

Kinetics & Equilibrium Diary

Kinetics and Equilibrium concern themselves with the energy of a chemical reaction, and where that energy was and goes to. Reactants of a chemical reaction have potential energy, but unless they are provided with a start up energy (the ACTIVATION ENERGY), the reaction will not start, or finish.

Most reactions we have done and observed have been "one way" reactions. That is the reactants become products, energy is either absorbed (endothermic) or released (exothermic) and the products that form are more or less permanent. The reason most reactions tend to go only one way is the energy involved. Once methane combusts with oxygen and forms the products of carbon dioxide and water, plus energy, the energy is released and will dissipate away. The energy is "gone", at least from the immediate area, and the ability to cause the reaction to go into reverse is lost.

We learned that matter cannot be created or destroyed in any chemical (or physical) process. Neither can energy. It can and has to be accounted for. It exists, it can be measured, and the chemistry requires us to manage this energy. Endothermic reactions absorb exact amounts of energy to go forward. Exothermic reactions release specific amounts of energy as well, all based upon the number of moles involved in the reactions. It is all very quantifiable and measurable. Lucky for us it will usually be fairly easy. We have Table I to tell us the exact ΔH , whether or not it is + or - signed (endo or exothermic). We also have potential energy diagrams, which show the change in potential energy from the REACTANTS to PRODUCTS. We are also lucky to have a reasonable teacher who is committed to teaching you all of this, and you are all quite bright.

COLLISION THEORY of chemical reactions

In theory, it is understood that the atoms and molecules need to have enough kinetic energy to crash into each other, at the proper orientation, to combine into new substances. If the energy is insufficient, the atoms or molecules just bump around but do not react. If the orientation is off, they also cannot combine. These collisions are the actual cause of chemical reactions to occur. The more collisions, the more reactions. The stronger and faster the particles move, the more likely that reactions can happen. Anything that encourages more, or stronger collisions will lead to faster chemical reactions.

The four main factors that affect the RATE of chemical reactions are as follows:

- Increase in Temperature. By adding to the kinetic energy of the chemical system, the result is more and stronger collisions. The rate of a chemical reaction is directly related to the kinetic energy (temperature) of the system.
- Increase in surface area of the reactants. By increasing this, you have more chances for reactants to bump into each other. The smaller the particles are, the more likely they will mix and collide into other particles. Rate of reaction is ALL ABOUT the most collisions.

- Increase in the concentration of the reactants. The more stuff you have bumping around, the more likely this stuff will collide into other reactants and cause a chemical reaction. Less concentration will of course lead to LESS COLLISIONS, which is bad for rates of reaction.
- The last factor that will affect the rate of reaction is the CATALYST. But, and this is an important difference, the catalyst effect is caused by its ability to lower the energy needed to start the reaction (the activation energy), and it has NOTHING TO DO WITH COLLISIONS. This is a very important distinction is how it changes the rate of a reaction than the previous 3 factors.

We did FOUR demo diagrams about these, recall them now:

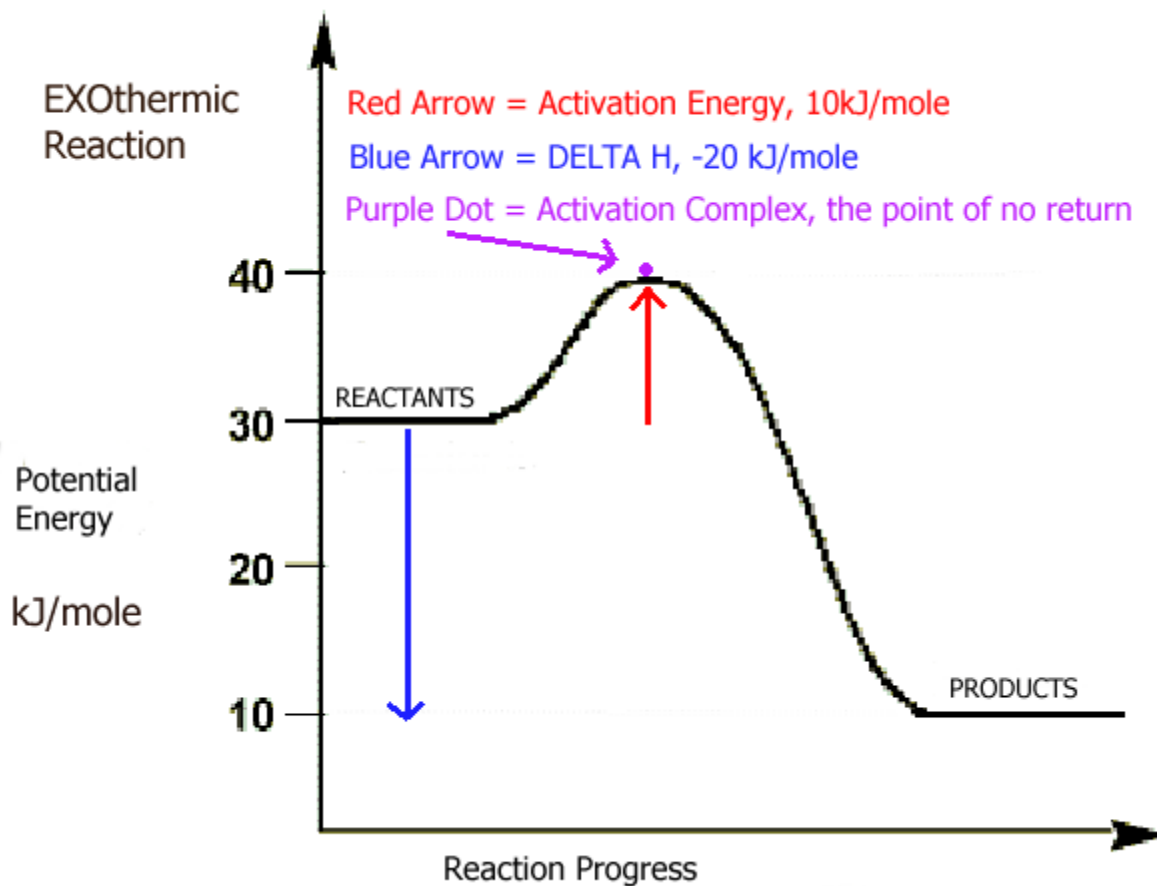
1. I placed an alka seltzer tablet into cold water, and into hot water. The one in the hot water fizzed much faster, and the tablet dissolved much faster. The higher kinetic energy in the hot water increased the rate of the reaction.
2. I added potassium iodide catalyst to hydrogen peroxide. It was decomposing very, very slowly, and exothermically. But it was happening SO SLOWLY, that no one could really notice this decomp reaction with their eyes. The catalyst sped up the reaction so much that the oxygen bubbled out rapidly, and a lot of heat was generated. So much that steam was produced from the other product, water. The exact same reaction happened with the catalyst, just MUCH FASTER. The speed let the heat all come out at once, making it capable of vaporizing some of the water at a rate we could see with our eyes.
3. I put the same mass of powdered sodium chloride into water as a solid chunk of salt. Of course, the solid chunk of salt dissolved MUCH SLOWER, because it had so much less surface area. When the particles are small, the surface area is much larger. That gives much more opportunity for the salt to actually solvate into the water and ionize.
4. I put oxygen into a balloon and filled up a test tube with the oxygen. I lit a wooden splint on fire, and blew it out. The wood tip glowed bright orange as the combustion reaction continued, much slower than before. The amount of oxygen in the air is about 20%, so the concentration of oxygen is actually fairly low in air, and with so much kinetic energy removed from the system (I blew out the fire), the chemical reaction stalled and stopped. When I did it again, but put the glowing tip of wood into the tube of pure oxygen, the wood burst back into flames. The combustion chemical reaction was too limited in the air with oxygen, but in the tube, the concentration of oxygen was WAY HIGHER. This shows that the concentration of reactants clearly affects the RATE OF A CHEMICAL REACTION.

