$$aA + bB \underset{\leftarrow}{\rightarrow} cC$$

rate: $$\frac{1}{\underset{\nwarrow \text{ negative}}{a}}\frac{d[A]}{dt} = \frac{1}{\underset{\nwarrow \text{ negative}}{b}}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt}$$

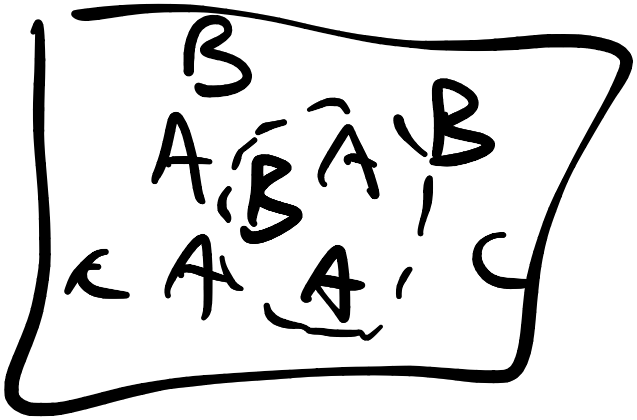
Want rate law, tells us the rate given current concentrations

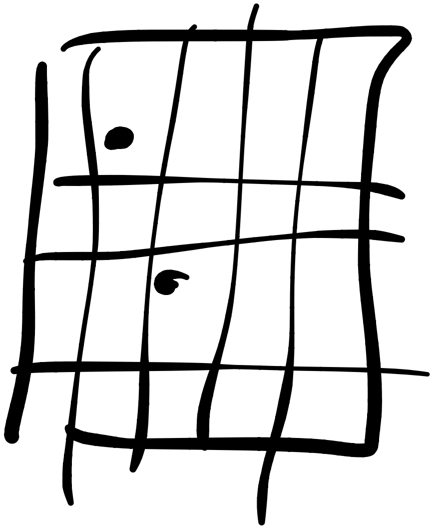
$$r(t) = k[A]^{m_A}[B]^{m_B} \ldots$$

one eqn for forward and one for backwards for elementary reaction:

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

$$2A + B \rightarrow C$$





$$K_{eq} = \frac{[C]_{eq}}{[A]^2_{eq}[B]_{eq}}$$ ← think about

rate has units of M/second
no matter what

<u>rate constants</u> have units
that differ
dep. on order rxn

1st order

$\cancel{a}A \rightarrow B$

$$\text{rate} = \cancel{-\frac{1}{a}}\frac{d[A]}{dt} = k[A]^1$$

$a = 1$

$k \sim \frac{1}{\text{sec}}$

2nd order

$2A \rightarrow B$

$$\text{rate} = -\frac{1}{2}\frac{d[A]}{dt} = k[A]^2 \qquad k \sim \frac{1}{M\,\text{sec}}$$

$A + B \rightarrow C$

2nd order

$\text{rate} = k[A]^1[B]^1 \qquad k \sim \frac{1}{M\,s}$

order sum of all the coefficients

↳ 2nd order overall

& 1st in A & 1st in B

Pathological example

$H_2 + Br_2 \rightarrow 2HBr$

$\text{rate} = k_1[H_2][Br_2]^{1/2} \cdot \left(1 + k_2[HBr][Br_2]^{-1}\right)$

How do we determine rate laws:

