

# Kinetics & Equilibrium BASICS

Kinetics and Equilibrium is the part of chemistry that measures the energy of a chemical reaction, and: where that energy was and where it 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, forget about finishing.

Most reactions we have done and observed have been “one way” reactions. They are “IRREVERSIBLE” or the “I” in TOPIC-B. 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 is “used up and it’s no longer available”. Methane combusts with oxygen, forming the products of carbon dioxide and water, plus energy. This energy is released and will dissipate away. The energy is “gone”, at least from the immediate area, and the energy that might 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 does not evaporate to nothing, and it 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  $\Delta H$ , whether or not it has a + or - sign (endo or exo-thermic).

We also have potential energy diagrams, which show the change in potential energy from the REACTANTS to PRODUCTS. Lucky for me that you are so 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:

- 1. Increase in Temperature. By adding to the kinetic energy of the chemical system, the result is more and stronger collisions. The rate of a reaction is directly related to the kinetic energy (temp) of the system.
- 2. 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.
- 3. 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.
- 4. The last factor that will affect the rate of reaction is the CATALYST. The important difference is that 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 demonstrations about these, try to recall them now:**

1. Alka Seltzer tablets into cold water, and Alka Seltzer tablets into hot water. In the hot water they fizzed (reacted) much faster, and the tablet dissolved much faster. The higher kinetic energy in the hot water increased the rate of the reaction. In cold water the reaction was less vigorous.
2. The addition of KI, potassium iodide catalyst into the slowly decomposing hydrogen peroxide. It decomposed very, very slowly. That is exothermic, but at that slow rate, we couldn't measure any heat release. The catalyst was able to speed up the reaction so much that the oxygen bubbled out rapidly, and a lot of heat was generated all at once. So much heat all at once that steam was produced by heating up 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. Using the same mass of powdered sodium chloride salt 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, as with the powdered salt, the surface area is much larger. That gives much more opportunity for the salt to actually solvate into the water and ionize.
4. When the test tube filled up with oxygen the glowing splint was able to re-ignite inside the concentrated oxygen. When the flame was blown out, the wooden tip glowed bright orange as the combustion reaction continued, much slower than before. Air is about 20%, so the concentration of oxygen is actually fairly low in air, and with so few oxygen molecules able to collide with this glowing wooden stick the chemical reaction stalled and stopped. When we 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 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.

There are only 2 kinds of PE diagrams, exothermic and endothermic. Just like we had only one kind of heating curve, and one kind of cooling curve (with different temperature scales), again here, we have just two kinds of diagrams (graphs) with different temperature scales. Also, one diagram goes “upwards”, and the other goes “downwards”.

## Exothermic Potential Energy Diagrams

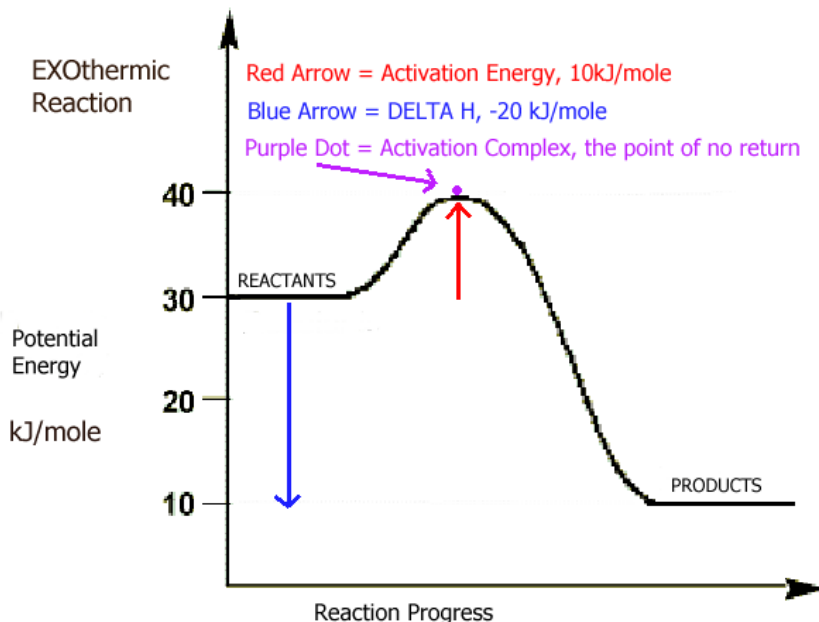
Note where the REACTANTS potential energy level is. It is flat until kinetic energy is added. The products have potential energy as well, and in an exothermic reaction, they have LESS potential energy than the reactants did. That is because the energy in a reaction like this is RELEASED. It's not lost, 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 in kilo-Joules per Mole, to make the reaction start. 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.

