

## Chemical Kinetics

### COLLISION THEORY OF REACTION RATES

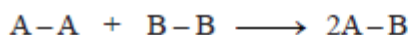
According to this theory, a **chemical reaction takes place only by collisions between the reacting molecules**. But not all collisions are effective. Only a small fraction of the collisions produce a reaction. The two main conditions for a collision between the reacting molecules to be productive are :

- (1) The colliding molecules must possess sufficient kinetic energy to cause a reaction.
- (2) The reacting molecules must collide with proper orientation.

Now let us have a closer look at these two postulates of the collision theory.

#### (1) The molecules must collide with sufficient kinetic energy

Let us consider a reaction



#### (2) The molecules must collide with correct orientation

The reactant molecules must collide with favourable orientation (relative position). **The correct orientation is that which ensures direct contact between the atoms involved in the breaking and forming of bonds.**

From the above discussion it is clear that : **Only the molecules colliding with kinetic energy greater than  $E_a$  and with correct orientation can cause reaction.**

### Temperature Dependence of Reaction Rate and Arrhenius Equation

We know that the kinetic energy of a gas is directly proportional to its temperature. Thus as the temperature of a system is increased, more and more molecules will acquire necessary energy greater than  $E_a$  to cause productive collisions. This increases the rate of the reaction.

In 1889, Arrhenius suggested a simple relationship between the rate constant,  $k$ , for a reaction and the temperature of the system.

$$k = A e^{-E_a/RT} \quad \dots(1)$$

This is called the **Arrhenius equation** in which  $A$  is an experimentally determined quantity,  $E_a$  is

the activation energy,  $R$  is the gas constant, and  $T$  is Kelvin temperature.

Taking natural logs of each side of the Arrhenius equation, it can be put in a more useful form :

$$\ln k = -\frac{E_a}{RT} + \ln A \quad \dots(2)$$

$$\log k = \frac{-E_a}{2.303 RT} + \log A \quad \dots(3)$$

If  $k_1$  and  $k_2$  are the values of rate constants at temperatures  $T_1$  and  $T_2$  respectively, we can derive

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right] \quad \dots(4)$$

### Calculation of $E_a$ Using Arrhenius Equation

In slightly rearranged form Arrhenius equation (2) can be written as

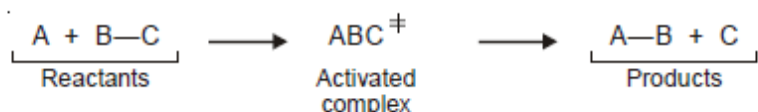
$$\ln k = -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln A \quad \dots(3)$$

$\uparrow \qquad \qquad \uparrow \qquad \qquad \uparrow$   
 $y \qquad = \qquad mx \qquad + \qquad b$

## TRANSITION STATE THEORY

The **transition state** or **activated complex theory** was developed by Henry Eyring (1935). This theory is also called the **absolute rate theory** because with its help it is possible to get the absolute value of the rate constant. The transition state theory assume that simply a collision between the reactant molecules does not really causes a reaction. During the collision, **the reactant molecules form a transition state or activated complex which decomposes to give the products.**

Thus,



The double dagger superscript ( $\ddagger$ ) is used to identify the activated complex.

The transition state theory may be summarised as follows :

- (1) In a collision, the fast approaching reactant molecules (A and BC) slow down due to gradual repulsion between their electron clouds. In the process **the kinetic energy of the two molecules is converted into potential energy.**
- (2) As the molecules come close, **the interpenetration of their electron clouds occurs which allows the rearrangement of valence electrons.**
- (3) A partial bond is formed between the atoms A and B with corresponding weakening of B – C bond. This leads to formation of an **activated complex** or **transition state**. The activated complex is momentary and decomposes to give the products (A–B + C)