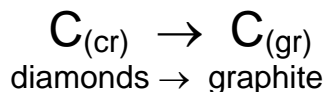




Lecture (7)

Kinetics, ElectroChem and Equilibrium

A very successful commercial claims that, "Diamonds are Forever." Nice thought but sorry, they are not. A diamond is the crystal form of carbon. But over time this crystal structure will fall apart and eventually turn into carbon in the graphite form. Luckily for the diamond sellers they will most likely never be sued for false advertising, as the rate of this reaction is VERY slow.



The study of the rates of reaction is called kinetics.

Here is another example, Ba^{+2} is toxic, but doctors give BaSO_4 to patients because the BaSO_4 is insoluble and will not dissolve quickly enough to release the toxic barium ion into your body.



Due to the equilibrium of this reaction the barium sulfate is insoluble, and will not put Ba^{+2} in the patients body.

Barium has an interesting property: it absorbs radiation. Barium shows up on x-rays very well. Just as a bone shows up on an x-ray film, wherever the barium is, it will show up. So, if you are having a problem with your intestinal tract you will be given BaSO_4 , to see if maybe your intestines are leaking into you body cavity.

So, diamond owners do not have to be worried about their diamonds turning into graphite for their mechanical pencils, as the reaction is so slow. Also, those patients having an upper GI don't have to worry about barium sulfate dissolving into toxic barium ion, as the barium sulfate will not be in their body long enough for it to dissolve.

Why Chemical Reactions Occur:

Chemical reactions occur because they are following fundamental laws of nature or because something forces them to react. So, when certain reactants are put together two options present themselves, they react or they don't.

The two fundamental laws of nature that are particularly important are:

- systems tend to attain a state of minimum energy
- systems tend to attain a state of maximum disorder



A system can be anything you designate as a system. It could be a solution in a 250 ml Erlenmeyer flask, a test tube you are heating, or your small intestines. Everything else in the universe would be considered the surroundings. So, systems tend to give energy to their surroundings and become less organized.

The energy of a system is termed enthalpy. The abbreviation is H. (unit kJ/mol)
The disorder of a system is termed entropy. The abbreviation is S. (unit kJ/mol·K)

If you think about these two laws, they follow common sense. What happens to something hot that you let sit around? It gets cold it loses enthalpy. Hot coffee can go cold in minutes. What happens to something organized if you don't do anything to it? It falls apart. A building not tended to will fall apart in months.

From these laws a system will want to lose H and gain S.

Spontaneous Reactions:

A spontaneous reaction occurs without cause favoring the formation of specific products under specific conditions. A nonspontaneous reaction **does not** occur without cause. For a nonspontaneous reaction to occur something must cause the reaction.

Josiah Willard Gibbs is one of the most influential scientists. His work spanned many fields, most specifically; math, physics and chemistry. His work in chemistry applies to the spontaneity of a reaction. He formulated an equation, which incorporated both enthalpy and entropy and set it equal to something called free energy. Even though Gibbs' work was incredibly important he only published in an obscure New England journal. The work was somewhat lost to the world until it was translated into ~~German and~~ French by Henri LeChatelier, where European scientists put this theories to work. Only after his death did the scientific community understand his real genius. The term free energy was given the abbreviation G and renamed Gibbs' Free Energy.

What Gibbs determined is that if a system frees energy, the reaction will be spontaneous.

The equation is as follows:

$$\Delta G = \Delta H - T\Delta S$$

The T stands for temperature in Kelvin. The importance of G is that it determines if a reaction will be spontaneous or nonspontaneous. If a reaction gives up free energy it is spontaneous, meaning G is negative, the reaction will occur. If a reaction takes in free energy it is nonspontaneous, under these conditions and the G is positive, the reaction does not occur. Gibbs' had formulated an expression that incorporated both laws that drive reactions, systems tend to



attain a state of minimum energy and systems tend to attain a state of maximum disorder. This equation leads to units of kJ/mol for Gibbs.

You may ask yourself, how do I know H and S? These values are found experimentally and will be in the CRC of Chemistry and Physics. Just as people experimented to determine the density of thousands of different substances, others have experimented to determine the S and H of other substances.



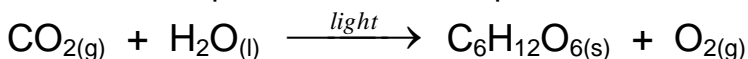
From this equation you don't actually have to know the values of H and S: only their sign and the temperature.

ΔG	ΔH	T	ΔS	
-	-	n/a	+	always spontaneous
+	+	n/a	-	never spontaneous
-	+	high	+	spontaneous
+	+	low	+	nonspontaneous
+	-	high	-	nonspontaneous
-	-	low	-	spontaneous

How do you know if the system has lost enthalpy? Enthalpy is really the sum of the heat in a system and the work that the system could do. An example of a systems ability to work can include its position, is it water above the dam or water at the bottom of the dam. Another example is a fluid under pressure; it could move something like a pellet in an air rifle.

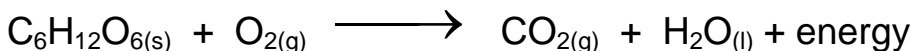
How do you know if a system has gained entropy? Entropy is a measure of disorder of a system, so is your system more or less organized. Ice turning to water is an example of a loss of order. Liquids are more disordered than solids. Along that same line, gases are more disordered than liquids. So, an ice cube melting in your home is an example of an increase in entropy.

The ability of plants to create sugar and oxygen from carbon dioxide and water with the input of light is one of the most important reactions on the planet. Is this vital reaction spontaneous or nonspontaneous?



It is nonspontaneous. Light is needed to drive the reaction, without light photosynthesis cannot occur. The system takes in energy; this increases the enthalpy, giving positive H, which is not favorable to a spontaneous reaction. Now lets look at the entropy. A gas and liquid combine to form a gas and a solid. These products are more organized than the reactants, giving a negative S, which is not favorable to a spontaneous reaction. If you look at the table above a +H with a -S will never be spontaneous.

But what about the reverse reaction?

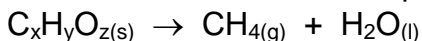


This reaction is spontaneous. This reaction is respiration of glucose/blood sugar. This system gives off energy, which is used by your cells, so H is negative that is favorable for spontaneous reactions. The reactants are solid and a gas and they



are converted into a liquid and a gas. This gives a positive S . If you look at the table above a $-H$ with a $+S$ will always be a spontaneous reaction. Your blood holds the glucose and you breathe in $O_{2(g)}$ and exhale $CO_{2(g)}$.