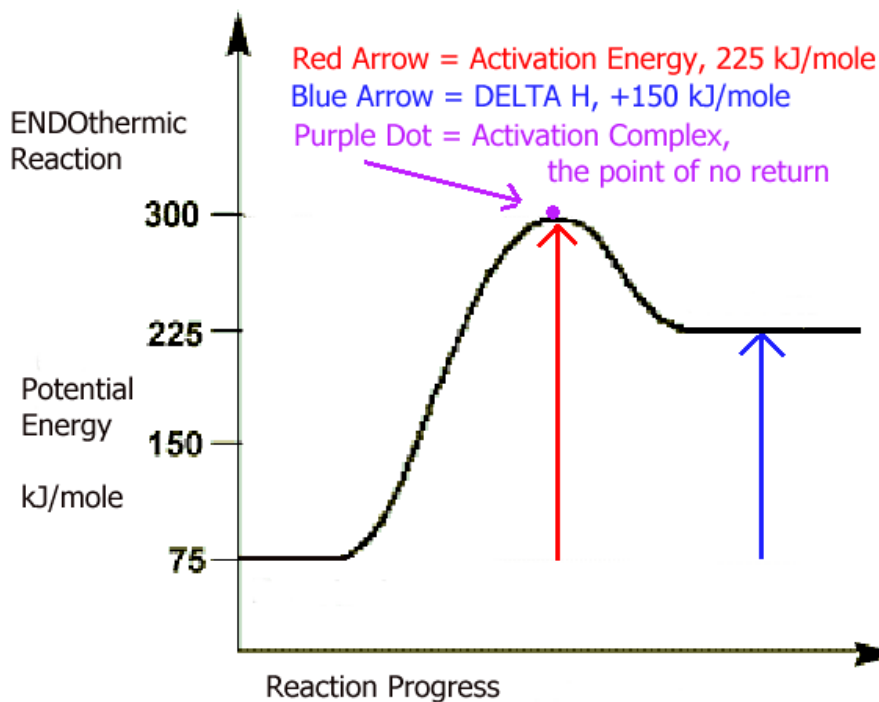
When the reactants secure enough activation energy, they very temporarily form into the activated complex. This is the in-between stage when reactants are not really reactants anymore, but they are not quite yet the products. (this is really just an additional vocabulary word). This activation complex 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  $\Delta H$ . The  $\Delta H$  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  $\Delta H$  values for 25 different reactions.



## The ENDOTHERMIC potential energy diagram



The ENDOTHERMIC potential energy diagram has all of the same parts, the big 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.

