Class 10.2
Chemical Kinetics

CHEM 102H
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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

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

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

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

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

First Order Reactions

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

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

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

Second Order, one reactant

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

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

This leads to:

$$\frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0} = kt \quad \text{or} \quad \boxed{\frac{1}{[\mathrm{A}]_t} = kt + \frac{1}{[\mathrm{A}]_0}}$$

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

Second Order, one reactant

$$\text{rate} = k[\mathrm{A}]^2$$

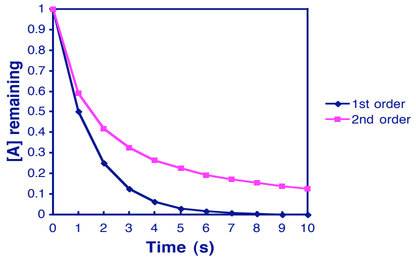
$$\frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = -k\,dt$$

This leads to:

$$\frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0} = kt \quad \text{or} \quad \boxed{\frac{1}{[\mathrm{A}]_t} = kt + \frac{1}{[\mathrm{A}]_0}}$$

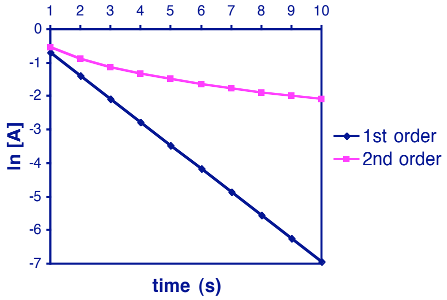
- <u>If second order kinetics apply</u>, a plot of 1/[A] vs. t will be a line with slope k.

1st vs. 2nd Order Kinetics

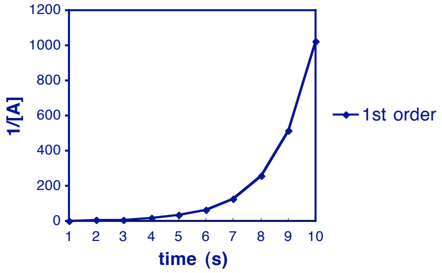


Both cases shown with *k* = 0.693

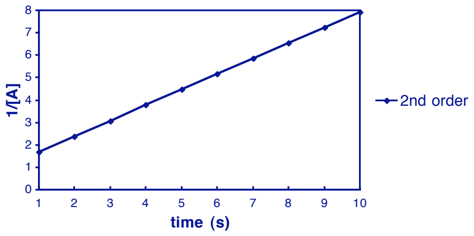
1st Order Test Plot: ln[A] vs. t



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



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



A Real Example ...

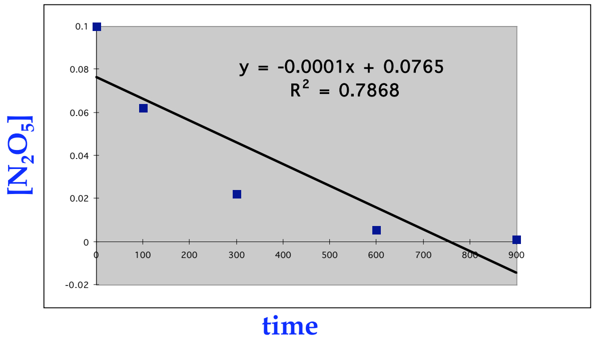
$2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$

- Experiment at T = 338 K gives:

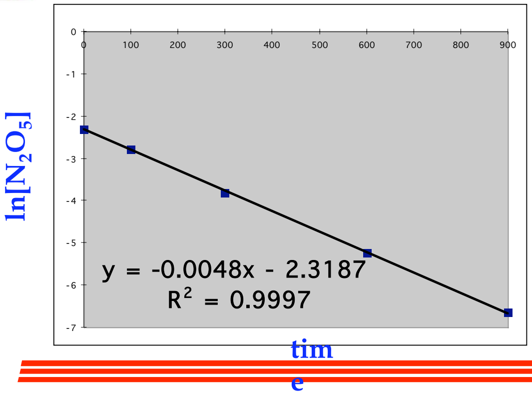
time (s)	$[N_2O_5]$ (M)
0	0.100
100.	0.0620
300.	0.0221
600.	0.0053
900.	0.0013

- Find rate law?

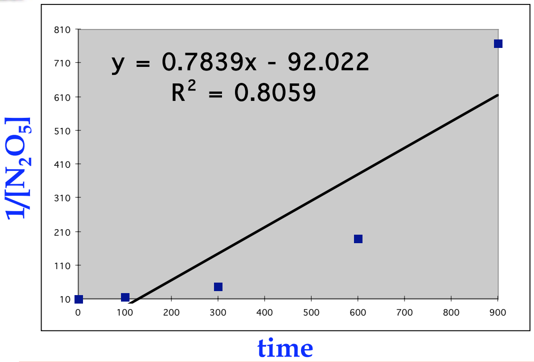
Zero Order?



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 $[N_2O_5] = (1/2)[N_2O_5]_0$?

Example.... (half-life)

$$t_{1/2} = \frac{1}{k} \ln \frac{[N_2O_5]_0}{(1/2)[N_2O_5]_0} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

- So with $k = 0.0048\ s^{-1}$, we get $t_{1/2} =$ 144 seconds
- This is called the “half-life” of the reaction.
- For a first order reaction, half-life is independent of initial amount.