

# Kinetics & Equilibrium BASICS

Kinetics and Equilibrium is the part of chemistry that measures the flow of energy through a chemical reaction, and also the rate of reaction, and finally the concept of dynamic equilibrium as it pertains to chemical reactions. We will examine the energy requirement to start a reaction, and the energy emitted by the reaction as well.

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.”

We learned that matter cannot be created or destroyed in any chemical (or physical) process. Neither can energy. Energy has to be accounted for. It exists, it can be measured, it can be transferred from one kind of energy to different kinds, and we need to keep track of it.

Endothermic reactions absorb an exact amount of energy to go forward.

Exothermic reactions release a specific amount of energy as well.

This is all based upon the number of moles involved in the reactions. It is all quantifiable and measurable. We have Table I to tell us how much energy is released, or absorbed by many different reactions. This change in energy is called the DELTA “H”, or  $\Delta H$ . The  $\Delta H$  must always have a sign, positive for endothermic reactions, and negative sign for exothermic ones.

We also will draw potential energy diagrams, which show the change in potential energy from the REACTANTS as they change into PRODUCTS.

## 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 faster the reaction. 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.

4 factors that affect the RATE of chemical reactions	
Increase in Temperature	Hotter particles move faster, causing more collisions, causing faster reactions. The rate of a reaction is directly related to the kinetic energy (temp) of the system.
Increase in Surface Area	More surface area leads to more collisions, and faster reactions. Smaller particles means “less waiting” for particles on the inside of larger particles to react after the outer ones do first.
Increase the Concentration	Stronger solutions have more ions or molecules per mL, leading to more collisions and of course, faster reactions. A lower molarity solute will lead to less collisions.
Catalysts	The use of catalysts do speed up chemical reactions, but they do not increase the collisions between particles. They do lower the energy needed to start the reaction (activation energy), or provide an alternate chemical pathway which is quicker.

## Table I — Heats of Reaction at 101.3 kPa and 298 Kelvin

Table I shows 6 combustion reactions, 12 synthesis reactions, and 6 ionic compounds forming a mixture (solution) in water. The last line of the table we will not discuss yet in our class.

All of these have what is called the DELTA “H”, or  $\Delta H$ . That is the change in heat of the reaction (or of the solution formation). All combustion reactions are exothermic, energy is emitted as a product. All of their  $\Delta H$  have negative signs. LOOK NOW at the 2nd line on the bottom of Table I. It says: “A minus sign indicates an exothermic reaction.”

Energy is not negative, or positive. The negative sign is your note that the energy is a product, it’s emitted.

The synthesis reactions have either negative or positive  $\Delta H$  values. Those with a +  $\Delta H$  are endothermic, they absorb energy when they occur. The reactions with a  $-\Delta H$  are exothermic (like the combustion reactions).

These  $\Delta H$  are called the HEATS OF REACTION (that’s the title of the table).

The six solution formations are also both positive or negative. Although these are not chemical reactions, they still have a  $\Delta H$  value as they either absorb or emit energy when the solutions form. Technically speaking, the  $\Delta H$  here ARE NOT heats of reaction, these are not chemical reactions. Here the  $\Delta H$  are the HEATS OF SOLUTION.

As a reminder, the first reaction, the combustion of methane, is exothermic. How exothermic? The  $\Delta H$  is  $-890.4$  kJ/mole, which means when one mole of methane combusts, this reaction emits 890.4 kilojoules of energy as a product.

Two moles of methane combusting releases  $2 \times 890.4$  kJ

3.50 moles of methane combusting releases  $3.50 \times 890.4$  kJ

The mole ratio for this reaction is 1:2:1:2, and the thermochemical mole ratio is 1:2:1:2: 890.4 kJ

All of the synthesis reactions can be reversed, that is you might combine CO and O<sub>2</sub> and form CO<sub>2</sub> which would release 566.0 kJ of energy.

Table I shows this:  $2\text{CO}_{(G)} + \text{O}_{2(G)} \rightarrow 2\text{CO}_{2(G)}$   $\Delta H$  is  $-566.0$  kJ/mole

Which means this:  $2\text{CO}_{(G)} + \text{O}_{2(G)} \rightarrow 2\text{CO}_{2(G)} + 566.0$  kJ (energy is emitted, exothermic)

But you can reverse this to:  $2\text{CO}_{2(G)} + 566.0$  kJ  $\rightarrow 2\text{CO}_{(G)} + \text{O}_{2(G)}$  (energy is absorbed, endothermic)

These reactions can all be “reversed” and the amount of energy is identical except that the sign for  $\Delta H$  changes. Endothermic reactions reverse to exo. Exothermic reactions reverse to endo.

