

# Introduction to Energy and Change

## Formulas & Theorems Covered Today:

- ★ Introduction to Thermodynamics
- ★ Law of Conservation of Energy
- ★ Heat vs. Temperature
- ★ Enthalpy Change Introduction
- ★ Physical Changes and Heat

## Homework:

🏠 Pg. 221-228

## Notes:

### Energy and Change

- Most physical and chemical changes and nuclear reactions are accompanied by a change in energy
- These changes are essential to life on Earth
- Some reactions, like cellular respiration, regulate body temperature by releasing heat, and some, like photosynthesis, require a net input of energy
- Even larger changes in energy are seen in nuclear reactions, which occur in the sun, and are what power all of life on earth
- The study of energy transfer is called thermodynamics
- Chemists are very much so interested in the branch of chemistry called thermochemistry

### Law of Conservation of Energy

- States that the total energy in the universe is constant
  - In other words energy cannot be created or destroyed but can be altered from one form to another

$$\Delta E_{\text{Universe}} = 0$$

- Energy can however be transferred from one substance to another
- Before scientists can study this transfer, they must define what part of the universe they are dealing with
- It is easiest for scientist to split the universe into two parts, the system and the surroundings
- The system is defined as the part of the universe that is being studied, be it a coffee cup, a single room, a sealed container etc.
- The surroundings are everything else
- From the equation above we derive the following two equations which are fundamental to studying thermochemistry and energy transformations

$$\Delta E_{\text{Universe}} = \Delta E_{\text{System}} + \Delta E_{\text{Surroundings}} = 0$$

$$\Delta E_{\text{System}} = -\Delta E_{\text{Surroundings}}$$

### Heat and Temperature

- Heat, (q), refers to the transfer of kinetic energy
- It is expressed in the same units as all other energy, Joules (J)
- Heat is always transferred from a warmer object to a cooler one
  - Ex1, A warm house loses heat in the winter to the outside
  - Ex2, A coffee cup loses heat to the room it is in
- Temperature (T) on the other hand, is a measure of the average kinetic energy of the particles that make up the substance or the system
- Temperature is basically a way of measuring how hot or cold something is and it can be expressed in several different units
  - °C, K, °F
- Recall that the conversion between the different temperature units is as follows

### Enthalpy and Enthalpy Change

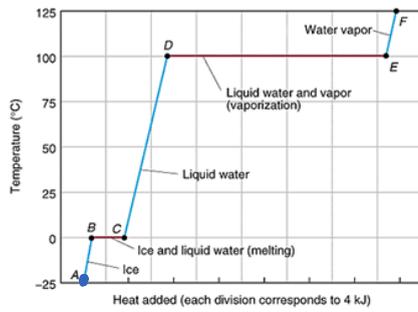
- The total internal energy of a substance is called its enthalpy (H)
  - More specifically it is the energy that is stored in the bonds of chemicals
- We will be looking at and working with the enthalpy change ( $\Delta H$ ) in this course
- Changes in enthalpy can occur during both physical and chemical processes
- We will start with physical processes today but will focus the majority of this unit on enthalpy changes if chemical processes

$$K = ^\circ C + 273.15$$
$$^\circ F = \left( ^\circ C \times \frac{9}{5} \right) + 32$$

### Physical Changes and Heat

- Enthalpy changes are associated with physical changes
- When you boil water, for example, it will heat up to 100°C (assuming standard pressure)
- Energy is still added to the system but the average kinetic energy (T) does not change

- Try this at home: with a thermometer and a pot of water, put a thermometer into some water and allow it to come to a boil.



- $\Delta H_{\text{vap}}$  - enthalpy change from liquid to gas
- $\Delta H_{\text{cond}}$  - enthalpy change from gas to liquid
- $\Delta H_{\text{melt}}$  - enthalpy change from solid to liquid
- $\Delta H_{\text{Freez}}$  - enthalpy change from liquid to solid

$$\Delta H_{\text{vap}} = -\Delta H_{\text{cond}}$$

$$\Delta H_{\text{melt}} = -\Delta H_{\text{Freez}}$$

#### Summary

After the lecture, summarize the main points of this lecture topic.

# Enthalpy Changes in Chemical Reactions

## Formulas & Theorems Covered Today:

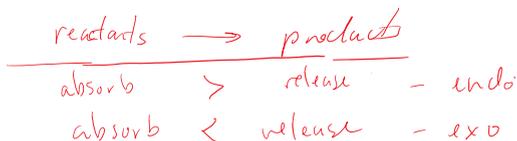
- ★ Energy requirements for reactions
- ★ 4 Ways to Represent thermochemical equations
- ★ Stoichiometry in Thermochemical Reactions
- ★ Nuclear Reactions

## Homework:

## Notes:

### Enthalpy Changes in Chemical Reactions

- In chemical reactions, enthalpy changes result from bonds breaking and bonds reforming
- When a reaction results in a net absorption of energy, we call that type of reaction endothermic
- When there is a net release of energy from bonds breaking and bonds forming, those reactions are called exothermic

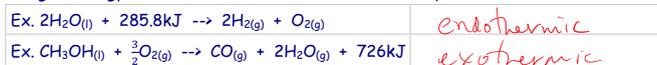


- The enthalpy change of a reaction can be denoted as  $\Delta H_{rxn}$
- This is dependant on conditions such as temperature, and if gases are involved, pressures
- When we calculate  $\Delta H_{rxn}$  it is usually done under standard conditions

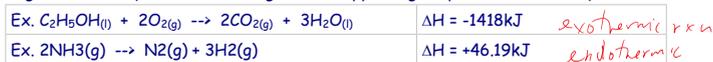
Standard Enthalpy of Reactions =  $\Delta H^\circ_{rxn}$

### Representation of Thermochemical Equations (4 Methods)

- By including an energy value as a term in the thermochemical equation



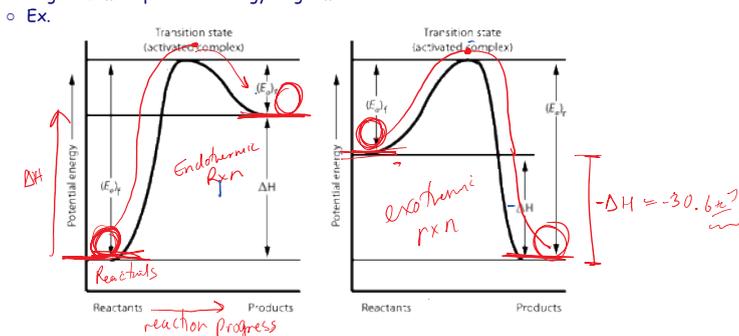
- By writing a chemical equation and stating its enthalpy change separate from the equation



- By stating the molar enthalpy of a specific reaction



- By drawing a chemical potential energy diagram



A formation rxn is one in which only one mole of a substance is produced by its elements in their standard states

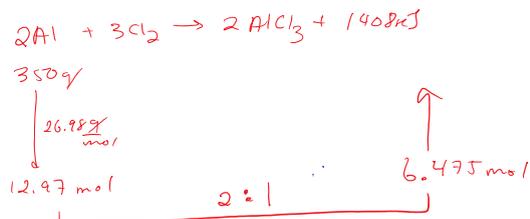
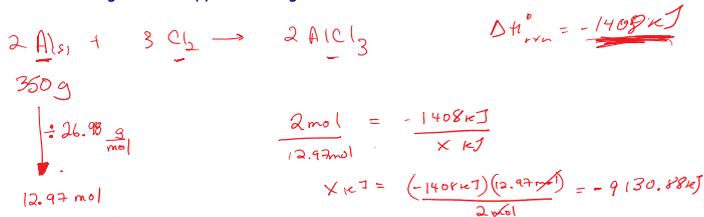
### Stoichiometry and Thermochemical Reactions

- The stoichiometry of thermochemical equations follows the same premise as the stoichiometry from your grade 11 course, the only difference is, is that you will now be calculating for the energy portion of your thermochemical equation rather than some other quantity

- Sample Problem 1 - Aluminum will react with chlorine gas to produce aluminum chloride shown in the balanced chemical equation below.



What is the change in enthalpy when 350g of aluminum react?

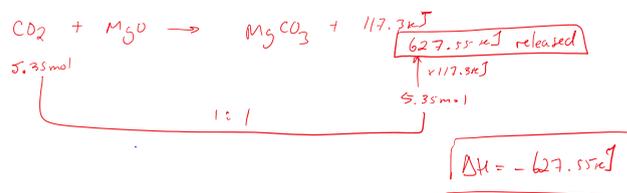


- Sample problem 2 - Consider the reaction:  $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$   $\Delta H = +117.3\text{ kJ}$

- Is heat absorbed or released in the reaction?
- What is the  $\Delta H$  for the reverse reaction?
- What is  $\Delta H$  when 5.35 moles of  $\text{CO}_2$  reacts with excess  $\text{MgO}$ ?



c.) What is  $\Delta H$  when 5.35 moles of  $\text{CO}_2$  reacts with excess  $\text{MgO}$ ?



