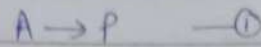
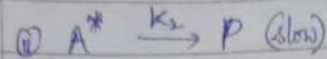
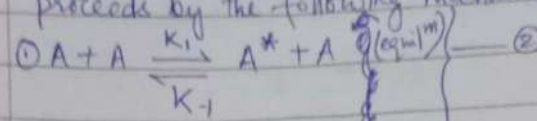


Lindemann Theory of Unimolecular Reactions :- (1922)

A unimolecular rxn



proceeds by the following mechanism :



Here A^* is the energized A molecule which has acquired sufficient vibrational energy to enable it to isomerize or decompose.

Step (1) involves a rapid equilibrium ~~rxn~~ rxn where in the forward rxn, a molecule A is activated by colliding with another A molecule and in the backward rxn, the excited molecule A is deactivated by colliding with another A molecule.

Step (2) represents another possibility of deactivation where the excited molecule is decomposed to give the products. Since step (2) is the slow and rate determining step, the rate at which products are formed will be determined by the unimolecular decay and hence first-order kinetics will be observed.

In the Lindemann mechⁿ, a time lag exists between the energization of A to A^* and the decomposition of A^* to products. During this time lag, A^* can be de-energized back to A . According to steady-state approximation (SSA) whenever a reactive species is produced as an intermediate in a chemical rxn,

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its rate of formation is equal to its rate of decomposition.

Here, the energized species A^* is short-lived.

Its rate of formation = $k_1[A]^2$ and
its rate of decomposition = $k_{-1}[A][A^*] + k_2[A^*]$.

Thus,

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A][A^*] - k_2[A^*] = 0 \quad \text{--- (4)}$$

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

The rate of the rxn is given by

$$r = -\frac{d[A]}{dt} = k_2[A^*] \quad \text{--- (5)}$$

Substituting eqⁿ (4) in (5), we get

$$r = \frac{k_1 k_2 [A]^2}{k_{-1}[A] + k_2} \quad \text{--- (6)}$$

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

$$r = \left(\frac{k_1 k_2}{k_{-1}} \right) [A] \quad \text{--- (7)}$$

which is the rate eqⁿ for a first-order rxn.

In gaseous rxn, $[A]$ is very large so $k_{-1}[A] \gg k_2$.

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

$$r = k_1[A]^2 \quad \text{--- (8)}$$

which is the rate equation for a second-order rxn. This is the low pressure limit.

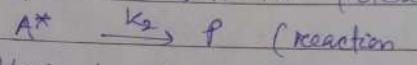
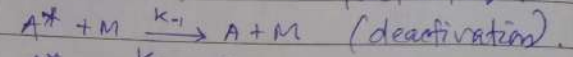
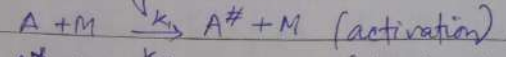
The experimental rate,
 $r = k_{uni} [A]$ — (7)

where k_{uni} = unimolecular rate constant.

Comparing equation (6) and (7),

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

Q. Consider the following Lindemann mechanism for the unimolecular decomposition of a molecule A in the presence of a species M (which may be an inert gas like helium or even A itself).



Using the steady-state approximation (s.s.a), derive the rate law for the formation of the product. We know that,

Q.11

$$r = -\frac{d[A]}{dt} = +\frac{d[P]}{dt} = k_2 [A^*] \quad \text{--- (1)}$$

Applying s.s.a. to the transient species A^* ,
 $k_1 [A][M] - k_{-1} [A^*][M] - k_2 [A^*] = 0$
or $k_1 [A][M] = (k_{-1} [M] + k_2) [A^*]$

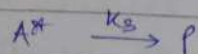
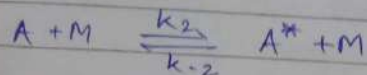
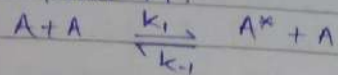
$$\Rightarrow [A^*] = \frac{k_1 [A][M]}{k_{-1} [M] + k_2} \quad \text{--- (2)}$$

Substituting (2) in (1), we get

$$r = k_1 k_2 \frac{[M][A]}{k_{-1} [M] + k_2}$$

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Q. Consider the following Lindemann mechanism for the unimolecular decomposition of a molecule A in the presence of an inert gas molecule M:



Applying the steady-state approximation to A^* , derive the rate law for the formation of the product.

