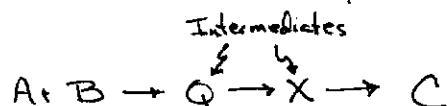$A + B \rightarrow C$ only tells us <u>stoichiometry</u>

Reactants $(A, B) \rightarrow$ decrease with time
Products $(c) \rightarrow$ increase with time

Intermediates $(?) \rightarrow$ increase, then decrease
As in: Intermediates
$$A + B \rightarrow Q \rightarrow X \rightarrow C$$

Things which <u>don't</u> change concentration:

Catalysts (enzymes, inhibitors, non-reactant factors)
Intermediates at steady state (definition of steady state)
Solvents
Species coupled to infinite pools (practically).

<u>ORDER OF A REACTION</u>

<u>If</u> the rate law is: $\nu = \dfrac{\partial c}{\partial t} = k A^2 B$

<u>then</u> the order of the reaction w/ respect to A is 2
                                                    B is 1
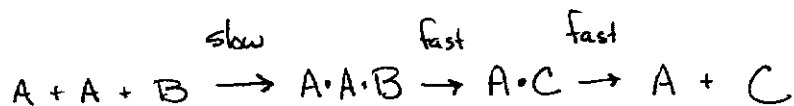
ie. the exponent of X in the <u>rate law</u>

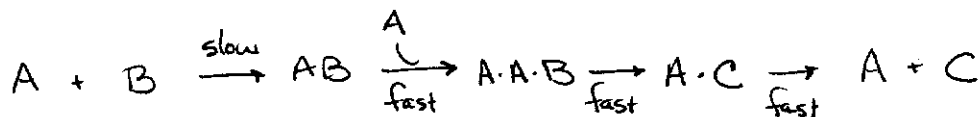<u>N.B.</u> The stoichiometry of a reaction tells us <u>nothing</u>
necessarily about the rate law.
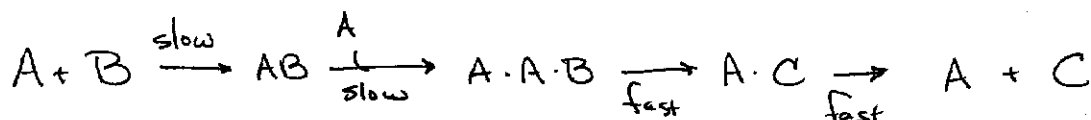
Perhaps $A + B \rightarrow C$

goes via

$$A + A + B \xrightarrow{\text{slow}} A \cdot A \cdot B \xrightarrow{\text{fast}} A \cdot C \xrightarrow{\text{fast}} A + C$$

in this case, one molecule of A
is a <u>reactant</u> (consumed)

but another molecule of A is a <u>catalyst</u>
(comes out unchanged)

$$A + B \xrightarrow{\text{slow}} AB \xrightarrow[\text{fast}]{A} A \cdot A \cdot B \xrightarrow{\text{fast}} A \cdot C \xrightarrow{\text{fast}} A + C$$

might show $\dfrac{dc}{dt} = v = k \, AB$

While

$$A + B \xrightarrow{\text{slow}} AB \xrightarrow[\text{slow}]{A} A \cdot A \cdot B \xrightarrow{\text{fast}} A \cdot C \xrightarrow{\text{fast}} A + C$$

would/could show something between the two

$$\dfrac{dc}{dt} = v = k \, A^{1.5} B \qquad (\text{Yikes!})$$

<u>ie</u>: it's <u>messy</u>.

Review $^{1)}$ IF $\quad \nu = k \, c_A^m \, c_B^n \, c_P^q$

$m, n,$ and q are the orders of the reaction with respect to A, B, and P, respectively.

2) Stoichiometry of a reaction does <u>not</u> tell you about the order of a reaction. <u>Must measure rates</u> as a function of concentrations

3) The order(s) of a reaction can <u>change</u> during the course of the reaction (eg. as substrate becomes low, the reaction may become more dependent on its conc).

