

Chemical Kinetics

UNIT V, BSc III year

Topic : Activation energy, collision theory
and it's limitation

... a small rise in temperature.

Concept of Activation Energy. Two important questions relating to reaction rates have been answered satisfactorily on the basis of the collision theory. We have also to answer two more questions based on simple laboratory observations :

(a) A mixture of oxygen and hydrogen (1 : 2 by volume) may remain as such at room temperature apparently without reacting. However, the moment an electric spark is passed through the mixture, the reaction proceeds instantaneously, almost explosively. Similarly, a mixture of methane and oxygen remains intact without reacting noticeably until a lighted match-stick is introduced into the mixture. Why is it so ?

(b) Even when the concentrations of reactants involved in two reactions may be the same, one reaction may be very fast and the other very slow (cf. effect of nature of reactants on rates of reactions, discussed in previous pages). Why is it so ?

We may answer these questions also on the basis of the collision theory by involving the concept of **activation energy**.

As has already been explained, there is a certain minimum energy (threshold energy) which the colliding particles (molecules or atoms) must acquire before they are capable of reacting. Most of the molecules, however, have much less kinetic energy than the threshold energy. The excess energy that the reactant molecules having energy less than the threshold energy must acquire in order to react to yield products is known as **activation energy**. Thus,

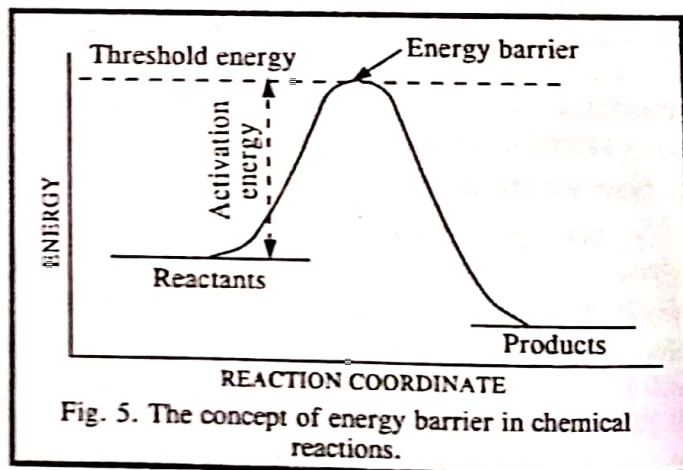
Activation Energy = Threshold energy — Energy actually possessed by molecules.

According to this concept, non-active molecules (having energy less than the threshold energy) can be 'activated' by absorption of extra energy. This extra energy is, evidently, the activation energy.

There is, thus, an **energy barrier** placed between reactants and products (Fig. 5). This barrier has to be crossed before reactants can yield products. This barrier determines the magnitude of threshold energy which reactant molecules must acquire before they can yield products.

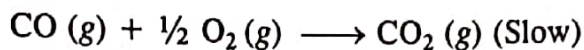
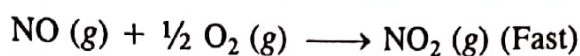
As is evident from Fig. 5, E_a is the activation energy of the reactants. They must absorb this much energy before they can react and change into products. The energy of the products is shown to be less than that of the reactants. This indicates that the reaction is exothermic.

Now we are in a position to answer questions (a) and (b) posed above. If a reaction, say,



between A and B is feasible, it will occur only if the required activation energy is supplied to the molecules. This is the reason that although the reaction between hydrogen and oxygen is highly feasible from the point of view of thermodynamics at the room temperature, yet it takes place at a noticeable rate only if the required activation energy in the form of an electric spark or heat is supplied to the reactants.

Further, different reactions require different amounts of activation energy. A reaction which requires a high activation energy is slow at ordinary temperatures. Consider the following two reactions :



The first reaction is fast at ordinary temperatures because it requires a comparatively low activation energy. The second reaction is slow because it requires a comparatively high activation energy.

It is thus evident that whether a given reaction is slow or fast at a given temperature depends on the activation energy of the reaction. A reaction which has lower activation energy will proceed at a faster rate, at a given temperature. Thus, differences in activation energies are largely responsible for observed differences in rates of different reactions. This answers question (2) posed above.

Effect of Catalyst. A catalyst is a substance that can increase the rate of a reaction but which itself remains unchanged in amount and chemical composition at the end of the reaction. When a catalyst is added, a new reaction path with a lower energy barrier is provided (cf. dotted curve in Fig. 6). Since the energy barrier is reduced in magnitude, a larger number of molecules of the reactants can get over it. This increases the rate of the reaction.

A catalyst does not alter the position of equilibrium in a reversible reaction. It simply hastens the approach of the equilibrium by speeding up both the forward and the backward reactions.

Calculation of Energy of Activation. The Arrhenius Equation. Arrhenius proposed the following empirical equation for calculating the energy of activation of a reaction having rate constant k at temperature T :

$$k = A e^{-E_a/RT} \quad \dots(59)$$

where E_a is called the **Arrhenius activation energy** and A is called the **Arrhenius pre-exponential factor**. Since the exponential factor in Eq. 59 is dimensionless, the pre-exponential factor A has the same units as the rate constant k . The units of k for a first order reaction are s^{-1} , which is the unit of frequency. Hence, A is also called the **frequency factor**. E_a and A are called the **Arrhenius parameters**.

