"A" students work
(without solutions manual)
~ 10 problems/night.

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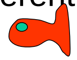
Module #14
Kinetics

FITCH Rules

General
- G1: Suzuki is Success
- G2. Slow me down
- G3. Scientific Knowledge is Referential
- G4. Watch out for Red Herrings



- G5. Chemists are Lazy

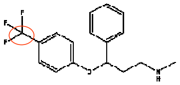
Chemistry
- C1. It's all about charge $E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$
- C2. Everybody wants to "be like Mike"
- C3. Size Matters $E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$
- C4. Still Waters Run Deep

- C5. Alpha Dogs eat first

Anti-depressants, work to inhibit seratonin uptake

http://chemfinder.cambridgesoft.com/

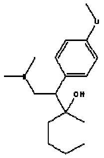
Prozac=
fluoxetine



Binds to human serum proteins:
Albumin and glycoprotein

Can build up in body; make you dizzy

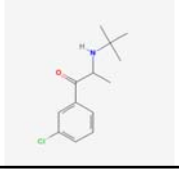
Effexor =
venlafaxine



Metabolized rapidly; user must take daily

How do we measure and
Report this effect, compare to others?

Wellbutrin=bupropion



This one works to inhibit dopamine
Reuptake; also metabolized rapidly

Look at structure and explain
Longevity in body

Question involves how fast a chemical reaction proceeds

$$aA + bB \xrightarrow{speed} cC + dD$$

As is usual,
define some sort of standard experimental measurement

Rule G3: Science is Referential

Determine what we need to measure/describe/hold constant

Begin with three "visual" experiments

1. **evaporation of water from a glass from blowing hot air in a desert**

$$H_2O_\ell \xrightarrow{speed} H_2O_g$$

2. radioactive decay of polonium
3. H_2 formation

Observe water level

Before we start our experiment

Calculate the molarity of water

$$\left(\frac{1g}{mL}\right)\left(\frac{1mole}{1+1+16\ g}\right)\left(\frac{1000mL}{1L}\right) = 55.55M$$

Memorize this Number!!!

Calculate number of moles/L of 1 atm gas phase

$$PV = nRT \qquad \frac{P}{RT} = \frac{n}{V}$$

$$\frac{n}{V} = \frac{1atm}{\left(0.082\frac{L\cdot atm}{mole\cdot K}\right)(25+273)}$$

$$\frac{n}{V} = 0.0408\frac{moles}{L}$$

Which one will be easiest to measure Concentration change?

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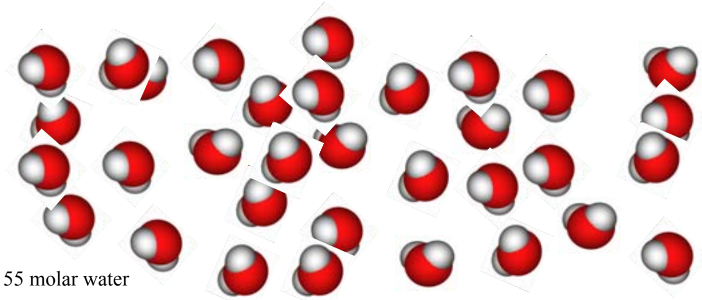
Module #14
Kinetics: Visualization

Visualization What do you observe?

$$H_2O_\ell \xrightarrow{speed} H_2O_g$$

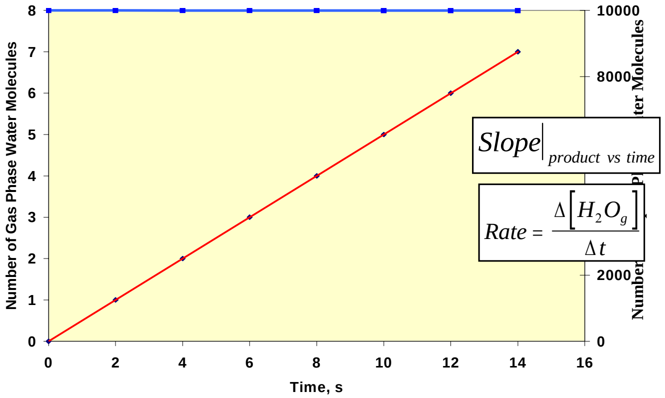
Time, s	#escapes
2	1
4	2
6	3
8	4
10	5
12	6



55 molar water

Visualization How should we measure this evaporation of water?

Number of gas phase water molecules vs time?
Number of liquid phase water molecules vs time? **NO change; 55 M**



$$Slope\Big|_{product\ vs\ time}$$

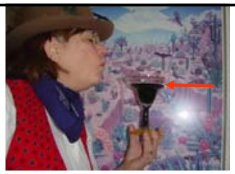
$$Rate = \frac{\Delta\left[H_2O_g\right]}{\Delta t}$$

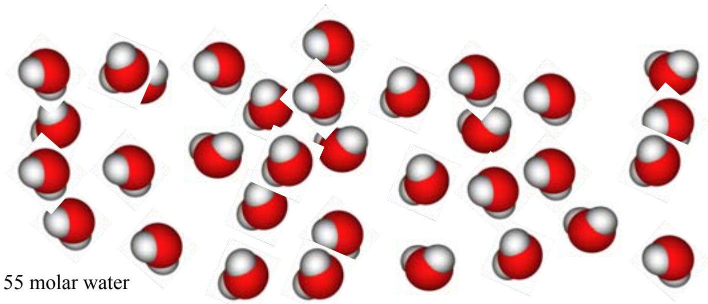
What kind of "measurement" (comparative number should we designate)?

Suppose we double the amount of water in the pot?

Will the rate change?

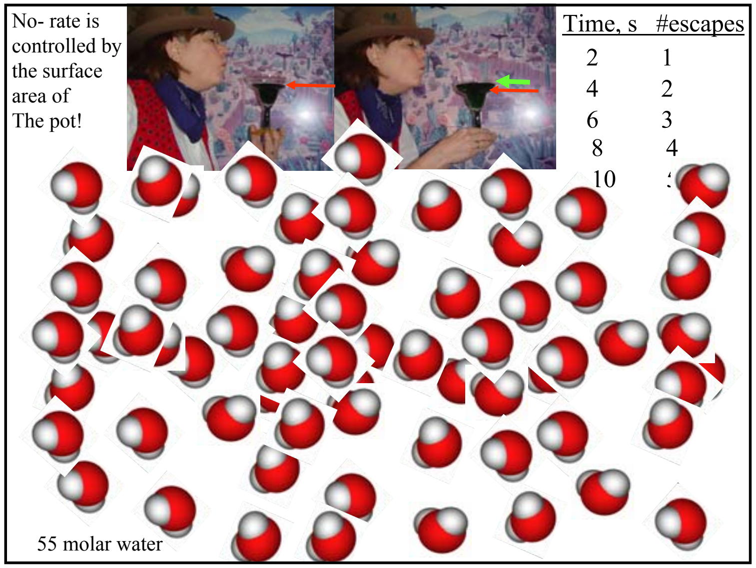
$H_2O_\ell \xrightarrow{speed} H_2O_g$


Observe water level


55 molar water

No- rate is controlled by the surface area of The pot!

Time, s	#escapes
2	1
4	2
6	3
8	4
10	[illegible]

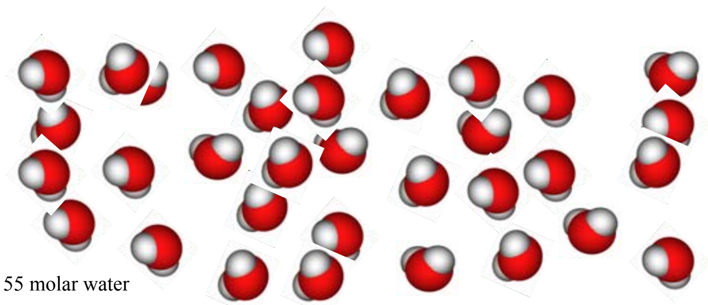

55 molar water

Visualization

Suppose we increase the velocity of the water molecules?

Will the rate change?

$H_2O_\ell \xrightarrow{speed} H_2O_g$


55 molar water

Visualization

What do you observe?

$H_2O_\ell \xrightarrow{speed} H_2O_g$

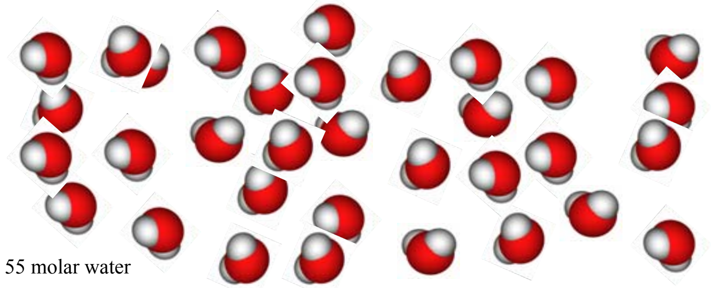
$Rate \propto T$

$\boxed{Rate \propto k_T}$

Prior experiment

Time, s	#escapes
2	1
4	2
6	3
8	4
10	5

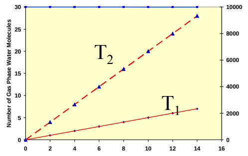
Time, s	#escapes
1	1
2	2
3	3
4	4
5	5
6	6


55 molar water

Visualization

First “visual” experimental results

$$H_2O_\ell \xrightarrow{speed} H_2O_g$$



$$\boxed{Rate = \frac{\Delta[\mathrm{Pr}\,oduct]}{\Delta t}}$$

$$\boxed{Slope = time\ independent}$$

$$\boxed{Rate \neq amount\ of\ water} \longleftrightarrow \boxed{Rate \propto [H_2O]^0 = 1}$$

$$\boxed{Rate \propto k_T}$$

Begin with three “visual” experiments

1. evaporation of water

$$H_2O_\ell \xrightarrow{speed} H_2O_g$$

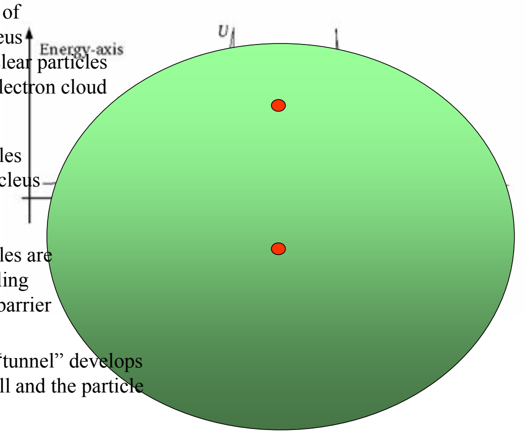
2. radioactive decay of polonium

$${}^{210}_{84}Po \xrightarrow{speed} {}^{4}_{2}He + {}^{206}_{92}Pb$$

3. H_2 formation

Rule G3: Science is Referential

An atom consists of
the nucleus
with nuclear particles
and an electron cloud



The nuclear particles
Are held in the nucleus
By an energy wall

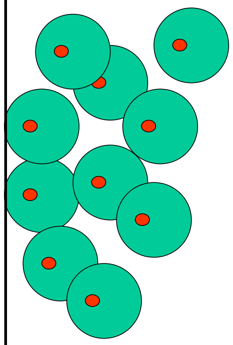
The nuclear particles are
Moving and tumbling
Inside the energy barrier

Occasionally, a “tunnel” develops
In the energy wall and the particle
escapes

The number of times a “tunnel” develops is proportional to the energy of
The particle

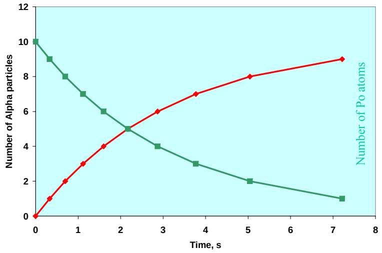
http://www.cop.ufl.edu/safezone/prokai/pha5100/radioact.htm

$${}^{210}_{84}Po \rightarrow {}^{4}_{2}He + {}^{206}_{92}Pb$$



Time, s	total alpha particles
0.33	1
0.699	2
1.12	3
1.6	4
2.17	5
2.87	6
3.77	7
5.04	8
7.21	9

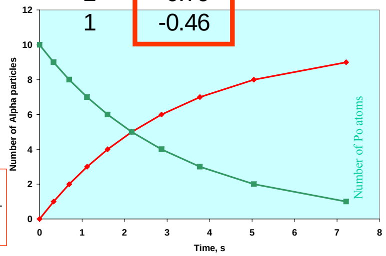
Who do we measure?
Alpha particles formed?
Polonium atoms remaining?



