Rate Laws (McQuarrie Ch28)

$$aA + bB \rightleftharpoons gG + hH$$

$\sum \nu_i I = 0$ eg $\nu_A = -a$

$\nu_G = g$

Reaction coordinate ξ

$$n_A(t) = n_A(0) + \nu_A \xi(t) = n_A(0) - a\xi(t)$$

$$n_G(t) = n_G(0) + \nu_G \xi(t) = n_G(0) + g\xi(t)$$

Eg:

$$n_A(t) = \underset{\curvearrowleft}{n_A}(0) + \nu_A \xi(t) = n_A(0) - a\xi(t)$$

$$\Delta n_A(t) = n_A(t) - n_A(0) = \nu_A \xi(t)$$

$$\Delta n_i(t) = \nu_i \xi(t)$$

limit where t is small

$$\xi = d\xi \qquad \Delta n = dn$$

differential

$$dn_i = \nu_i d\xi$$

$$dn_i = \nu_i \, d\xi$$

"divide" both sides by dt

$$\frac{dn_i}{dt} = \nu_i \frac{d\xi}{dt} \Rightarrow \frac{d\xi}{dt} = \frac{1}{\nu_i} \frac{dn_i}{dt}$$

Divide both sides by volume V

$$\underbrace{\frac{1}{V} \frac{d\xi}{dt}}_{\uparrow \text{ rate of reaction at time t}} = \frac{1}{\nu_i} \frac{d[I]}{dt} \qquad \boxed{\nu(t)}$$

$$\frac{1}{V}\frac{d\xi}{dt} = \frac{1}{\nu_i}\frac{d[I]}{dt}$$

Eg $2NO\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$

$$v(t) = -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{1}{1}\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$$

<u>Want</u> a rate law

tells us rate at time t

given concentrations

$$2NO\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$$

Elementary Reaction direct collision between molecules reacting form product, no hidden steps

$$v(t) = K\,[A]^{|\nu_A|}\,[B]^{|\nu_B|} \ldots$$

$$v(t) = k\,[NO]^2\,[O_2]^1$$

Rate law for this reaction

For most reaction, can't guess rate law, have to determine using experiments

Note: $v(t)$ always has the same units $\frac{1}{V}\frac{d\xi}{dt}$

$$\text{units} \quad \frac{\text{mole}}{\text{liter}} \cdot \frac{1}{s} = M/s \;\Lleftarrow\; \frac{\text{mol}}{s \cdot \underset{\underset{\text{liter}}{\uparrow}}{(\text{dm})^3}}$$

units of k depend on reaction

Don't know rate law, guess:

$$v(t) = K[A]^{m_A}[B]^{m_B} \cdots$$

Order is $m_A + m_B + \cdots$

m_A order in A, m_B order in B

For example

$$2NO + O_2$$

$$K[NO]^2[O_2]$$

3rd order

2nd order in NO

1st order in O_2

$$v(t) = K [A]^{m_A} [B]^{m_B}$$

v units of M/s

0th order reaction

		units of k
0	$v(t) = K$	M/s
1st	$v(t) = k[A]$	$1/s$
2nd	$v(t) = K[A]^2$ $= K[A][B]$	$1/M \cdot \frac{1}{sec}$

Can also have rate laws
aren't in this form

$$H_2 + Br_2 \rightarrow 2HBr$$

$$v(t) = \frac{k'[H_2][Br_2]^{1/2}}{1+k''[HBr][Br_2]^{-1}}$$

↳ multi step reaction

Next chapter: reaction mechanisms

How do we determine rate laws using experiments

① Method of isolation

$$aA + bB \rightarrow \underline{\qquad\qquad}$$

$$v = k\,[A]^{m_A}\,[B]^{m_B}$$

Make A in excess (a lot)

$$k[A]_0^{m_A} \equiv k'$$

$$\left[\, k[B]_0^{m_B} \equiv k'' \,\right]$$

$$v(t) = k'[B]^{m_B}$$

$$-\frac{1}{b}\frac{d[B]}{dt} = v(t)$$ Measure

give us k' & m_B

$$\ln(\underline{v(t)}) = \underset{\uparrow}{m_B} \ln\underline{[B]} + \underset{\uparrow}{\ln(k')}$$