POTENTIAL ENERGY DIAGRAMS

As you might expect, it would be sensible to be able to graph the energy flow in a chemical reaction, including some units and numbers. There are 2 basic kinds of graphs, both are potential energy diagrams. They show the potential energy of the reactants and products at all times during the chemical reaction. These two kinds of graphs are exothermic and endothermic potential energy diagrams. It is important to see the

difference, and recognize these differences so you can determine what the energy flow in a reaction is, just by looking over the diagram/graph.

The EXOTHERMIC diagram first. It has many similarities to the endothermic, but we'll see them soon enough.



Note where the REACTANTS potential energy level is. It is flat until kinetic energy is added. The products have potential energy as well, and in an exothermic reaction, they have LESS potential energy than the reactants did. That is because the energy in a reaction like this is RELEASED. It's not lost, it is released from the chemicals into the environment in a specific quantity, based upon the moles of reactants.

The energy needed to start a reaction is called the ACTIVATION ENERGY. This is the minimum amount of energy needed (kilo-Joules per Mole) to make the reaction happen. This is an investment of energy and a minimum amount is required for reactions to occur. If too little energy is applied, the reactants may be warmed up, but they will not react.

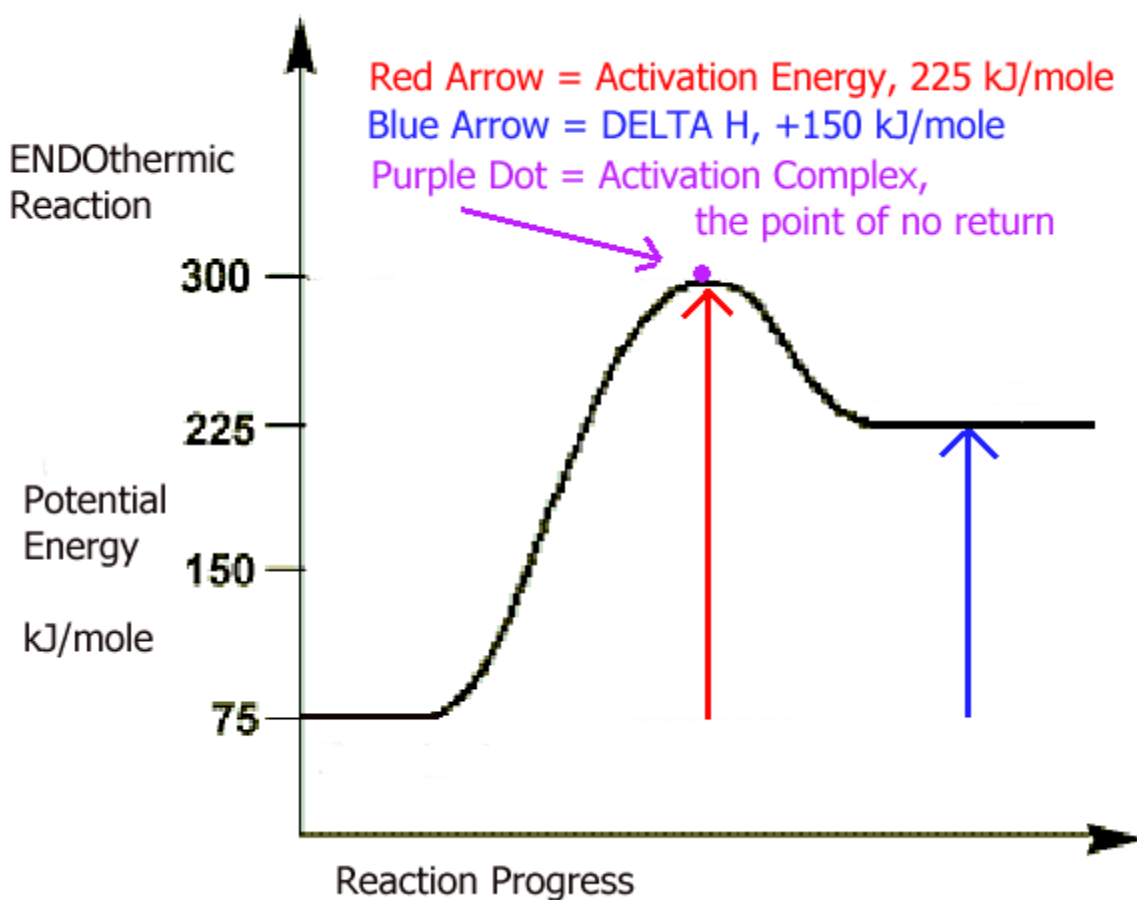
When the reactants secure enough activation energy, they very temporarily form into the activated complex. This is the in-between stage when reactants are not really reactants anymore, but they are not quite yet the products. (this is really just an additional vocabulary word). This activation complex forms exactly at the top of the curve of the potential energy diagram.

