Kinetics, Thermodynamics and Equilibrium

Word	Definition
Activated complex	The species that are formed and decomposed during the mechanism, also called the intermediate.
Activation energy	The energy that must be added to the reactants to allow them to react and form the activated complex.
Catalyst	A chemical that is added to a reaction to eliminate steps in the mechanism and increase the reaction rate and decrease the activation energy without being consumed itself.
Effective collision	A collision between reactant particles that results in a chemical reaction taking place.
Enthalpy	The total amount of potential energy stored in a substance.
Endothermic	A reaction that absorbs and stores energy from its surrounding environment.
Entropy	A system's state of disorder. Entropy increases as temperature increases. Entropy increases as a substance is heated from a solid to a liquid to a gas.
Equilibrium	A system where the rate of forward change is equal to the rate of the reverse change.
Exothermic	A reaction that releases stored energy into its surrounding environment.
Favored	A change in a thermodynamic property that contributes towards the reaction being spontaneous.
Gibbs free energy	The total amount of energy available in a system to do work. It is a combination of both enthalpy and entropy.
Heat of reaction	The net gain or loss of potential energy during a chemical reaction.
Inhibitor	A chemical that is added to a reaction to add steps to the mechanism and decrease the reaction rate and increase the activation energy without being consumed itself.
Kinetics	The study of reaction mechanism and reaction rate.
Mechanism	The pathway or series of steps a reaction takes on its way to forming product.
Nonspontaneous	A change that requires a constant input of energy to occur, or the change will stop or reverse itself.
Reaction rate	The amount of reactant consumed per unit of time.
Spontaneous	A change that, once started, continues the rest of the way on its own.
Thermodynamics	The study of heat flow during physical and chemical changes.
Unfavored	A change in a thermodynamic property that contributes towards the reaction being nonspontaneous.

1) Kinetics (HW: p. 23)

Essential Question: How do reactions happen in the first place, and how fast do they go?

How Reactions Happen
Chemical kinetics - the study of reaction mechanisms and rates (how reactions occur, and how long they take)

Mechanism - the "pathway" the reaction takes - a series of steps that leads from product to reactant.

a) Particles of reactant must collide in order to react
b) These collisions must occur with enough energy (activation energy) to react
c) The molecules must be oriented properly to react.
d) Collisions that satisfy both requirements that lead to the commencement of the reaction are called **effective collisions.**

The mechanism can occur in a series of steps, each involving electron shifts as old bonds are broken and new bonds are formed.

For the imaginary reaction 2 A + B --> A_2B, a possible mechanism might be

STEP 1: A + B --> AB (one of the two molecules of A reacts with the one molecule of B to form an intermediate molecule, AB)

STEP 2: A + AB --> C (the remaining molecule of A reacts with the intermediate molecule AB to form the final product, C)

NET: 2 A + B --> C (when considering the net equation, AB is found on both sides, and therefore cancels out)

For the reaction $H_2 + I_2 \rightarrow 2\ HI$:

STEP 1: $H_2 \rightarrow 2\ H$ (the bonds between the hydrogen atoms must break by absorbing energy)

STEP 2: $I_2 \rightarrow 2\ I$ (the bonds between the iodine atoms must break by absorbing energy)

STEP 3: $2\ I + 2\ H \rightarrow 2\ HI$ (H would rather bond to I than to itself, so the atoms rearrange for this to happen. New bonds form, which releases energy)

NET: $H_2 + I_2 \rightarrow 2\ HI$ (2 H and 2 I are formed in steps 1 and 2, then used up in step 3. 2 H and 2 I are the intermediates, also known as the activated complex)

Mechanism is like taking different roads to the same place. Depending on which road you take, it takes a different amount of time to reach your destination. **The only way to know what the mechanism really is would be to do an experiment.**

Rate-determining step: the slowest step dictates the overall speed of the reaction. If there are eleven steps, ten of which are very fast, the other step, the slow one, determines the rate of the reaction.

FACTORS THAT AFFECT REACTION RATE BY CHANGING THE MECHANISM

1) Catalyst - speeds up a reaction by changing one or more steps in the mechanism to shorten the mechanism. Generally lowers the activation energy, allowing the reaction to proceed at a faster rate. Catalysts are not consumed by the reaction. This is like finding a shortcut when driving!

Dissolving ionic compounds in water before undergoing a double replacement reaction speeds up the reaction. Water is the catalyst and does not get used up by the reaction.

Esters are complex organic molecules that can be used for adding odor or flavor to products. The ester pentyl ethanoate, for example, is the molecule that is produced by overripe bananas and is used to flavor artificially flavored banana products such as Laffy Taffy. It is formed when ethanoic acid reacts with 1-pentanol, a five-carbon alcohol. This is a covalent reaction, and therefore very, very slow. This reaction could take weeks to happen, even under heat. Add a couple of drops of concentrated sulfuric acid and the reaction will take a few minutes. The sulfuric acid acts as a catalyst, and is not used up by the reaction. It has to be extracted from the product before it is used in food.

2) Inhibitor - slows down a reaction by adding additional steps to the mechanism - acts as a "roadblock" or detour. Generally increases the activation energy. After all, if you have to take a detour, it uses more gas to get to you destination! Inhibitors are not consumed by the reaction.

Some metals like aluminum, copper, zinc and silver will form a protective oxide coating called a patina when exposed to the oxygen in air. This oxide coating protects the metal underneath from further corrosion. On the other hand, iron does not form this patina. Iron oxidizes to form rust, which digs out pits in the metal, weakening it. To protect iron and steel that will be exposed to the weather, like chicken-wire or chain-link fences and roofing nails, the iron or steel is electroplated with zinc. The zinc coating will form a patina, which protects the zinc, which protects the fence so it doesn't rust out and the roofing nail so that the roof doesn't fall off. Another way to protect iron or steel is to paint it. Cars use a hard enamel and exposed metal around the house can be protected with rustproofing paint, which prevents oxygen from getting to the metal.

Reaction Rate - the speed at which reactant is transformed into product. It is generally measured in terms of amount of reactant consumed over a period of time. On the molecular level, it is measured in terms of number of effective collisions per unit time. The more effective collisions there are, the faster the rate will be. At the industrial level, it is important that the reactions take the shortest time possible to reach the purest product with the least expenditure of energy. It is therefore important to study methods of increasing reaction rate. **Anything that will speed up the rate of collisions will increase the rate of the reaction.**

FACTORS AFFECTING THE RATE OF REACTION BY CHANGING THE NUMBER OF COLLISIONS

In industry, the push is to maximize product while minimizing cost. A faster reaction rate will tend to lower costs, since it means a larger output in less time. Let's study the ways reaction rates can be speeded up.

1) Nature of Reactants

Depending on what the reactants are, it will take different amounts of energy to elicit an effective collision.

IONIC REACTIONS OCCUR VERY FAST, especially if the reactants are in solution so that the ionic bonds are already broken. Remember how fast the precipitate formed in the double replacement reactions?

COVALENT REACTIONS OCCUR VERY SLOW. Some of them can take days. Covalent bonds are a lot more difficult to break than ionic bonds, and thus require more energy. Molecules are also a lot more complicated in structure than ionic crystals. Most reactions that take place in living organisms are covalent reactions. In order to speed them up without having to use a lot of energy, organic catalysts called **enzymes** are used. The oxidation of glucose to form carbon dioxide and water vapor would cause the glucose to catch on fire if you tried it in a beaker, but in the body, it takes place in the mitochondria of the cells. Instead of the energy released causing a fire, enzymes take that energy and store it in chemical bonds in molecules of ATP or in fat molecules.

2) Temperature
This directly affects the speed of the colliding particles. The higher the temperature, the faster the particles are moving, and therefore they collide with more energy. This gives more effective collisions in the same unit time, increasing the rate of reaction.

WHICH HAS A HIGHER RATE OF COLLISIONS? CARS TRAVELLING AT 30 MPH OR 100 MPH?

If you want to preserve batteries that you are not using, put them in the refrigerator. This will slow down the chemical reaction so that the batteries last longer. Try using a Walkman in sub-freezing temperatures. You might notice that the tape…plays…a…lot…slower…than…usual. Devices that have moving parts that run on batteries usually have an operating range of temperatures.

The Bunsen burner heats up reactants. Why? To get the molecules to move faster and collide more frequently so that the reaction happens faster and you don't have to sit around all day waiting for it to finish reacting!

3) Concentration
This affects the orientation of the colliding particles. The more particles there are in a given volume, the greater the chance for collision, the greater the chance for proper orientation, the greater the chance for effective collisions, and the higher the rate. An increase in pressure for gases is the same as an increase in concentration, since the gas molecules are being pushed closer together, resulting in more collisions and a faster rate.

WHICH HAS A HIGHER RATE OF COLLISIONS? A PARKING LOT WITH 10 CARS OR 100?

Acids are generally compounds containing H^+ ions dissolved in water. When reacting acids with metals (like in the demonstration that filled up the balloon where hydrochloric acid reacted with zinc metal to produce the hydrogen gas), the higher the concentration of the acid is, the more collisions there will be between the acid molecules and the metal, making the reaction faster. Highly concentrated acid will eat away metals faster.

4) Surface area
The more surface that is exposed, the more surface that can undergo effective collisions. Crushing a salt cube to dissolve it exposes fresh surface to react. Smaller particles of the same mass of a large cube of substance have a higher surface area. Affects only solid reactants, since liquids and gases have maximum surface area (no chunks to break up).

Take two bricks four feet apart and throw them at each other. Now, break those bricks up into twenty pieces each and throw the pieces at each other from four feet away. Which situation will give you a better chance of a collision? If you have more pieces, there is a better chance of collision. This is why higher surface area (smaller particles) gives a faster reaction.