Time, s	total " particles	**average** "slope$_{\text{at time t}}$
0	0	
0.33	1	$\frac{1-0}{0.33-0s} = 3.03s^{-1}$
0.699	2	$\frac{2-1}{0.699-0.33s} = 2.71s^{-1}$
1.12	3	$\frac{3-2}{1.12-0.699s} = 2.38s^{-1}$
1.6	4	2.07
2.17	5	1.75
2.87	6	1.43
3.77	7	1.11
5.04	8	0.79
7.21	9	0.46

^{210}Po	s^{-1} aver.Po slope
10	
9	-3.03
8	-2.71
7	-2.39
6	-2.07
5	-1.75
4	-1.43
3	-1.11
2	-0.79
1	-0.46

What do you “see”?



$$slope = \frac{particles_{final} - particles_{initial}}{t_{final} - t_{initial}}$$

We are considering this reaction

$$^{210}_{84}Po \xrightarrow{speed} {}^{4}_{2}He + {}^{206}_{92}Pb$$

$$slope_{Product} = rate_{Product} = \frac{[Product]_{final} - [Product]_{initial}}{t_{final} - t_{initial}} = \frac{\Delta[P]_{f-i}}{\Delta t_{f-i}}$$

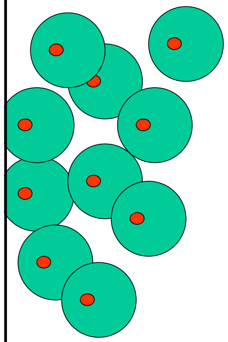
$$slope_{reactant} = rate_{reactant} = \frac{[Reactant]_{final} - [Reactant]_{initial}}{t_{final} - t_{initial}} = \frac{\Delta[R]_{f-i}}{\Delta t_{f-i}}$$

$$rate = \frac{\Delta[P]_{f-i}}{\Delta t_{f-i}} \boxed{= -} \frac{\Delta[R]_{f-i}}{\Delta t_{f-i}}$$

What will happen in our Polonium experiment if we double the amount of Po, present?

$$^{210}_{84}Po \rightarrow {}^{4}_{2}He + {}^{206}_{92}Pb$$

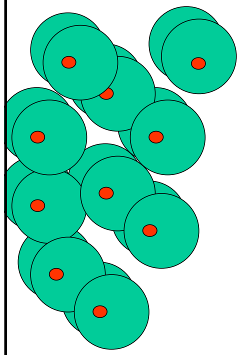
Time, s	total alpha particles
0.33	1
0.699	2
1.12	3
1.6	4
2.17	5
2.87	6
3.77	7
5.04	8
7.21	9



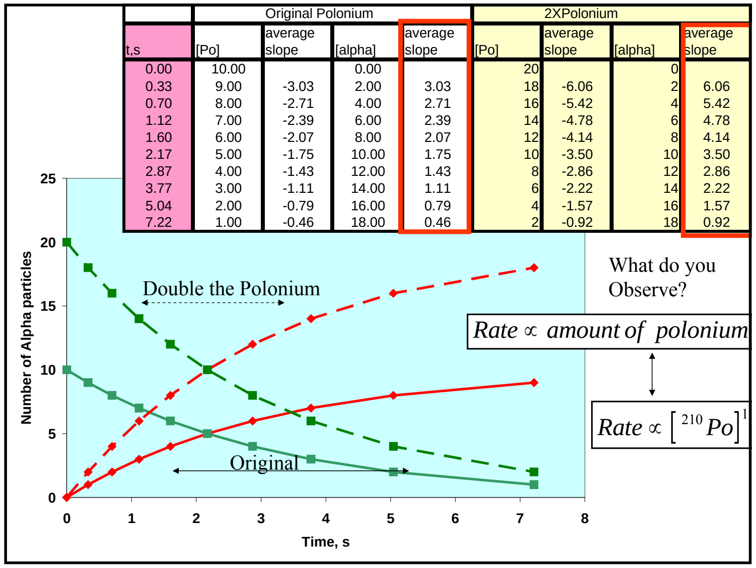
What will happen in our Polonium experiment if we double the amount of Po, present?

$$^{210}_{84}Po \rightarrow {}^{4}_{2}He + {}^{206}_{92}Pb$$

Time, s	total alpha particles	Double Time, s	Double total alpha particles
0.33	1	0.33	2
0.699	2	0.699	4
1.12	3	1.12	6
1.6	4	1.6	8
2.17	5	2.17	10
2.87	6	2.87	12
3.77	7	3.77	14
5.04	8	5.04	16
7.21	9	7.21	18



What do you observe?

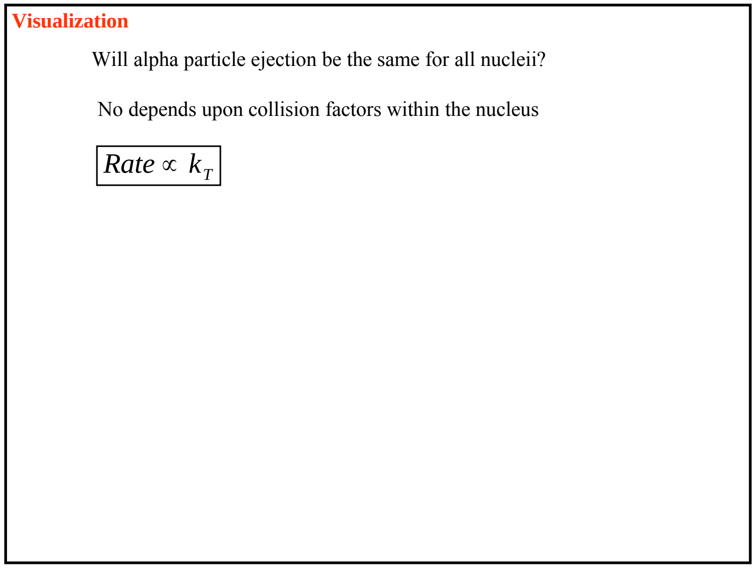


	Original Polonium				2XPolonium			
t,s	[Po]	average slope	[alpha]	average slope	[Po]	average slope	[alpha]	average slope
0.00	10.00		0.00		20		0	
0.33	9.00	-3.03	2.00	3.03	18	-6.06	2	6.06
0.70	8.00	-2.71	4.00	2.71	16	-5.42	4	5.42
1.12	7.00	-2.39	6.00	2.39	14	-4.78	6	4.78
1.60	6.00	-2.07	8.00	2.07	12	-4.14	8	4.14
2.17	5.00	-1.75	10.00	1.75	10	-3.50	10	3.50
2.87	4.00	-1.43	12.00	1.43	8	-2.86	12	2.86
3.77	3.00	-1.11	14.00	1.11	6	-2.22	14	2.22
5.04	2.00	-0.79	16.00	0.79	4	-1.57	16	1.57
7.22	1.00	-0.46	18.00	0.46	2	-0.92	18	0.92

What do you Observe?

$$\boxed{Rate \propto amount\ of\ polonium}$$

$$\boxed{Rate \propto \left[{}^{210}Po\right]^1}$$

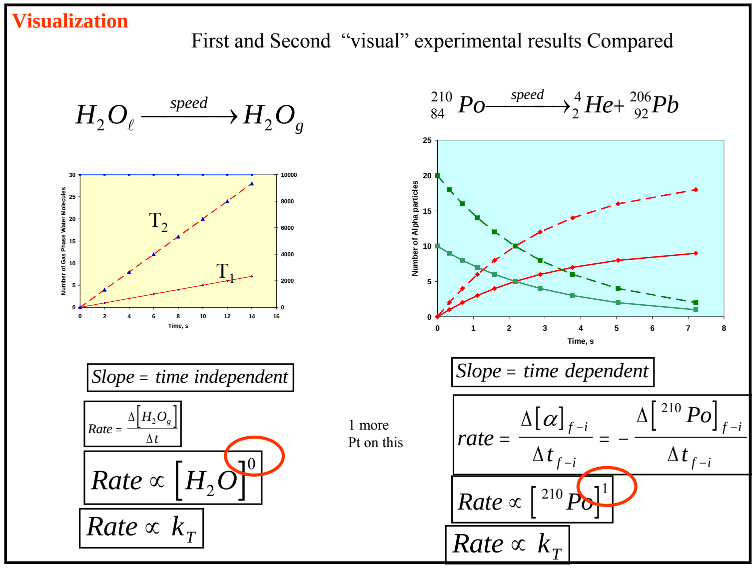


Visualization

Will alpha particle ejection be the same for all nucleii?

No depends upon collision factors within the nucleus

$$\boxed{Rate \propto k_T}$$



Visualization

First and Second "visual" experimental results Compared

$$H_2O_\ell \xrightarrow{speed} H_2O_g$$

$${}^{210}_{84}Po \xrightarrow{speed} {}^{4}_{2}He + {}^{206}_{92}Pb$$

$$\boxed{Slope = time\ independent}$$

$$\boxed{Rate = \frac{\Delta\left[H_2O_g\right]}{\Delta t}}$$

$$\boxed{Rate \propto \left[H_2O\right]^0}$$

$$\boxed{Rate \propto k_T}$$

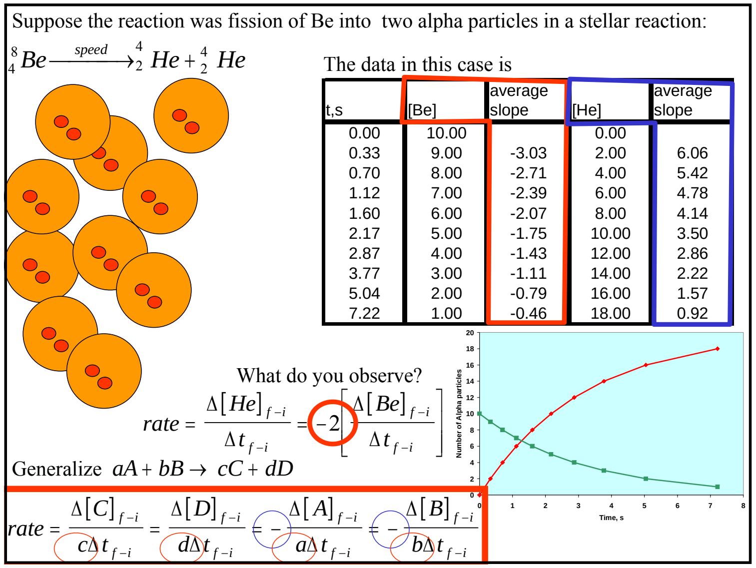
1 more
Pt on this

$$\boxed{Slope = time\ dependent}$$

$$\boxed{rate = \frac{\Delta[\alpha]_{f-i}}{\Delta t_{f-i}} = -\frac{\Delta\left[{}^{210}Po\right]_{f-i}}{\Delta t_{f-i}}}$$

$$\boxed{Rate \propto \left[{}^{210}Po\right]^1}$$

$$\boxed{Rate \propto k_T}$$



Suppose the reaction was fission of Be into two alpha particles in a stellar reaction:

$${}^{8}_{4}Be \xrightarrow{speed} {}^{4}_{2}He + {}^{4}_{2}He$$

The data in this case is

t,s	[Be]	average slope	[He]	average slope
0.00	10.00		0.00	
0.33	9.00	-3.03	2.00	6.06
0.70	8.00	-2.71	4.00	5.42
1.12	7.00	-2.39	6.00	4.78
1.60	6.00	-2.07	8.00	4.14
2.17	5.00	-1.75	10.00	3.50
2.87	4.00	-1.43	12.00	2.86
3.77	3.00	-1.11	14.00	2.22
5.04	2.00	-0.79	16.00	1.57
7.22	1.00	-0.46	18.00	0.92

What do you observe?

$$rate = \frac{\Delta[He]_{f-i}}{\Delta t_{f-i}} = -2\left[\frac{\Delta[Be]_{f-i}}{\Delta t_{f-i}}\right]$$