### Energy and Nuclear Reactions

- These reactions are extremely powerful reactions dealing with the net release of energy
- Take for example the energy that is released from the sun
- It is able to fry an egg on the sidewalk and the sun is some 150,000,000km from earth
- The nuclear reactions that are taking place in the sun, and similarly, those that take place on Earth, result in some transformation of nuclei
  - The nuclei can change in one of two ways
    - They can either join to form larger atoms in reactions called fusion reactions (like what we find in the sun)
    - They can also split to form smaller atoms in reactions called fission reactions (like what we find in our power plants, or in atomic bombs)
- In these reactions, we see mass that is converted into pure energy
- The most famous equation of all time is what is used to determine how much energy can actually be released from these thermonuclear reactions

$$E=MC^2$$

- Einstein's famous equation states that mass and energy are interconvertable
- Without knowing too much about the derivation of the equation, we can see that even if a small amount of mass is present, a huge amount of energy can still be released
- The bomb that was dropped on the city of Hiroshima in 1945 had approximately 600-860mg of plutonium that was converted into energy
- The key here is to remember that even a small amount of mass contains enormous amounts of energy

### Summary

After the lecture, summarize the main points of this lecture topic.

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# Enthalpy of Reaction by Experiment

## Formulas & Theorems Covered Today:

- ★ Enthalpy by Experiment
- ★  $q = mC\Delta T$
- ★  $-q_{\text{lost}} = q_{\text{gained}}$
- ★ Bomb calorimetry
- ★  $\Delta H = \frac{-q}{n}$

## Homework:



## Notes:

### Enthalpy of Reaction by experiment

- To measure the heat that is associated (enthalpy) with a reaction, chemists often times use insulated systems so that the surroundings have negligible effects on the results of the reactions
- These insulated systems are called calorimeters
- They are able to determine the heat change by measuring temperature
- To be able to do this they need to know how much energy a substance is able to absorb
- The amount of energy that is required to raise the temperature of one gram of a substance by one degree is called the specific heat capacity (C) \*
- The values of the specific heat capacity for many substances are tabulated and can be used to solve problems
- The units for the specific heat capacity can be seen below  $C_{\text{water}} = 4.184 \frac{\text{J}}{\text{g}\cdot^{\circ}\text{C}}$

$$C = \frac{J}{\text{g}\cdot^{\circ}\text{C}}$$

- The specific heat capacity, mass of the substance absorbing or releasing heat, and the temperature change can be used to determine the heat that is lost or gained by a chemical or physical processes through the following equation

$$q = mC\Delta T$$

*heat* ←  $q$      ←  $m$  *mass*     ←  $C$  *specific heat capacity*     ←  $\Delta T$  *change in temp*

- Ex1. If a 35g copper block at 25°C absorbs 128J of heat, what will the new temperature of the copper block be? ( $C_{\text{copper}} = 0.385 \frac{\text{J}}{\text{g}\cdot^{\circ}\text{C}}$ )

$$\begin{aligned}
 m &= 35\text{g} \\
 t_i &= 25^{\circ}\text{C} \\
 q &= 128\text{J} \\
 C_{\text{Cu}} &= 0.385 \frac{\text{J}}{\text{g}\cdot^{\circ}\text{C}} \\
 t_f &= ?
 \end{aligned}$$

$$\begin{aligned}
 q &= mC\Delta t \\
 q &= mC(t_f - t_i) \\
 \frac{q}{mC} &= t_f - t_i \\
 \left[ \frac{q}{mC} \right] + t_i &= t_f
 \end{aligned}$$

$$34.5^{\circ}\text{C} = t_f$$

$$\left[ \frac{128\text{J}}{(35\text{g})(0.385 \frac{\text{J}}{\text{g}\cdot^{\circ}\text{C}})} \right] + 25^{\circ}\text{C} = t_f$$

- Sometimes there are instances when two substances at two different temperatures come into contact with one another
- In these instances, one of the objects will lose heat while the other will gain heat
- This will continue to happen until the temperature of both objects becomes the same
- Since the one of the objects will be losing while the other is gaining heat, it can be stated that the heat that is gained by one object is lost by the other using the following equation

$$-q_{\text{lost}} = q_{\text{gained}}$$

- Ex2. A 220g piece of plastic ( $C_{\text{plastic}} = 0.965 \frac{\text{J}}{\text{g}\cdot^{\circ}\text{C}}$ ) at 84°C is placed in 120g of water ( $C_{\text{water}} = 4.184 \frac{\text{J}}{\text{g}\cdot^{\circ}\text{C}}$ ). If the final temperature of the mixture is 31°C, what is the initial

temperature of the water?

$$\begin{array}{ll} \text{lose} & \text{gain} \\ C_p = 0.965 \frac{\text{J}}{\text{g}^\circ\text{C}} & C_v = 4.184 \frac{\text{J}}{\text{g}^\circ\text{C}} \\ m = 220\text{g} & m = 120\text{g} \\ t_i = 24^\circ\text{C} & t_f = ? \\ & t_x = 31^\circ\text{C} \end{array}$$

$$-q_{\text{lost}} = q_{\text{gained}}$$

$$-mC_p\Delta t = mC_v\Delta t$$

$$\left[ \frac{-mC_p\Delta t}{mC_v} \right] - t_f = -t_i$$

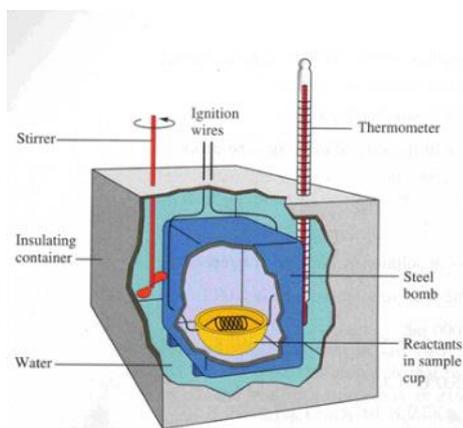
$$\left[ \frac{(220\text{g})(0.965 \frac{\text{J}}{\text{g}^\circ\text{C}})(31^\circ\text{C} - 24^\circ\text{C})}{(120\text{g})(4.184 \frac{\text{J}}{\text{g}^\circ\text{C}})} \right] - 31^\circ\text{C} = -t_i$$

$$-8.59^\circ\text{C} = -t_i$$

$$8.59^\circ\text{C} = t_i$$

### Bomb Calorimeters

- Sometimes there are experiments that are too dangerous to do in a standard coffee cup calorimeter, for instance the heat of combustion of many compounds
- Heat of combustion is the amount of heat that is given off when a certain amount of a substance is burned in the presence of oxygen
- It is measured by placing a known mass of a compound in a steel container called a constant-volume bomb calorimeter (or bomb calorimeter for short)
- The structure is shown below in the diagram as it is a steel container, whose volume does not change but what changes in these experiments is the pressure



- The calorimeter is filled with oxygen before the sample is placed in the cup
- The sample is then ignited electrically, and the heat produced by the reaction can be accurately determined by measuring the temperature increases in the known amount of surrounding water
- Because no heat enters or leaves the system throughout the process, heat lost by the reaction must be equal to the heat gained by the calorimeter and the water and so we can then write that:

$$q_{\text{reaction}} = q_{\text{water}} + q_{\text{calorimeter}}$$

- We also know that a good calorimeter has the amount of heat that it can absorb as predetermined and is given as  $C\Delta T$
- We can then simplify this by saying that:

$$q_{\text{reaction}} = mC_{\text{water}}\Delta T + C_{\text{calorimeter}}\Delta T$$

- Ex3. A sample of 0.850g of carbon in the form of graphite is burned in oxygen in a bomb calorimeter. The temperature of the calorimeter increases from 25.72°C to 27.85°C. The bomb calorimeter contains 2500mL of water and the bomb has a rated heat capacity of 950  $\frac{\text{J}}{^\circ\text{C}}$ . Determine how much heat was released in the reaction?