Crushed garlic has more surface area than a whole clove of garlic, so it will give its flavor to the food you put it in more readily.

10. grams of zinc powder will react faster with 2.0 M hydrochloric acid than a 10. gram chunk of mossy zinc.

Take two cars, both unpainted. One is in perfect condition, the other has been scratched up. The one that has been scratched up has more surface exposed than the one in perfect condition, and will therefore rust faster.

2) Potential Energy Diagrams (HW: p. 24-27)

Essential Question: Why do you have to strike a match just right to get it to light?

Energy Changes in Chemical Reactions: Potential Energy Diagrams

CHEMICAL EQUATIONS

A + B ---> C + D
reactants products

In chemical reactions, reactants react to form products with an associated release or absorption of energy.

1) ENDOTHERMIC (absorption of energy)

A + B + ENERGY ---> C + D
↑
energy absorbed as reactant

a) Heat is absorbed by the reactants.
b) This heat is **absorbed** from the environment surrounding the reaction, and the temperature of the surroundings decreases.
c) The products have more energy than the reactants after absorption. This energy is **stored** in the chemical bonds of the products
d) This excess energy stored in the products makes the products chemically **unstable** and highly reactive. Nitroglycerine, TNT and plastic explosive are all formed through highly endothermic reactions, the excess energy stored in the bonds and easily reactive.

General Example:

For the reaction A + B → C:

If H_A = 40 kJ and H_B = 20 kJ, then the reactants have a total of 60 kJ. If H_C = 110 kJ, then (110-60 =) 50 kJ of heat must have been absorbed by the reactants. The reaction can therefore be rewritten to show this energy change as follows:

A + B + 50 kJ → C:

This way, the total energy on both sides is the same, 110 kJ. This satisfies the Law of Conservation of Energy

Example from Reference Table I:

N_2 (g) + O_2 (g) → 2 NO (g) ΔH = +182.6 kJ

The plus sign in front of the 182.6 kJ indicates that this reaction is endothermic, that energy was absorbed. This energy can be placed on the reactants side, as follows:

Table I
Heats of Reaction at 101.3 kPa and 298 K

$N_2(g) + O_2(g) \longrightarrow 2NO(g)$	+182.6

*Minus sign indicates an exothermic reaction.

N_2 (g) + O_2 (g) + 182.6 kJ → 2 NO (g)

This shows that N_2 and O_2 absorb 182.6 kJ in order to form NO. NO, therefore, has 182.6 kJ more energy stored in its bonds than N_2 and O_2 combined. NO is an unstable product.

2) EXOTHERMIC (release of energy)

A + B ---> C + D + ENERGY
↑
energy released as a product

a) Heat is released as a product.
b) This heat is released into the environment surrounding the reaction, causing the temperature of the surroundings to increase.
c) The products have less energy than the reactants after release.
d) Since the products have less energy stored in their chemical bonds, they are more stable than the reactants were. Burning paper is exothermic. The ash formed by the burning is not flammable and will not burn.

General Example:

For the reaction A + B → C:

If H_A = 60 kJ and H_B = 40 kJ, then the reactants have a total of 100 kJ. If H_C = 30 kJ, then (100- 30 =) 70 kJ of heat must have been released as a product. The reaction can therefore be rewritten to show this energy change as follows:

A + B → C + 70 kJ

This way, the total energy on both sides is the same, 100 kJ. This satisfies the Law of Conservation of Energy

Example from Reference Table I:

C (g) + O_2 (g) → CO_2 (g) ΔH = -393.5 kJ

The minus sign in front of the 393.5 kJ indicates that this reaction is exothermic, that energy was released. This energy can be placed on the products side, as follows:

Table I
Heats of Reaction at 101.3 kPa and 298 K

$C(s) + O_2(g) \longrightarrow CO_2(g)$	−393.5

*Minus sign indicates an exothermic reaction.

C (g) + O_2 (g) → CO_2 (g) + 393.5 kJ

This shows that C and O_2 had 393.5 kJ more stored in their bonds than CO_2 has, and that the difference in energy was released as CO_2 was formed. C is a stable product.

IN ADDITION:

This reaction shows the SYNTHESIS of **one mole** of CO_2. This synthesis reaction releases 393.5 kJ. If we were to synthesize **2.3 moles** of CO_2, how many kJ would be released?

2.3 ~~moles~~ X -393.5 kJ/~~mole~~ = - 905.05 = - **910 kJ**

If we were to DECOMPOSE one mole of CO_2, what would the energy change be? Well, since decomposition is simply the reverse of synthesis, the heat flow is reversed. Energy is released when CO_2 forms, so energy must be absorbed in order to decompose it!

If $\Delta H_{synthesis}$ = -393.5 kJ/mole, then $\Delta H_{decomposition}$ +393.5 kJ/mole

Potential Energy Diagrams: graph that shows what happens to potential energy as a reaction goes from start to finish. The basic order of things is this:

1) All reactions start with reactants, so the PE starts at the Heat of Reactants level.
2) Activation energy must be added to the reactants to get the reaction to start. This represents the energy needed to have effective collisions between reactant particles. This raises the level of PE in the reaction to the Heat of Activated Complex (intermediate) level.
3) The activated complex is very temporary and breaks down to form the products. This lowers the level of PE to the Heat of Products level.

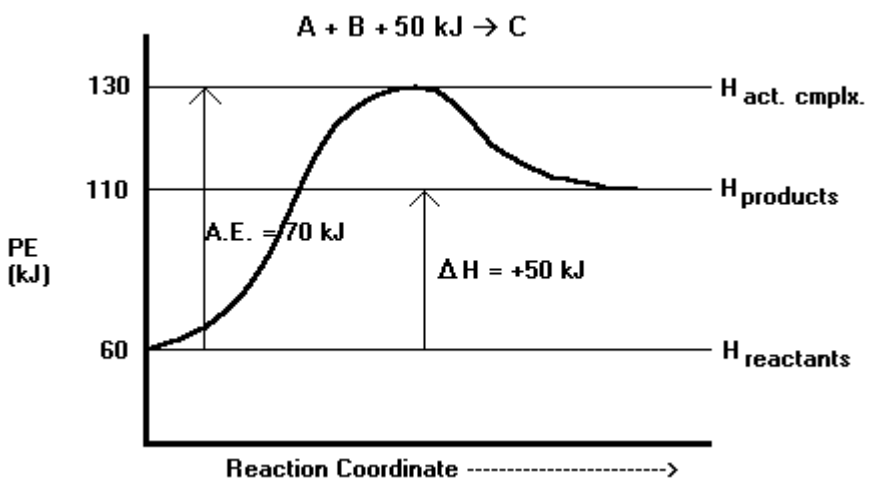
There are seven things that must be labeled in a PE Diagram:

1) The Axes (Y axis is **PE in kJ** and the X axis is the **Reaction Coordinate**…a fancy way for saying unmeasured time, or "as the reaction goes from start to finish". The Reaction Coordinate has no units.
2) The PE Levels: **Heat of Reactants**, **Heat of Products** and **Heat of Activated Complex**
3) The energy changes: **activation energy** (arrow from Heat of Reactants to Heat of Activated Complex) and **ΔH** (arrow from Heat of Reactants to Heat of Products).

1) Endothermic: Energy is absorbed by the reactants, so the net amount of potential energy increases.

For the reaction A + B + 50 kJ → C:

Experimentation has determined that the combined heats of A and B is 60 kJ. This is the Heat of Reactants. It has also been determined that the heat of C is 110 kJ. This is the Heat of Products. Further experimentation shows that the reactants require 70 kJ of energy be added to them in order to react. This is the Activation Energy (A.E.). Adding this amount of energy to the reactants yields the activated complex, which has its own Heat of Activated Complex, which is always the highest energy level in any reaction. Since the reaction started at 60 kJ and ended at 110 kJ, there is a net increase of 50 kJ in this reaction, called the ΔH. Below is a properly labeled PE Diagram for this reaction:



If a catalyst is added to this reaction, it will decrease the activation energy by removing steps from the mechanism. As a result, the Heat of the Activated Complex will also decrease. The opposite will happen if an inhibitor is added.

Note these things from the above graphic example:

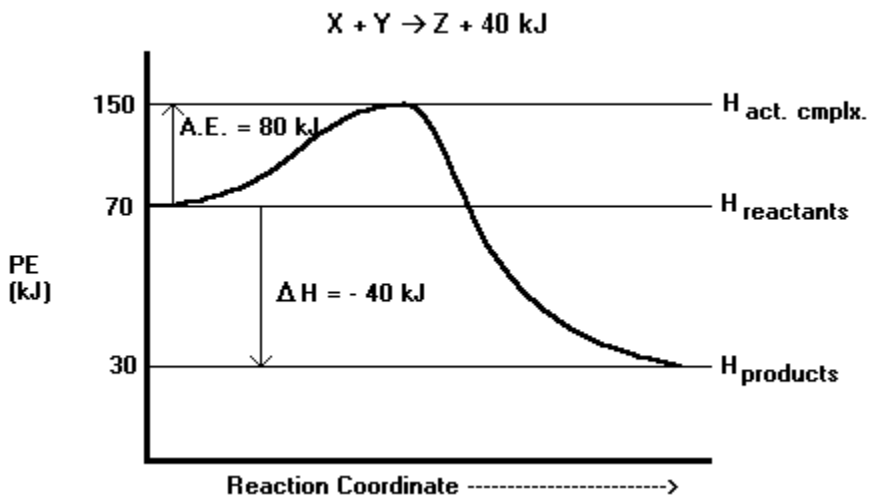
1) There is a net increase in potential energy, absorbed from the surrounding environment's kinetic energy. The temperature (which, as you know, measured the average kinetic energy) of the surrounding environment decreases.

