

LINDEMANN THEORY OF UNIMOLECULAR REACTIONS

It is assumed that activation of molecules in unimolecular reaction is due to its collisions. It means that the reactions should follow the second order kinetics due to number of collision is proportional to the square of the concentration.

Lindemann's theory:

Lindemann suggested that

- (i) Reactant molecules are activated by collisions with one another, some of the molecules may possess sufficient energy to pass the final products without receiving any additional energy, such molecules are termed as activated molecules.
- (ii) If the rate of activated molecules to convert into the products is slow as compared with the rate with which activated molecules are deactivated by collisions, a stationary concentration of activated molecules may be formed. As the activated molecules are in equilibrium with the normal molecules, the concentration of activated molecules will be proportional to that of normal molecules, therefore, it follows that the rate of reaction is proportional to the concentration of activated molecules which in turn is proportional to first power of the concentration of normal molecules as the two types - are in equilibrium with each other it means that reaction is of 1st order.

Case I

At high Pressure :

It means that $k_3 [A]$ can be neglected in comparison with $k_2 [A]$ $k_3 [A]$ is far greater than k_2

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

Thus reaction is of 1st order

Case II

At low pressure :

k_3 may be neglected in comparison with k_2 Hence k_3 is ^{far} greater than k_2 . Therefore,

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

Hence the reaction is of 2nd order.

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Unid Decomposition:

Decomposition of activated molecule may be represented as

$$A^* \xrightarrow{k_3} \text{Products}$$

where k_3 is the first order constants.

As the concentration of A^* is so small that according to steady state treatment $\frac{d[A^*]}{dt}$ is equal to zero.

i.e. $\frac{d[A^*]}{dt} = 0$ (I)

But the rate of formation of A^* is given by

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

(II)

Applying condition of equation (I) to eqn (II) we get

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

or, $k_1[A]^2 = k_2[A][A^*] + k_3[A^*]$

or, $k_1[A]^2 = [A^*] (k_2[A] + k_3)$

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

Since the rate of reaction will be proportional to the concentration of the activated molecules,

$$\frac{d[A]}{dt} = k_3[A^*] \quad \text{--- (IV)}$$

Substituting equation (III) in eqn (IV), we get

$$\frac{d[A]}{dt} = \frac{k_3 k_1 [A]^2}{k_2 [A] + k_3} = k' [A] \quad \text{--- (V)}$$

(ii) At low pressure, the collisions can not maintain a supply of activated molecules, therefore the rate of reaction will depend upon the rate of activation and hence is proportional to the square of concentration of reacting molecules. Thus the reaction becomes of the 2nd (second) order at low pressure.

Mathematical Formulation of Lindemann's Theory :-

(i) Activation by collisions :-

by collision is represented by



where A = Normal molecule and A* = Activated molecule which possesses sufficient energy to pass into the products.

∴ Rate of activation = $k_1 [A]^2$

where k_1 = Specific rate constant of the second order reaction.

(ii) Deactivation by collision :-

The process of deactivation may be represented as



∴ Rate of deactivation = $k_2 [A]^2$ where the rate of deactivation is slow as compared with the rate of activation