$$q = ?$$

$$m_v = 2500\text{g}$$

$$q = ?$$

$$M_w = 2500g$$

$$C_w = 4.184 \frac{J}{g^\circ C}$$

$$C_c = 950 \frac{J}{g^\circ C}$$

$$\Delta T = 27.85^\circ C - 25.72^\circ C = 2.13^\circ C$$

$$\begin{aligned} q &= mC_w \Delta T + C_c \Delta T \\ &= (2500g) \left( 4.184 \frac{J}{g^\circ C} \right) (2.13^\circ C) + \left( 950 \frac{J}{g^\circ C} \right) (2.13^\circ C) \\ &= 24303.33 J \quad \text{or} \quad 24.3033 kJ \end{aligned}$$

## Enthalpy of Reaction

- Once we have learned to calculate the heat given off by some physical or chemical process, we can then use that to calculate the enthalpy for that process
- To do this, we simply take the negative of our  $q$  and divide it by the number of moles
- The reason that we do this is because in any given investigation, whether it is a lab or a problem from a problem set, we are given, or know, how much of a substance we started with and thus we are able to determine the enthalpy of that reaction based on the number of moles that reacted
- This particular enthalpy is called the molar enthalpy of reactions because the resulting units will be given in  $\frac{kJ}{mol}$ 
  - Let us use the question from above and determine what is the enthalpy of combustion for graphite is?

$$\Delta H_{comb} = \frac{-q}{n}$$

$$\begin{aligned} n &= \frac{m}{M_w} \\ n &= \frac{0.850g}{12.01 \frac{g}{mol}} \\ n &= 0.071 mol \end{aligned}$$

$$\begin{aligned} \Delta H_{comb} &= \frac{-q}{n} \\ &= \frac{-24303.33 J}{0.071 mol} \\ &= -343000 J/mol \end{aligned}$$

$$\text{OR}$$
$$\boxed{= -343 \frac{kJ}{mol}}$$

$6.02 \times 10^{23}$  particles of graphite

## Summary

After the lecture, summarize the main points of this lecture topic.

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# Bond Energies and Enthalpy of Reactions

## Formulas & Theorems Covered Today:

- ★ Bond Energies
- ★  $\Delta H_{rxn} = \sum \Delta H_{bonds\ broken} - \sum \Delta H_{bonds\ formed}$
- ★
- ★

## Homework:



## Notes :

### Bond Energies

- Bond energies, also known as bond enthalpy, is the energy that is required to break a chemical bond
- These are usually expressed in  $\frac{kJ}{mol}$  measured at SATP (100kPa, 298k)
- The exact bond energy depends on the molecular environment in which the bonds exist, that is why they are standardized at SATP
- The tabulated values in text books are therefore average values based on a variety of temperatures and pressures
- To calculate the enthalpy of a chemical reaction from the bond energies, the following equation can be used

$$\Delta H_{rxn} = \sum \Delta H_{bonds\ broken} - \sum \Delta H_{bonds\ formed}$$

- This equations states that the difference of the sum of all the energy of the bonds broken and the sum of all the energy of the bonds formed will produce the enthalpy of the reaction
- If you recall from last class that in order for bonds to break, energy must be absorbed (put into the reaction) and when bonds form, energy is released
- Therefore, if the sum of the enthalpy of the bonds formed is larger than that of the enthalpy of the bonds broken, then the reaction will be exothermic because there will be a net release of energy giving us a  $-\Delta H$
- The opposite is also true, that when the enthalpy of the bonds broken is larger than that of the enthalpy of the bonds formed, the reaction will be endothermic because there will be a net absorption of energy.

- Ex1. Using the provided bond energies, find the enthalpy of the reaction for the combustion of hydrogen gas.

**Bond Energies**

H-H  $436 \frac{kJ}{mol}$

O=O  $499 \frac{kJ}{mol}$

H-O  $463 \frac{kJ}{mol}$

→

←

$2 H_2 + O_2 \rightarrow 2 H_2O$

$\Delta H_{rxn}^{\circ} = \sum n \Delta H_{bonds}^{\circ} - \sum w \Delta H_{bonds}^{\circ}$

$= \left[ (2 mol)(436 \frac{kJ}{mol}) + (1 mol)(499 \frac{kJ}{mol}) \right] - (4 mol)(463 \frac{kJ}{mol})$

$\Delta H_{rxn}^{\circ} = -481 kJ$

**Summary**

After the lecture, summarize the main points of this lecture topic.

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# Hess's Law of Heat Summation

Formulas & Theorems Covered Today:



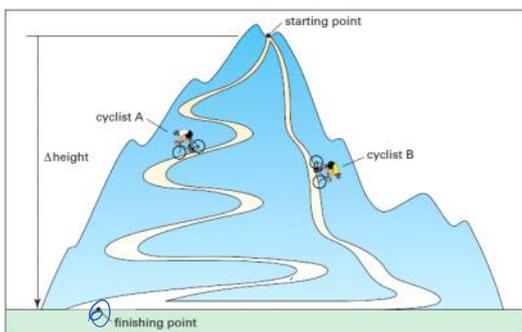
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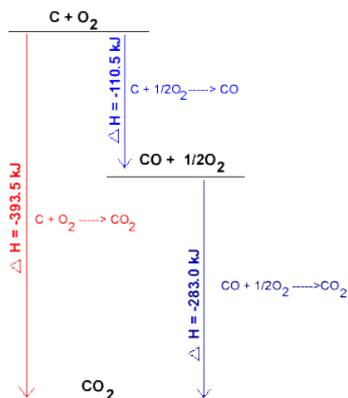
## Notes:

### Hess's Law of Heat Summation

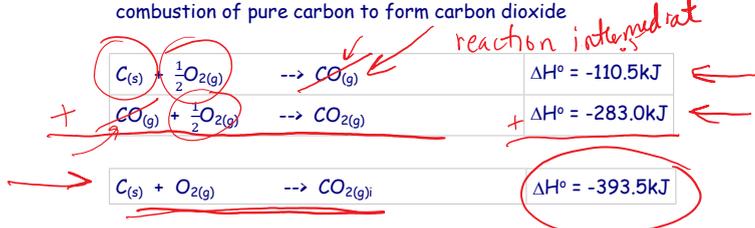
- In the previous section we talked about using experiment to determine the heat transferred in a chemical reaction
- To do this we use a simple calorimeter
- In class and in the majority of instances, we use these only for dilute aqueous solutions
- There are however many, non-aqueous chemical reactions, and there are even those reactions that release so much energy that it would be unsafe to perform them using our calorimeters
- Chemists can use Hess's Law in order to determine the heats of summation
- Hess's Law states that the enthalpy change in a physical or chemical process depends only on the beginning conditions (the reactants) and the end conditions (the products)
- The intermediate steps do not change the heats produced
- You can use the following diagram to help explain pictorially what Hess's law states



- We can think about some chemical reactions as happening in two or more steps and the sum total of all the steps will allow us to determine the overall reaction
- If the beginning and the end conditions (reactants and products) are all that is required to determine the overall enthalpy of the reaction, then summing the individual steps of a chemical reaction should give us the overall enthalpy of the reaction



- Ex1. Use the following equations to determine the overall enthalpy of reaction for the combustion of pure carbon to form carbon dioxide

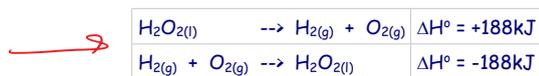


## Combining Chemical Equations Algebraically

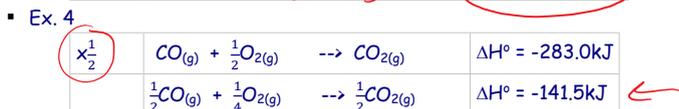
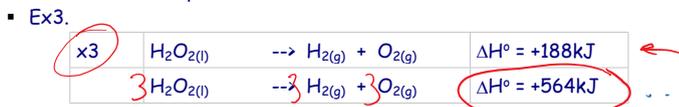
- Sometimes you will be given a set of equations that, when added together, does not yield the

target equation

- In these instances, the intermediate equations will have to be manipulated in order to sum to give us the final target equation
- There are two types of transformations that you can use to manipulate intermediate equations to yield the target equation
  - The first way in which you may want to manipulate an equation is reversing the equation
  - If you wish to reverse the equation, simply multiply the enthalpy by -1
    - Ex2.