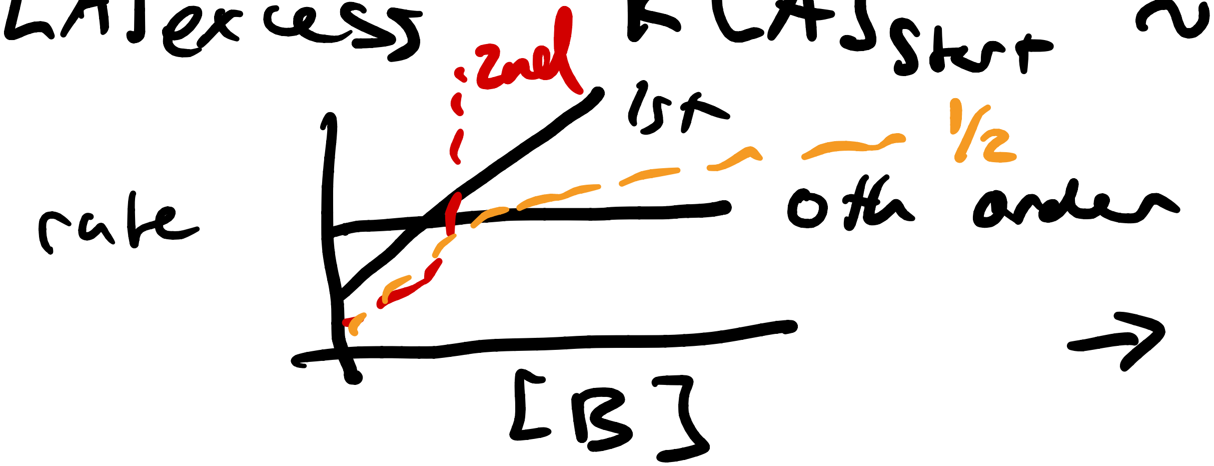
1st: method of isolation

$$aA + bB \rightarrow$$

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

Make 1 reactant in huge excess

$[A]_{excess}$ $\quad k[A]^{m_A}_{start} \sim$ constant



$\rightarrow m_B$ by fitting

& then, do the recurse to get m_A

once you know m_A & m_B

any of measurements of

rate give k

eg $r(t) = k[A]^{3/2}[B]^{2/3}$

get k from concentrations & rate measurements

② method of initial rates

$$aA + bB \rightarrow \_\_\_\_$$

$$r_{initial} = k\,[A]_{init}^{m_A}\,[B]_{init}^{m_B}$$

	rate	A	B
1	— r_1	1 mM	1 mM
2	— r_2	1 mM	2 mM
3	—	2 mM	1 mM
4	—		
5	—		

$= 2?$

$$\frac{r_2}{r_1} = \left(\frac{[B]_2}{[B]_1}\right)^{m_B} \Rightarrow m_2 = \frac{\ln(r_2/r_1)}{\ln([B]_2/[B]_1)}$$

$$r_{init} = k[A]^{m_A}[B]^2 \leftarrow \text{guess}$$

$$\underbrace{\frac{r_3}{r_2}}_{\#} = \frac{[A]_3^{m_a}}{[A]_2^{m_a}} \underbrace{\left(\frac{[B]_3}{[B]_2}\right)^2}_{\#}$$

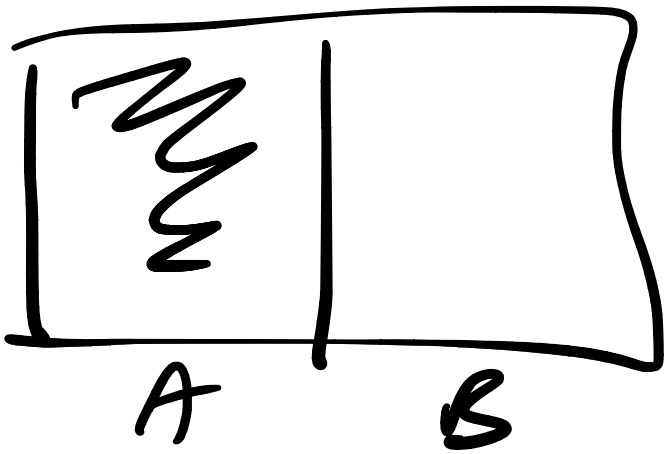
A_3/A_2

$\#$

eg $8 = 2^{m_A} \cdot 4 \Rightarrow m_A = 1$

limitation:

can't do this when mixing is slow



How does concentration look vs time?

