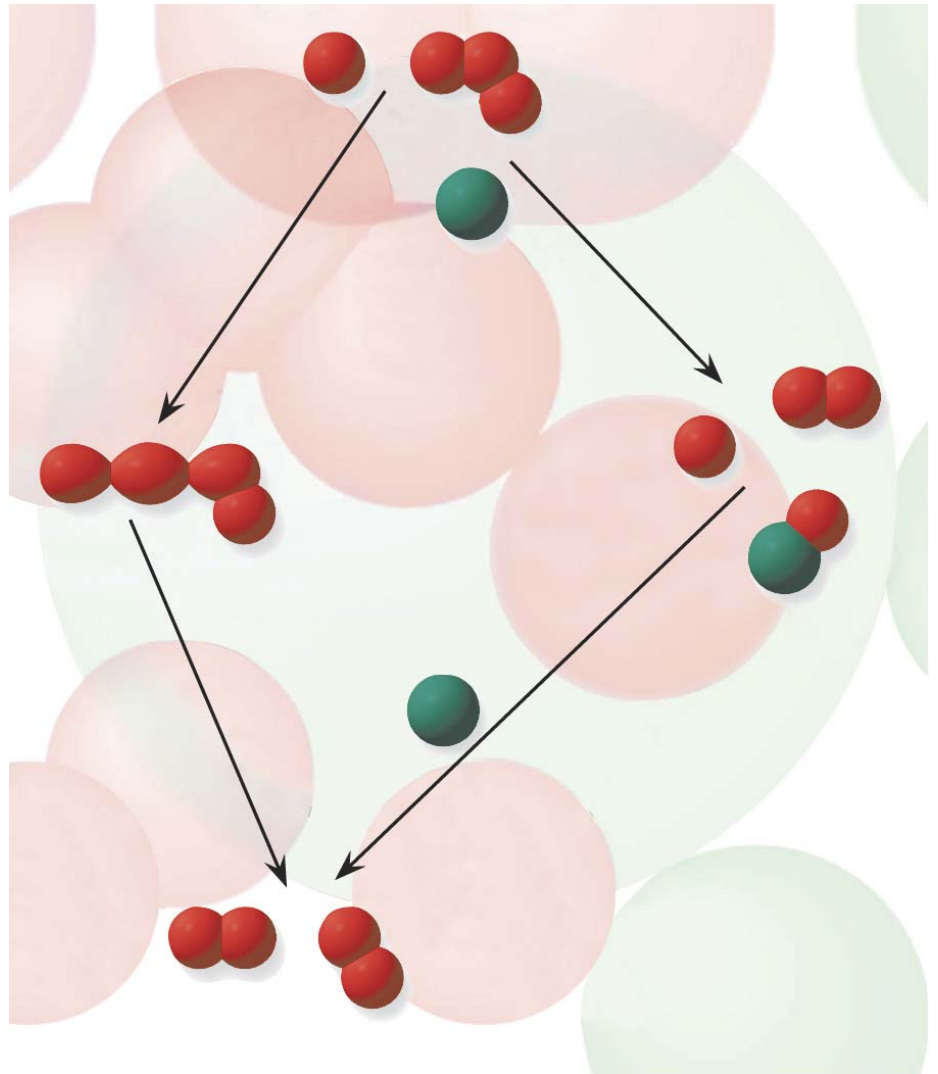


# Lecture 12 – Chapter 15, Section 4

## Experiments

- Experimental rate laws
- First order
- Second order
- Method of Isolation
- Method of Initial Rates



# Rate Laws can be predicted from

- 0% 1. Reaction stoichiometry
- 0% 2. Phase of the moon
- 0% 3. Reaction mechanisms
- 0% 4. Collision rates