- The second way that you may want to manipulate an equation is by multiplying it by a whole number or a fraction in order to give you the desired intermediate equation
- If you wish to multiply an intermediate equation, you must multiply the enthalpy associated with that equation as well

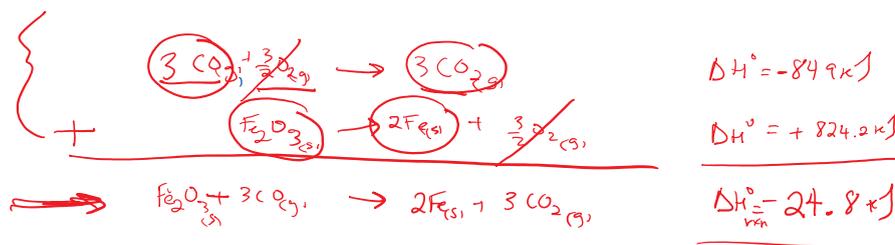
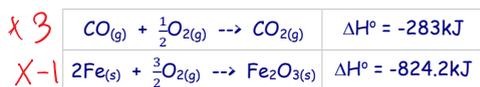


### Sample Problems

- Ex4. One method of obtaining metallic iron is to react Iron (III) Oxide with carbon monoxide, producing carbon dioxide and elemental iron as shown in the following equation



Determine the enthalpy change given the following two intermediate steps



### Summary

After the lecture, summarize the main points of this lecture topic.

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# Enthalpy of Formation

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## Formulas & Theorems Covered Today:

★  $\Delta H^{\circ}_f = \Sigma(n\Delta H^{\circ}_f \text{ products}) - \Sigma(n\Delta H^{\circ}_f \text{ reactants})$



## Homework:

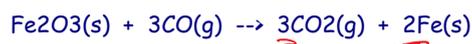


### Notes:

- As we have discussed before, molar enthalpies of formation are the energy that is absorbed or received when one mole of a substance is created from its elements in their standard states
- The standard molar enthalpy's of formations of many compounds are found tabulated and can be found in your text books or can be found in the package that was given to you at the beginning of the semester
- The enthalpy of any element in its standard state is 0 including all diatomic molecules as they already exist in standard states
- To calculate the enthalpy of a reaction, the following equation can be used:

$$\Delta H^{\circ} = \Sigma(n\Delta H^{\circ}_f \text{ products}) - \Sigma(n\Delta H^{\circ}_f \text{ reactants})$$

- Using this equation, you can calculate the enthalpy change of any reaction by adding the heats of formation of the products and subtracting them from the sum of the heats of formation of the reactants
  - Ex1. Determine the enthalpy change of the following reaction given the following information



$$\begin{aligned}\Delta H^{\circ}_f \text{ Fe}_2\text{O}_3(\text{s}) &= -824.2 \frac{\text{kJ}}{\text{mol}} \\ \Delta H^{\circ}_f \text{ CO}(\text{g}) &= -110.5 \frac{\text{kJ}}{\text{mol}} \\ \Delta H^{\circ}_f \text{ CO}_2(\text{g}) &= -393.5 \frac{\text{kJ}}{\text{mol}} \\ \Delta H^{\circ}_f \text{ Fe}(\text{s}) &= 0 \frac{\text{kJ}}{\text{mol}}\end{aligned}$$

$$\begin{aligned}\Delta H^{\circ}_{\text{rxn}} &= \Sigma n\Delta H^{\circ}_f \text{ prod} - \Sigma n\Delta H^{\circ}_f \text{ react} \\ &= \left( (0 \frac{\text{kJ}}{\text{mol}})(2 \text{ mol}) + (-393.5 \frac{\text{kJ}}{\text{mol}})(3 \text{ mol}) \right) - \left( (-824.2 \frac{\text{kJ}}{\text{mol}})(1 \text{ mol}) + (-110.5 \frac{\text{kJ}}{\text{mol}})(3 \text{ mol}) \right) \\ &= -24.8 \text{ kJ}\end{aligned}$$

# Expressing and Measuring Reaction Rates

Formulas & Theorems Covered Today:



Homework:



Notes:

## Expressing and Measuring Reaction Rates

- The change in the amount of reactant or product over time is known as the reaction rate
- Consider how we express rates elsewhere, such as an Olympic 100m runner runs the 100m race in approximately 10s
- This would mean that he/she would run on average about  $10 \frac{m}{s}$
- Rates can also be expressed in chemical reactions that show changes in chemical quantities over time

$$\frac{\text{mol}}{\text{L} \cdot \text{s}}$$

- Chemists express reaction rates in several ways
- They rate can be the amount of a reactant that is consumed, or the amount of production of a product over a given amount or time

○ Ex1. Rate =  $\frac{\Delta \text{mol}}{\Delta t} = \frac{\text{mol}}{\text{s}}$

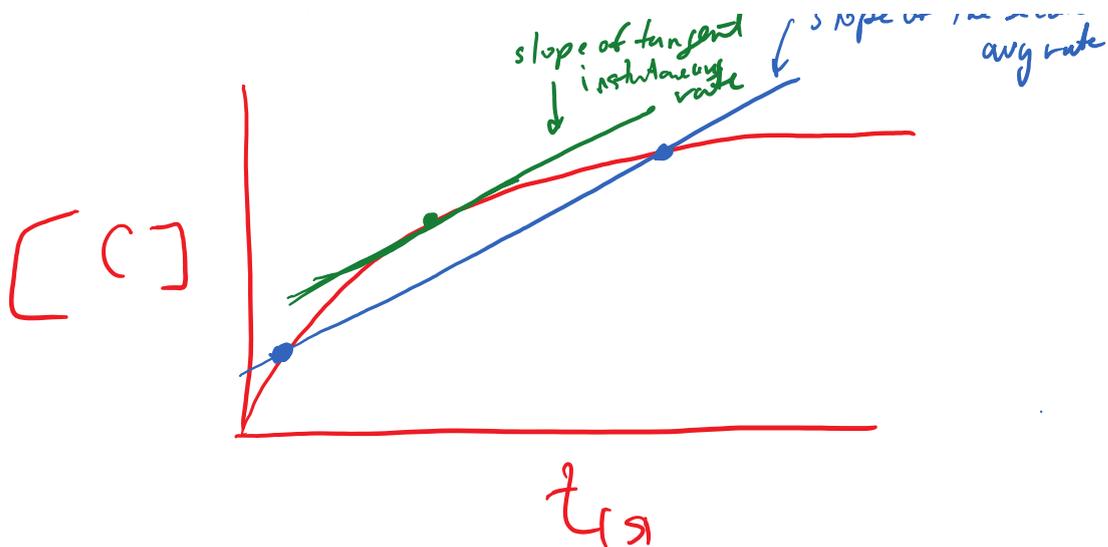
- In the gaseous or in aqueous states it is often times easier to express these rates using molarity instead of just using the mole

○ Ex2. Rate =  $\frac{\Delta [A]}{\Delta t} = \frac{\text{mol}}{\text{L} \cdot \text{s}}$

- Reaction rates will always yield a positive value
- If we are referring to the rate at which some product is being produced, then we are dealing with an increase in the amount of that substance
- On the other hand if we are referring to the rate at which some reactant is being consumed, it is still going to be a positive value, it just means that it is decreasing by that much

## Average and Instantaneous Rates of Reactions

slope of tangent  
instantaneous rate  
slope of the secant  
avg rate



Dinitrogen pentoxide,  $N_2O_5$ , decomposes to form  $NO_2 + O_2$



The rate at which  $NO_2$  is produced is  $5 \times 10^{-6} \frac{\text{mol}}{\text{L}\cdot\text{s}}$ , what is the rate of consumption of  $N_2O_5$ ? What is the rate of production of  $O_2$ ?

$$\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2} \frac{\Delta[NO_2]}{\Delta t}$$

$$\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4} \frac{\Delta[NO_2]}{\Delta t}$$

$$\begin{aligned} \frac{\Delta[N_2O_5]}{\Delta t} &= \frac{1}{2} \frac{\Delta[NO_2]}{\Delta t} = \frac{1}{2} \left( 5 \times 10^{-6} \frac{\text{mol}}{\text{L}\cdot\text{s}} \right) \\ &= 2.5 \times 10^{-6} \frac{\text{mol}}{\text{L}\cdot\text{s}} \end{aligned}$$

$$\begin{aligned} \frac{\Delta[O_2]}{\Delta t} &= \frac{1}{4} \frac{\Delta[NO_2]}{\Delta t} = \frac{1}{4} \left( 5 \times 10^{-6} \frac{\text{mol}}{\text{L}\cdot\text{s}} \right) \\ &= 1.25 \times 10^{-6} \frac{\text{mol}}{\text{L}\cdot\text{s}} \end{aligned}$$



# Theories of Reaction Rates

## Formulas & Theorems Covered Today:

- ★ Theories of Reaction Rates
- ★ Factors affecting rates of reactions
- ★ Collision Theory
- ★ Beyond Collision Theory

## Homework:



Notes:

