Lindemann's Theory of Unimolecular Reactions

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

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

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$$\frac{d[A^*]}{dt} = K_1[A]^2 - K_{-1}[A^*][A] - K_2[A^*]$$

CHEM

Lindemann's Theory of Unimolecular Reactions

PRI

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$$K_1[A]^2 = K_{-1}[A^*][A] + K_2[A^*]$$

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$$\frac{dP}{dt} = K_2[A^*]$$

$$\boxed{r = \frac{K_2 K_1[A]^2}{K_{-1}[A] + K_2}}$$

Case(i) Reactt conc ↑ P ↑

$$K_{-1}[A] >> K_2$$

$$rate = \frac{K_1 K_2 [A]^2}{K_{-1}[A]}$$

$$rate = K(A)^1$$

first order

Case ii) reactt conc ↓

Product ↑

$$K_2 >> K_{-1}[A]$$

$$\text{rate} = \frac{\cancel{K_2} K_1 (A)^2}{\cancel{K_2}}$$

$$\text{rate} = K_1 [A]^2$$

2nd or

Kinetics of Reversible

$$A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} B$$

K inverse 1

initial time	a	0
at time t	$(a-x)$	x

rate for forward reaction $r = k_1 (a-x)$

backward " $r = k_{-1} x$

Net rate of formation of B $\frac{dx}{dt} = k_1 (a-x) - k_{-1} x$ — (1)

Substract the backward reaction rate from forward reaction rate

Kinetics of Reversible or opposite Reactions

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

k inverse 1

rate for forward reaction $r = k_1 (a-x)$

backward " $r = k_{-1}\, x$

initial time a 0

at time t $(a-x)$ x

$\boxed{\text{Net rate of formation of B}}$ $\dfrac{dx}{dt} = k_1 (a-x) - k_{-1} x$ — ①

Substract the backward reaction rate from forward reaction rate

After some time equilibrium will be stabilized.

at equilibrium suppose the conc. of $B = x_e$

the Conc. of A at equilibrium is $(a-x_e)$

$$k_1 (a-x_e) = k_{-1}\, x_e$$

So ... putting this value in eq ①

$$k_1(a - x_e) = k_{-1}\, x_e$$

So $\boxed{k_{-1} = \dfrac{k_1(a-x_e)}{x_e}}$ → Now putting this value in eq (1)

So $$\frac{dx}{dt} = k_1(a-x) - \frac{k_1(a-x_e)}{x_e}\cdot x$$

$$\frac{dx}{dt} = \frac{k_1 a(x_e - x)}{x_e}$$

$$\int_0^x \frac{dx}{x_e - x} = \frac{k_1 a}{x_e}\,[t]_0^t$$

$$\cancel{\ln \frac{x_e}{x_e - x} = \frac{k_1 a}{x_e}}$$

$$-[\ln(x_e - x)]_0^x = \frac{k_1 a}{x_e}\,[t]_0^t$$

... variables at same side.

$$-\left[\ln(x_e - x)\right]_0^x = \frac{k_1 a}{x_e}\left[t\right]_0^t$$

$$\ln\left(\frac{x_e}{x_e - x}\right) = \frac{k_1 a t}{x_e}$$

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thus $\boxed{k_1 = \frac{x_e}{at} \ln \frac{x_e}{x_e - x}}$