Generalize $aA + bB \rightarrow cC + dD$

$$rate = \frac{\Delta[C]_{f-i}}{c\Delta t_{f-i}} = \frac{\Delta[D]_{f-i}}{d\Delta t_{f-i}} = -\frac{\Delta[A]_{f-i}}{a\Delta t_{f-i}} = -\frac{\Delta[B]_{f-i}}{b\Delta t_{f-i}}$$

Begin with three “visual” experiments

1. evaporation of water

$$H_2O_\ell \xrightarrow{speed} H_2O_g$$

2. radioactive decay of polonium

$$^{210}_{84}Po \xrightarrow{speed} {}^{4}_{2}He + {}^{206}_{92}Pb$$

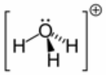
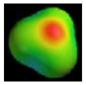
3. H_2 formation

$$H_3O^+_{aq} + H_3O^+_{aq} \xrightarrow{speed} H_{2,g} + H_2O$$

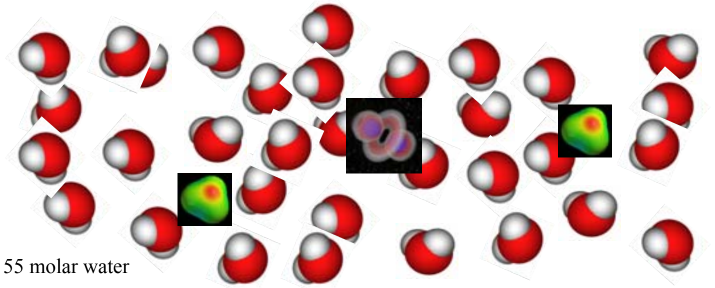
Visualization

http://www.princeton.edu/~chm333/2002/spring/FuelCells/images/hydrogen_molecule.jpg

$$H_3O^+_{aq} + H_3O^+_{aq} \xrightarrow{speed} H_{2,g} + 2H_2O$$


This reaction is very different
Need to get two reactants to collide in order to produce the produc
Postulate: rate " collisions,
Collisions " individuals/volume (conc.), velocity in solution



55 molar water

Visualization

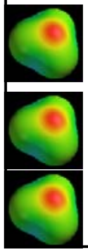
$$H_3O^+_{aq} + H_3O^+_{aq} \xrightarrow{speed} H_{2,g} + 2H_2O$$

Consider a single molecule colliding with a side

$$rate \propto collision\ probability$$

$$collision\ probability_{molecule\,1} \propto [molecule_1]$$

$$collision\ probability_{molecule} \propto velocity$$

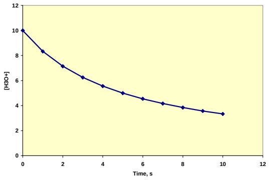


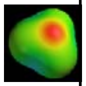
$$H_3O^+_{aq} + H_3O^+_{aq} \xrightarrow{speed} H_{2,g} + 2H_2O$$

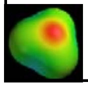
$$probability\ of\ two\ hitting\ each\ other \propto velocity[molecule][molecule]$$

$$rate \propto [H_3O]^2$$

$$rate \propto k_T$$



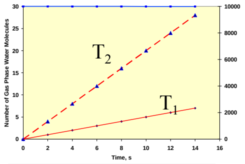




First, Second, and Third "visual" experimental results Compared

$$H_3O^+_{aq} + H_3O^+_{aq} \xrightarrow{speed} H_{2,g} + H_2O$$

$$H_2O_\ell \xrightarrow{speed} H_2O_g$$



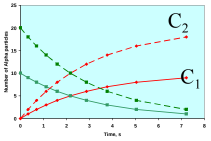
$$Slope = time\ independent$$

$$Rate = \frac{\Delta[H_2O_g]}{\Delta t}$$

$$Rate \propto [H_2O]^0$$

$$Rate \propto k_T$$

$$^{210}_{84}Po \xrightarrow{speed} {}^4_2He + {}^{206}_{92}Pb$$

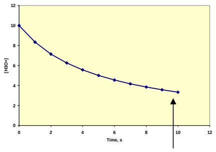


$$Slope = time\ dependent$$

$$rate = \frac{\Delta[\alpha]_{f-i}}{\Delta t_{f-i}} = -\frac{\Delta[{}^{210}Po]_{f-i}}{\Delta t_{f-i}}$$

$$Rate \propto [{}^{210}Po]^1$$

$$Rate \propto k_T$$



Shape is different

$$rate \propto [H_3O]^2$$

$$Rate \propto k_T$$

How are we going to get something to compare for Rule G3: **Science is Referential?**

$$\boxed{rate = k[A]^m}$$

k=rate constant, T dependent

m=order, accounts for number of participants

"A" students work
(without solutions manual)
~ 10 problems/night.

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Module #14
Kinetics: end of "visualizing"

Comparison Numbers: order

FITCH Rules

General
- G1: Suzuki is Success
- G2. Slow me down
- **G3. Scientific Knowledge is Referential**
- G4. Watch out for Red Herrings

- G5. Chemists are Lazy

Chemistry
- C1. It's all about charge $E_{el} = k\left(\frac{q_1q_2}{r_1+r_2}\right)$
- C2. Everybody wants to "be like Mike"
- C3. Size Matters $E_{el} = k\left(\frac{q_1q_2}{r_1+r_2}\right)$
- C4. Still Waters Run Deep

- C5. Alpha Dogs eat first

$$\boxed{aA \to cC + dD}$$

$$\boxed{rate = k[A]^m}$$

$$rate_{measured} = \frac{\Delta[C]}{c\Delta t} = \frac{\Delta[D]}{d\Delta t}$$

$$rate_{measured} = -\frac{\Delta[A]}{a\Delta t}$$

k=rate constant, T dependent

m=order, accounts for role number of participants play

m= order, an integer from 0 to usually no more than 2
often stoichometric coefficient "a" or "b"

We now have defined
our measurement
change in concentration with change in time
our comparison numbers
k
m
How will we calculate the comparison numbers?

1. Monitor change in conc.
2. Calculate the Rate
3. **Determine the Order of the reaction**
4. Write the complete rate expression.
5. Calculate the rate constant
6. Calculate the half life
7. Retire to the Bahamas

$$rate_1 = k[A_1]^m$$

$$rate_2 = k[A_2]^m$$

$$\frac{rate_2}{rate_1} = \frac{k[A_2]^m}{k[A_1]^m} = \left(\frac{[A_2]}{[A_1]}\right)^m$$

$$\frac{rate_2}{rate_1} = \left(\frac{[A_2]}{[A_1]}\right)^m$$

$$\boxed{\log\left(\frac{rate_2}{rate_1}\right) = m\log\left(\frac{[A_2]}{[A_1]}\right)}$$

You could also do the following

$$\boxed{\log\left(\frac{rate_2}{rate_1}\right) = m\log\left(\frac{[A_2]}{[A_1]}\right)}$$

Look for a concentration Multiple

$$[A_2] = x[A_1]$$

$$\boxed{\frac{rate_2}{rate_1} = \left(\frac{x[A_1]}{[A_1]}\right)^m = x^m}$$

For example if we double the conc:

Zero order

$$\frac{rate_2}{rate_1} = 2^m = 2^0 = 1 \qquad rate_1 = rate_2$$

First order

$$\frac{rate_2}{rate_1} = 2^m = 2^1 = 2 \qquad rate_2 = 2rate_1$$

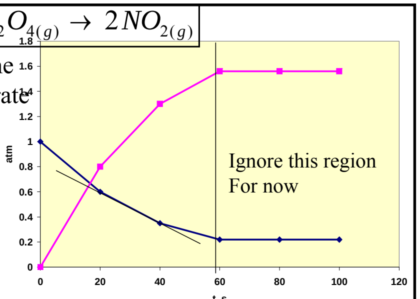
Second order

$$\frac{rate_2}{rate_1} = 2^m = 2^2 = 4 \qquad rate_2 = 4rate_1$$

ExampleCalculation: determine m and k for this reaction

$$N_2O_{4(g)} \rightarrow 2NO_{2(g)}$$

1. Measure concentration vs time
2. Calculate the instantaneous rate
   or
3. Calculate the average rate
4. Calculate the order



$$\log\left(\frac{rate_2}{rate_1}\right) = m\log\left(\frac{[A_2]}{[A_1]}\right)$$

$$\log\left(\frac{0.02}{0.0125}\right) = m\log\left(\frac{[0.6]}{[0.35]}\right)$$

$$0.204 \overset{?}{=} m(0.234)$$

$$\frac{0.204}{0.234} \approx 1 = m$$

$$rate_{average} = -\frac{[A]_{t_2} - [A]_{t_1}}{a(t_2 - t_1)}$$

$$rate_{average} = -\frac{0.6-1}{20-0} = --0.02$$

s	N2O4, atm	NO2, atm
0	1	0
20	0.6	0.8
40	0.35	1.3
60	0.22	1.56
80	0.22	1.56
100	0.22	1.56

s	N2O4, atm	average rate
0	1	
20	0.6	0.02
40	0.35	0.0125
60	0.22	0.0065

---

1. Measure concentration vs time
2. Calculate the average rate
3. Calculate the order

$$N_2O_4 \rightarrow 2NO_2$$

$$m = 1$$

4. Write the rate expression

$$rate = k[N_2O_4]^1 = k[N_2O_4]$$

5. Calculate the rate constant, using the most convenient data

s	N2O4, atm	average rate	k
0	1		
20	0.6	0.02	0.033
40	0.35	0.0125	0.036
60	0.22	0.0065	0.030

$$02\frac{atm}{s} = k(0.06atm)$$

What are the sources
Of variability in our
Calculation?

$$\frac{0.02\frac{atm}{s}}{(0.6atm)} = 0.033\frac{1}{s}$$

"A" students work
(without solutions manual)
~ 10 problems/night.

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Module #14
Kinetics: end of "visualizing"

**Comparison Numbers:
Half life**

Change Calculation to Something
Policy Makers Understand

How long does it take for me to get rid of ½ of the original amount of stuff?

½ life = $t_{1/2}$

Math Phobic
Can sleep through the next 4 slides

Derivation: Half lives

m=0, 1, and 2

$$-\frac{\Delta[A]}{\Delta t} = k[A]^m$$

Solve for
1. Conc. Vs time
2. time at ½ conc.

$$-\frac{\Delta[A]}{[A]^m} = k\Delta t$$

$$\int\left[-\frac{\Delta[A]}{[A]^m}\right] = \int k\Delta t$$

Derivation: Half lives

$$\int\left[-\frac{\Delta[A]}{[A]^m}\right] = \int k\Delta t$$

For m=0

$$\int\left[-\frac{\Delta[A]}{1}\right] = \int k\Delta t$$

$$\int\left[\frac{\Delta[A]}{1}\right] = -\int k\Delta t$$

$$[A]_t - [A]_o = -kt$$

$$\boxed{[A]_t = [A]_{t=0} - kt}$$

Allow reaction to consume ½ of original

$$\tfrac{1}{2}[A]_{t=0} = [A]_{t=0} - kt$$

$$\tfrac{1}{2}[A]_{t=0} = kt_{1/2}$$

$$\boxed{\frac{[A]_{t=0}}{2k} = t_{1/2}}$$

Derivation: Half lives

$$\int\left[-\frac{\Delta[A]}{[A]^m}\right] = \int k\Delta t$$

For m=1

$$\boxed{\ln[A]_t - \ln[A]_{t=0} = -kt}$$

$$\ln\left(\frac{[A]_t}{[A]_{t=0}}\right) = -kt$$

$$\frac{[A]_t}{[A]_{t=0}} = e^{-kt}$$

Allow reaction to consume ½ of original

$$\ln\left(\frac{\tfrac{1}{2}[A]_{t=0}}{[A]_{t=0}}\right) = -kt$$

$$\ln\left(\frac{1}{2}\right) = -kt_{\frac{1}{2}}$$

$$\frac{-0.693}{-k} = t_{\frac{1}{2}}$$

$$\boxed{\frac{0.693}{k} = t_{\frac{1}{2}}}$$

Derivation: Half lives

$$\int\left[-\frac{\Delta[A]}{[A]^m}\right] = \int k\Delta t$$

For m=2

$$\int\left[-\frac{\Delta[A]}{[A]^2}\right] = \int k\Delta t$$

$$\int -[A]^{-2}\,dt = -kt$$

$$-\left(\frac{[A]^{-2+1}}{-2+1}\right) = -kt$$

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

$$\left.\frac{1}{[A]}\right|_t = -kt$$

$$\boxed{\frac{1}{[A]_t} - \frac{1}{[A]_{t=o}} = kt}$$

Allow reaction to consume ½ of original

$$\frac{1}{\tfrac{1}{2}[A]_{t=0}} - \frac{1}{[A]_{t=o}} = kt_{\frac{1}{2}}$$

$$2 - 1 = k[A_o]t_{\frac{1}{2}}$$

$$\boxed{\frac{1}{k[A_o]} = t_{\frac{1}{2}}}$$

$\boxed{aA \rightarrow cC + dD}$ $\boxed{rate = k[A]^m}$

Order, m	Rate expression	**UNITS Of k**	$t_{1/2}$	Concentration vs Time	Example
0	$rate = k[A]$	$\frac{M}{s}$	$t_{1/2} = \frac{[A_o]}{2k}$	$[A_t] = [A_0] - kt$	$H_2O_\ell \rightarrow H_2O_g$
1	$rate = k[A]^1$	$\frac{1}{s}$	$t_{1/2} = \frac{0.693}{k}$	$\ln[A_t] = \ln[A_o] - kt$	${}^{210}_{84}Po \rightarrow {}^{4}_{2}He + {}^{206}_{92}Pb$
2	$rate = k[A]^2$	$\frac{1}{Ms}$	$t_{1/2} = \frac{1}{k[A_o]}$	$\frac{1}{[A]} - \frac{1}{[A_0]} = kt$	$2H_3O^+_{aq} \rightarrow H_{2,g} + H_2O$

Units of rate constant vary!!!!!