The difference in potential energy between the reactants and products is the ΔH . The ΔH is always negative in an exothermic reaction, because the products always have less

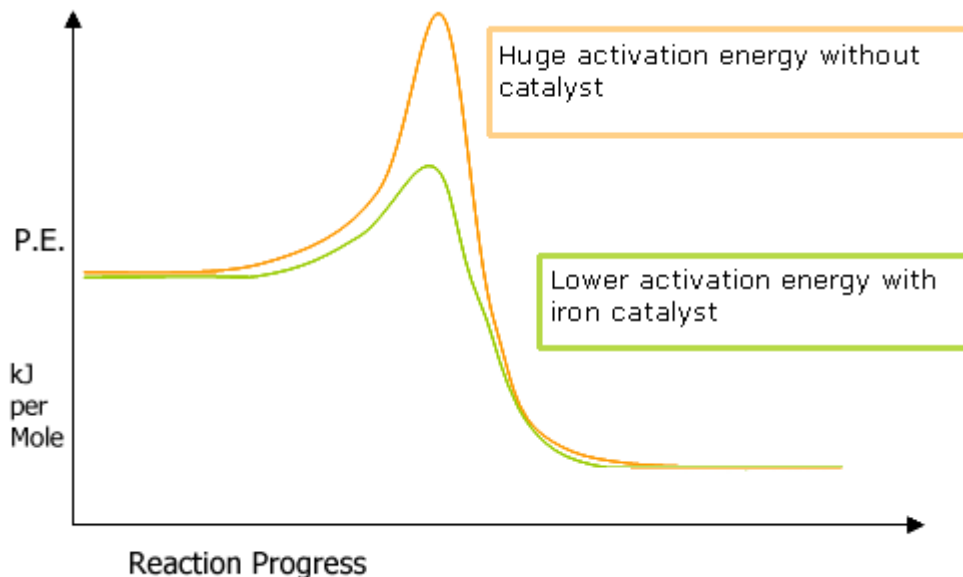
potential energy than the reactants started with (the extra energy is jettisoned into the environment).

The units of energy are kJ/mole. Use the graphs Y-axis to measure the actual energy values, or use Table I to get the exact ΔH values for 25 different reactions.

The ENDOTHERMIC potential energy diagram has all of the same parts, but the difference is that the products have MORE potential energy than the reactants did. In order for this to happen, this extra energy has to be absorbed from the immediate environment and put into the products. That is why endothermic reactions feel "colder", they are quite literally sucking energy into the chemistry from the surroundings, taking this kinetic energy and converting it into potential energy stored in the products. (pretty cool, and a pretty cool metaphor too).



A catalyst (as you remember) only lowers the activation energy for a chemical reaction. It does not change the potential energy of the reactants or products at all. This means that the addition of a catalyst does not change the ΔH either. ONLY the activation energy level needed to start the reaction is lowered. The catalyst added to this diagram and is shown as the GREEN line. Without a catalyst is with the ORANGE line. a DOTTED line.



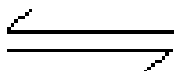
An inhibitor will of course inhibit or slow or even stop a chemical reaction. Often they block the catalyst from working, but can also work by blocking the reaction itself.

