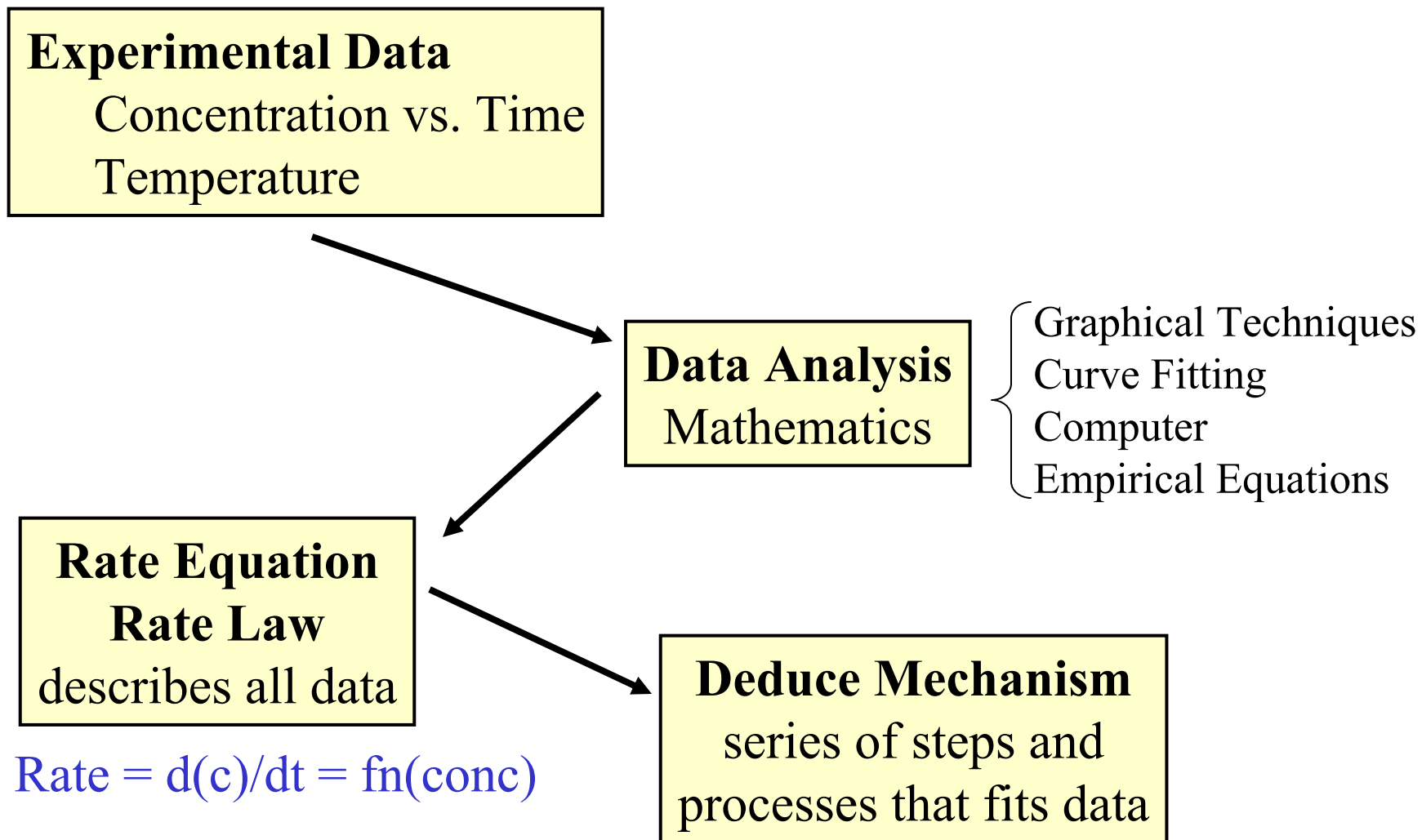
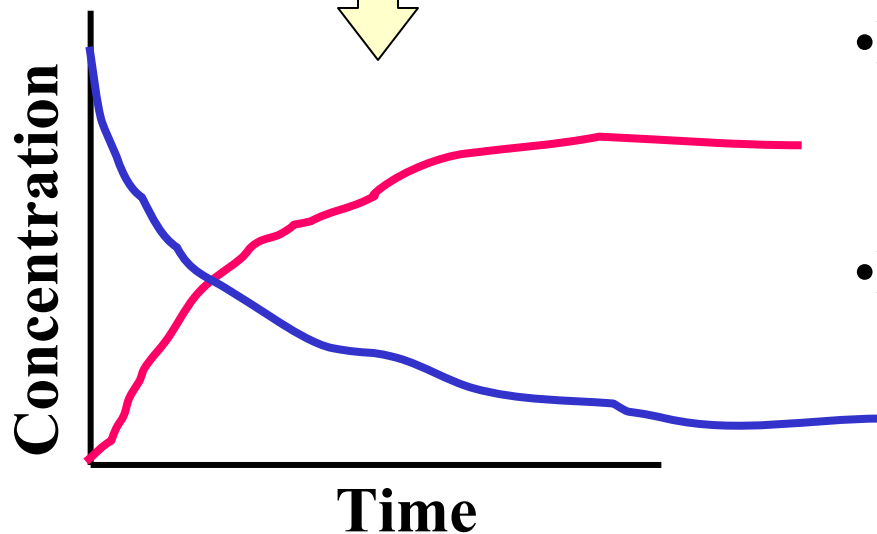
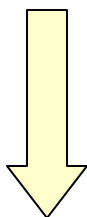


Kinetics and the Scientific Method



Analysis of Kinetic Data

| Conc R | Conc P | time | rate |
|--------|--------|------|------|
| --- | --- | --- | --- |
| --- | --- | --- | --- |
| --- | --- | --- | --- |



- Best smooth curve to fit all data
don't just "connect-the-dots"
- Slope measured at points
- Long time range (at least $2-3+ t_{1/2}$)
- If possible – conc of all reactants & products
- Rate Equation or Rate Law –
mathematical expression
describing the curves
- Deduce a mechanism consistent
with the data and rate law

The Rate Equation

Simple 1 step reaction $A \longrightarrow B$

Time rate of loss of A = time rate of gain of B

- Careful of stoichiometric coefficients in balanced equation
- Careful of algebraic sign

Rate is time rate of change of concentration

Rate is the slope at various times and concentration on a conc. vs time plot

Rate = $-d(A)/dt = +d(B)/dt$ () or [] denotes molar conc M

Units: conc/time = moles/lit/sec = M/sec (vol: lit, cm³, dm³, etc.)

For gases – pressure is proportional to moles/lit

(gas law $PV=nRT$ or $P=[n/V]RT$ and n/V is concentration)

So for gasses pressure (atm, Torr, etc.) often substituted for moles/liter

The Rate Equation

Experimental observations in late 1800's showed general equation

$$\text{Rate} = k[\text{Reactant 1}]^x[\text{Reactant 2}]^y[\text{Reactant 3}]^z$$

Reaction **order** for each reactant is x, y, z

Over all order = $x+y+z$

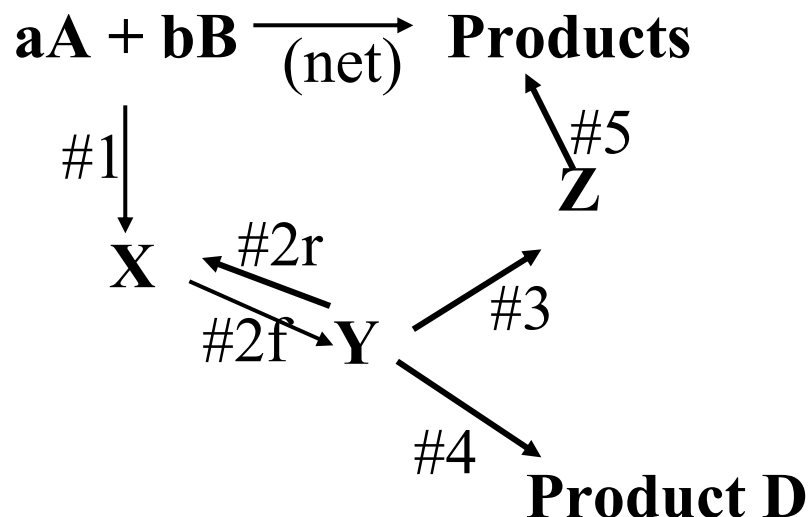
Rate Constant = k

- The goal is to fit this expression to the experimental data, describing the concentration vs. time graphs and solve for k, x, y, z, \dots
- Rate is a function of reactant concentration, not product
- Product concentration may appear in overall (net) kinetic equations for multi-step reactions with reversible steps $A \rightarrow B \rightleftharpoons C \rightarrow D$

Rate Equations

Careful not to confuse individual steps in a multi-step process with the overall or net reaction described by the balanced equation

X, Y, Z are Intermediates
(energy wells) short or long lived (determined by depth of well and height of barrier)



- Overall (net) reaction is what we observe in the lab
- Rate equation for overall reaction may be complex
- Rate equation for each step or elementary reaction is generally has a simple order=1 or 2 or $\frac{1}{2}$ or 0 and only reactant concentrations appear

Elementary Step vs. Rate Equation

Elementary Steps and Their Rate Laws

| Molecularity | Elementary Step | Rate Law |
|---------------------|---|----------------------------|
| <i>Unimolecular</i> | $A \longrightarrow \text{products}$ | $\text{Rate} = k[A]$ |
| <i>Bimolecular</i> | $A + A \longrightarrow \text{products}$ | $\text{Rate} = k[A]^2$ |
| <i>Bimolecular</i> | $A + B \longrightarrow \text{products}$ | $\text{Rate} = k[A][B]$ |
| <i>Termolecular</i> | $A + A + A \longrightarrow \text{products}$ | $\text{Rate} = k[A]^3$ |
| <i>Termolecular</i> | $A + A + B \longrightarrow \text{products}$ | $\text{Rate} = k[A]^2[B]$ |
| <i>Termolecular</i> | $A + B + C \longrightarrow \text{products}$ | $\text{Rate} = k[A][B][C]$ |

Multistep reactions may have overall rate equations much different than these elementary one step reactions

Rate Constant k

$$\text{Rate} = k[\text{R}_1]^x[\text{R}_2]^y[\text{R}_2]^z$$

Units of k $[\text{moles/liter/sec}] \cdot [\text{liter/mol}]^{\text{order}}$

| | | | |
|----------------|--|----|----------------------------------|
| First order | time^{-1} | | sec^{-1} |
| Second order | liter/mole/time | or | $\text{M}^{-1}\text{sec}^{-1}$ |
| Third order | $\text{liter}^2/\text{mole}^2/\text{time}$ | or | $\text{M}^{-2}\text{sec}^{-1}$ |
| One half order | $\text{liter}^{1/2}\text{mole}^{-1/2}\text{time}^{-1}$ | or | $\text{M}^{-1/2}\text{sec}^{-1}$ |
| Zero order | moles/liter-time | or | M sec^{-1} |

Stoichiometric Relations & Rate Equations

If - Balanced Equation $A + 3B = 4C$

Then - $d[C]/dt = -4d[A]/dt = -4/3 d[B]/dt$

Rate = $-d[A]/dt = 1/4d[C]/dt$

the rate of loss of A is $1/4$ the rate of gain of C

- The rate equation may not “look like” the stoichiometry of the overall balanced equation if there are multiple elementary steps
- Depends on the Mechanism not the Balanced Overall Equation

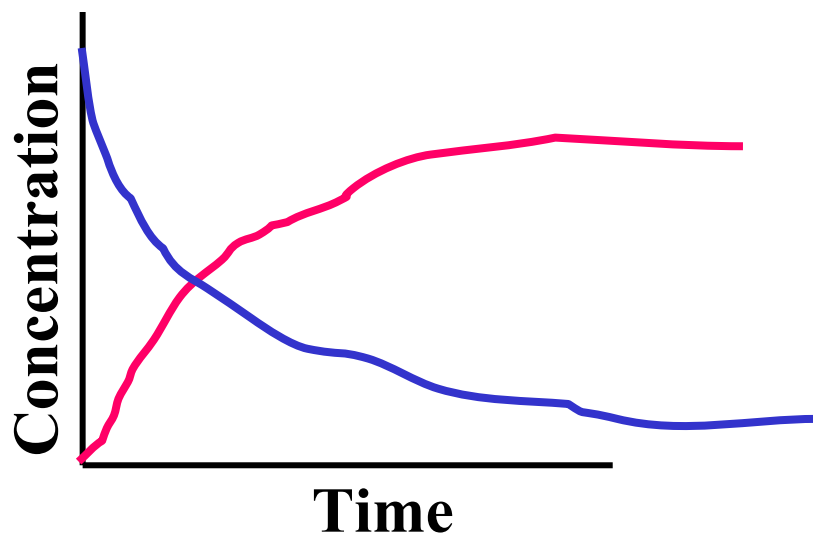
$A + 3B = 4C$ could be $A+B=D$ $D+B=E$ $E+B=F$ $F+B=G$ $G=4C$
or, etc. etc.....