Let's look at simple classes of reactions:

$$\frac{\partial C_P}{\partial t} = k_o$$

Q: What's the order with respect to A?

A: $\emptyset$

$$\frac{\partial C_P}{\partial t} = k_o A^0$$

Integrate:

let $C = C_P$
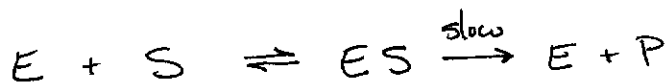
$$dC_P = k_o \, dt$$

$$\int_{C_1}^{C_2} dC_P = k_o \int_{t_1}^{t_2} dt$$

$$C_2 - C_1 = k_o (t_2 - t_1)$$

$$C_2 = C_1 + k_o (t_2 - t_1)$$

<u>examples</u>   at saturating substrate, reactions can
be independent of conc of substrate

<u>why?</u> What does saturating mean?

$$E + S \rightleftharpoons ES \xrightarrow{\text{slow}} E + P$$

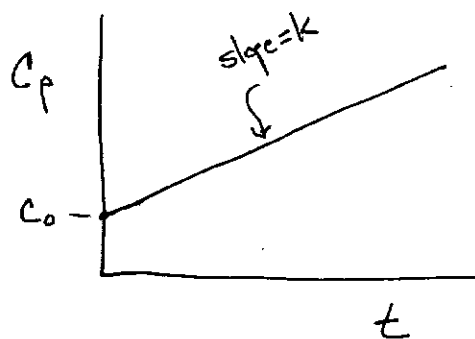Le Chatelier says: at very high S, all E
is pushed to ES.
Increasing S further can't make more ES!

Plot data

$$C_p = C_0 + k_0(t-0)$$

$$v = \frac{\partial C_p}{\partial t} = -\frac{\partial C_s}{\partial t}$$

$$= \frac{\partial P}{\partial t} = -\frac{\partial S}{\partial t}$$ (replace all C_p by P
C_A by A
etc.)

slope = k

C_p

C_0 —

t

Units of k_0
are $\dfrac{conc}{time} \Rightarrow \dfrac{molar}{sec}$

FIRST ORDER REACTIONS

$$\frac{dc}{dt} = k_1 C$$

$$A \longrightarrow B$$

$$v = \frac{-\partial A}{\partial t} = \frac{\partial B}{\partial t} = k_1 A$$

Integrate:
$$-\frac{\partial A}{A} = k_1 \partial t$$

$$-\int \frac{\partial A}{A} = k_1 \int \partial t$$

$$\ln A = -k_1 t + C$$

determine C by limiting conditions.
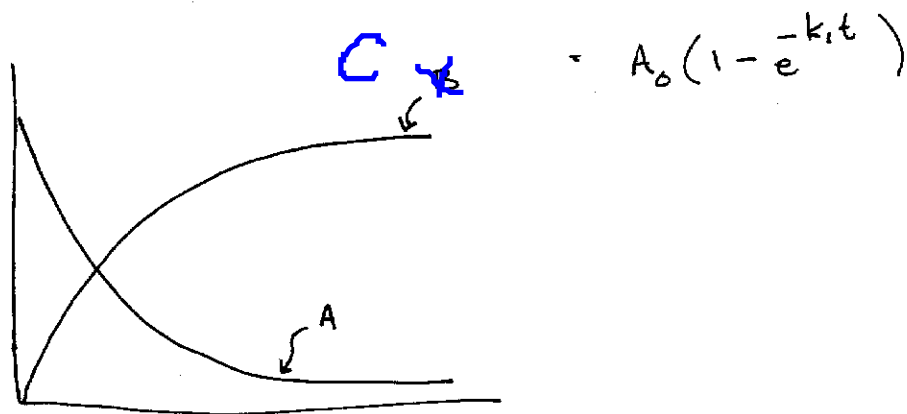
e.g. $\ln A_0 = -k_1(0) + C$

∴ $C = \ln A_0$

$$\ln A - \ln A_0 = -k_1 t$$

$$A/A_0 = e^{-k_1 t} \qquad\qquad A = A_0 e^{-k_1 t}$$

Conc of A decreases exponentially with time.

