Chem 1B Objective 5:
Understand factors that determine reaction rate and describe reaction rate with rate law, order, rate constant, and activation energy.

<u>Key Ideas</u>: Important in preserving food, curing cement, combustion.
Rate - How fast does a reaction occur? Reaction occurs when reactants collide with sufficient energy and correct orientation for bonds break/form.
Rate depends on T and [ ] and catalyst.

Rate law: rate = $- \Delta [\ ] / \Delta t = k [\ ]^x$ where x = order

Rate constant = k depends on T ($k = Ae^{-Ea/RT}$)

Activation energy is speed bump. See reaction energy diagram.

Consider the following common reactions,

http://www.physicscentral.com/experiment/physicsathome/electricwhirlpool.cfm

http://hiox.org/13831-bunsen-burner-day.php

a. dissolution of salt in water b. combustion of methane

(i) Is the reaction fast or slow? How do you know?

(ii) Is heat absorbed or released? How do you know?

(iii) Does the reaction occur spontaneously? How do you know?

Energy Is Involved In Every Chemical Reaction

<u>Heat (q) and Thermochemistry</u>

Energy supplied (gained) is <u>Endothermic</u> (q is +).
Energy released (lost) is <u>Exothermic</u> (q is -).

1. a. When bonds break, energy is
   (i) required (ii) supplied (iii) released (iv) absorbed

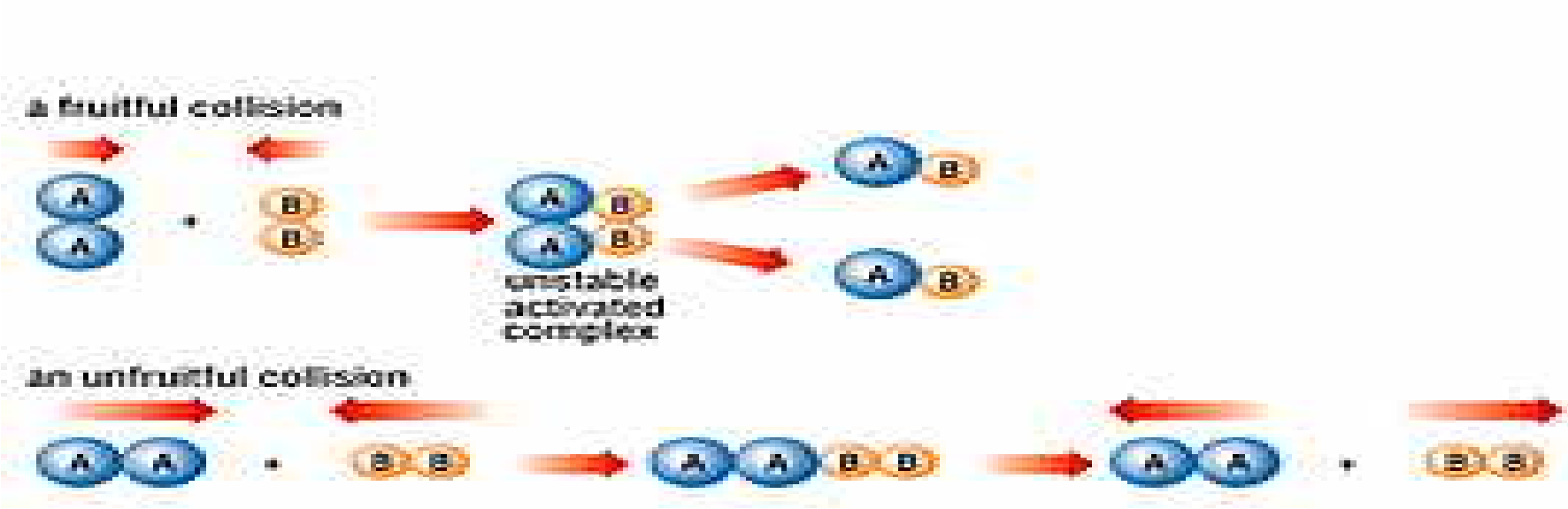
b. When bonds form, energy is
(i) required (ii) supplied (iii) released (iv) absorbed

c. Most reactions are
(i) exothermic (ii) endothermic (iii) neither

A Chemical Reaction Occurs When:

Atoms/molecules collide with ***sufficient*** energy and correct orientation for bonds to break/form.

Collision Theory



Every Chemical Reaction Involves Energy

Does A Reaction Occur?
Thermodynamics
<u>2 Driving Forces</u>:
Enthalpy
Entropy

How Fast Does A Reaction Occur?
Kinetics (rate of reaction)
<u>3 Factors</u>:
Temperature
Concentration
Catalyst

A chemical reaction occurs if energetics are ***<u>favorable</u>***.
This means reaction is:

(i) exothermic and slow
(ii) exothermic and fast
(iii) endothermic and slow
(iv) endothermic and fast

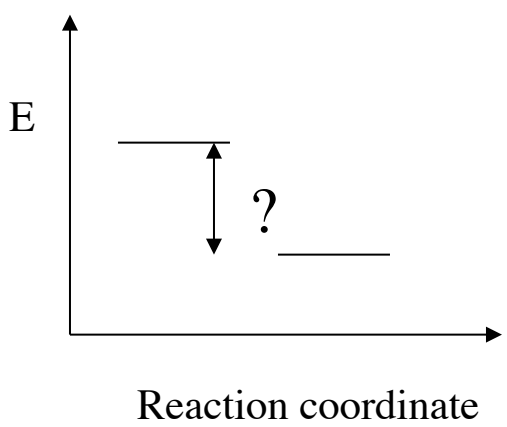
<u>2 Driving Forces</u>

Determine Whether A Reaction Occurs

<u>Enthalpy</u> (Hess' Law)
Is wood burning an exothermic or endothermic reaction?

<u>Entropy</u>
Remember the tossed salad?

Which reaction energy diagram represents the wood burning rxn?



