Rate Laws (McQuarrie Ch 28)

Previously $aA + bB \rightleftharpoons gG + hH$

said $\sum \nu_i I = 0$ where $\nu_A = -a$ e.g.

$\nu_g = +g$

There is a reaction coordinate ξ

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

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

In differential form

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

This means if $d\xi$ moles of reaction occur,

the moles of products increase by $\nu_i d\xi$

or reactants decrease by $\nu_i d\xi$

Now we are interested in kinetics, how fast does this occur

$dn_i = \nu_i \, d\xi$, "divide by" dt

ν_i ≈ constant

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

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

If we want concentration units, divide by total volume

$$\underbrace{\frac{1}{V}\frac{d\xi}{dt}}_{\text{rate of reaction } v(t)} = \frac{1}{\nu_i}\frac{d[I]}{dt}$$

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

one way

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

if we can measure any of these concentrations vs time, we can get the rate from the slope

Want a rate law, something that tells us the rate given only the current concentrations

Reaction laws often have the form

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

For **Elementary Reactions**, direct collission between molecules, no hidden steps

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

But for a given reaction, has to be determined experimentally

Note: $v(t)$ always has units of

$$\text{Molar/sec} = \frac{\text{mol}}{L\,\text{sec}} = \frac{\text{mol}}{(dm)^3\,\text{sec}} \quad \leftarrow \text{in book}$$

$1\,ml = 1\,(cm)^3 \Rightarrow 1\,L = 1000\,(cm)^3 = 1000\left(\frac{dm}{10}\right)^3 = dm^3$

$1\,dm = 10^{-1}\,m = 10\,cm$

so units of k depend on reaction mechanism!

Order of reaction $= \sum m_i$

So $2NO + O_2$ reaction is

3rd order in total, 2nd in NO & 1st in O_2

	k units
0th order:	M/s
1st order	1/s etc
2nd order	1/s M

Can have fractions too for complex reactions

Can also have non-intuitive rate laws that don't have a simple order

$$H_2 + Br_2 \rightarrow 2HBr$$

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

↑ multistep process, next lecture

How to measure rate laws

① Method of isolation: $aA + bB \rightarrow$ ___

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

Make A in huge excess, so $k[A]_0^{m_A} \equiv k'$ is approximately a constant

Then measure $v(t)$ for several B to get k' and m_B

then switch to an excess of B

Then should have k, m_A, m_B

(2) Method of initial rates

Can't always have a big excess

If we have measurements of eg $d[A]/dt$ for several $[A]_0, [B_0]$

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

More accurate for $\Delta t \to 0$

Can do two measurements

$$v_1 = k[A]_0^{m_a}[B]_1^{m_b}$$

$$v_2 = k[A]_0^{m_a}[B]_2^{m_b}$$

then $$v_1/v_2 = \left(\frac{[B]_1}{[B]_2}\right)^{m_b}$$

($[B]_1$: measured; $[B]_2$: measured)

$$m_B = \ln(v_1/v_2) \,/\, \ln([B]_1/[B]_2)$$

and then same for M_a

Do example as extra exercise

★ sometimes the time to mix is limiting process, and then we can't find reaction mechanism this way this will be solved by relaxation methods

First!