Many spontaneous reactions occur in the body, here is another. The decomposition of organic matter is a spontaneous reaction. The result is sometimes an unfortunate spontaneous release of gas, the smelly kind.



This is a decomposition reaction, one reactant becomes two products with the reactant being a solid and the products are a liquid and a gas. The entropy of the system has increased considerably.

Reaction Rates:

The speed at which a reaction occurs is called the reaction rate.

- Reaction rates are very important.
 - A doctor wants to know how long a patient must wait for certain drug to take effect. When will the pain subside, or when will the anesthesia take effect?
 - A partygoer wants to know how long he must wait before the alcohol he has consumed has been metabolized out of his system. When can I drive?
 - A chemistry student wants to know how long this lab will take.

The equation for the average rate of a reaction over a given period of time is as follows:

$$rate = \frac{\Delta C}{\Delta t}$$

Where **C** is concentration of the reactant and **t** is time.

The **f** and **i** stand for final and initial.

$$rate = \frac{C_f - C_i}{t_f - t_i}$$

So, if you know how much you started with and how much you ended with and the time it took for this to occur, you can calculate the average rate of this reaction.

Problems:

- If you begin with a 5M solution of H_2O_2 , which will decompose into water and oxygen gas, and in 45 minutes you have a 1.5M reaction, what is the rate of this reaction?

Remember: M means moles per liter



$$rate = \frac{1.5M - 5M}{45 \text{ min}} = -.07M / \text{min}$$

- If you know the rate of your reaction is .001M per minute how long will it take the concentration of the antidepressant lithium ion in the bloodstream to become ineffective? After taking a pill the patients initial concentration will be .1M. Once levels have dropped to .005M the lithium has lost its ability to regulate mood.

$$time = \frac{.1M - .005M}{.001 \frac{M}{\text{min}}} = 95 \text{ min}$$

Rule of Thumb:

For temperature changes, the reaction rate double every 10 degree increase in temperature. If you get 3 grams of product at 15°C you will get 12 grams at 35°C.

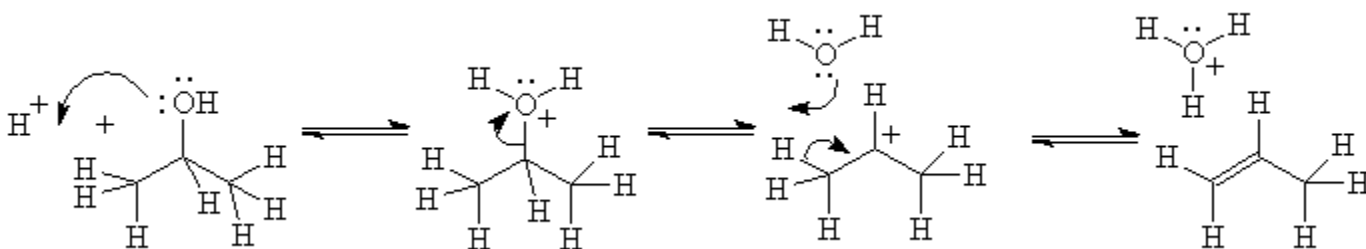
Molecular Collisions:

For a reaction to occurs three conditions must be met at exactly the same time:

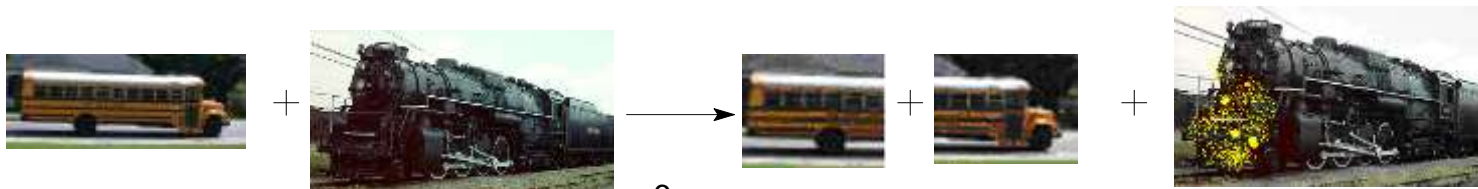
1. The reactants must collide, except in decomposition reactions.
2. The reactants must have enough energy for the reaction to occur.
3. The reactants must hit in a specific manner or orientation.

The detailed depiction of how the molecules collide is called a reaction mechanism.

Here is an example of a reaction mechanism, the reaction of an acid with 2-propanol also know as isopropyl alcohol or rubbing alcohol.



Here is another more morbid, but much more visual and fun example. How do a train and school bus react to give a train with engine damage and a school bus in two pieces?





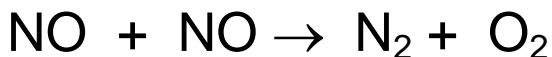
If you look back to the three conditions required for a reaction to occur, we can relate them to this terrible accident. Condition number one requires that the train must collide with the bus. Condition number two requires that the train and bus collide with enough energy for the reaction to occur, meaning the train must hit the bus with enough energy, not merely tap the bus. The third condition requires that the train and bus hit with the proper orientation. If the bus hit the side of the train, it will not slice the train in half. The train must t-bone the bus. Hopefully this visual will help you to remember the condition required for a reaction to occur.

Following the above rules we can reason:

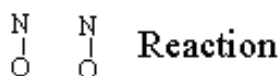
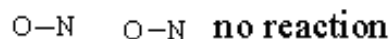
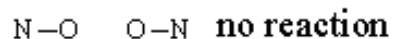
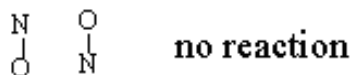
- Gaseous and aqueous reactants are better able to react as they can move around and run into each other. Except for their surfaces, two solids have a difficult time reacting. Also, gases and liquids can only interact with surface of the solid. For a car to rust through, the first layer of rust must flake off to expose the underlying layer of steel.
- If you have a solid with a lot of surface area you will have a good reaction. For example, iron dust will be oxidized quickly enough in air that it will keep you hands warm while skiing. Grain elevators explode when fine dust particles ignite.
- Increasing the concentration of the reactants will give the reactants a better chance of running into each other.
- Increasing the temperature of the system will give the reactants more energy. Reactants must overcome a barrier of energy called activation energy. Any increase in temperature will bring the reactants closer to overcoming this barrier energy.
- The reactants must hit with proper orientation as shown in the reaction of nitrogen monoxide to produce nitrogen gas and oxygen gas.