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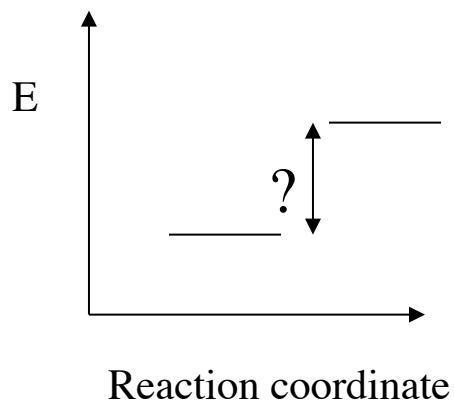


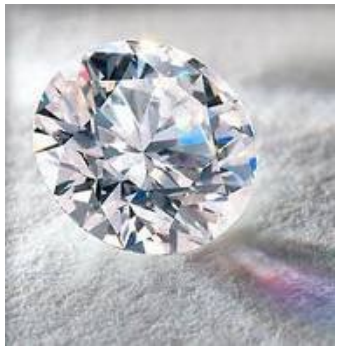
Each of the following reactions occur.
Which Reaction is Fast? Which Reaction is Slow?

Grass growing

Wood burning

Iron rusting

Fireworks:
$S + KNO_3 + C \rightarrow$



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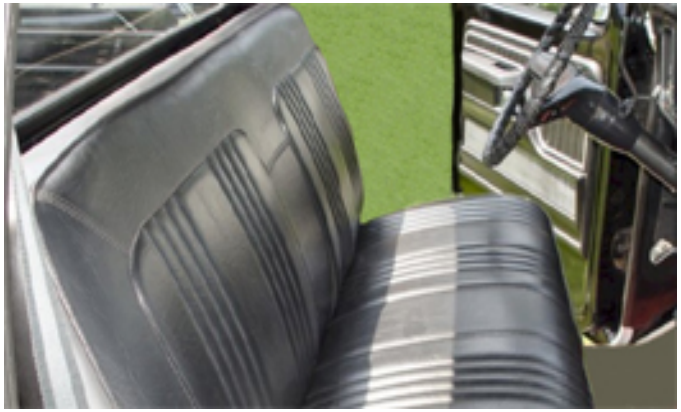
Diamond turning into graphite

Control of Reaction Rate Is Very Important!

Food spoilage



Vinyl seat cover cracks

Concrete setting

Ozone destruction

Objective: Identify the factors that determine rate

Atoms/molecules collide with sufficient energy and correct orientation for bonds to break/form.

Three factors determine (control) the rate of reaction:

1. Temperature
2. Concentration
3. Catalyst

Which factor increases the energy of the reaction?
Which factor increases the frequency of collisions?

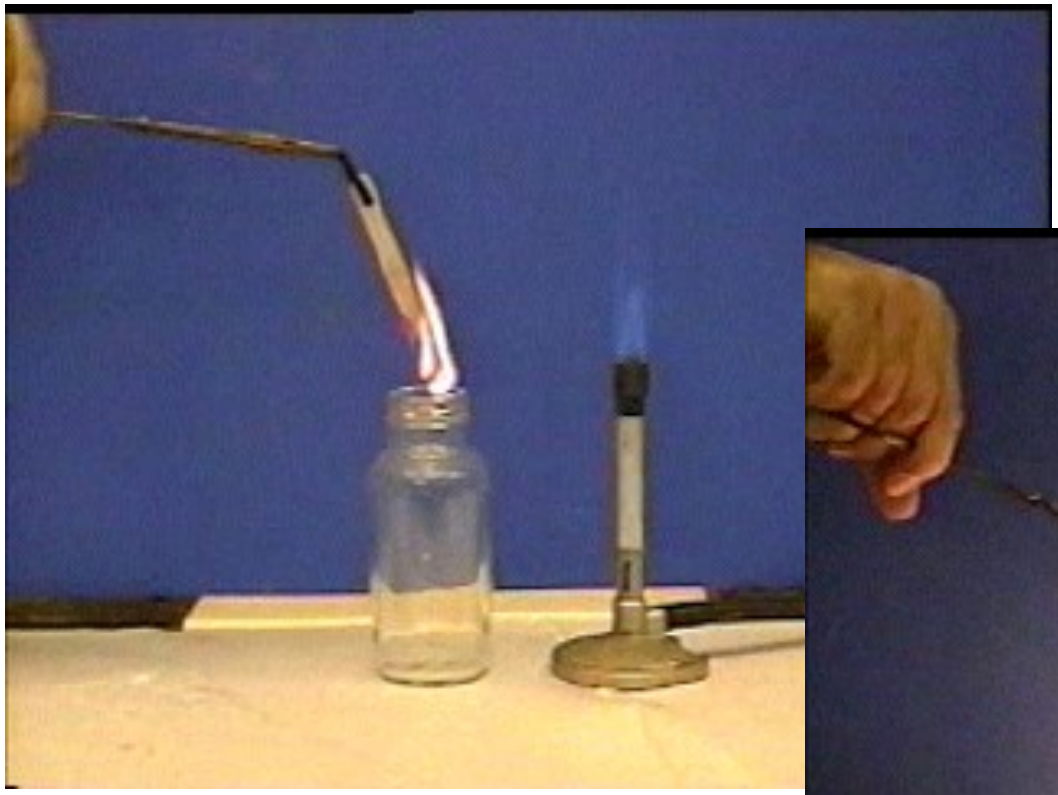
Animations: effect of T and [ ] on rate
http://www.glencoe.com/sec/science/chemistry/mc/wwwlinks/chapter17.shtml

