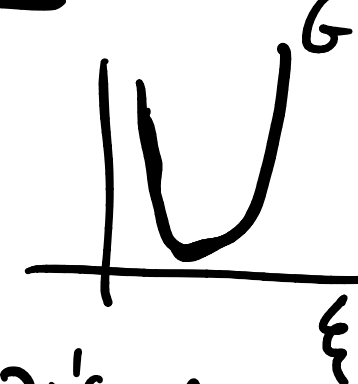
# Rate Laws ( Ch 28 McQuarrie)

$$aA + bB \rightleftharpoons cC + dD$$

Reaction coordinate $\xi$

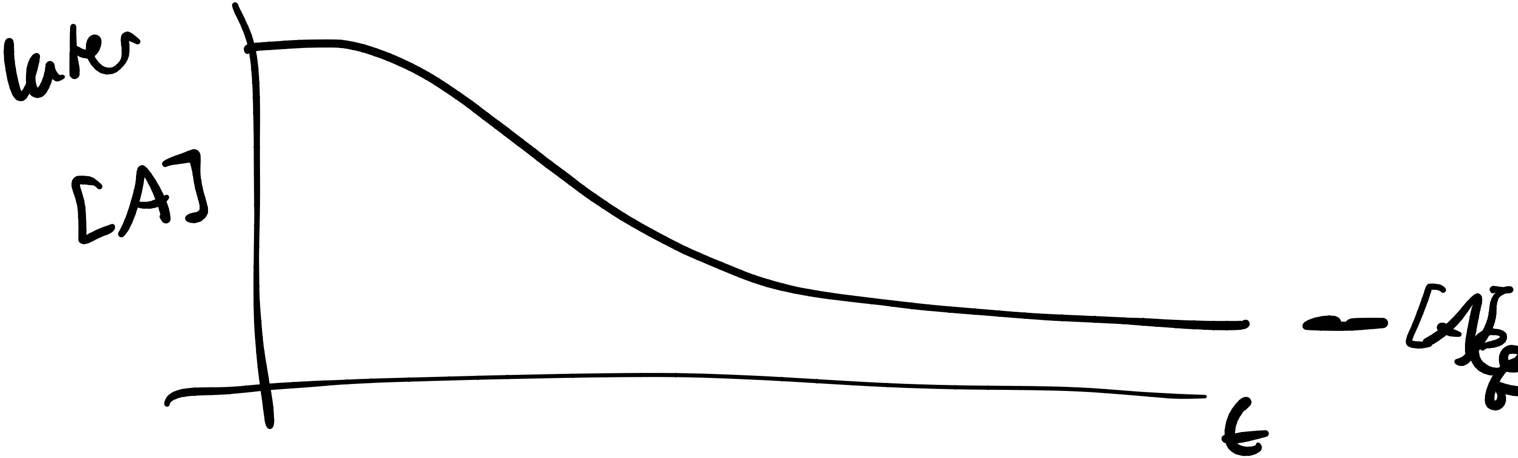



$\nu$'s neg for reactants

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

$$\vdots$$

$$n_D(t) = n_D(0) + \underset{+d}{\nu_D}\, \xi(t)$$




$$\lim_{t \to 0} \frac{n_A(t) - n_A(0)}{t} = \frac{\nu_A[\xi(t) - \xi(0)]}{t}$$

$$dn_A/dt = \nu_A \, d\xi/dt$$

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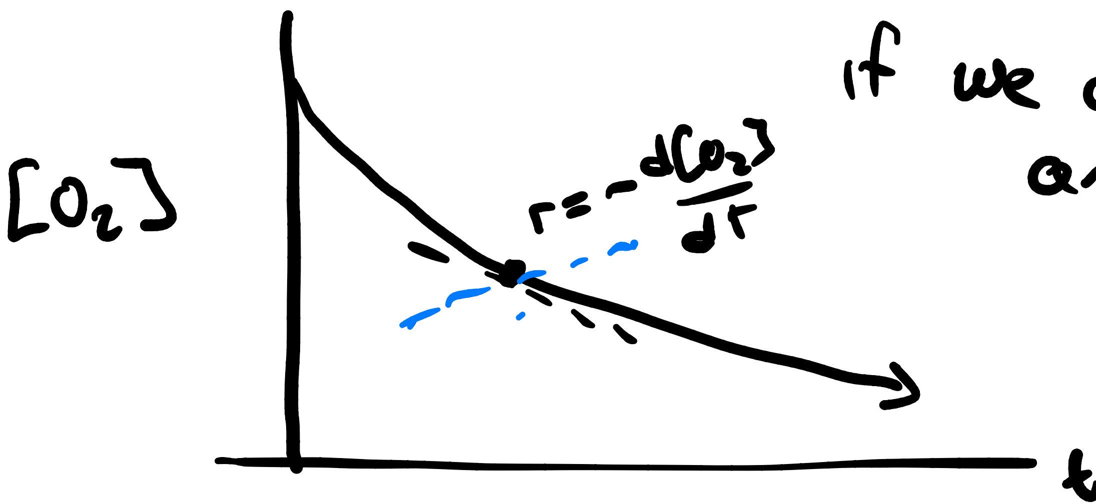
$$\frac{d\xi/dt}{V} = \frac{\frac{1}{\nu_A}\, dn_A/dt}{V} = \frac{\frac{1}{\nu_B}\frac{dn_B}{dt}}{V} \cdots$$

<u>reaction rate</u>

$$r(t) = \frac{1}{V}\frac{d\xi}{dt}$$

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

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




if we can measure any concentration

Goal: a <u>rate law</u> tells us the rate given just concentrations

Usually looks like

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

Special case - <u>elementary reaction</u>

reactants collide with eachother

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

so could be

$$= k [NO]^2 [O_2]$$

**Key** Have to determine rate law experimentally

Eg $H_2 + Br_2 \Rightarrow 2HBr$

actually a multistep process

