B.Sc. (Hons) Part II

CHEMICAL KINETICS

Paper : III A Physical Chemistry

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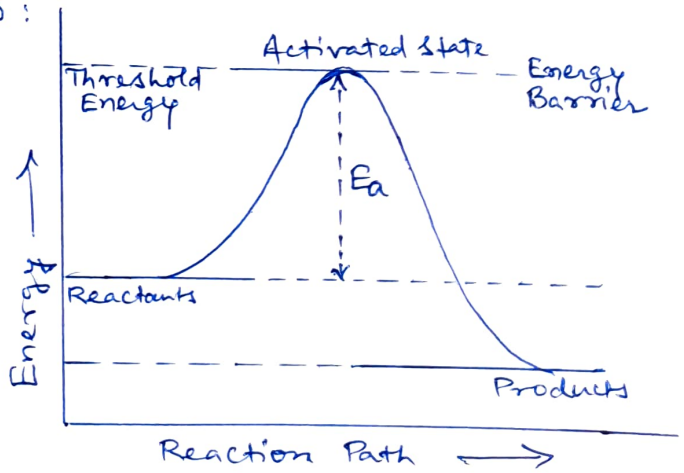
Energy of Activation, Ea :—

Appearance of Ea factor in the Arrhenius equation leads to the fact that before the reaction occurs, reactant molecules must be activated, i.e. they possess energy in excess of a certain amount. These activated molecules will then collide and lead to the reaction to yield products. Collisions between molecules which are not activated, will be of no use and no reaction will take place. The minimum energy which the molecules must have in order to react before the reaction takes place is known as the Activation Energy.

It follows from the concept of activation that reactants are not directly converted into products. The molecules first acquire energy to form an activated complex and then this activated complex decomposes into products.

Reactants $\rightleftharpoons$ Activated complex $\longrightarrow$ Products

In other words, there exists an energy barrier between the reactants and products. If the reactant molecules can cross the energy barrier, they will be converted into products. This can be shown in the figure given below :



It is evident from the figure that there is a certain minimum energy (threshold energy) which the colliding molecules must acquire before they are capable of reacting. Most of the molecules,

however, have much less kinetic energy than the threshold energy. This excess energy that the reactant molecules must acquire in order to react to yield products is known as activation energy, Ea.

i.e. Ea = Threshold Energy − Energy actually possessed by reactant molecules

Thus, there is an energy barrier placed between reactants and products. This barrier has to be crossed before reactants yielding products. Only those molecules which collide with a kinetic energy greater than Ea are able to get over the barrier and react. The molecules colliding with kinetic energies less than Ea fail to surmount the barrier. The collisions between them are unproductive and the molecules simply bounce off one another.

Therefore, the energy of activation, Ea, is defined as the minimum amount of extra energy required by reactant molecules to get converted into product molecules.

Recommended Books :—

1. Principles of Physical Chemistry
   By Puri, Sharma and Pathania
2. A Textbook of Physical Chemistry
   By K. K. Sharma and L. K. Sharma
3. Essentials of Physical Chemistry
   By Bahl, Bahl and Tuli.

Collision Theory of Reaction Rates :-

There are two important theories of reaction rates. These are (i) the Collision Theory developed by van't Hoff and Arrhenius and (ii) the Activated Complex Theory (or Transition State Theory).

Why such a small rise of temperature speeds up a reaction to such a large extent can be explained on the basis of the collision theory.

According to the collision theory, for chemical reactions to take place, there must be collisions between the reactant molecules. However, most of the collisions taking place between molecules are ineffective. The important postulate of the collision theory is that only those collisions result in chemical reaction in which colliding molecules are associated with a certain minimum energy. The two main conditions for a collision between reacting molecules to be productive are :

a. The colliding molecules must possess sufficient kinetic energy to cause a reaction, and
b. The reacting molecules must collide with proper orientation.

The molecules must collide with sufficient kinetic energy : Let us consider a reaction

$$A_2 + B_2 \longrightarrow 2AB \quad \text{or}$$

$$A-A + B-B \longrightarrow 2A-B$$

A chemical reaction occurs by breaking bonds between the atoms of the reacting molecules and by forming new bonds in the product molecules. It means for an effective collision (i.e. the collision which results in the formation of products), the colliding molecules must possess a certain minimum value of energy, called threshold energy. The molecules having energy equal to threshold energy are called active molecules, while others as passive molecules. Passive molecules

may be made active by supplying them a definite amount of energy which is equal to activation energy, E_a.

E_a = Threshold Energy − Energy possessed by reactant molecules.

When temperature of reaction mixture is increased passive molecules gain activation energy to become active. It means only molecules that collide with a kinetic energy greater than E_a are able to cross the energy barrier and react.

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