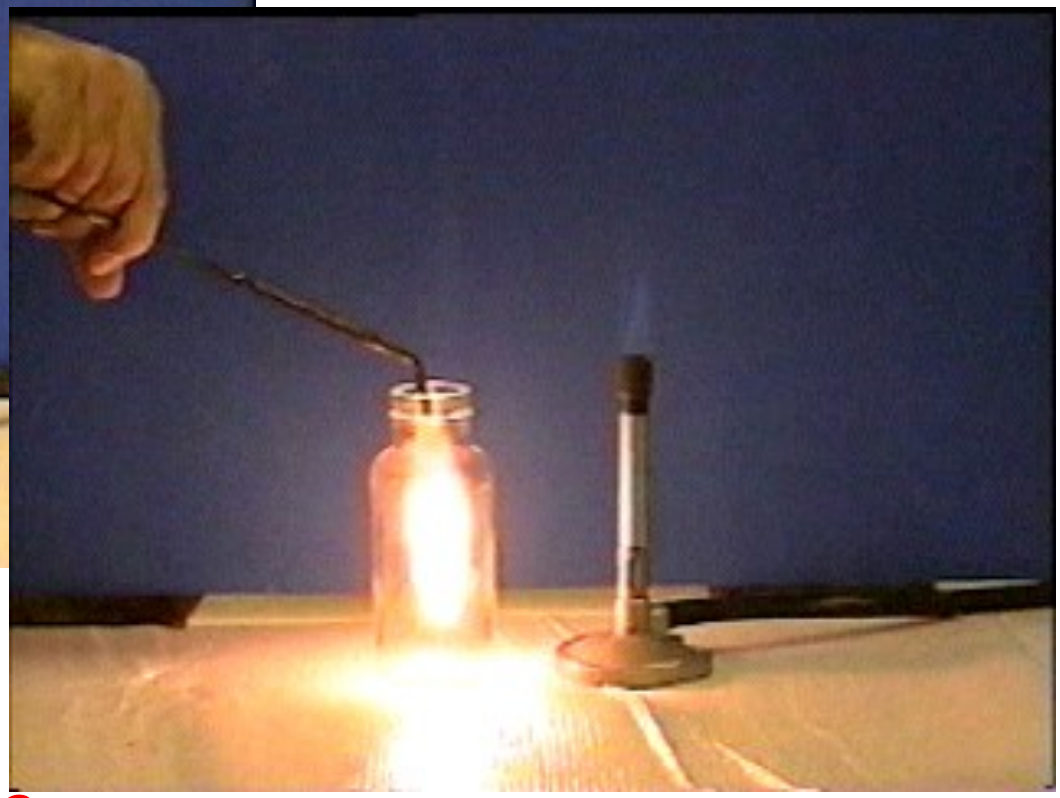
<u>Objective</u>: Identify the factors that determine rate
Atoms/molecules collide with sufficient energy and correct orientation for bonds to break/form.

How to increase the energy of the reaction?
How to increase the frequency of collisions?

Compare

Wood burning in air: (http://www.angelo.edu/faculty/kboudrea/demos/burning_splint/burning_splint.htm)





What is happening?

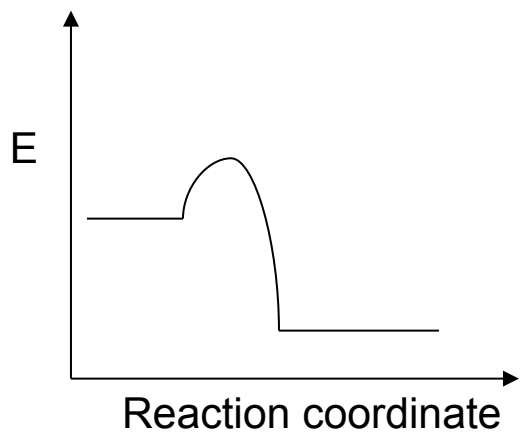
What factor changes rate?

Wood burning in pure oxygen:
http://www.youtube.com/watch?v=N5soi2DnX44

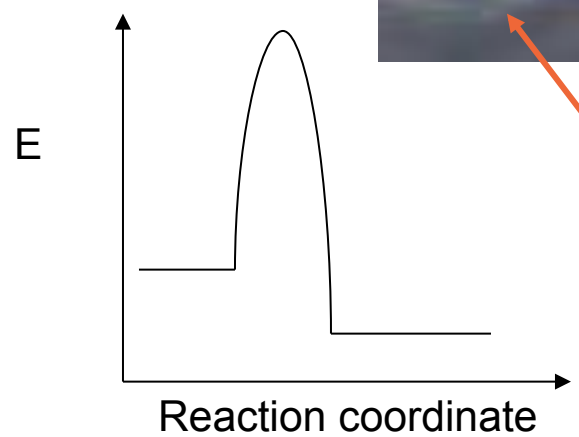
Objective: Relate rate to activation energy

Wood + O_2 ---> CO_2 + H_2O

This reaction is ____ fast or slow _____.
Is the ***Activation Energy*** (speed bump) large or small?
Which reaction energy diagram represents this reaction best?



Fast

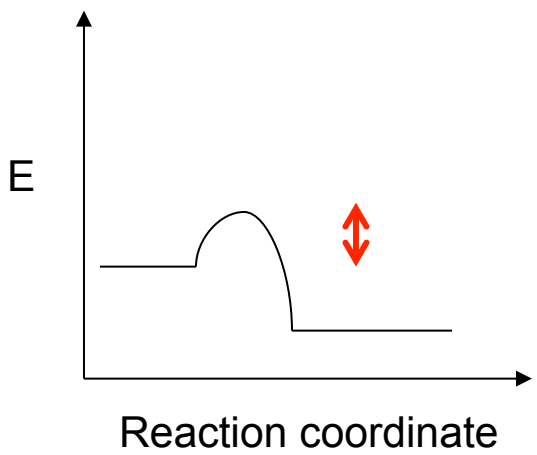


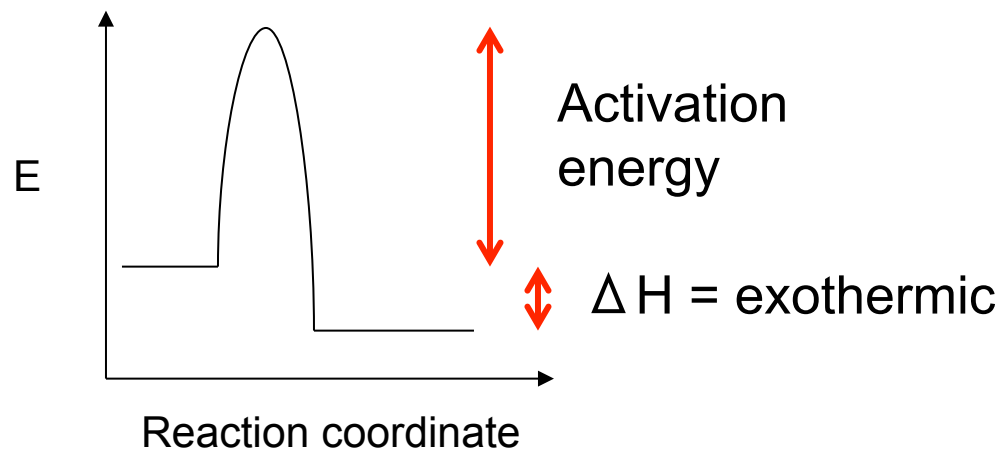
Slow

To go from here to there as fast as you can …

How can this reaction be slowed down?

What does the reaction energy diagram for the iron rusting reaction look like?