### Theories of Reaction Rates

- In the previous section we discussed the relationship between the concentration of reactants and the reaction rate
- Why is it that the reaction rate increases with concentration?
- Why is it that the reaction rate increases with surface area? Or temperature?
- One way of looking at these questions and the answers to these questions is by beginning to understand Collision Theory
- Before we answer these questions we must answer "what causes a reaction to occur?"
- The obvious answer to this is that a reaction occurs because of some type of collision between reacting particles
- The whole idea of a collision between particles is the basis for Collision Theory
- **In order for a reaction to occur, reacting particles must collide with one another**

### The effect of Concentration on Reaction Rate

- If a collision is necessary for a reaction to happen, then the more particles that are present, the greater the tendency of a reaction to proceed forward
- Think about cars on a road, let's say we compare the city of Toronto and the town of Hearst
- Toronto is a city of 5 million people or so while Hearst is a town with a population of 5000
- With a greater population, you would expect that there are more cars on the road
- The more cars on the road, the greater the chance of a collision occurring
- This can be directly related to concentration and its effect on the rate of a reaction, the more concentrated a solution, or a gas, the more likely it is to collide with other reacting particles and thus a faster reaction rate

### Surface Area and Collision Theory

- With a greater surface area, there is a greater opportunity for collision to occur and therefore the rate of a reaction will increase
- When you are trying to relate surface area to the rate of a reaction, you can think about a tiny packet of sugar dissolving in water, versus a cube of sugar dissolving in water
- We know from experience that a packet of sugar (containing the same amount of sugar as a cube of sugar) will dissolve faster because of the overall surface area of all the particles
- The same concept can be used with respect to us chewing food

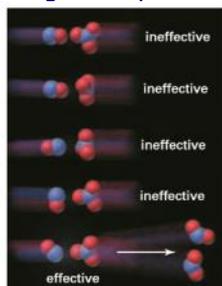
### Beyond Collision Theory

- A collision is necessary for a reaction to happen however we must also ask ourselves do all collisions cause a reaction to go to completion? (That is do all colliding particles produce products?)
- The simple answer is no, not every collision of reacting particles will yield products and so we can say that not all collisions will be successful
- In order to facilitate this, we can think about those collisions between cars that we had previously discussed
- Think about a car accident, and for simplicity, let us consider that a "successful" collision is one in which the front bumper of a car is torn off
- Do all accidents produce that result?
- What are the necessary conditions in order for that result to happen?
- The simple answer to that is that no, not all car accidents will yield a torn off front bumper

- From this we can deduce the following
  - For a collision to be effective (to produce products)**
    - You need the correct orientation of reacting particles
    - You need sufficient collision energy

### Orientation

- Reacting particles must collide with the proper collision orientation, which is called collision geometry

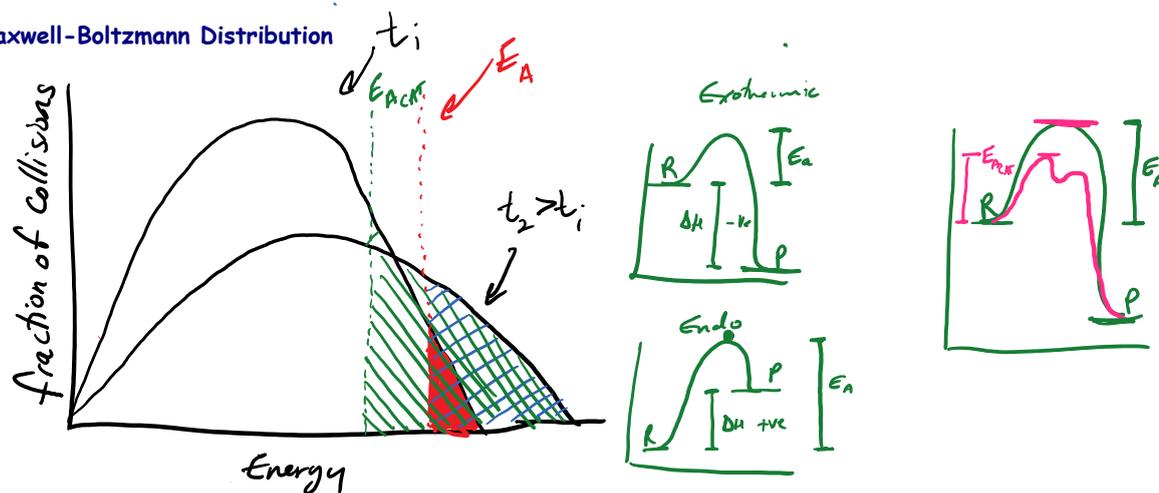


**Figure 6.9** Only one of these five possible orientations of NO and NO<sub>2</sub> will lead to the formation of a product.

### Activation Energy

- The second factor that contributes to a reaction is the collision energy
- The reactants must collide not only with the correct geometry, but must also collide with enough energy to break the bonds and then ultimately reform them
- Most chemical reactions only have a very small number of collisions that have sufficient energy and the correct geometry to have a successful reaction occur
- That amount of energy that is the "minimum amount" of collision energy that is required to make a reaction successful is called the activation energy,  $E_a$
- The collision energy is dependent on the kinetic energy of the reacting particles (which is where temperature comes into play)

### Maxwell-Boltzmann Distribution



# Transition State Theory

Formulas & Theorems Covered Today:



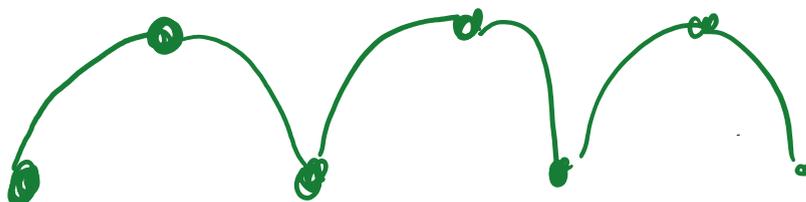
Homework:

🏠 Question #13-16, pg 294

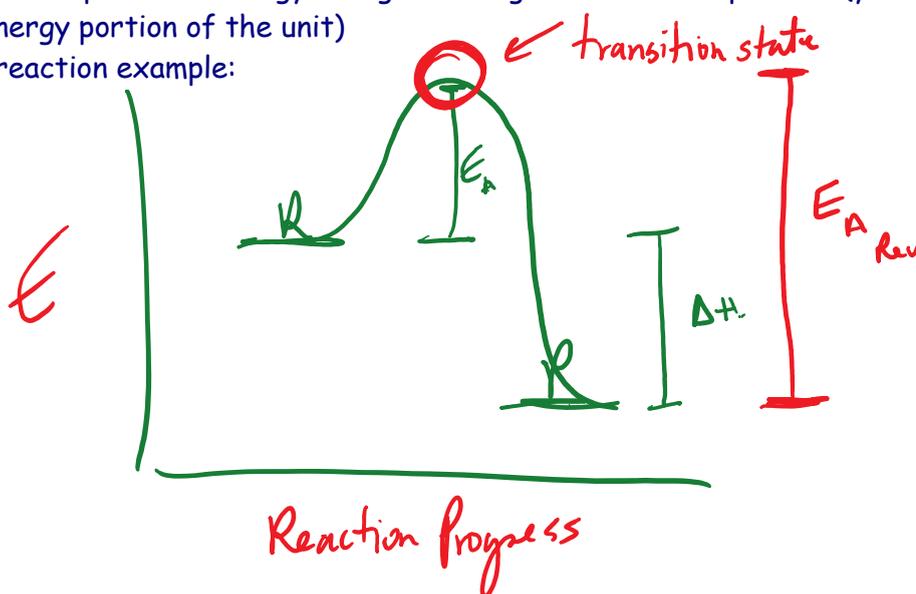
Notes:

## Transition State Theory

- This theory is used to tell us what happens to molecules when they collide in a reaction.
- Kinetic energy is transferred into potential energy: Law of conservation of energy
- Think of a bouncing basketball:

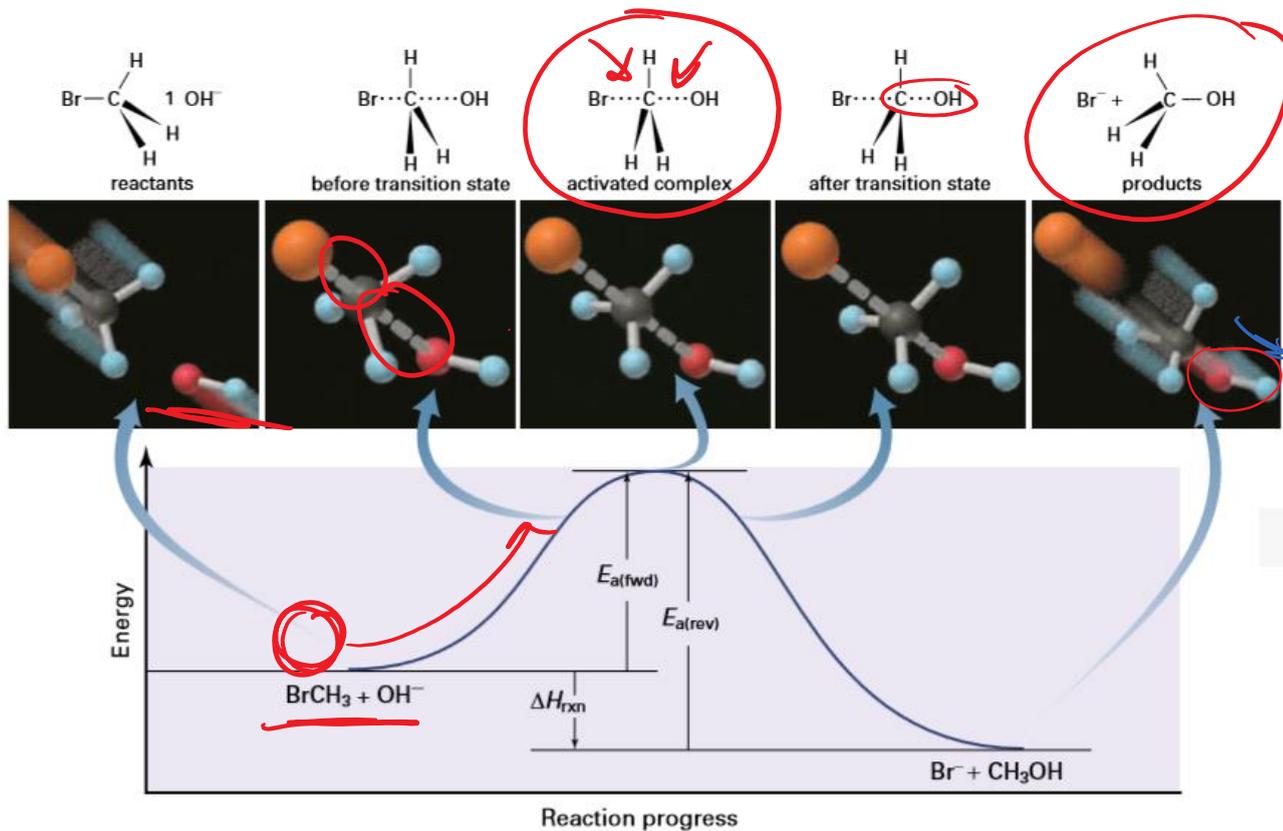


- The kinetic energy of the ball is transformed into potential energy, then back to kinetic as the ball bounces
- A potential energy diagram can be used to show changes in potential energy during a chemical reaction.
- It graphs how the potential energy changes through the reaction process (you have seen this during the energy portion of the unit)
- Exothermic reaction example:



- $\Delta H$  = Enthalpy change
- $E_{a(fwd)}$  = Activation energy of the forward reaction
- $E_{a(rev)}$  = Activation energy of the reverse reaction

- Here, the reactants have a higher potential energy than the products: The products release energy as heat, and have less potential energy and more kinetic energy than the reactants.
- Activation energy: The minimum energy required for a successful reaction between colliding molecules
- Transition state: Top of the activation energy barrier (the "hill")
- The activated complex is the chemical species that exists at the transition state
- This species is neither reactant nor product and is very unstable due to its partial bonds



# Rate Law

Formulas & Theorems Covered Today:

- ★ Reactant Concentrations and Rates
- ★ Reaction Orders
- ★

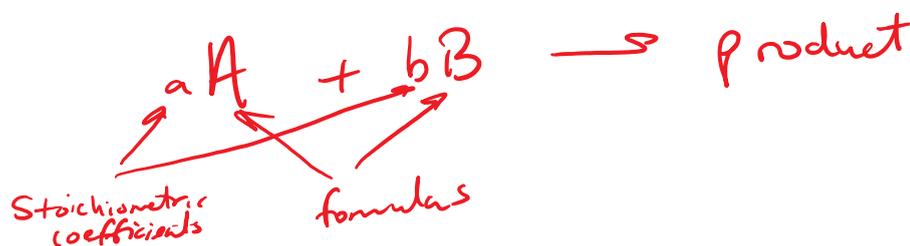
Homework:



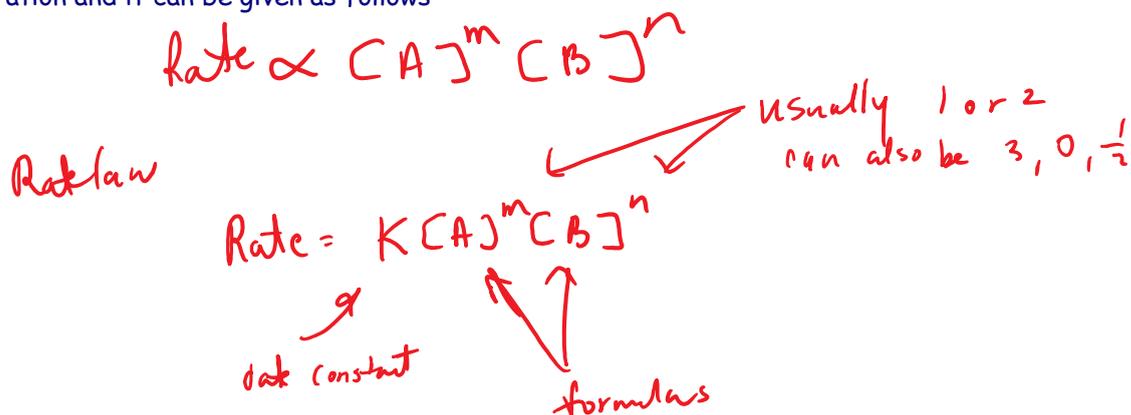
Notes:

Rate Law: Reactant Concentration and Rates

- The rate of a reactions depends on several factors as we have learned
- One factor that we are very interested in is the concentration and we have learned that as the concentration increases, so too does the rate
- Consider the following general formula



If we use this equation, we can create an expression for the dependence of rate on concentration and it can be given as follows



- "m" and "n", the exponents from above, are what are used in order to determine the order of the reaction
- These are usually a 1 or 2 but values of 0, 3 and even fractions can occur
- These exponents are determined by experiment as we will learn next class
- If the sum of the exponents is a 1, then we consider that to be a first order reaction
- If the sum of the exponents is a 2, then we consider that to be a second order reaction, and so on
- The value of the exponent tells us how the concentration effects the initial rate of the reaction

- For a zero order exponent - there is no effect on the initial rate
- For a first order exponent - as the concentration doubles, so too does the rate
- For a second order exponent - as the concentration doubles, the rate quadruples
- For a third order exponent - as the concentration doubles, the rate increases eightfold

- For a first order exponent - as the concentration doubles, so too does the rate
- For a second order exponent - as the concentration doubles, the rate quadruples
- For a third order exponent - as the concentration doubles, the rate increases eightfold

### The Rate Constant "K"

- The magnitude of the reaction constant indicates the speed of the reaction
- A small "k" value indicates a slow reaction and a large "k" value indicates a fast reaction
- The units of "k" change depending on the overall order of the reaction
- Below is a sample of how to calculate the rate law constant's units
- Ex1.  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

$$\text{Rate} = k[\text{N}_2\text{O}_5]^1$$

↑

$$\frac{\text{mol}}{\text{L}\cdot\text{s}} = k \left( \frac{\text{mol}}{\text{L}} \right)^1$$

$$\left( \frac{\text{mol}}{\text{L}\cdot\text{s}} \right) \left( \frac{\text{L}}{\text{mol}} \right) = k = \frac{1}{\text{s}} \text{ or } \text{s}^{-1}$$

↓  
1st  
order  
rxn

- Ex2.  $2\text{HI} \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$

$$\text{Rate} = k[\text{HI}]^2$$

$$\frac{\text{mol}}{\text{L}\cdot\text{s}} = k \left( \frac{\text{mol}}{\text{L}} \right)^2$$

$$\frac{\text{mol}}{\text{L}\cdot\text{s}} = k \frac{\text{mol}^2}{\text{L}^2}$$

$$\left( \frac{\text{mol}}{\text{L}\cdot\text{s}} \right) \left( \frac{\text{L}^2}{\text{mol}^2} \right) = k = \frac{\text{L}}{\text{mol}\cdot\text{s}}$$