or

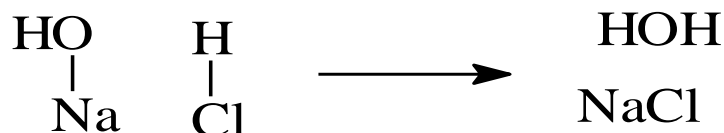


the nitrogen monoxides must line up properly for this reaction to occur



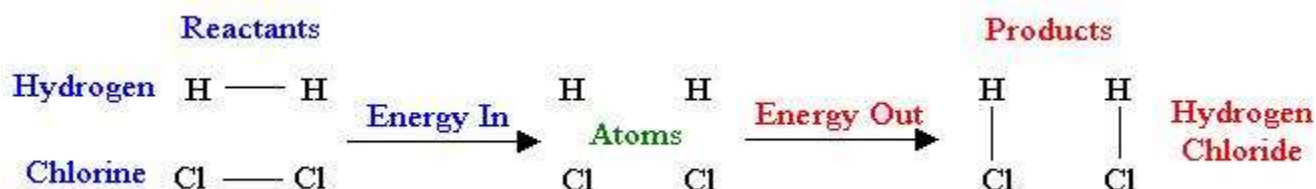
Example:

Hydrochloric acid, stomach acid, is neutralized by sodium hydroxide, drain cleaner. The resulting products are sodium chloride and water. Draw how these two reactants would have to hit in order for the reaction to occur.



Example:

Hydrogen gas and chlorine gas, in there elemental states converting to hydrochloric acid. Is this entropically friendly? Does entropy increase?



Rate Law and the Order of Reactants:

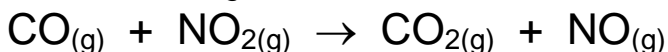
Sorry, but the rate law isn't actually a law and the order of reactants isn't actually the order they react. The rate law is a mathematical equation which allows a person to determine the rate at which a reaction will take place, based on the concentration of the reactants. The order of reactants describes the factor by which a particular reactant changes the rate of the reaction. What follows is the general form for a rate law.

$$\text{rate} = k [\text{A}]^x [\text{B}]^y [\text{C}]^z$$



k is the rate constant, which is **only** dependant upon the temperature of the given reaction. The capital letters in the brackets are the reactant in moles per liter and the superscripts for each reactant are the orders of each reactant.

For the following reaction:



Here is the rate law:

$$\text{rate} = k [\text{CO}]^1 [\text{NO}_2]^1$$

This reaction is said to be first order with respect to both carbon monoxide and nitrogen dioxide, and second order overall. To determine the overall reaction order, add each of the reacts order together.

The rate constant, orders of reactants and the rate law must all be determined experimentally. What follows is a table of data, from which, the above rate law was determined.

	initial [CO]	initial [NO ₂]	rate
trial	$\frac{\text{mol}}{\text{liter}}$	$\frac{\text{mol}}{\text{liter}}$	$\frac{\text{mol}}{\text{liter} \cdot \text{hours}}$
#1	5.1×10^{-4}	$.35 \times 10^{-4}$	3.4×10^{-8}
#2	5.1×10^{-4}	$.7 \times 10^{-4}$	6.8×10^{-8}
#3	5.1×10^{-4}	$.18 \times 10^{-4}$	1.7×10^{-8}
#4	10.2×10^{-4}	$.35 \times 10^{-4}$	6.8×10^{-8}
#5	20.4×10^{-4}	$.35 \times 10^{-4}$	13.6×10^{-8}

The method by which one goes about determining each of the reactant's order is to do multiple trials of the same experiment, varying initial concentrations of the reactants and observing changes in the rate. An important point is to hold all the reactants concentrations constant and vary one at a time. This way you know that any changes in the rate will be due to just the reactants whose concentration you changed.

So, looking at the above table in trials #1 and #2, the [CO] was held constant and the [NO₂] was doubled. Trial #2 is twice as concentrated in NO₂ as trial #1. Look at the rate for each trial. Trial #2 reacted twice as fast as trial #1. This implies that NO₂ is a first order reactant. Since doubling the concentration doubled the rate the exponent over the concentration must be 1. To confirm this look at trials #1 and #3. The [NO₂] was cut in half and the rate was twice as slow. What about the other reactant? Well, we must look at a trial where the [NO₂] was held constant and the [CO] was changed. Trials #4 and #5 fit this description. Trial #5 has double the [CO] of trial #4 and the rate has also doubled. This tells you that the order of CO is also 1.



From the above information we can calculate the rate constant too. What we need to do is solve for k and input the data for a trial. We should do this for each trial and take the average k value to be our rate constant for this reaction at this temperature.

$$\text{rate} = k [\text{CO}]^1 [\text{NO}_2]^1$$

$$k = \frac{\text{rate}}{[\text{CO}]^1 [\text{NO}_2]^1}$$

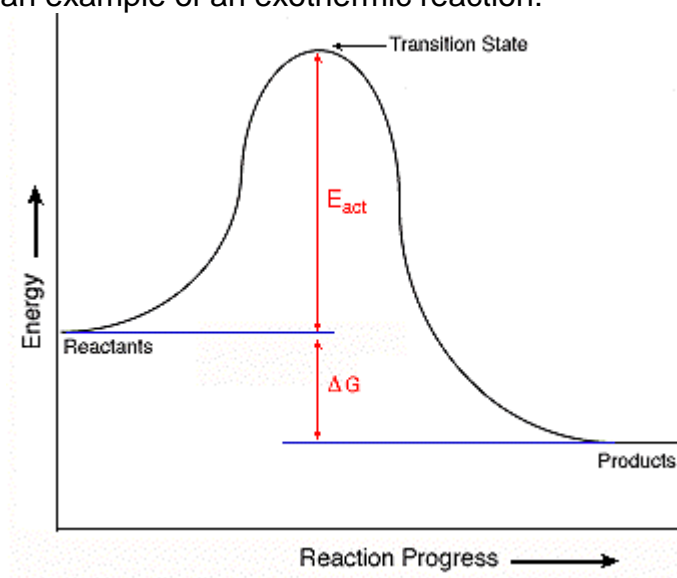
$$k = \frac{3.4 \times 10^{-8}}{[5.1 \times 10^{-4}]^1 [3.5 \times 10^{-4}]^1} = 1.9$$

