Chemical Kinetics

CHEM 102
T. Hughbanks

Integrated Rate Laws

- From initial concentrations & rate law, we can predict all concentrations at any time *t*.
- Mathematically, this is an initial value problem involving a (usually) simple differential equation.

Simplest Case: First Order

$$A \rightarrow 2P \qquad \text{rate} = -\frac{d[A]}{dt} = k[A]$$

By integrating, we can get an equation relating concentration and time:

$$\int_{[A]_0}^{[A]_t} \frac{d[A]'}{[A]'} = -k\int_0^t dt'$$

$$\ln\frac{[A]_t}{[A]_0} = -kt$$

First Order Reactions

$$\ln\frac{[A]_t}{[A]_0} = -kt$$

$$\frac{[A]_t}{[A]_0} = e^{-kt} \quad \text{so} \quad [A]_t = [A]_0 e^{-kt}$$

- From this, see that a plot of ln[A] vs. t will be a line with a slope of $-k$.

Half-Lives of radioisotopes

$^{3}_{1}H$	12.3 y	$^{235}_{92}U$	7.1×10^{8} y
$^{14}_{6}C$	5.73×10^{3} y	$^{238}_{92}U$	4.5×10^{9} y
$^{15}_{6}C$	2.4 s	$^{137}_{55}Cs$	30.17
$^{40}_{19}K$	1.26×10^{9} y	$^{131}_{53}I$	8.05 d
$^{90}_{38}Sr$	28.1 y	$^{226}_{88}Ra$	1.60×10^{3} y
$^{60}_{27}Co$	5.26 y		

Example

Hydrogen peroxide decomposes into water and oxygen in a first-order process.

$$H_2O_2(aq) \rightarrow H_2O(l) + \frac{1}{2} O_2(g)$$

At 20.0 °C, the ½-life for the reaction is 3.92×10^{4} seconds. If the initial concentration of hydrogen peroxide is 0.52 M, what is the concentration after 7.00 days (6.048×10^{5} s)?

Second Order, one reactant

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

$$\frac{d[\text{A}]}{[\text{A}]^2} = -k\,dt \quad \Rightarrow \quad \int_{[\text{A}]_0}^{[\text{A}]_t} \frac{d[\text{A}]'}{[\text{A}]'^2} = -k\int_0^t dt'$$

This leads to:

$$\frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_0} = k\,t \quad \text{or} \quad \boxed{\frac{1}{[\text{A}]_t} = k\,t + \frac{1}{[\text{A}]_0}}$$

- If second order kinetics apply, a plot of 1/[A] vs. t will be a line with slope k.

Second Order, one reactant

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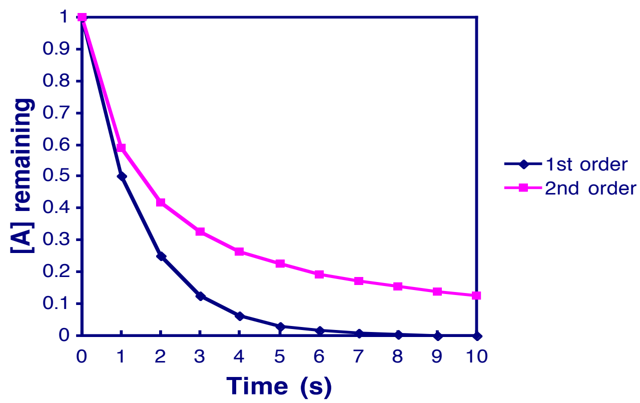
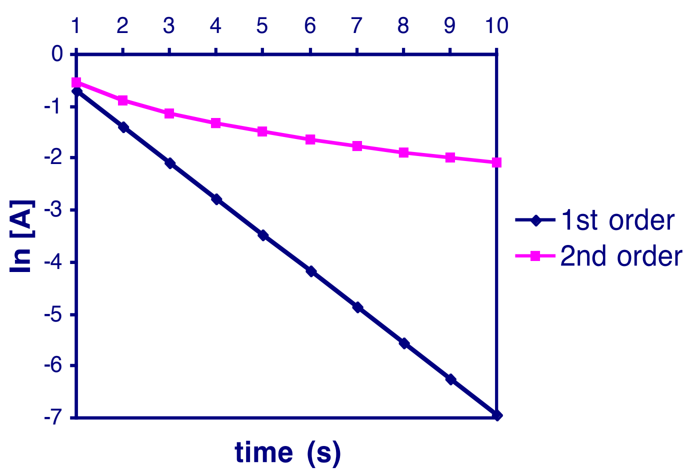
- If second order kinetics apply, a plot of 1/[A] vs. t will be a line with slope k.

