dominate this field of investigation.

[1] Collision Theory of Bimolecular Reactions

If every collision between reacting gases were to result in chemical combination, the velocity of the reaction would be far greater than the one actually observed by experiments. Therefore, this theory received a serious setback. But the concepts of activated molecules and activation energy given by Arrhenius led to the revival of this theory in a modified form.

The postulates of the collision theory are:

(1) A reaction occurs on the collision of two molecules only if they possess a certain minimum amount of energy in excess to the normal energy of the molecules.

(2) The collisions between the molecules other than activated molecules do not lead to chemical reaction at all.

(3) The minimum energy in excess to their normal energy which the molecules must possess before chemical reaction on collision is known as and equal to the activation energy.

The probability that a molecule will possess energy in excess of an amount E per mole at a temperature T is given by the Boltzmann factor, $e^{-E/RT}$. If the energy is restricted to two components for a single molecule or two components for each of the two molecules making a total of two square terms, then the fraction of molecules which have energy in excess of E is actually equal to $e^{-E/RT}$.

For a chemical reaction to occur when two molecules collide, it is supposed that molecules must have energy greater than E_1 and the other than E_2, where $E_1 + E_2 = E = $ energy of activation. The probability of collisions is then given by

$$e^{-(E_1 + E_2)/RT} = e^{-E/RT}$$

For simplicity, this is the condition that a pair of molecules must have the energy necessary for the reaction. Consider a biomolecular gaseous reaction, e.g.,

$$2HI\ (g) \rightleftharpoons H_2\ (g) + I_2\ (g)$$
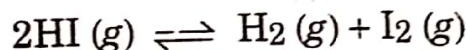
The reaction for the present purpose can be considered to take place in the forward direction—a correct assumption only in the initial stages of the reaction. Evidently, two

molecules of HI must collide with each other, before the bonds existing between H and I can break to form new bonds between H and H; I and I. This gives rise to one molecule each of H_2 and I_2.

If z' is the number of molecules per ml of the gas taking part in binary collisions per second and E be the energy of activation, then the reaction velocity is given by

$$\frac{dx}{dt} = z' e^{-E_1/RT}$$

If n number of molecules of the same kind are involved in the biomolecular reaction, then

$$\frac{dx}{dt} = kn^2$$

Hence

$$z' e^{-E/RT} = kn^2$$

or

$$k = \frac{z'}{n^2} e^{-E_1/RT} \qquad \qquad ...(1)$$

Now z' is twice the number of molecular collisions per ml per second, as two molecules take part in every collision. Hence,

$$z' = 4 n^2 \sigma^2 \left(\frac{\pi RT}{M}\right)^{1/2}$$

where, σ is the molecular collision diameter and M is the molecular weight.

Therefore, equation (1) reduces to

$$k = \frac{4n^2 \sigma^2}{M} \left(\frac{\pi RT}{M}\right)^{1/2} e^{-E_1/RT}$$

$$= 4\sigma^2 \left(\frac{\pi RT}{M}\right)^{1/2} e^{-E_1/RT} \qquad \qquad ...(2)$$

$$= Z e^{-E_1/RT}$$

where $Z = 4\sigma^2 \left(\frac{\pi RT}{M}\right)^{1/2}$ and is known as **collision number**. It is defined as, '*number of collisions per second when there is only one mole of reactant per unit volume*'.

On taking logarithm of equation (2), we get

$$\log k = \log \left[4\sigma^2 \left(\frac{\pi RT}{M}\right)^{1/2}\right] - \frac{E}{RT}$$

Differentiating the above expression with respect to temperature, we get

$$\frac{d \log k}{dT} = \frac{1}{2T} + \frac{E}{RT^2} \qquad \qquad ...(3)$$

Neglecting $\frac{1}{2T}$ (as in most cases $2T$ is small as compared to E/RT^2), then equation (3) reduces to

$$\frac{d \log k}{dT} = \frac{E}{RT^2} \qquad \dots(4)$$

This equation is identical with Arrhenius equation. If the value of σ (collision diameter) is known, the collision number (Z) can be calculated. It is thus possible to compare it with the experimental value of the frequency factor.