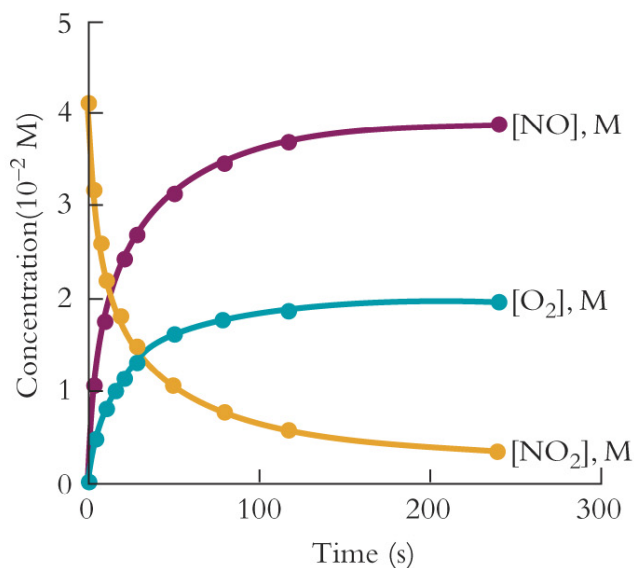
# Understanding Reactions

1. Have some overall reaction
2. Dream up (hypothesize) one or more likely reaction mechanisms
3. Derive rate law corresponding to each mechanism
4. Measure experimental rate law
5. Rule out impossible mechanisms
6. Devise further experiments if necessary

# Connecting Rate Law to Experiment

- Reaction rate we had before:  $\text{Rate} = \frac{1}{d} \frac{\Delta[\text{D}]}{\Delta t}$

- Experimentally we measure  $[\text{D}]$  at various times



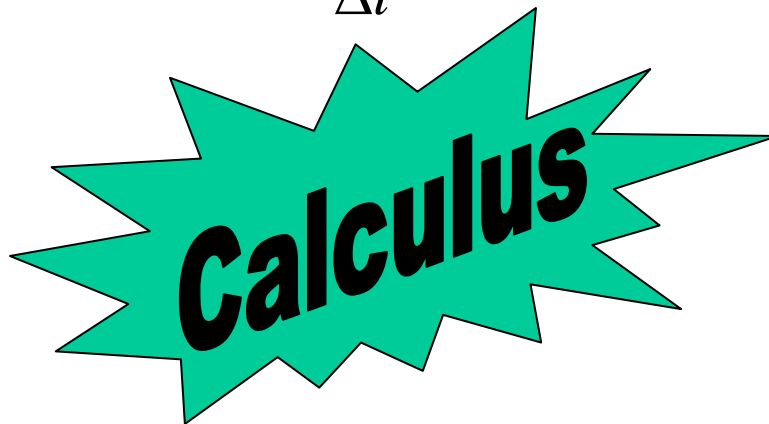
Time (s)	0	5.0	10	15	20	30	50	80	120	240
$[\text{NO}_2]$ ( $10^{-2}$ M)	4.1	3.1	2.5	2.1	1.8	1.4	1.0	0.70	0.50	0.30
$[\text{NO}]$ ( $10^{-2}$ M)	0	1.0	1.6	2.0	2.3	2.7	3.1	3.4	3.6	3.8
$[\text{O}_2]$ ( $10^{-2}$ M)	0	0.50	0.80	1.0	1.1	1.3	1.6	1.7	1.8	1.9

- We would like to convert rate law from  $\Delta$ concentration just to concentration

# Integrated Rate Laws

- Calculus makes this possible (thank goodness for mathematicians). For a first-order rate law...

$$\text{Rate} = \frac{\Delta[\text{NO}_2]}{\Delta t} = k[\text{NO}_2]$$



$$\ln\left(\frac{[\text{NO}_2]_0}{[\text{NO}_2]}\right) = kt$$

or

$$[\text{NO}_2] = [\text{NO}_2]_0 e^{-kt}$$

# First-order Rate Laws

- General form of the rate law and integrated rate law

$$\text{Rate} = \frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]$$

$$\ln\left(\frac{[\text{A}]_0}{[\text{A}]}\right) = kt$$

or

$$[\text{A}] = [\text{A}]_0 e^{-kt}$$

# First-order Rate Laws

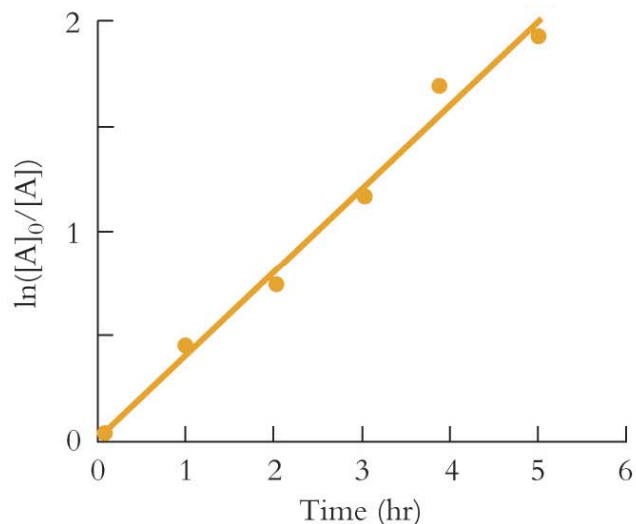
- Note that the integrated form is linear