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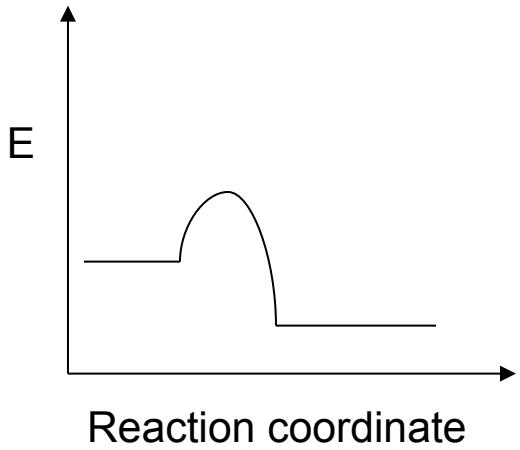
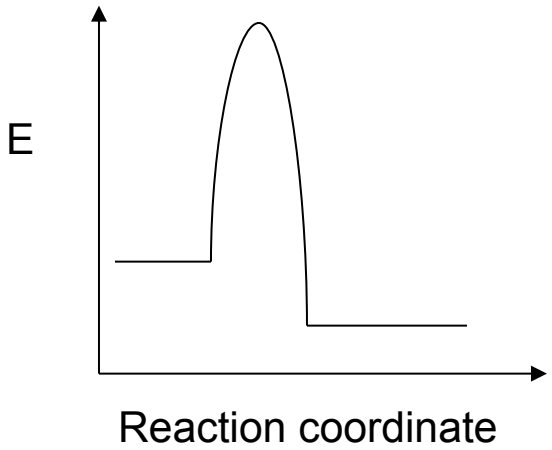
What does the reaction energy diagram for the diamond --> graphite reaction look like?





Objective: Describe How Fast A Reaction Occurs

Fast/Slow → Speed → Rate

Physics: $\text{rate} = \dfrac{\Delta\ \text{distance}}{\Delta\ \text{time}}$

Chemistry: $\text{rate} = \dfrac{\Delta\ \text{concentration}}{\Delta\ \text{time}}$

Objective: Describe How Fast A Reaction Occurs

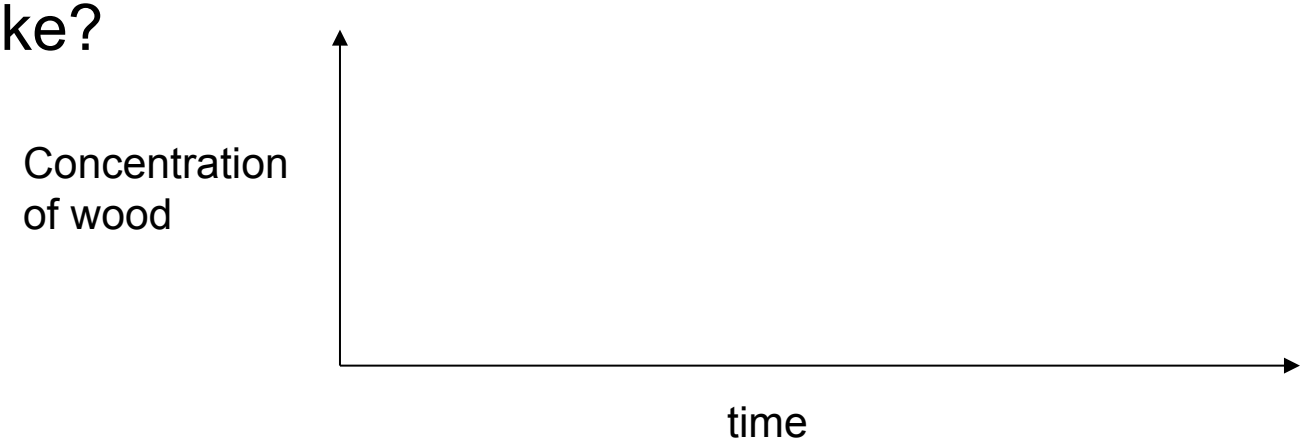
Chemistry: $$\text{rate} = \frac{\Delta \text{ concentration}}{\Delta \text{ time}}$$

$$\text{Wood} + O_2 \text{ ---> } CO_2 + H_2O$$

From Chem 1A:

Initial amount	10	10	0	0
Amount that reacts	5	5		
Amount left over	5	5		

As wood burns, what does the concentration of wood vs. time graph look like?



Objective: Describe How Fast A Reaction Occurs

Chemistry: $$\text{rate} = \frac{\Delta \text{ concentration}}{\Delta \text{ time}}$$

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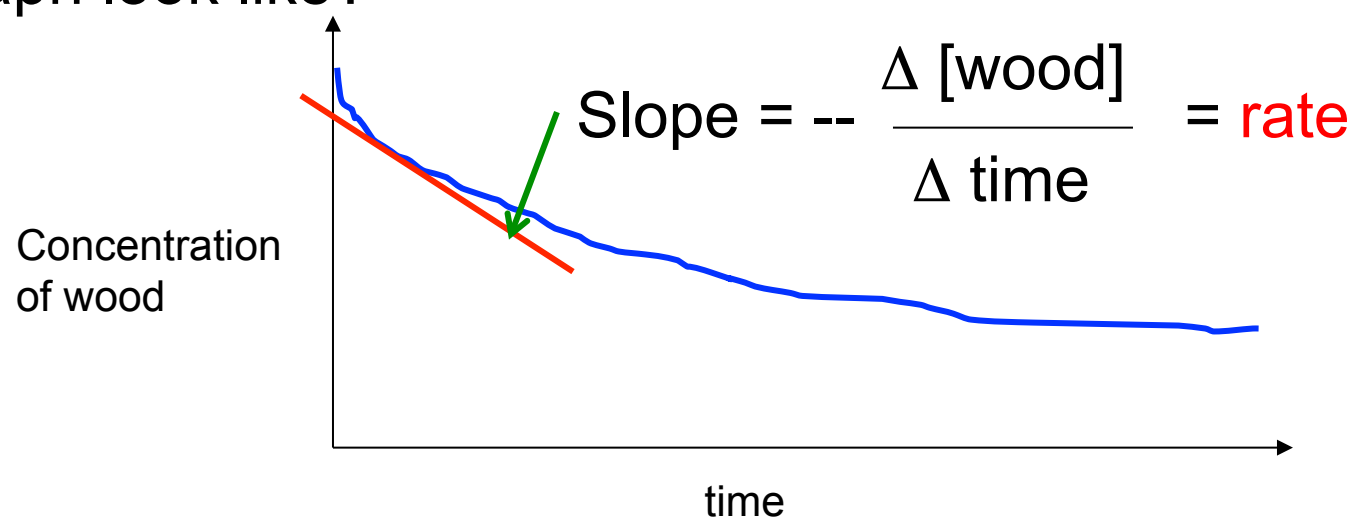
As wood burns, what does the concentration of wood vs. time graph look like?