If we calculate the rate constant for each trial the value is $1.9 \text{ M}^{-1} \text{ hr}^{-1}$

Energy Diagrams:

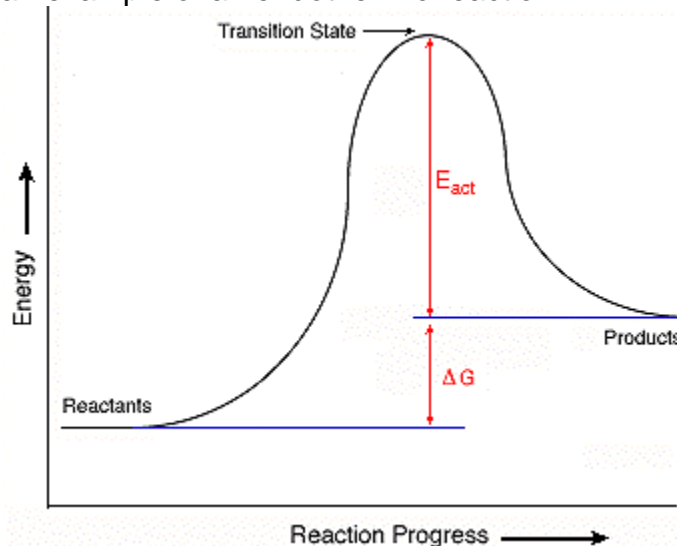
Energy diagrams are also called reaction progress diagrams as they depict the energy of the chemicals involved in the reaction through out the course of the reaction.

The following is an example of an exothermic reaction:





The following is an example of an endothermic reaction:



As you can see there is a hill of energy you must over come, again, this barrier energy is named activation energy. The activation energy is the energy needed during the transition from one form to another. The ΔG energy and the E_{act} are the total amount of energy needed to over come for this reaction to occur. But only the ΔG is the total change in energy from reactants to products.

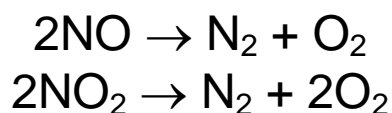
Factors Affecting the Rates of Reactions:

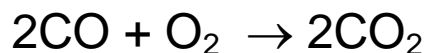
Now we can conclude that there are 4 factors that affect the rate a reaction will occur.

1. The nature of the reactants: solid, liquid, gas, aqueous.
2. The concentration of the reactants.
3. The temperature of the reactants.
4. The presents of a catalyst.

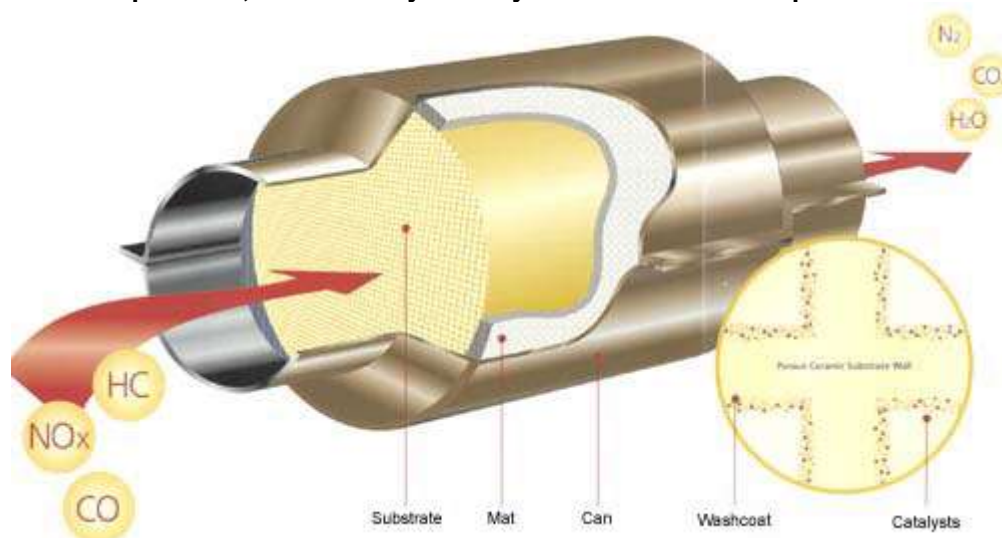
The first three we have already discussed. The last deals with the orientation of the reactants upon impact with each the other.

A catalyst assists a reaction by orienting the reactants. Sometimes this is done by allowing the reactants to sit on the surface of the catalyst, carbon monoxide gas and oxygen can be converted to carbon dioxide or nitrogen monoxide or nitrogen dioxide, both smog gases, can be converted into nitrogen gas and oxygen gas.





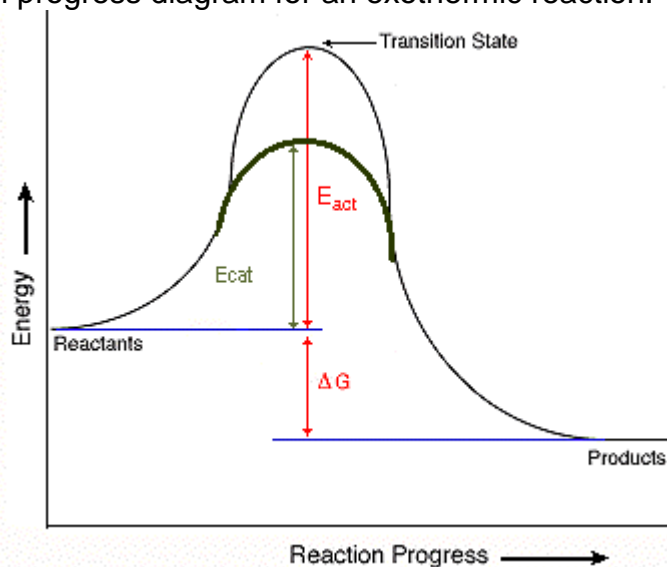
these reactions are assisted by the surface of a car's catalytic converter; the catalyst is platinum, which is why a catalytic converter is so expensive



The catalyst does all of this without being consumed in the reaction. In the end the catalyst is exactly as it began the reaction, ready to be used again. The catalytic converter on your car will never wear out.

The catalyst is involved in the transition state. It helps bring the reactants together, like a mediator.