Make B in excess $v(t) = k''[A]^{m_A}$

$$\ln(v(t)) = m_A \ln[A] + \ln(k'')$$

But - can't always have a big excess

② Method of initial rates

$[A]_0$, $[B]_0$

$$v(t) \approx -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = k[A]_0^{m_A}[B]_0^{m_B}$$

Do multiple measurements

$$\left.\begin{aligned} v_1 &= k[A]_0^{m_A}[B]_1^{m_B} \\ v_2 &= k[A]_0^{m_A}[B]_2^{m_B} \end{aligned}\right\} \text{2 experiments}$$

a) $$\left.\begin{aligned} v_1 &= k\,[A]_0^{m_A}\,[B]_1^{m_B} \\ v_2 &= k\,[A]_0^{m_A}\,[B]_2^{m_B} \end{aligned}\right\}\ \text{2 experiments}$$

$$\underset{\nearrow\ \text{measure}}{v_1/v_2} = \Bigg(\underset{\nwarrow\ \text{determine}}{\frac{[B]_1}{[B]_2}}\Bigg)^{m_B} \leftarrow \text{unknown}$$

$$m_B = \ln(v_1/v_2)\Big/\ln\left(\frac{[B]_1}{[B]_2}\right)$$

b) Do same to get m_A

c) $v(t) = k[A]_x^{m_A}[B]_y^{m_B}$

a&b we got m_A, m_B

	$v(t)$	$[A]$	$[B]$	$[A]^{m_A}[B]^{m_B}$
expt 1	—	—	—	—
expt 2	—	—	—	-
expt 3	—	—	—	—