This series of elementary steps is the Mechanism

Each elementary step has a rate equation.

The overall reaction can be describe by an overall rate equation.

Mathematical Analysis



Simple Equation – only 1 reactant
 $nA = \text{products}$

Slope at each point of Conc v. Time graph is the rate at that point

Method of Integration:

Rate of disappearance of A = $-d(A_0 - x_a)/dt = d[x]dt = k[A_0 - x]^n$

A_0 = concentration of A at time $t=0$ (initial concentration)

x = amount of A lost after time t

$A_0 - x$ = amount of A remaining at time t

Rate Equation (differential form) $-d(A_0 - x_a)/dt = d[x]dt = k[A_0 - x]^n$

Integrated Rate Equation

Rate Equation (differential form) $-d(A_0 - x_a)/dt = d[x]dt = k[A_0 - x]^n$
single reactant “A” more complex if other reactants “B”, etc.

Differential – how something changes with something else $\Delta y/\Delta x$ or dy/dx

Integration (boundary condition $x=0$ at $t=0$) see integration tables

$$\text{for } n \neq 1 \quad k = [1/(t(n-1))] [(1/(A_0 - x)^{n-1} - 1/(A_0^{n-1}))]$$

$$\text{for } n = 1 \quad k = [1/t] \ln[A_0/(A_0 - x)]$$

$$\text{Remember } \ln_e X = 2.303 \log_{10} X$$

Differential and Integrated Rate Equations

| Order | Reaction | Rate law ($x = [P]$) | Integrated form | $t_{1/2}$ |
|------------|--------------------------------------|---------------------------|---|---|
| 0 | $A \rightarrow P$ | $dx/dt = k_0$ | $k_0 t = x$ for $x \leq [A]_0$ | $[A]_0/2k_0$ |
| 1 | $A \rightarrow P$ | $dx/dt = k_1[A]$ | $k_1 t = \ln \left\{ \frac{[A]_0}{[A]_0 - x} \right\}$ | $(\ln 2)/k_1$ |
| 2 | $A \rightarrow P$ | $dx/dt = k_2[A]^2$ | $k_2 t = \frac{x}{[A]_0([A]_0 - x)}$ | $1/k_2[A]_0$ |
| | $A + B \rightarrow P$ | $dx/dt = k_2[A][B]$ | $k_2 t = \left\{ \frac{1}{[B]_0 - [A]_0} \right\} \times \ln \left\{ \frac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0} \right\}$ | |
| | $A + 2B \rightarrow P$ | $dx/dt = k_2[A][B]$ | $k_2 t = \left\{ \frac{1}{[B]_0 - 2[A]_0} \right\} \times \ln \left\{ \frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0} \right\}$ | |
| | $A \rightarrow P$ with autocatalysis | $dx/dt = k_2[A][P]$ | $k_2 t = \left\{ \frac{1}{[A]_0 - [P]_0} \right\} + \ln \left\{ \frac{[A]_0([P]_0 + x)}{([A]_0 - x)[P]_0} \right\}$ | |
| 3 | $A + 2B \rightarrow P$ | $dx/dt = k_3[A][B]^2$ | $k_3 t = \left\{ \frac{1}{2[A]_0 + [B]_0} \right\} \times \left\{ \frac{2x}{[B]_0([B]_0 - 2x)} \right\} + \left\{ \frac{1}{2[A]_0 - [B]_0} \right\}^2 \times \ln \left\{ \frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0} \right\}$ | |
| $n \geq 2$ | $A \rightarrow P$ | $dx/dt = k_n[A]^n$ | $k_n t = \frac{1}{n-1} \left\{ \left(\frac{1}{[A]_0 - x} \right)^{n-1} - \left(\frac{1}{[A]_0} \right)^{n-1} \right\}$ | $\frac{2^{n-1} - 1}{(n-1)k_n[A]_0^{n-1}}$ |

Rate equation is a differential equation that can be integrated

see integration tables in math table book or Handbook of Chem and Physics and also tables in kinetics texts such as Laidler, and others

Experimental Kinetics



Collect data on how concentrations change with time

direct measurement of concentration or something proportional to concentration

Analyze data to arrive at a rate equation that describes the data and determine reaction order “n” and rate constant “k”

graphical analysis is a powerful tool

it pictorially shows trends and error size

Data must be collected over a wide time range to

Data Analysis for a Reaction



Rate Data for Reaction of C₄H₉Cl with Water

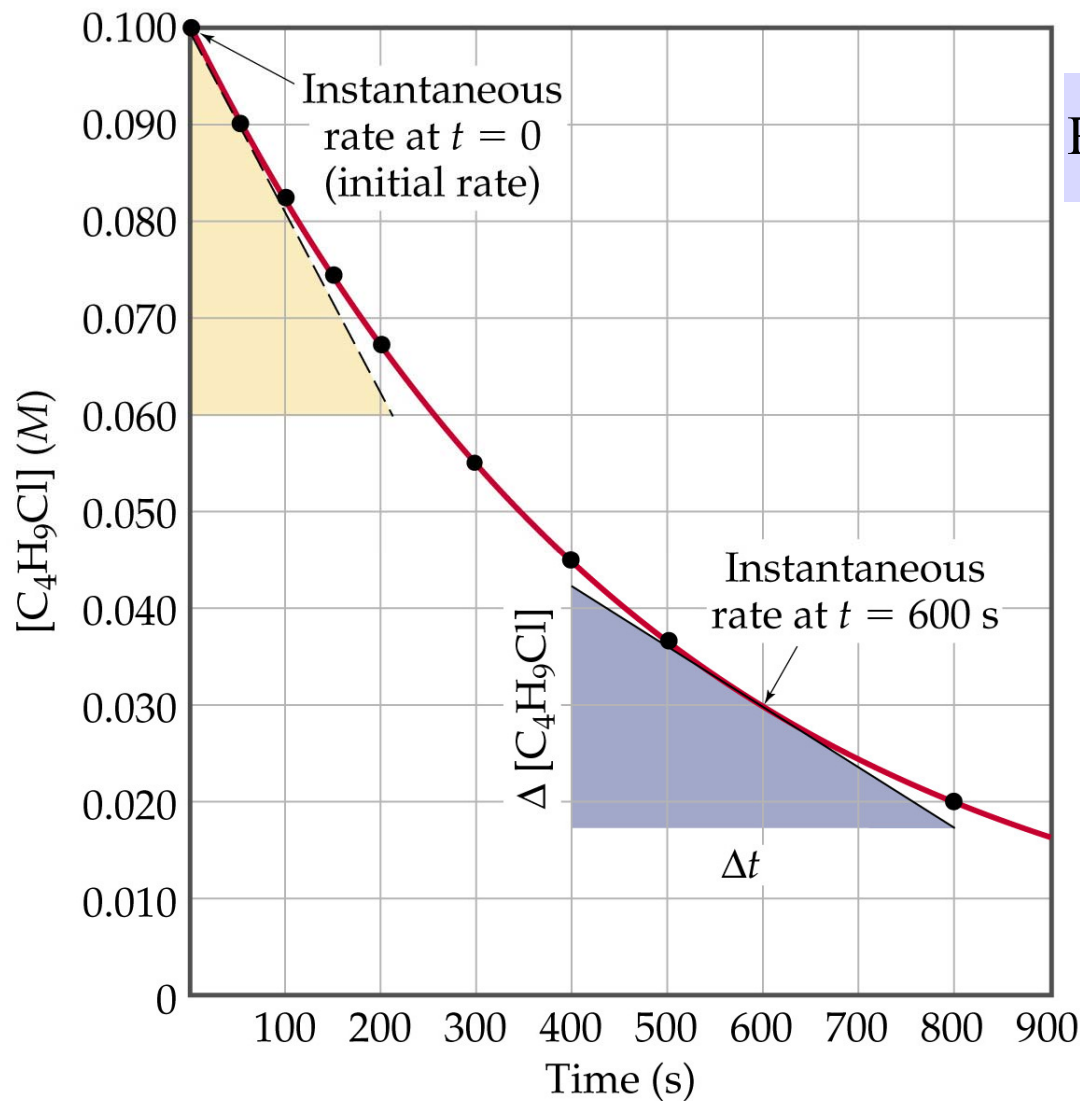
| Time, t (s) | [C ₄ H ₉ Cl] (M) | Average Rate (M/s) |
|---------------|--|------------------------|
| 0.0 | 0.1000 | 1.9×10^{-4} |
| 50.0 | 0.0905 | 1.7×10^{-4} |
| 100.0 | 0.0820 | 1.6×10^{-4} |
| 150.0 | 0.0741 | 1.4×10^{-4} |
| 200.0 | 0.0671 | 1.22×10^{-4} |
| 300.0 | 0.0549 | 1.01×10^{-4} |
| 400.0 | 0.0448 | 0.80×10^{-4} |
| 500.0 | 0.0368 | 0.560×10^{-4} |
| 800.0 | 0.0200 | |
| 10,000 | 0 | |

Calculated Rates

Conc at which these rates apply is the avg conc of the two conc values used to calculate the rate

Observed Experimental Data

Data Analysis for a Reaction (contd)



$$\text{Rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

Rate is slope of concentration vs. time curve

Slope/rate is $d(\text{conc})/d(\text{time})$ at each point on the curve

Rate decreases with time and concentration of reactant

First Order Rate Equation

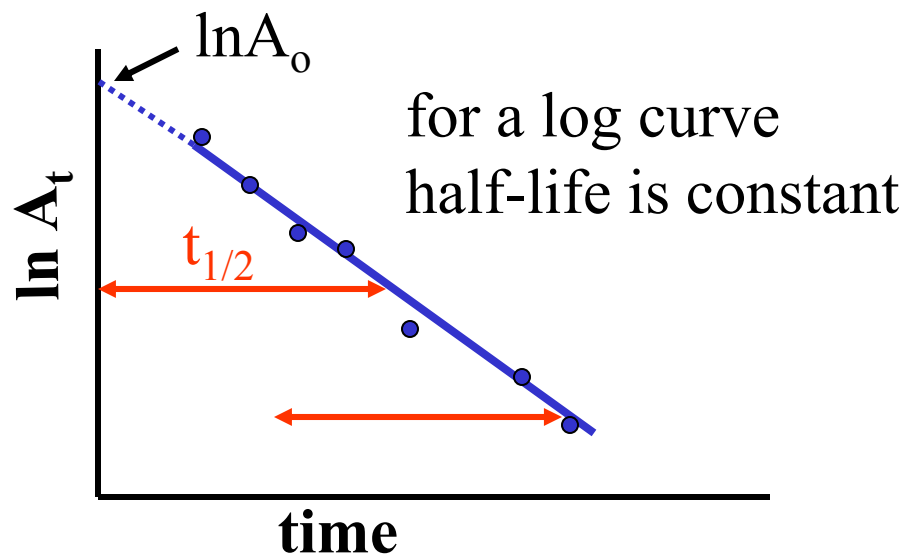
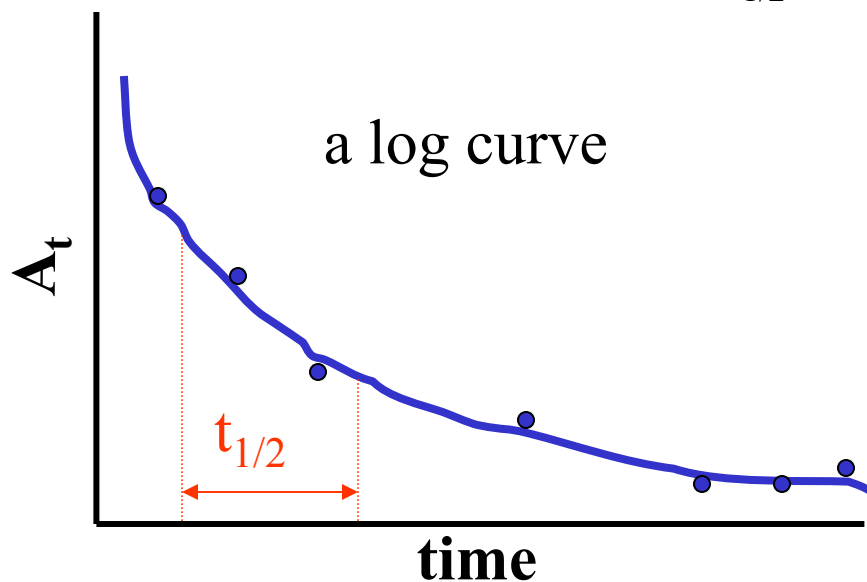
for the very simple reaction **A = Products**

$$d[A]/dt = -k[A] \quad \text{differential form}$$

$$k = [1/t] \ln[A_0/(A_0-x)] \quad \text{where } A_0-x=A_t \quad \text{integral form}$$

$$\ln A_0 - \ln A_t = kt \quad \text{or} \quad \ln A_t = -kt + \ln A_0$$
$$y = mx + b$$