2) The products have more energy stored in their bonds than the reactants. This makes the products more unstable than the reactants.

2) Exothermic: Energy is released as a product, so the net amount of potential energy decreases.

For the reaction X + Y → Z + 40 kJ:

Experimentation has determined that the combined heats of X and Y is 70 kJ. This is the Heat of Reactants. It has also been determined that the heat of C is 30 kJ. This is the Heat of Products. Further experimentation shows that the reactants require 80 kJ of energy be added to them in order to react. This is the Activation Energy (A.E.). Adding this amount of energy to the reactants yields the activated complex, which has its own Heat of Activated Complex, which is always the highest energy level in any reaction. Since the reaction started at 70 kJ and ended at 30 kJ, there is a net decrease of 50 kJ in this reaction, called the ΔH. Below is a properly labeled PE Diagram for this reaction:



If a catalyst is added to this reaction, it will decrease the activation energy by removing steps from the mechanism. As a result, the Heat of the Activated Complex will also decrease. The opposite will happen if an inhibitor is added.

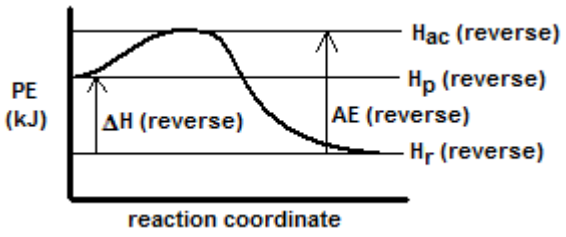
Note these things from the above graphic example:

1) There is a net decrease in potential energy, which is released into the surrounding environment as kinetic energy. The temperature (which, as you know, measured the average kinetic energy) of the surrounding environment increases.

2) The products have less energy stored in their bonds than the reactants. This makes the products more stable than the reactants.

Reactions are REVERSIBLE. Synthesis can be reversed…it's called DECOMPOSITION. With enough energy, any reaction can be reversed.

When a reaction is reversed, the products become the reactants. The reaction coordinate goes from right to left instead of left to right. Note that the exothermic forward reaction has a very small activation energy, but that the reverse reaction (being endothermic) has a much greater activation energy. Also note that the forward reaction's ΔH arrow should be a downwards one, as the forward reaction goes from higher PE to lower PE. On this diagram, the arrow for the ΔH for the reverse reaction goes UP instead.



3) Equilibrium Systems (HW: p. 27, 28)

Essential Question: How have humans impacted the equilibrium system that is the biosphere?

EQUILIBRIUM: a state of **rate** balance between two opposing changes. **The rate of the forward change is equal to the rate of the reverse change.**

Most reactions are reversible:

A + B → C + D + energy forward
C + D + energy → A + B reverse

A + B ⇔ C + D + energy when the rate of the forward reaction equals the rate of the reverse reaction, a state of equilibrium is reached. The double arrow is used to indicate that BOTH reactions are occurring simultaneously.

Forward reaction: N_2 (g) + 3 H_2 (g) → 2 NH_3 (g) + 92 kJ

Reverse reaction would be: 2 NH_3 (g) + 92 kJ → N_2 (g) + 3 H_2 (g)

Equilibrium is written as: **N_2 (g) + 3 H_2 (g) ⇔ 2 NH_3 (g) + 92 kJ**

Imagine walking up a down escalator. Now, walk fast enough so that the rate of you going up is equal to the rate of the escalator going down. You have now reached dynamic equilibrium. Even though you appear to onlookers to be going nowhere, you are still moving, and so is the escalator.

Imagine walking on an exercise treadmill. The idea is for you to walk forward as fast as the treadmill's belt is moving backward. Assuming endless energy, you will be able to maintain this equilibrium forever…unless someone comes in and knocks you off, or the phone rings, an earthquake happens or a large meteor crashes into your home.

PROPERTIES OF SYSTEMS AT EQUILIBRIUM

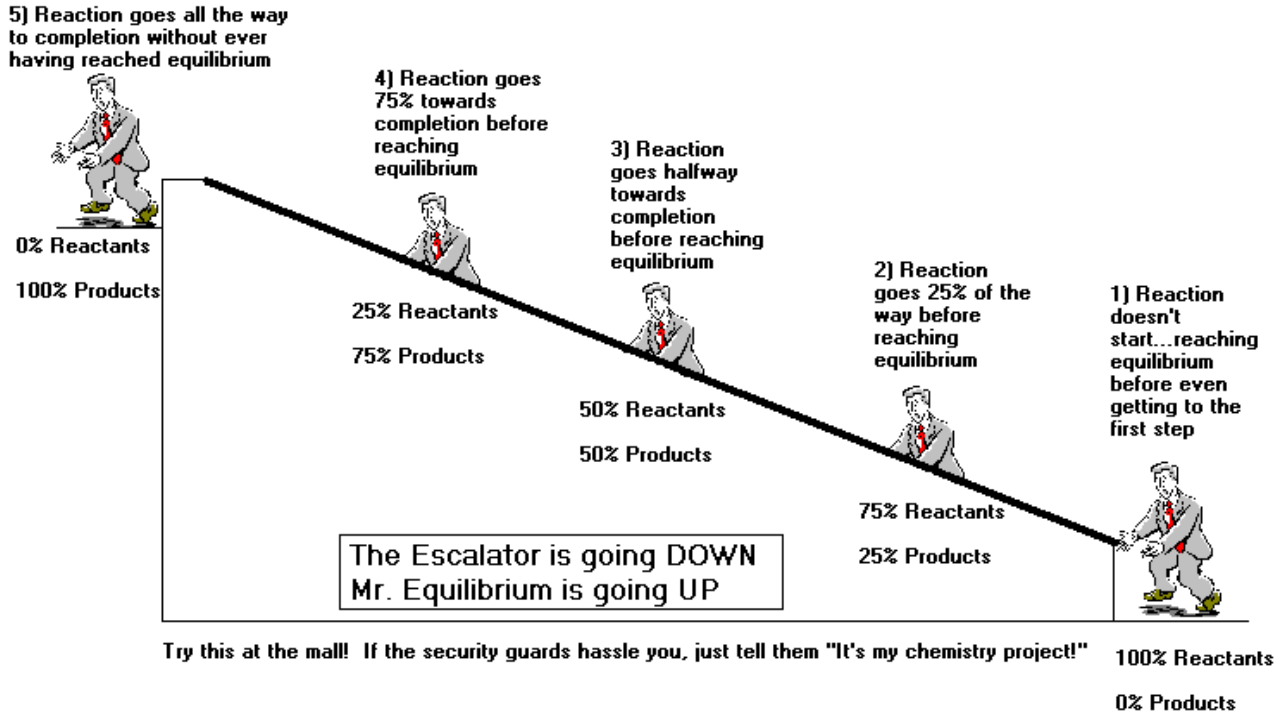
1) Equilibrium is **dynamic** (in motion), with molecules of reactant reacting to form molecules of product at the same rate at which molecules of product react to form molecules of reactant. The system is in constant motion, but the equal rates give the impression that the system is at a standstill.

2) Equilibrium can only occur in a **closed system**, that is, the system is set apart and sealed from the environment, so that nothing gets in or out.

3) As long as the system is closed, a system at equilibrium will remain that way forever. Changing any conditions of the equilibrium will change the equilibrium.

4) Equilibrium occurs at different concentrations of product and reactant. Depending on the nature of the species involved, assuming that one starts with the forward reaction, the rate of the reverse reaction will increase as product is formed by the forward reaction. When the rates are equal, equilibrium occurs. This may occur at different concentrations of product and reactant.

Going up the down escalator: This diagram shows different points at which a system can reach equilibrium:



TYPES OF EQUILIBRIUM

1) Chemical Equilibrium: The rate of the forward reaction is equal to the rate of the reverse reaction.

The Haber Process: used to manufacture ammonia. Why ammonia? To make lots of different cleaning products. This is a multi-billion dollar industry, all based on this simple equilibrium:

N_2 (g) + 3 H_2 (g) ⇔ 2 NH_3 (g) + heat

This reaction produces ammonia, but some of the ammonia decomposes to form its original elements. When the rate of synthesis equals the rate of decomposition, this system will be at equilibrium. It is possible to apply stresses to this equilibrium to force it to produce more ammonia.

The ratio of amount of product to the amount of reactant at equilibrium is called the **EQUILIBRIUM CONSTANT**. It is a number that represents how far the reaction went before reaching equilibrium.

K_{eq} = [products] / [reactants], where [ ] stands for concentration.

Mass Action Expression: a ratio of the concentration of the products to the concentration of the reactants. Used to determine the degree to which the forward reaction proceeded before equilibrium was established.

aA + bB ⇔ cC + dD, where the lower case letters represent the coefficients of the substances in the reaction

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Products over reactants, coefficients become exponents, concentrations are multiplied

For the equilibrium $2\ SO_2\ (g) + O_2\ (g) \Leftrightarrow 2\ SO_3\ (g)$, the mass action expression would be set up as:

$K_{eq} = [SO_3]^2 / [SO_2]^2\ [O_2]$

For the equilibrium $CaCl_2\ (s) \Leftrightarrow Ca^{+2}\ (aq) + 2\ Cl^{-1}\ (aq)$, the mass action expression would be set up as:

$K_{eq} = [Ca^{+2}]\ [Cl^{-1}]^2 / [CaCl_2]$

For the equilibrium $2\ O_3\ (g) \Leftrightarrow 3\ O_2\ (g)$, the mass action expression would be set up as:

$K_{eq} = [O_2]^3 / [O_3]^2$

Equilibrium Constant (K_{eq}): the numerical ratio derived from plugging the equilibrium concentrations of the products and reactants and working through the algebra of the mass-action expression

Assume that for the system at equilibrium A + B <==> 2C + energy, the equilibrium concentrations of the species are [A] = 2 M [B] = 5 M [C] = 10 M. What is K_{eq}?