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

$$y = \ln\left(\frac{[A]_0}{[A]}\right)$$

$$x = t$$

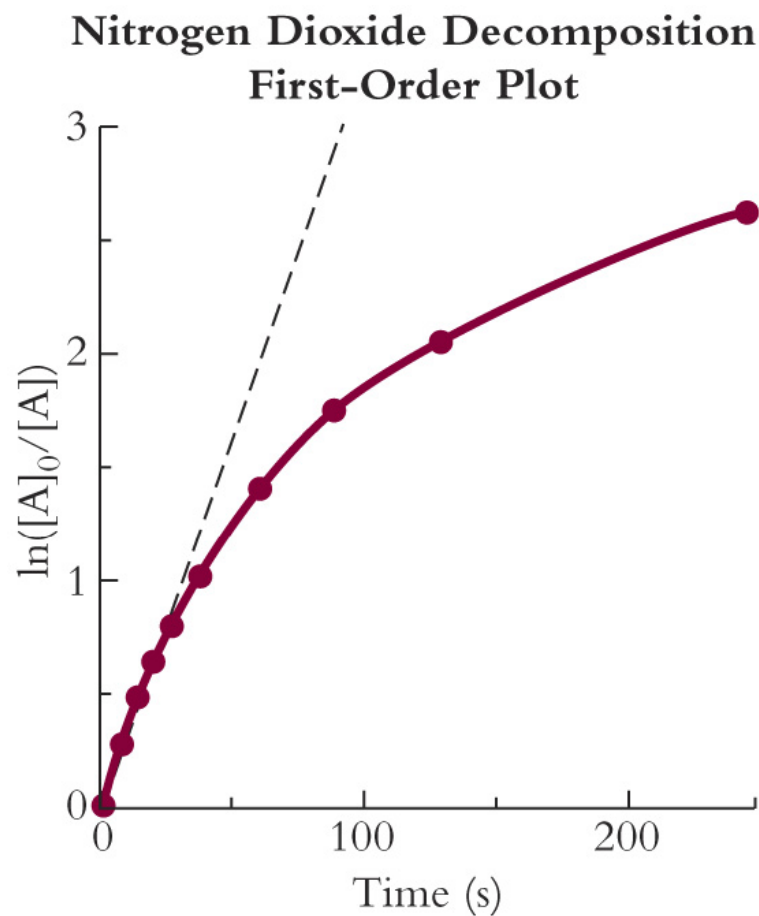
$$\text{slope} = k$$



Time (hr)	$[C_5HBr]$ (M) <sub>11</sub>	$[C_5H_{11}Br]_0/[C_5H_{11}Br]$	$\ln([A]_0/[A])$
0	0.150	1.00	0
1.00	0.099	1.52	0.42
2.00	0.073	2.05	0.72
3.00	0.047	3.19	1.16
4.00	0.028	5.36	1.68
5.00	0.022	6.82	1.92

# Not first order?

- If reaction is not first order, plot will not look linear





# Half-life

- Amount of time it takes for  $\frac{1}{2}$  of reactant to be used up (or half of product to form)
- For first-order  $\frac{1}{2}$ -life is independent of concentration
- Always same time to use up  $\frac{1}{2}$  of stuff
- Why the number  $e$  is so special
- Examples:
  - Radioactivity
  - Photochemistry
  - Some reactions