2nd  
order  
rxn

- Ex3.  $2\text{ClO}_2(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{ClO}_3^-(\text{aq}) + \text{ClO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$

$$\text{Rate} = k[\text{ClO}_2]^2[\text{OH}^-]^1$$

$$\frac{\text{mol}}{\text{L}\cdot\text{s}} = k \left( \frac{\text{mol}}{\text{L}} \right)^2 \left( \frac{\text{mol}}{\text{L}} \right)^1$$

$$\frac{\text{L}^2}{\text{mol}^2\cdot\text{s}}$$

$$\frac{\text{mol}}{\text{L}\cdot\text{s}} = k \left( \frac{\text{mol}^2}{\text{L}^2} \right) \left( \frac{\text{mol}}{\text{L}} \right)$$

$$\frac{\text{mol}}{\text{L}\cdot\text{s}} = k \left( \frac{\text{mol}^3}{\text{L}^3} \right)$$

$$\left( \frac{\text{mol}}{\text{L}\cdot\text{s}} \right) \left( \frac{\text{L}^3}{\text{mol}^3} \right) = k = \frac{\text{L}^2}{\text{mol}\cdot\text{s}}$$

3rd  
order

## Initial Rates Method and Half-Life

Formulas & Theorems Covered Today:

★ Rate Law and Initial Rates Method

★  
★

Homework:



Notes:

### Initial Rates Method

- "m" and "n" must be determined experimentally
- To do this, we must run the experiment many times, slightly changing concentrations of each of the reactants to determine the overall rate law
- All other factors and conditions, including temperature, pressure, etc., remain constant
- We then measure the initial rate of the reaction and the ratio of concentration change to reaction rate is compared to give us the rate law exponents
- Ex1. Recall that we used the following rate law



$$\text{Rate} = k [\text{N}_2\text{O}_5]^1$$

Experiment	[Initial] $\text{N}_2\text{O}_5$ ( $\frac{\text{mol}}{\text{L}}$ )	Initial Rate ( $\frac{\text{mol}}{\text{L}\cdot\text{s}}$ )
1	0.01	$4.8 \times 10^{-6}$
2	0.02	$9.6 \times 10^{-6}$
3	0.03	$1.5 \times 10^{-5}$

$$\text{Rate} = k [\text{N}_2\text{O}_5]^m$$

$$\text{Rate} = k (0.01 \frac{\text{mol}}{\text{L}})^m = 4.8 \times 10^{-6} \frac{\text{mol}}{\text{L}\cdot\text{s}}$$

$$\text{Rate} = k (0.02 \frac{\text{mol}}{\text{L}})^m = 9.6 \times 10^{-6} \frac{\text{mol}}{\text{L}\cdot\text{s}}$$

$$\frac{4.8 \times 10^{-6} \frac{\text{mol}}{\text{L}\cdot\text{s}}}{9.6 \times 10^{-6} \frac{\text{mol}}{\text{L}\cdot\text{s}}} = \frac{k (0.01 \frac{\text{mol}}{\text{L}})^m}{k (0.02 \frac{\text{mol}}{\text{L}})^m}$$

$$\frac{1}{2} = \left( \frac{0.01 \frac{\text{mol}}{\text{L}}}{0.02 \frac{\text{mol}}{\text{L}}} \right)^m = \left( \frac{1}{2} \right)^m \quad m=1$$

Determine The Rate Constant

$$\text{Rate} = k [\text{N}_2\text{O}_5]^1$$

$$4.8 \times 10^{-6} \frac{\text{mol}}{\text{L}\cdot\text{s}} = k (0.01 \frac{\text{mol}}{\text{L}})^1$$

$$\frac{4.8 \times 10^{-6} \frac{\text{mol}}{\text{L}\cdot\text{s}}}{0.01 \frac{\text{mol}}{\text{L}}} = k = \boxed{4.8 \times 10^{-4} \text{ s}^{-1}}$$

$$4.8 \times 10^{-4} \frac{1}{\text{s}}$$

- Ex2. Sample Problem

Chlorine Dioxide reacts with hydroxide ions to produce chlorate and chlorite ions and liquid water in the following reaction



The following data was collected from experiment. Use the data to determine the rate law for the reaction

Experiment	[Initial] $\text{ClO}_{2(\text{aq})}$ ( $\frac{\text{mol}}{\text{L}}$ )	[Initial] $\text{OH}^{-}(\text{aq})$ ( $\frac{\text{mol}}{\text{L}}$ )	Initial Rate ( $\frac{\text{mol}}{\text{L}\cdot\text{s}}$ )
1	0.015	0.025	$1.3 \times 10^{-3}$
2	0.015	0.050	$2.6 \times 10^{-3}$
3	0.045	0.025	$1.16 \times 10^{-2}$

$$\text{Rate} = k [\text{ClO}_2]^m [\text{OH}^-]^n$$

$$1.3 \times 10^{-3} \frac{\text{mol}}{\text{L}\cdot\text{s}} = k (0.015 \frac{\text{mol}}{\text{L}})^m (0.025 \frac{\text{mol}}{\text{L}})^n$$

$$2.6 \times 10^{-3} \frac{\text{mol}}{\text{L}\cdot\text{s}} = k (0.015 \frac{\text{mol}}{\text{L}})^m (0.050 \frac{\text{mol}}{\text{L}})^n$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^n \quad n = 1$$

$$1.3 \times 10^{-3} \frac{\text{mol}}{\text{L}\cdot\text{s}} = k (0.015 \frac{\text{mol}}{\text{L}})^m (0.025 \frac{\text{mol}}{\text{L}})^n$$

$$1.16 \times 10^{-2} \frac{\text{mol}}{\text{L}\cdot\text{s}} = k (0.045 \frac{\text{mol}}{\text{L}})^m (0.025 \frac{\text{mol}}{\text{L}})^n$$

$$\frac{1}{9} = \left(\frac{1}{3}\right)^m \quad m = 2$$

$$\text{Rate} = k [\text{ClO}_2]^2 [\text{OH}^-]$$

$$1.3 \times 10^{-3} \frac{\text{mol}}{\text{L}\cdot\text{s}} = k (0.015 \frac{\text{mol}}{\text{L}})^2 (0.025 \frac{\text{mol}}{\text{L}})$$

$$k = \frac{1.3 \times 10^{-3} \frac{\text{mol}}{\text{L}\cdot\text{s}}}{(0.015 \frac{\text{mol}}{\text{L}})^2 (0.025 \frac{\text{mol}}{\text{L}})} = k = 231 \frac{\text{L}^2}{\text{mol}^2 \cdot \text{s}}$$

$$\text{Rate} = \left(231 \frac{\text{L}^2}{\text{mol}^2 \cdot \text{s}}\right) [\text{ClO}_2]^2 [\text{OH}^-]$$

### Half Life

- Half-life is the time that is needed to cause half of the reactants mass or concentration to react
- This is of particular importance to drug companies as they often times have to measure how long a drug stays in the body
- There is an entire branch of chemistry, in particular, pharmacology, called pharmacokinetics which deals with the kinematics of pharmaceuticals and included in that is half-life calculations
- When we measure half-life, we always refer to it in seconds
- The half-life of any first order reaction is always constant
- Second and  $n^{\text{th}}$  order reactions have changing half-lives and require different equations

$$\text{Rate} = k [A]^1$$

- This particular expression has a half-life that is independent of the initial concentration (in other words the half-life is constant).
- The time that it takes for half of a material to disappear is given by the following equation

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

Ex3. The half-life of a given first order reaction is said to be 10min, determine the rate constant for this reaction with the correct units

$$10 \text{ min} = 600 \text{ s} = \frac{\ln 2}{k}$$

$$k = \frac{0.693}{600 \text{ s}} = 0.001155 \text{ s}^{-1}$$

$$10 \text{ min} = 600 \text{ s} = \frac{1}{k}$$

$$k = \frac{\ln 2}{600 \text{ s}}$$

$$k = 1.155 \times 10^{-3} \text{ s}^{-1}$$

$$\begin{aligned} & 1 \text{ yr} \\ & 86400 \text{ s/day} \\ & 31557600 \text{ s} \\ & \text{yr} \end{aligned}$$

# Reaction Mechanisms and Catalysts

Formulas & Theorems Covered Today:

- ★ Molecularity
- ★ Reaction Mechanisms
- ★ Catalysts

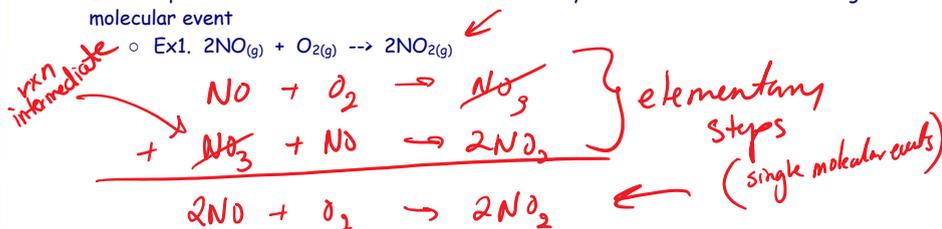
Homework:



Notes:

## Reaction Mechanisms and Catalysts

- The rate mechanism is a series of steps that makes up an overall reaction
- Each step in a rate mechanism is called an elementary reaction and it involves a single molecular event



- When elementary reactions are added together, as shown above, you get the overall reaction
- Any molecules or ions that are formed by the elementary reactions are called reaction intermediates and are consumed by the subsequent elementary reactions

## Molecularity

- The term molecularity refers to the number of reactant particles taking part in a chemical reactions
- More specifically, it is the number of molecules or ions that participate in something that we call the rate determining step

1 - Unimolecular	$\text{Cl}_{2(g)} \rightarrow 2\text{Cl}_{(g)}$
2 - Bimolecular	$\text{CO}_{(g)} + \text{NO}_{3(g)} \rightarrow \text{CO}_{2(g)} + \text{NO}_{2(g)}$ $2\text{NOCl} \rightarrow 2\text{NO}_{(g)} + \text{Cl}_{2(g)}$
3 - Termolecular	$2\text{NO}_{(g)} + \text{O}_{2(g)} \rightarrow 2\text{NO}_{2(g)}$

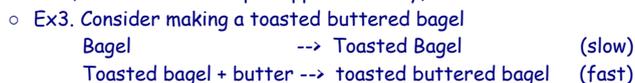
## Rate Law Equations for Elementary Reactions

- We have recently learned that the rate law equations must be determined experimentally
- Elementary reactions are the exceptions to that rule
- In elementary reactions, the rate law exponents, which would normally be determined by experiment, are the same as the stoichiometric coefficients associated with the reaction

$\text{A} \rightarrow \text{Products}$	Rate = $k[\text{A}]$
$\text{A} + \text{B} \rightarrow \text{Products}$	Rate = $k[\text{A}][\text{B}]$
$2\text{A} \rightarrow \text{Products}$	Rate = $k[\text{A}]^2$
$2\text{A} + \text{B} \rightarrow \text{Products}$	Rate = $k[\text{A}]^2[\text{B}]$

## Rate Determining Step

- Elementary reactions that sum to give us an overall reactions more often than not have different rates
- The fact that they have different rates also means that their must also be one of the elementary reactions that is slower than all the others
- The reactions that is slower than all the others is called the rate determining step
- This step, of all the elementary reactions, determines the overall rate of reaction
- We assume, that all other steps happen instantly, while this one takes the longest time



- In this example above, the slow step is toasting the bagel
- The fast step is the buttering of that bagel

## Sample Problem

Consider the following reaction

### Sample Problem

Consider the following reaction



The rate law that was determined by experiment was found to be as follows

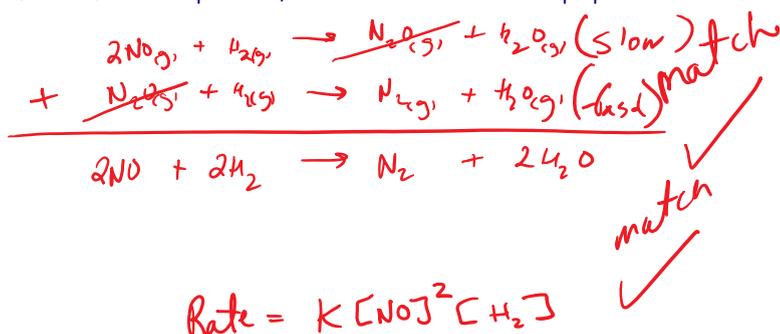
$$\text{Rate} = k[\text{NO}_{(g)}]^2[\text{H}_2]$$

A chemist proposes the following mechanism below

Step 1:	$2\text{NO}_{(g)} + \text{H}_{2(g)} \rightarrow \text{N}_2\text{O}_{(g)} + \text{H}_2\text{O}_{(g)}$	(slow)
Step 2:	$\text{N}_2\text{O}_{(g)} + \text{H}_{2(g)} \rightarrow \text{N}_{2(g)} + \text{H}_2\text{O}_{(g)}$	(fast)

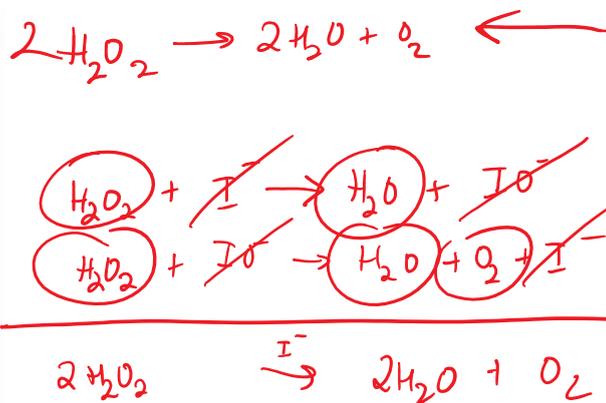
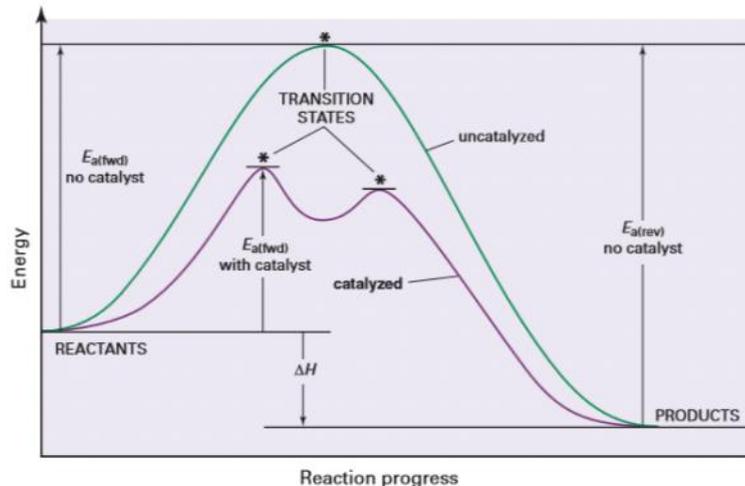
Determine if this is a reasonable rate mechanism

- To solve problems like these, we must first add the elementary reactions from the reaction mechanisms together to see if they will sum to give us the overall reaction
- Second we must determine whether the rate law determined by experiment matches the rate law from the slow step in the reaction mechanism
- If both of these steps match, then the reaction mechanism proposed is reasonable



### Catalysts

- These are substances that increase the rate of a chemical reaction without being consumed by the chemical reaction
- These are extremely important to modern industries and are found even in natural systems
- Catalysts work by reducing the activation energy for a chemical reaction and does this by producing an alternate mechanism for the reaction to happen

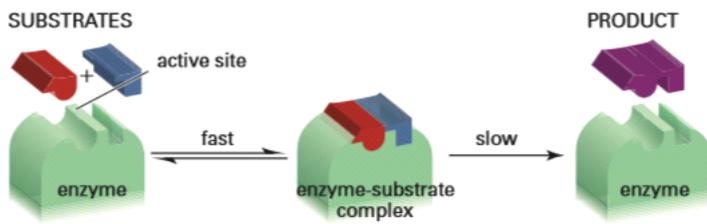


- Catalysts can exist as either heterogeneous catalysts or homogeneous
- A heterogeneous catalyst is in a different phase than the reactants where as a homogeneous catalyst is in the same phase as the reactants

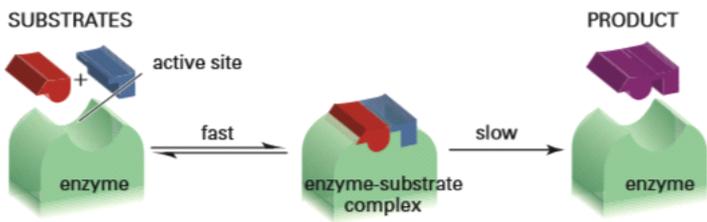
### Biological Catalysts

- Our bodies are quite dependent on catalyzed reactions
- Enzymes are large molecules in our bodies, produced by our cells, that help us get reactions moving in the forward direction
- These enormous proteins, which can have masses in the thousands to hundreds of thousands of grams per mole, have only a small portion of the molecule that is dedicated to catalyzing reactions

- The small area in which reactions happen is called an active site and that site works one or more molecules called substrates
- There are two models for how these enzymatic systems work
  - Lock and Key model
  - Induced fit model



**A** Lock-and-key model



**B** Induced-fit model