1st order kinetics

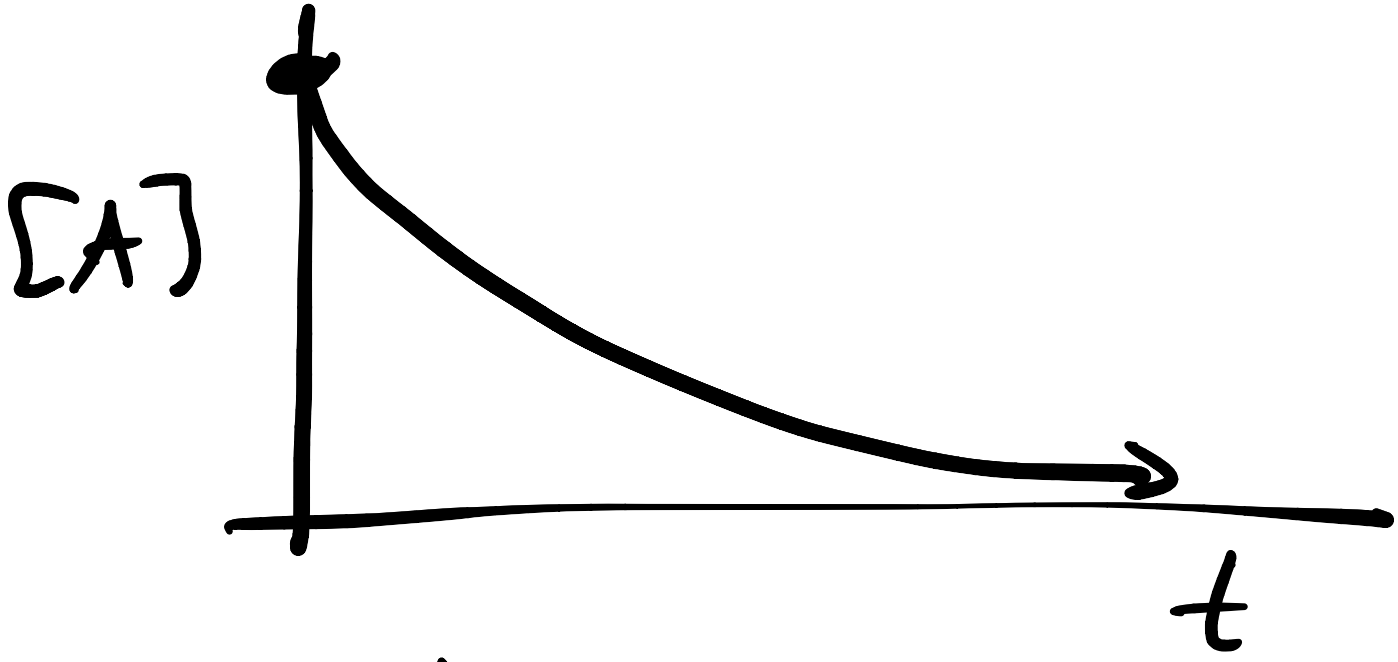
$A \rightarrow$ ______

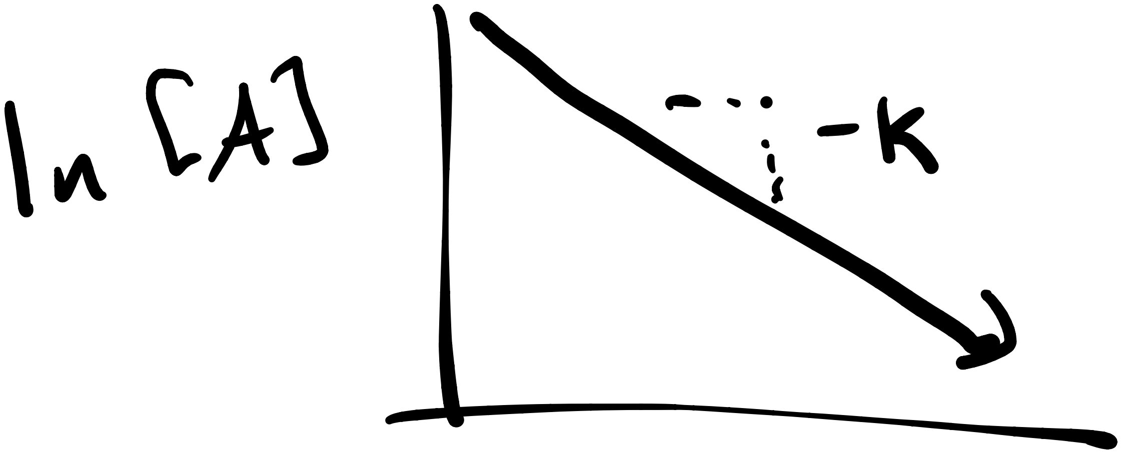
rate of loss of A

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

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

no reverse reaction





get rate
const from
slope

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

special property →

$\frac{1}{2}$ left :

$$\frac{1}{2}\cancel{[A](0)} = \cancel{[A](0)}\,e^{-kt}$$

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

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