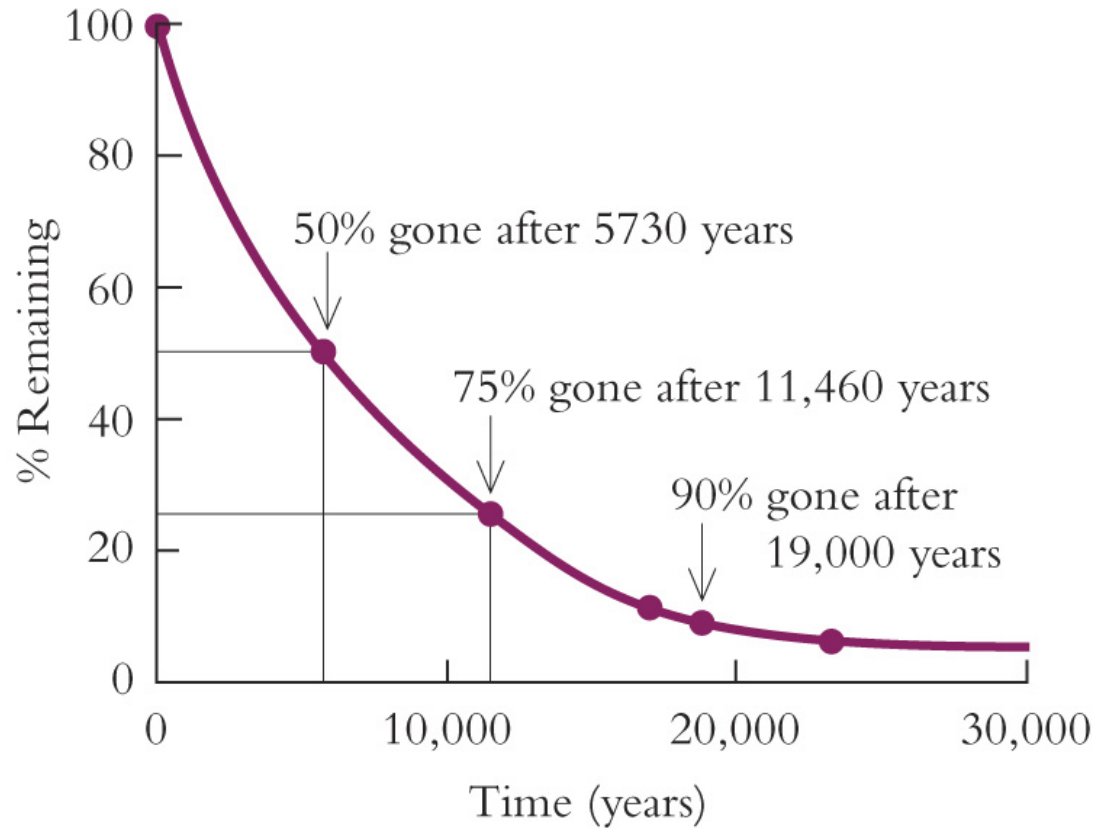
$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

$$\ln\left(\frac{[A]_0}{\frac{1}{2}[A]_0}\right) = kt_{\frac{1}{2}}$$

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

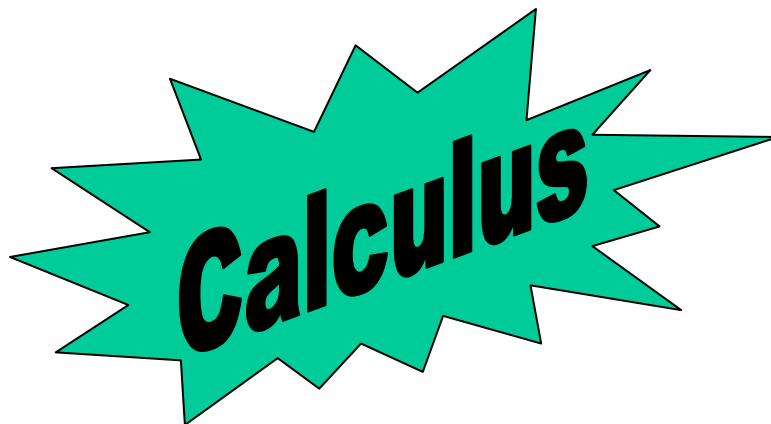
$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

# Half-life



# Second-order Rate Law

$$\text{Rate} = \frac{\Delta[A]}{\Delta t} = k[A]^2$$



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

or

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

A second-order reaction will look linear if we plot  $t$  as  $x$  and what as  $y$ ?

