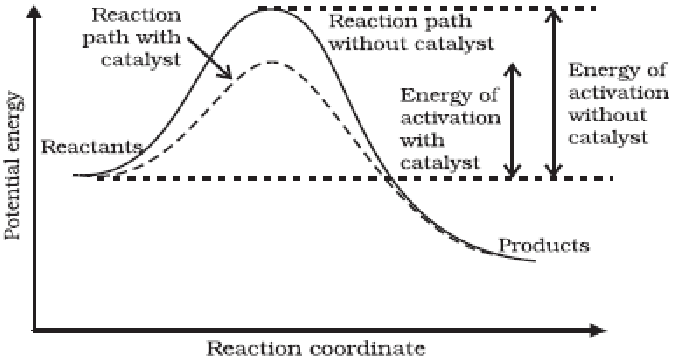

Fig. 7: Effect of catalyst on activation energy

(Source: Fig. 4.11, page no. 115, Chapter 4: Chemical Kinetics, NCERT Textbook)

It is clear from Arrhenius equation (1) that lower the value of activation energy caused by the catalyst higher will be the rate of a reaction.

For example, in ozone cycle, the depletion of ozone to oxygen speeds up in the presence of chlorine (Fig. 8). Chlorine breaks down the ozone molecule to form a little stable intermediate chlorine oxide (ClO) which readily decomposes to oxygen molecule and chlorine.

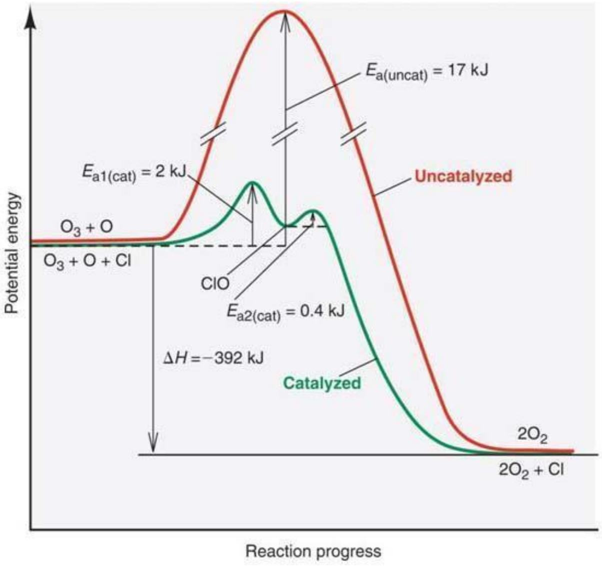

Fig. 8: Effect of catalyst (chlorine) on depletion of ozone

(Source: http://images.slideplayer.com/13/4174704/slides/slide_91.jpg)

A small amount of the catalyst can catalyse a large amount of reactants. A catalyst does not alter Gibbs energy, ΔG of a reaction. It catalyses spontaneous reactions but does not catalyse non-spontaneous reactions. It is also found that a catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster, that is, it catalyses the forward as well as the backward reactions to the same extent so that the equilibrium state remains same but is reached earlier.

Collision Theory of Chemical Reactions

Though Arrhenius equation is applicable under a wide range of circumstances, collision theory, which was developed by Max Trautz and William Lewis in 1916 -18, provides a greater insight into the energetic and mechanistic aspects of reactions. It is based on the kinetic theory of gases. According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other. The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (*Z*). Another factor which affects the rate of chemical reactions is activation energy (as we have already studied). For a bimolecular elementary reaction

A + B → Products

rate of reaction can be expressed as

$$Rate = Z_{AB} e^{\frac{-E_a}{RT}} \qquad (6)$$

where Z_{AB} represents the collision frequency of reactants, A and B and $e^{-Ea/RT}$ represents the fraction of molecules with energies equal to or greater than E_a. Comparing (6) with the Arrhenius equation, we can say that A is related to collision frequency.