① 1st order reactions decay exponentially

$A \rightarrow bB + cC$

If $v(t) = -\frac{1}{1}\frac{d[A]}{dt} = k[A]$

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

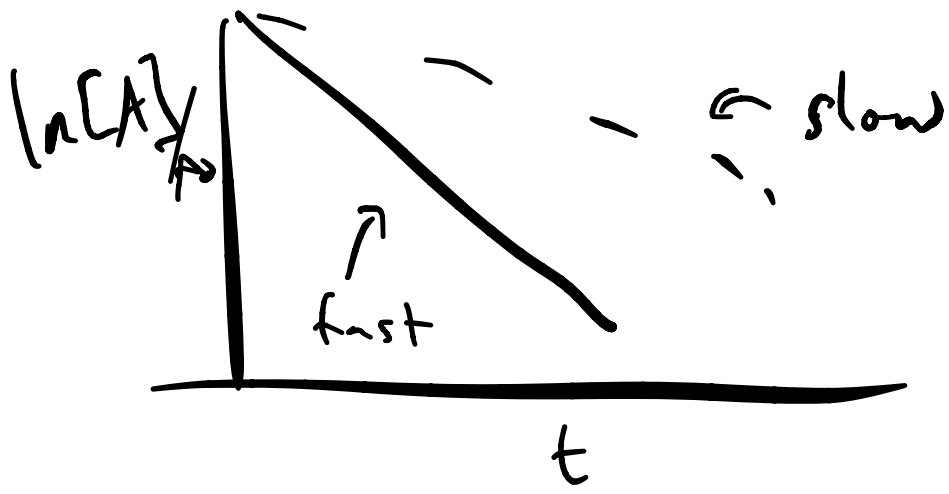
$$\Rightarrow \ln [A]/[A]_0 = -kt$$

$$\text{or } [A] = [A_0]e^{-kt}$$

k has units of ^{1}/time

If this is case

ln [A](t) is linear in t



Special property of first order

$$[A](t_{1/2}) = [A]_0/2$$

$$\ln(1/2) = -k t_{1/2}$$

$$t_{1/2} = \text{half life} = \ln 2/k \approx \frac{0.693}{k}$$

independent of initial concentration!

See: eg radio carbon dating

Example 26-3: rak for products

suppose $A \rightarrow bB$

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

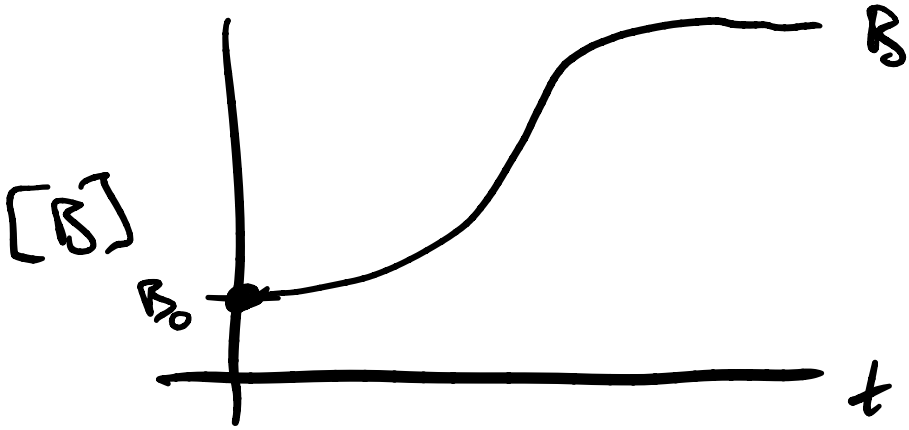
$$\text{so } \frac{d[B]}{dt} = bk[A] = bk[A]_0 e^{-kt}$$

integrating,

$$[B](t) = [B]_0 + bk[A_0]\int_0^t e^{-kt}\,dt$$

$$t\ \frac{-1}{k}e^{-kt}\Big|_0^t$$

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



if no reverse reaction this is what exponential growth looks like

2nd Order

$$-\frac{d[A]}{dt} = k[A]^2 \Rightarrow \frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