Data over long time interval ($2-3+ t_{1/2}$) required to “prove” that the log plot is linear



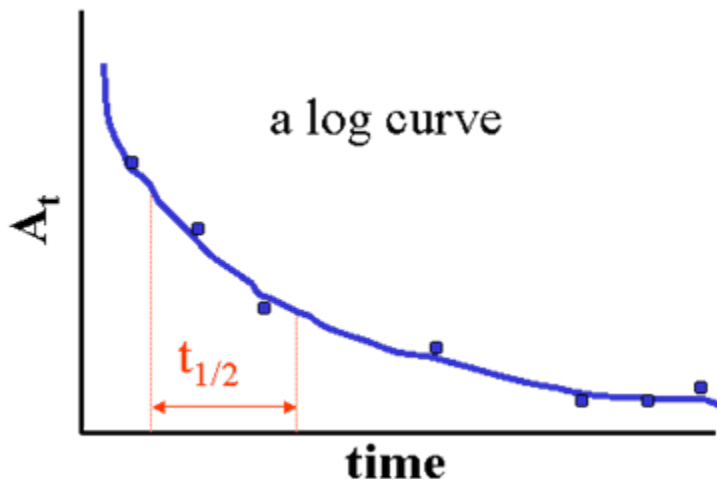
Half-Life of a First Order Reaction

Time for concentration to drop to one half of its value = $t_{1/2}$

Nature of a logarithmic relationship (since $\ln 2 = 0.693$)

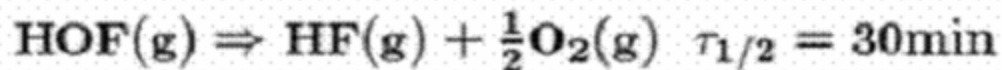
For first order reactions: $t_{1/2} = 0.693/k$ $k = 0.693/t_{1/2}$

For first order reactions Half-Life remains constant over time of reaction and is independent of concentration - this is not true for other orders



- If it is first order then data fits a log or ln curve and anywhere you measure $\frac{1}{2}$ life you get the same value.
- Not true for other than 1st order reactions
- For first order processes, if the concentration of reactant doubles the rate doubles
- Good quick test to determine order

Observed Experimental Half-Life Hypofluorous Acid HOF



At $t = 0$ $p_{\text{HOF}} = 100$ torr at $25\text{C} = 298\text{K}$ $V = 1\text{L}$

What P after 30 min and after 45 min?

$$-\frac{d[\text{HOF}]}{dt} = k[\text{HOF}]$$

After 30 min half the HOF has decomposed producing equal amount of HF and half O_2 .

$$P = 50 + 50 + 25 = 125 \text{ torr}$$

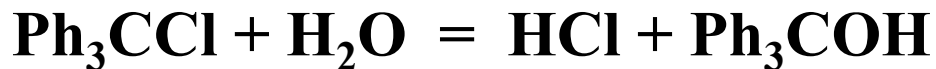
After 45 min? $45/30 = 1.5$ half times. Thus,

$$p_{\text{HOF}} = 35.4, \quad p_{\text{HF}} = 64.6, \quad p_{\text{O}_2} = 32.3 \quad \text{and} \quad P = 132.3 \text{ torr.}$$

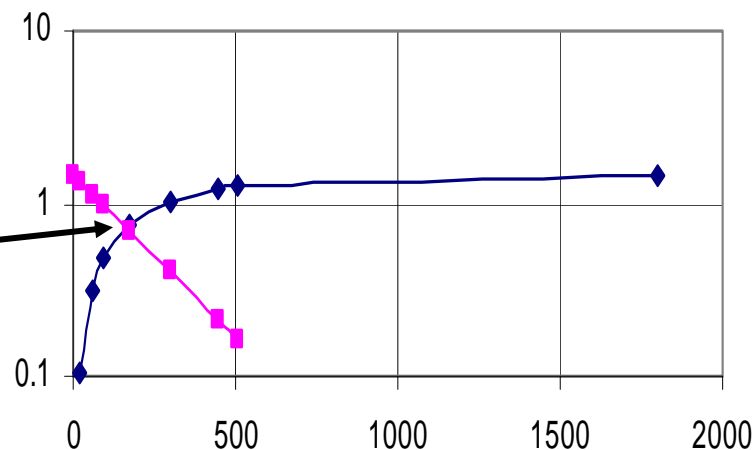
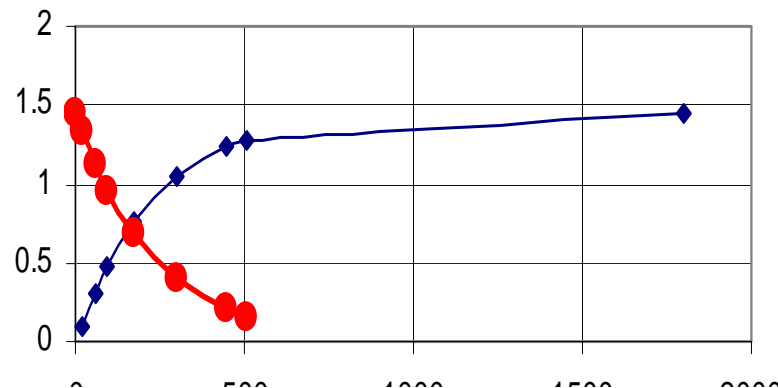
First Order Reaction – Example – real data

Hydrolysis of triphenylmethyl chloride

Swain, C.G., Scott, C., Lohman, K. N.;
JACS 75, 136 (1953)



| Time (sec) | [H+] conc x 10e3 | [Ph3CL] concx10e3 |
|------------|------------------|-------------------|
| 0 | | 1.44 |
| 18 | 0.104 | 1.34 |
| 57 | 0.312 | 1.13 |
| 93 | 0.484 | 0.96 |
| 171 | 0.757 | 0.68 |
| 298 | 1.04 | 0.4 |
| 448 | 1.23 | 0.21 |
| 508 | 1.28 | 0.16 |
| 1800 | 1.44 | |



Assuming first order

Slope = -4.3×10^{-3}

$k = 4.3 \times 10^{-3} \text{ sec}^{-1}$

$t_{1/2} = 160 \text{ sec}$

| | | | | | | |
|------------|-----|-----|-----|-------------|---------|-----|
| Conc [M] 1 | 1/2 | 1/4 | 1/8 | 1/16=0.0625 | 0.03125 | |
| Time (sec) | 0 | 160 | 320 | 480 | 640 | 800 |

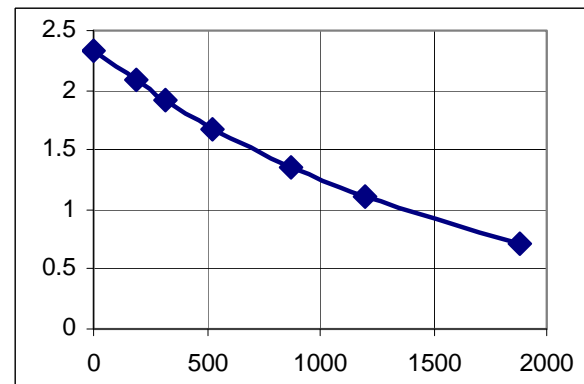
First Order Reaction – Example – real data

Rate of decomposition of dinitrogen pentoxide
in carbon tetrachloride at 45 C

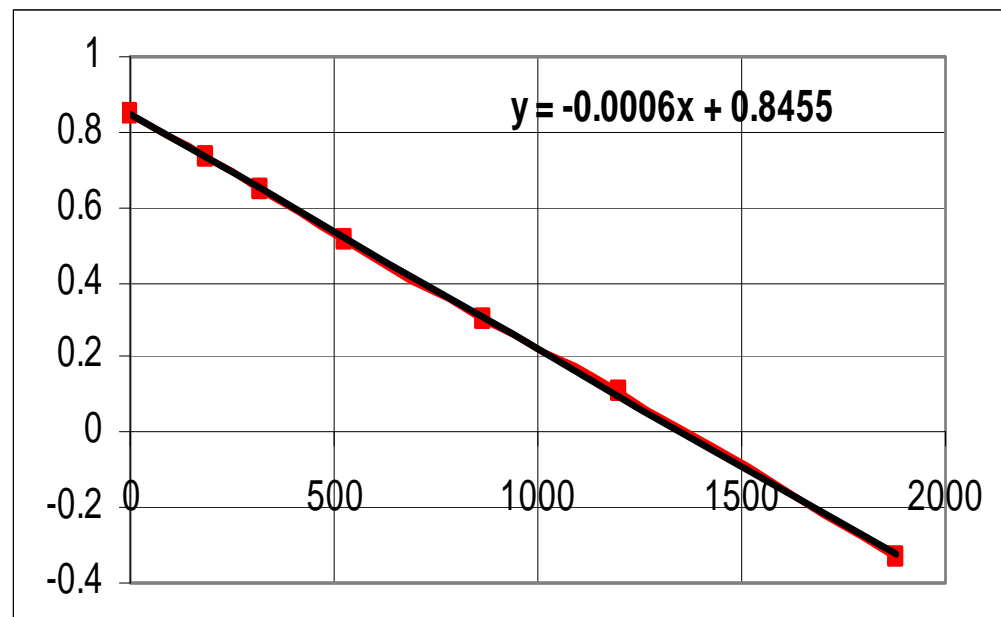


H. Eyring & F. Daniels;

JACS, 52, 1472 (1930)



| Time (min) | N ₂ O ₅ [M] | ln N ₂ O ₅ |
|------------|-----------------------------------|----------------------------------|
| 0 | 2.33 | 0.845868 |
| 184 | 2.08 | 0.732368 |
| 319 | 1.91 | 0.647103 |
| 526 | 1.67 | 0.512824 |
| 867 | 1.35 | 0.300105 |
| 1198 | 1.11 | 0.10436 |
| 1877 | 0.72 | -0.3285 |



First Order Reaction – Example (contd)



$$\text{Rate} = \Delta\text{N}_2\text{O}_5 / \Delta t$$

Rate decreases with time since concentration of reactants decrease with time and rate is proportional to reactant concentration for first order reactions

| Time (min) | N2O5 [M] | delta N2O5 | delta N2O5/delta t |
|------------|----------|------------|--------------------|
| 0 | 2.33 | | |
| | 2.205 | 0.25 | 0.00136 |
| 184 | 2.08 | | |
| | 1.995 | 0.17 | 0.00126 |
| 319 | 1.91 | | |
| | 1.79 | 0.24 | 0.00116 |
| 526 | 1.67 | | |
| | 1.51 | 0.32 | 0.00094 |
| 867 | 1.35 | | |
| | 1.23 | 0.24 | 0.00072 |
| 1198 | 1.11 | | |
| | 0.915 | 0.39 | 0.00057 |
| 1877 | 0.72 | | |

(red is extrapolated)

If first order:

Ratio of any two rates ($\Delta\text{conc}/\Delta t$) follows ratio of conc. at those rates
If first order, if reactant conc doubles rate doubles, etc.