In doing this the transition state does not require as much energy. In other words a catalyst will lower the activation energy of a reaction. The result is shown in the following reaction progress diagram for an exothermic reaction.



The green line in the transition state is showing the new barrier energy, the new amount of activation energy needed for this reaction to occur. This reaction has a significantly higher probability of happening as the energy it needs to overcome has decreased.





Electro Chemistry:

Spontaneous reactions will happen with no outside influence. An everyday example would be a battery. You simply allow the ends of a battery to touch and a chemical reaction will occur. The reaction is called an electrochemical reaction, as electrons move from one substance to another. These substances are normally metals and metal ions. Common names for batteries are nickel – cadmium, lithium ion and lead - acid.

The concept of Gibbs free energy to electrochemical cells is applied by the Activation Series. This series lists which metals are most reactive, most likely to be involved in a spontaneous reaction. In other words you can use this list to predict how two metals will react. Each element on the list replaces from a compound any of the elements below it. The larger the interval between elements, the more vigorous or energetic the reaction. Those higher on the list are more reactive as they are more likely to give up their valence electrons. Look at the top of the list; you find group I and II metals. Looking at the periodic table, what properties do these metals have? They want to give up those valence electrons to complete their outer energy level. Once more, these metals only need to give up one or two electrons to complete their energy levels. They are itching to get rid of those electrons.

Metal	Oxidation Reaction
Lithium	$\text{Li(s)} \longrightarrow \text{Li}^+(\text{aq}) + \text{e}^-$
Potassium	$\text{K(s)} \longrightarrow \text{K}^+(\text{aq}) + \text{e}^-$
Barium	$\text{Ba(s)} \longrightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{e}^-$
Calcium	$\text{Ca(s)} \longrightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{e}^-$
Sodium	$\text{Na(s)} \longrightarrow \text{Na}^+(\text{aq}) + \text{e}^-$
Magnesium	$\text{Mg(s)} \longrightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{e}^-$
Aluminum	$\text{Al(s)} \longrightarrow \text{Al}^{3+}(\text{aq}) + 3\text{e}^-$
Manganese	$\text{Mn(s)} \longrightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{e}^-$
Zinc	$\text{Zn(s)} \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$
Chromium	$\text{Cr(s)} \longrightarrow \text{Cr}^{3+}(\text{aq}) + 3\text{e}^-$
Iron	$\text{Fe(s)} \longrightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$
Cobalt	$\text{Co(s)} \longrightarrow \text{Co}^{2+}(\text{aq}) + 2\text{e}^-$
Nickel	$\text{Ni(s)} \longrightarrow \text{Ni}^{2+}(\text{aq}) + 2\text{e}^-$
Tin	$\text{Sn(s)} \longrightarrow \text{Sn}^{2+}(\text{aq}) + 2\text{e}^-$
Lead	$\text{Pb(s)} \longrightarrow \text{Pb}^{2+}(\text{aq}) + 2\text{e}^-$
Hydrogen	$\text{H}_2(\text{g}) \longrightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$
Copper	$\text{Cu(s)} \longrightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$
Silver	$\text{Ag(s)} \longrightarrow \text{Ag}^+(\text{aq}) + \text{e}^-$
Mercury	$\text{Hg(l)} \longrightarrow \text{Hg}^{2+}(\text{aq}) + 2\text{e}^-$
Platinum	$\text{Pt(s)} \longrightarrow \text{Pt}^{2+}(\text{aq}) + 2\text{e}^-$
Gold	$\text{Au(s)} \longrightarrow \text{Au}^{3+}(\text{aq}) + 3\text{e}^-$



All metals above HYDROGEN are replaced by H^+ ion metal ions and H_2 gas.

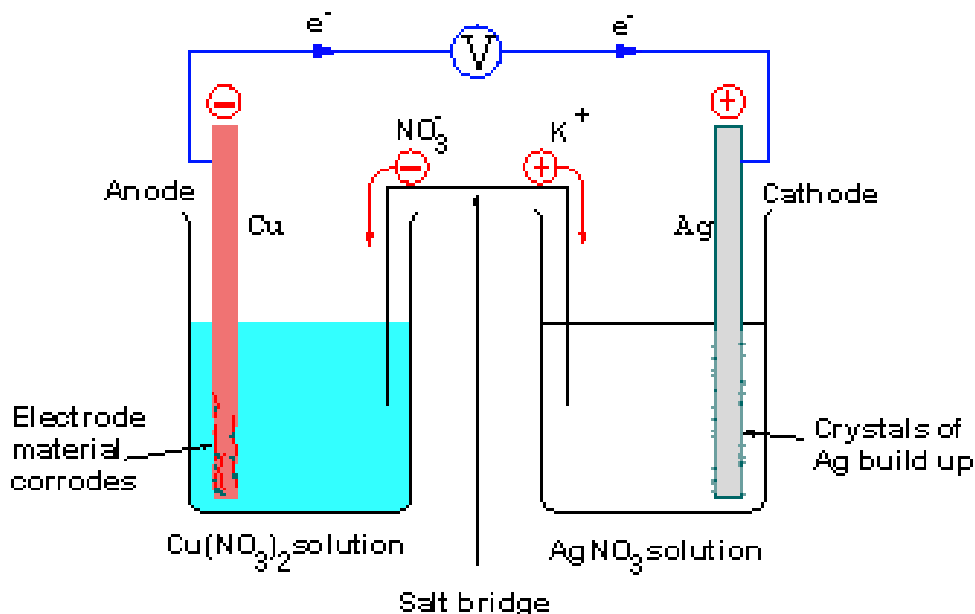
In other words, if you put any of the metals above HYDROGEN in an acid, they will dissolve into cations and hydrogen gas bubbles will form.

Getting back to our discussion on batteries, a battery is a redox reaction between two metals. Remember a redox reaction is an oxidation-reduction reaction, meaning one substance is oxidized, loses electrons, and one substance is



reduced, gains electrons. This may seem backwards, but keep in mind that the oxidation number is what is being reduced, and when a substance gains an electron, its charge is reduced, hence the substance is said to be reduced.

The first batteries were called galvanic or voltaic cells, we will refer to them simply as cells. These cells consisted of two beakers filled with an ionic solution, two pieces of metal, a wire and a salt bridge. See below.