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

## Important to consider units

$r(t)$ always has units $\frac{M}{s} = \frac{mol}{L\,s}$

$$\frac{mol}{L\,s} = \frac{mol}{(dm)^3\,s}$$

$dm = 10\,cm$

$ml = cm^3$

$$r(t) = k\,[A]^{m_A}\,[B]^{m_B} \cdots$$

$2NO + O_2$

$2^{nd}$ in NO

$1^{st}$ in $O_2$

nth order reaction – $n = \sum m_i$

Units of k

| | $k$ |
|---|---|
| 0th order reaction | $M/s$ |
| 1st order reaction | $1/s$ |
| 2nd order | $1/sM$ |
| etc | |

most common

# How do we figure out rate laws

① method of isolation

$$aA + bB \rightarrow$$

$$r(t) = k[A]^{m_A}[B]^{m_B}$$

what are $k, m_A, m_B$?

first make $[A]$ in huge excess

second make $[B]$ in huge excess

$$r(t) = \underline{k' [B]^{m_B}}$$

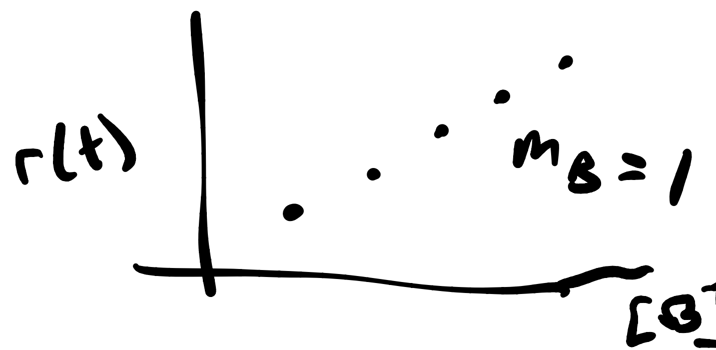
A exess

$$k' = k[A]^{m_A}$$

$$r(t) = k'' [A]^{m_A}$$

$$k'' = k[B]^{m_B}$$

for several values of B

② method of initial rates

Get measurements $d[A]/dt$
right after mixing
for different $[A]_0, [B]_0$

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

$$r_1 = k[A]_0^{m_A}[B]_1^{m_b}$$

$$r_2 = k[A]_0^{m_A}[B]_2^{m_b} \Rightarrow \underbrace{\frac{r_2}{r_1}}_{\text{measure}} = \left(\frac{[B]_2}{[B]_1}\right)^{\overline{m_b}}$$

measure

$\overline{\text{measure}}$

$$m_B = \ln(r_1/r_2) / \ln([B]_1/[B]_2)$$

...