What happens to the rate as the reaction proceeds?

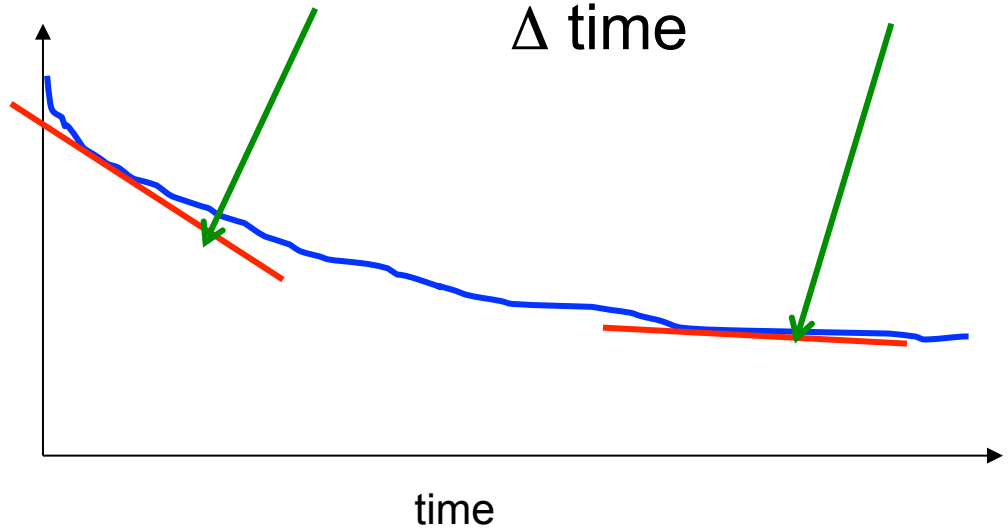
Animation: http://www.wwnorton.com/college/chemistry/chemistry3/ch/15/chemtours.aspx

Objective: Describe How Fast A Reaction Occurs

Chemistry: $\text{rate} = \dfrac{\Delta \text{ concentration}}{\Delta \text{ time}}$

$$\text{Wood} + O_2 \text{ ---> } CO_2 + H_2O$$

$$\text{Slope} = -\dfrac{\Delta\,[\text{wood}]}{\Delta \text{ time}} = \text{rate}$$



As reaction proceeds, compare Slopes.

Slope decreases ➔ rate decreases

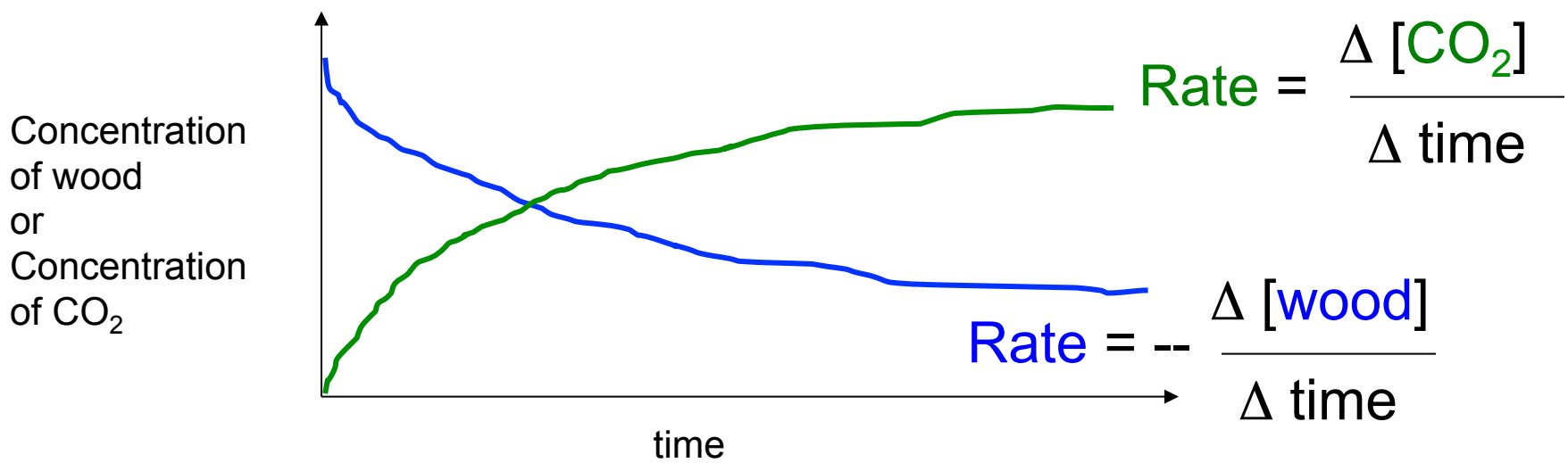
What does concentration of CO_2 vs. time look like?

Objective: Describe How Fast A Reaction Occurs

Chemistry: $\text{rate} = \dfrac{\Delta \text{ concentration}}{\Delta \text{ time}}$

$$\text{Wood} + O_2 \text{ ---> } CO_2 + H_2O$$

	Wood	O_2	CO_2	H_2O
Initial amount	10	10	0	0
Amount that reacts	5	5		
Amount that forms			5	5



<u>Objective</u>: Quantify Reaction Rate with a **<u>Rate Law</u>**

Wood + O_2 ---> CO_2 + H_2O

Rate Law: $\text{rate} = -\dfrac{\Delta\,[\text{wood}]}{\Delta\,\text{time}} = k\,[\text{wood}]^x\,[O_2]^y$

(-) sign refers to rate of <u>dis</u>appearance of wood

k = rate constant (changes with T)

x and y = reaction order Determined by Experiment!

Rate law is determined by Experiment!

<u>Objective</u>: Quantify Reaction Rate with a **<u>Rate Law</u>**

$$\textbf{Wood} + O_2 \text{ ---> } CO_2 + H_2O$$

Rate Law: $\text{rate} = -\dfrac{\Delta\,[\text{wood}]}{\Delta\,\text{time}} = k\,[\text{wood}]^x\,[O_2]^y$

Rate Factors:

Change [ ] ----> rate changes

Change Temperature ---> k changes ---> rate changes

Rate law is determined by Experiment!