The potential energy is sometimes called free energy as well.

Dynamic Equilibrium

Some reactions are more easily reversed than others. In fact some can alternate back and forth over and over again, in a sort of balanced way. When the rate of the forward reaction is equal to the rate of the reverse reaction, this chemical system is said to be in dynamic equilibrium. That means, always changing and always equal at the same time.

When a chemical system is in dynamic equilibrium (sometimes just called equilibrium), it can appear that NOTHING is happening. This is of course totally untrue, both chemical reactions are taking place over and over, at the same rate. Reactants form products. These products are also reactants when the reaction reverses and they form into new products, which are the original reactants. Energy is often added on one side or the other. Rather than a single arrow head for a chemical reaction, we use the double arrow head.



That particular symbol is not in my computer, so I often use the \rightleftharpoons symbol to represent dynamic equilibrium.

The reaction that reads left to right is called the forward reaction. Going right to left is called the reverse. One reaction will be exothermic, and the energy will be part of the products of that reaction. The other reaction would be endothermic, since the energy is part of the reactants. See below:



The forward reaction is synthesis, and endothermic since the energy is going into the chemistry to form the product. The ΔH for the forward reaction is not known exactly, but it is positive.

The reverse reaction is the decomposition of AB into A and B, and releases energy, so the reverse reaction is exothermic. The ΔH for the reverse reaction is not known exactly, but it is negative.

When a reaction is at dynamic equilibrium, this balance can be disrupted by three ways:

- changing the temperature (adding or removing energy)
- changing the pressure (this only affects the gases in the reaction)
- changing the concentration of reactants

The addition of a catalyst will not change an equilibrium, but will rather bring it to equilibrium faster.

Equilibrium is a state that can exist depending upon the conditions. When these conditions are altered (change temp, pressure, or concentrations of reactants), this equilibrium will adjust to the new conditions and create a new dynamic equilibrium at these new conditions. Every time you adjust the conditions, the dynamic equilibrium will make an adjustment to relieve the stress you have applied.

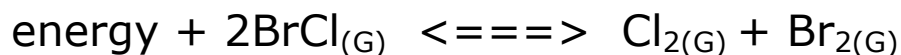
This seems basic in thought, and was made into a real chemical theory by a French chemist known as LeChatelier. **LeChatelier's Principle states:**

“When a stress is added to a system at equilibrium, this system will shift to relieve this stress, and a new dynamic equilibrium will form at the new conditions.”

Wow, that is really profound! He's going to be famous INDEFINITELY because it is so right.

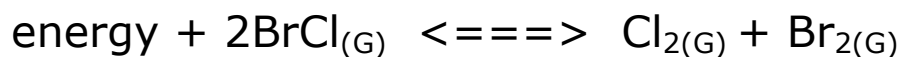
When you have a chemical reaction in dynamic equilibrium, you can adjust the temperature, pressure, or concentrations of reactants, and you can predict which way the equilibrium will shift (temporarily) until a new equilibrium is reached.

For example, this reaction will be examined in detail now.



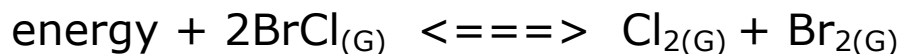
forward reaction

1. left to right
2. endothermic (energy is added to reactants, no energy release in products)
3. decomposition reaction (big substance forms 2 or more smaller substances)



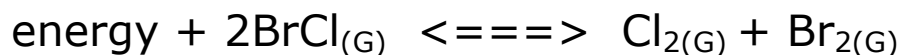
reverse reaction

1. right to left
2. exothermic (energy is released as a product, no energy with the reactants)
3. synthesis reaction (2 or more smaller reactants for larger product)



Increase Temperature shifts equilibrium to the right, additional energy will further decompose the bromine chloride into chlorine and bromine.

Decrease Temperature shifts equilibrium to the left because less energy in the system will slow the decomposition reaction. Both of these shifts will be TEMPORARY, lasting only until a new dynamic equilibrium is reached at the new temperature conditions.



