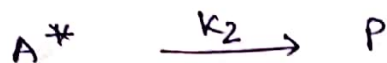
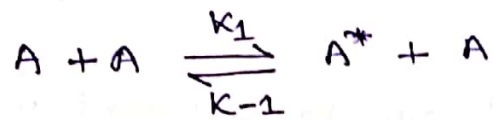


* Lindemann Theory of Unimolecular reaction:-

A/c to this theory -

A unimolecular reaction $A \longrightarrow P$ proceeds

to following mechanism -



Here, A^* is the energized 'A' molecule which has acquired sufficient vibrational energy to enable it to ~~is~~ decompose.

In the first step, the energized molecule A^* is produced by collision with another molecule 'A'.

The rate constant for the energized step is k_1 . After the production of A^* , it can either be de-energized back to 'A' where rate constant is k_{-1} . Here, its vibrational energy is transferred to the kinetic energy of an 'A' molecule or be decomposed to product where rate constant is k_2 .

A/c to steady-state approximation, a reactive species is produced as an intermediate in a chemical reaction. its rate of formation is equal to rate of decomposition.

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

$$\text{Rate of decomposition} = k_{-1} [A] [A^*] + k_2 [A^*]$$

$$\text{Thus, } \frac{d[A^*]}{dt} = k_1 [A]^2 - k_{-1} [A] [A^*] - k_2 [A^*] = 0 \quad \text{--- (1)}$$

$$\therefore [A^*] = \frac{k_1 [A]^2}{k_{-1} [A] + k_2} \quad \text{--- (2)}$$

The rate of reaction is given by -

$$r = \frac{-d[A]}{dt} = k_2 [A^*] \quad \text{--- (3)}$$

Substituting eqs- (2) in eqs- (3) we get,

$$r = \frac{k_1 k_2 [A]^2}{k_{-1} [A] + k_2} \quad \text{--- (4)}$$

If $k_{-1} [A] \gg k_2$ then k_2 term in the denominator can be neglected.

$$\therefore r = \frac{k_1 k_2}{k_{-1}} [A] \quad \text{--- (5)}$$

It is the rate equation for a first-order reaction. In a gaseous reaction.

At very high pressure -

$[A]$ is very large so that $k_1 [A] \gg k_2$.

If $k_2 \gg k_{-1} [A]$ then $k_{-1} [A]$ can be neglected.

$$\therefore r = k_1 [A]^2 \quad \text{--- (6)}$$

It is the rate equation for 2nd order reaction.

But experimental rate is -

$$r = k_{uni} [A] \quad \text{--- (7)}$$

Where, k_{uni} = Unimolecular rate constant.

On combining eqs- (4) and eqs- (7) we get,

$$k_{uni} \equiv k^1 = \frac{k_1 k_2 [A]}{k_{-1} [A] + k_2} = \frac{k_1 k_2}{k_{-1} + k_2 / [A]} \quad \text{--- (8)}$$