The reaction occurring in this cell is spontaneous from the copper metal to the silver metal. We can predict this as copper lies above silver on the Activity series. Again, metals higher on the list are more reactive; they more easily give up their electrons. In this reaction each copper atom becomes a copper ion by giving up two electrons. These electrons are accepted by two different silver ions to make two silver atoms. The electrons spontaneously flow from the copper metal to the silver ions.

The side where the oxidation occurs is named the anode and the side where the reduction occurs is named the cathode. Remember this as anode and oxidation both begin with a vowel and cathode and reduction both begin with a consonant.

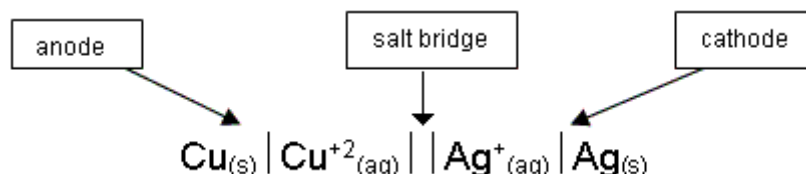
Spontaneously at the anode copper metal will change to copper (II) ion dissolve into the beaker's solution. While on the cathode side silver ions are changing into silver metal and plating the cathode.

The wire is used to allow the electrons to transfer. The salt bridge must be used to maintain charge balance, and is a tube simply filled with a salt-water solution. Without a salt bridge, electrons would be leaving the anode and a positive charge would build up in the anode beaker, while electrons being added to the cathode would cause a positive charge to build up in the cathode beaker. Nature does

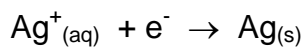
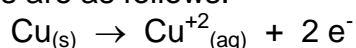


not allow this to occur. All substances must have electro neutrality. Each time one electron enters the cathode a potassium ion, from the salt bridge, enters the cathode. This is the addition of one negative and one positive, leaving the beaker with no overall charge.

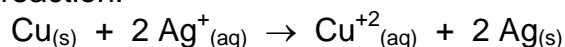
There is short hand notation for cells. For this copper-silver cell the notation is as follows:



The salt bridge divides this reaction into two halves. They are referred to as half reactions. The half reactions are as follows:

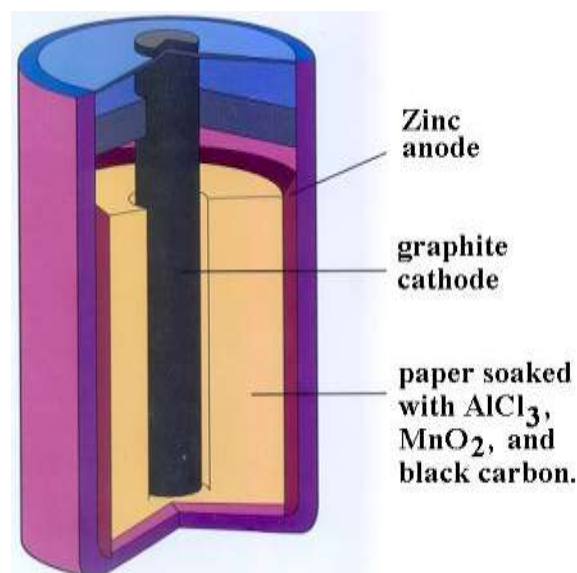


If we now add these reactions up, ensuring we balance charge we will come to the following overall reaction:



Looking at this galvanic cell you should say to yourself, I have seen many a battery but none that look like that. Today's batteries are much smaller, but the same components are found in all batteries. Instead of having beakers filled with solution, a battery replaces the beakers with a can inside of another can. The solutions are replaced with a paste or gel. Since these batteries do not have a solution, they are named "dry" cell batteries.

The first dry cell developed by the German chemist Carl Gassner in 1888, consisted of a zinc can that served both as a container and as the anode. The cathode, a carbon (graphite) rod, was immersed in a manganese dioxide/carbon black mixture. It was separated from the zinc container by a folded paper sack, soaked in a solution of ammonium chloride, which acted as the electrolyte. During use the zinc casing of the battery was gradually consumed by the chemical reaction. A sealant prevented evaporation of water from the electrolyte and the admission of oxygen.



Using the activity series we can predict which metal will be reduced and which metal will be oxidized, but what about the voltages? How does a person determine what voltage a cell composed of two random metals will produce?



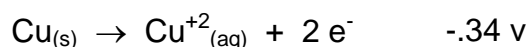
There is another list of metals, based on the activity series and the experimentally determined voltages. The list is written in two ways. One method is to list all reactions as reduction, gaining of electrons, and the other is as an oxidation, losing of electrons. Below find a reduction potential table.



Table of Reduction Potentials

Cathode (Reduction) Half-Reaction	Standard Potential E° (volts)
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.04
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.92
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ca}(\text{s})$	-2.76
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.38
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$	-0.74
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.41
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.40
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.23
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13
$\text{Fe}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.04
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	0.15
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightarrow \text{Cu}^+(\text{aq})$	0.16
$\text{AgCl}(\text{s}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	0.22
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34
$\text{Cu}^+(\text{aq}) + \text{e}^- \rightarrow \text{Cu}(\text{s})$	0.52
$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$	0.54
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	0.77
$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Hg}(\text{l})$	0.80
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.80
$\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Hg}(\text{l})$	0.85
$\text{ClO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.90
$2\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}(\text{aq})$	0.90
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$	1.07
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	1.36
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \rightarrow \text{Ce}^{3+}(\text{aq})$	1.44
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.78
$\text{Co}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Co}^{2+}(\text{aq})$	1.82
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$	2.87

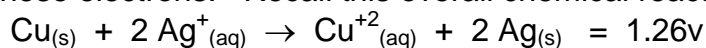
To determine the voltage of our cell you add the voltages produced by each half reaction.





$$\text{Total Voltage} = -.34\text{v} + .80\text{v} + .80\text{v} = 1.26\text{v}$$

The reason the voltage for the copper half reaction is negative is in the reduction potential table the reaction is written backwards of what is actually occurring. So, the voltage magnitude is the same but the sign is reversed. The silver voltage is added twice because the copper gives up two electrons, so the silver ions must accept both of these electrons. Recall this overall chemical reaction:



I cannot say I have ever seen a dry cell battery consisting of copper and silver. Why do you think they do not exist? Cost, weight and voltage. The cost and weight would be too much, while the voltage output would be too small.

Most car batteries are of the lead acid type. These batteries have the ability to produce large amounts of power. But you wouldn't want to drag around a 40-pound cell phone. The most recent battery development in mobile phones is the lithium ion battery. Why do you think lithium makes a good battery component? It is the lightest metal, it is the most active metal and it is not too expensive.

