



## Chapter 14 Kinetics & Equilibrium Diary

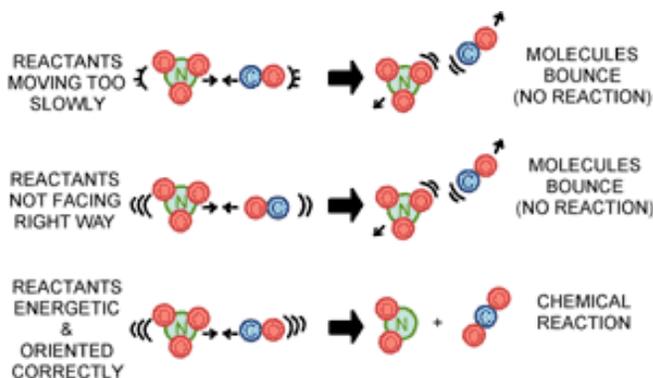
Kinetics and Equilibrium concern themselves with the energy of a chemical reaction, and where that energy was and goes to. Reactants of a chemical reaction have potential energy, but unless they are provided with a start up energy known as the ACTIVATION ENERGY, the reaction will not start, or finish.

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 related to the energy involved. For example, 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. Energy exists, can be measured, and 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.

### Collision Theory

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. They must come together for their valence electrons to interact. 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:*

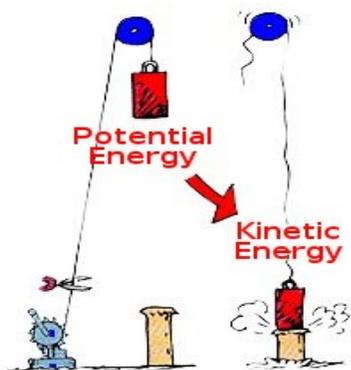
- **Increase in Temperature.** By adding to the kinetic energy of the chemical system, the result is more and stronger collisions. Particles move faster as temperature increases and collide more often. The rate of a chemical reaction is directly related to the kinetic energy (temperature) of the system.
- **Increase in surface area of the reactants.** By increasing surface area, 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 molecules you have bumping around, the more likely these particles 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.
- **Adding a CATALYST.** A catalyst's 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. Catalysts are a necessary part of all biological reactions. Without them the activation energy would take too long to be reached and reactions would move to slow. Biological catalysts are known as ENZYMES.

▶ **Video: A chemical catalyst in action** [Genie in a bottle](#) (control click)

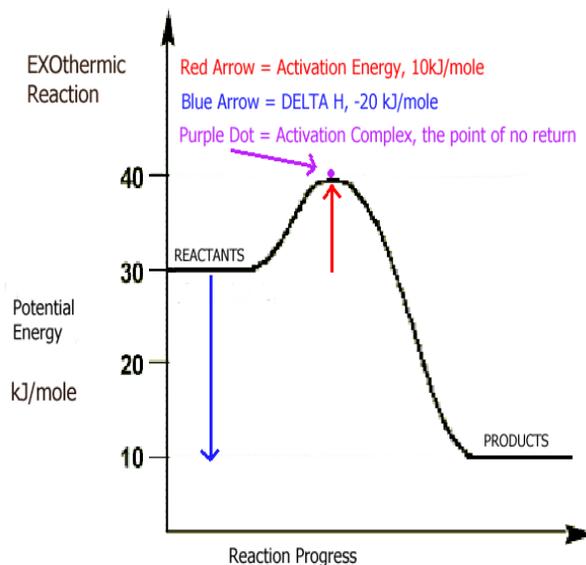
## Potential Energy Diagrams



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, however, both are potential energy diagrams. They show the potential energy of the reactants and products at all times during the chemical reaction. The 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

Note where the REACTANTS potential energy level is. It is flat until kinetic energy is added. The products have potential energy as well. In an exothermic reaction, the products have LESS potential energy than the reactants. It 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 (kilojoules per Mole) to make the reaction happen. This is an



investment of energy. A minimum amount of energy is required for reactions to occur. If too little energy is applied, the reactants will not react.

When the reactants secure enough activation energy, they form a very temporary **Activated complex**. This is the in-between stage when reactants are not really reactants anymore, but they are not quite yet the products. 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  $\Delta H$ , known as the **Heat of reaction**. 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 released into the environment. The units of energy for  $\Delta H$  are kJ/mole. You can use the graph's Y-axis to measure the actual energy values, or use Table I to get the exact  $\Delta H$  values for 25 different reactions.

**Reference Table I** Lets use see exothermic reactions with their negative  $\Delta H$ , and also the endothermic reactions with their positive  $\Delta H$ . This is just a list of 25, there are thousands of thermo-chemical reactions in the universe.