K_{eq} = $[C]^2$ / [A] [B] = $[10]^2$ / [2] [5] = 100 / 10 **= 10** K_{eq} has no units, it is simply a ratio.

Evaluating K_{eq} values

The value of K_{eq} tells us how much product is formed before equilibrium is attained.

The greater the value of K_{eq}, the greater the concentration of products at equilibrium, therefore, the further the reaction went before reaching equilibrium

Imagine that escalator we looked at on the first page (diagrammed on the previous page). Imagine that the bottom of the escalator represents the 100% reactants (what you have when the reaction starts) and the top of the escalator represents 100% products (what you have when the reaction goes to completion without reaching equilibrium).

Therefore, the following chart describes K_{eq} and its relationship to how far the reaction went before reaching equilibrium:

Value of K_{eq}	**[Products] <> [Reactants]**	**…before reaching equilibrium.**
$K_{eq} = 0$	[Products] < [Reactants]	The reaction does not start at all...
K_{eq} is less than 1	[Products] < [Reactants]	The reaction goes a little way…
$K_{eq} = 1$	[Products] = [Reactants]	The reaction goes halfway…
K_{eq} is more than 1	[Products] > [Reactants]	The reaction goes most of the way…
K_{eq} = infinity	[Products] > [Reactants]	The reaction goes to completion…

Place the following equilibrium constants in order from which system goes the least far towards completion before reaching equilibrium to which system goes the furthest towards completion before reaching equilibrium:

a) $K_{eq} = 3.4 \times 10^{-5}$ b) $K_{eq} = 5.7 \times 10^{7}$ c) $K_{eq} = 9.3 \times 10^{-9}$ d) $K_{eq} = 2.1 \times 10^{9}$

Correct order: Go by exponents first. **c, a, b, d**

2) Solution Equilibrium: formed when a solution is saturated. The rate of dissolving equals the rate of precipitating.

$NaCl\ (s) \Leftrightarrow Na^{+1}\ (aq) + Cl^{-1}\ (aq)$

When sodium chloride is first placed in the water, the salt dissolves. As the concentration of dissolved ions increases, some of those dissolved ions will rejoin each other and form a precipitate, which is almost immediately re-dissolved. Eventually, all of the water molecules will be engaged in holding ions apart and no more salt can go into solution until some ions come out of solution as precipitate. The rate of dissolving equals the rate of precipitating. This is called a saturated solution. If you place a salt cube in a beaker of saturated sodium chloride solution, the cube will change shape over time as ions precipitate onto the cube from solution as salt from the cube dissolves. This demonstrates very well the dynamicity of systems at equilibrium.

Dissociation Of Electrolytes (M = metal, A = nonmetal that forms anion)

$MA\ (s) \Leftrightarrow M^{+}\ (aq) + A^{-}\ (aq)$
$M_2A\ (s) \Leftrightarrow 2\ M^{+}\ (aq) + A^{-2}\ (aq)$
$MA_2\ (s) \Leftrightarrow M^{+2}\ (aq) + 2\ A^{-}\ (aq)$
$MA\ (s) \Leftrightarrow M^{+2}\ (aq) + A^{-2}\ (aq)$
$M_2A_3\ (s) \Leftrightarrow 2\ M^{+3}\ (aq) + 3\ A^{-2}\ (aq)$

Where the (s) reactants represent the undissolved solid that sits at the bottom of the container and the ions on the product side represent the dissolved ions in solution.

$NaCl\ (s) \Leftrightarrow Na^{+1}\ (aq) + Cl^{-1}\ (aq)$ $\qquad K_{eq} = [Na^{+1}]\ [Cl^{-1}] / [NaCl]$

$Li_2SO4\ (s) \Leftrightarrow 2\ Li^{+1}\ (aq) + SO_4^{-2}\ (aq)$ $\qquad K_{eq} = [Li^{+1}]^2\ [SO_4^{-2}] / [Li_2SO_4]$

$Mg(NO_3)_2\ (s) \Leftrightarrow Mg^{+2}\ (aq) + 2\ NO_3^{-1}\ (aq)$ $\qquad Keq = [Mg^{+2}]\ [NO_3^{-1}]^2 / [Mg(NO_3)_2]$

The higher the Keq for the dissolving is, the more product that is formed and therefore the more ions that are dissolved in the solvent the higher the solubility.

SOLUBILITY PRODUCT CONSTANT

Some salts have very strong attractions between their ions, and it takes a lot of solvent molecules to break them apart. For these solutions, solution equilibrium is established at a low concentration of dissolved ions. The concentration is so small that the change is insignificant when compared to the concentration of undissolved solid. It's kind of like taking a dump truck full of the ionic compound and dumping it into a pond. If it is nearly insoluble, perhaps only a cup or so of the salt will be enough to saturate the whole lake, and any more would form a precipitate. Since the concentration of dissolved ions is so tiny, the K_{eq} of all salts of this type (called mostly insoluble) would = 0. Since this would be of no use to us in comparing relative solubilities of these mostly insoluble salts. Instead, we use the equilibrium constant **K_{sp}, the solubility product constant**. This constant consists of the concentrations of the dissolved ions, and is used for comparing the relative solubilities of mostly insoluble salts. The concentration of undissolved salt is ignored.

$K_{sp} = [M^{+}]\ [A^{-}]$

$AgCl\ (s) \Leftrightarrow Ag^{+1}\ (aq) + Cl^{-1}\ (aq)$ $\qquad K_{sp} = [Ag^{+1}]\ [Cl^{-1}]$

$Li_2CO_3\ (s) \Leftrightarrow 2\ Li^{+1}\ (aq) + CO_3^{-2}\ (aq)$ $\qquad K_{sp} = [Li^{+1}]^2\ [CO_3^{-2}]$

The more soluble the salt is, the higher the concentration of dissolved ions will be. Since larger numbers will be multiplied together, the value of Ksp will be larger in a more soluble salt.

AE Reference Table D

Solubility Product Constants for Nearly Insoluble Salts at 1 atm and 298 K

Adapted from New York State Chemistry Regents Reference Tables, 1987 Revision, Reference Table M

Salt	Solubility Product Constant, K_{sp}
AgBr	5.0×10^{-13}
AgCl	1.8×10^{-10}
Ag_2CrO_4	1.1×10^{-12}
AgI	8.3×10^{-17}
$BaSO_4$	1.1×10^{-10}
$CaSO_4$	9.1×10^{-6}
Li_2CO_3	2.5×10^{-2}
$PbCl_2$	1.6×10^{-5}
$PbCO_3$	7.4×10^{-14}
$PbCrO_4$	2.8×10^{-13}
PbI_2	7.1×10^{-9}
$ZnCO_3$	1.4×10^{-11}

$CaSO_4$ (Ksp = 9.1×10^{6}) is a more soluble salt than $PbCO_3$ (Ksp = 7.4×10^{14}) but a less soluble salt than $PbCl_2$ (Ksp = 1.6×10^{5}).

3) Physical Equilibrium (Phase Equilibrium): The rate of the forward phase change equals the rate of the reverse phase change.

This takes place at the phase change temperature. The melting point of water is $0^{o}C$. At that temperature, H_2O (s) molecules undergo melting at the same rate as H_2O (l) molecules undergo freezing.

4) Will A Reaction Happen On Its Own Once Started? (HW: p. 29, 30)

Essential Question: What do you do when mom says "no" but dad says "yes"?

SPONTANEOUS CHEMICAL CHANGES - reactions that proceed of their own accord once initiated. These reactions are handy for manufacturing processes! Imagine…what will cost less money to make; a product formed from a reaction that happens all by itself once started, or a product that requires a constant addition of energy to manufacture? If you can find a spontaneous reaction to make your product, you can charge less for it…or invest the difference into research and development into new products!

In order for a chemical reaction to be spontaneous, there has to be a balance between two factors:

1) ENTHALPY - the heat content of the system. Nature favors reactions that undergo a decrease in enthalpy.

When you let go of a ball that you hold in your hand, it falls. This is a spontaneous decrease in **enthalpy**.

Nature favors reactions that have a net **decrease** in PE, so EXOTHERMIC reactions are favored. Most exothermic reactions are spontaneous. Most endothermic reactions are nonspontaneous, and they require a constant input of energy to keep them going.

Table I
Heats of Reaction at 101.3 kPa and 298 K

$C(s) + O_2(g) \longrightarrow CO_2(g)$	−393.5

*Minus sign indicates an exothermic reaction.

This reaction is exothermic, and is therefore FAVORED.

Table I
Heats of Reaction at 101.3 kPa and 298 K

$N_2(g) + O_2(g) \longrightarrow 2NO(g)$	+182.6

*Minus sign indicates an exothermic reaction.

This reaction is endothermic, and is therefore UNFAVORED.

Imagine you are on a bike at the top of a hill. Once you kick off, you can go down the hill with no further input of energy. This is a spontaneous exothermic change.

Imagine you are on a bike at the bottom of a hill. To get to the top, you have to continuously put in energy. If you stop, you will slide back to the bottom of the hill. This is a nonspontaneous endothermic change.

Once a match is struck, it continues burning on its own, without any further input of energy, until the reactants have completely reacted. This is a spontaneous exothermic change.

