Chemical Kinetics (or Reaction Rates)

I. Collison Theory of Reactions
   i. **Demo**: Lycopodium power and Iron filings
   ii. Computer Lab: Factors Affecting Reaction Rates
   iii. Reaction Rates
      I. Reactions occur when two or more atoms and or molecules collide with sufficient energy and in the correct orientation.
      II. Factors which affect reaction rates
         i. Surface area of solid reactants. Why?

         ii. Concentration of reactants. Why?

         iii. Temperature of reactants. Why?

         iv. Catalysts
            a. A catalyst is a substance which speeds up the rate of reaction without being used up in the reaction. You will have the same amount of catalyst at the beginning and end of a reaction, but the reaction will occur much more quickly.
            b. Catalyst examples:
               1. Most of the enzymes in your body are catalysts. Many of the chemical reactions that are necessary for life to occur run too slowly without being catalyzed by an enzyme. Without catalysts we could not exist.

2. The catalytic converter that is part of all modern car exhaust systems. This turn many of the pollutants (primarily hydrocarbon (C-H) fragments and carbon monoxide (CO) in the exhaust into carbon dioxide (CO_2) and water (H_2O).
3. When you generated oxygen from hydrogen peroxide earlier this year you used a Manganese metal catalyst.

   $2\ H_2O_2 \text{ ---> } 2\ H_2O + O_2$

   Notice that the Mn (Manganese) is not written as part of this reaction. That is because it is not consumed during the reaction. It can be reused over and over again.

4. Chlorine atoms from CFCs (chlorofluorocarbons) catalyze the breakdown of ozone into oxygen: $O + O_3 \text{ ---> } 2\ O_2$

c. See some catalyzed reactions:
1. Film: Forensic Catalysis
2. Film: Formic Acid Decomposition

iv. Lab: Iodine Clock Reaction

v. Homework: Using descriptions of what must be happening on a molecular level, explain why concentrated acids are much more dangerous than ones that have been diluted by water.

II. Chemical Potential Energy

i. **Demo**: Various Types of Potential Energy

ii. Types of Potential Energy

I. Potential energy is a type of energy that is "hidden" in some way. It is a type of energy that can be converted to other forms and often is related to some attractive or pushing forces.

i. Elastic Potential Energy

a. Anything that can act like a spring or a rubber band can have elastic potential energy.
b. Let's take the rubber band for example. To stretch the rubber band you have to use energy. That energy has now been turned into elastic potential energy. To get that energy back, just let go of the rubber band and its potential energy is converted

primarily into kinetic energy.

c. Springs work the same way, but you can either stretch or compress them. Wind-up watches store potential energy in an internal spring when you wind them and slowly use this energy to power the watch.