$T_{1/2}$ varies!!!

Conc. Vs Time varies!!!

$$rate_{measured} = \frac{\Delta[C]}{c\Delta t} = \frac{\Delta[D]}{d\Delta t}$$

$$rate_{measured} = -\frac{\Delta[A]}{a\Delta t}$$

Determining Order Example Calculation From the data we Have acquired in preceding analysis determine the **half life** of The reaction

$$N_2O_{4(g)} \rightarrow 2NO_{2(g)}$$

---

1. Measure concentration vs time
2. Calculate the average rate
3. Calculate the order
4. Write the rate expression
5. Calculate the rate constant, using the most convenient data
6. Calculate the half life

$$N_2O_4 \rightarrow 2NO_2$$

$m = 1$

$$rate = k\left[N_2O_4\right]^1$$

$$k = 0.033\frac{1}{s}$$

For a 1st order $\boxed{\frac{0.693}{k} = t_{\frac{1}{2}}}$

$$t_{\frac{1}{2}} = \frac{0.693}{0.033\frac{1}{s}} = 20.79s$$

7. Testify in front of Congress; retire to Bahamas

Honorable Senator, "Dinitrogen tetroxide half life is 21s."

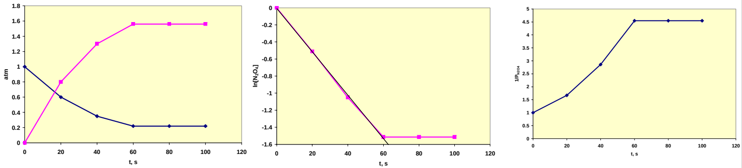
A second method for getting the order, rate constant, and half life

Order, m	Rate expression	**UNITS Of k**	$t_{½}$	Concentration vs Time	Example
0	$rate = k[A]^0$	$\frac{M}{s}$	$t_{½} = \frac{\left[A_o\right]}{2k}$	$\left[A_t\right] = \left[A_0\right] - kt$	$H_2O_\ell \rightarrow H_2O_g$
1	$rate = k[A]^1$	$\frac{1}{s}$	$t_{½} = \frac{0.693}{k}$	$\ln\left[A_t\right] = \ln\left[A_o\right] - kt$	${}^{210}_{84}Po \rightarrow {}^{4}_{2}He + {}^{206}_{92}Pb$
2	$rate = k[A]^2$	$\frac{1}{Ms}$	$t_{½} = \frac{1}{k\left[A_o\right]}$	$\frac{1}{[A]} - \frac{1}{\left[A_0\right]} = kt$	$2H_3O^+_{aq} \rightarrow H_{2,g} + H_2O$

As an example calculation use the dinitrogen tetroxide data

$$N_2O_{4,g} \rightarrow 2NO_{2,g}$$

s	N2O4, atm	NO2, atm	1/N2O4	ln N2O4
0	1	0	1	0
20	0.6	0.8	1.67	-0.51
40	0.35	1.3	2.86	-1.05
60	0.22	1.56	4.55	-1.51
80	0.22	1.56	4.55	-1.51
100	0.22	1.56	4.55	-1.51



$$rate = k[A]^0$$

$$\left[A_t\right] = \left[A_0\right] - kt$$

$$rate = k[A]^1$$

$$\ln\left[A_t\right] = \ln\left[A_o\right] - kt$$

$$rate = k[A]^2$$

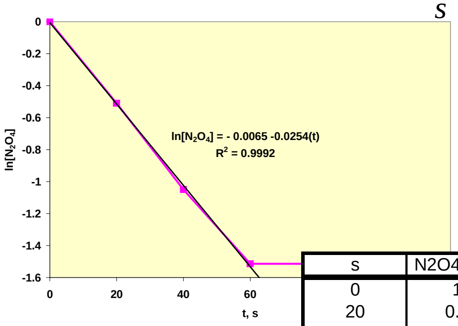
$$\frac{1}{[A]} - \frac{1}{\left[A_0\right]} = kt$$

1st order reaction

$$rate = k[A]^1$$

$$\ln\left[A_t\right] = \ln\left[A_o\right] - kt$$

$$\ln P_{N_2O_4,t} = \ln P_{N_2O_4,t=0} - kt$$
$$\ln P_{N_2O_4,t} = \ln(1) - kt$$
$$\ln P_{N_2O_4,t} = 0 - kt$$
$$k = 0.0254\frac{1}{s}$$



Which data do you
Think is more
Reliable?

$$k = 0.0254\frac{1}{s}$$

Or the other method

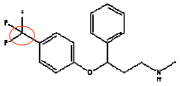
s	N2O4, atm	average rate	k
0	1		
20	0.6	0.02	0.033
40	0.35	0.0125	0.036
60	0.22	0.0065	0.030

Anti-depressants, work to inhibit seratonin uptake

Can now compare molecules by comparing
Their ½ lives

http://chemfinder.cambridgesoft.com/

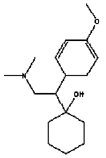
Prozac=
fluoxetine



Binds to human serum proteins:
Albumin and glycoprotein

$t_{1/2}$ = 4-6 days after chronic dosing

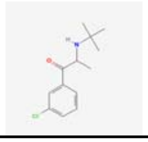
Effexor =
venlafaxine



Metabolized within 1.3 hours from
Plasma (no binding to human serum
Proteins)

$t_{1/2}$=5±2 hours

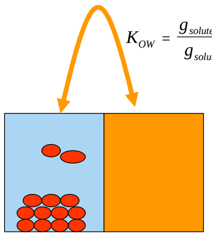
Wellbutrin=bupropion



$t_{1/2}$=20hours

Reference Data for Risk Assessment

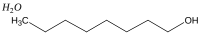
$$C_g = kP_g$$



$$K_{OW} = \frac{g_{solute/L\,octanol}}{g_{solute/L\,water}}$$

$$s = \frac{g_{solute}}{g_{H_2O}}$$

octanol



Set a reference state to compare all chemicals

solubility in water (s)
solubility between water and octanol (K_{ow})
K_H
$t_{1/2}$ marine water, marine sediment, soils

for 2 compounds (one
A toxic compound and one a
pharmaceutical

find, listing source of data
s
K_{ow}
K_H
$t_{1/2}$ sediment, soil,
marine water
Find info from REACH and
from US sources on
risk assessment

Written portion of paper should Relate the structure of the Compound to the comparison Numbers via topics such as

a) Intermolecular forces
b) Free radicals (unbonded electrons)
c) Any additional information which you find interesting enough to wow your future mate in life

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Your Paper Assignment Important Dates:

1. **Friday Feb. 16** – Finalize and submit names of group (no more than 3)
2. **Monday Mar 12** – submit the three compound names and associated CAS (Chemical Abstract Service) numbers
3. **April 11 Wednesday** – submit the short paper

Paper Style

1. 1-2 **typed** pages
2. **Chemical figures** should be obtained from web by screen capture or by download of chemical drawing (e.g. see the NIST site). Hand drawn figures will be given a slight negative marking
3. **Equations** should be typed using word equation editor

Grading Points

20 points total (3.8% of class total)
Failure to turn in paper lowers total class grade by ½ grade point (e.g. A to A-)

"A" students work
(without solutions manual)
~ 10 problems/night.

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Module #14
Kinetics: example calculation

Example Calc. 1 - Determine the order, the rate constant, and half life

$$HI \rightarrow products \qquad \boxed{rate = k[A]^m}$$

T(h)	[HI]
0	1
2	0.5
4	0.33
6	0.25

$$rate_{measured} = -\frac{\Delta[A]}{a\Delta t}$$

$$rate_{measured} = -\frac{0.5-1}{2-0} = -\left(\frac{-0.5}{2}\right) = 0.25$$

Example Calc. 1 - Determine the order, the rate constant, and half life

$$HI \rightarrow products$$

$$\frac{0.25}{0.04} = 6.25$$

T(h)	[HI]	Ave. Rate
0	1	
2	0.5	0.25
4	0.33	0.0835
6	0.25	0.04

x2

$$m > 1$$

$$guess: m \approx 2$$

$$rate = k[HI]^2$$

$$k = \frac{[HI]^2}{rate}$$

$$k = \frac{[0.5]^2}{0.25} = \frac{1}{M \cdot hr}$$

$$\frac{rate_2}{rate_1} = 2^m = 2^0 = 1 \qquad rate_1 = rate_2$$

$$\frac{rate_2}{rate_1} = 2^m = 2^1 = 2 \qquad rate_2 = 2rate_1$$

$$\frac{rate_2}{rate_1} = 2^m = 2^2 = 4 \qquad rate_2 = 4rate_1$$

$$t_{1/2} = \frac{1}{k[A_o]}$$

$$t_{1/2} = \frac{1}{\left(\frac{1}{M \cdot hr}\right)[1M]} = 1hr$$

Alternative method use the shape of concentration vs time

$$rate = k[HI]^2$$

O order $[A_t] = [A_0] - kt$

1 order $\ln[A_t] = \ln[A_o] - kt$

2 order $\frac{1}{[A]} - \frac{1}{[A_0]} = kt$

k=slope of appropriate equation

$$slope = k = \frac{(2-1)}{(2-0)} = 0.5\frac{1}{M \cdot hr}$$

$$t_{1/2} = \frac{1}{k[A_o]} \qquad t_{1/2} = \frac{1}{0.5\frac{1}{Mhr}[1M]} = 2hr$$

T(h)	[HI]	ln[HI]	1/[HI]
0	1	0	1
2	0.5	-0.69	2
4	0.33	-1.1	3
6	0.25	-1.39	4

Which of these makes a straight line function?

Method 1: average rates	Method 2 Concentration Plots
$m \approx 2$	$m = 2$
$rate = k[HI]^2$	$rate = k[HI]^2$
$k = \frac{[0.5]^2}{0.25} = 1$	$slope = k = \frac{(2-1)}{(2-0)} = 0.5\frac{1}{M \cdot hr}$
$t_{1/2} = \frac{1}{\frac{1}{M\cdot}[1M]} = 1hr$	$t_{1/2} = \frac{1}{0.5\frac{1}{M \cdot hr}[1M]} = 2hr$

Which is better and why?
Will it always be better?

"A" students work
(without solutions manual)
~ 10 problems/night.