To decompose water into hydrogen and oxygen (as done in an earlier demo) requires constant input of energy. Once energy input is stopped, the reaction will stop and ,in many cases, reverse itself.

2) ENTROPY - the randomness (disorder) of the system. Nature favors reactions that undergo an INCREASE in entropy.

Substances undergo an increase in entropy as the temperature increases, as evidenced by the organization of particles in the various phases of matter at the different temperatures. Since entropy increases as temperature increases, the gas phase has the most entropy and the solid phase has the least entropy. Gas molecules move randomly, and solid molecules are locked into regular-shaped crystal lattices.

Nature favors reactions that INCREASE IN PHASE.

$$2C(s) + 3H_2(g) \longrightarrow C_2H_6(g)$$

This reaction starts with solid and gas, and ends up as all gas. The entropy INCREASES, and this is favored.

$$4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$$

This reaction starts as a solid and a gas, and ends up as all solid. The entropy DECREASES, and this is UNFAVORED.

Spontaneous Reactions: in order for a reaction to be spontaneous, nature has to favor the factors. If both factors are unfavored, the reaction will be nonspontaneous.

1) If BOTH factors are FAVORED, the reaction is SPONTANEOUS at ALL temperatures.

$$2C(s) + 3H_2(g) \longrightarrow C_2H_6(g) \qquad -84.0$$

This reaction has a $-\Delta H$. This reaction is EXOTHERMIC, which is ***favored***.

This reaction starts with a solid and a gas, and ends up as all gas. This reaction increases in entropy, which is ***favored***.

Since both factors are favored, this reaction will ALWAYS be spontaneous, at all temperatures.

2) If BOTH factors are UNFAVORED, the reaction is NONSPONTANEOUS at ALL temperatures. The only way to make these reactions happen is to constantly put in energy.

$$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad +66.4$$

This reaction has a $+\Delta H$. This reaction is ENDOTHERMIC, which is ***unfavored***.

This reaction starts with three moles of gas and ends up with only 2 moles of gas. Due to there being less gas flying around, the ENTROPY DECREASES, which is ***unfavored***.

Since both factors are unfavored, this reaction will ALWAYS be nonspontaneous at all temperatures. In order to turn nitrogen and oxygen into nitrogen dioxide, energy must be constantly put in to the reaction.

3) If ENTHALPY is FAVORED, but ENTROPY is UNFAVORED, then the reaction will only be spontaneous at LOW temperatures. Above a certain temperature, the reaction will stop being spontaneous.

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g) \qquad -566.0$$

This reaction has a $-\Delta H$. This reaction is EXOTHERMIC, which is ***favored***.

This reaction starts with a solid and a gas and ends u p as a solid. The ENTROPY DECREASES, which is ***unfavored***.

This reaction will only be spontaneous at LOW temperatures. .

4) If ENTHALPY is UNFAVORED, but ENTROPY is FAVORED, then the reaction will only be spontaneous at HIGH temperatures. Below a certain temperature, the reaction will stop being spontaneous.

$$NH_4NO_3(s) \xrightarrow{H_2O} NH_4^+(aq) + NO_3^-(aq) \qquad +25.69$$

This reaction has a $+\Delta H$. This reaction is ENDOTHERMIC, which is ***unfavored***.

This reaction starts out as a solid, but then dissolves into ions that are free to move around. Entropy increases, which is ***favored***.

This is very typical of dissolving salts in water. Often, the change is endothermic, but the change in entropy is high enough to overcome that. This is one reason why salts are more soluble at higher temperatures!

<u>Why does water ice melt at temperatures above 0°C?</u>

H_2O (s) → H_2O (l) +6.01 kJ (334 J/g X 18.0 g/mole)

This change has a $+\Delta H$ (heat of fusion). This is ENDOTHERMIC, which is ***unfavored***.

This change starts with a solid and ends up as a gas. The entropy increases, which is ***favored***.

These kinds of changes are spontaneous at HIGH temperatures (see #4, above). This means that this change is nonspontaneous at temperatures below 0°C, but from 0°C on up, this reaction will take place without having to add any energy. **This is why the melting point of water is 0°C!**

Gibbs Free Energy: energy available to do work in a reaction. Nature favors a decrease in free energy.

When you start mowing the lawn, you have a certain amount of energy. As you mow the lawn, your energy reserves decrease. You have less energy available to do work. You are expending your potential energy (exothermic, favored) and your body temperature is increasing (increase in entropy, favored). Nature therefore favors this change.

The two thermodynamic quantities of enthalpy change (ΔH) and entropy change (ΔS) are related by the Gibbs Free Energy Equation, $\Delta G = \Delta H - T \Delta S$.
Why $T \Delta S$? Because ΔS is measured in kJ/K and you need to cancel out the K…which is temperature!

A/E Reference Table C

Energies of Formation of Compounds at 1 atm and 298 K

(Adapted from New York State Reference Table G, January 1987 Revision. Energies in kcal/mol converted to kJ/mol, rounded to nearest whole number)

All of the compounds below were formed by synthesis reaction. To determine the energies of decomposition, simply reverse the signs.

Compound	Enthalpy of Formation (ΔH_f) in kJ/mol	Free Energy of Formation (ΔG_f) in KJ/mol
Al_2O_3 (s)	-1674	-1581
NH_3 (g)	-46	-16
$BaSO_4$ (s)	-1472	-1361
$Ca(OH)_2$ (s)	-985	-898
CO_2 (g)	-393	-394
CO (g)	-110.	-137
$CuSO_4$ (s)	-771	-661
C_2H_6 (g)	-84	-33
C_2H_4 (g)	+52	+68
C_2H_2 (g)	+227	+209
HF (g)	-271	-273
HI (g)	+26	+2
ICl (g)	+18	-5
PbO (s)	-215	-188
MgO (s)	-601	-569
NO (g)	+90.	+87
NO_2 (g)	+33	+51
KCl (s)	-436	-409
NaCl (s)	-411	-384
SO_2 (g)	-296	-300.
H_2O (g)	-242	-228
H_2O (l)	-285	-237

The quantity ΔG is Gibbs Free Energy, an indication of the total available energy in the reaction. **Nature favors a decrease in the total available energy**, so when conditions of enthalpy and entropy are such that ΔG is negative, the reaction will be spontaneous. These conditions, which are adapted from the charts on the previous page, will exist when:

a) ΔH is negative (favored) and $T\Delta S$ is positive (favored):

Reaction goes to completion, spontaneous at ALL temperatures

b) ΔH is negative (favored) and $T\Delta S$ is negative (unfavored) with less magnitude than ΔH

Reaction is spontaneous at LOW temperatures, can reach equilibrium

c) ΔH is positive (unfavored)and $T\Delta S$ is positive (favored) with greater magnitude than ΔH

Reaction is spontaneous at HIGH temperatures, can reach equilibrium

If ΔH is positive and $T\Delta S$ is negative, the reaction will never be spontaneous at ANY temperature, and will never reach equilibrium.

THINGS YOU CAN DO WITH THE GIBBS FREE ENERGY EQUATION

1) Calculating ΔG

For the fictitious reaction A + B → C + 30.0 kJ at 25°C (298 K):

If ΔH for this reaction is –30.0 kJ and ΔS is –0.010 kJ/K, calculate ΔG and determine if this reaction is spontaneous or nonspontaneous.

$\Delta G = \Delta H - T \Delta S$ = (-30.0 kJ) – [(298 K) x (-0.010 kJ/K)] = **-27 kJ**

Since ΔG is negative, this reaction is spontaneous.

2) Using AE Reference Table C To Determine Spontaneity of Reactions

If a reaction has a negative ΔG listed in this table, the reaction is spontaneous. Reversing the reaction will require the addition of energy.

If a reaction has a positive ΔG listed in this table, the reaction is nonspontaneous. Reversing the reaction will result in a spontaneous reaction.

Discharging a battery is spontaneous, and therefore has a negative ΔG. Recharging the battery is the reverse reaction, and requires constant input of energy from a recharger to work, therefore has a positive ΔG.

According to AE Table B, forming one mole of NH_3 has a ΔG of –16 kJ, and is therefore spontaneous. Decomposing NH_3, on the other hand, would have a ΔG or +16 kJ and would require at least that amount of energy to force it to work.

3) Determining a Reaction's ΔS

AE Reference Table C gives the ΔH, ΔG and temperature. Using these, we can determine the ΔS by rearranging the Gibbs equation using simple algebra thusly:

1) Original equation: $\Delta G = \Delta H - T \Delta S$
2) adding $T \Delta S$ to each side gives $\Delta G + T \Delta S = \Delta H$
3) subtracting ΔG from each side gives $T \Delta S = \Delta H - \Delta G$
4) Dividing both sides by T gives $\mathbf{\Delta S = (\Delta H - \Delta G)/T}$

Calculate the ΔS for CO.

$\Delta S = (\Delta H - \Delta G)/T = [(-110 \text{ kJ}) – (-137 \text{ kJ})] / 298 \text{ K} =$ **+0.0906 kJ/K**.

Because ΔH is negative (favored) and ΔS is positive (favored), this reaction will be spontaneous at all temperatures.

Calculate the ΔS for C_2H_4.

$\Delta S = (\Delta H - \Delta G)/T = [(+52 \text{ kJ}) – (+168 \text{ kJ})] / 298 \text{ K} =$ **-0.39 kJ/K**.

Because ΔH is positive (unfavored) and ΔS is negative (unfavored), this reaction will never be spontaneous at any temperature. It will always be nonspontaneous.

Calculate the ΔS for ICl.

$\Delta S = (\Delta H - \Delta G)/T = [(+18 \text{ kJ}) – (-5 \text{ kJ})] / 298 \text{ K} =$ **+0.044 kJ/K**.