Taking logs of Eq. 59, we have

$$\ln k = -E_a/(RT) + \ln A \quad \dots(60)$$

From Eq. 60, it is evident that a plot of $\ln k$ versus the reciprocal of absolute temperature ($1/T$) would give a straight line with slope $= -E_a/R$ and intercept $= \ln A$.

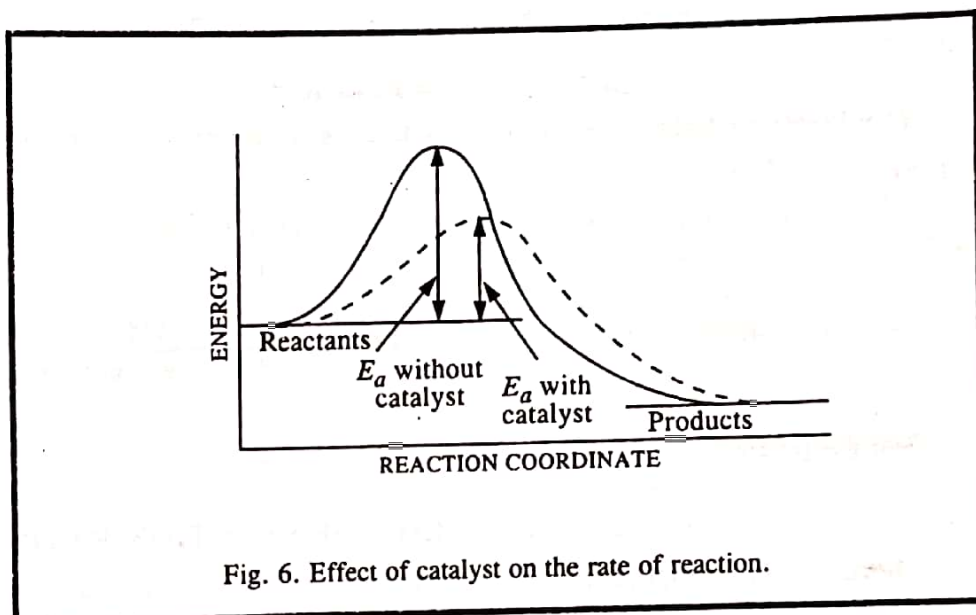


Fig. 6. Effect of catalyst on the rate of reaction.

Differentiating Eq. 60 with respect to temperature, we have

$$d \ln k / dT = E_a / RT^2 \quad \dots(61)$$

Integrating Eq. 61 between temperatures T_1 and T_2 when the corresponding rate constants are k_1 and k_2 , respectively and assuming that E_a is constant over this temperature range, we obtain

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \quad \dots(62)$$

This is the **integrated Arrhenius equation**. Thus, knowing the rate constants at two different temperatures, the energy of activation E_a can be readily determined.

Example 13. The rate constant of a second order reaction is $5.70 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C and $1.64 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 40°C . Calculate the activation energy and the Arrhenius pre-exponential factor.

Solution : Substituting the given data in Eq. 62, we have

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \quad \text{or} \quad E_a = R (\ln k_2 / k_1) \left[\frac{T_1 T_2}{T_2 - T_1} \right]$$

$$\therefore E_a = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \left[\ln \frac{1.64 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}{5.70 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}} \right] \times \left[\frac{298 \text{ K} \times 313 \text{ K}}{313 \text{ K} - 298 \text{ K}} \right]$$

$$= 54478 \text{ J mol}^{-1} = \mathbf{54.478 \text{ kJ mol}^{-1}}$$

To calculate the Arrhenius pre-exponential factor A , we incorporate one of the given data in Arrhenius equation, viz., $k = A e^{-E_a / RT}$. Thus,

$$\ln k = \ln A - E_a / RT \quad \text{or} \quad \ln A = \ln k + E_a / RT$$

$$\text{At } T = 298 \text{ K, } k = 5.7 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$\therefore \ln A = \ln (5.7 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) + \frac{54478 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}$$

$$\therefore A = \mathbf{2.01 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

Note that the units of A are the same as those of the rate constant.

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:

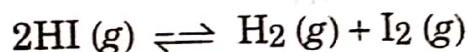
- (1) A reaction occurs on the collision of two molecules only if they possess a certain minimum amount of energy in excess to the normal energy of the molecules.
- (2) The collisions between the molecules other than activated molecules do not lead to chemical reaction at all.
- (3) The minimum energy 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.,



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 H₂ and I₂.

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

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

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

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

Therefore, equation (1) reduces to

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

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

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

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

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

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) $2\text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2$	56,000	58,000
(2) $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$	44,000	44,000
(3) $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$	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 ($k = Ae^{-E/RT}$) 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 :



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,

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

According to thermodynamics, we have

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

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.