Looking back to the activity series, can you see why gold is an important and expensive metal? Gold plated cables or computer parts are not as susceptible to oxidation even when running current through them at high temperatures.



The Statue of Liberty gets its green colored skin from the copper that its exoskeleton is made of. But the statue gets most of its structural support from steel beam, steel is mostly iron.

Oxidation or rusting occurs when oxygen gas is allowed to contact a metal when the metal is wet. The copper skin is not copper colored, its green color comes from the copper (II) oxide that forms on its surface. Hence, the skin of the statue is covered in $\text{CuO}_{(\text{s})}$. Once the entire surface has been oxidized the interior copper is protected.

Iron on the other hand is a metal that continues to undergo a reaction after the surface of the iron has oxidized. This oxidation or rust can permeate through the beams destroying the structural integrity of the statue.



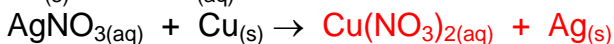
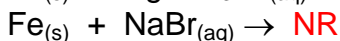
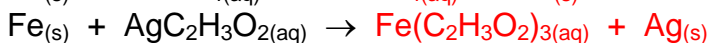
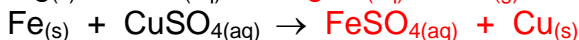
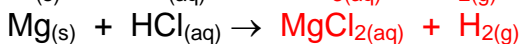
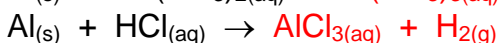
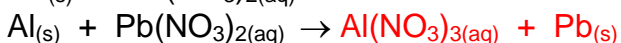
Which of the metals would you consider to be most active? Which metal weakens fastest, the Fe or the Cu? Fe will react before Cu. But the New York port authority doesn't want the Cu or Fe to rust. How can they stop this from occurring? Employ a metal that is more active than either Cu or Fe. To prevent rusting, paint with zinc dust was used. Why?

Iron beams are coated with this zinc paint so that oxygen reacts with the zinc and not the iron. Zn has higher activity series thus protects the iron beams. The oxygen will not rust the iron until all of the zinc has been oxidized. The zinc is sacrificing itself for the iron. And since the zinc is being oxidized, the zinc is referred to as a sacrificial anode.

Often a person will hammer a rod of zinc or magnesium into the ground close to metal structure and attach a wire from the structure to the rod, so that any oxides of Fe will be exchanged by having the O₂ prefer to react with Zn to form ZnO or Mg to form MgO. Zinc and magnesium have a greater affinity to O₂ and thus draws O₂ away from the metal structure and towards itself. This is another example of a metal sacrificing itself to spare another metal from corrosion.

Predicting Redox Reactions:

Using the activity series, complete the following reactions, if no reaction will occur write NR.

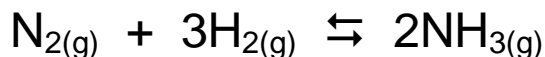


The reactions you have written as NR will react, but not spontaneously. Energy must be put into the reaction for it to proceed. This reaction is endothermic, taking in energy. An example would be the recharging of a battery.

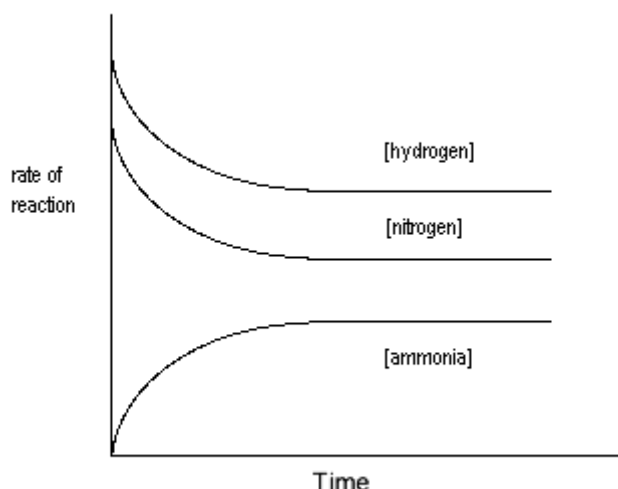
Equilibrium:

Up to now we have discussed reactions as if they go in one direction. This is not the case as many reactions are performing a balancing act between the products and the reactants.

A reaction from the background information from the last lab showed the Haber process.



- Once this has proceeded reached equilibrium the reaction produces more ammonia by combining the hydrogen and nitrogen and at the same time the ammonia is breaking down to produce more nitrogen and hydrogen.
- There is no change in the overall concentration of any of the gases, as soon as one NH_3 breaks down a set of nitrogen and hydrogen gases come together.
- The [brackets] around the gases in the following plot mean concentration, specifically moles per liter or molarity. If you see $[\text{H}_2]$ this means the concentration of hydrogen gas in moles per liter.



- As you can see if we put H_2 and N_2 gas in the same container their concentrations will decrease while the concentration of ammonia increases. But eventually the concentrations stop changing. At that point the reaction has reached equilibrium.

Problem:

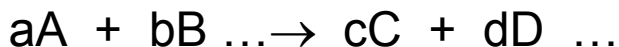
Hydrofluoric acid, HF is a weak acid and only some of the molecules break up. It forms equilibrium between the molecule HF and the ions of hydrogen and fluoride.

1. Write the chemical equation for this equilibrium reaction.
2. Create a drawing presenting the changes in concentration of HF, H^+ and F^- .

answers not given in these notes, see me if you have a question on this problem

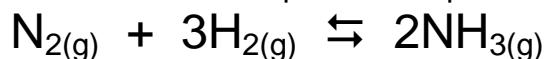
Equilibrium Equation and Equilibrium Constant:

There is an equation used to describe the equilibrium for a given reaction. The general form of this equation for this generalized reaction, is given as follows:



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

- The equilibrium constant, K, is a measure of the progress of a reaction. How far is this equilibrium reaction shifted to the products or reactants?
- K, again, is dependant **only** on temperature.
- A large K value, greater than 1, indicates more product than reactant.
- A small K value, smaller than 1, indicates more reactant than product.
- For our Haber process reaction the equilibrium equation would be as follows:



$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

One interesting aspect of the equilibrium equation is that the values in the equation are always present in terms of moles per liter. This is fine for gases and solutions but solids and pure liquids are not measured in terms of moles per liter. For this reason you will never see an equilibrium equation written with a solid or pure liquid.