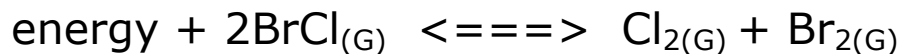
Increased Pressure will shift equilibrium towards the side of less number of moles of gas. In fact in this reaction, there are 2 moles of bromine chloride at left, and one mole each of chlorine and bromine at right. 2 moles = 2 moles, so in this reaction, change in pressure will not have an affect here.

Decreased Pressure will have no affect on this system for the same reason stated just above.

When there are different numbers of moles on either side of the double arrows, an increased pressure will push the reaction towards the lower number of moles of gas. Less moles of gas take up less room, so it would relieve this stress by forming into less moles.

A decreased pressure would push the reaction in the other way, less pressure would "encourage" the formation of more moles of gas.

Both of these shifts, towards or away from more or less moles of gas is TEMPORARY, it just lasts until a NEW DYNAMIC EQUILIBRIUM is reached.



a change in concentration of reactants will also (temporarily) shift the equilibrium of the system.

Increased BrCl will tend to cause MORE decomposition to happen, so more BrCl shifts the equilibrium to the right. A decrease in BrCl will do the opposite, shifting to the left.

Increased Cl₂ will tend to cause MORE synthesis (more collisions due to higher concentration) so the equilibrium will shift to the left. That is until the new equilibrium is reached. Decreased Cl₂ will do the opposite and shift the equilibrium to the right.

Increased Br₂ will tend to cause MORE synthesis (more collisions due to higher concentration) so the equilibrium will shift to the left. That is until the new equilibrium is reached. Decreased Br₂ will do the opposite and shift the equilibrium to the right.

Energy is in fact a reactant, but it was covered in change in temperature above.

ENTROPY

entropy is the measure of disorder, or chaos, in a system.

Technically it is quantifiable, with a complex equation, but that is outside the scope of our class. Entropy is measurable and comparable.

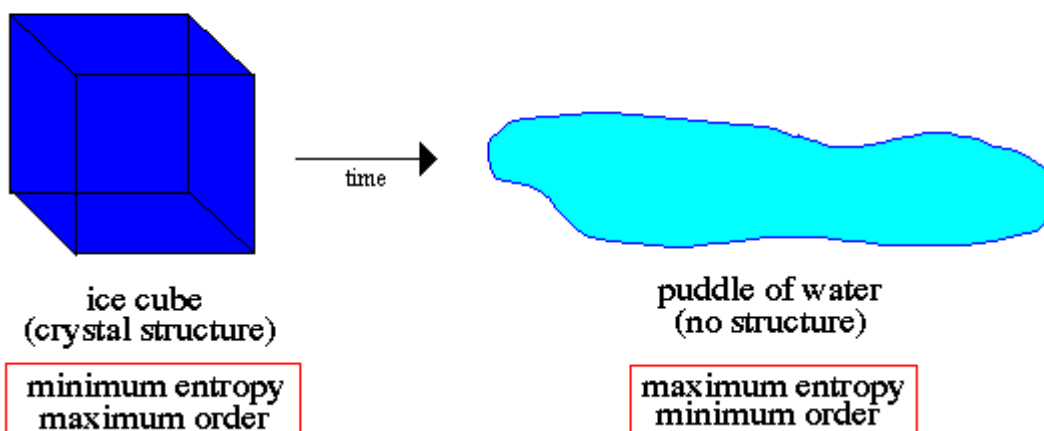
We can compare entropy by looking at water in its three phases.

Solid ice has low entropy because the molecules are not moving much at all.

Gas steam has the highest entropy because the molecules are blasting around like crazy.

Liquid water is medium, it has medium entropy compared to solid and gas phase.

Entropy



Another thought on entropy is that larger particles have less entropy than smaller particles. Octane has lower entropy than methane or propane.

Fewer molecules have lower entropy than many molecules.

The universe, and all of chemistry, tend towards higher and higher entropy. Things are breaking down into smaller particles, the universe is falling apart. Energy dissipates, particles spread out.