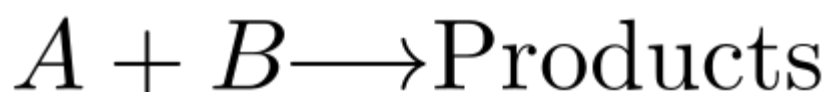


Collision Theory of Chemical Reactions

The Arrhenius equation explains the effect of temperature on the rate constant of a chemical reaction but does not describe how reactant molecules are transformed into products. This limitation was addressed by the development of the **collision theory**, which provides a molecular interpretation of reaction rates. The theory was developed independently by Max Trautz (1916) and William Lewis (1918) and is mainly applicable to simple bimolecular reactions occurring in the gaseous state.

According to collision theory, molecules are in continuous random motion and therefore collide with one another repeatedly. However, the occurrence of a collision does not necessarily result in a chemical reaction. Only those collisions that possess sufficient energy and occur with a proper orientation lead to the formation of products. Such collisions are known as **effective collisions**. Thus, the rate of a chemical reaction depends on the number of effective collisions taking place per unit time rather than on the total number of collisions.

Consider the bimolecular reaction



The molecules of A and B must first collide before any chemical transformation can occur. During the collision, the old bonds are weakened and new bonds begin to form. If the molecules possess sufficient energy and approach each other in a favourable orientation, products are formed; otherwise, the molecules simply separate without undergoing any chemical change.

Postulates of Collision Theory

1. The reacting molecules are assumed to behave as **hard, rigid spheres** moving randomly in all directions. This assumption is known as the **hard-sphere model**.
2. A chemical reaction can occur only when the reactant molecules collide with one another.
3. Not every collision results in a chemical reaction. Most collisions are ineffective because the necessary conditions for reaction are not satisfied.
4. For a collision to be effective, the colliding molecules must possess kinetic energy equal to or greater than the **activation energy** of the reaction.
5. The molecules must collide with a proper orientation so that the reacting atoms or functional groups come into close contact and the required bond rearrangement can take place.
6. The rate of a chemical reaction is directly proportional to the number of effective collisions occurring per unit time.

According to the hard-sphere model, each molecule possesses a definite effective size. The minimum distance between the centres of two molecules at the instant of collision is called the **collision**

diameter. If the effective diameters of molecules A and B are d_A and d_B , respectively, then the collision diameter for the pair is

$$d_{AB} = \frac{d_A + d_B}{2}$$

The collision diameter determines the effective size of the molecules during a collision and influences the probability of molecular encounters.

The area presented by one molecule for collision with another is known as the **collision cross-section**. For two spherical molecules, it is given by

$$\sigma = \pi d_{AB}^2$$

A larger collision cross-section increases the probability of collision because the molecules occupy a larger effective area during their motion.

Since both molecules are moving, the collision process depends upon their **relative velocity** rather than the velocity of either molecule alone. An increase in the relative velocity increases the number of molecular encounters and therefore increases the collision frequency.

The number of collisions occurring per unit volume per unit time is known as the **collision frequency**, represented by Z . It depends upon the concentration of the reactants, their collision cross-section, and their relative speed. Consequently, increasing the concentration or temperature generally increases the collision frequency.

Although collision frequency is important, only a fraction of these collisions is capable of producing products. Molecules must possess sufficient energy to overcome the activation energy barrier. According to the Maxwell-Boltzmann distribution, the fraction of molecules having energy greater than or equal to the activation energy is represented by

$$e^{-E_a/RT}$$

Even when this energy requirement is satisfied, the molecules must approach each other in a suitable orientation. This orientation requirement is represented by the **steric factor** or **probability factor**,

denoted by P . Its value always lies between zero and one.

$$0 < P \leq 1$$

For simple molecules, the value of P is usually close to unity, whereas for complex molecules it may be much smaller because only a limited number of orientations lead to product formation.

Taking into account the collision frequency, activation energy and steric factor, the rate constant for a bimolecular gaseous reaction is expressed by the collision theory equation

$$k = PZ e^{-E_a/RT}$$

This equation shows that the rate constant depends on three important factors: the number of molecular collisions, the fraction of molecules possessing sufficient energy to overcome the activation energy barrier, and the probability that the molecules collide with the proper orientation.

Limitations of Collision Theory

- It is mainly applicable to simple bimolecular reactions in the gaseous state.
- The theory assumes molecules to be rigid spheres, whereas real molecules possess complex shapes and electron distributions.
- The orientation factor is introduced empirically and cannot always be predicted accurately.
- The theory does not describe the formation of the activated complex during a reaction.
- It is less successful for reactions occurring in solution and for reactions involving complex molecular mechanisms.