Chemistry Honors – Lesson 4 Chemical Kinetics and Equilibrium

When studying a chemical reaction, it is important to consider not only the chemical properties of the reactants, but also the conditions under which the reaction occurs, the **mechanism** (or steps) by which it takes place, the rate at which it occurs, and the **equilibrium** (or steady state) toward which it proceeds.

Reaction Mechanisms

The **mechanism** of a reaction is the actual series of steps through which a chemical reaction occurs. Not all the steps are show in the overall reaction. Consider the following reaction :

Overall Reaction: $A_2 + 2 B \rightarrow 2 AB$

This equation implies that two molecules of B collides with one molecule of A_2 to make two molecules of AB. But suppose that the reaction actually took two steps:

Step 1:	$A_2 + B> A_2 B$	(slow)
Step 2:	$A_2B + B> 2 AB$	(fast)

When you add these two reactions together, you get the Overall Reaction listed above. A_2B does not show up in the Overall Reaction because it is neither a reactant or a product, but an **intermediate**. Intermediates can be hard to detect or observe, but their existence can be supported through experiments. The slowest step in a proposed mechanism is called the **rate-determining step** because the Overall Reaction cannot go faster than that step.

Reaction Rates

Rate is another way to say how much something changes over time. Speed and acceleration are rates where speed is a rate of changing distance over time and acceleration is a rate of velocity change over time. In a chemical reaction, the reaction rate is described as the disappearance of reactants or appearance of products over time.

	Decrease in concentration of reactants	Increase in concentration of products
Reaction rate =	= =	=
	Time	Time

Consider the reaction $2A + B \rightarrow C$, where one molecule of C is made from 2 molecules of A and 1 molecule of B. Thus from our equation, the rate using the product C is $\Delta[C]/\Delta t$ (that reads "change in the concentration of C over the change in time"). Since the reactants are decreasing during the reaction, a negative sign is put in the front, so

using B it would look like $-\Delta[B]/\Delta t$. Since molecules of A are used up twice as fast, you divide the rate by 2 to make it equal to the other rates:

$$A[A] \quad \Delta[B] \quad \Delta[C]$$

$$Rate = -1/2 \quad ----- = \quad ------ = \quad ------$$

$$\Delta t \quad \Delta t \quad \Delta t$$

In general, for the reaction: aA + bB - -> cC + dD

$$A[A] \qquad \Delta[B] \qquad \Delta[C] \qquad \Delta[D]$$

$$Rate = -1/a - ---- = -1/b - ---- = 1/c - ---- = 1/d - -----$$

$$\Delta t \qquad \Delta t \qquad \Delta t \qquad \Delta t$$

Rate is expressed in the unites of moles per liter per second (mol/L x s) or molarity per second (M/s)

Reaction Orders

Chemical reactions are often classified based on the **order** of the reaction. Using the general reaction aA + bB - cC + dD:

- 1. **Zero-order reactions** A zero-order reaction has a constant rate, which is independent of the reactants' concentrations.
- 2. **First-order reactions** A first-order reaction has a rate which is proportional to the concentration of a reactant. Thus if a reactant's concentration is doubled, then the rate of the reaction is also doubled.
- 3. Second-order reactions A second-order reaction has a rate proportional to the product of the concentration of two reactants or the square of one reactant

Factors Affecting Reaction Rate

The rate of a chemical reaction can depend heavily on the environment of where the reaction is taking place. The rate of a reaction will increase if there is an increase in the collisions of the reactants or a stabilization of intermediates or **transition states** (old bonds are in the middle of being broken while new ones are forming).

- 1. **Reactant Concentrations** The greater the concentrations of the reactants (the more particles per volume), the greater the chance will be for collisions of the reactants. Therefore the reaction rate will increase for all but zero order reactions.
- Temperature For nearly all reactions, the reaction rate will increase as the temperature of a system/reaction increases. Since the temperature is a measure of the particles' average kinetic energy, increasing the temperature increases how fast the molecules are moving around and providing enough energy to form products.
- 3. **Medium** The rate of reaction may also be affected by the medium in which it takes place. If the surroundings of a molecule is thick and hard to move through,

then the slower it will be fore molecules to find each other and collide with enough energy.

4. **Catalysts** – Catalysts are substances that increase reaction rates without being used up or consumed. They help the reactants collide in the right way, stabilize the transition states and/or the intermediates, and generally makes it easier to form the products. This increases the overall reaction rate if the rate-determining step is the formation and breaking of bonds. This is especially important in biology and biological reactions.

<u>Equilibrium</u>

So far, reaction rates have been discussed under the assumption that the reactions were **irreversible** (only goes from reactants to products). A **reversible** reaction is one where products can react/breakdown to form the reactants. When there is no **net** or overall change in the concentrations of the products and reactants after reacting for a while, it is said to be in equilibrium. This is not to say that when a reaction is in equilibrium, nothing is happening. During equilibrium, products are still being formed and broken down but at an equal rate. Equilibrium can be thought of as a balance between two reaction directions. Consider the following:

 $A \iff B$

At equilibrium, the concentrations of A and B stay the same, but the reactions A-->B and B--> A occur at the same rate.

Le Chatelier's Principle

Henry Louis Le Chatelier was a French chemist that stated "a system to which a stress is applied tends to change to relieve the applied stress". This rule is known as **Le Chatelier's Principle**. It is used to determine the direction in which a reaction at equilibrium will go when changes (such as concentration or temperature) are made.

1. **Changes in concentration** – When the concentration of a species (either reactant or product) is increased, the equilibrium shifts away from that species. What that means is the reaction balance will be uneven and proceed in the direction decreasing the species in order to reestablish a new equilibrium. In the reaction:

$$A + B \leq = > C + D$$

If the concentration of A or B is increased, the reaction would proceed to use up more A and B to make products C and D (shifting the equilibrium towards C and D). Conversely, if the concentration of C and D were increased, the equilibrium would shift to make more A and B. Similarly if you removed product C and D, the equilibrium would shift to make more C and D.

2. Changes in temperature – Temperature can also be considered a "species" in a reaction. In an exothermic reaction, heat is produced as a product of the reaction.

In an **endothermic** reaction, heat is consumed as a reactant to allow for the reaction to proceed. Consider the following exothermic reaction:

$$A \leq B + heat$$

If this reaction system were placed in an ice bath, its temperature would decrease, driving the reaction to the right to replace the heat lost. Conversely, if the reaction were placed in a boiling-water bath, the reaction equilibrium would shift to the left due to the increased "concentration" of heat.