Skip 342-352

11/5/01

FIRST ORDER

$$\frac{dC}{dt} = kC$$

$$A \rightarrow B$$

$$-\frac{dA}{dt} = kA$$

Special treatments

$$A = A_0 e^{-k_1 t}$$

HALF-LIFE

$$\frac{1}{2} A_0 = A_0 e^{-kt_{1/2}}$$

$$\ln \frac{1}{2} = -\ln 2 = -kt_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k}$$

RELAXATION TIME

$$\tau = \frac{1}{k}$$

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

CLASSIC EXAMPLE

Radioactive Decay

- $t_{1/2}$ commonly used

2^{ND} Order

$$v = \frac{dC}{dt} = kC^2 \quad \text{or} \quad \frac{dC}{dt} = kAB$$

$$A + A \rightarrow P$$

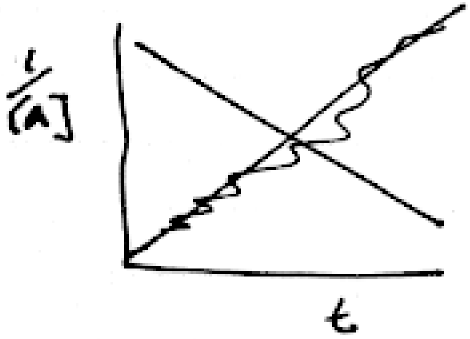
$$-\frac{dA}{dt} = k[A]^2$$

As Before

$$\int_0^f -\frac{dA}{A^2} = \int_0^f k\,dt$$

$$\frac{1}{[A]_f} - \frac{1}{[A]_0} = kt_f - kt_0 \qquad t_0 = 0 \quad t_f = t$$

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



HALF-LIFE

$$\frac{1}{\frac{1}{2}[A]_0} = \frac{1}{[A_0]} + kt_{1/2}$$

$$t_{1/2} = \frac{1}{k_2[A]_0}$$

Note: $t_{1/2}$ for 1^{ST} order was independent of starting condition–

$t_{1/2}$ for 2^{ND} order depends on starting conditions – less generally useful.

Class II $A + B \rightarrow P$

$$-\frac{dA}{dt} = kAB$$

<u>FOR $[A] \neq [B]$</u> (if $[A] = [B]$, then it's previous case)

Let x = amount reacted

$$A = A_0 - x$$
$$B = B_0 - x$$

$$-\frac{dA}{dt} = \frac{dx}{dt} = k(A_0 - x)(B_0 - x)$$

$$\int \frac{dx}{(A_0 - x)(B_0 - x)} = \int k\,dt$$

ugly (look it up)

~~$\frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} = k_2 t$~~

$A_0 \neq B_0$ ~~$a \neq b$~~

$$\frac{1}{A_0 - B_0} \ln \frac{B_0(A_0 - x)}{A_0(B_0 - x)} = k_2 t$$

FOR MORE COMPLICATED RATE LAWS,
THINGS GET STILL UGLIER
... and then
NOT SOLVABLE DIRECTLY
... BUT
WE <u>CAN</u> DEAL WITH...

Determining the Order and Rate Constant

Plot conc vs time in a different ways

↳ Straight Lines for:

			Rate vs time
	0th order	: c vs t	$\frac{dc}{dt} \propto k$
	1st order	: $\ln c$ vs t	$\propto kc$
(A^2)	2ND order	: $\frac{1}{c}$ vs t	$\propto kc^2$
(AB)	2ND order	: $\ln(C_A/C_B)$ vs t	$\propto kAB$
A^n	nth order	: $\frac{1}{C^{n-1}}$ vs t	$\propto kc^n$

Method of initial rates

Measure velocity under conditions where the concentrations of reactants don't change in concentration significantly.

Measure v at different $[A]_0$

If we double $[A_0]$ and

rate does not change then 0th order
doubles $(2)^1$ then 1st order
quadruples $(2)^2$ then 2ND order

etc. CLASSIC

RE-ITERATE

N.B.

Knowledge of the stoichiometry of a reaction DOES NOT tell us about rate laws or kinetic mechanism

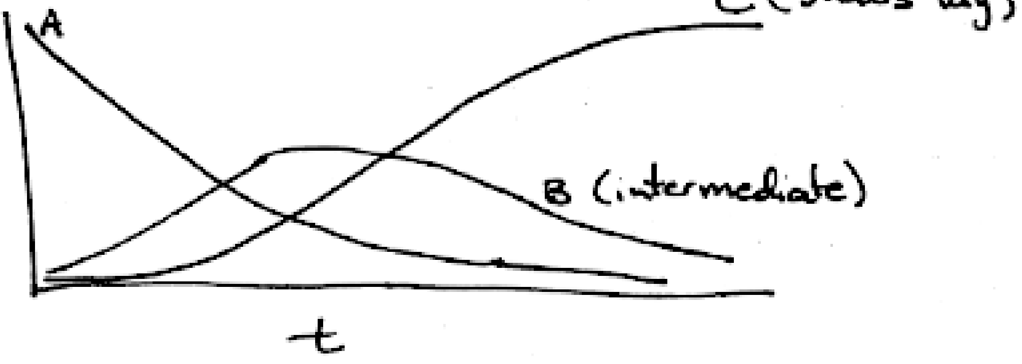
Knowledge of rate laws or kinetic mechanism DOES NOT tell us about stoichiometry of the reaction.

See pp 341-343

MULTI-STEP REACTIONS

Parallel $$A \begin{array}{l} \xrightarrow{k_1} B \\ \xrightarrow[k_2]{} C \end{array}$$ p. 343

Series First Order $A \xrightarrow{k_1} B \xrightarrow{k_2} C$



Reactions get more complex

$A \rightleftharpoons B$ (include reverse step)

$A \rightleftharpoons B \rightarrow C$ ugly if treat for all times, OK at steady state

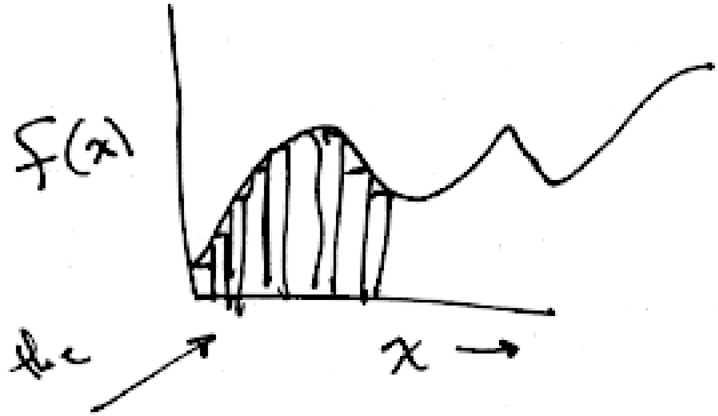
$$\left\{ \begin{array}{l} A + B \rightleftharpoons C \rightarrow E \\ A + I \rightleftharpoons D \end{array} \right.$$

and more...

Simple approaches we've outlined here for direct (analytical) solutions don't work

But we can do integrations (even *really* ugly ones) *numerically*.

In the same way that you can calculate integrals *numerically*



Area under the curve is the integral.