Chemical Kinetics (or Reaction Rates)

- I. Handout: Chemical Kinetics Note Packet
- II. Collision Theory of Reactions
 - i. Lab: Iodine Clock Reaction
 - ii. Computer Lab: Sections 1,2, and 3 of the Chemical Reactions Activity
 - iii. Handout: Questions for above computer labs on reaction rate
 - iv. 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 (CO2) and water (H2O).
- 3. When you generated oxygen from hydrogen peroxide earlier this year you used a Manganese metal catalyst.

2 H2O2 ---> 2 H2O + O2

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 + O3 ---> 2 O2
- c. See some catalyzed reactions:
 - 1. Film: Forensic Catalysis
 - 2. Film: Formic Acid Decomposition
- v. **Demo**: Lycopodium power and Iron filings
- vi. **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.

III. Chemical Potential Energy

- i. Strong and Weak Bond Overview
 - I. There are two major bond types: weak bonds between molecules, and strong bonds between atoms.
 - II. Weak bonds van der Waals bonds
 - i. All atoms and molecules have a weak attraction for each other. This is called the van der Waals attraction
 - ii. All liquids and some solids are formed through this kind of weak bond.
 - iii. Hydrogen bonds which are commonly referred to in biology, which hold our two strands of DNA together, and help shape proteins into their proper conformation, fall into this category.

- III. Strong bonds ionic and covalent
 - i. When two atoms bond together very strongly they do so via either a covalent bond or an ionic bond.
 - ii. These bonds are MUCH stronger than the weak van der Waals bonds that help molecules to stick to each other.



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.



Types of Energy For a Spring

- 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, chemical energy is converted into other forms of energy, 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** chemical energy there is between the bonded atoms.

Strong bonds have low chemical energy and weak bonds have high chemical energy.

- e. Lot's of heat and/or light energy is released when very strong bonds form, because much of the chemical 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 which is converted into chemical energy when the bond is broken.
- f. See an example below of how a chemical reaction converts chemical energy into heat and light energy:



Converting Chemical Energy to Heat and Light Energy				
	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	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	0-0	0-0	The O-H bond is even stronger than the H-H or O-O.
	The chemical energy converted here is small because the bonds formed are weak.	The amount of chemical potential energy released above is much greater than what is released during the formation of weak van der Waals bonds.		

- a. **Computer Lab: Section 4** of the Chemical Reactions Activity
- b. **Computer Lab**: Forming a Single Bond
- c. Computer Lab: Breaking a Single Bond

iii. Chemical Reactions and Potential Energy

- I. 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 chemical 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):



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 chemical energy, therefore some of that chemical energy must be converted to heat and light as the stronger bonds form.

Also, note that the reaction could be run in reverse, but heat and light energy must be absorbed and converted to chemical 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:



Simplified Chemical Energy Graph

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 heat energy, the new bonds must be stronger or more stable than the old bonds. If this is true, some of the chemical 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.

a. Homework: Chemical Potential Energy in Chemical Reactions

iv. 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 Ea. 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 H2 and O2 gives off so much energy that it can supply the left over reactants with the activation energy needed to form water causing a chain reaction which makes the rest of the hydrogen and oxygen react. 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 HCI, H2O, and NI3
- b. Film: Activation Energy and Bonding
- c. Computer Lab: Section 5 of the Chemical Reactions Activity
- d. **Computer Lab**: Activation energy and Chemical Energy
- e. **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.
- v. 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 turns many of the pollutants (primarily hydrocarbon (C-H) fragments and carbon monoxide (CO) in the exhaust) into carbon dioxide (CO2) and water (H2O).
- iii. When you generated oxygen from hydrogen peroxide earlier this year you used a Manganese metal catalyst.

2 H2O2 ---> 2 H2O + O2

Notice that the MnO2 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 (chlorofluorocarbons) catalyze the breakdown of ozone into oxygen: O + O3 ---> 2 O2
- 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. Computer Lab: Section 6 of the Chemical Reactions Activity

b. Homework: Activation Energy

IV. Equilibrium

- i. Lab: Penny Lab
- ii. Computer Lab: Section 7 of the Chemical Reactions Activity
- iii. Chemical Equilibrium



II. Why don't we write the equation as: 2 H2 + O2 - 2 H2O

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:

to show that it is mostly water that is formed.

However, so little water breaks up to form hydrogen and oxygen that it is OK, and considered correct IV. to write the equation as:

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? Why? $2 \text{ NO2} \longrightarrow \text{N2O4}$ $\begin{array}{c} 2 \text{ NO2} \longleftarrow \text{N2O4} \\ 2 \text{ NO2} \longrightarrow \text{N2O4} \\ \end{array}$

- VII. If we start with all NO2, then they will collide and start to form N2O4. At first the likelyhood of two N2O4 molecules colliding will be small, but eventually the N2O4 will build up in concentration until it will be common for them to collide. Because they can almost as easily break up into NO2 as NO2 can combine to form N2O4 the reaction will start to go to the left. Eventually, you will have just as much N2O4 forming as NO2 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 you add heat the reaction will go in the direction which will use up that heat (convert it to chemical energy). If you remove heat, then the reaction will go in the direction that produces heat (converts chemical to heat energy).
 - 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.

III. Let's consider the following equilibrium reaction:



- 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 N2O4?
 - iv. What would happen if you removed N2O4?

v. What would happen if you added a catalyst?

- a. **Demo**: NO2 <--> N2O4 tubes
- b. Lab: Le Chetalier part 1 and 2
- c. **Film**: The Harber Process
- V. Handout: Chemical Kinetic Review with Answers