<u>Objective</u>: Quantify Reaction Rate with a **<u>Rate Law</u>**

Wood + O_2 ---> CO_2 + H_2O

Rate Law: $\text{rate} = -\dfrac{\Delta\,[\text{wood}]}{\Delta\,\text{time}} = k\,[\text{wood}]^x\,[O_2]^y$

x and y = reaction order
Determined by Experiment!

1. What does <u>reaction order</u> mean?

Reaction Order Tells Us:

a. What happens to rate when [ ] changes,

b. the # of Particles of Each Reactant Involved in the **Reaction Mechanism**

Rate Law → Reaction Mechanism

1. What does <u>reaction order</u> mean?

Reaction Order Tells Us:

a. What happens to rate when [ ] changes,

E.g., A + B ---> products rate law: rate = $k\,[A]^1\,[B]^2$

If [A] is doubled and [B] is constant, rate will

(i) stay the same (ii) DOUBLE (iii) triple (iv) quadruple

$$\frac{\text{Rate of Exp 2}}{\text{Rate of Exp 1}} = \frac{k\,[2]^1\,[1]^2}{k\,[1]^1\,[1]^2} = ??$$

If [A] is constant and [B] is doubled, rate will

(i) stay the same (ii) double (iii) triple (iv) quadruple

<u>Objective</u>: Determine rate law

The Rate Law Is Determined By Experiment!

Method (i):

<u>Step 1</u>: Change [ ] of one reactant, keep other reactant [ ] constant, measure rate. Do <u>several</u> experiments.

<u>Step 2</u>: Compare rate with change in [ ] to determine the order of the reaction with respect to each reactant. Calculate the rate constant, k.

A + B ---> products

	[A],M	[B],M	rate, M/sec
Experiment 1	1	1	10
Experiment 2	2	1	20
Experiment 3	1	2	40
Experiment 4	5	?	50

Rate law: rate = $k\,[A]^x\,[B]^y$

What is x? y? k?

Combustion of Methane:

$$CH_4\ (g) + 2\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (g)$$

1. What is the rate law?

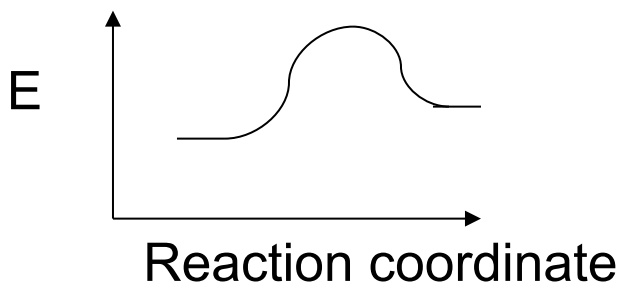
a) Rate = k $[CH_4]^x\ [CO_2]^y$

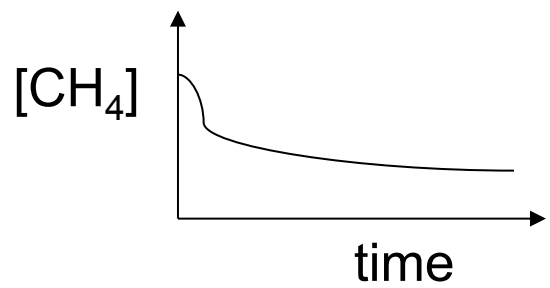
b) Rate = k $[CH_4]^x\ [O_2]^y$

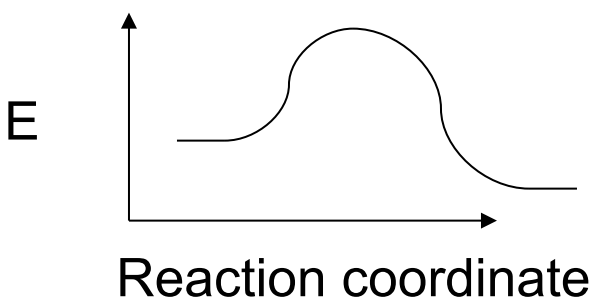
c) Rate = k $[CO_2]^x\ [H_2O]^y$

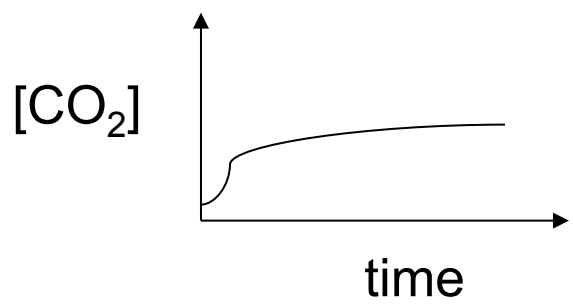
2. Which diagram represents the reaction energy diagram?

3. Which diagram represents the change in concentration of CO_2?









Lab 3: The Kinetics of the Iodine Clock Reaction

Mix two colorless solutions together. After some time, the solution turns **Blue**. The Iodine Clock Reaction is three reactions:

$$IO_3^- + 3\ HSO_3^- \text{ ---> } I^- + 3\ SO_4^{2-} + 3\ H^+ \qquad (1)$$

$$5\ I^- + 6\ H^+ + IO_3^- \text{ ---> } 3\ I_2 + 3\ H_2O \qquad (2)$$

$$I_2 + \text{starch ----> blue solution (indicator)} \qquad (3).$$

These three reactions occur at different rates. Which reaction is the fastest? Give reasons.

(a) Reaction (1) (b) Reaction (2) (c) Reaction (3)

In Reaction (1), which reactant is the limiting reactant? Why?

Iodine clock reaction (1)

	IO_3^- +	$3\ HSO_3^-$ ---> I^- + $3\ SO_4^{2-}$ + $3\ H^+$
	10 ml	10 ml
	0.02 M	0.002 M
Initial moles		
Moles reacts		
Moles leftover		

Rate law: rate = -- $\dfrac{\Delta\,[IO_3^-]}{\Delta\ \text{time}}$ = $k\,[IO_3^-]^x\,[HSO_3^-]^y$

<u>How is rate measured so x and y and k can be determined?</u>

$\Delta[IO_3^-] = [IO_3^-]_{t=0} - [IO_3^-]_{t=blue}$

Δt = time for solution to turn blue

<u>Objective</u>: Determine rate law

The Rate Law Is Determined By Experiment!