Solⁿ

The rate of formation of product is given by

$$r = k_3 [A^*] \quad \text{--- (i)}$$

Applying s.s.a to A^* ,

$$k_1 [A]^2 - k_{-1} [A^*] [A] + k_2 [A] [M] - k_{-2} [A^*] [M] - k_3 [A^*] = 0$$

$$\Rightarrow k_1 [A]^2 + k_2 [A] [M] = [A^*] \{ k_{-1} [A] + k_{-2} [M] + k_3 \}$$

$$[A^*] = \frac{k_1 [A]^2 + k_2 [A] [M]}{k_{-1} [A] + k_{-2} [M] + k_3} \quad \text{--- (ii)}$$

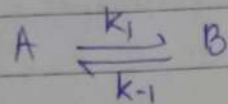
Substituting ~~the~~ eqⁿ (ii) in (i), we get

$$r = k_3 [A^*] = \frac{k_3 (k_1 [A]^2 + k_2 [A] [M])}{k_{-1} [A] + k_{-2} [M] + k_3} //$$

1. Opposing or Reversible Reactions.
2. Consecutive Reactions.
3. Competing or Parallel Reactions and
4. Chain Reactions.

1. Kinetics of Opposing or Reversible Reactions :-

Considers a simple opposing reaction in which the forward and reverse rxns are both first-order:



where k_1 and k_{-1} are the constants of the forward and the reverse rxns, respectively.

Let a be the initial concentration of the reactant A. Then,

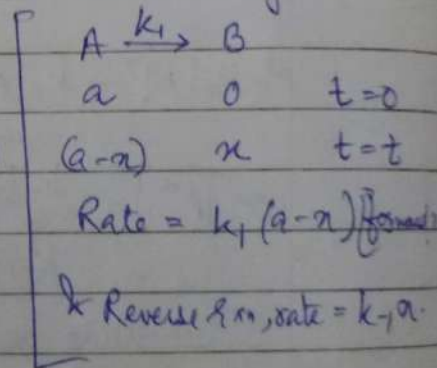
after time t , the concⁿ of A will be $(a-x)$

and that of the product B will be x . The rate of the forward rxn is equal to $k_1(a-x)$

while that of reverse rxn is $k_{-1}x$.

Hence, rate of formation of B,

$$\frac{dx}{dt} = k_1(a-x) - k_{-1}x \quad \text{--- (1)}$$



the net rate is zero, then

$$k_1(a-x) - k_{-1}x = 0 \quad \text{--- (i)}$$

$$k_1(a-x) = k_{-1}x \quad \text{--- (ii)}$$

$$\Rightarrow k_{-1} = k_1 \left(\frac{a-x}{x} \right) \quad \text{--- (iv)}$$

Substituting the value of k_{-1} in eq. (i), we get

$$\frac{dx}{dt} = k_1(a-x) - k_1 \left(\frac{a-x}{x} \right) x \quad \text{--- (v)}$$

$$= k_1 \left(\frac{ax - ax - a^2 + ax}{x} \right)$$

$$= k_1 \left(\frac{x^2 - a^2}{x} \right) \quad \text{--- (vi)}$$

Separating the variables, we have

$$\frac{dx}{x^2 - a^2} = \frac{a}{x} k_1 dt \quad \text{--- (vii)}$$

Integrating (vii), we get

$$-\ln(x-a) = \frac{a}{x} (k_1 t + I) \quad \text{--- (viii)}$$

where I = constant of integration.

$$x^2 - \frac{a^2}{x} \ln(x-a) = k_1 t + I \quad \text{--- (ix)}$$

At $t=0$, $x=a$, so that

$$I = -\frac{a^2}{a} \ln a \quad \text{--- (x)}$$

Substituting the value of I ^{from} (x) in eq. (ix), we get

$$-\frac{a^2}{a} [\ln(x-a)] = k_1 t - \frac{a^2}{a} \ln a$$

$$\text{or } k_1 t = \frac{a^2}{a} \ln \left(\frac{x}{a} \right)$$

$$\text{or } k_1 = \frac{a^2}{at} \ln \left(\frac{x}{a} \right) \quad \text{--- (xi)}$$

(11)

$$\begin{aligned} \therefore (k_1 + k_{-1}) &= k_1 + k_{-1} \left(\frac{a - a_e}{n_e} \right) \quad [\therefore \text{from (10)}] \\ &= \frac{n_e k_1 + k_{-1} a - k_{-1} n_e}{n_e} = \frac{k_1 a}{n_e} \\ &= \frac{1}{t} \ln \left(\frac{n_e}{n_e - x} \right) \quad [\therefore \text{from (10)}] \\ &= \frac{k_1 a}{n_e} - \frac{1}{t} \ln \frac{n_e}{n_e - x} \end{aligned}$$

$$(k_1 + k_{-1}) = \frac{1}{t} \ln \frac{n_e}{n_e - x} - \frac{k_1 a}{n_e} \quad \text{--- (11)}$$

Then, from k_1 , a and n_e , the rate constant, k_{-1} for the reverse rxn can be calculated.