$\Bigg\}\ k$

$k_{est\,1}, k_{est\,2}, k_{est\,3}$

Limitation here: for slowish reactions

First order reactions

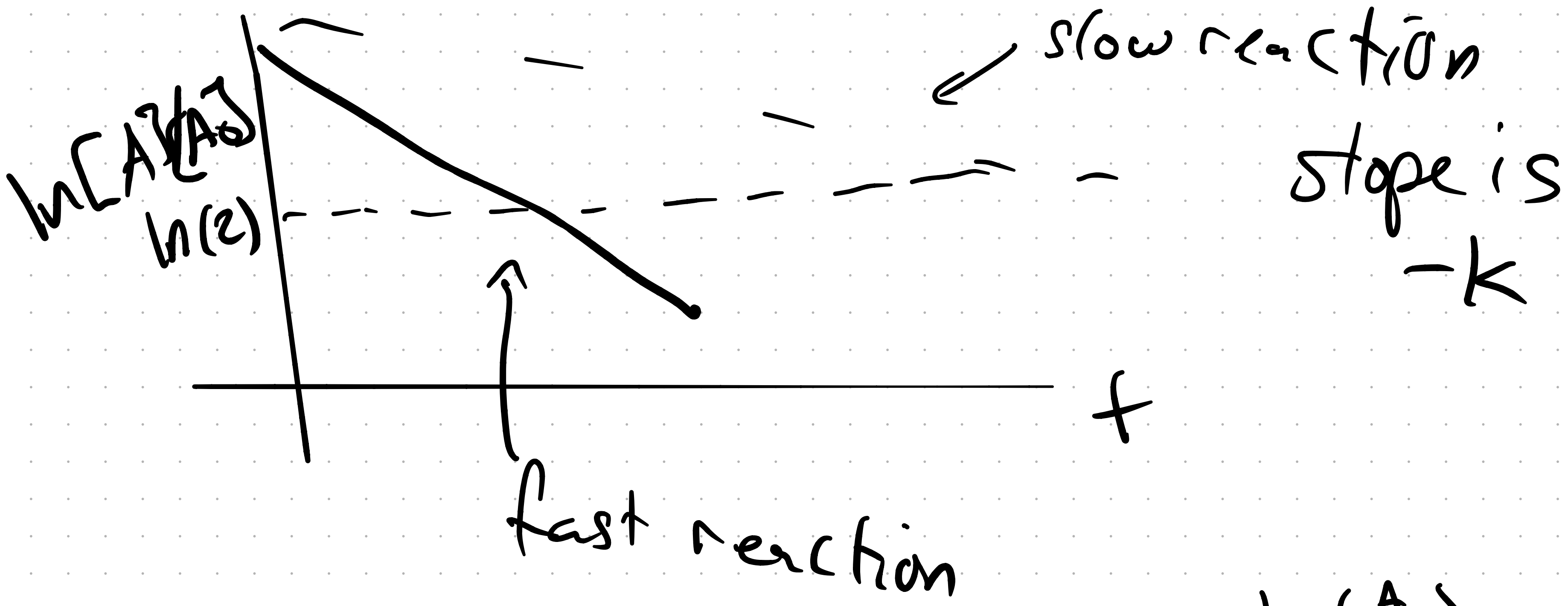
$$A \rightarrow aB + cD + \ldots$$

$$\nu(t) = k[A]$$

$$= -\frac{d[A]}{dt} = k[A] \Rightarrow \frac{1}{[A]}\frac{d[A]}{dt} = -k$$

$$[A](t) = [A]_0 e^{-kt}$$

plot $\ln\left([A](t)/[A]_0\right)$ vs t is linear



$$\ln\left(\frac{A}{A_0}\right) = -kt$$

Special property

$$[A](t_{1/2}) = \frac{1}{2}[A_0]$$

$$\ln(1/2) = -k t_{1/2} \Rightarrow t_{1/2} = \frac{\ln(2)}{k} \approx \frac{0.693}{k}$$

time is independent of initial concentration

$A \to aB$ Example 28-3

$$-\frac{dA}{dt} = \underline{\underline{k[A] = \frac{1}{b}\frac{d[B]}{dt}}}$$

$$\frac{d[B]}{dt} = bk[A] = bk[A]_0\, e^{-kt}$$

$$B(\tau) - B(0) = \int_0^{\tau} dt\; bk[A]_0\, \underline{\underline{e^{-kt}}}$$

$$\int e^{-kt} = -\frac{1}{k}e^{-kt}$$

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$$\int e^{-kt} = -\frac{1}{k} e^{-kt}$$

$$= b[A]_0 \left(1 - e^{-k\tau}\right)$$

$$[B](\tau) = [B]_0 + b[A]_0 \left(1 - \underline{\underline{e}}^{-k\tau}\right)$$

2nd order

k[A][B]?

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

check

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

plot $\frac{1}{[A]}$ vs time, slope = rate constant

$$t_{1/2} = \frac{1}{k[A]_0}$$

depends on how much you start with

Reversible Reactions

$$A \underset{k_{-1}}{\overset{k}{\rightleftharpoons}} B$$ as example

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} \Rightarrow \frac{d[A]}{dt} + \frac{d[B]}{dt} = 0$$

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

$$[A] + [B] = \text{constant}$$

$$[A] + [B] = \text{const}$$

start expriment with $[B]_0 = 0$

$$[B] = [A]_0 - [A]$$

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

$$= -(k+k_{-1})[A] + k_{-1}[A]_0$$

check

$$[A] - [A]_{eq} = ([A]_0 - [A]_{eq})e^{-(k+k_{-1})t}$$

$$[A]-[A]_{Eq}=\left([A]_0-[A]_{Eq}\right)e^{-(k+k_{-1})t}$$