Method (i):

<u>Step 1</u>: Change [ ] of one reactant, keep other reactant [ ] constant, measure rate. Do <u>several</u> experiments.

<u>Step 2</u>: Compare rate with change in [ ] to determine the order of the reaction with respect to each reactant. Calculate the rate constant, k.

a. Chang, 6th ed., Problem 14.15

b. Chang, 6th ed., Problem 14.16

c. Lab 3 Iodine Clock Reaction (1)

$$IO_3^- + 3\ HSO_3^- \text{ ---> } I^- + 3\ SO_4^{2-} + 3\ H^+$$

Exam 1

March 2, 2017

<u>Last 30 minutes of class</u>

Open Book and Notes

Exam 2 will cover Objectives 1 through 6.

1. Identify organic functional groups, draw skeletal structures, and distinguish between the same compound, isomers, and resonance structures.
2. Understand organic oxidation reactions and ester reactions.
3. Identify the chemical forces in ionic and molecular solutions.
4. Predict solution properties based on colligative properties
5. Understand factors that determine reaction rate and describe reaction rate with rate law, order, rate constant, and activation energy.
6. Describe reaction mechanisms and relate mechanism to rate law and reaction energy diagram.

2. Rate constant, k, is constant if T is constant.
What happens to k as the reaction temperature changes?

E.g., A + B ---> products rate law: rate = k $[A]^1$ $[B]^2$

Arrhenius equation: $k = A e^{-Ea/RT}$

where k = rate constant

A = collision factor

E_a = activation energy in J/mole

R = gas constant = 8.31 J/mole K

T = temperature in K

Which rate factor (T, [ ], or catalyst) is related to this equation?

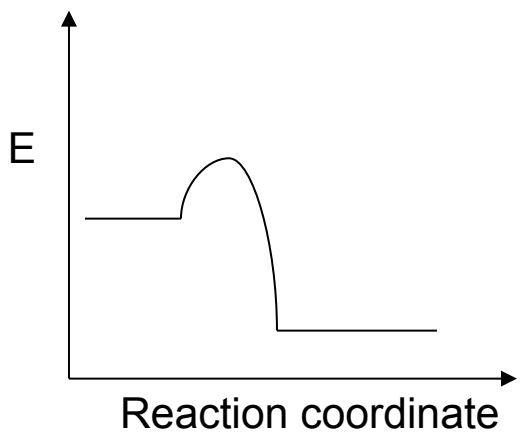
As T increases =====> Rate Constant ___ Increases or decreases _____

Objective: Relate rate to activation energy

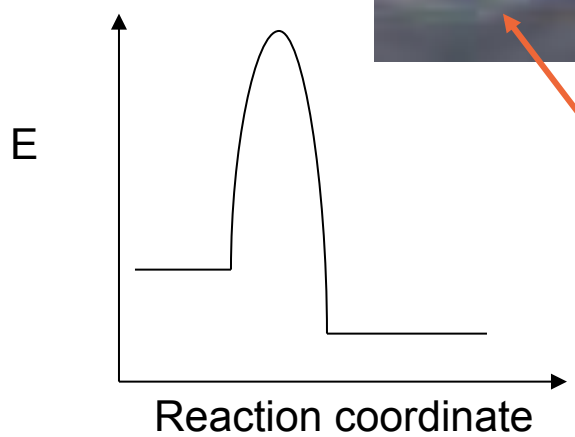
Wood + O_2 ---> CO_2 + H_2O

This reaction is fast.

Activation Energy (speed bump) is small.



Fast



Slow

To go from here to there as fast as you can …

2. Rate constant, k, is constant if T is constant.
As T increases =====> Rate Constant Increases

E.g., A + B ---> products rate = $k\,[A]^1\,[B]^2$

Arrhenius equation: $k = A\,e^{-Ea/RT}$

If you know k at <u>one</u> T and want to know k at a <u>different</u> T, use Arrhenius equation.

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

Objective: use Arrhenius equation to calculate k at different T

General Rule: rate doubles with every 10°C increase in T

Typical E_a = 50 kJ/mole
What happens to k if T increases from 300 K to 310 K?

Use Arrhenius equation ($k = A e^{-Ea/RT}$) to calculate k.

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

T_1 = 310 K, T_2 = 300 K, E_a = 50,000 J/mole, R = 8.31 J/mole K
Solve for k_1/k_2

Answer = k_1/k_2 = 2

<u>Objective</u>: Determine the Activation Energy, E_a

E_a of a Reaction is Determined by Measuring the Rate and k at Different Temperatures

Arrhenius equation: $k = A e^{-Ea/RT}$

Take ln of both sides: $\ln k = \ln A - E_a/RT$

Measure k and different T

Graph your data:

a) k vs. T b) ln k vs. T c) ln k vs. 1/T d) E_a vs. k

Slope = _____.

Lab 3: **What is E_a of Iodine Clock Reaction?**

Measure rate at different T.
Calculate k at different T.
Graph _____ vs. _____
Determine E_a from _____.

Lab Practical:
Your group will be assigned a time.
Identify/calculate the [ ] and T to make this reaction turn blue in your assigned time.
Mix the reactants in front of the lab class ==> **ONE** chance only.

Summary: What is the difference between reaction rate, reaction order, and rate constant?

Consider the reaction: A + B --> C

1. Rate law does not tell you:

a. Order b. rate constant c. exothermic

2. 0th order in B means if [B] doubles,

a. Rate doesn't change b. rate doubles c. rate triples

3. Rate constant, k, changes with

a. Concentration b. time c. temperature

4. k varies with T ($k = A e^{-Ea/RT}$) means:

a. As T increases, k decreases

b. $E_a > 0$

c. E_a changes with Temperature

Objective: Determine rate law

The Rate Law Is Determined By Experiment!

Method (ii) Uses Integrated Rate Equations

(see Chang, 6th ed., Chapter 14.3)

Measure [ ] at different times in one experiment.

Step 1: Assume reaction is ____ order.
Step 2: Use Integrated rate equations to graph data.
Step 3: If graph is a straight line, assumed reaction order is correct. Calculate k.

Example: Consider the reaction: A --> products
a. Using method (ii), how would you determine the rate law?