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Module #14
Kinetics: Multiple Reactants

Few reactions are of the form:

$$aA \rightarrow products$$
$$rate = k[A]^m$$

$$\boxed{\log\left(\frac{rate_1}{rate_2}\right) = m\log\left(\frac{[A_1]}{[A_2]}\right)}$$

Most are of the form:

$$aA + bB \rightarrow products$$
$$rate = k[A]^m[B]^n$$

Overall order
=m+n

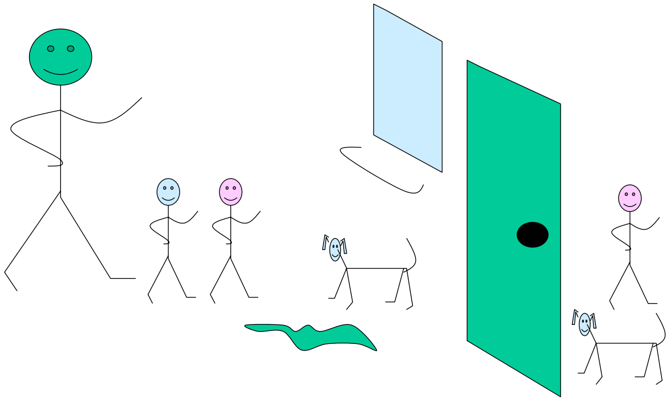
$a \neq m$
$b \neq n$ Ojo

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$
$$rate = k\left[(CH_3)_3CBr\right]^m\left[OH^-\right]^n$$

How can we determine both m and n?

A. Stupid Analogy for proportions

How do I know which child (or dog) is responsible for the towels never staying on the towel rack?



Hold one child and one dog constant and measure the rate of towel to floor events, repeat with dog; repeat with other child

Example Calculation 2

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

$$rate = k\left[(CH_3)_3CBr\right]^m\left[OH^-\right]^n$$

[OH$^-$]	[(CH$_3$)$_3$CBr]	Rate
0.050M	0.50M	0.005M/s
0.050	1.0	0.01
0.050	1.50	0.015
0.050	2.00	0.02
0.050	1.00	0.01
0.10	1.00	0.01
0.15	1.00	0.01
0.20	1.00	0.01

Divide and Conquer

Make one guy constant and compare rates as other guy varies

$$\log\left(\frac{rate_1}{rate_2}\right) = m\log\left(\frac{[A_1]}{[A_2]}\right)$$

$$\log\left(\frac{0.005\frac{M}{s}}{0.01\frac{M}{s}}\right) = m\log\left(\frac{0.050M(CH_3)_3CBr}{1.0M(CH_3)_3CBr}\right)$$

$\log(0.5) = m\log(0.5)$

$m = 1$ order with respect to (CH$_3$)$_3$CBr

[OH$^-$]		[(CH$_3$)$_3$CBr]		Rate
0.050M	Hold constant	0.50M	Study this	0.005M/s
0.050		1.0		0.01
0.050		1.50		0.015
0.050		2.00		0.02
0.050		1.00		0.01
0.10		1.00		0.01
0.15		1.00		0.01
0.20		1.00		0.01

What data will We use to get Order of OH?

[OH$^-$]		[(CH$_3$)$_3$CBr]		Rate
0.050M		0.50M		0.005M/s
0.050		1.0		0.01
0.050		1.50		0.015
0.050		2.00		0.02
0.050	Study this	1.00	Hold constant	0.01
0.10		1.00		0.01
0.15		1.00		0.01
0.20		1.00		0.01

$$\log\left(\frac{rate_1}{rate_2}\right) = m\log\left(\frac{[A_1]}{[A_2]}\right)$$

$$\log\left(\frac{0.01\frac{M}{s}}{0.01\frac{M}{s}}\right) = m\log\left(\frac{0.050MOH}{1.0MOH}\right)$$

$\log(1) = m\log(0.5)$

$0 = m\log(0.5)$

$m = 0$

Zero order with respect to OH$^-$

[OH$^-$]	[(CH$_3$)$_3$CBr]	Rate
0.050M	0.50M	0.005
0.050	1.0	0.01
0.050	1.50	0.015
0.050	2.00	0.02
0.10	1.00	0.01
0.15	1.00	0.01
0.20	1.00	0.01

(ease of calculation)

$$0.01\frac{M}{s} = k(1M)^1(0.05M)^0$$

Now calculate the rate constant using:

$$0.01\frac{M}{s} = k(1M)$$

$$rate = k\left[(CH_3)_3CBr\right]^m\left[OH^-\right]^n$$

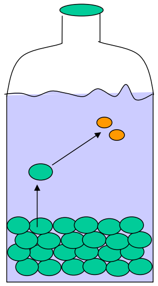
$$k = 0.01\frac{1}{s}$$

Which data should we use?

http://www.cop.ufl.edu/safezone/prokai/pha5100/zeroord.htm

Example Calc. 3. A prescription for a liquid aspirin preparation is called for. It is to contain 6.5 g /100 ml. The solubility of aspirin at 25^{o}C is 0.33 g/100 ml; therefore, the preparation will contain solid aspirin as a suspension which will control the aqueous concentration of aspirin.. The other ingredients in the prescription cause the product to have a pH of 6.0. The first-order rate constant for aqueous aspirin degradation in this solution is $4.5x10^{-6}$ sec^{-1}. Calculate the zero-order rate constant for the suspension..

Determine the shelf life for the liquid prescription, assuming that the product is satisfactory until the time at which the solid has decomposed to 90% of its original concentration (i.e., 10% decomposition) at 25^{o}C.



1. Draw a mental picture
2. "Translate" into chemistry

$$aspirin_s \xrightarrow{k_o} aspirin_{aqueous} \xrightarrow{k_1} products$$

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http://www.cop.ufl.edu/safezone/prokai/pha5100/zeroord.htm

Example Calc. 3. A prescription for a liquid aspirin preparation is called for. It is to contain 6.5 g/100 ml. The solubility of aspirin at 25^{o}C is 0.33 g/100 ml; therefore, the preparation will contain solid aspirin as a suspension which will control the aqueous concentration of aspirin.. The other ingredients in the prescription cause the product to have a pH of 6.0. The first-order rate constant for aqueous aspirin degradation in this solution is $4.5x10^{-6}$ sec^{-1}. Calculate the zero-order rate constant for the suspension..

Determine the shelf life for the liquid prescription, assuming that the product is satisfactory until the time at which the solid has decomposed to 90% of its original concentration (i.e., 10% decomposition) at 25^{o}C.

Know	Don't Know	Red Herrings?
	$k_{m=0}$	$pH = 6$

$$\boxed{aspirin_s \xrightarrow{k_o} aspirin_{aqueous} \xrightarrow{k_1} products}$$

$$rate = -\frac{\Delta\left[Aspirin_{aq}\right]}{\Delta t} = k_{m=1}\left[Aspirin_{aq}\right] = \frac{4.5x10^{-6}}{s}\left[Aspirin_{aq}\right] = \left(\frac{4.5x10^{-6}}{s}\right)\left(\frac{0.33g_{aspirin}}{100mL}\right)$$

$$K_{solubility} = \frac{\left[Aspirin_{aq}\right]}{\left[Aspirin_s\right]} = \left[Aspirin_{aq}\right] = s = \frac{0.33g_{aspirin}}{100mL}$$

We have just shown that the rate is constant!

That is, a zero order rx!

$$rate_o = k_o = 4.5x10^{-6}\frac{1}{s}\left[\frac{0.33g}{100mL}\right] = 1.5x10^{-6}\frac{g}{mL\cdot s}$$

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http://www.cop.ufl.edu/safezone/prokai/pha5100/zeroord.htm

Example Calc. 3. A prescription for a liquid aspirin preparation is called for. It is to contain 6.5 g/100 ml. The solubility of aspirin at 25^{o}C is 0.33 g/100 ml; therefore, the preparation will contain solid aspirin as a suspension which will control the aqueous concentration of aspirin.. The other ingredients in the prescription cause the product to have a pH of 6.0. The first-order rate constant for aqueous aspirin degradation in this solution is $4.5x10^{-6}$ sec^{-1}. Calculate the zero-order rate constant for the suspension..

Determine the shelf life for the liquid prescription, assuming that the product is satisfactory until the time at which the solid has decomposed to 90% of its original concentration (i.e., 10% decomposition) at 25^{o}C.

Know	Don't Know
$k_0 = 1.5x10^{-6}\frac{g}{mL\cdot s}$	$t_{10\%\,decomposed}$

For zero order reaction

$$\left[A_t\right] = \left[A_0\right] - kt \qquad \left[A_t\right] = 0.9\left[A_0\right]$$

$$0.9\left[A_0\right] = \left[A_0\right] - \left(1.5x10^{-6}\frac{g}{mL\cdot s}\right)\left(t_{90\%remains}\right)$$

$$0.9\left[A_0\right] - \left[A_0\right] = -\left(1.5x10^{-6}\frac{g}{mL\cdot s}\right)\left(t_{90\%}\right)$$

$$-0.10\left[A_o\right] = -\left(1.5x10^{-6}\frac{g}{mL\cdot s}\right)\left(t_{90\%}\right)$$

$$t_{90remains\%} = \frac{-0.10\left[A_0\right]}{-1.5x10^{-6}\frac{g}{mL\cdot s}}$$

$$t_{90\%remains} = \frac{0.10\left[6.5\frac{g_{aspirin\,solid}}{100mL}\right]}{1.5x10^{-6}\frac{g}{mL\cdot s}}$$

$$t_{90\%remains} = 4.3x10^{5}s = 5.0days$$

"A" students work
(without solutions manual)
~ 10 problems/night.

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Module #14
Kinetics: Activation Energy

A CLOSER LOOK AT RATES

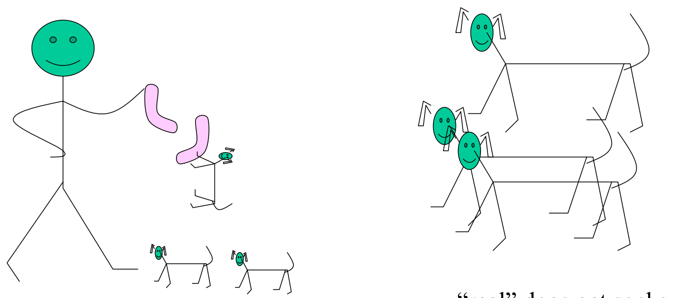
Rate should be proportional to SUCCESSFUL collisions

1. Number of collisions
   1. Concentration increases collisions
   2. Velocity increases number of collisions per time, Z
2. Successful collisions
   1. With sufficient energy to break the bonds (~>200 kJ) f_{Energy}
   2. **With appropriate orientation, P**

$$\boxed{k = PZf_{Energy}}$$

A. Stupid Analogy

How fast can a sock go from a human to a dog?



Ankle biters

“real” dogs get socks

Will depend upon the type of dogs and their ability to have **successful collisions**!!!

$$CO + NO_2 \rightarrow CO_2 + NO$$

$$O \equiv C + O - N = O \rightarrow O = C = O + N =$$

No reaction because C is not oriented toward the oxygen

Orientation matters

A CLOSER LOOK AT RATES

Rate should be proportional to SUCCESSFUL collisions

1. Number of collisions
   1. Concentration increases collisions
   2. **Velocity increases number of collisions per time, Z**
- Successful collisions
  - With sufficient energy to break the bonds (~>200 kJ) f_{Energy}
  - With appropriate orientation, P

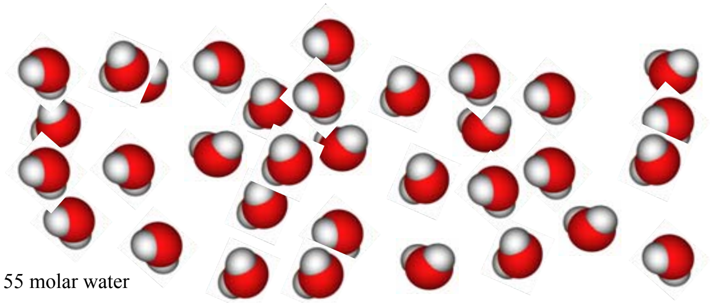
$$\boxed{k = PZf_{Energy}}$$

Visualization

Suppose we increase the velocity of the water molecules?