The **most endothermic** reaction on table I is  $C_2H_4(g)$  forms, and takes in 227.4 kJ of energy.

The **most exothermic** reaction by far is when octane combustion and releases energy. It takes 2 moles octane produce 10943 kJ; one mole octane would release half that amount of energy or 5471.5 kJ is released.

Imagine a heating pad put onto your achy elbow. The pad undergoes a chemical reaction that is exothermic ( $-\Delta H$ ), releasing heat. The heat, or kinetic energy goes from the pad into your elbow. You feel good.

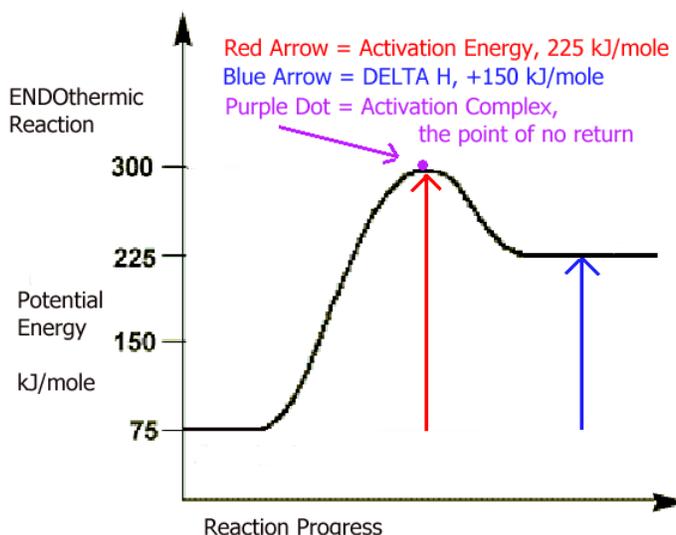
If you rather a cold pad, those reactions that undergo endothermic reactions ( $+\Delta H$ ), and the pad is cold. Place it on your twisted ankle. The pad does not "send" cold to your ankle, rather the heat from your ankle is transferred to the pad.

*Using Table I:*

How much heat is absorbed when 2.50 moles of NaOH is dissolved into water?

The  $\Delta H$  for this reaction on Table I for NaOH dissolving into water is +44.51 kJ. That is for ONE MOLE of sodium hydroxide. The mole ratio is when one mole NaOH is dissolved into water it absorbs that many kilojoules of energy. You have 2.50 moles here. The ratio would be this way:

|  |  |   |
|--|--|---|
| <sup>1</sup><br>$\frac{1 \text{ mole NaOH}}{44.51 \text{ kJ}}$ | <sup>2</sup><br>$\frac{2.50 \text{ moles NaOH}}{X \text{ kJ}}$ | <sup>3</sup><br>Cross multiply and solve for X kilojoules of energy |
| <sup>4</sup><br>$X = (44.51\text{kJ})(2.50\text{mol})$         | <sup>5</sup><br>$X = 111.275 \text{ kJ}$                       | <sup>6</sup><br>With 3 SF:<br>111 kJ energy <b>absorbed</b>         |



## The ENDOTHERMIC diagram

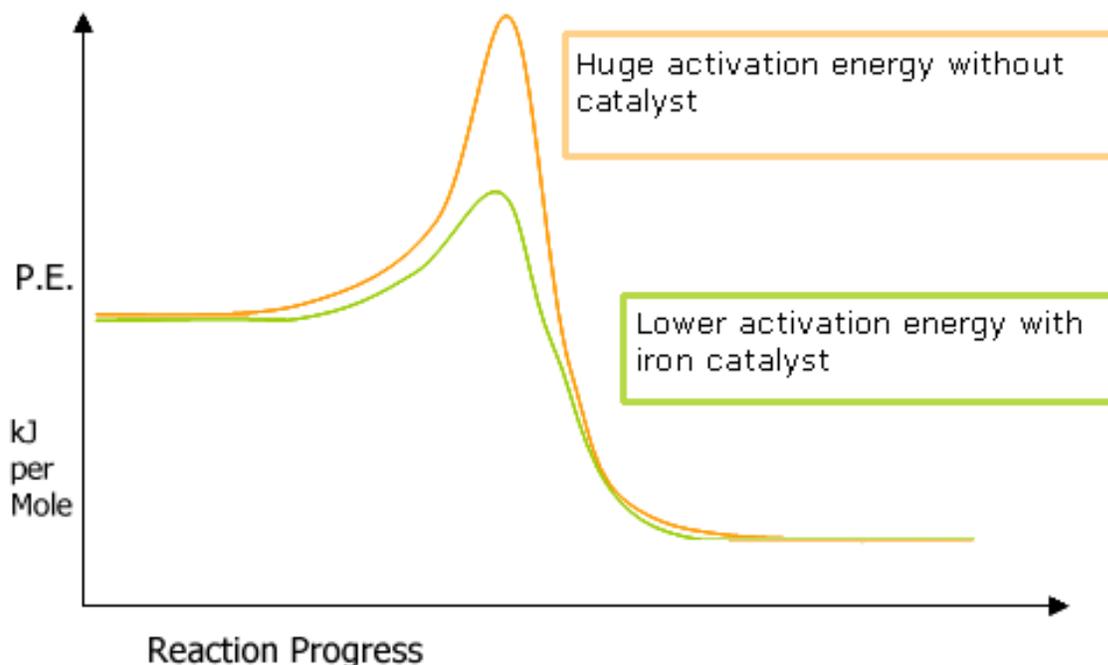
The endothermic potential energy diagram has all of the same parts as the exothermic one, however, the difference is that the products have MORE potential energy than the reactants did. In order for this to happen, this extra energy has to be absorbed from the immediate environment and put into the products. That is why endothermic reactions feel "colder", since they are quite literally sucking energy into the chemistry from the surroundings. They take this kinetic energy and convert it into potential energy stored in the products.