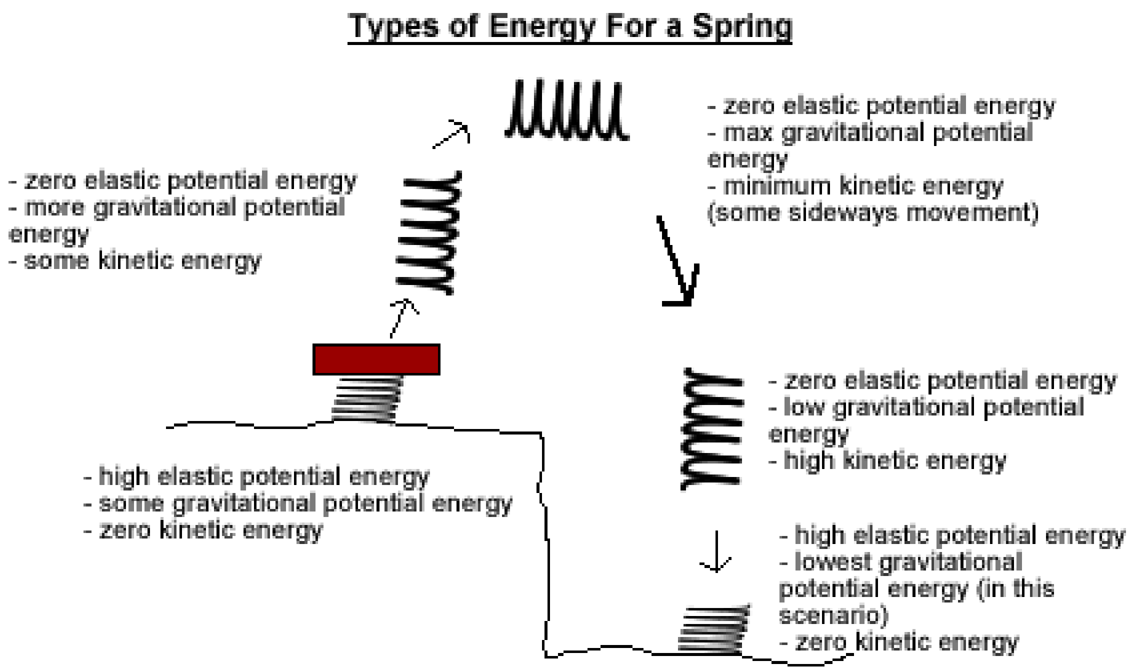
ii. Gravitational Potential Energy

a. There is a constant attractive force between the Earth and everything surrounding it, due to gravity.

b. To lift something off the ground it takes energy, so just by lifting an object, that object now has higher gravitational potential energy.

c. Gravitational potential energy is typically converted into kinetic energy (an object falling) before it is converted into any other type of energy.

d. Hydroelectric power is generated this way. As the water falls, it turns a turbine, which pushes electrons around, creating an electric current.



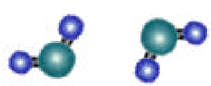
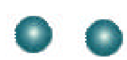
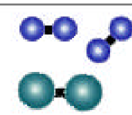
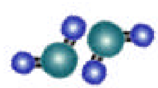
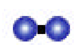
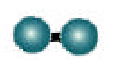
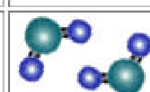
iii.Chemical Potential Energy

a. A chemical bond can be thought of as an attractive force between atoms.
b. Because of this, atoms and molecules can have chemical potential energy.
c. Anytime two atoms form a strong covalent or ionic bond or two molecules form a weak van der Waals bond, energy is released, usually in the form of heat and light.
d. The amount of energy in a bond is somewhat counterintuitive - the **stronger** or more stable the bond, the **less** potential energy there is between the bonded atoms.

Strong bonds have **low potential energy** and **weak bonds** have **high potential energy**.

e. Lot's of heat and/or light energy is released when very strong bonds form, because much of the potential energy is converted to heat and/or light energy. The reverse is true for breaking chemical bonds. It takes more energy to break a strong bond than a weak bond. The breaking of a bond requires the absorption of heat and/or light energy.

Comparison of High and Low Chemical Potential Energy for Various Bonds

	weak van der waals bond formation	strong covalent bond formation	strong covalent bond formation	breaking of weaker covalent bonds to form stronger covalent bonds
higher chemical potential energy				
lower chemical potential energy				 The O-H bond is even stronger than the H-H or O-O.
	The difference between the high and low is small because of the weak bond formation.	The amount of chemical potential energy released above is much greater than what is released during the formation of weak van der Waals bonds during condensing or freezing.		

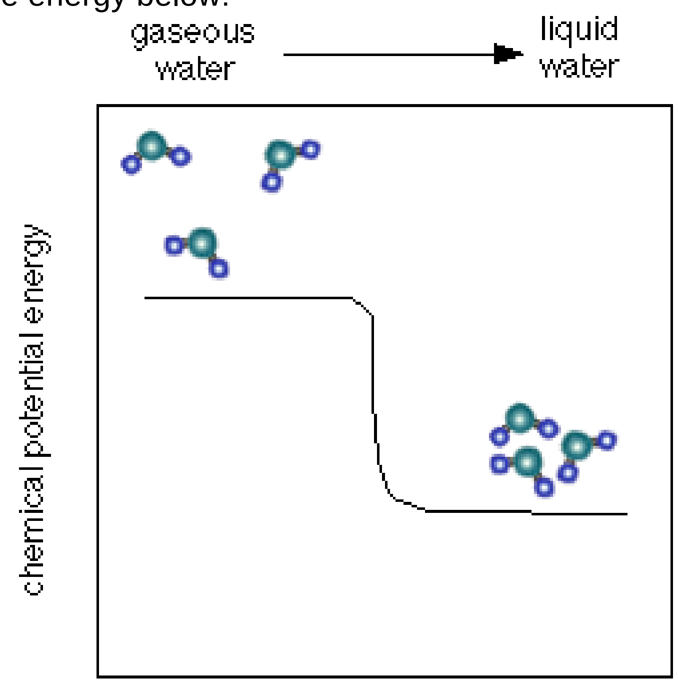
iii. Phase Change and Chemical Potential Energy