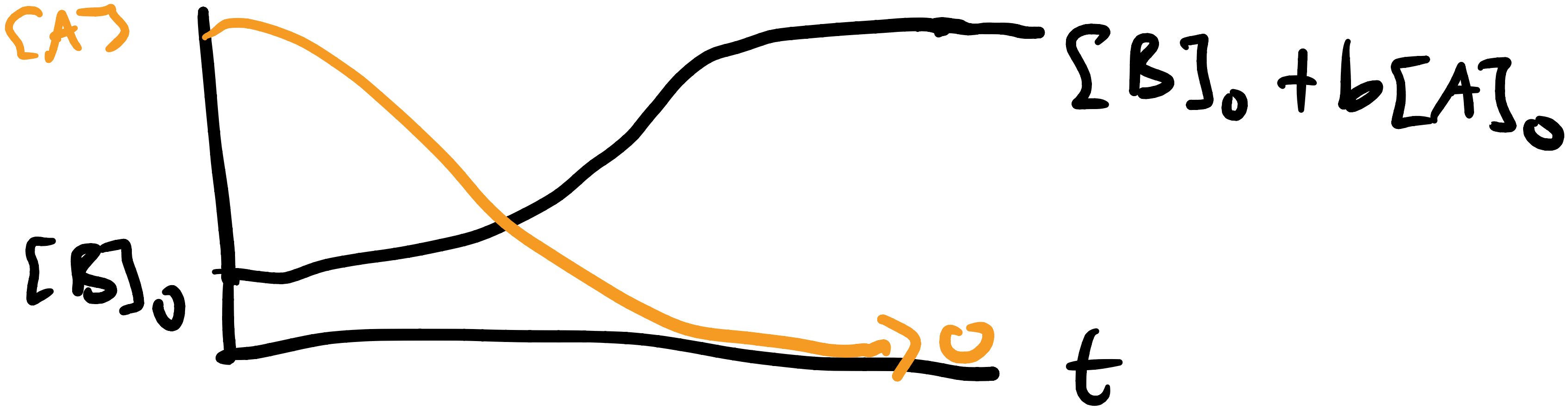
Example 28-3

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

$$\frac{d[B]}{dt} = b\left(r_{\text{forward}}\right)$$

$$= b \cdot k[A] = bk[A_0]e^{-kt}$$

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



2nd order

$$2A \rightarrow \text{——}$$

$$-\frac{1}{2}\frac{d[A]}{dt} = k[A]^2 \quad = -\frac{1}{2}\frac{d[A]}{dt}$$

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

$$\int -\underbrace{\frac{1}{2}\frac{1}{[A]^2}\,d[A]}_{\frac{1}{[A]}\Big|_{A_0}^{A(t)}} = \int k\,dt$$