Rate is proportional to first power of concentration

Thus first order reaction **Rate = k(conc A)¹**

(if second order rate would be proportional to square of concentration)

Reaction Order from Data

Reaction order may be deduced by determining the effect of concentration on the rate of reaction

- in a single reaction over time
- in various identical reactions with different concentrations

Example:

- If doubling concentration doubles rate – first order
- If doubling concentration increases rate 4x – second order
- A reacting is n th order if doubling the concentration causes an 2^n increase in rate

Rate is a Function of Concentration

- In general rates increase as concentration of reactants increase.



Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25°C

| Experiment Number | Initial NH_4^+ Concentration (M) | Initial NO_2^- Concentration (M) | Observed Initial Rate (M/s) |
|-------------------|---|---|-----------------------------|
| 1 | 0.0100 | 0.200 | 5.4×10^{-7} |
| 2 | 0.0200 | 0.200 | 10.8×10^{-7} |
| 3 | 0.0400 | 0.200 | 21.5×10^{-7} |
| 4 | 0.0600 | 0.200 | 32.3×10^{-7} |
| 5 | 0.200 | 0.0202 | 10.8×10^{-7} |
| 6 | 0.200 | 0.0404 | 21.6×10^{-7} |
| 7 | 0.200 | 0.0606 | 32.4×10^{-7} |
| 8 | 0.200 | 0.0808 | 43.3×10^{-7} |

Rate is a Function of Concentration

- For the reaction



we note

- as $[\text{NH}_4^+]$ doubles with $[\text{NO}_2^-]$ constant the rate doubles,
 - as $[\text{NO}_2^-]$ doubles with $[\text{NH}_4^+]$ constant, the rate doubles,
 - we conclude rate $\propto [\text{NH}_4^+][\text{NO}_2^-]$.
 - reaction is first order in ammonium ion, first order in nitrate ion and is overall second order
- Rate law determined by experimental observation:

$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$

First Order Reaction - Example

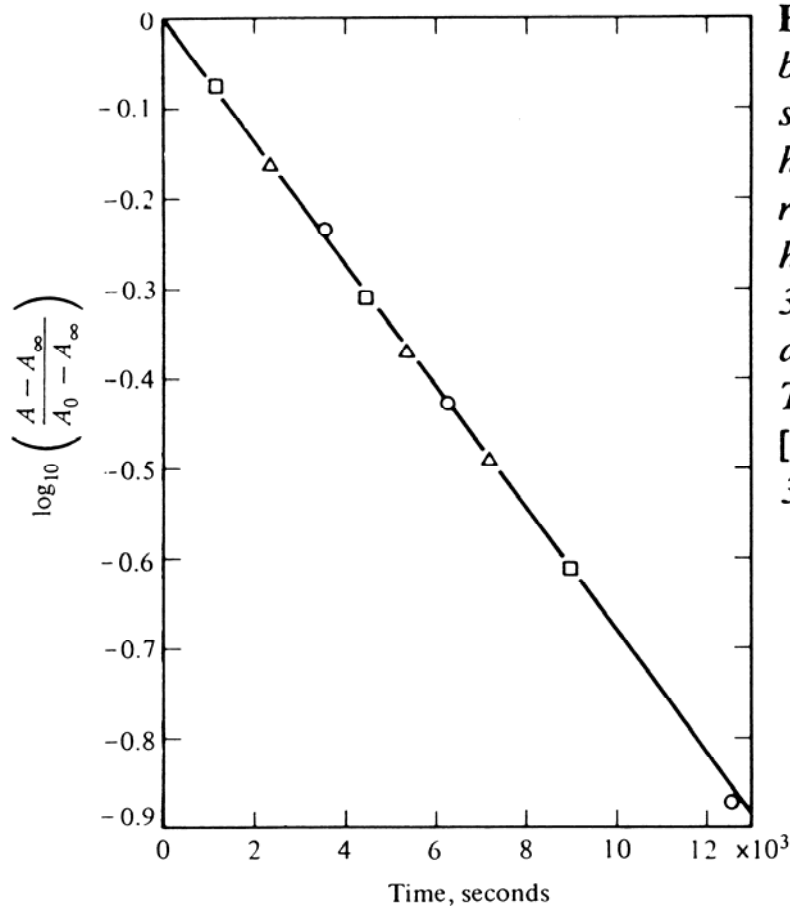


Figure 1.2. The first-order thermal decomposition of 2,2'-azo-bis-isobutyronitrile in toluene at 80.4°C. The absorbance of the solution at the start is A_0 , that at time t is A , and that after 24 hours is A_{∞} . Hence, the quantity $A - A_{\infty}$ is proportional to reactant concentration. The absorption spectrum of the nitrile has a peak at 345 nm, while the data shown were obtained at 360 nm (\circ), 370 nm (\square), and 380 nm (\triangle). The three sets of data are normalized by use of the ratio $(A - A_{\infty})/(A_0 - A_{\infty})$. The rate constant found from this plot is $1.55 \times 10^{-4} \text{ sec}^{-1}$. [From M. Talat-Erben and S. Bywater, J. Am. Chem. Soc. 77, 3712 (1955).]

$$k = 1.55 \times 10^{-4} \text{ sec}^{-1}$$

$$\text{Half-Life} = t_{1/2} = 4470 \text{ sec}$$
$$74.5 \text{ min}$$
$$1.24 \text{ hr}$$

Data covers 2.7 half-lives – enough time and concentration drop to determine if data is logarithmic (linear plot of $\log(c)$ vs t) or some other shape curve in which case it would not be a first order reaction, but rather some other order reaction

Second Order Reactions – 1 reactant (simplest case)

A = Products

Differential form of rate equation $d[A]/dt = -k[A]^2$

Integrated form of rate equation $1/(A_t) - 1/(A_0) = kt$

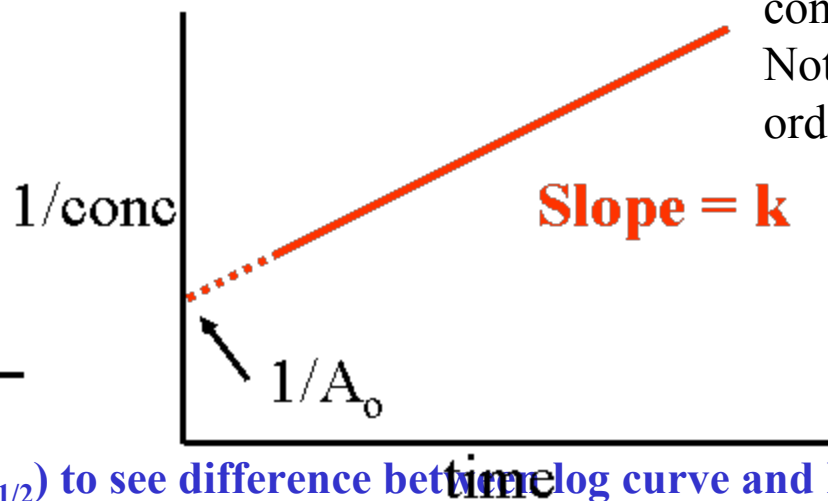
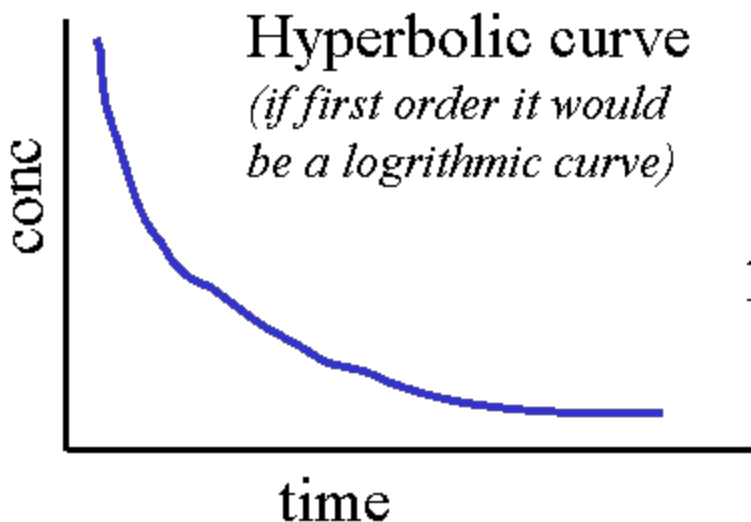
$$1/(A_t) = kt + 1/(A_0)$$

$$y = mx + b$$

or $(A_t) = (A_0)/[1+kt(A_0)]$

$$t_{1/2} = 1/k(A_0)$$

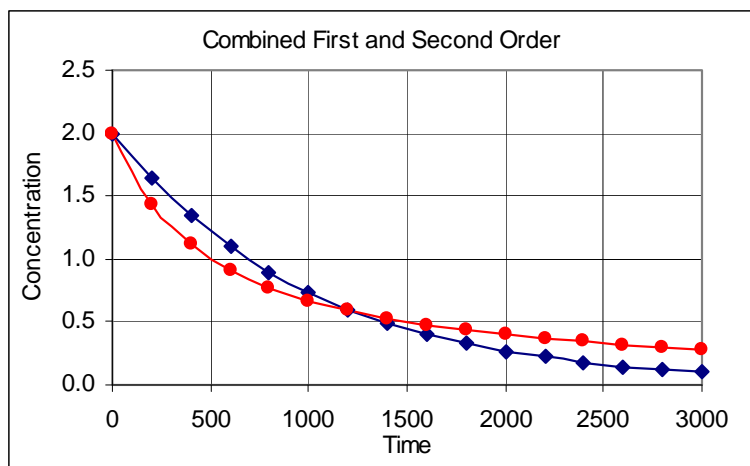
Note: half-life of 2nd order process is a function of conc and time. Not true of 1st order process



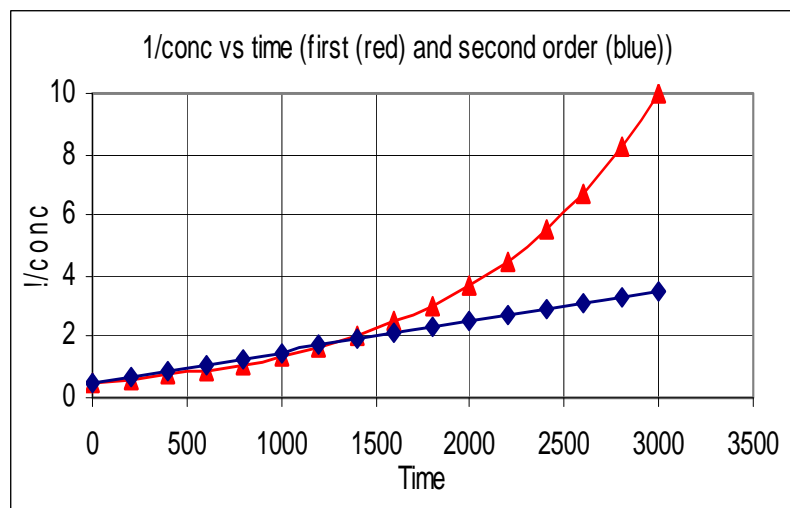
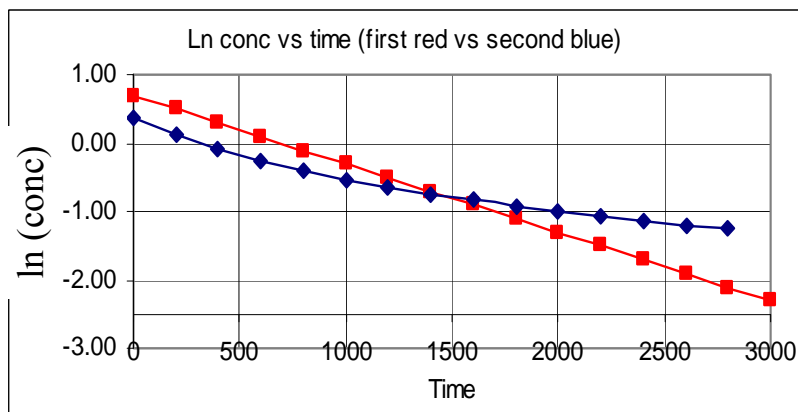
Need data over long time interval (2-3+ $t_{1/2}$) to see difference between log curve and hyperbola

Difference between First and Second Order

| First Order | | | | | Second Order | |
|-------------|-------|------------|-----|--|--------------|-------|
| k= | 0.001 | half life= | 693 | | k= | 0.001 |
| A initial = | 2 | | | | A initial = | 2 |
| t max = | 3000 | | | | t max = | 3000 |