do again

$$m_A = \ln(r_3/r_4) / \ln([A]_3/[A]_4)$$

const B

only need min 3 reactions

☆ example

Time to mix, could be limiting
can't use these techniques

## Relaxation methods

How fast something decays to equilibrium

1st order & second order reactions

① 1st order reactions

$A \to bB + cC$ [eg nuclear decay]

exponential relaxation

$$r(t) = -\frac{1}{1}\frac{d[A]}{dt} = K[A]$$

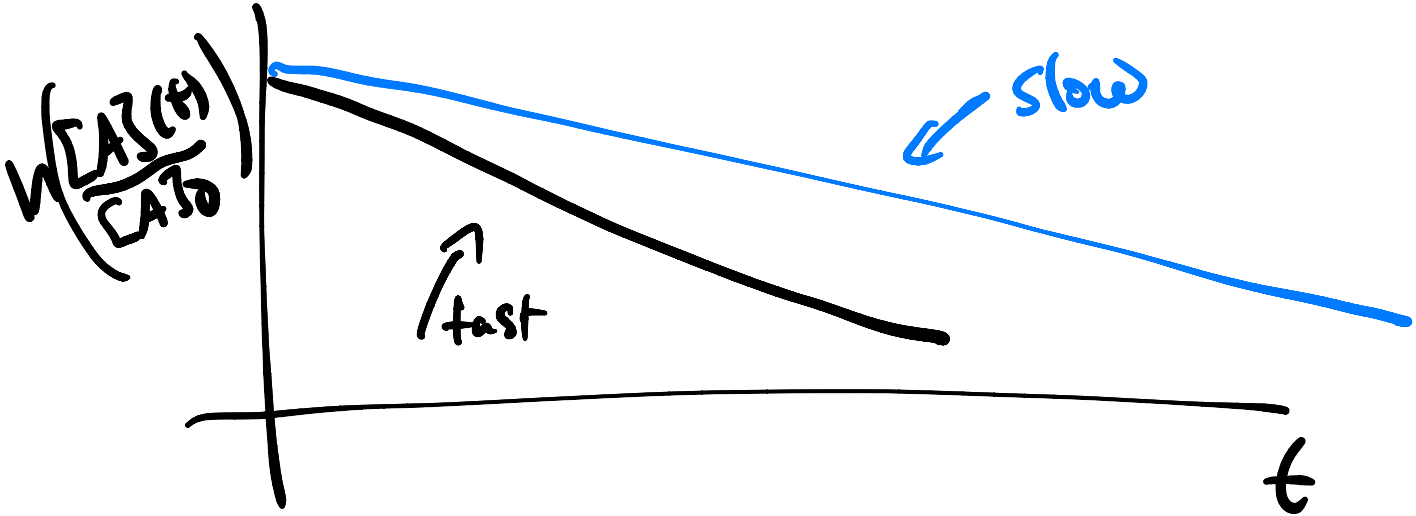
$$\frac{1}{[A]}\frac{d[A]}{dt} = -K$$

$$\int \frac{1}{[A]} \frac{d[A]}{dt} dt = \int_{t_0}^{t_1} -k \, dt$$

$$\ln \left\{ [A](t_1) / [A](t_0) \right\} = -k\Delta t$$

$$[A](\Delta t) = [A]_0 e^{-k\Delta t}$$

k has units of 1/time



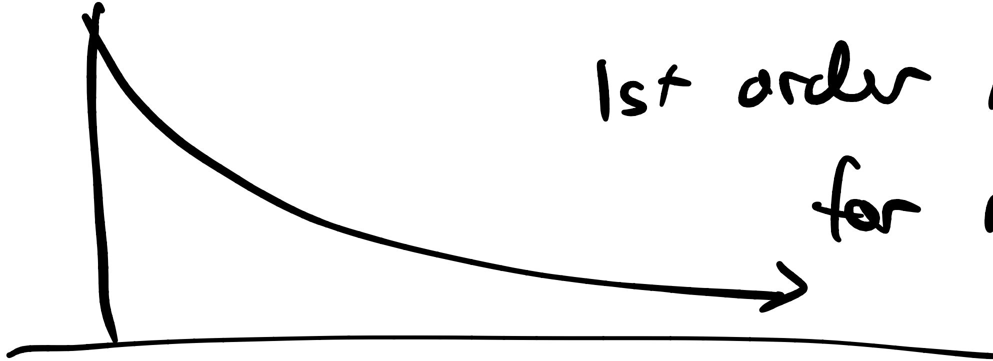

$$[A](t) = [A](0)e^{-kt}$$

when is it halfused up

$$1/2 = e^{-kt_{1/2}}$$

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

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



1st order reaction for reactant

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