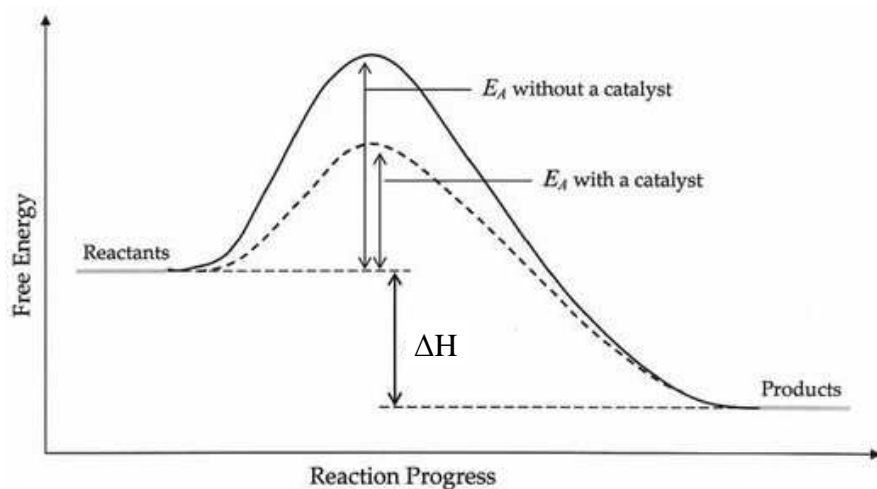
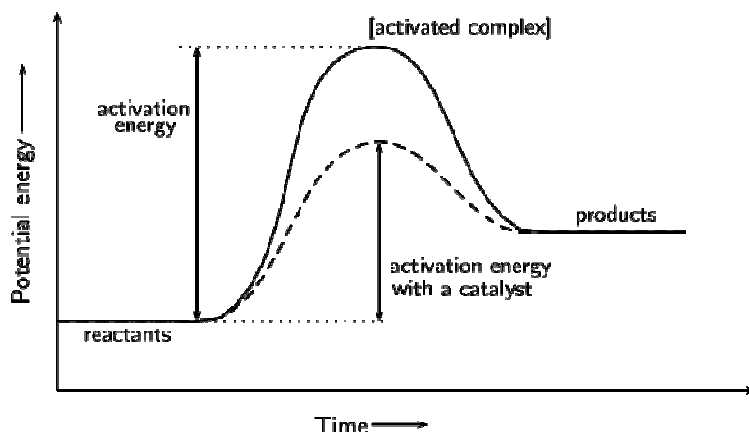
That's pretty cool, and it's a pretty cool metaphor too.

When a catalyst is used, it 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  $\Delta H$  either. ONLY the activation energy level needed to start the reaction is lowered. The catalyst added to this diagram and is shown as the DOTTED line. Without a catalyst is with the SOLID line above.

This diagram shows how the catalyst lowers the necessary activation energy of this endothermic reaction.

With exothermic reactions, the catalyst has a similar impact (see below).

$E_A$  means Energy of Activation



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.

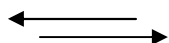
## Dynamic Equilibrium

Most chemical reactions you have seen so far are “irreversible” meaning once they occur, they stay done. The products form, the products do not spontaneously revert back into the reactants. They can't, as the energy required is insurmountable without help from a scientist.

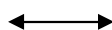
Some reactions are more easily reversed than others, the energy required to go forward, or even in reverse is low enough, and similar enough, that air temperature is sufficient to push reactions in either direction. Some reactions can alternate back and forth over and over again, in a sort of balanced 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 that symbol to represent dynamic equilibrium.



Sometimes I will use



In our class ANY reaction that is provided with that double arrow will be considered to be in dynamic equilibrium, even if you might not think that it's possible. In high school we sometimes use reactions that are not reversible, but we use this double arrow anyway, to help you think. It's "not real" but it will help you think. The double arrow MEANS THAT THE REACTION IS REVERSIBLE in this moment.

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  $\Delta H$  for the forward reaction is not known exactly, but it is definitely positive.

The reverse reaction is the decomposition of AB into A and B, and releases energy, so the reverse reaction is exothermic.

The  $\Delta H$  for the reverse reaction is not known exactly, but it is surely 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.

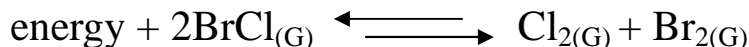
This seems basic in thought, and was made into a real chemical theory by a French chemist named LeChatelier.

**LeChatelier's Principle states:**

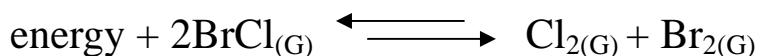
“When a stress is added to a system at equilibrium,  
this system will shift to relieve this stress,  
and a new dynamic equilibrium will form at the new conditions.”

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 the new dynamic equilibrium is reached.

