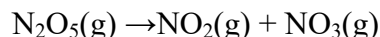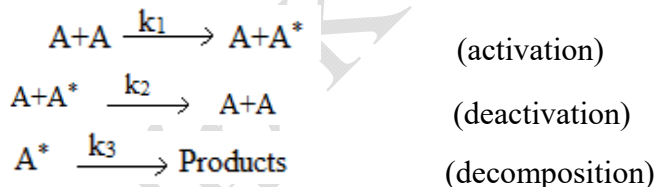❖ **Theory of Unimolecular Reactions**

The collision theory and the absolute reaction rate theory satisfactorily account for the biomolecular reaction. However, a number of unimolecular gaseous reactions have been studied, which were found to be of first order as , for example, the decomposition of N_2O_5

$N_2O_5(g) \rightarrow NO_2(g) + NO_3(g)$

If the energy of activation of these first order reactions is believed to come from biomolecular collisions then the question that arises is how these reactions occur. To investigate the kinetics of such reactions , Lindemann in 1922 proposed that the behavior of unimolecular reactions can be explained on the basis of biomolecular collisions. It is proposed that when the reactant molecules are activated by collisions with other molecules there may be a time lag before decomposition of the activated molecules. In other words, the activated molecules do not decompose immediately into products but remain in the activated state for a finite time. During this time –lag, the energized molecules may lose their extra energy in a second biomolecular collision or it may be deactivated to ordinary molecules. Consequently, the rate of the reaction will not be proportional to all the molecules activated but only to those which remain active. The process of activation or deactivation by collisions may be represented by the following mechanism:

$$A+A \xrightarrow{k_1} A+A^* \quad \text{(activation)}$$

$$A+A^* \xrightarrow{k_2} A+A \quad \text{(deactivation)}$$

$$A^* \xrightarrow{k_3} \text{Products} \quad \text{(decomposition)}$$

where A is an inactive molecule and A^* the activated molecule. The rate at which A will disappear is proportional to the concentration of A^* , viz.,

$$-\frac{d[A]}{dt} = k_3[A^*] = k_1[A]^2 - k_2[A][A^*] \quad \text{.....................(101)}$$

Since $[A^*]$ is not known and it is necessary to obtain it in terms of [A] this can be done with the help of steady state principle. According to this, it is assumed that in the steady state the concentration of the intermediate (activated complex) is small and does not change with time , i.e, the rate of formation and the rate of decomposition of the intermediate are equal, i.e,

$$k_1[A]^2 - k_2[A][A^*] - k_3[A^*] = 0$$
$$k_1[A]^2 - k_2[A][A^*] = k_3[A^*]$$

$$[A^*] = \frac{k_1[A]^2}{k_2[A] + k_3}$$

Hence,

$$-\frac{d[A]}{dt} = \frac{k_3 k_1 [A]^2}{k_3 + k_2[A]}$$

………………………………(102)

Equation (102) predicts two limiting possibilities.

Case I: When $k_2[A] \gg k_3$ Eq. (102) reduces to

$$-\frac{d[A]}{dt} = \frac{k_3 k_1}{k_2}[A]$$

which is a first order rate equation. This corresponds to a situation in which the concentration of A is high enough to produce appreciable deactivation of A^* by collisions with A so that the rate of deactivation $k_2[A][A^*]$ is appreciably large in comparison to the rate of decomposition, $k_3[A^*]$.

Case II: When $k_3 \gg k_2[A]$ i.e rate of decomposition is large as compared to the rate of deactivation Eq. (102) becomes

$$-\frac{d[A]}{dt} = k_1 [A]^2$$

In such cases the reaction should be of second order. This situation corresponds to low concentration of A where the rate of activation becomes slow and hence the rate controlling.

In gaseous reaction as the pressure of the system is decreased, the deactivation, $k_2[A][A^*]$, decreases . At low pressure, therefore, the conditions for the first order kinetics fail and $k_2[A]$ is no longer greater than k_3. Thus the first order kinetics is replaced by the second order kinetics.

…………………………………..**End***…………………………………………………