$$kt\Big|_0^{t}$$

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

A+B -> ___

probs 28-24

28-25

plot $\frac{1}{[A]}$ vs time

slope gives k

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

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

depends on
starting conc

Reversible rxns (not on exam)

$$A \rightleftharpoons B$$

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

@ eq

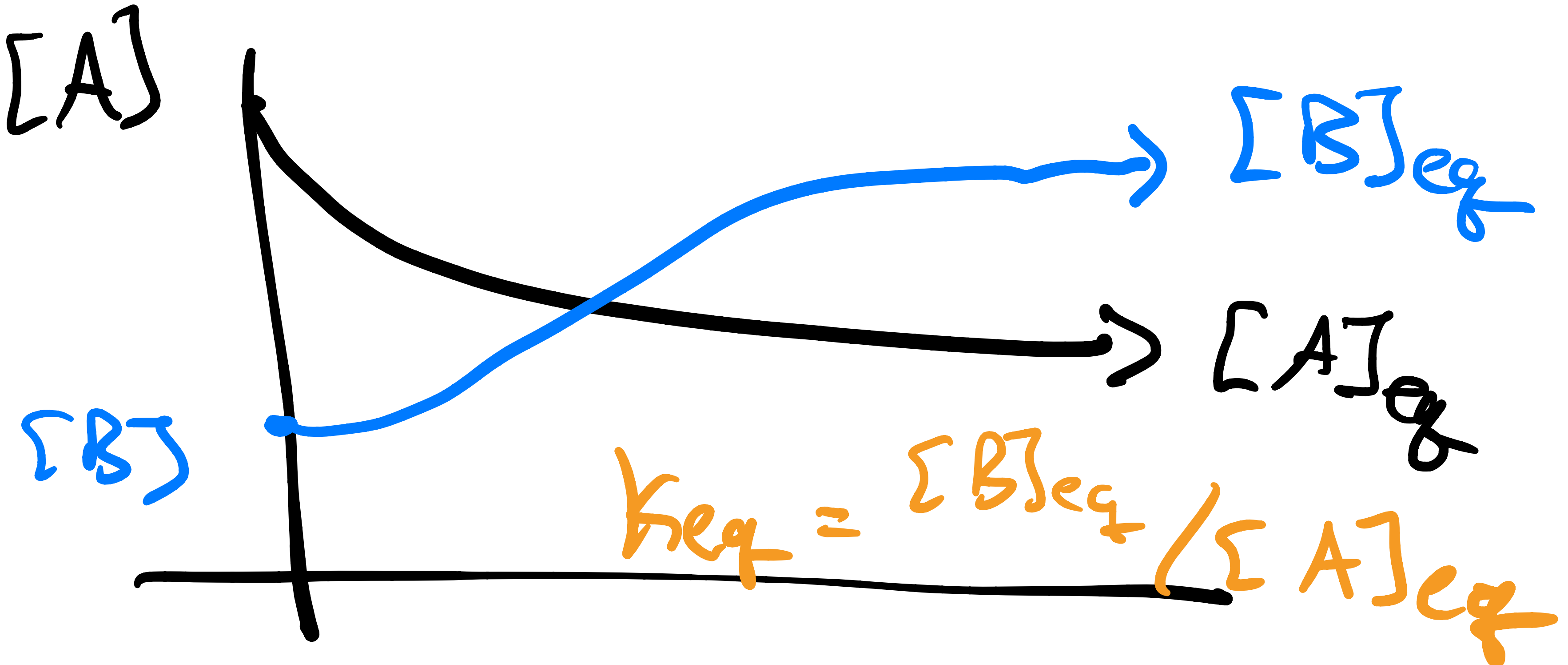
$$-\frac{d[A]}{dt} = k_f[A] - k_b[B]$$

$[A] + [B]$ constant

Can solve .....

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

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



$K_{eq} = [B]_{eq} / [A]_{eq}$