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

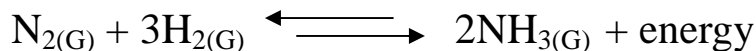


1. The forward reaction runs left to right
2. The forward reaction is endothermic  
(energy is added to reactants, no energy released with products)
3. The forward reaction is the decomposition reaction (a bigger substance forms 2 or more smaller substances)
4. The reverse reaction runs right to left
5. The reverse reaction is exothermic  
(energy is released as a product, no energy added to the reactants)
6. The reverse reaction is a synthesis reaction (2 smaller reactants form 1 larger product)



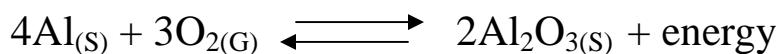
7. increase temp shifts forward
8. decrease in temperature (cooling) causes a reverse shift

Both of these shifts (#7 and #8) will be TEMPORARY, lasting only until a new dynamic equilibrium is reached at the new temperature that the system changed to. Then a new dynamic equilibrium starts.



9. increase in pressure shifts towards the LESS number of moles of gas (they'll be less pressurized).  
There are 4 moles of gas at left but only 2 moles of gas at right.
10. decreased Pressure will shift towards MORE moles of gas.
11. When there are the SAME number of moles of gas on both sides (like with the reaction at the top of the page, any increase or any decrease of pressure has NO EFFECT, the pressure balances out, and a

All 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, which occurs quickly if the conditions change and become stable in regard to new temp or new pressure, etc.



Adding + removing reactants (or products) will also (temporarily) shift the equilibrium of the system.

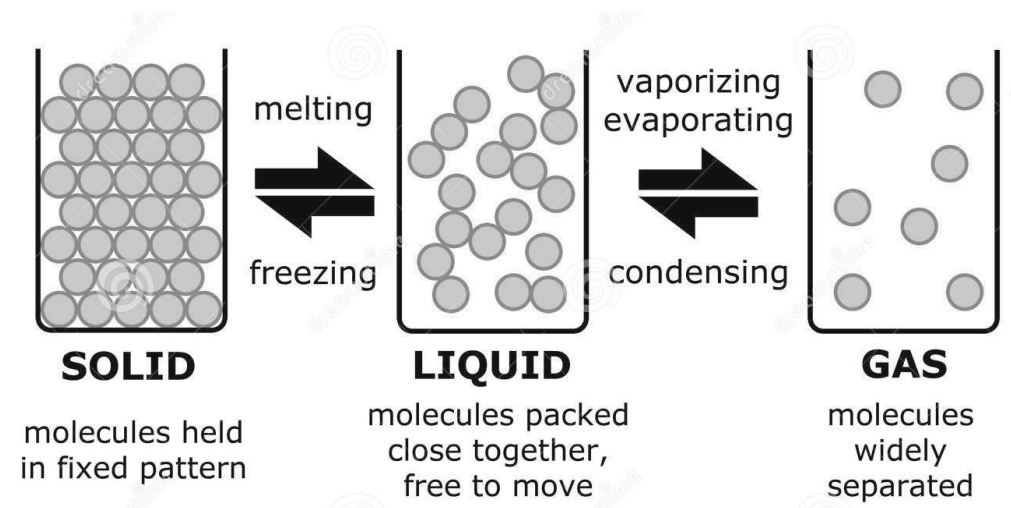
12. Add Al shifts forward (more collisions between Al and oxygen)  $\longrightarrow$
14. Add  $\text{O}_2$ , same thing happens  $\longrightarrow$
15.  $\longleftarrow$  Add  $\text{Al}_2\text{O}_3$ , shift reverse, more decomposition possible.
16.  $\longleftarrow$  add energy, more decomposition (energy is a reactant for reverse reaction)
17. remove energy, shift forward, less decomp possible without energy  $\longrightarrow$
18.  $\longleftarrow$  remove Al (or remove  $\text{O}_2$ ) shift reverse because less synthesis is possible.

## 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. Liquid water is medium, it has medium entropy compared to solid and gas phase. Gas steam has the highest entropy because the molecules are blasting around like crazy.



Another thought on entropy is that larger particles have less entropy than smaller particles when they are at the same conditions of pressure and temperature. Octane ( $\text{C}_8\text{H}_{18}$ ) has lower entropy than propane ( $\text{C}_3\text{H}_8$ ), but methane ( $\text{CH}_4$ ) has the lowest entropy of these three gases.

Fewer molecules have lower entropy than more molecules.

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