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

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

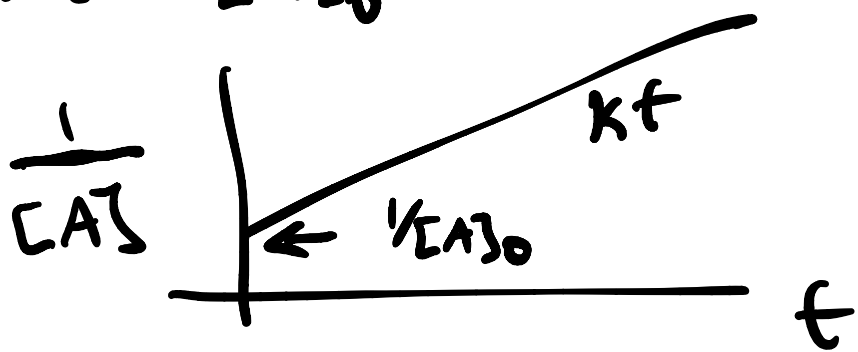
$$[B](t) = [B]_0 + b[A]_0(1 - e^{-kt})$$

# 2nd order

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

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

$\frac{1}{2[A]_0}$




$[r(t) = k[A][B]]$

28-24

-25

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

$$A \rightleftarrows B \qquad k_f \;\&\; k_b$$

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} \quad \text{at equilibrium}$$

$[A] + [B]$ is constant

$$\frac{d[A]}{dt} = -k_f[A] + k_b[B]$$

$C - [A]$

$C - [B]$

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

Assume start from all A, $[B]=0$

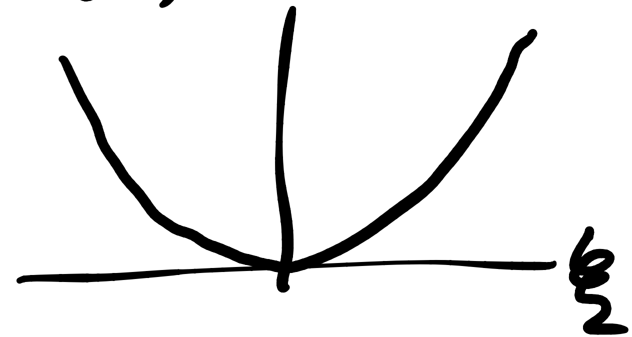
$$\frac{d[A]}{dt} = -k_f[A] + k_b([A]_0 - [A])$$

$$= -(k_f + k_b)[A] + k_b[A]_0$$

sub $u = (k_f + k_b)[A] - k_b[A]_0$

use $k_f[A]_{eq} = k_b[B]_{eq}$

$$\underbrace{[A]-[A]_{eq}}_{\xi} = ([A]_0 - [A]_{eq})e^{-k_{rxn}t}$$




$$k_{rxn} = k_b + k_f$$