1^{st} vs. 2^{nd} Order Kinetics

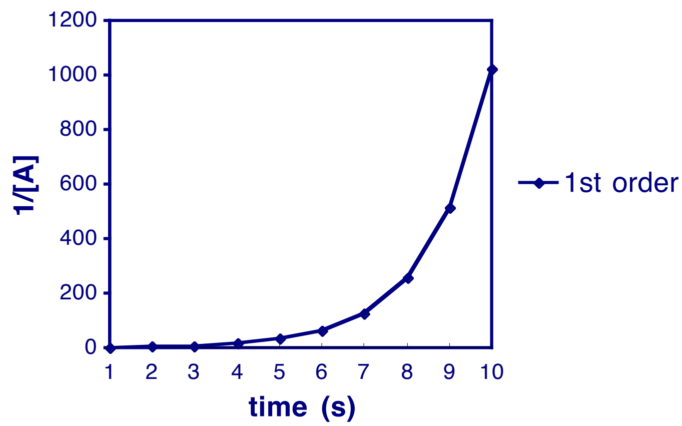


Both cases shown with k = 0.693 (Which is not terribly meaningful since units differ!)

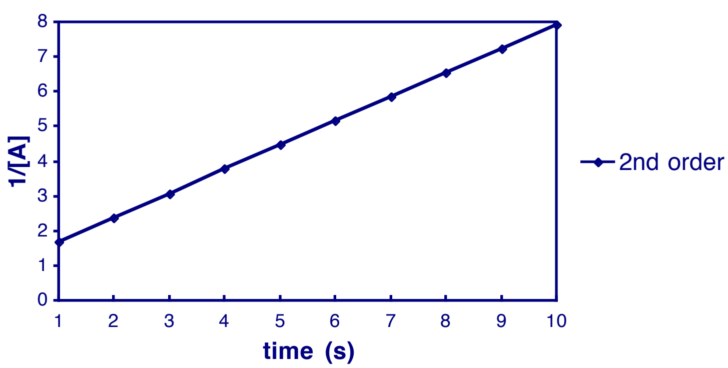
1^{st} Order Test Plot: ln[A] vs. t



2^{nd} Order Test Plot: 1/[A] vs. t



2^{nd} Order Test Plot: 1/[A] vs. t



A Real Example ...

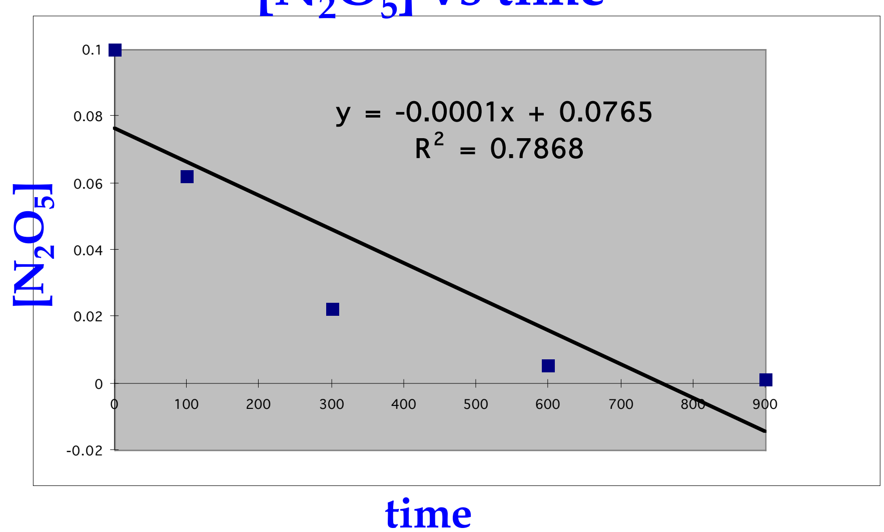
$$2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$$