Will the rate change?

$$H_2O_\ell \xrightarrow{speed} H_2O_g$$



55 molar water

Visualization

What do you observe?

$$H_2O_\ell \xrightarrow{speed} H_2O_g$$

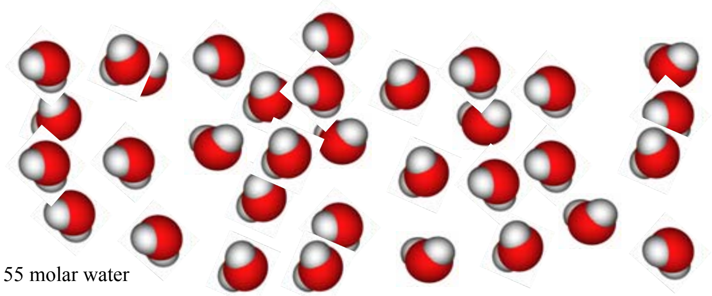
$Rate \propto T$

$\boxed{Rate \propto k_T}$

Prior experiment

Time, s	#escapes
2	1
4	2
6	3
8	4
10	5

Time, s	#escapes
1	1
2	2
3	3
4	4
5	5
6	6



55 molar water

Derivation

From earlier chapter we learned gas phase velocities

$$u_{rms} = \sqrt{\frac{3kT}{g_{molecule}}}$$

Notice how this function shows up in the number Of collisions of molecule A and B per cm³ in 1s

$$Z_{AB} = \rho^2 n_A n_B \sqrt{8\pi\left(\frac{kT}{g_{molecule,A}}\right) + 8\pi\left(\frac{kT}{g_{molecule,B}}\right)}$$

Number of molecules per cm³

Related to distance between molecules that results in a collision, usually 2 to 3 A

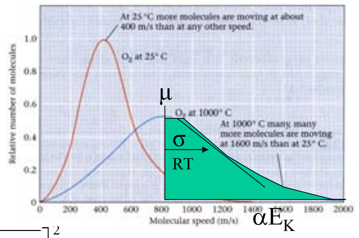
$$k = P\left\{\underbrace{\rho^2 n_A n_B \sqrt{8\pi\left(\frac{kt}{g_{molecule,A}}\right) + 8\pi\left(\frac{kt}{g_{molecule,B}}\right)}}_{Z}\right\} f_{Energy}$$

From earlier chapter we learned of kinetic energy:

$$E_k = \frac{1}{2}mv^2$$

$$u_{rms} = \sqrt{\frac{3kT}{g_{molecule}}}$$

Maxwell's Distribution



$$E_k = \frac{1}{2}m_{ass\ of\ molecule}\left[\sqrt{\frac{3kT}{mass\ of\ molecule}}\right]^2$$

$$E_k = \left(\frac{1}{2}m_{ass\ of\ molecule}\right)\left(\frac{3kT}{mass\ of\ molecule}\right)$$

$$E_k = \left(\frac{3kT}{2}\right)$$

However, only a **fraction** of molecules at a given temperature Have that average speed, and therefore, Average energy

If you assume a normal distribution for the "bell curve" you can calculate the fraction of molecules with an energy above the average value

$$f(x) = e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$$

$$f(x) = e^{-\frac{E_{molecule}}{kT}} = e^{-\frac{E_{mole}}{RT}}$$

Review

Derivation

$$k = \underbrace{P}_{\text{orientation}}\underbrace{\left\{\rho^2 n_A n_B\sqrt{8\pi\left(\frac{kT}{g_{molecule,A}}\right)+8\pi\left(\frac{Tt}{g_{molecule,B}}\right)}\right\}}_{\text{Collision frequency}}\underbrace{\left(e^{-\frac{E_A}{RT}}\right)}_{\text{Fraction of molecules with Enough energy to break bond}}$$

orientation

Collision frequency

Fraction of molecules with
Enough energy to break bond

Both are temperature dependent, which is most?

Relative number of collisions at 2 temperatures (310 and 300K), for an activation energy Of 40 kcal/mol (~10kJ/mol – just barely the energy of a hydrogen bonds)

$$\left(\frac{T_2}{T_1}\right)^{1/2} = \left(\frac{310}{300}\right)^{1/2} = 1.015$$

Relative Fraction of molecules with sufficient energy to break bonds at two temps

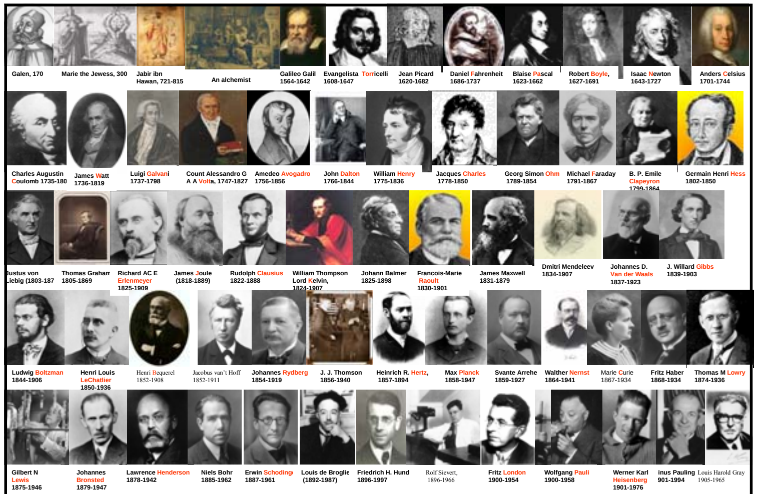
$$\frac{\exp^{\frac{-E_a}{R(310\text{K})}}}{\exp^{\frac{-E_a}{R(300\text{K})}}} = \exp^{\frac{-E_a}{R(310\text{K})}-\frac{-E_a}{R(300\text{K})}} = 8.7$$

Much more significant

$$\boxed{k = A\left(e^{-\frac{E_A}{RT}}\right)}$$

Arrhenius Eq.

Orientation and # of collisions



Fitch Rule G3: Science is Referential

$$rate \propto k_T \qquad \boxed{k = Ae^{-\left[\frac{E_a}{RT}\right]}} \qquad \boxed{R = 8.31\frac{J}{mol \cdot K}}$$

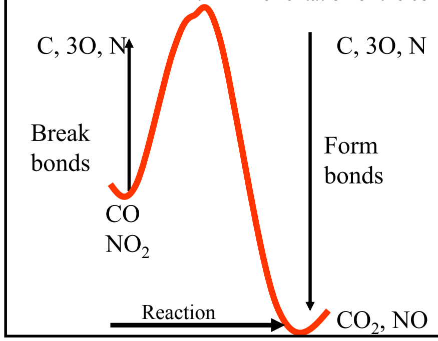
Arrhenius Equation

E_a an activation energy

accounts for successful collisions based on energy sufficient to break bonds

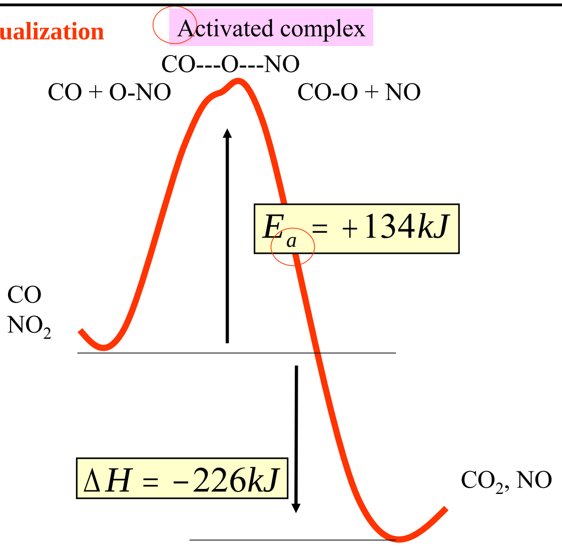
A – pre-exponential factor accounts

1. total number of collisions (velocity and temperature)
2. orientation of the collisions



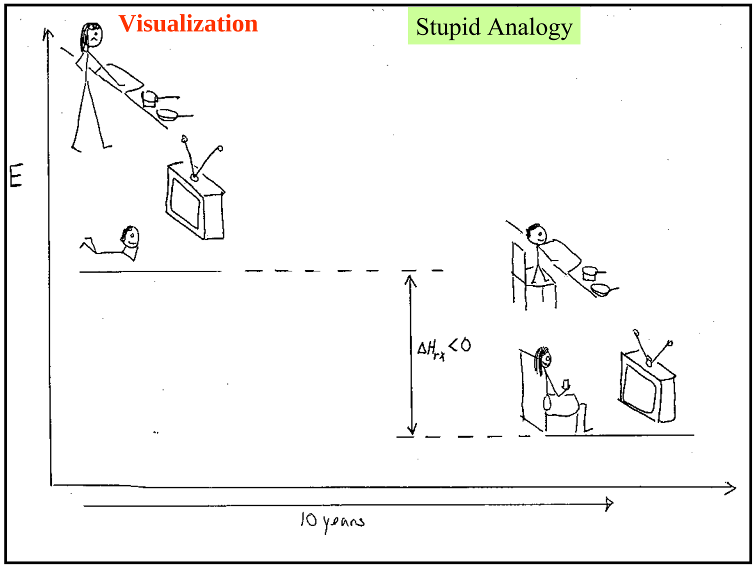
Chemist use this model
To create reaction "maps"

Visualization

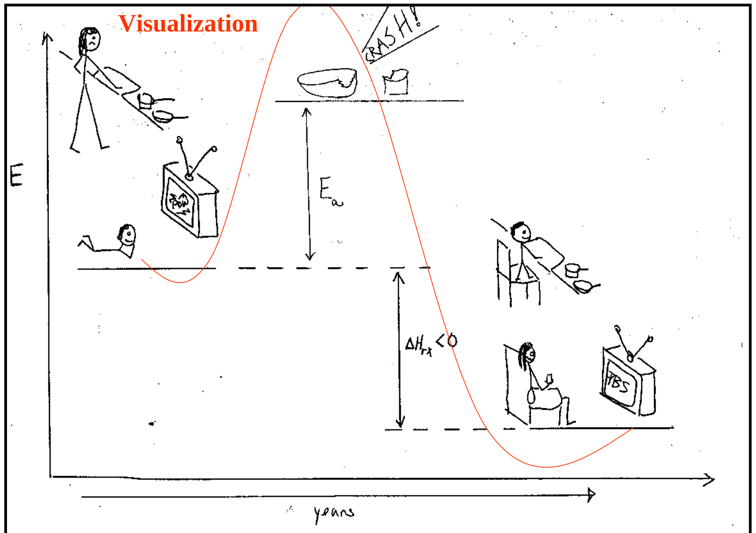


Visualization

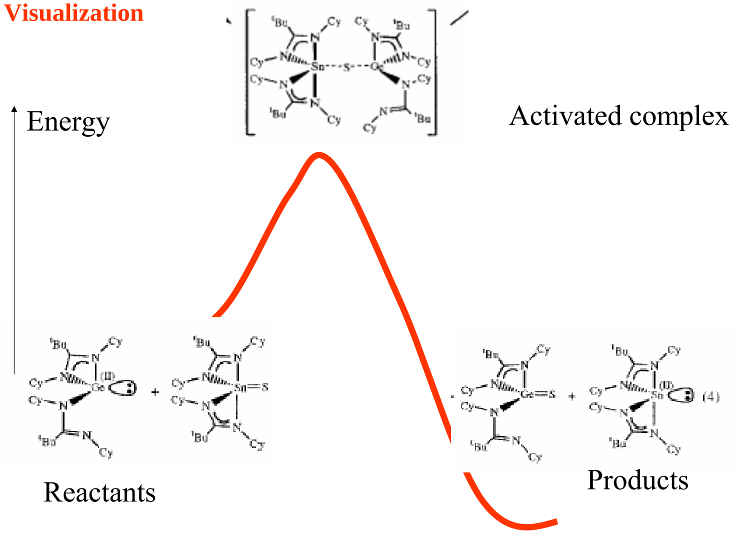
Stupid Analogy



Visualization



Visualization



Energy

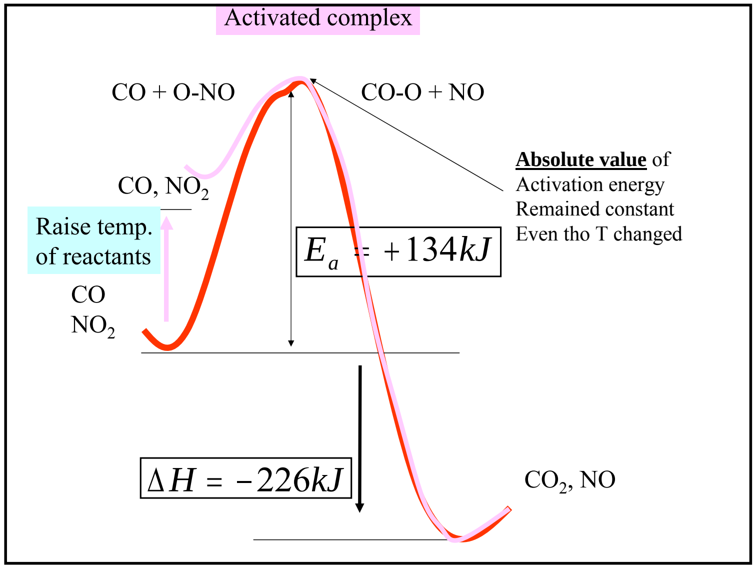
Activated complex

Reactants

Products

ACTIVATION ENERGY

1. ≡ energy in to make rx go
2. ≡E_a
3. Units = kJ
4. $E_a > 0$
5. E_a proportional rx rate
   - a) E_a small; rate large
   - b) Absolute value of E_a independent of T, [ ] hmmm, that doesn't seem right?