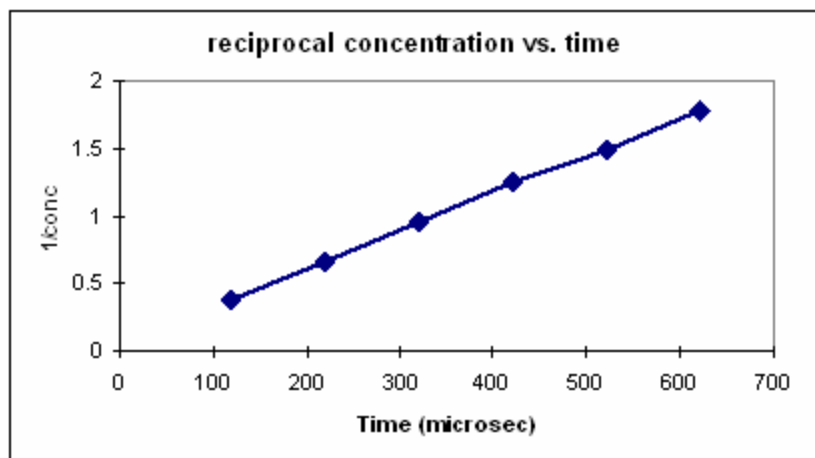
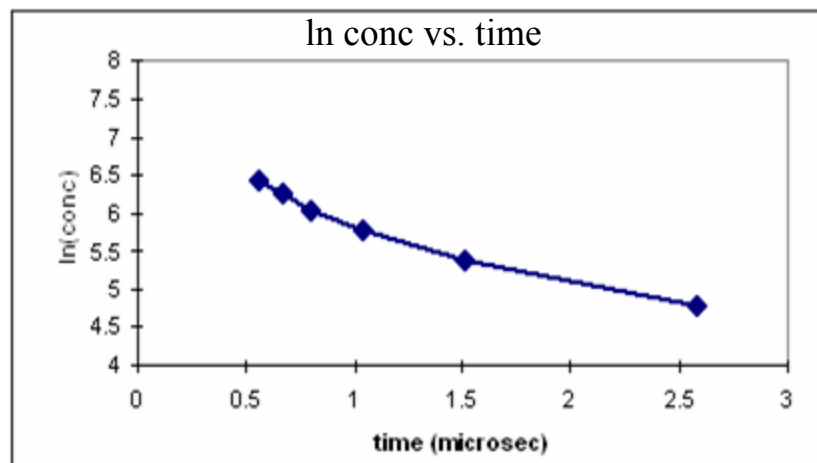
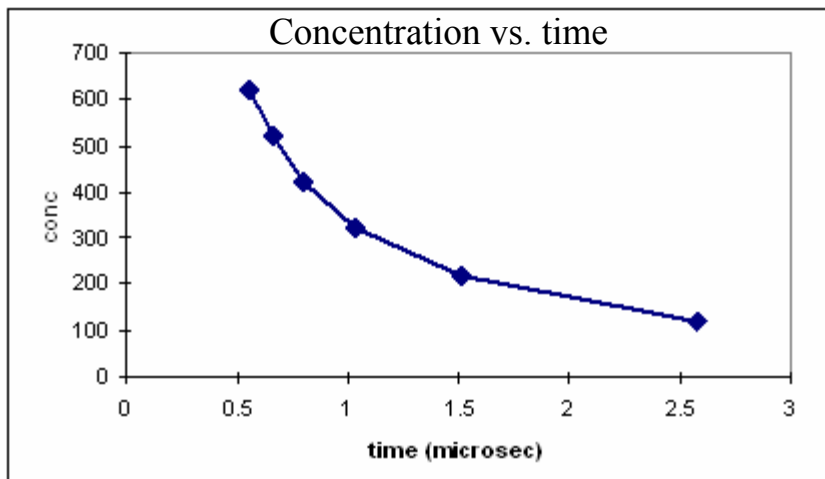
red is first order data
blue is second order data



Note: if you don't have enough data over a long enough time you can't tell the difference

Difference between First and Second Order

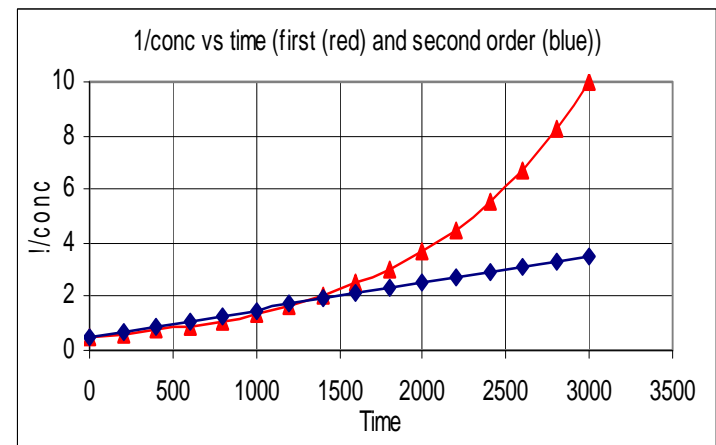
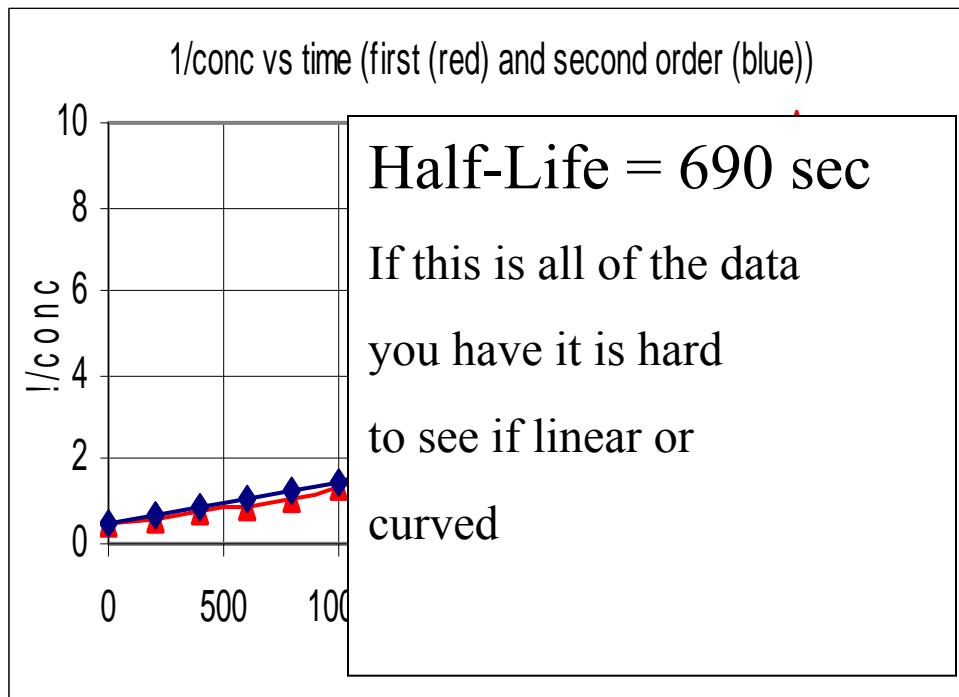
| | | | | | | | |
|--|--|------|------|------|-----|------|------|
| Concentration (moles/lit) | | 120 | 220 | 320 | 420 | 520 | 620 |
| Time (microsec)(you mult. each x10 ⁻⁵) | | 2.58 | 1.51 | 1.04 | 0.8 | 0.67 | 0.56 |



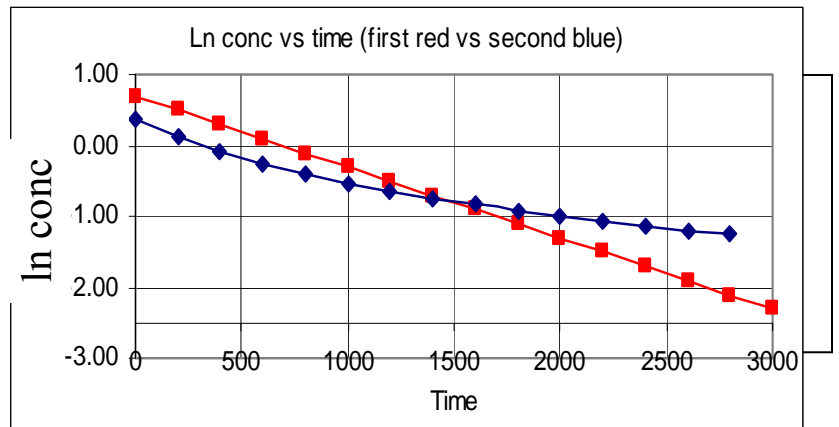
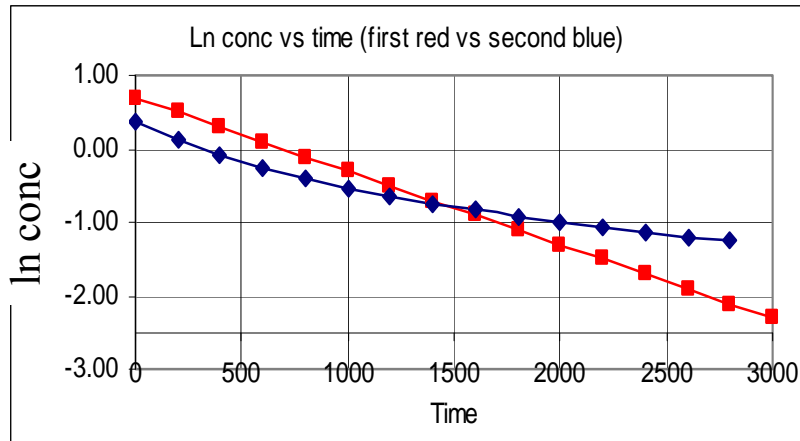
- You need sufficient data over a long enough time period to see deviations from linear.
- It is easier to see deviations from linear than deviations from a curve

Effect of “not-enough-data”

The longer the time interval over which data is collected, the lower concentration becomes and the more difficult it is to accurately make concentration measurements. However, with not enough time or drop in concentration it is difficult to see differences between orders. Curves can look straight, hyperbolas can look like log curves, etc.



Effect of “not-enough-data”



As a general rule – try to collect time/conc data over 3+ half lives
 This means concentration drops to less than 12.5% of initial concentration

100% - 50% - 25% - 12.5% - 6.25% - 3.125% - 1.56% -----
 half lives 1 2 3 4 5 6 -----

Second Order Reactions – two reactants

A + B = Products mathematically more complex than 1 reactant

$$dx/dt = k[A_0 - x][B_0 - x] \quad x = \text{amount reacted in time } t$$

$$1/(A_0 - B_0) \ln \{ (B_0(A_0 - x)) / (A_0(B_0 - x)) \} = kt$$

Graphical Analysis

$$\{1/(A_0 - B_0)\} [\ln \{ (B_0(A_0 - x)) / (A_0(B_0 - x)) \}] \quad \text{vs. } t$$

Slope = k

We try to find something we can graph that is linear which gives us what we want like rate constant k

If initial concentrations of A and B are the same $A_0 = B_0$

Then the equation becomes the same as for 1 reactant

$$d[A]/dt = -k[A]^2 \quad \text{or} \quad 1/(A_t) = kt + 1/(A_0)$$

This is simpler.

