

Lecture No: 6

KINETIC THEORIES

Kinetic theories explain how the chemical reactions occur. The aim of these theories is to calculate the rate of any reaction by using the properties of the reactant molecules. The results of the calculations give not only the rates of the chemical reactions but they also give quantitative and qualitative information on the identities and the relative concentrations of the reaction products.

1. Unimolecular Reactions

At the beginning of the 20th century, no scientist could explain how unimolecular reactions occur. A unimolecular reaction is the breaking of a molecule into fragments;



To achieve this, A must gain sufficient energy to surmount the energy barrier. Excess energy gets into a particular vibrational degree of freedom. This vibration then produces dissociation of the molecule into fragments. There were few suggestions on the problem:

- **1st suggestion:** It was suggested that this energy is supplied by radiation. If this hypothesis were true, then in the absence of light, no reaction would occur. But, experiments proved it wrong, because there are many unimolecular reactions that occur in the dark.
- **2nd suggestion:** Another suggestion is that A gains energy through collisions. But, then the rate constant becomes proportional to the square of the concentration. This would make the reaction second-order, whereas it is observed that most of the unimolecular reactions are first-order.

2. Lindemann's Theory

Lindemann explained the occurrence of unimolecular reactions by his famous mechanism. The proposed mechanism consists of three steps;



The first step is the *activation*. A collides with another A molecule to produce an activated molecule. A* has an excess energy, while the remaining molecule is deficient in energy. The activated molecule may be *deactivated* by collision or it may *decompose* into products. The rate of disappearance of A is;

$$\text{Rate} = -\frac{d[A]}{dt} = k_2[A^*]$$

[A*] may be calculated by using "Steady-State Approximation", because A* is an intermediate. It is formed in the first step and consumed in the second and third steps;

$$\frac{d[A^*]}{dt} = 0 = -k_{-1}[A^*][A] + k_1[A]^2 - k_2[A^*]$$

and

$$\text{Rate} = \frac{k_1 k_2 [A]^2}{k_{-1}[A] + k_2}$$

There are two limiting cases:

- **Rate of Decomposition >> Rate of Deactivation**

$$k_2[A^*] \gg -k_{-1}[A^*][A]$$

In this case, the rate equation may be written as;

$$\text{Rate} = k_1[A]^2$$

The kinetics is second-order. So, the activated molecule does not decompose immediately.

- **Rate of Deactivation >> Rate of Decomposition**

$$k_{-1}[A^*][A] \gg k_2[A^*]$$

In this case, the rate equation takes the form;

$$Rate = \frac{k_1 k_2}{k_{-1}} [A]$$

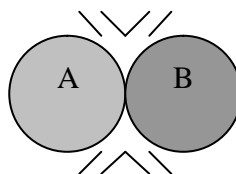
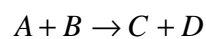
The kinetics is first-order. This indicates that the activated molecule loses its excess energy through collisions. It does not decompose immediately.

There is a **time lag** between activation and decomposition steps. In that time, the activated molecule arranges its geometry into a particular configuration in order to produce the products. But, most of the activated molecules lose their excess energy through collisions and deactivate. Only a very small fraction of the activated molecules are able to have the suitable geometry and to decompose to yield the products.

In a gas-phase reaction, high pressures increase the number of collisions, the rate is first-order. At lower pressures, the number of collisions decreases, the rate becomes second-order. The apparent first-order rate constant decreases at low pressures.

3. Collision Theory

The collision theory is applicable only to bimolecular elementary reactions;



If reaction occurs with every collision, then the rate is equal to the number of collisions between A and B per unit time, per unit volume;

$$Rate = Z_{AB} = \left(\frac{s_A + s_B}{2} \right)^2 \sqrt{\frac{8p(m_A + m_B)k_B T}{m_A m_B}} [A][B]$$

where;

$s_A + s_B$: molecular diameters
 m_A, m_B : molecular masses
 $[A], [B]$: # of molecules per unit volume

But, every collision does not result in the reaction but only those collisions in which the colliding molecules exceeds E^* . The fraction in which the energy exceeds E^* is proportional to $e^{-E^*/RT}$. Then, the rate constant may be written as;

$$k = \left(\frac{s_A + s_B}{2} \right)^2 \sqrt{\frac{8p(m_A + m_B)k_B T}{m_A m_B}} e^{-E^*/RT}$$

The collision theory predicts the rate constants satisfactorily for reactions which involve simple molecules. But, for larger molecules the rates tend to be smaller than the theory predicts. To account for this, an additional factor is inserted into the above expression. This factor is called "the probability factor". Its value is around 10^{-5} , and indicates that even those collisions having the required energy may not produce the reaction. The molecules have to collide in a particular configuration. Complex molecules will have less chance of colliding in the correct orientation.