$Z(n_1, n_2, \ldots)$ → implicit dependence on t

$$\frac{dZ}{dt}$$

$CH_3COOC_2H_5 \longrightarrow CH_3COOH + C_2H_5OH$

NaOH

Z → vol of

$$\text{Rate} = k[A]^{\alpha}[B]^{\beta}\ldots$$

$$H_2 + Br_2 \rightleftharpoons 2HBr$$

$$\text{Rate} = k\frac{[H_2][Br]^{1/2}}{1 + m[H_2][Br_2]}$$

Determine the rate law

$$A \rightarrow \text{products}$$

$$-\frac{d[A]}{dt} = k[A] \quad \text{(Lindemann)}$$

$$[A](t) = [A]_0 e^{-kt} \longrightarrow \text{conc}$$

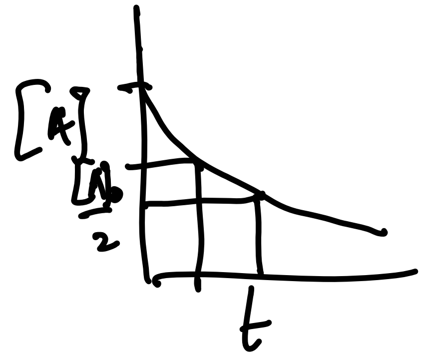
$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$

Half-life – $t_{1/2}$

$$\boxed{t_{1/2} = \frac{0.693}{k}}$$

$\text{Rate} = k[N_2O_5]$

$$-\frac{d[A]}{dt} = k[A]^2$$



$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

$$t_{1/2} \propto \frac{1}{[A]_0^{(n-1)}}$$

$A + B \rightleftharpoons$ Products

$$-\frac{d[A]}{dt} = k[A][B]$$

$$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[A][B]_0}{[B][A]_0}$$

$$\text{Rate} = k[A]^{\alpha}[B]^{\beta} \ldots$$

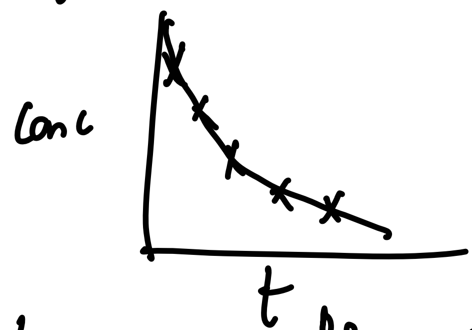
Method of Isolation

Conc of all but one species is high

$$\text{Rate} = k'[A]^{\alpha}$$

$$-\frac{d[A]}{dt} = -\frac{\Delta[A]}{\Delta t}$$ for small times

Method of isolation in combination with the method of half-lives



Opposing reaction

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \quad / \quad A + B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C + D$$

$$-\frac{d[A]}{dt} = k_2[A][B] - k_{-2}[C][D]$$

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]$$

At $t = 0$, $[B] = 0$

$$[B](t) = [A]_0 - [A]$$

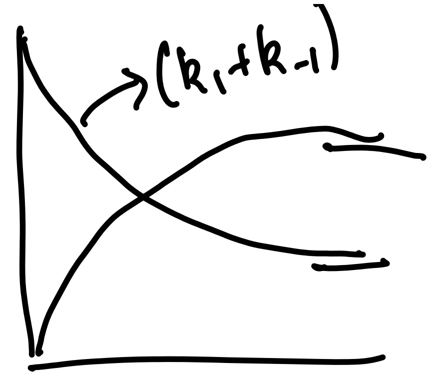
$$-\frac{d[A]}{dt} = (k_1 + k_{-1})[A] - k_{-1}[A]_0$$