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

20% 1.  $1/[A]$

20% 2.  $1/[A] - 1/[A]_0$

20% 3.  $1/[A]_0$

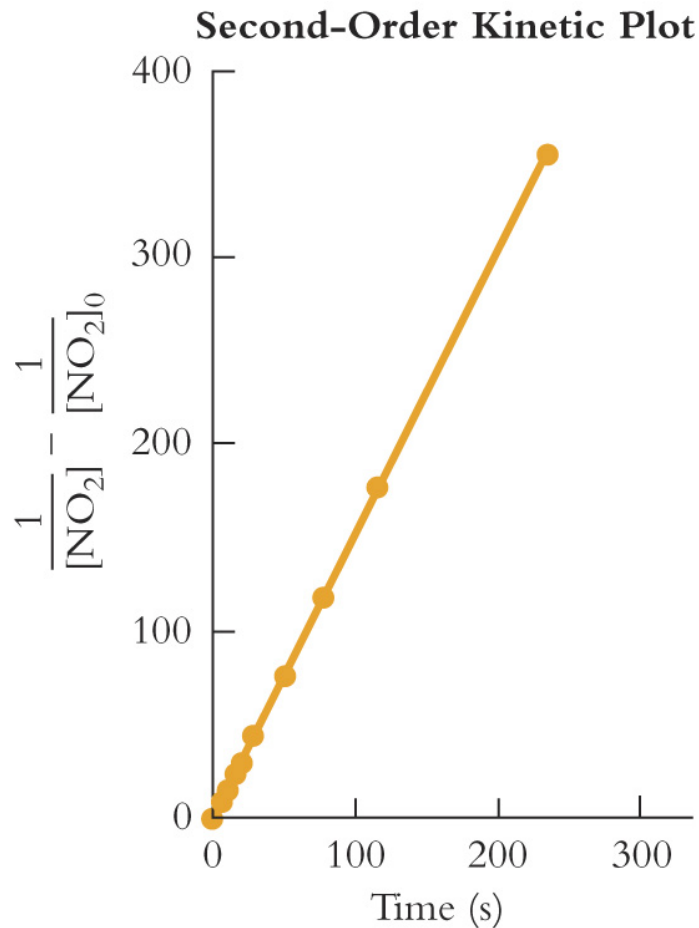
20% 4.  $k$

20% 5.  $kt$

1	2	3	4	5
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# Second-order Rate Laws