## Catalysts

A catalyst 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 GREEN line. Without a catalyst is with the ORANGE line. a DOTTED line.

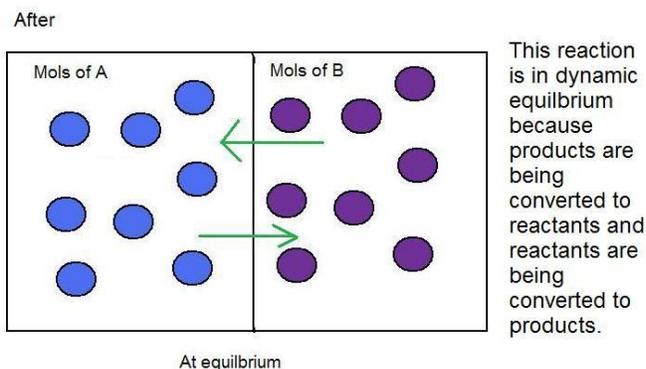
An **inhibitor** will of course inhibit or slow or even stop a chemical reaction. Often they block the catalyst from working, but can also work by blocking the reaction itself.

The potential energy is sometimes called free energy as well.



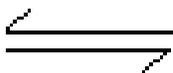
## Dynamic Equilibrium

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.



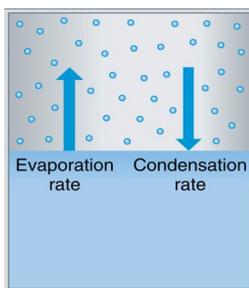
The symbol " $\rightleftharpoons$ " also represents dynamic equilibrium.

A reaction that reads left to right is called the forward reaction. Reading a reaction from right to left is called the reverse. If a reaction is endothermic in the forward reaction the energy will be part of the reactants of that reaction. The reverse reaction would be exothermic, since the energy would then become part of the products. For example:



The forward reaction is a synthesis reaction that is endothermic since the energy is going in as a reactant to form the product. The  $\Delta H$  for the forward reaction would be a positive value.

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 would be negative since the energy would become part of the products.

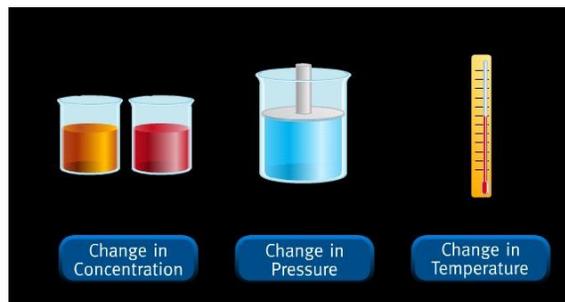


**This dynamic equilibrium exists at changes of phase of matter!**  
 The evaporation rate equals the condensation rate of water in our atmosphere. That's why you do not see water droplets everywhere all the time!

## Out of Balance..Now what?

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 by lowering the activation energy needed to start the reaction.