I. There is chemical potential energy in the weak van der Waals bonds as well as in the strong ionic and covalent bonds.

II. Because the van der Waals bond/attraction is so much weaker there is much less chemical potential possible here, but it is a major factor in the energy of phase changes.

III. As you can see below, the chemical potential energy of water is less than that of water vapor (or steam) which helps to explain why steam burns can be so severe. Not only is the steam hot, but it tends to condense into a liquid when it touches something. When forming a liquid the chemical potential energy that is released when the van der Waals bonds form can add substantial heat energy to the process of heat transfer from the water molecules to whatever they are condensing on.

IV. See a diagram of the energy below:



V. A process that releases chemical potential energy as heat is called exothermic.
VI. A process that absorbs heat to reduce chemical potential energy is called endothermic.
VII. Whenever a change of state occurs energy is either absorbed or released
   i. An **exothermic** process **releases heat**.
   ii. An **endothermic** process **absorbs heat**.
VIII. Below is a table of common phase changes and their associated energy

Process	**Name of phase change**	**Energy flow**
solid -> liquid		
liquid -> solid		
liquid -> gas		
gas -> liquid		
solid -> gas		
gas -> solid		

IX. In endothermic phase changes the energy is used to overcome the weak intermolecular bonds.
X. In exothermic phase changes some chemical potential energy is released as heat energy when the weak intermolecular bonds form.
a. Computer Lab: Exploring chemical potential energy in phase changes.
b. Lab: Sodium Thiosulfate Lab

c. Lab: Butane Lab

d. Lab: Ice to Steam Lab

e. Homework: Chemical Potential Energy and Phase Changes

f. The nature of boiling

I. Boiling occurs when molecules have enough kinetic energy to separate from each other.

II. Two forces hold molecules and atoms in a condensed state

i. Pulling forces from the intermolecular attractions.

ii. Pushing forces from the pressure applied on all surfaces of the liquid (from both the container and the gas above the liquid)

III. Below is an interactive graph that displays what happens when you alter the temperature, pressure, and type of substance with varying intermolecular forces. The red line depicts the amount of energy needed by a molecule to break free from the liquid state. **See if you can demonstrate two distinctly different circumstances in which you have created the conditions for boiling. Sketch these graphs and describe the boiling environment.**

VI. The boiling point occurs when enough molecules have enough energy to break free from their intermolecular forces and the external pressure keeping them together. This can be achieved in several ways.

i. You can heat the substance so that enough molecules break free.

ii. You can lower the pressure on a substance to make it easier for the molecules to break free with the energy they already posses.

iii. Some combination of either i or ii.