At equilibrium,

$$k_{-1}[A]_0 = (k_1 + k_{-1})[A]_{eq}$$

$$-\frac{d}{dt}([A] - [A]_{eq}) = (k_1 + k_{-1})([A] - [A]_{eq})$$

$$\frac{[B]_{eq}}{[A]_{eq}} = \frac{k_1}{k_{-1}} = K$$ [A]



$$H^+ + OH^- \rightleftharpoons H_2O$$

25°C → 35°C

Relaxation kinetics - Manfred Eigen

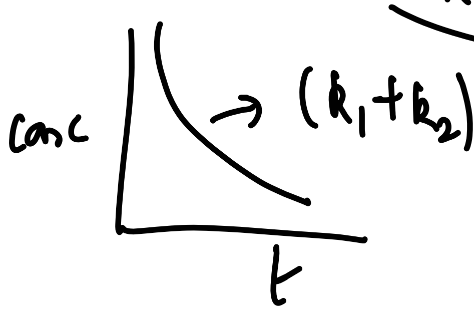
Parallel reactions

$$A \xrightarrow{k_1} B$$
$$A \xrightarrow{k_2} C$$

$$-\frac{d[A]}{dt} = (k_1+k_2)[A]$$

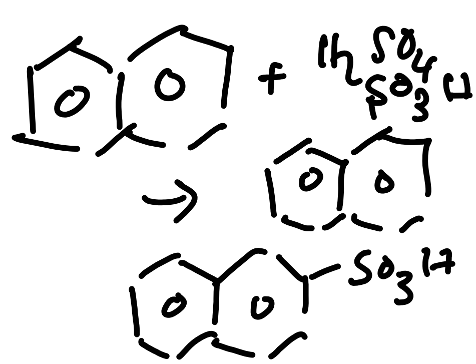
$$[A] = [A]_0 e^{-(k_1+k_2)t}$$

$$\frac{d[B]}{dt} = k_1 [A]_0 e^{-(k_1+k_2)t}$$



$$\frac{[C]}{[B]}(t) = \frac{k_2}{k_1}$$

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$
$$A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C$$



$k_1 = 1/s \quad k_2 = 1000/s$

At short times, $[C] >> [B]$

$k_{-1} = 0.001/s \quad k_{-2} = 100/s$

$\frac{k_1}{k_{-1}} = 1000 \qquad \frac{k_2}{k_{-2}} = 10$

Kinetic vs Thermodynamic control

Consecutive Reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

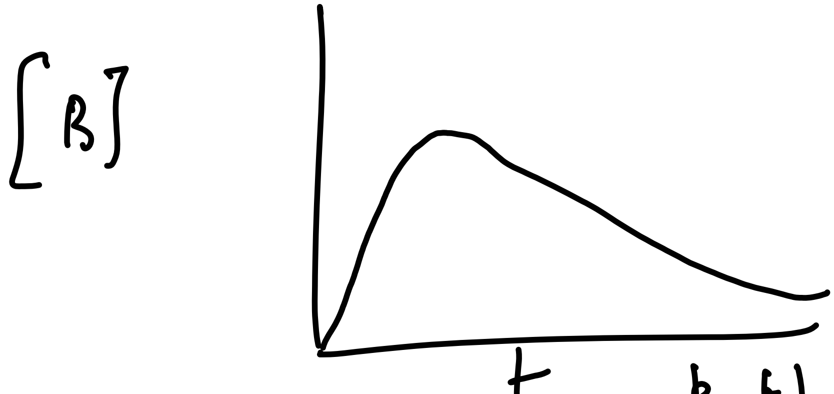
$$-\frac{d[A]}{dt} = k_1 [A]$$

$$-\frac{d[B]}{dt} = k_2 [B] - k_1 [A]$$

$$\frac{d[C]}{dt} = k_2 [B]$$

$$[A] = [A]_0 e^{-k_1 t}$$

$$-\frac{d[B]}{dt} = k_2 [B] - k_1 [A]_0 e^{-k_1 t}$$



$$[B](t) = \frac{k_1[A]}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

Two limiting cases: $k_1 \ll k_2$

→ Rate determining step