Because ΔH is positive (unfavored) and ΔS is positive (favored), this reaction will be spontaneous at temperatures at which $T\Delta S$ is larger than ΔH and nonspontaneous at temperatures at which $T\Delta S$ is smaller than ΔH.

4) Determining the temperature at which a reaction becomes spontaneous (Equilibrium temperature)

At equilibrium, both the forward and reverse reactions are spontaneous, and occur at the same rate. ΔG equals 0 at this temperature, which means that the reaction can go forward or reverse.

1) Original equation: $\Delta G = \Delta H - T \Delta S$
2) Set ΔG equal to zero: $0 = \Delta H - T \Delta S$
3) Add $T \Delta S$ to both sides: $T \Delta S = \Delta H$
4) Divide both sides by ΔS: $\mathbf{T = \Delta H/\Delta S}$

Determine the temperature at which ICl reaches equilibrium.

$T = \Delta H/\Delta S = (+18 \text{ kJ}) / (+0.044 \text{ kJ/K}) =$ **410 K**

Since ΔS is positive (favored), increasing the temperature will make the reaction more favorable. Therefore, this reaction is spontaneous at all temperatures above 410 K and nonspontaneous at all temperatures below 410 K.

5) Changing Equilibrium (HW: p. 31, 32)

Essential Question: How can you make an equilibrium work to your advantage?

Equilibrium systems are dynamic, meaning they are constantly in motion. Equilibrium must be in a closed system, or the system cannot remain at equilibrium. But sometimes you don't want your system to be at equilibrium! How irritating it would be if you went to all the trouble to make a product, just to have it decompose back into the reactants again and reach equilibrium! How can you force a system at equilibrium to do what YOU want it to? That's right! Make equilibrium work for YOU!!!

Le Chatelier's Principle

If a system at equilibrium is subjected to a stress (any factor that affects reaction rate, like temperature, concentration and pressure for gases), the equilibrium will shift in a way that relieves the stress, in the direction of whichever reaction was made faster by the stress. This will cause a change in concentration of both the reactants and products until the equilibrium is re-established.

FORWARD SHIFT →

Reactants ⇔ Products

← REVERSE SHIFT

Stress	Shift	Change In Concentration
Adding reactant	This increases the number of collisions between reactant particles, making the **FORWARD** reaction go faster.	Reactants: decrease Products: increase
Removing reactant	This decreases the number of collisions between reactant particles, making the **REVERSE** reaction faster than the forward reaction.	Reactants: increase Products: decrease
Adding product	This increases the number of collisions between product particles, making the **REVERSE** reaction go faster.	Reactants: increase Products: decrease
Removing product	This decreases the number of collisions between product particles, making the **FORWARD** reaction faster than the reverse reaction.	Reactants: decrease Products: increase
Increasing Temperature	This favors the ENDOTHERMIC reaction, causing the equilibrium to shift **AWAY FROM THE SIDE WITH HEAT** to absorb the excess energy,	This depends on the direction of shift. **IF THE SHIFT IS TOWARDS THE PRODUCTS, THEN PRODUCTS WILL INCREASE AND REACTANTS WILL DECREASE.** **IF THE SHIFT IS TOWARDS THE REACTANTS, THEN REACTANTS WILL INCREASE AND PRODUCTS WILL DECREASE.**
Decreasing Temperature	This favors the EXOTHERMIC reaction, causing the equilibrium to shift **TOWARDS FROM THE SIDE WITH HEAT** to release energy,	
Increasing Pressure (gases only)	This causes the system to bring the pressure back down by shifting **TOWARDS THE SIDE WITH FEWER MOLES OF GAS** on it.	
Decreasing Pressure (gases only)	This causes the system to bring the pressure back UP by shifting **TOWARDS THE SIDE WITH MORE MOLES OF GAS** on it.	

Catalysts, inhibitors and surface area have NO EFFECT on systems at equilibrium. They allow a system to get TO equilibrium faster, but once there, they affect both reactions equally, meaning that the equilibrium will not be changed.

Application of Determining Direction of Equilibrium Shift

For the equilibrium N_2 (g) + 3 H_2 (g) ⇔ 2 NH_3 (g) + heat:

Stress	Shift	Change In Concentration
Add N_2 (g)	FORWARDS Add a reactant, shift to products	N_2: decreases H_2: decreases NH_3: increases
Remove N_2 (g)	REVERSE Remove a reactant, shift to reactants	N_2: increases H_2: increases NH_3: decreases
Add H_2 (g)	FORWARDS Add a reactant, shift to products	N_2: decreases H_2: decreases NH_3:
Remove H_2 (g)	REVERSE Remove a reactant, shift to reactants	N_2: increases H_2: increases NH_3: decreases
Add NH_3 (g)	REVERSE Add a product, shift to reactants	N_2: increases H_2: increases NH_3: decreases
Remove NH_3 (g)	FORWARDS Remove a product, shift to products	N_2: decreases H_2: decreases NH_3: increases
Increase Temperature	REVERSE Increase T, shift away from heat	N_2: increases H_2: increases NH_3: decreases
Decrease Temperature	FORWARDS Decrease T, shift towards heat	N_2: decreases H_2: decreases NH_3: increases
Increase Pressure	FORWARDS Increase P, shift to side with fewer moles of gas	N_2: decreases H_2: decreases NH_3: increases
Decrease Pressure	REVERSE Decrease P, shift to side with more moles of gas	N_2: increases H_2: increases NH_3: decreases

For the solution equilibrium KNO_3 (s) + 34.89 kJ ⇔ K^{+1} (aq) + NO_3^{-1} (aq):

What happens to the concentration of K^{+1} (aq) when the temperature is increased?

Stress: Increasing temperature
Shift: Away from heat, FORWARDS
Change In Concentration: Since the shift is TOWARDS K^{+1}, **the concentration of K^{+1} INCREASES.**

What happens to the concentration of NO_3^{-1} (aq) when the temperature is decreased?

Stress: Decreasing temperature
Shift: Towards heat, REVERSE
Change In Concentration: Since the shift is AWAY from NO_3^{-1}, **the concentration of NO_3^{-1} DECREASES.**

For the equilibrium $2\ CO\ (g) + O_2\ (g) \Leftrightarrow 2\ CO_2\ (g) + 566\ kJ$:

What happens to the concentration of CO_2 (g) when CO (g) is added to the equilibrium system?

Stress: Increasing concentration of a REACTANT
Shift: Away from reactant, FORWARDS
Change In Concentration: Since the shift is TOWARDS CO_2, **the concentration of CO_2 INCREASES.**

What happens to the concentration of O_2 (g) when CO_2 (g) is removed from the equilibrium system?

Stress: decreasing concentration of a PRODUCT
Shift: Towards product, FORWARDS
Change In Concentration: Since the shift is AWAY from O_2, **the concentration of O_2 DECREASES.**

What happens to the concentration of CO (g) when pressure is increased?

Stress: Increasing pressure
Shift: Towards side with fewer moles of gas, FORWARDS
Change In Concentration: Since the shift is AWAY from CO, **the concentration of CO DECREASES.**

For the equilibrium system $N_2\ (g) + 2\ O_2\ (g) + 66.4\ kJ \Leftrightarrow 2\ NO\ (g)$:

List five things that can be done that will result in an increase in the concentration of NO (g).

Desired shift: to make more NO, you must shift towards NO, so shift FORWARDS.

How can the equilibrium be shifted FORWARDS?

a) Add N_2: (adding reactant makes the reaction go forwards)
b) Add O_2: (adding reactant makes the reaction go forwards)
c) Remove NO: (removing product makes the reaction go forwards)
d) Increase Temperature: (adding heat makes the reaction shift away from heat)
e) Increase Pressure: (adding pressure shifts the equilibrium towards the side with fewer moles of gas)

For the equilibrium system $NaCl\ (s) + 3.88\ kJ \Leftrightarrow Na^{+1}\ (aq) + Cl^{-1}\ (aq)$:

List four things that can be done that will result in an increase in the concentration of NaCl (s).

Desired shift: to make more NaCl, you must shift towards NaCl, so shift REVERSE.

a) Remove NaCl: (removing a reactant makes the reaction shift reverse)
b) Remove heat: (removing heat makes the reaction shift towards heat)
c) Increase Na^{+1} (by adding a salt solution that contains Na^{+1}): (adding a product makes the reaction shift reverse)
d) Increase Cl^{-1} (by adding a salt solution that contains Cl^{-1}): (adding a product makes the reaction shift reverse)

Student Name:_____ Grades: _____, _____, _____, _____, _____
Kinetics PE Diag Equilib Spont LeChat

1) Kinetics Homework

1) Create a possible mechanism for the reaction:

$$C + S_2 \rightarrow CS_2$$

Step 1) break any existing bonds:_____→ _____

Step 2) Two atoms combine to form the intermediate:_____ → _____

Step 3) The last atom combines with the intermediate to form the final compound: _____→_____

2) Explain how the following will affect the reaction rate (increase, decrease, remains the same):

a) Adding N_2 (g) to the reaction $N_2 + 3\ H_2 \rightarrow 2\ NH_3$ (g) _____

b) Removing H_2 (g) from the reaction $N_2 + 3\ H_2 \rightarrow 2\ NH_3$ (g) _____

c) Increasing the pressure on the reaction N_2 (g) + 3 H_2 (g) → 2 NH_3 (g) _____

d) Using powdered NaCl instead of large crystal NaCl in a reaction _____

e) Adding water catalyst to a double replacement reaction _____

f) Adding $CuSO_4$ inhibitor to a reaction of acid and metal _____

g) Increasing pressure on Na (s) + $ZnSO_4$ (aq) → Na_2SO_4 (aq) + Zn (s) _____

3) Given the following reaction mechanism and observed rates, circle the rate-determining step:

Step	Time
1	0.0002 sec
2	0.0343 sec
3	4.7771 sec
4	0.0089 sec
5	0.9880 sec

3) Place three 5.0 gram samples of sugar in three different 50.0 mL samples of pure water in three different insulated cups, all at 50.0 °C. Sample A is a single cube of sugar, Sample B is granulated sugar and Sample C is powdered sugar. Which sample will dissolve slowest? Explain, in terms of *effective collisions*.