1. Lab: Warm water in syringe experiment

2. **Demo**: Low Pressure Boiling

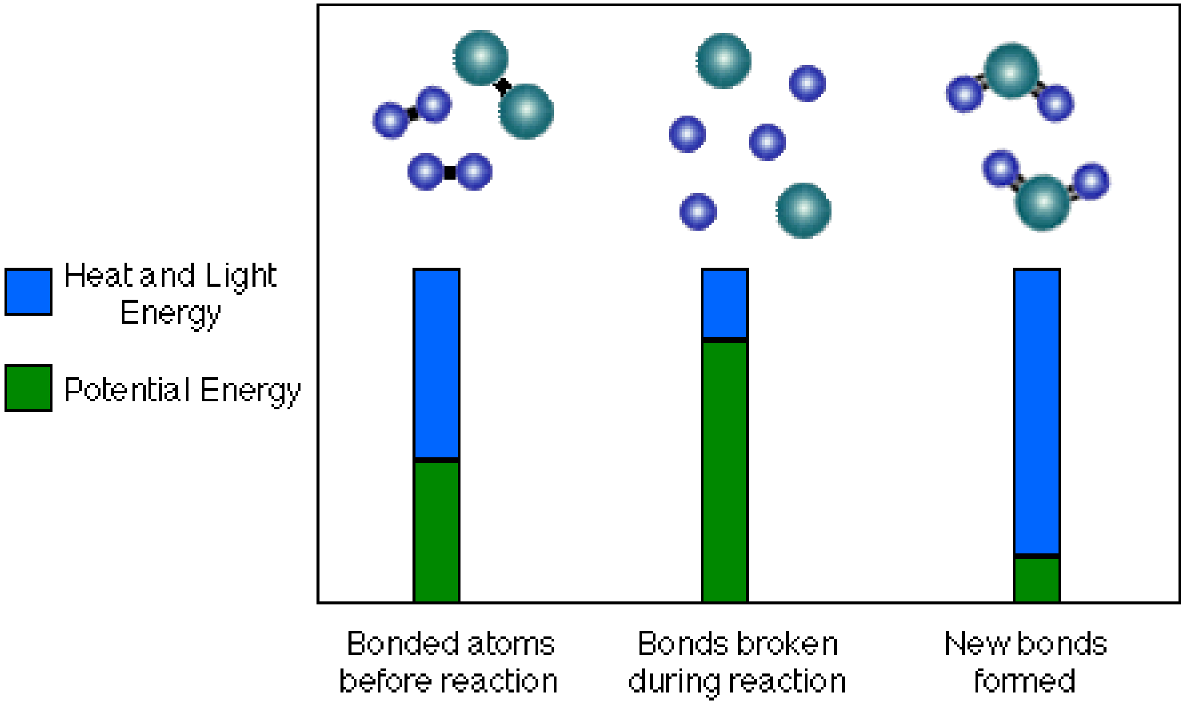
3. Homework: Write up ideas of what is happening in the low pressure boiling demo

iv. Chemcial Reactions and Potential Energy

I. Potential Energy in chemical reactions is a little more complicated than in phase changes. Often you have to break some bonds first before you can form new bonds. See the example of how water is formed from reacting hydrogen molecules with oxygen molecules below.

II. Most chemical reactions are exothermic. In that case, the newly bonded atoms have lower potential energy than the previously bonded atoms. This means that, after the reaction is done, more of the energy in the system exists as heat or light than before the reaction. See the diagram below of Hydrogen (H-H) and Oxygen (O-O) reacting to form Water (H-O-H):

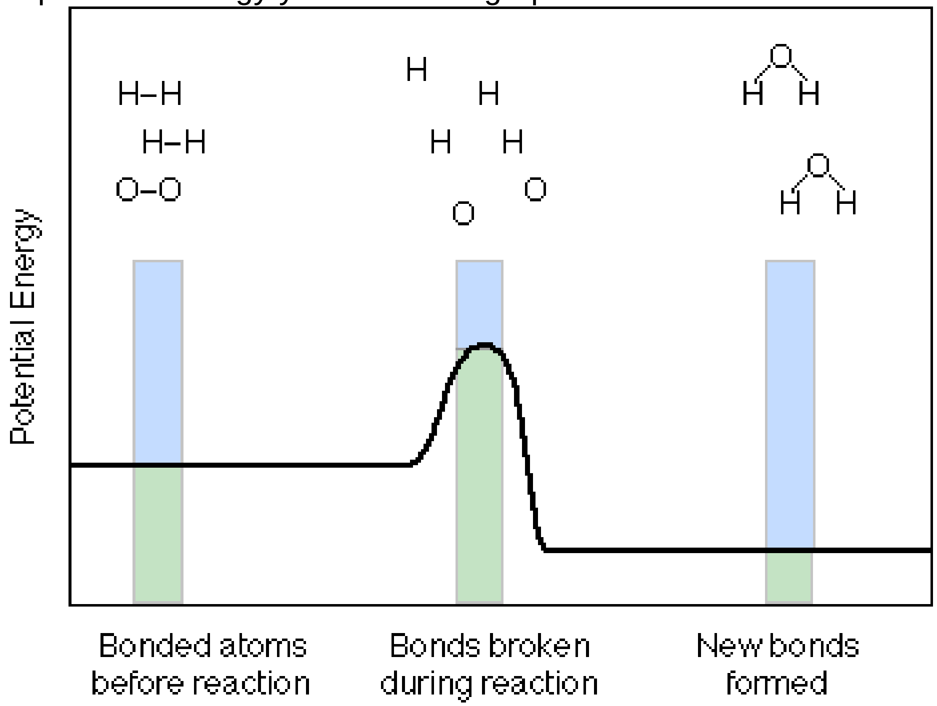
In chemical notation the reaction is written: $2\ H_2 + O_2$ -------------------------------> $2\ H_2O$