If the bimolecular reaction involves two molecules of different species, then the collision number (Z) is given by

$$Z = \sigma^2 \left| 8\pi RT \left(\frac{M_1 + M_2}{M_1 M_2}\right)^{1/2} \right|$$

where M_1 and M_2 are the respective molecular weights of different species.

The equations developed are applicable to simple homogeneous reactions but will not apply to heterogeneous reactions or chain reactions. A plot between $\log k$ and $1/T$ will not be exactly linear, but less deviations are observed on plotting $\log k/T^{1/2}$ against $1/T$.

Reactions	E (calculated) in calories	E (experimental) in calories
(1) $2N_2O \rightarrow 2N_2 + O_2$	56,000	58,000
(2) $2HI \rightarrow H_2 + I_2$	44,000	44,000
(3) $H_2 + I_2 \rightarrow 2HI$	40,000	39,500

The success of the collision theory can be judged from the above table in which the activation energies calculated according to equation ($k = Ac^{-E/RT}$) as well as those based upon experimental data have been compared. It will thus be seen that there is a very good agreement between the calculated and experimental values.

[I] Failures of Collision Theory

However, there are certain reactions where the experimental and calculated values differ, e.g., the reaction between vapours of ethanol and acetic anhydride, combination of two molecules of ethylene etc.

In the bimolecular polymerisation of ethylene, the reaction occurs only once in about 2,000 collisions between activated molecules. In the polymerisation of 1 : 3 butadiene the reaction occurs only once in about 10,000 collisions between activated molecules.

[II] Steric Factor

A sufficient number of slow reactions are known which show that the phenomenon is limited to few instances and the equation $k = Ze^{-E/RT}$ reduces to,

$$k = PZe^{-E/RT}$$

where P = *probability factor or steric factor*, which makes allowances for effects causing deviations from the ideal behaviour. The value of P varies from unity to 10^{-8} depending upon the nature of the reaction.

Anomalies were also found to exist in liquid systems. These were assumed to be due to solvent effects, but in some cases these were found to be present in gaseous systems also. Several weaknesses of collision theory have been found in recent years.

(1) Firstly, attempts to correlate the value of P-probability factor-with the structure and properties of reacting molecules have not been successful.

(2) Secondly, on this basis it is not possible to advance an explanation for abnormally high rates.

(3) Thirdly, a logical weakness is observed when reversible reactions are considered. Consider the following reaction :

$$X + Y \underset{k_1}{\overset{k_1}{\rightleftharpoons}} XY$$
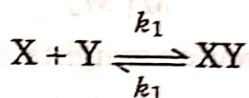
For the forward reaction : $k_1 = P_1 Z_1 e^{-E_1/RT}$

For the backward reaction : $k_2 = P_2 Z_2 e^{-E_2/RT}$

Since, $K = k_1 / k_2$, we have,

$$K = \frac{P_1 Z_1 e^{-E_1/RT}}{P_2 Z_2 e^{-E_2/RT}} , \text{ i.e., } K = \frac{P_1 Z_1}{P_2 Z_2} . e^{(E_1 - E_2)/RT}$$

According to thermodynamics, we have

$$K = e^{-\Delta G/RT} = e^{-\Delta S/RT} . e^{-\Delta H/RT}$$

where, ΔG = increase in free energy, ΔS = increase in entropy,

ΔH = increase in heat content.

Comparing these expressions for K it is clear that $e^{-(E_1 - E_2)/RT}$ and $e^{-\Delta H/RT}$ correspond with one another. If the molecules of the reactants and products are of comparable dimensions, $Z_1 = Z_2$, so that entropy term $e^{-\Delta S/RT}$ must be equal to P_1/P_2. It is, therefore, not sufficient to correlate the probability of certain reacting groups being together in collision. They should be interpreted in terms of entropy factor.