4) Place three identical 5.0 g cubes of sugar into three different 50.0 mL samples of pure water in three different insulated cups. Cup A contains water at 20°C, Cup B contains water at 10°C and Cup C contains water at 40°C. In which cup will the sugar dissolve fastest? Explain, in terms of *effective collisions*.

2) Potential Energy Diagrams Homework

A) Here we have three reactions with two blank spaces each. Energy in kJ belongs in one of the two spaces. Based on Reference Table I, place the heat of reaction in the appropriate blank space and leave the other space blank. Also state if the reaction is EXOthermic or ENDOthermic and identify the products formed as either being STABLE or UNSTABLE compared to the reactants that formed them.

Reaction	EXOthermic or ENDOthermic?	STABLE or UNSTABLE products?
N_2 (g) + 3 H_2 (g) + _____ → 2 NH_3 (g) + _____		
N_2 (g) + 2 O_2 (g) + _____ → 2 NO_2 (g) + _____		
H_2 (g) + I_2 + _____ (g) → 2 HI (g) + _____		

B) Answer the following questions, based on Reference Table I for the formation of NO (g) from its elements:

1) How many moles of NO are formed in the reaction shown on Table I?_____

2) What is the heat of synthesis, in kJ/mole for NO? Show your work:_____=_____

3) How many kJ are absorbed when 4.5 moles of NO are formed? Show work:_____=_____

4) How many kJ are released when 2.7 moles of NO are decomposed?_____=_____

5) 0.020 grams of N_2 (g) are completely reacted with O_2 to form NO.

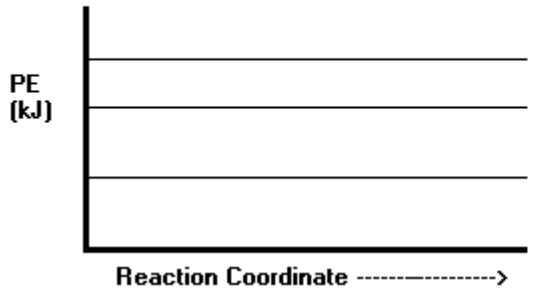
a) How many moles of NO will form?_____=_____

b) How many kJ of heat will be absorbed?_____=_____

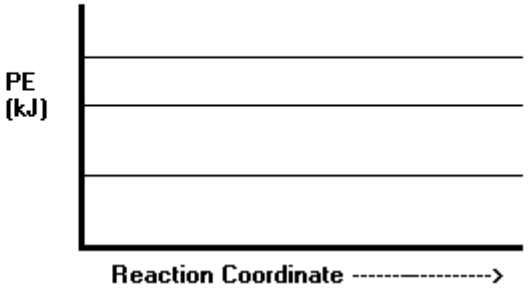
c) If this reaction is carried out in 50.0 g of water at 20.0°C, what will the final temperature of the water be?

6) For the following blank PE Diagrams, sketch the shape of the noted curves and label the $H_{reactants}$, $H_{products}$, $H_{activated\ complex}$, activation energy and ΔH. You do not have to put any numbers in.

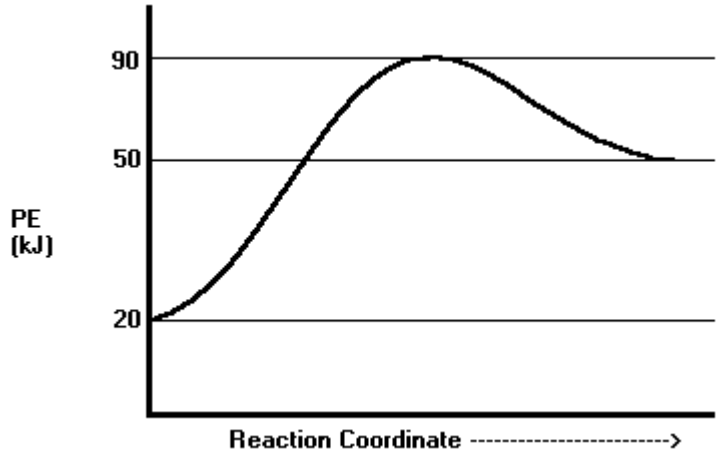
a) Draw and label the PE Diagram for the FORWARD reaction.



b) Draw and label the PE Diagram for the REVERSE reaction.



C) For the following PE Diagram, answer the questions below:



_____1) What is the heat of reactants?
a) 20 kJ b) 50 kJ c) 90 KJ d) 30 kJ

_____2) What is the heat of the products?
a) 20 kJ b) 50 kJ c) 90 KJ d) 30 kJ

_____3) What is the heat of the activated complex?
a) 20 kJ b) 50 kJ c) 90 KJ d) 30 kJ

_____4) What is the activation energy for this reaction?
a) 90 kJ b) 70 kJ c) 30 KJ d) 40 kJ

_____5) What is the ΔH of this reaction?
a) + 30 kJ b) – 30 kJ c) +70 kJ d) -70 kJ

_____6) What type of reaction is this?
a) exothermic b) endothermic c) both d) neither

_____7) What is the activation energy for the reverse reaction?
a) 90 kJ b) 70 kJ c) 30 KJ d) 40 kJ

_____8) What is the ΔH of the reverse reaction?
a) + 30 kJ b) – 30 kJ c) +70 kJ d) -70 kJ

9) Draw a dashed curved line on the above diagram to indicate what the PE curve would look like if an inhibitor was added to this reaction.

10) Is this reaction exothermic or endothermic? How can you tell?_____

11) Which is more stable in this reaction; the reactants or the products? How can you tell?_____

_____

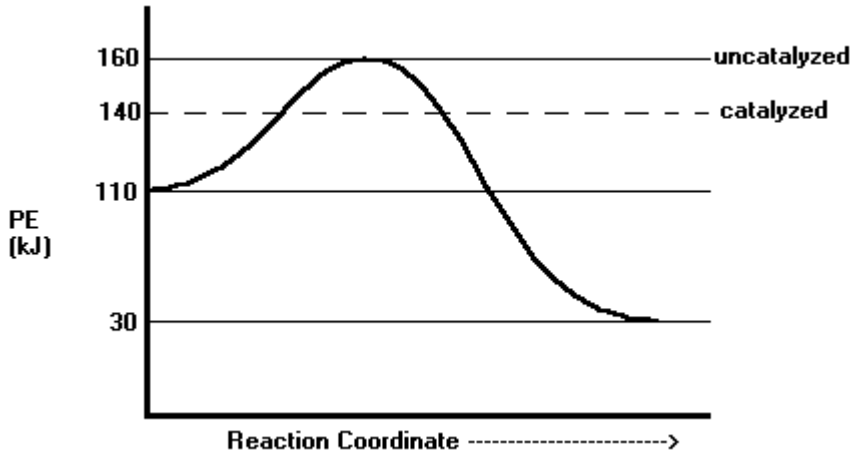
12) If this reaction is carried out in a tub of water at 25°C, will the temperature of the water increase or decrease? Why?

_____

13) Will this reaction occur if the reactants are given 40 kJ of activation energy? Explain._____

_____

D) For the following PE Diagram, answer the questions below:



_____1) What is the heat of reactants?
a) 30 kJ b) 110 kJ c) 140 KJ d) 160 kJ

_____2) What is the heat of the products?
a) 30 kJ b) 110 kJ c) 140 KJ d) 160 kJ

_____3) What is the heat of the activated complex for the uncatalyzed reaction?
a) 30 kJ b) 110 kJ c) 140 KJ d) 160 kJ

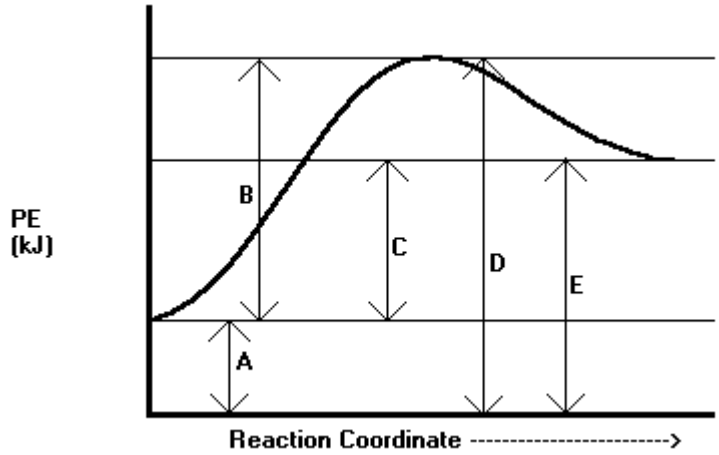
_____4) What is the activation energy for the catalyzed reaction?
a) 30 kJ b) 110 kJ c) 140 KJ d) 160 kJ

_____5) What is the ΔH of this reaction?
a) + 80 kJ b) – 80 kJ c) +130 kJ d) -130 kJ

_____6) What type of reaction is this?
a) exothermic b) endothermic c) both d) neither

7) Draw a dashed curved line on the above diagram to indicate what the PE curve would look like if a catalyst was added to this reaction, using the catalyzed reaction line as your guide.