- Experiment at T = 338 K gives:

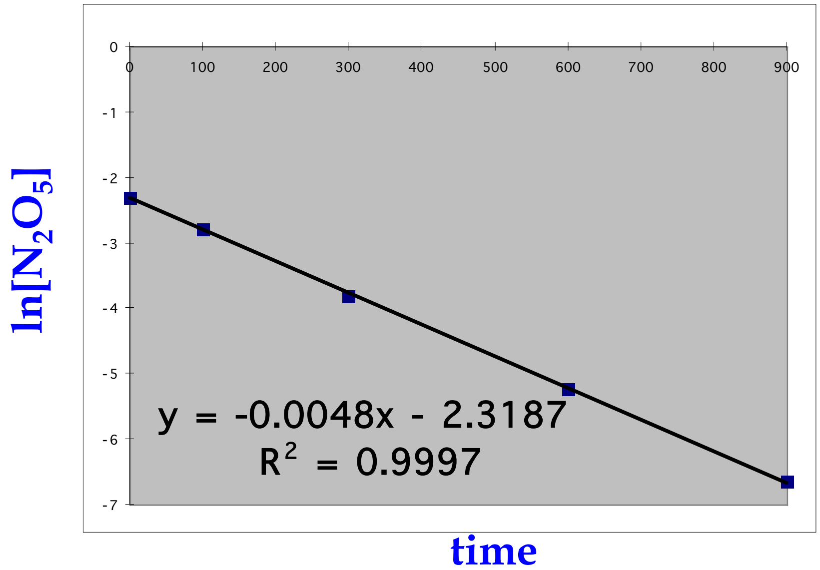
time (s)	$[N_2O_5]$ (M)
0	0.100
100.	0.0620
300.	0.0221
600.	0.0053
900.	0.0013

- Find rate law?

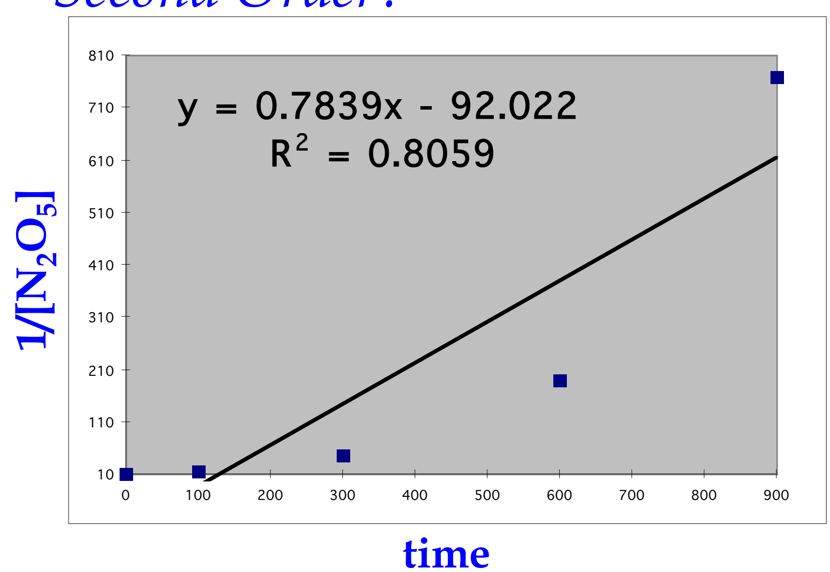
$[N_2O_5]$ vs time



First Order?



