* Lindemann Theory of Unimolecular reaction :-

A/c to this theory -

A unimolecular reaction $A \longrightarrow P$ proceeds

the following mechanism -

$$A + A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} A^* + A$$

$$A^* \xrightarrow{K_2} P$$

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

Rate of formation $= K_1[A]^2$

Rate of decomposition $= K_{-1}[A][A^*] + K_2[A^*]$

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

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

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

At very high pressure –

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

If $k_2 >> k_{-1}[A]$ 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,

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