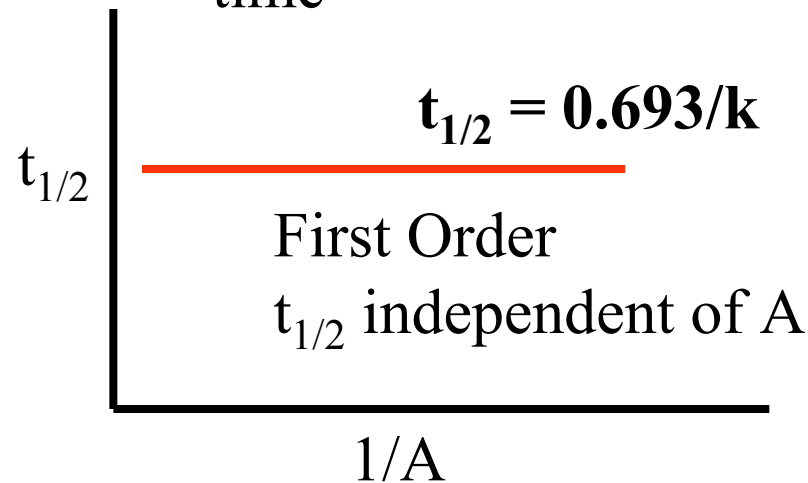
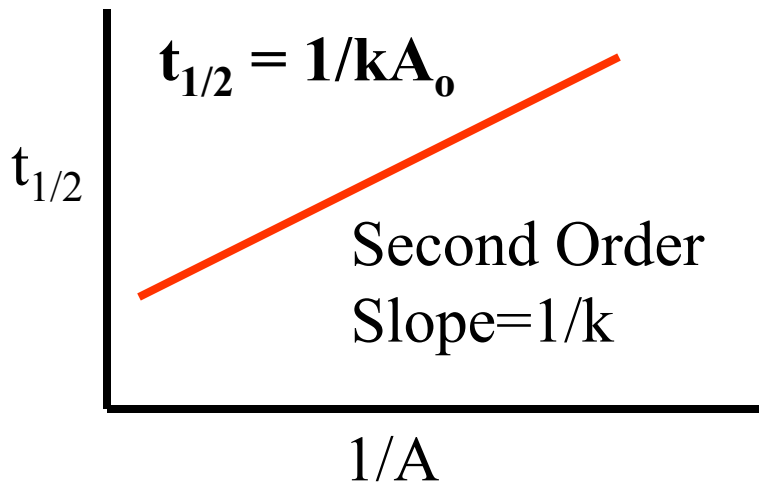
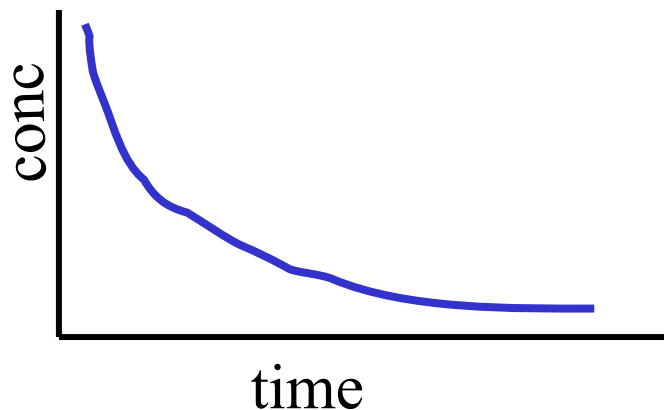
Often experimental conditions are adjusted to make $A_0 = B_0$

Second Order – Method of Half Lives

Half life of a second order reaction is a function of the continuously changing concentration. $t_{1/2} = 1/kA_0$

Measure half-life at various concentration (times) during reaction

| Conc A | time | $t_{1/2}$ |
|--------|------|-----------|
| --- | --- | --- |
| --- | --- | --- |
| --- | --- | --- |

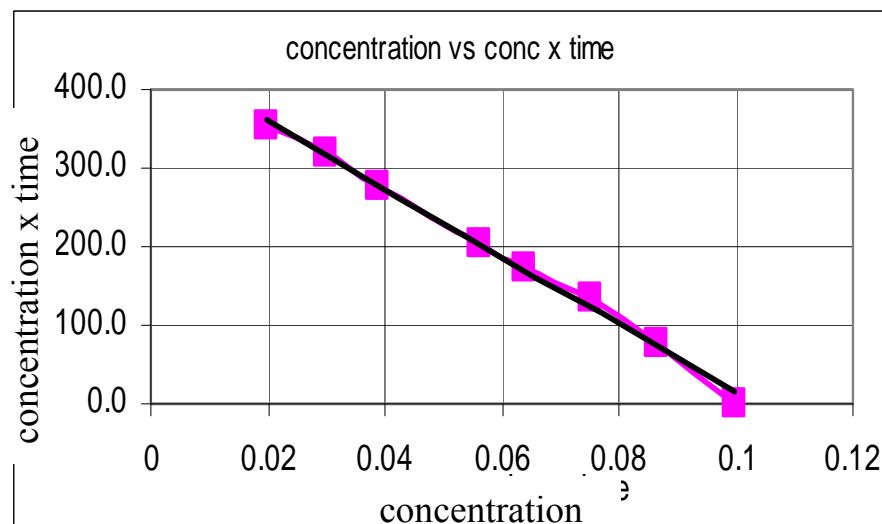
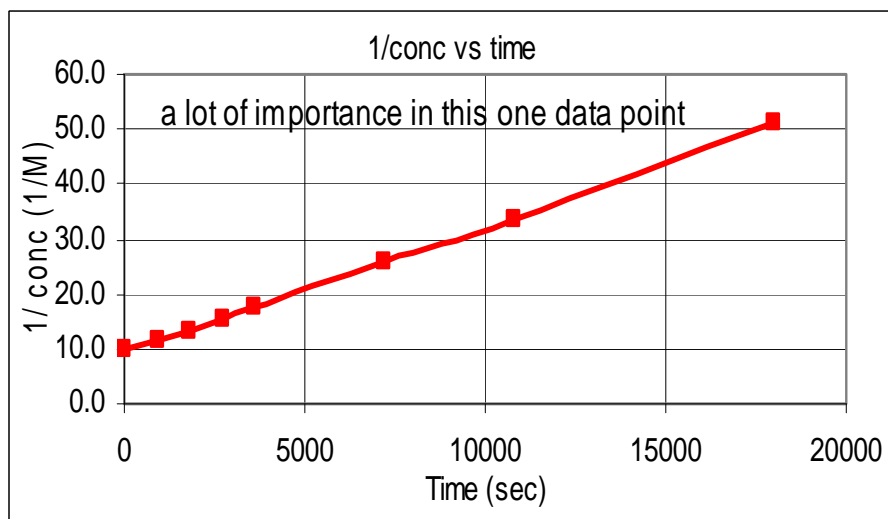
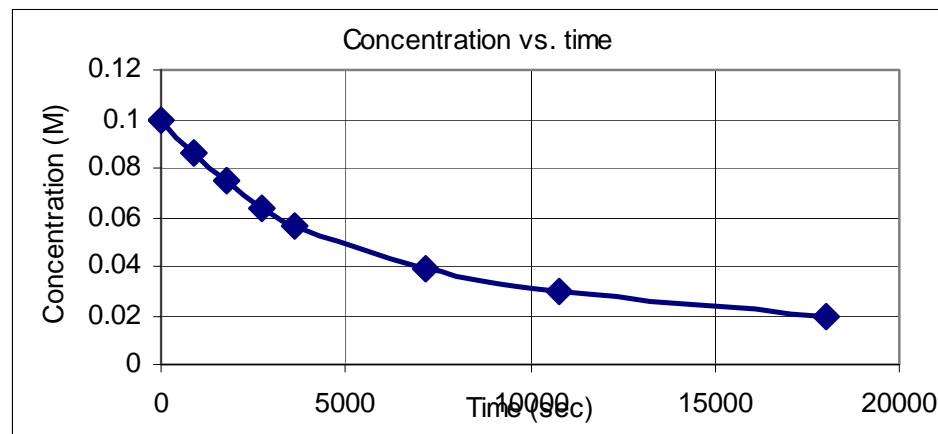


Second Order – reaction example

Disproportionation of p-toluenesulfinic acid (ArSO_2H)

| time s | ArSO ₂ H M | ArSO ₂ H 1/M | ArSO ₂ H Mxtime |
|--------|-----------------------|-------------------------|----------------------------|
| 0 | 0.1 | 10.0 | 0.0 |
| 900 | 0.0863 | 11.6 | 77.7 |
| 1800 | 0.0752 | 13.3 | 135.4 |
| 2700 | 0.064 | 15.6 | 172.8 |
| 3600 | 0.0563 | 17.8 | 202.7 |
| 7200 | 0.0387 | 25.8 | 278.6 |
| 10800 | 0.0297 | 33.7 | 320.8 |
| 18000 | 0.0196 | 51.0 | 352.8 |

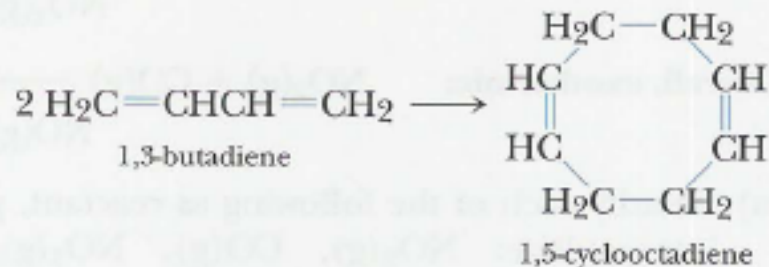
Kice & Bowers-JACS 84, 605 (1962)



Same information, less emphasis on one data point

Second Order Reaction Example

Butadiene, $C_4H_6(g)$, dimerizes when heated, forming 1,5-cyclooctadiene, C_8H_{12} . The data in the table were collected

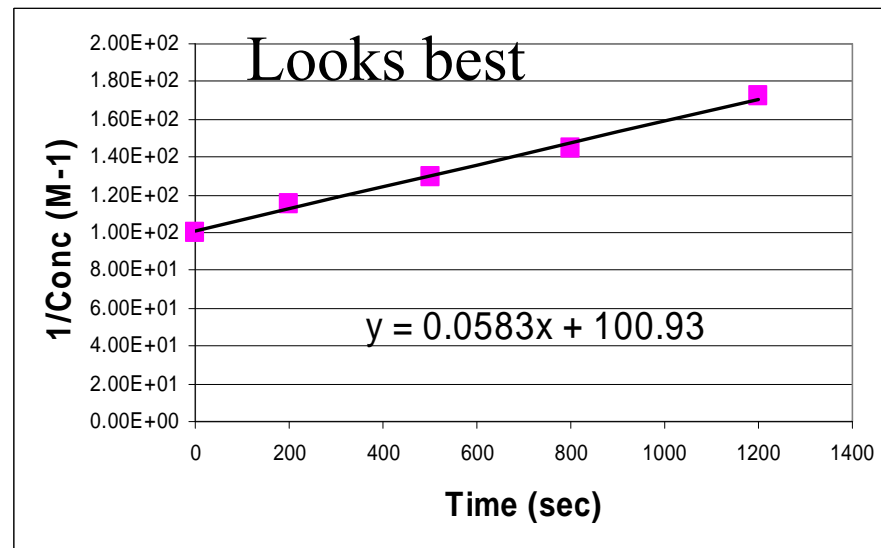
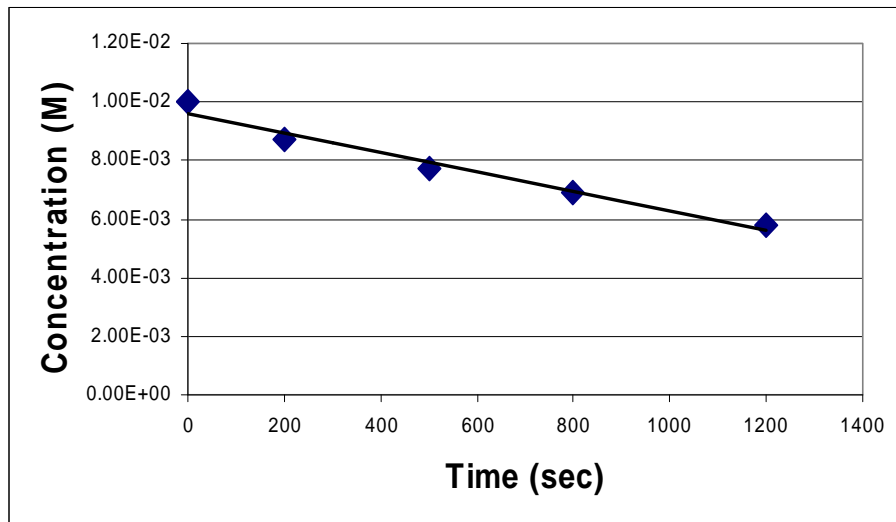


| $[C_4H_6]$ (mol/L) | Time (s) |
|-----------------------|-------------|
| 1.0×10^{-2} | 0 |
| 8.7×10^{-3} | 200 |
| 7.7×10^{-3} | 500 |
| 6.9×10^{-3} | 800 |
| 5.8×10^{-3} | 1200 |