- Integrated form is linear again



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

$$y = \frac{1}{[A]} - \frac{1}{[A]_0}$$

$$x = t$$

$$\text{slope} = k$$

$$\text{intercept} = 0$$

OR

$$y = \frac{1}{[A]}$$

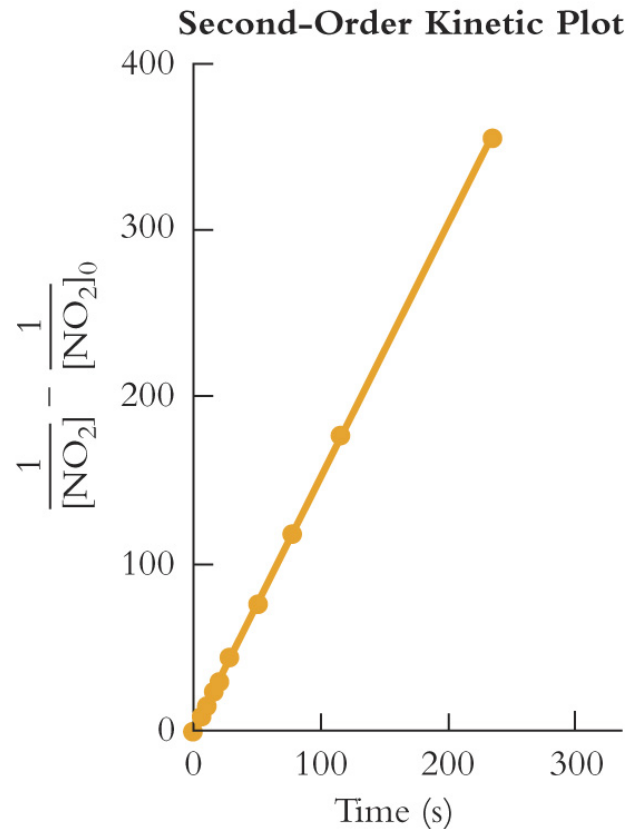
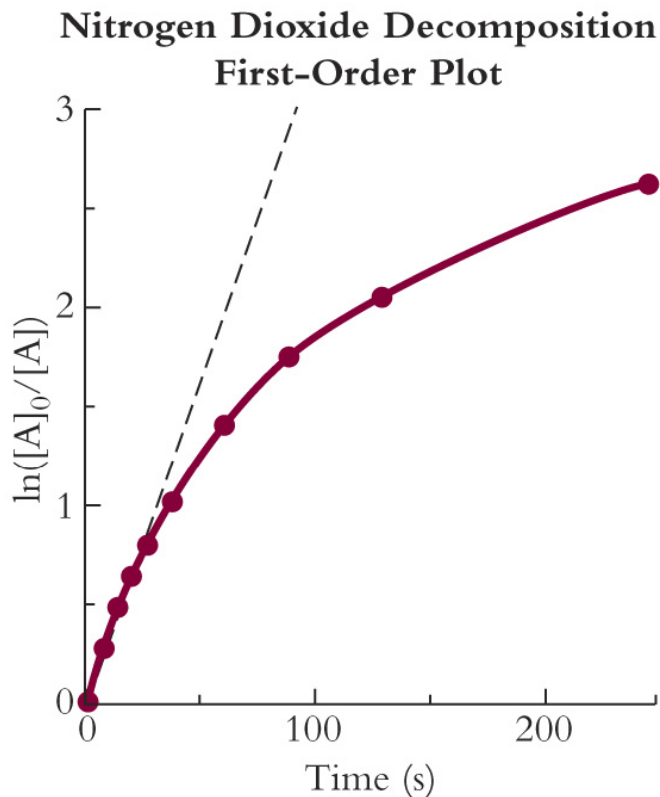
$$x = t$$

$$\text{slope} = k$$

$$\text{intercept} = \frac{1}{[A]_0}$$

Recall  $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$  reaction

- Two different mechanisms gave two different rate laws
  - Mechanism I predicted:  $\text{Rate}_I = k[\text{NO}_2]$
  - Mechanism II predicted:  $\text{Rate}_{II} = k[\text{NO}_2]^2$



# Half-life

- Can derive half-life for second-order reaction
- But, half-life depends on concentration
  - Not nearly as useful as first-order
  - Not usually used, so don't worry about it

# Zero-order

- Zero-order reactions also happen

$$\text{Rate} = k$$

$$[A]_0 - [A] = kt$$

or

$$[A] = -kt + [A]_0$$

$$y = [A]_0 - [A]$$

$$x = t$$

$$\text{slope} = k$$

OR

$$y = [A]$$

$$x = t$$

$$\text{slope} = -k$$

$$\text{intercept} = [A]_0$$

- Higher-order reactions also common



# Summary of Integrated Rate Laws

Order	Rate Law	Concentration Dependence	Linear Plot
0	Rate = $k$	$[A]_o - [A] = kt$	$[A]_o - [A]$ vs. $t$
1	Rate = $k[A]$	$\ln\left(\frac{[A]_o}{[A]}\right) = kt$	$\ln\left(\frac{[A]_o}{[A]}\right)$ vs. $t$
2	Rate = $k[A]^2$	$\frac{1}{[A]} - \frac{1}{[A]_o} = kt$	$\frac{1}{[A]} - \frac{1}{[A]_o}$ vs. $t$

Note that we have ignored effects of product concentrations.

This is OK for some reactions, but generally we need to consider concentrations of all components (not right now)

# Multiple components

- What if rate law has multiple things in it?

$$\text{Rate} = k[\text{A}]^y[\text{B}]^z$$

- Different methods used to determine  $y$  and  $z$ .
  - Isolation
  - Initial Rates
  - Others

# Method of Isolation

- Do experiments with one component in huge excess
  - Concentration is effectively constant



$$\text{Rate} = k[A]^y[B]^z$$

Initially  $[A]_0 = 5 \times 10^{-3} \text{ M}$  and  $[B]_0 = 1 \times 10^{-5} \text{ M}$

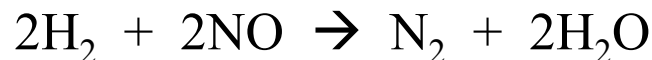
When reaction is complete...

