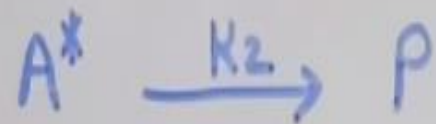
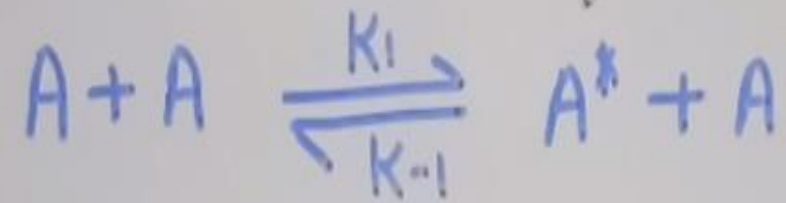
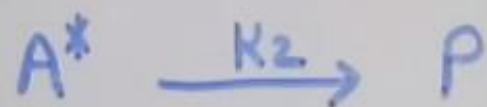
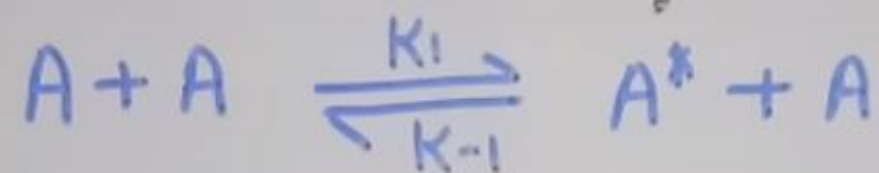


Lindemann's Theory of Unimolecular Reactions

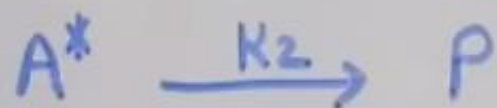
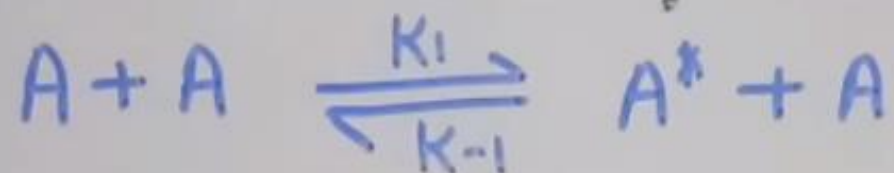


Lindemann's Theory of Unimolecular Reactions



$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*]$$

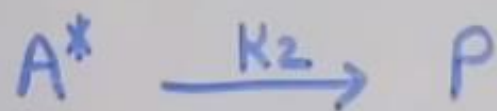
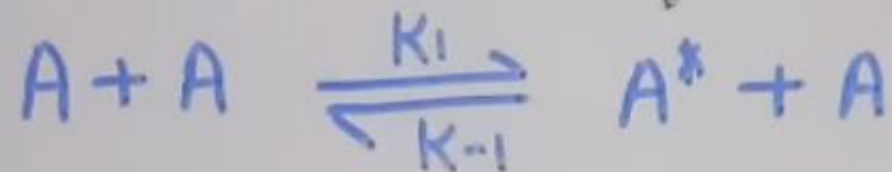
Lindemann's Theory of Unimolecular Reactions



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

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

Lindemann's Theory of Unimolecular Reactions

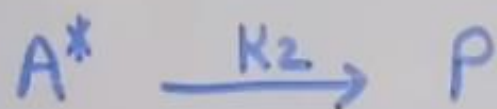
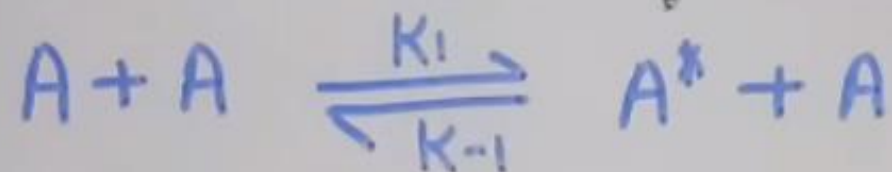


$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] = 0$$

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

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

Lindemann's Theory of Unimolecular Reactions



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

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

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

$$\frac{dP}{dt} = k_2[A^*]$$

$$\boxed{\mathcal{R} = \frac{k_2 k_1 [A]^2}{k_{-1}[A] + k_2}}$$

Case (i)

React conc \uparrow $P \uparrow$

$$K_{-1}[A] \gg K_2$$

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

$$\text{rate} = K[A] \rightarrow \text{first order}$$

Case ii)

reactant conc \downarrow

Product \uparrow

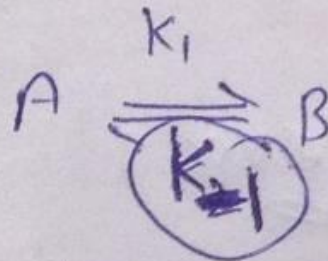
$$K_2 \gg K_{-1}[A]$$

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

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

2nd order

Kinetics of Reversible



$k_{\text{reverse } 1}$

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

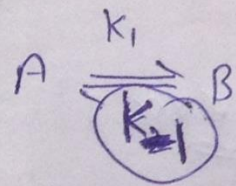
rate ~~of~~ ^{for} forward reaction $r = k_1 (a-x)$

backward $r = k_{-1} x$

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

↓
Subtract the backward reaction rate
from forward reaction rate

Kinetics of Reversible or opposite reactions



$k_{\text{inverse 1}}$

initial time a 0

at time t $(a-x)$ x

rate ~~of~~ 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

↓
Subtract 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 $\xrightarrow{\hspace{2cm}}$

putting this value in eq. ①

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

So

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

Now putting this value in eq ①

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

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

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

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

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

variables at same side

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

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

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

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

thus

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