- (a) Use a graphical method to verify that this is a second-order reaction.
- (b) Calculate the rate constant for this reaction.

see graphs next slide

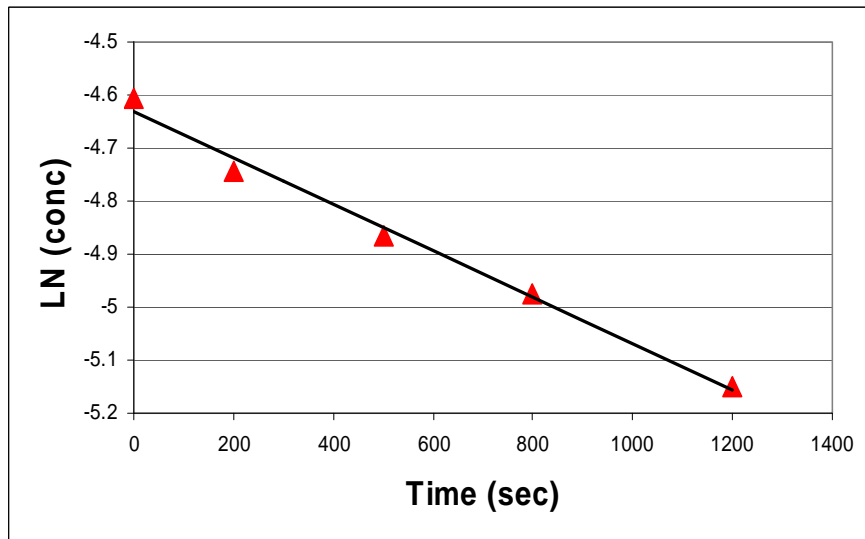
Second Order Reaction Example



Probably second order with rate constant = 0.58 L/mol-sec

Data at longer time is needed to be sure it is second order

Don't confuse "scatter" with "trend" in a graph



Differential Method (*Method of Slopes*)

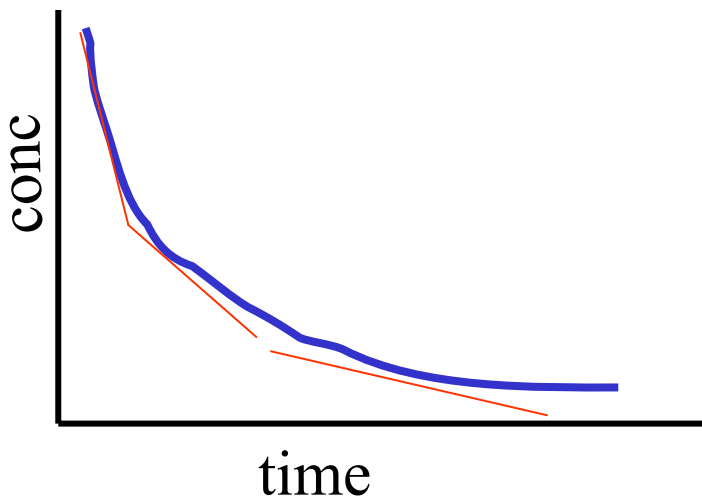
Determine rate (slope) at various times during a reaction

$$\text{Rate} = k (\text{conc})^n$$

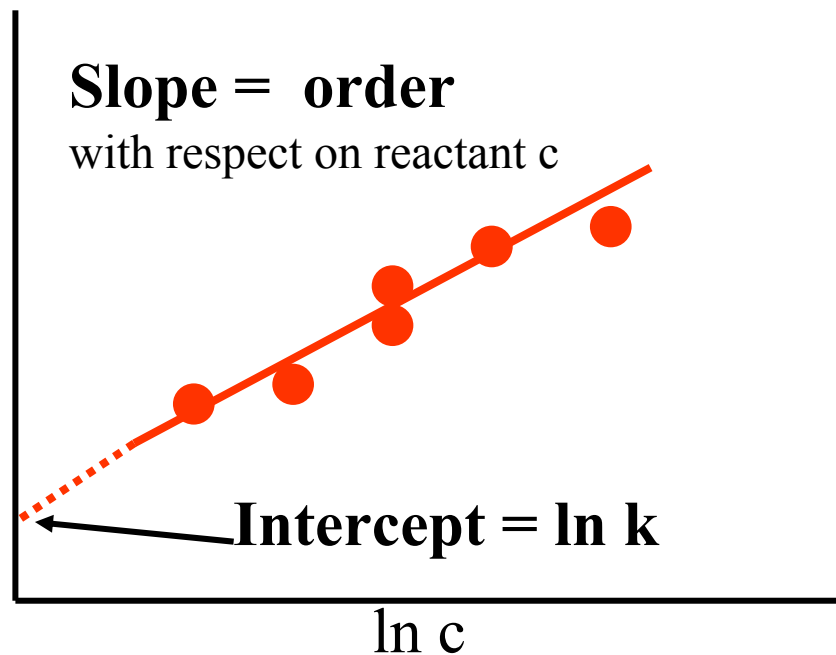
$$\ln(\text{Rate}) = \ln k + n \ln(\text{conc})$$

$$y = b + mx$$

| Conc R | Conc P | time | rate |
|--------|--------|------|------|
| --- | --- | --- | --- |
| --- | --- | --- | --- |
| --- | --- | --- | --- |



ln rate

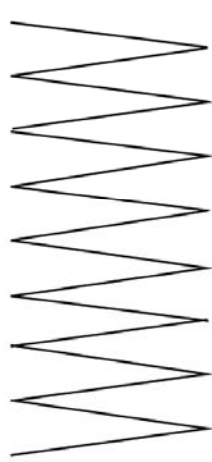


Calculation of rates in spreadsheets
 Careful of significant figures
 Accuracy and log-log plots

Example – Differential Method



Rate Data for Reaction of $\text{C}_4\text{H}_9\text{Cl}$ with Water

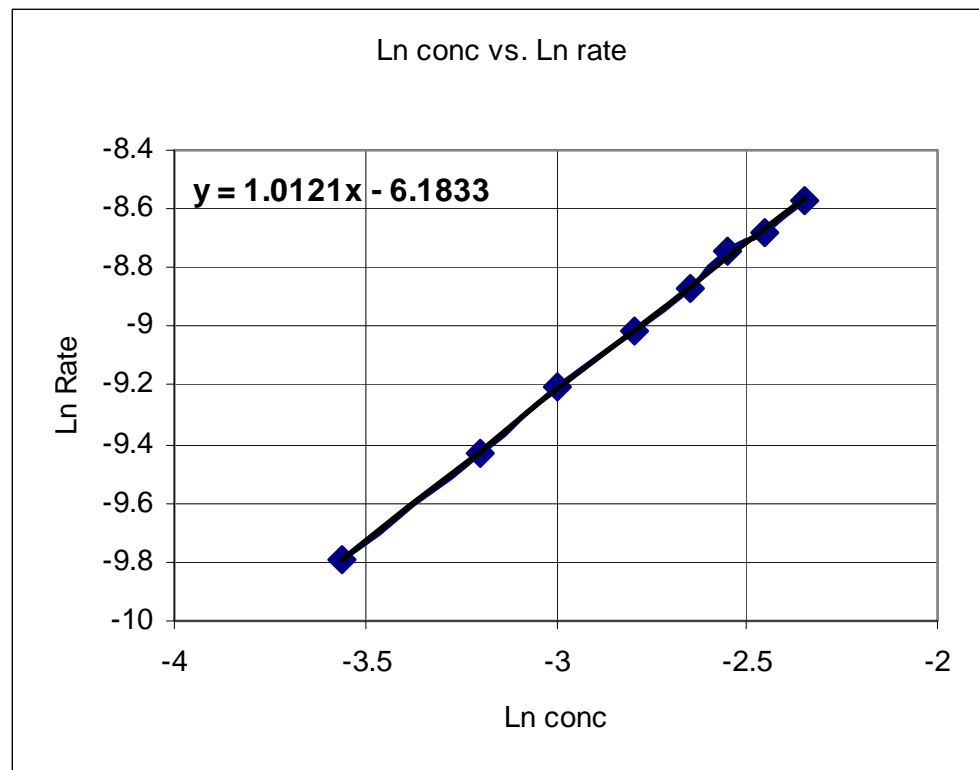
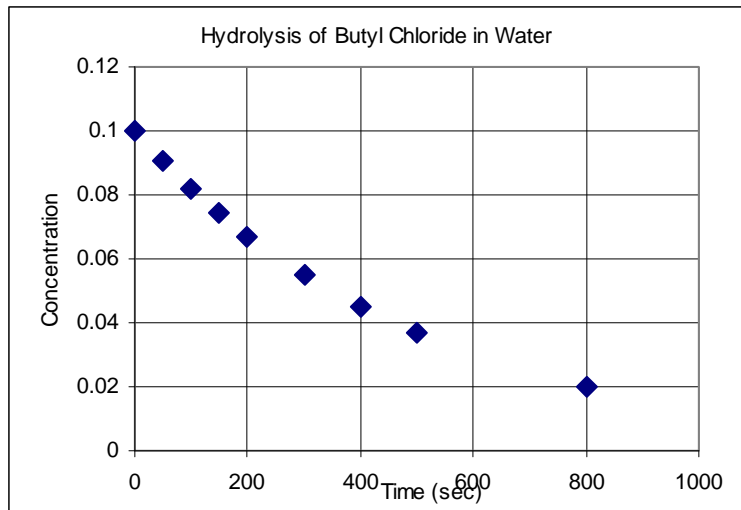
| Time, t (s) | $[\text{C}_4\text{H}_9\text{Cl}]$ (M) | Average Rate (M/s) | Conc at that rate | |
|---------------|---------------------------------------|---|------------------------|--------|
| 0.0 | 0.1000 |  | 1.9×10^{-4} | 0.0952 |
| 50.0 | 0.0905 | | 1.7×10^{-4} | 0.0862 |
| 100.0 | 0.0820 | | 1.6×10^{-4} | 0.0781 |
| 150.0 | 0.0741 | | 1.4×10^{-4} | 0.0706 |
| 200.0 | 0.0671 | | 1.22×10^{-4} | 0.0610 |
| 300.0 | 0.0549 | | 1.01×10^{-4} | 0.0498 |
| 400.0 | 0.0448 | | 0.80×10^{-4} | 0.0408 |
| 500.0 | 0.0368 | | 0.560×10^{-4} | 0.0284 |
| 800.0 | 0.0200 | | | |
| 10,000 | 0 | | | |