$$[A]_f = 4.99 \times 10^{-3} \text{ M} \quad \text{and} \quad [B]_f = 0 \text{ M}$$

- Now we can measure concentration of [B] with time and make plots to determine  $z$
- Repeat with [B] in huge excess to determine  $y$

# Method of Initial Rates

- If possible, measure reaction rate over very short time period
- If time period is short enough, concentrations of all reactants are approximately constant
- Vary initial concentration of one component to determine reaction order



<u>Experiment</u>	<u>[H<sub>2</sub>]</u>	<u>[NO]</u>	<u>Initial rate</u>
1	0.001 M	0.002 M	$1.2 \times 10^{-4}$ M/s
2	0.001 M	0.003 M	$1.8 \times 10^{-4}$ M/s
3	0.002 M	0.002 M	$4.8 \times 10^{-4}$ M/s

Doubling [H<sub>2</sub>] increases rate by 4. So [H<sub>2</sub>] is second-order

# Initial Rates

$$\text{Initial Rate 1} = 1.2 \times 10^{-4} \text{ M/s} = k(0.001\text{M})^y (0.002\text{M})^z$$

$$\text{Initial Rate 2} = 1.8 \times 10^{-4} \text{ M/s} = k(0.001\text{M})^y (0.003\text{M})^z$$

divide

$$\frac{1.2 \times 10^{-4} \text{ M/s}}{1.8 \times 10^{-4} \text{ M/s}} = \frac{k(0.001\text{M})^y (0.002\text{M})^z}{k(0.001\text{M})^y (0.003\text{M})^z}$$

$$\frac{2}{3} = \left( \frac{0.002}{0.003} \right)^z$$

$$\ln\left(\frac{2}{3}\right) = z \ln\left(\frac{0.002}{0.003}\right)$$

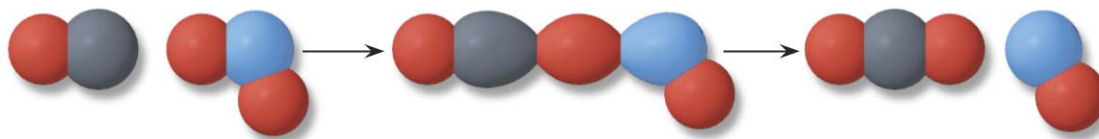
$$z = 1$$

# Mechanisms

- Recall mechanisms explain reactions in detail
- True mechanism must have the following behaviors:
  - Mechanism is composed of one or more elementary reactions that are uni-, bi-, or termolecular
  - Sum of individual steps must yield overall reaction stoichiometry
  - Mechanism must be consistent with experimental rate law
- Multiple mechanisms may yield the same rate law
  - Agreement with experiment does NOT prove a mechanism is correct
  - Disagreement with experiment DOES prove a mechanism incorrect

# Rate-determining step

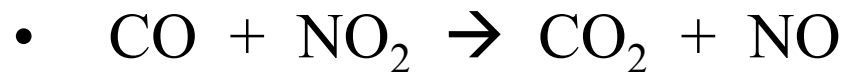
- Already discussed importance of rate-determining step
- Have done several examples with rate-determining step was
  - The only step of a one-step mechanism
  - The first step of a multi-step mechanism
- In these cases we get an overall rate law that matches the rate-determining elementary reaction
- We'll do one more example like this...



One step mechanism

1. CO collides with  $\text{NO}_2$
2. CO steals an O
3. Result is  $\text{CO}_2$  and NO

So elementary reaction is same as overall reaction





What is the rate law corresponding to this 1-step mechanism?



- 0%** 1. Rate =  $k[\text{CO}]$
- 0%** 2. Rate =  $k[\text{NO}_2]$
- 0%** 3. Rate =  $k[\text{CO}][\text{NO}_2]$
- 0%** 4. Rate =  $k[\text{CO}_2][\text{NO}]$
- 0%** 5. Rate =  $k[\text{CO}][\text{NO}_2][\text{CO}_2][\text{NO}]$

1	2	3	4	5
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# Today

- Finish CAPA #7

# Wednesday

- Seminar 4:00 Schaap 1000
- Start/Finish CAPA #8
- Work on previous chapters...