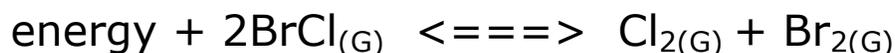
Equilibrium is a state that can only exist depending upon the conditions. When these conditions are altered (change temp, pressure, or concentrations of reactants), this equilibrium will adjust to the new conditions and create a new dynamic equilibrium at these new conditions. Every time you adjust the 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.”**

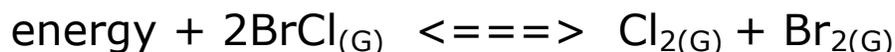
When you have a chemical reaction in dynamic equilibrium, you can adjust the temperature, pressure, or concentrations of reactants, and you can predict which way the equilibrium will shift (temporarily) until a new equilibrium is reached.

Let's examine this reaction in detail...



### Forward reaction

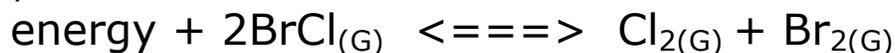
1. left to right
2. endothermic (energy is added to reactants, no energy release in products)
3. decomposition reaction (big substance forms 2 or more smaller substances)



### 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)

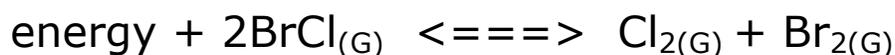
Let's now apply a stressor ...



### **Temperature & energy**

**Increased Temperature(energy)** shifts equilibrium to the right, additional energy will further decompose the bromine chloride into chlorine and bromine.

**Decreased 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.



### **Gases & Pressure**

**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.

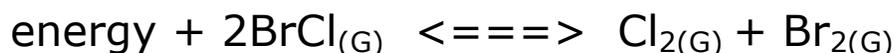
**Decreased Pressure** will have no affect on this system for the same reason stated just above.

### **Pressure & moles**

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 of molecules.

A **decreased pressure** would push the reaction in the opposite direction, since 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 are TEMPORARY. It just lasts until a NEW DYNAMIC EQUILIBRIUM is reached.



### **Concentration changes**

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

**Increased BrCl(reactant)** will tend to cause MORE decomposition to happen, The equilibrium shifts to the right. A decrease in BrCl will do the opposite, shifting to the left.

**Increased Cl<sub>2</sub>** will tend to cause MORE synthesis (more collisions due to higher concentration) so the equilibrium will shift to the left until the new equilibrium is reached. Decreased Cl<sub>2</sub> will do the opposite and shift the equilibrium to the right.

**Increased  $Br_2$**  will tend to cause MORE synthesis (more collisions due to higher concentration) so the equilibrium will shift to the left until the new equilibrium is reached. Decreased  $Br_2$  will do the opposite and shift the equilibrium to the right.

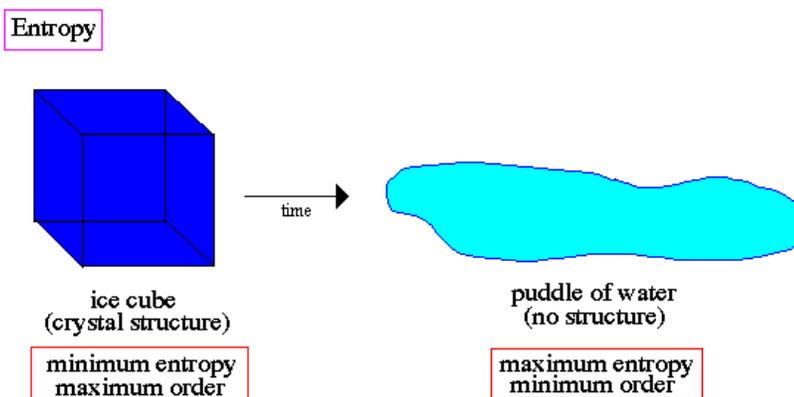
## Entropy

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

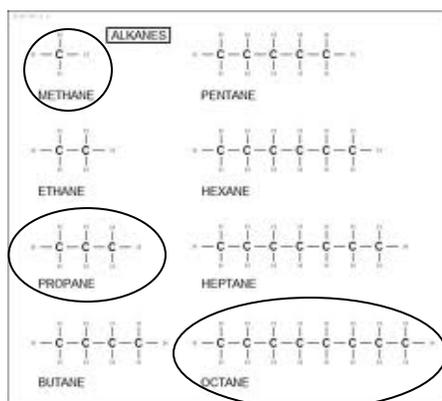
Technically it is quantifiable, with a complex equation, but that is outside the scope of our class. Entropy is measurable and comparable.

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.*



**Large particles** have **less entropy** than smaller particles. Octane(8 Carbon alkane) has lower entropy than methane(1 Carbon alkane) or propane(3 Carbon alkane)



**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, and the universe is falling apart. Energy dissipates, and then particles spread out.

*Best of all, if you happen to keep a messy bedroom, you can remind your parents that the universe prefers disorder!!! It's all Chemistry!*