$$\text{Rate} = k (\text{conc})^n$$

$$\ln(\text{Rate}) = \ln k + n \ln(\text{conc})$$

$$y = b + mx$$

Differential Method



$$\text{Rate} = k (\text{conc})^n$$

$$\ln(\text{Rate}) = \ln k + n \ln(\text{conc})$$

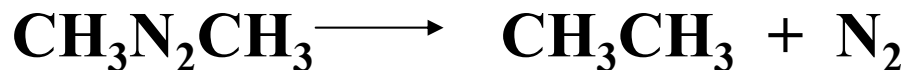
$$y = b + mx$$

Order = 1

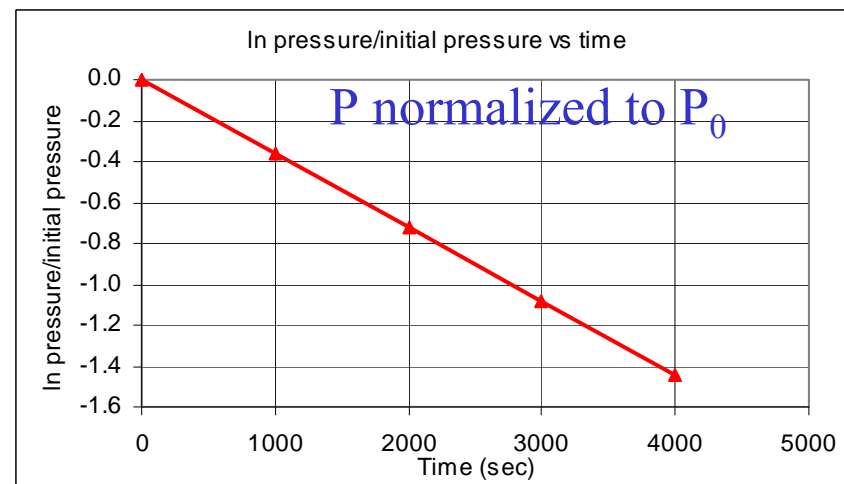
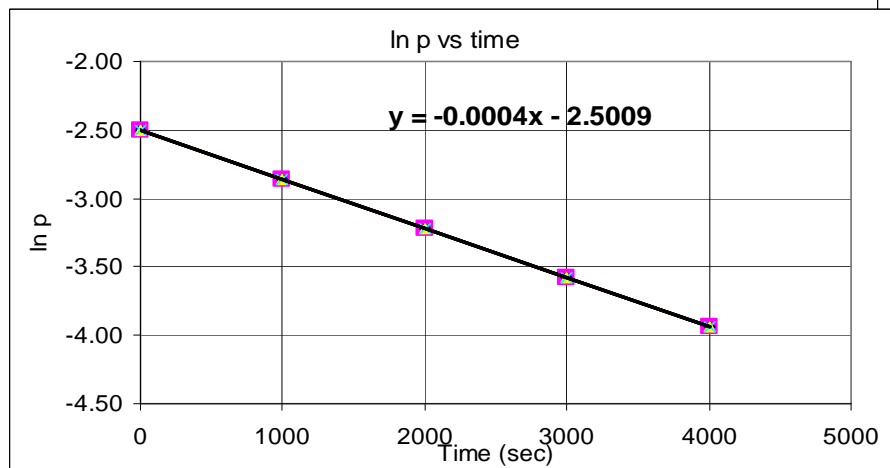
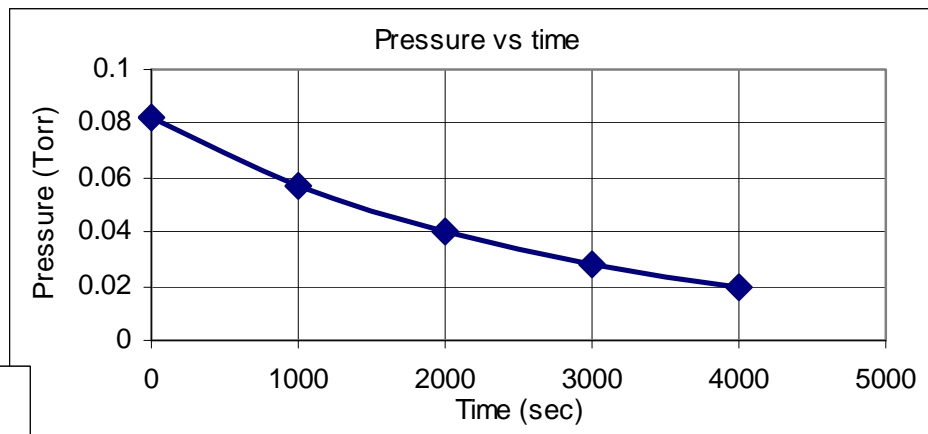
$\ln(k) = -6.188$ so $k = 0.00206 \text{ sec}^{-1}$

Experimental Example

Decomposition of azomethane at 600°C



| Time sec | Press(azomethane) Torr | ln p | ln(p/p ₀) |
|----------|------------------------|-------|-----------------------|
| 0 | 0.082 | -2.50 | 0.00 |
| 1000 | 0.0572 | -2.86 | -0.36 |
| 2000 | 0.0399 | -3.22 | -0.72 |
| 3000 | 0.0278 | -3.58 | -1.08 |
| 4000 | 0.0194 | -3.94 | -1.44 |



First Order $k=3.6 \times 10^{-4} \text{ sec}^{-1}$
Half-life = 1900 sec (32 min)

Complex Kinetics – Multiple Steps

For elementary 1 step process $d\text{Conc}/d\text{Time} = k(\text{Conc Reactants})^n$

for a multistep process

(most reactions of interest can be very complex)

example $2A \rightleftharpoons B \rightleftharpoons C$ each of the 4 arrows have a rate equations

$dB/dt = -k_1 A^2$ rate of formation of B from 2A loss of A gain of B

$dA/dt = k_2 (1/2B)^1$ reverse rate of formation of A from B

$dC/dt = k_3 B^1$ rate of forming C from B

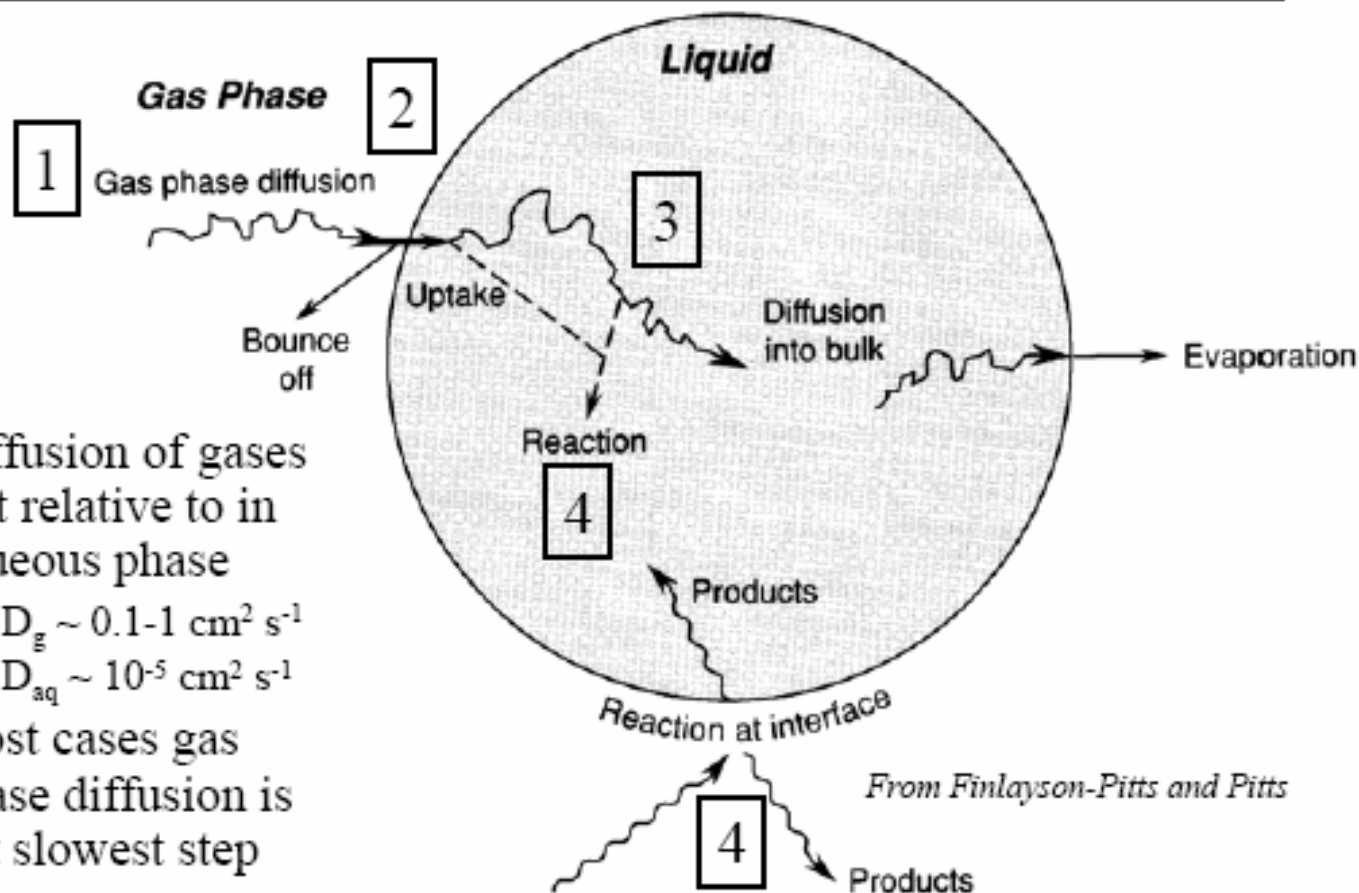
$dB/dt = -k_4 C^1$ reverse rate of forming B from C

This gives a set of simultaneous differential equations with 4 k's

Use experimental data to solve these simultaneous differential equations for all of the k's

Gas Reacting with Species in Liquid Droplet

Uptake and Reaction of Gases in Liquids



- Diffusion of gases fast relative to in aqueous phase
 - $D_g \sim 0.1-1 \text{ cm}^2 \text{ s}^{-1}$
 - $D_{aq} \sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
- Most cases gas phase diffusion is not slowest step

Example
Multi-step
process

Slowest
step in
multi-step
reaction
determines
overall
observed
rate

FIGURE 5.12 Schematic diagram of uptake and reaction of gases in liquids.

D

Elementary Steps vs. Overall Reaction

- Overall reaction is a series of simple elementary steps
- Order of an elementary step fits stoichiometry of that step
- Order of overall reaction (observed) many not fit stoichiometry of overall reaction

Simple Example-



overall process



Observed overall order is the rate of loss of A or formation of products

elementary step 1 is 1st, step 2 is 1st
step 3 is 2nd.

If steady state conc of C is small (if C is short lived) and A is high, step 3 may appear to be 1st (pseudo-first order)

Types of Elementary Reactions

- Unimolecular reactions



$$-dn_A/dt = dn_B/dt = dn_C/dt = k n_A$$



$$-dn_A/dt = (1/2)dn_B/dt = k n_A$$

k is in units of s^{-1}

- Bimolecular reactions



$$-dn_A/dt = -dn_B/dt = dn_C/dt = dn_D/dt = k n_A n_B$$



$$(-1/2)dn_A/dt = dn_B/dt = dn_C/dt = k n_A^2$$

k is in units of $cm^3 \text{ molecule}^{-1} s^{-1}$

- Termolecular reactions



$$-dn_A/dt = -dn_B/dt = dn_C/dt = k n_A n_B n_M$$



$$(-1/2)dn_A/dt = dn_B/dt = k n_A^2 n_M$$

k is in units of $cm^6 \text{ molecule}^{-2} s^{-1}$

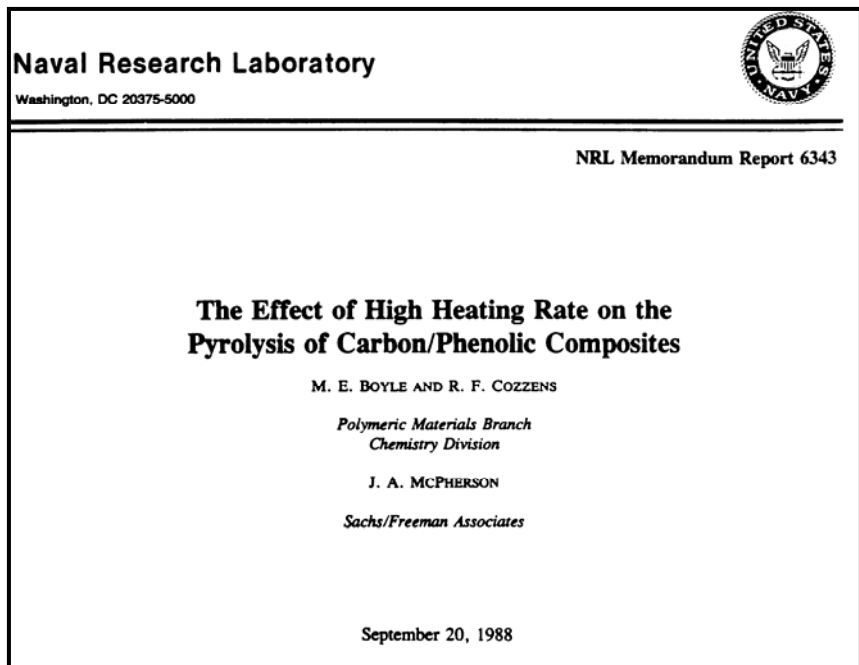
Most overall reactions are a series of multiple elementary reactions

Overall reaction order could be the same as the order of the slowest in a series of steps, but if several steps have similar rates but different orders, the overall order could be complex and not simply 1 or 2.

Very Complex Multistep Reactions

Many reactions are really many processes and multi-steps all taking place at the same time. We may only see (experimental) an “**over all process**”. Kinetic equations describe that process.

Discussions of an Example of a complex overall process with many steps:



Kinetic equations can be useful for modeling behavior of systems even if the actual step-by-step mechanism is too complex to understand.