Suppose, b moles of B is present initially. Then, the net rate of formation of B is given by

$$\frac{dx}{dt} = k_1(a - x) - k_{-1}(b + x) \quad \text{--- (12)}$$

Since at equilibrium, $\frac{dx}{dt} = 0$, hence

$$k_1(a - x_e) = k_{-1}(b + x_e) \quad \text{--- (13)}$$

$$\text{or } k_{-1} = k_1 \left(\frac{a - x_e}{b + x_e} \right) \quad \text{--- (14)}$$

Substituting the value of k_{-1} in eqⁿ (12), we get

$$\begin{aligned} \frac{dx}{dt} &= k_1(a - x) - k_1 \left(\frac{a - x_e}{b + x_e} \right) (b + x) \\ &= k_1 \left\{ \frac{(a - x)(b + x_e) - (a - x_e)(b + x)}{b + x_e} \right\} \\ &= k_1 \left\{ \frac{ab + ax_e - bx - x_e^2 - ab - ax + bx_e + x_e^2}{b + x_e} \right\} \end{aligned}$$

(IV)

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$$= k_1 \left\{ \frac{a(ae-a) + b(ae-a)}{b+ae} \right\}$$

$$= k_1 \frac{(a+b)(ae-a)}{b+ae} = k_1 \left(\frac{a+b}{b+ae} \right) (ae-a) \quad \text{--- (xvi)}$$

Separating the variables,

$$\left(\frac{b+ae}{a+b} \right) \left(\frac{da}{ae-a} \right) = k_1 dt \quad \text{--- (xv)}$$

Integrating eqⁿ (xv), we get.

$$\left(\frac{b+ae}{a+b} \right) [-\ln(ae-a)] = k_1 t + I \quad \text{--- (xvi)}$$

At $t=0$, $a=0$, we have

$$I = \left(\frac{b+ae}{a+b} \right) (-\ln ae) \quad \text{--- (xvii)}$$

Substituting I from eqⁿ (xvii) in eqⁿ (xvi),

we get

$$\left(\frac{b+ae}{a+b} \right) [-\ln(ae-a)] = k_1 t + \left(\frac{b+ae}{a+b} \right) (-\ln ae)$$

$$\Rightarrow k_1 = \frac{b+ae}{t(a+b)} \cdot \ln \left(\frac{ae}{ae-a} \right) \quad \text{--- (xviii)}$$

Again from eqⁿ (xv),

$$k-1(b+ae) = k_1(a-ae)$$

$$\Rightarrow k_1 b + k-1 ae = k_1 a - k_1 ae$$

$$\Rightarrow ae(k_1 + k-1) = k_1 a - k_1 b$$

$$\Rightarrow q_e = \frac{k_1 a - k_2 b}{k_1 + k_2} \quad \text{--- (xix)}$$

Substituting (xix) in eqⁿ (xviii), we get

$$k_1 = \frac{b + \frac{(k_1 a - k_2 b)}{k_1 + k_2} \ln \left(\frac{q_e}{m_e - q_e} \right)}{t(a+b)}$$

$$\Rightarrow k_1 = \frac{b(k_1 + k_2) + (k_1 a - k_2 b)}{t(a+b)(k_1 + k_2)} \ln \left(\frac{q_e}{m_e - q_e} \right)$$

$$= \frac{b k_1 + a k_2}{t(a+b)(k_1 + k_2)} \ln \left(\frac{q_e}{m_e - q_e} \right)$$

$$\Rightarrow k_1 = \frac{k_1 (a+b)}{t(a+b)(k_1 + k_2)} \ln \left(\frac{q_e}{m_e - q_e} \right)$$

$$\Rightarrow \boxed{k_1 + k_2 = \frac{1}{t} \ln \left(\frac{q_e}{m_e - q_e} \right)} \quad \text{--- (xx)}$$