E) For the following PE Diagram, what does each arrow represent?



a) Heat of Reactants _____

b) Heat of Products _____

c) Activation Energy _____

d) ΔH _____

e) Heat of Act. Cmplx _____

f) Sketch a dashed line to indicate the effect of adding a catalyst.

3) Equilibrium Systems Homework

1) Write the reverse reactions for the following:

a) $2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (g) + 483.6\ kJ$ _____

b) $2\ C\ (s) + H_2\ (g) + 227.4\ kJ \rightarrow C_2H_2\ (g)$ _____

_____2) What has to be equal at equilibrium?

a) the mass of the products and reactants
b) the volume of the products and reactants
c) the concentration of the products and reactants
d) the rates of formation of the products and reactants

_____3) A stoppered bottle contains 20 grams of liquid water and 20 grams of water vapor. Does equilibrium exist?

a) Yes, the amount of each component is equal
b) Yes, the bottle is stoppered
c) Only if the rates of evaporation and precipitation are equal
d) Only if a) and b) are both true
e) Only if b) and c) are both true

_____4) What word is used to describe a solution at equilibrium?

a) saturated b) unsaturated c) supersaturated d) wet

5) Write the mass-action expressions for the following systems at equilibrium:

a) $2\ NO_2\ (g) \Leftrightarrow 2\ NO\ (g) + O_2\ (g)$

b) $N_2\ (g) + 3\ H_2\ (g) \Leftrightarrow 2\ NH_3\ (g)$

c) $Zn(NO_3)_2\ (s) \Leftrightarrow Zn^{+2}\ (aq) + 2\ NO_3^{-1}\ (aq)$

6) Given the following mass action expressions, write the equations for the equilibrium systems:

a) $K_{eq} = [N_2][O_2]^3 / [NO_3]^2$

b) $K_{eq} = [Au^{+3}][NO_3^{-1}]^3 / [Au(NO_3)_3]$

7) Given the following systems at equilibrium and the equilibrium concentrations of each species, calculate the equilibrium constant. All work must be shown.

a) $2\ NO_2\ (g) + O_2\ (g) \Leftrightarrow 2\ NO_3\ (g)$ $[NO_2] = 4.0\ M$ $[O_2] = 2.0\ M$ $[NO_3] = 1.5\ M$

8) Complete the following chart:

K_{eq} for a system at equilibrium	Are there more products or reactants at equilibrium?	How do you know?
a) 4.8×10^{-4}		
b) 7.2×10^{8}		
c) 9.8×10^{-11}		
d) 1.7×10^{15}		
e) 5.5×10^{2}		

9) Using the letters a-e from the chart above, place the K_{eq}'s in order from the reaction that goes least to completion before reaching equilibrium to the reaction that goes the most to completion before reaching equilibrium.

_____, _____, _____, _____, _____

9) For each of the following ionic compounds, write the dissociation equation and the mass-action expression for the resulting solution equilibrium for K_{sp}.

Salt	Dissociation Equilibrium	K_{sp} Expression
Na_2SO_4	Na_2SO_4 (s) ⇔ 2 Na^{+1} (aq) + SO_4^{-2} (aq)	$K_{sp} = [Na^{+1}]^2[SO_4^{-2}]$
KBr		
Li_2CO_3		
$PbCO_3$		
$PbCl_2$		
$Zn_3(PO_4)_2$		
Ag_3PO_4		

10) Place the following salts in order from least soluble to most soluble, using AE Reference Table B.

$BaSO_4$, $PbCl_2$, PbI_2, AgBr, $ZnCO_3$, Li_2CO_3, AgCl

_____, _____, _____, _____, _____, _____, _____

11) Explain why you put the salts in #2, above, in the order that you did.

4) Will A Reaction Happen On Its Own Once Started? Homework

A) Does entropy increase or decrease in the following phase changes and reactions? Are these favored or unfavored changes?

Reaction	Entropy Increase or Decrease?	Favored or Unfavored?
CO_2 (s) → CO_2 (g)		
I_2 (g) → I_2 (s)		
C (s) + O_2 (g) → CO_2 (g)		
4 Al (s) + 2 O_2 (g) → 2 Al_2O_3 (s)		
2 CO (g) + O_2 (g) → 2 CO_2 (g)		
2 H_2 (g) + O_2 (g) → 2 H_2O (l)		

B) Water freezes only at temperatures of 0°C and below: H_2O (l) → H_2O (s) + 6.01 kJ

1) Is this an increase or decrease in entropy?_____

2) Is this change favored or unfavored?_____

3) When water freezes, is this exothermic or endothermic?_____

4) Is this change favored or unfavored?_____

_____5) Which explanation correctly describes why water only spontaneously freezes at temperatures BELOW 0°C? Make sure your answer is consistent with your answers above.

a) The favored entropy factor is greater than the unfavored enthalpy factor.
b) The favored entropy factor is less than the unfavored enthalpy factor.
c) The unfavored entropy factor is greater than the favored enthalpy factor.
d) The unfavored entropy factor is less than the favored enthalpy factor.

C) You have a NiMH AAA rechargeable battery in your mp3 player. After a while, the battery indicator shows that the battery is losing its charge (running out of "juice") and needs to be recharged, which you do by placing the battery into a recharger and plugging it into the outlet in your room. After a few hours, the charger shows that the battery is now full, so you take it out and put it back in your mp3 player and rock to the tunes.

a) Is discharging the battery (by having it powered on) spontaneous or nonspontaneous? Why?

b) Is recharging the battery (by plugging it into the wall socket) spontaneous or nonspontaneous? Why?

4) For the formation of PbO:

a) Using AE Reference Table A, calculate the ΔS value for PbO.

b) Calculate the ΔG of the formation of PbO if the temperature is 400 K. Is the reaction spontaneous at this temperature?

5) For the decomposition of NO:

a) Calculate the ΔS of decomposition for NO (g) using AE Reference Table A.

b) At what temperature will the decomposition of NO reach equliibrium?

6) Using AE Reference Table A, determine if the following reactions are spontaneous or nonspontaneous at 298K:

a) $N_2 + 3\ H_2$ ---> $2\ NH_3$ _____

b) NH_3 ----> $N_2 + 3\ H_2$ _____

c) $N_2 + 2\ O_2$ ----> $2\ NO_2$ _____

d) $2\ NO_2$ ----> $N_2 + O_2$ _____

5) Changing Equilibrium Homework

A) For each of the following systems at equilibrium, predict the effect of a given change on the concentration of the specific substances. First, draw an arrow in the direction of the equilibrium shift next to the stated change.

Write **I** if the concentration increases, **D** if the concentration decreases, and **R** if the concentration remains the same.

I) $2\ NH_3\ (g) + heat \Leftrightarrow N_2\ (g) + 3\ H_2\ (g)$

1) Stress: increase in $[N_2]$. Direction of Shift:_____
What is the resulting effect on the concentration of:

a) $[NH_3]$_____

b) $[H_2]$_____

2) Stress: increase in temperature Direction of Shift:_____
What is the resulting effect on the concentration of:

a) $[N_2]$_____

b) $[NH_3]$_____

3) Stress: increase in pressure Direction of Shift:_____

a) What is the resulting effect on the number of moles of N_2_____

b) What is the resulting effect on the number of moles of NH_3_____

II) $2\ NO\ (g) \Leftrightarrow N_2\ (g) + O_2\ (g) + heat$

4) Stress: decrease in $[O_2]$ Direction of Shift:_____
What is the resulting effect on the concentration of:

a) $[N_2]$_____

b) [NO]_____

5) Stress: decrease in temperature Direction of Shift:_____
What is the resulting effect on the concentration of:

a) $[O_2]$_____

b) [NO]_____

6) Stress: increase in pressure Direction of Shift:_____

a) What is the resulting effect on the number of moles of O_2_____

b) What is the resulting effect on the number of moles of NO_____

C) Complete the following questions by CIRCLING THE ANSWER OF YOUR CHOICE:

Given the equilibrium N_2 (g) + 3 H_2 (g) ⇔ 2 NH_3 (g) + heat :

a) If N_2 is added to the system at equilibrium, which direction will the equilibrium shift?

1. Forward 2. Reverse

b) If H_2 is removed from the system at equilibrium, which direction will the equilibrium shift?

1. Forward 2. Reverse

c) If NH_3 is added to the system at equilibrium, which direction will the equilibrium shift?

1. Forward 2. Reverse

d) If temperature is decreased to the system at equilibrium, which direction will the equilibrium shift?

1. Forward 2. Reverse

e) If pressure is increased to the system at equilibrium, which direction will the equilibrium shift?

1. Forward 2. Reverse

f) If H_2 is removed from the system at equilibrium, what will happen to the concentrations of (circle your choice for each)

1. N_2 {increase} {decrease} {remain the same}

2. NH_3 {increase} {decrease} {remain the same}

g) If NH_3 is removed from the system at equilibrium, what will happen to the concentrations of (circle your choice for each)

1. N_2 {increase} {decrease} {remain the same}

2. H_2 {increase} {decrease} {remain the same}

D) Given the equilibrium system H_2 (g) + I_2 (g) + 53.0 kJ ⇔ 2 HI (g), list four things that can be done to result in an increase in the concentration of HI (g).

1)_____ 2)_____

3)_____ 4)_____

E) Given the equilibrium system NaOH (s) ⇔ Na^{+1} (aq) + OH^{-1} (aq) + 44.51 kJ, list four things that can be done to result in an increase in the concentration of NaOH (s).

1)_____ 2)_____

3)_____ 4)_____