Notice that the proportion of heat and light energy after the new bonds form is greater than it was before. In other words, heat and light energy are released as the reaction is completed. On average the bonds in the Water (H-O-H) molecules are stronger than those of the Hydrogen (H-H) and Oxygen (O-O) molecules. Because the (H-O) bonds in water are stronger, they have less potential energy, therefore some of that chemical potential energy must be converted to heat and light.

Also, note that the reaction could be run in reverse, but heat and light energy must be absorbed and converted to chemical potential energy in order to break up water to form Hydrogen and Oxygen.

If we just graph the potential energy you will see a graph that looks like this:



vii. **Film:** [Releasing energy in ionic bond formation.]

viii. **Film:** [Releasing energy in molecular bond formation.]

ix. In summary, during a reaction some chemical bonds are broken and new ones are formed. In order for a chemical reaction to produce energy, the new bonds must be stronger or more stable than the old bonds. If this is true, some of the potential energy that was present when atoms were more weakly bonded together must be released as heat and/or light to form the new more stable bonds. A chemical reaction happens in several steps:

a. First, energy of some form, usually heat or light, is absorbed by two bonded atoms. This causes them to separate, **breaking their chemical bond** and **increasing their chemical potential energy**. (Some of the heat or light energy was converted to chemical potential energy.)
b. Then, two different atoms collide with each other. As these two atoms get closer together, they begin to **form a chemical bond**, **decreasing the chemical potential energy** and releasing heat and/or light energy.

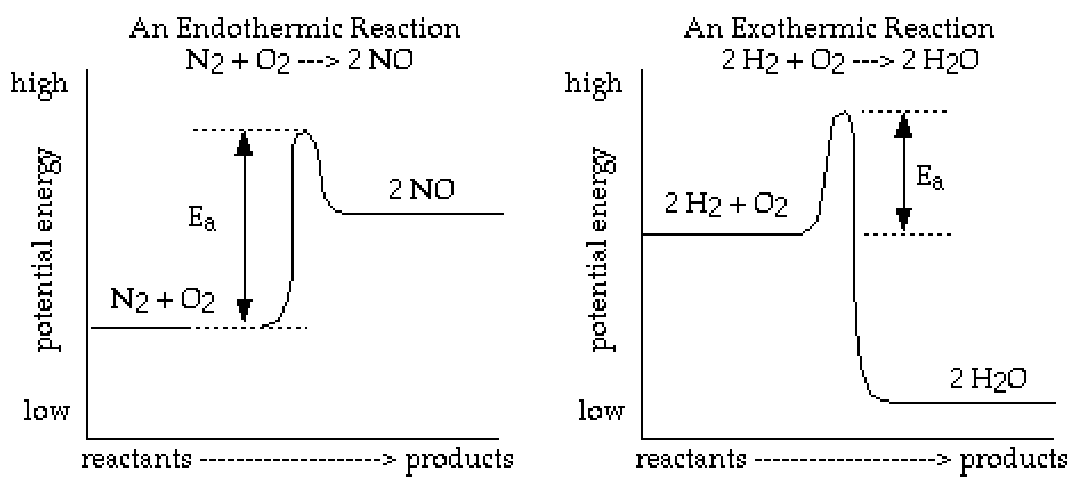
Your body stores its energy in the ATP molecule. Explore the process of storing and retrieving energy by going to this web page. (Netscape Required.)

a. **Computer Lab Demo**: Chemical Potential Energy and Covalent Bond Formation
b. Handout: Energy Storage in Your Body

c. Homework: Chemical Potential Energy in Chemical Reactions

v. Activation Energy

I. As mentioned before, to get a reaction to happen bonds usually have to be broken first. This takes some energy, usually in the form of heat (fast moving molecules or atoms colliding) or light.
II. The energy needed to break the initial bonds of the reactants is called the Activation Energy and is abbreviated E_a. Below is a picture of two different reactions and how the chemical potential energy of the substances changes during the reaction.