Second Order?



Example...

- Graphs show us that the reaction is first order, so:

  rate = $k[N_2O_5]$
- We can also find k from slope of graph: $\ln [N_2O_5] = \ln [N_2O_5]_0 - kt$
- So slope is equal to $-k$. Fit gives us:

  $k = 0.0048\ s^{-1}$

Example …. (half life)

- At what time will the $[N_2O_5]$ be equal to one-half of its original value?
- Use integrated rate law, solved for *t*:

$$t = \frac{1}{k} \ln \frac{[N_2O_5]_0}{[N_2O_5]}$$

- The question asks, what is *t* when $[N_2O_5] = (1/2)[N_2O_5]_0$?

Radioactive Half-Life: 1st Order Kinetics

Elements that decay via radioactive processes do so according to 1st order kinetics:

Element:	**Half-life:**
$^{238}_{92}\text{U} \rightarrow ^{238}_{92}\text{Th} + ^{4}_{2}\alpha$	4.5×10^{9} years
$^{14}_{6}\text{C} \rightarrow ^{14}_{7}\text{N} + ^{0}_{-1}\beta$	5730 years
$^{131}_{53}\text{I} \rightarrow ^{131}_{54}\text{Xe} + ^{0}_{-1}\beta$	8.05 days

notes: $^{0}_{-1}\beta$ is an electron, $^{4}_{2}\alpha$ is a $^{4}_{2}\text{He}$ nucleus.

Radioactive Half-Life: 1st Order Kinetics

Tritium decays to helium by beta (β) decay:

$$^{3}_{1}\text{H} \rightarrow ^{0}_{-1}e + ^{3}_{2}\text{He}$$

The half-life of this process is 12.3 years

Starting with 1.50 mg of ^{3}H, what quantity remains after 49.2 years?

Radioactive Half-Life: 1st Order Kinetics

Recall that that the rate constant for a 1st order process is given by:

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

$$\frac{[A]_t}{[A]_0} = e^{-kt} \longrightarrow [A]_t = [A]_0 \times e^{-kt}$$

$$[^3H]_t = 1.50 \text{ mg} \times e^{-\frac{0.693}{12.3\,years} \times 49.2 \text{ years}}$$

$$= 0.094 \text{ mg}$$

Radioactive Half-Life: 1st Order Kinetics

Notice that 49.2 years is 4 half-lives…

$$\frac{49.2}{12.3} = 4$$

After 1 half life: $\frac{1.50 \text{ mg}}{2}$ = 0.75 mg remains

After 2 half life's: $\frac{1.50 \text{ mg}}{4}$ = 0.38 mg remains

After 3 half life's: $\frac{1.50 \text{ mg}}{8}$ = 0.19 mg remains

After 4 half life's: $\frac{150 \text{ mg}}{16}$ = 0.094 mg remains

Another Example … (half life)

- ^{14}C measurements on the linen wrappings from the Dead Sea Scrolls suggest that the scrolls contain about 80.3% of the ^{14}C expected in living tissue. How old are the scrolls if the half-life for the decay of ^{14}C is 5.73×10^3 years?

Note: Radiocarbon dating relies on the uptake of ^{14}C into living tissue and subsequent decay after the death of the organism. ^{14}C is produced at a steady rate by cosmic ray absorption:

$${}_{0}^{1}n + {}_{7}^{14}\mathrm{N} \rightarrow {}_{6}^{14}\mathrm{C} + {}_{1}^{1}p \quad (\text{decay: } {}_{6}^{14}\mathrm{C} \rightarrow {}_{7}^{14}\mathrm{N} + {}_{-1}^{0}e^{-} + \nu)$$