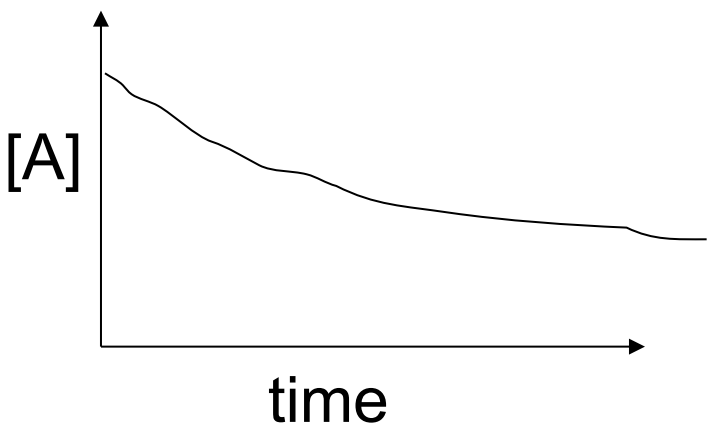
Method (ii) Uses Integrated Rate Equations

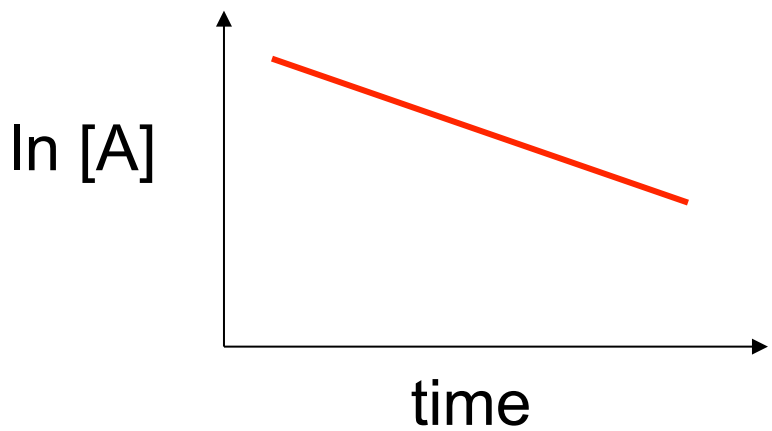
a. Using method (ii), how would you determine the rate law?
Assume A --> products reaction is **1st order** in A

So $\text{rate} = -\dfrac{\Delta[A]}{\Delta t} = k\,[A]$ ===> do math (diff equation)

Integrated rate equation: $\ln \dfrac{[A]_t}{[A]_o} = -k\,t$

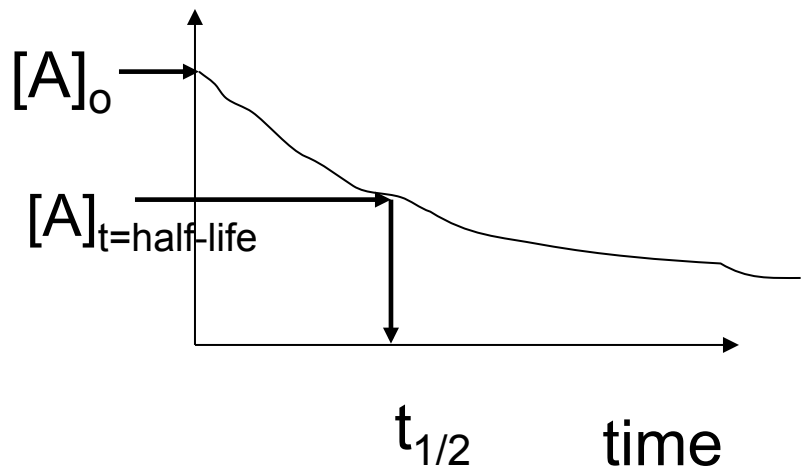
Graph ln [A] vs. t
If graph gives a straight line, then reaction is 1st order in A.





b. What is the **half-life** of this reaction?

at half-life, $t_{1/2}$, $[A]_{t=half\text{-}life} = 0.5\ [A]_o$



$$\ln \frac{[A]_t}{[A]_o} = -k\,t$$

For 1st order reaction, $\mathbf{t_{1/2} = ??}$

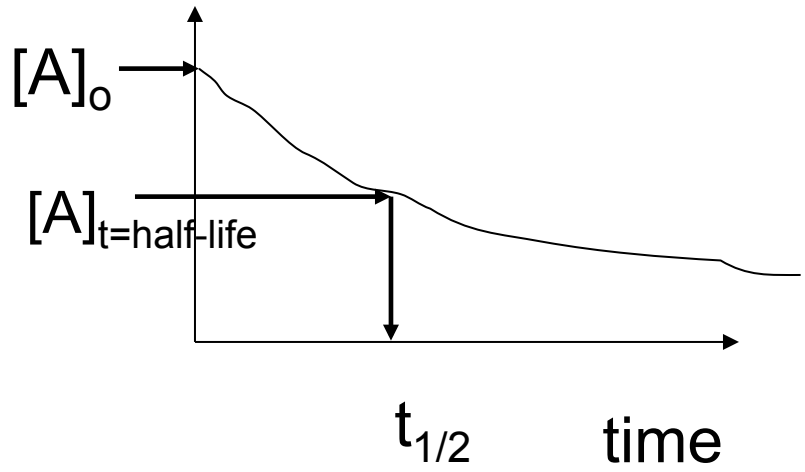
At half-life,

$[A]_{t=half\text{-}life} = 0.5\ [A]_o$

$\ln(0.5\ [A]_o/[A]_o) = -k\,t_{1/2}$

$\ln(0.5) = -k\,t_{1/2}$

Solve for $t_{1/2}$



Half-life for a 1st order reaction means:

a. 1/2 of this class is over
b. $t_{1/2} = 0.693/k$
c. cat has 8.5 lives left

Would you want your DNA to stay coiled or to uncoil?

3×10^9 base pairs divided into 23 chromosomes

base to base distance = 0.34 nm

2 strands coiled in alpha helix shape, DNA length = 2 - 3 m

$\approx 10^{14}$ cells in human body, each cell $\approx 10\ \mu m$

The uncoiling of DNA is a first order process with an activation energy of 430 kJ/mole. At 60°C, the half-life is estimated to be 2 minutes.

a. Write a chemical equation that represents this reaction. Then, write the rate law for this reaction.

b. Calculate the half-life at normal body temperature, 37 °C.

c. What is the chemical force that holds the DNA in its coiled state? Is the uncoiling of DNA favored by enthalpy or entropy or both? Give reasons.

d. Is the uncoiling of DNA spontaneous at 37°C? Give reasons.

e. Draw a reaction energy diagram for the uncoiling of DNA.