III. Notice that the endothermic reaction needs a continual input of energy to continue reacting. However, the reaction between H_2 and O_2 gives off so much energy that it can supply the left over reactants with the activation energy needed to form water and complete the reaction. Once this reaction is started with a spark or a flame it continues until there are no more reactants.

IV. Exothermic reactions with a very low activation energy will occur spontaneously, and one's that tend to give off a lot of energy tend to be very reactive or even explosive.

a. **Demo**: Making HCl, H_2O, and NI_3

b. **Film**: Activation Energy and Bonding

vi. Catalysts

I. A catalyst is a substance which speeds up the rate of reaction without being used up in the reaction. You will have the same amount of catalyst at the beginning and end of a reaction, but the reaction will occur much more quickly.

II. Catalyst examples:

i. Most of the enzymes in your body are catalysts. Many of the chemical reactions that are necessary for life to occur run too slowly without being catalyzed by an enzyme. Without catalysts we could not exist.

ii. The catalytic converter that is part of all modern car exhaust systems. This turn many of the pollutants (primarily hydrocarbon (C-H) fragments and carbon monoxide (CO) in the exhaust into carbon dioxide (CO_2) and water (H_2O).

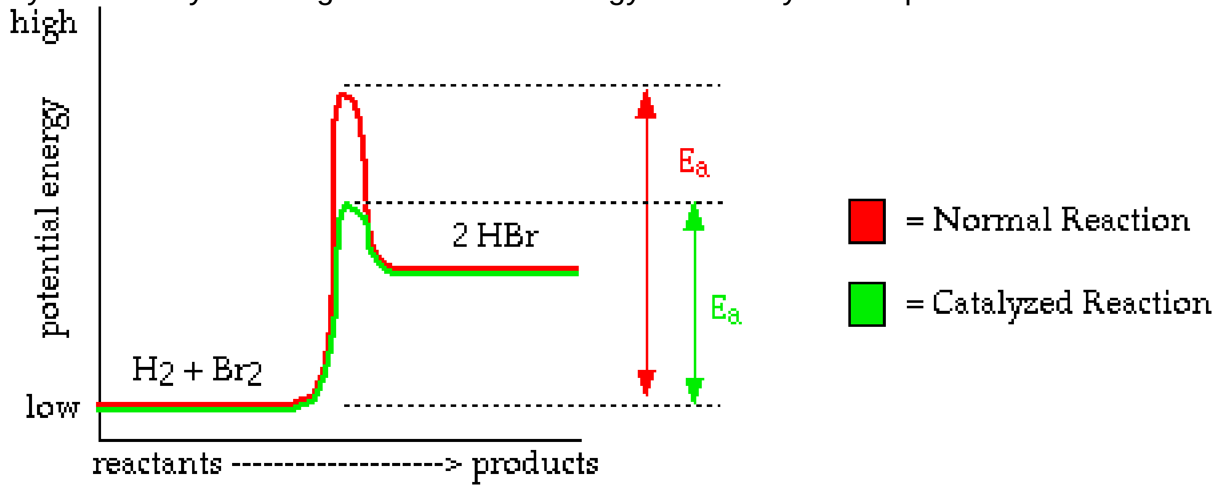
iii. When you generated oxygen from hydrogen peroxide earlier this year you used a Manganese metal catalyst.

$2\ H_2O_2 \text{ ---> } 2\ H_2O + O_2$

Notice that the MnO_2 is not written as part of this reaction. That is because it is not consumed during the reaction. It can be reused over and over again.

iv. Chlorine atoms from CFCs (chloroflourocarbons) catalyze the breakdown of ozone into oxygen: $O + O_3 \text{ ---> } 2\ O_2$

III.A catalyst works by lowering the activation energy necessary to complete a reaction



IV. Because it takes less energy to form products, the reaction occurs more quickly.

V. **Film**: Catalysts and Activation Energy

VI. **Film**: Hydrogen Catalysis

a. **Homework:** Activiation Energy

b. Computer Lab: Exploring Potential Energy Curves in Reactions

c. **Homework:** Draw potential energy curves for the following situations:

1. an exothermic reaction that is likely to be completely spontaneous
2. a reaction which would require a constant input of energy to complete
3. an exothermic reaction with a high activation energy
4. an endothermic reaction with a low activation energy
5. a reaction in which the reactants and products contain approximately but not exactly the same chemical potential energy.
6. two curves - one representing a catalyzed reaction, and one representing the same reaction without a catalyst.