Problem:

Write the equilibrium equation for the decomposition of HF acid, which breaks down into H^+ and F^- ions.

$$K = \frac{[H^+][F^-]}{[HF]}$$

The K value for this reaction is 7.2×10^{-4} which side of this reaction is favored, reactants or products? $7.2 \times 10^{-4} = .00072$



- The reactants, the number are really small which means the denominator is much larger than the numerator.
- What this is saying is that only 1 out of every 1389 hydrofluoric acid breaks apart.
- I got this by inverting the .00072, $\frac{1}{.00072} = 1389$

Water separates similar to this HF.

We can calculate the K value for any given equilibrium reaction if we know the concentrations of all involved chemical.

Consider the equilibrium: $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$

At a certain temperature the Haber reaction has come to equilibrium in a 4-liter container. The vessel contains 1.6 moles of NH_3 , .80 Moles of N_2 , and 1.20 moles of H_2 . What is the value of K?

$$K = \frac{\left[\frac{1.60}{4} \right]^2}{\left[\frac{.80}{4} \right] \left[\frac{1.20}{4} \right]^3} = 29.6$$

Problem:

Given that the K value for the dissociation of HF is 7.2×10^{-4} what is the concentration of H^+ going to be if the concentration of HF was measured to be .5M.

- The concentration of H^+ and F^- has to be the same. For every HF that separates you get one H^+ and one F^- . So you can create the following equation:

$$7.2 \times 10^{-4} = \frac{[\text{X}][\text{X}]}{[.5]}$$

Solve for X and you know your concentration of H^+ and F^- .

$\text{X} = .01897$ Therefore $[\text{H}^+] = .01897\text{M}$

Le Chatelier's Principle:

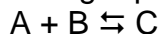
- Le Chatelier's Principle analyzes the factors which effect the equilibrium position, in other words what makes the equilibrium shift toward the reactants or the products.
- The equilibrium constant, K, is set in stone for that temperature, the reaction in equilibrium will shift to set the concentrations to reestablish the proper K value.
- The rule is the equilibrium will shift in order to suppress any change in the system.
- The following 3 changes will cause the equilibrium to shift.



1. Change in the Temperature
2. Change in Volume of the Container
3. Change in Concentration for any of the chemicals involved.

The mathematical representation of this theory can be found in the following equations.

Using the reactions and its corresponding equilibrium expression:



$$K = \frac{[C]}{[A] \cdot [B]}$$

Lets say for a given temperature the K value is 2, and the concentrations are as follows:

$$A = .4M$$

$$B = .1M$$

$$C = .08M$$

The equilibrium expression will be set us as follows.

$$K = \frac{[.08]}{[.4] \cdot [.1]} = 2$$

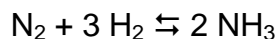
We now remove some of the product C reducing its concentration. How does the reaction shift to oppose this change? It must reestablish the equilibrium by converting some of the reactants into products. In doing so, the reestablished equilibrium has maintained the K value of 2.

$$K = \frac{[.04]}{[.25] \cdot [.08]} = 2$$

One important aspect of Le Chatelier's Principle is that the addition of a catalyst will not shift the equilibrium; it will only increase the rate at which the equilibrium is maintained.

The following examples demonstrate the use of Le Chatelier's Principle.

Example #1 - which way will the equilibrium shift if more H₂ is added to this reaction at equilibrium.



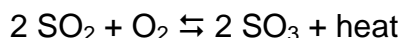
Answer - the H₂ amount goes up (by adding it), therefore according to LeChatelier's Principle, the reaction will try and use up the added H₂. It does so by shifting the position of equilibrium to the right. This makes more NH₃ by using up N₂ and H₂



Example #2 - using the same reaction, which way will the equilibrium shift if some NH_3 is removed from the reaction when it is at equilibrium.

Answer - according to LeChatelier's Principle, the chemical system will attempt to replace the lost NH_3 . The stress was to remove NH_3 , so the opposite is to replace it. The equilibrium position will shift to the right in order to replace some of the lost NH_3 .

Example #3 - which way will the equilibrium shift if the system temperature goes up (heat is added)?

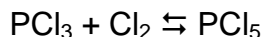


Answer - even though heat is not a thing, for the purposes of LeChatelier's Principle, you can treat it as if it has physical existence. Since heat is added, the reaction will shift to try and use up some of the added heat. In order to do this, the reaction must shift to the left.

Example #4 - using the same reaction, which way will the equilibrium shift if heat is removed (that is, the temperature goes down)?

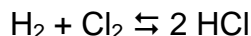
Answer - the reaction will attempt to do the opposite of what the stress was. Since the stress was to remove heat, the reaction will shift to the right to generate more heat (replacing only a part of what was lost).

Example #5 - the container holding the following reaction (already at equilibrium) has its volume suddenly reduced by half. Which way will the equilibrium shift to compensate?



Answer - since the volume went down, this means the pressure went up. The reaction will try to lessen the pressure by shifting to the side with the lesser number of molecules. This means a shift to the right because for every PCl_5 molecule made, two molecules are used up. The lesser the number of total molecules in the container, the lesser the pressure.

Example #6 - the container holding the following reaction (already at equilibrium) has its volume suddenly increased. Which way will the equilibrium shift to compensate?





Answer - neither side is favored over the other since both sides have the same number of total molecules (two). No matter which way the reaction shift, the total number of molecules would remain unchanged. In cases like this, where there are an equal number of molecules on each side, the equilibrium would remain unchanged by the change in pressure (in either direction).

Example #7 - the system below is already at equilibrium when a catalyst is added to the system. What happens to the position of the equilibrium? Does it shift right, left, or no change?



Answer - there will be no change in the equilibrium. BOTH (with emphasis on both) the forward and the reverse reactions are speeded up. A catalyst just gets you to equilibrium faster; it doesn't affect the final position of equilibrium like changing the concentration would.

Subscripts of K:

There are many forms of the equilibrium constant and many subscripts are employed. Here are a few we will be using:

K_{eq} – equilibrium constant – may be used in all equilibrium reactions, expresses to what extent the reactants turn into products.

K_{a} – acid – expresses to what extent an acid will separate.

K_{b} – base – expresses to what extent a base will separate.

K_{w} – water – expresses to what extent water separates.

K_{sp} – solubility product – express to what extent a solid will dissolve in a solvent.