Absolute value of Activation energy Remained constant Even tho T changed

$$\boxed{E_a = +134kJ}$$

$$\boxed{\Delta H = -226kJ}$$

How could you calculate Ea?

$$k = Ae^{-\left[\frac{E_a}{RT}\right]}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

$$\ln k_1 + \frac{E_a}{RT_1} = \ln A = \ln k_2 + \frac{E_a}{RT_2}$$

$$\ln k_1 - \ln k_2 = \frac{E_a}{RT_2} - \frac{E_a}{RT_1}$$

$$\boxed{\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

Clausius-Clapeyron Equation
for the kinetic model of
gas vaporization
from a liquid!!!!!!,

$$\boxed{\ln\left[\frac{P_2}{P_1}\right] = \left[\frac{-\Delta H_{vaporization}}{R}\right]\left[\frac{1}{T_2} - \frac{1}{T_1}\right]}$$

$$R = 0.0821\frac{L \cdot atm}{mol \cdot K}$$

$$R = 8.31\frac{J}{mol \cdot K}$$

$$R = 8.31x10^3 \frac{g \cdot m^2}{s^2 \cdot mol \cdot K}$$

Activation Energy Example Calculation : The experimental rate constant for the reaction of iodide ion with methyl bromide is $7.70x10^{-3}$ L/mol·s at 50°C and $4.25x10^{-5}$ L/mol·s at 0°C. Calculate the activation energy and the pre-exponential factor.

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$k = Ae^{-\left[\frac{E_a}{RT}\right]}$$

$$R = 8.31\frac{J}{mol \cdot K}$$

$$\ln\left[\frac{7.70x10^{-3} \frac{L}{mol \cdot s}}{4.25x10^{-5} \frac{L}{mol \cdot s}}\right] = \frac{E_a}{8.31\frac{J}{mol \cdot K}}\left(\frac{1}{0+273}\frac{1}{K} - \frac{1}{50+273}\frac{1}{K}\right)$$

Be careful, be very very careful

$$\ln[181] = \frac{E_a}{8.31\frac{J}{mol \cdot K}}\left(\frac{1}{273}\frac{1}{K} - \frac{1}{323}\frac{1}{K}\right)$$

$$43.207\frac{J}{mol \cdot K} = E_a\left(0.000567\frac{1}{K}\right)$$

$$\boxed{76{,}200\frac{J}{mol} = E_a}$$

Activation Energy Example Calculation : The experimental rate constant for the reaction of iodide ion with methyl bromide is $7.70x10^{-3}$ L/mol·s at 50°C and $4.25x10^{-5}$ L/mol·s at 0°C. Calculate the activation energy and the pre-exponential factor.

$$k = Ae^{-\left[\frac{E_a}{RT}\right]}$$

$$R = 8.31\frac{J}{mol \cdot K}$$

$$\boxed{76{,}200\frac{J}{mol} = E_a}$$

$$7.70x10^{-3} \frac{L}{mol \cdot s} = Ae^{-\left[\frac{76{,}200\frac{J}{mol}}{\left(8.31\frac{J}{mol \cdot K}\right)(323K))}\right]}$$

$$7.70x10^{-3} \frac{L}{mol \cdot s} = Ae^{-[23.389]}$$

$$\frac{7.70x10^{-3} \frac{L}{mol \cdot s}}{e^{-23.389}} = A$$

$$\frac{7.70x10^{-3} \frac{L}{mol \cdot s}}{4.685x10^{-13}} = A$$

$$\boxed{A = 1.64x10^4 \frac{L}{mol \cdot s}}$$

This number represents orientation
And collisions

"A" students work
(without solutions manual)
~ 10 problems/night.

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Module #14
Kinetics: Catalysis

CATALYSIS

1. Want to make reaction go faster.

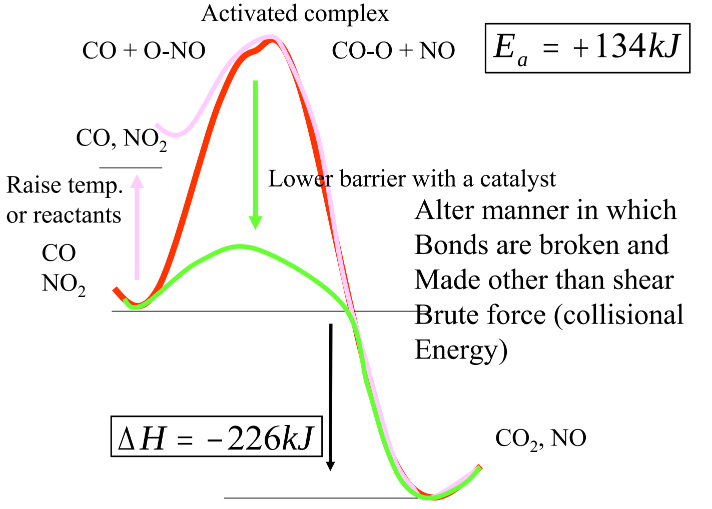
   (Eat dinner at 5 instead of 10)

2. Two choices:

   a) Raise energy of reactants close to E_a

   b) Decrease E_a (CATALYSIS)

Two ways to speed up reaction:



Activated complex

CO + O-NO

CO-O + NO

$E_a = +134kJ$

CO, NO_2

Raise temp.
or reactants

CO
NO_2

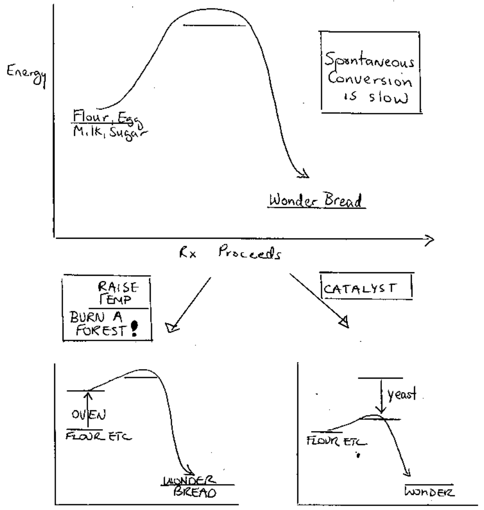
Lower barrier with a catalyst

Alter manner in which
Bonds are broken and
Made other than shear
Brute force (collisional
Energy)

$\Delta H = -226kJ$

CO_2, NO

Visualization



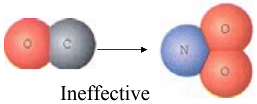
Catalysts work by:

Stupid Analogies

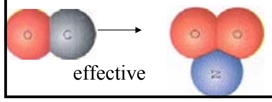
1. **Dating Service**: Bringing reactants together (increasing number of collisions, without requiring an increase in temp)

2. **Dating Service** tailored to specific populations ensuring proper orientation of reactants (increasing the number of **effective** collisions); also facilitates energy of bond making

Because the job of the dating service (catalyst) to facilitate the reaction there is **no net loss** in dating Services with number of marriages



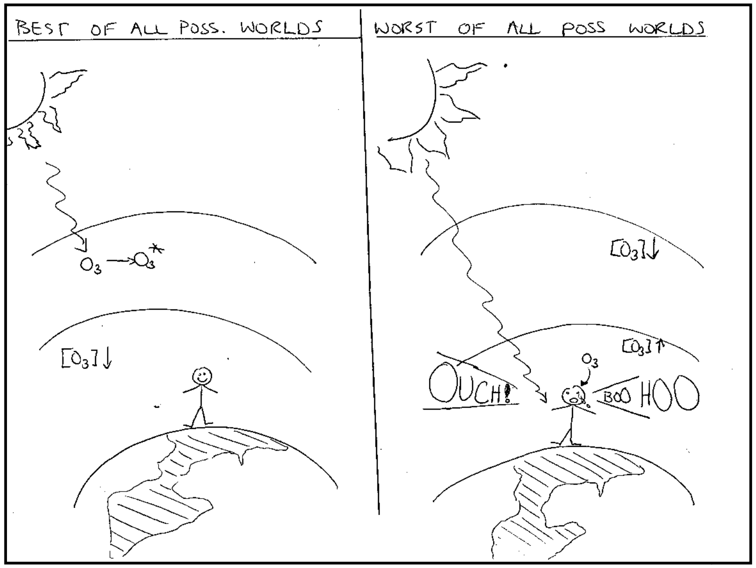
Ineffective



effective

Catalyst is not consumed in rx.

Example: smog, ozone, and catalytic converters



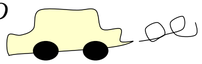
FLASHBACK

$\Delta H = -890kJ$ $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

Heat transferred
from system to surroundings

	$\Delta E_{system} = q + w$	q	w	"efficiency"
Bunsen burner	-885kJ	-890kJ	+5kJ	
Automobile Engine	-885kJ	-665kJ	-220kJ	25%

$N_2 + O_2 \xrightarrow{\text{heat}} 2NO$



Lung/Eye Damage: Ozone excess in Lower Atmosphere

$$NO + 2O_2 \rightarrow O_3 + NO_2$$

$$NO_2 + light \rightarrow NO + :\ddot{\underset{..}{O}}:$$

Happy Camper?

No, **Unhappy** camper

Not Consumed By reaction

$$O + O_2 \rightarrow O_3$$

Net Reaction?

$$3O_2 \rightarrow 2O_3$$

NO is a catalyst

Has an intermediate bond energy with oxygen

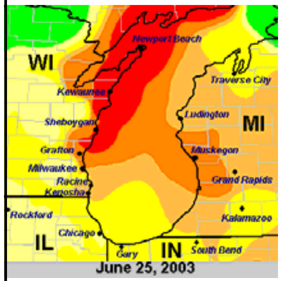
Allowing it to carry oxygen, and to release it

---

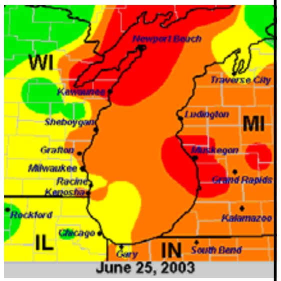
http://www.epa.gov/airnow/showmaps.html?/airnow/2003/20030624/8p-super.gif

Lower Atmosphere Ozone Concentrations for Lake Michigan

Red = unhealthy, >125 ppb

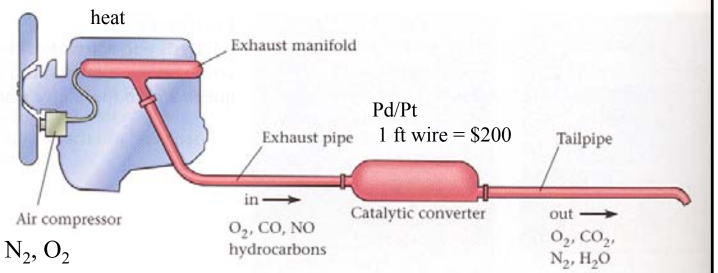


1 hour peak average concentration



8 hour peak average concentration

One solution: reduce NO from engine back to N_2



N_2, O_2

$$2NO \rightarrow N_2 + O_2$$

Ox # +2 -2 0 0

What Kind of Reaction Is this?