III. Equilibrium

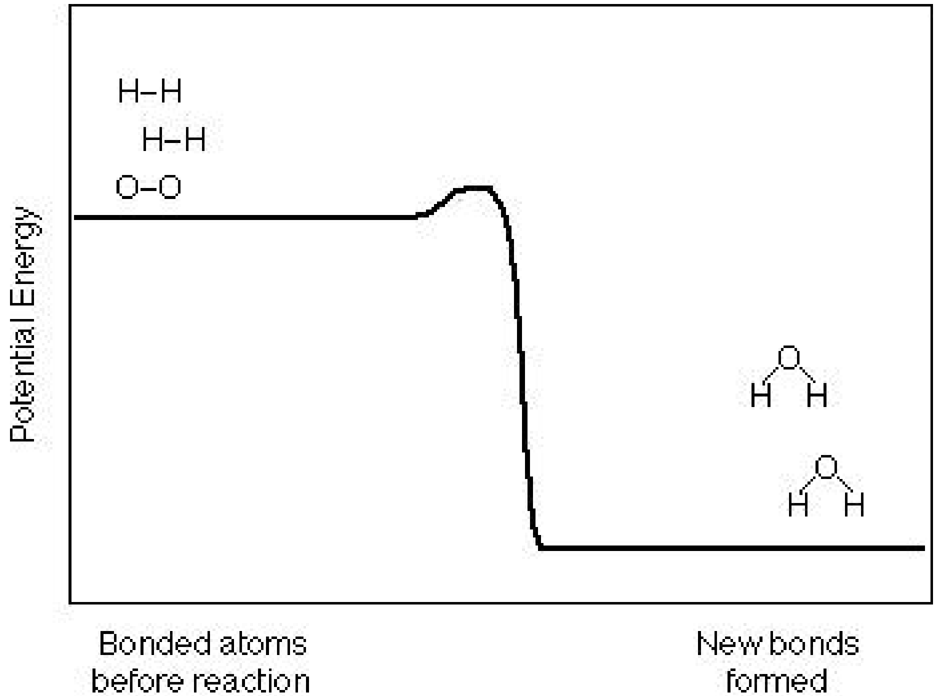
i. Lab: Penny Lab

ii. Computer Lab: Equlibrium

iii. Chemical Equlibrium

I. Often we talk about reactions as if you mix a couple of things together to produce one or more new substances. For example, we say that Hydrogen and Oxygen can combine to make Water and write the chemical equation as:

$$2\ H_2 + O_2 \longrightarrow 2\ H_2O$$



II. Why don't we write the equation as: $2\ H_2 + O_2 \longleftarrow 2\ H_2O$

In other words, why is it less likely that water breaks up to form hydrogen and oxygen than it is for hydrogen and oxygen to form water?