Since $A + B = A_0$ then $C = A_0 - A$

(with C written in blue over B)

$$C = A_0 (1 - e^{-k_1 t})$$

Radioactive decay is a classic example of this

Conventions

When is half the reagent (A) used up?
Call this time $t_{1/2}$ ⟵ HALF-TIME

Then

$$A_{1/2} = \frac{1}{2} A_0 = A_0 e^{-k_1 t_{1/2}}$$

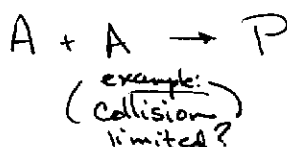$$\frac{1}{2} = e^{-k_1 t_{1/2}}$$

$$-\ln 2 = -k_1 t_{1/2}$$

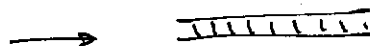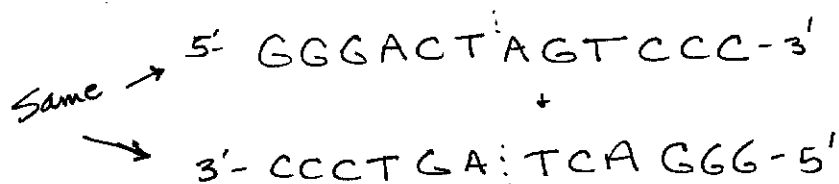$$t_{1/2} = \frac{\ln 2}{k_1}$$ ⟸ Often used as an alternative to k_1

They are interchangeable.
(inter convertible, really)

2ND Order Reactions $A + A \rightarrow P$

example:
(collision limited?)

$$v = k_2 A^2$$

or for $A + B \rightarrow P$

$$v = k_2 AB$$ ⟸ ~~B~~ 2ND order overall
1ST order w/ resp to A
1ST order w/ resp to B

Same → 5' GGGACTAGTCCC-3'
+   ⟶   IIIIIIII
3'-CCCTGATCAGGG-5'

"Class 1" — 2ND order in one species

Integrate $\quad v = k_2 A^2 = -\dfrac{\partial A}{\partial t}$

$$-\frac{dA}{A^2} = k_2\, dt$$

$$-\int \frac{dA}{A^2} = k_2 \int dt$$

$$\frac{1}{A} = k_2 t + C$$

At $t=0$, $A = A_o$ $\qquad \dfrac{1}{A_o} = k_2(0) + C \qquad \therefore\ C = \dfrac{1}{A_o}$

$$\frac{1}{A} = k_2 t + \frac{1}{A_o} \qquad\qquad A = \frac{1}{k_2 t + \frac{1}{A_o}}$$

$$\frac{1}{A} - \frac{1}{A_o} = k_2 t \qquad\qquad = \frac{A_o}{\frac{k_2}{A_o} t + 1}$$

"Class 2" — 2ND order **overall**. $\qquad A + B \rightarrow P$

$$v = k_2 A B \qquad \text{let} \quad \begin{matrix} A = A_o - x \\ B = B_o - x \end{matrix} \qquad x = P$$

$$\frac{dP}{dt} = \frac{dx}{dt} = k_2(A_o - x)(B_o - x)$$

$$\int \frac{dx}{(A_o - x)(B_o - x)} = \int k_2\, dt$$

Consult your Calculus book

$$\frac{1}{A_o - B_o} \ln \frac{B_o(A_o - x)}{A_o(B_o - x)} = k_2 t \qquad \text{for } A \neq B$$

$$\left(\begin{matrix} \text{for } A = B, \\ \text{use "Class I"} \end{matrix}\right)$$

Solve for x (FUN!)