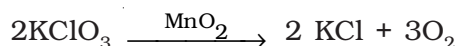


$$\begin{aligned}\log k_2 &= \log k_1 + \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \\ &= \log(1.60 \times 10^{-5}) + \frac{209000 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left[\frac{1}{600 \text{ K}} - \frac{1}{700 \text{ K}} \right] \\ \log k_2 &= -4.796 + 2.599 = -2.197 \\ k_2 &= 6.36 \times 10^{-3} \text{ s}^{-1}\end{aligned}$$

4.4.1 Effect of Catalyst

A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent chemical change. For example, MnO_2 catalyses the following reaction so as to increase its rate considerably.



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.

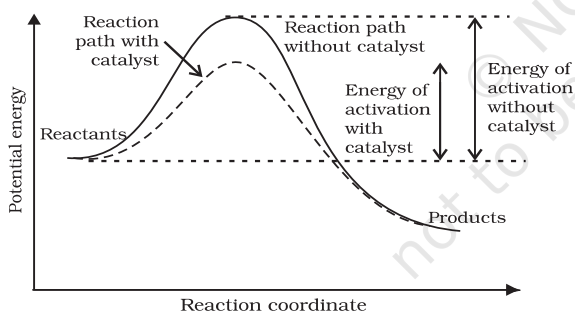


Fig. 4.11: Effect of catalyst on activation energy

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. 4.11.

It is clear from Arrhenius equation (4.18) that lower the value of activation energy faster will be the rate of a reaction.

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 the 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.

4.5 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 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



rate of reaction can be expressed as

$$\text{Rate} = Z_{AB} e^{-E_a/RT} \quad (4.23)$$

where Z_{AB} represents the collision frequency of reactants, A and B and $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a . Comparing (4.23) with Arrhenius equation, we can say that Z is related to collision frequency.

Equation (4.23) 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*) 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. 4.12. The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed.

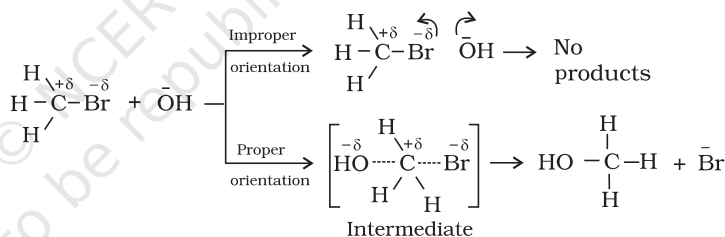
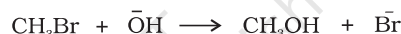


Fig. 4.12: Diagram showing molecules having proper and improper orientation

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.,

$$\text{Rate} = PZ_{AB} e^{-E_a/RT}$$

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.

* Threshold energy = Activation Energy + energy possessed by reacting species.