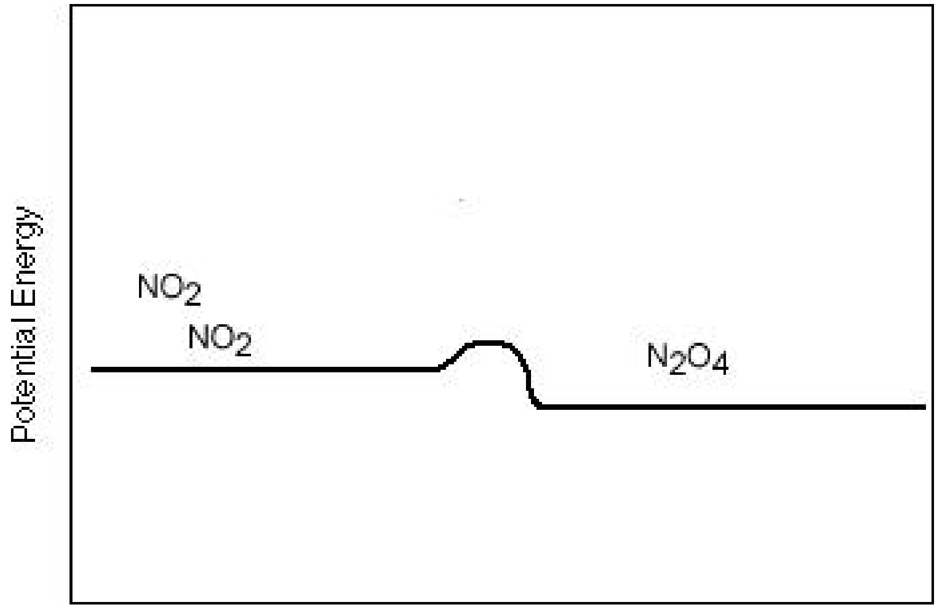
III. In fact, there is a very small chance that water could break up to form hydrogen and oxygen. Maybe we should write the chemical equation as:

$$2\ H_2 + O_2 \rightleftharpoons 2\ H_2O$$

to show that it is mostly water that is formed.

IV. However, so little water breaks up to form hydrogen and oxygen that it is OK, and considered correct to write the equation as: $2\ H_2 + O_2 \longrightarrow 2\ H_2O$

V. However, now consider the following reaction in which the potential energy of the reactants and the products are almost the same, making the activation energy almost equal from left to right as it is from right to left:



VI. Which do you think is the best way to write the equation for the above chemical reaction?

$$2\ NO_2 \longrightarrow N_2O_4$$
$$2\ NO_2 \longleftarrow N_2O_4$$
$$2\ NO_2 \rightleftharpoons N_2O_4$$

VII. If we start with all NO_2 , then they will collide and start to form N_2O_4. At first the likelyhood of two N_2O_4 molecules colliding will be small, but eventually the N_2O_4 will build up in concentration until it will be common for them to collide. Because they can almost as easily break up into NO_2 as NO_2 can combine to form N_2O_4 the reaction will start to go to the left. Eventually, you will have just as much N_2O_4 forming as NO_2 forming. In other words, the reaction will go left and right at the same rate, reaching an equilibrium.

VIII. All reactions are equilibrium reactions. However, many (like the formation of water from hydrogen and oxygen) are much more likely to happen one direction that we think of these reactions as only going in that direction. For those reactions it is OK to use a single arrow.

IX. For reactions in which a significant amount of product and reactants are constantly being formed we use the double arrow to indicate the behavior of this equilibrium.

iv. Le Chetalier's Principle

I. Le Chetalier studied equilibrium systems and determined that: **A system in equilibrium will respond to stress in such a way as to counteract that stress**.

II. There are several ways to stress a chemical equilibrium:

i. Add or remove heat: If a reaction is endothermic then adding heat will increase it's rate, if exothermic the reverse reaction will be favored.

ii. Add or remove various reactants or products: because reactions occur when molecules collide, adding more of one type of molecule will favor its collision with other molecule, thus increasing the probability that it will react.

iii. Raise or lower the pressure for reactions which involve gasses: Assuming the reaction vessel remains at a constant volume the only way to respond to increased pressure would be to form fewer moles of gas. Reactions which reduce the number of gaseous molecules would be favored under increased pressure. The opposite is true for reduced pressure.

iv. Add a catalyst which increases the rate of one reaction over the other: if a catalyst only accelerates a reaction in one particular direction, then a new equilibrium will be reached under these new conditions.

III. Let's consider the following equilibrium reaction:

$$2\,NO_2 \rightleftharpoons N_2O_4 + \text{energy}$$

brown colorless

IV. As written this reaction is exothermic from left to right and endothermic from right to left.

i. What would happen if you heated this system?

ii. What would happen if you increased the pressure on this system?

iii. What would happen if you added more N_2O_4?

iv. What would happen if you removed N_2O_4?

v. What would happen if you added a catalyst?

a. **Demo**: NO_2 <--> N_2O_4 tubes
b. Lab: LeChetalier part 1 and 2
c. **Film**: The Harber Process

IV. Handout: Chemical Kinetic Review