Equation (6) predicts the value of rate constants fairly accurately for the reactions that involve atomic species or simple molecules but for complex molecules significant deviations are observed. The reason could be that all collisions do not lead to the formation of products. The collisions in which molecules collide with sufficient kinetic energy (called threshold energy which is the sum of the activation energy and the energy possessed by reacting species) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as effective collisions.

For example, formation of methanol from bromoethane depends upon the orientation of reactant molecules as shown in Fig. 9. The proper orientation of reactant molecules leads to bond formation whereas improper orientation makes them simply bounce back and no products are formed.

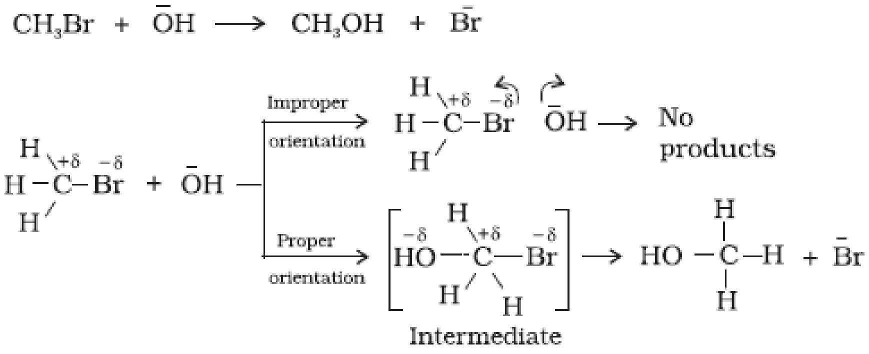

Fig. 9: Diagram showing molecules having proper and improper orientation

(Source: Fig. 4.12, page no. 116, Chapter 4: Chemical Kinetics, NCERT Textbook)

To account for effective collisions, another factor P, called the probability or steric factor is introduced. It takes into account the fact that in a collision, molecules must be properly oriented i.e.,

$$Rate = P.Z_{AB}e^{\frac{-E_a}{RT}}$$

Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

Collision theory also has certain drawbacks as it considers atoms/molecules to be hard spheres and ignores their structural aspect. You will study details about this theory and more on other theories in your higher classes.

Example 6: In certain reactions, large fraction of molecules possess more energy than the threshold energy, still the reactions proceed with slow rate. Explain.

Solution: According to collision theory of chemical reactions, a collision will be an effective one when the particles possess minimum activation energy and a correct alignment. In this case, the particles possess more energy than the threshold energy but still the reaction is slow. The reason is that the collisions are not taking place in proper orientation.

Summary

In this module, we have learnt about the effect of temperature and catalyst on the rate of a reaction. Temperature dependence of rate constant is described by Arrhenius equation (k = $Ae^{-Ea/RT}$ or $lnk = \frac{-E_a}{RT} + lnA$). E_a corresponds to the activation energy and is given by the energy difference between activated complex and the reactant molecules, and A (Arrhenius factor or pre-exponential factor) corresponds to the collision frequency. The equation clearly shows that increase of temperature or lowering of E_a will lead to an increase in the rate of a reaction. This increase in reaction rate, due to rise in temperature, is in consequence of the increased number of effective collisions per unit time with temperature. Catalyst is a substance which provides an alternate pathway for the formation of a product readily and thus increases the rate of a reaction. A catalyst actually, lowers the activation

energy by providing an alternate path for the reaction. Catalysts are chemically involved in the reaction mechanism but get regenerated before completion of the reaction. We have learnt in this module that a reaction occurs due to collisions. This defines the collision theory of the reactions. For a collision to be effective, a particle must have minimum activation energy and a correct alignment. The number of collisions per second per unit volume of a reaction is called collision frequency (Z). Thus, Arrhenius equation can be written as: $k = Z_{AB}\, e^{-Ea/RT}$.

According to collision theory, another factor P called steric factor which refers to the orientation of molecules which collide, is important and contributes to effective collisions, thus modifying the Arrhenius equation to $k = P \,.\, Z_{AB}\, e^{-Ea/RT}$.