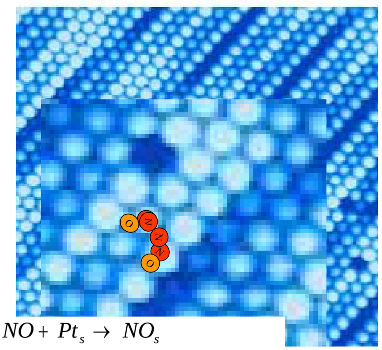
4 electrons are transferred from O to N

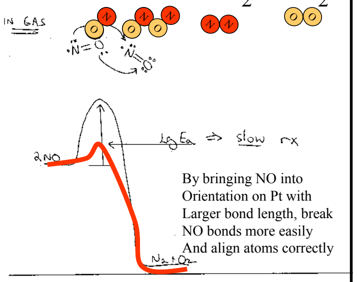
4e + 2 molecules

Is this probable?

Scanning tunneling image of Pt surface

$$2NO \rightarrow N_2 + O_2$$





By bringing NO into Orientation on Pt with Larger bond length, break NO bonds more easily And align atoms correctly

$$NO + Pt_s \rightarrow NO_s$$

Slow ste

$$NO_s + Pt_s \rightarrow N_s + O_s \qquad k = 5.00x10^{20}\frac{mol}{cm \cdot s}e^{-\frac{107.8kJ/mol}{RT}} = 4.91x10^{20}\frac{mol}{cm \cdot s}$$

$$N_s + N_s \rightarrow N_2 + Pt_s + Pt_s \qquad k = 3.70x10^{21}\frac{mol}{cm \cdot s}e^{-\frac{113.9kJ/mol}{RT}} = 3.63x10^{21}\frac{mol}{cm \cdot s}$$

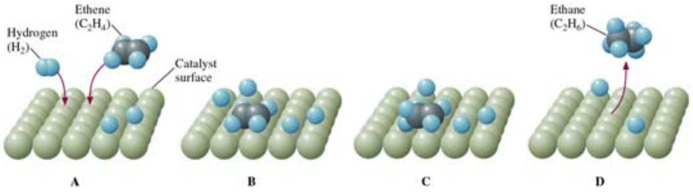
$$O_s + O_s \rightarrow O_2 + Pt_s + Pt_s \qquad k = 3.70x10^{21}\frac{mol}{cm \cdot s}e^{-\frac{232.2kJ/mol}{RT}} = 3.56x10^{21}\frac{mol}{cm \cdot s}$$

Slow step

$NO_s + Pt_s \rightarrow N_s + O_s$ $\qquad k = 5.00x10^{20} \frac{mol}{cm \cdot s} e^{-\frac{107.8kJ/mol}{RT}} = 4.91x10^{20} \frac{mol}{cm \cdot s}$

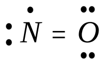
To keep step 1 from being slow design to maximize number of NO encounters with Pt

$NO + Pt_s \rightarrow NO_s$



More on NO reactivity

NO is an "antioxidant", scavenging electron containing intermediates mediating oxidative stress in organisms.



Are e on N happy campers?

NO – looking for partners

For example if your hemoglobin is delivering O$_2$ but happens to produce O_2^- by an actual reaction with the Fe(II) acting as the delivery boy to give Fe(III) which no longer carries oxygen, NO can come along and straighten out the problem by an oxidation/reduction reaction
http://www.pnas.org/cgi/content/full/100/16/9196

Induces vasodilation Produced by the innermost cell layer of the arteries, diffuses rapidly distances of microns, into underlying muscles cells and regulates their contractions to open the flow of the blood. Found to play a role in **male impotence**.
http://nobelprize.org/nobel_prizes/medicine/laureates/1998/press.html
Robert F. Furchgott, Louis J. Ignarro and **Ferid Murad**

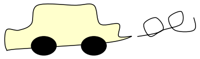
Plays a role in the **immune system**: cytokine-activated macrophages can produce high concentrations of NO in order to kill target cells such as bacteria or tumor cells. NO-mediated cytotoxicity is often associated with the formation of nitrosyl-thiol complexes in enzymes within the target cell. NO has been shown to kill cells by disrupting enzymes involved in the Kreb's cycle, DNA synthesis and mitochondrial function. http://www.sgul.ac.uk/depts/immunology/~dash/no/role.html

NO not only produces ozone; but can act as a catalyst to Destroy ozone in upper atmosphere

$$\left.\begin{array}{c} O_3 \rightarrow O_2 + O \\ O_3 + O \rightarrow 2O_2 \\ \hline 2O_3 \rightarrow 3O_2 \end{array}\right\}$$

"spontaneous ozone loss"
Is slow

$N_2 + O_2 + heat \rightarrow 2NO$



Notice that NO is not Part of final reaction: not consumed

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$O + NO_2 \rightarrow NO + O_2$$
$$\overline{O + O_3 \rightarrow 2O_2}$$

Another reaction catalyzing upper atmosphere ozone loss

$2O_3 \rightarrow 3O_2$ *slow*

Spontaneous pathway

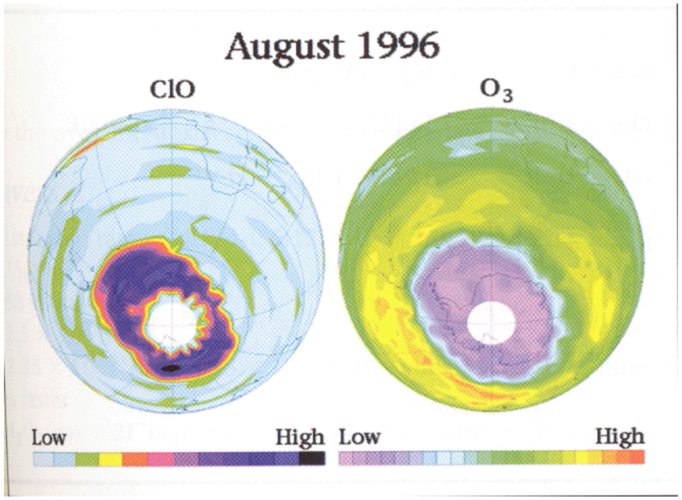
Catalyzed pathway

$$O_3 + Cl_g \rightarrow O_{2(g)} + ClO_{(g)} \qquad 5.2x10^9 \left.\frac{L}{mol \cdot s}\right|_{220K}$$

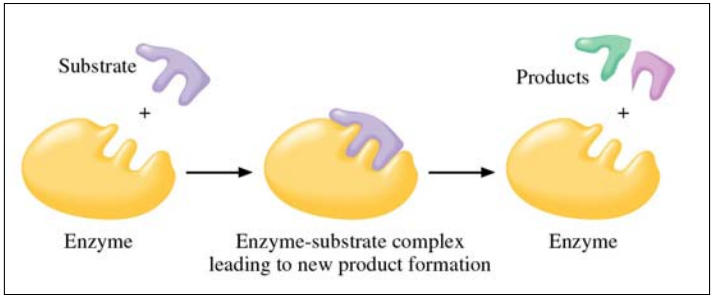
Slow step
Is pretty fast

$$ClO_g + O_g \rightarrow Cl_{(g)} + O_{2(g)} \qquad 2.6x10^{10} \left.\frac{L}{mol \cdot s}\right|_{220K}$$

$$O_3(g) + O_{(g)} \rightarrow 2O_2$$



Enzyme action (lock-and-key model).



Enzymes are catalysts in biochemical reactions

Catalysis Example Problems

Which of the these reactions appear to involve a catalyst? In those cases where a catalyst is present, tell whether it is homogeneous or heterogeneous.

$$CH_3CO_2CH_{3,aq} + H_2O_\ell \rightarrow CH_3COOH_{3,aq} + CH_3OH_{aq}$$

$$rate = k\left[CH_3CO_2CH_{3,aq}\right]\left[H_2O^+\right]$$

$$H_{2g} + I_{2g} \rightarrow 2HI_g$$

$$rate = \left[H_{2g}\right]\left[I_{2,g}\right]$$

"A" students work
(without solutions manual)
~ 10 problems/night.

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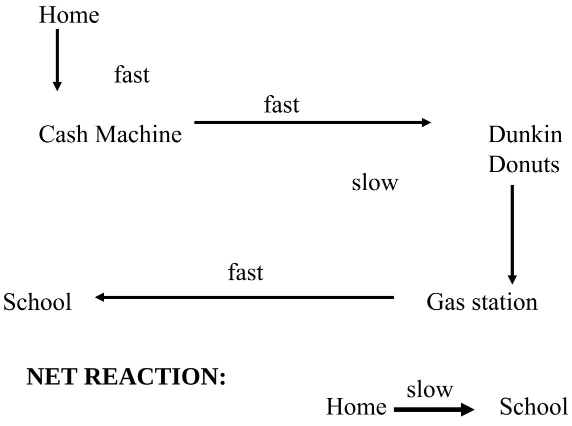
Module #14
Kinetics: Reaction Mechanism

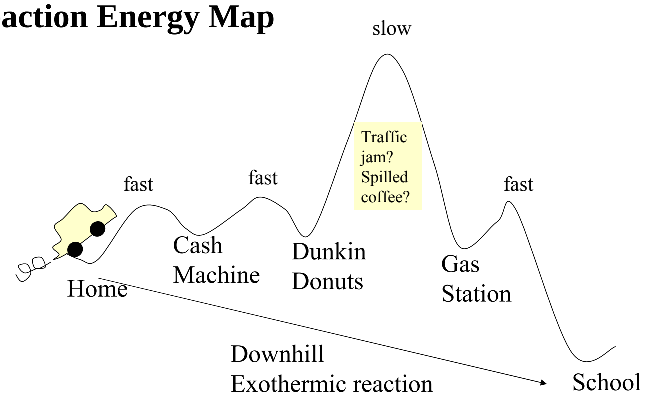
Reaction Mechanism



NET REACTION:

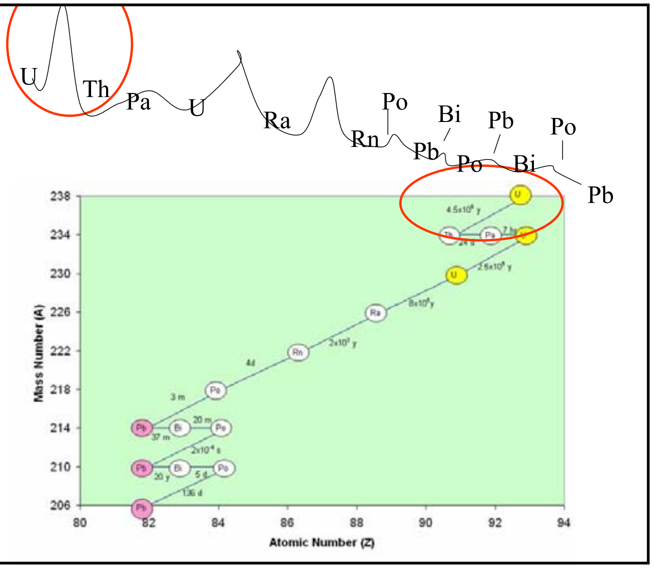
Home $\xrightarrow{slow}$ School

Reaction Energy Map



Downhill
Exothermic reaction
Driven by love of Chemistry

But reaction is slow!!!



Example: Ozone

Express the reaction rate for:

$$O_3 \rightarrow O_2 + \cancel{O} \qquad fast$$
$$O_3 + \cancel{O} \rightarrow 2O_2 \qquad slow$$
$$\overline{2O_3 \rightarrow 3O_2 \qquad ?}$$

What is the rate expression?
What is the rate?

Wrong answer: $\cancel{rate = k[O_3]^2}$

From the overall reaction

$$\boxed{rate = k[O_3]^m[O]^n}$$

From the slow step!!

Example Problem: Reaction Mechanism

Reaction	Rate	
$2A + B \rightleftarrows C$	fast	
$C \rightleftarrows D$	fast	
$D \rightarrow 2E$	slow	
$2E + F \rightleftarrows G$	fast	
$2A + B + F \rightarrow G$	slow	Net reaction

From **net reaction**
WE PREDICT

$rate = k[A]^2[B][F]$

WE OBSERVE

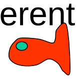
$rate = k[D]$

IS THIS A PROBLEM?

FITCH Rules

General

G1: Suzuki is Success
G2. Slow me down
G3. Scientific Knowledge is Referential
G4. Watch out for Red Herrings



G5. Chemists are Lazy

Chemistry

C1. It's all about charge $E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$
C2. Everybody wants to "be like Mike"
C3. Size Matters $E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$
C4. Still Waters Run Deep

C5. Alpha Dogs eat first

"A" students work
(without solutions manual)
~ 10 problems/night.

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Module #14
Kinetics

End