plot of $\frac{1}{[A]}$ vs time, slope gives rate

half life: $\frac{2}{[A]_0} = \frac{1}{[A]_0} + k t_{1/2}$

$t_{1/2} = \frac{1}{k[A]_0}$, depends on initial concentrations

$v(t) = k[A][B]$ addressed in homework 28-24, 28-25

Reversible Reactions

$A \rightleftarrows B$ example

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0 \text{ @ eq}$$

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

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

if $[B]_0 = 0$, then $[B] = [A]_0 - [A]$

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

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

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

$u = (k+k_{-1})[A] - k_{-1}[A]_0 \qquad u(0) = k[A]_0$

$du = (k+k_{-1})\,d[A]$

$\Rightarrow \frac{du}{u} = -(k+k_{-1})\,dt$

$\ln u/u_0 = -(k+k_{-1})t$

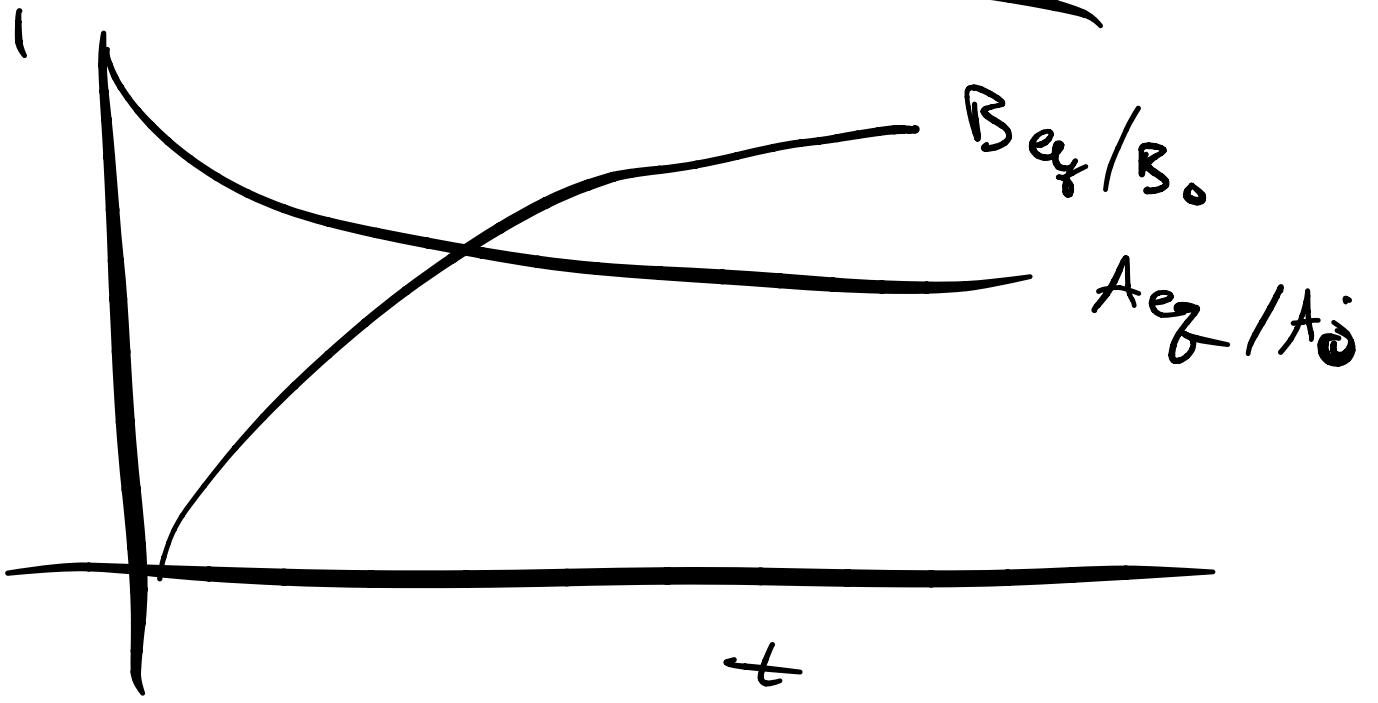
$(k+k_{-1})[A] - k_{-1}[A]_0 = k[A]_0 e^{-(k+k_{-1})t}$

As $t \to \infty$ goes to eq

@ eq $k[A]_{eq} = k_{-1}[B]_{eq}$

$$[A]_0 = \frac{(k + k_{-1})[A]_{eq}}{k_{-1}} \Rightarrow [A]_{eq} = \frac{k_{-1}[A]_0}{k + k_{-1}}$$

$$\text{So } [A] - [A]_{eq} = \frac{k}{k + k_{-1}} [A_0] e^{-(k + k_{-1})t}$$

$$[A]_0 - [A]_{eq} = \frac{k[A]_0}{k + k^{-1}}$$

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