Find this one now...  $\text{NaCl}_{(S)} \xrightarrow{\text{water}} \text{Na}^{+1}_{(AQ)} + \text{Cl}^{-1}_{(AQ)}$   $\Delta H$  is  $+3.88$  kJ/mole

When table salt, sodium chloride dissolves and ionizes in water to form salt water, it will absorb a bit of energy and get a touch cooler (only 3.88 kJ per mole of NaCl). When salty water evaporates away, this is completely reversed.

$\text{Na}^{+1}_{(AQ)} + \text{Cl}^{-1}_{(AQ)} \rightarrow \text{NaCl}_{(S)} + \text{H}_2\text{O}_{(G)}$  *which evaporates away*  $\Delta H$  is  $-3.88$  kJ/mole

# POTENTIAL ENERGY DIAGRAMS

We can show the flow of energy in a chemical reaction in a graph called a Potential Energy diagram.

They show the energy in the bonds of the reactants and products at all times during the chemical reaction. The 2 kinds are exothermic potential energy diagrams, and endothermic potential energy diagrams.

They are very similar (and different). Understand them to tell them apart. 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.

## Exothermic Potential Energy Diagrams

The Y axis shows potential energy in kilojoules per mole. The X axis label is always about the start and end of the reaction. Here it's "reaction progress", but you will see "time of reaction" or "reaction pathway"/

Find REACTANTS. This shows the potential energy that is in the reactants. This is inherent, it is how much energy these reactants have. It's a constant and it's in a book, but we will NOT have to know the exact numbers. It stays constant, or flat, forever, the potential can't change, it's due to what the reactants are.

When you add energy, you heat up the reactants, they gain potential. For instance, if your reactants are explosive when they react, hotter reactants have a greater potential to explode. They can only react if they get ENOUGH energy to react. That amount is the "top of the hill" energy called the "ACTIVATION ENERGY". Less than that amount makes the reaction almost happen, but the whole AE is needed for reaction to proceed.

Once the reaction gets to "the top of the hill" it cannot be stopped and it proceeds to form products.

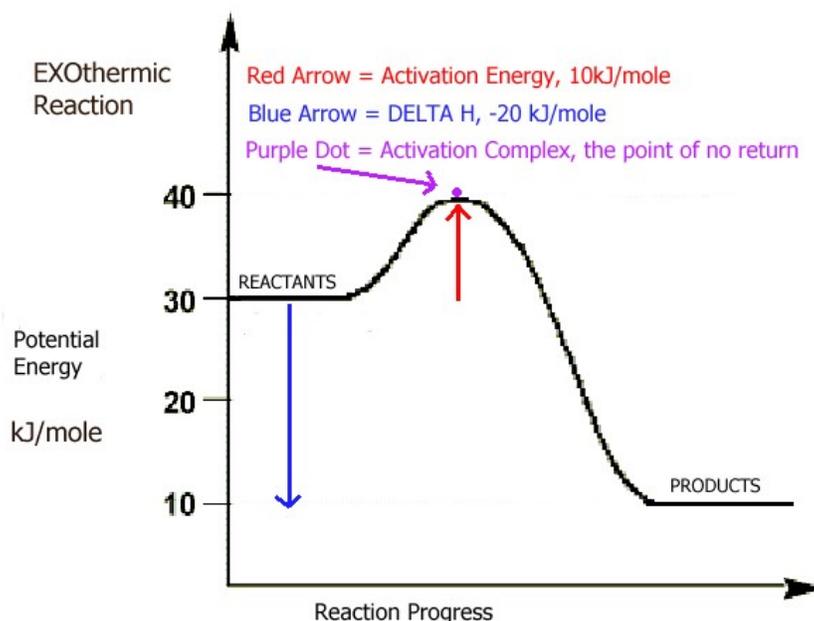
Here the products have less energy than the reactants started with. Where did that energy go? It was released, exothermically. It's not lost, it is released from the reaction into the environment. And it's in ratio the balanced equation from table I (or other tables).

When the reactants secure the activation energy, they 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 activation complex forms exactly at the top of the curve of the potential energy diagram. It lasts a nanosecond.

The difference in potential energy between the reactants and products is the  $\Delta H$ .

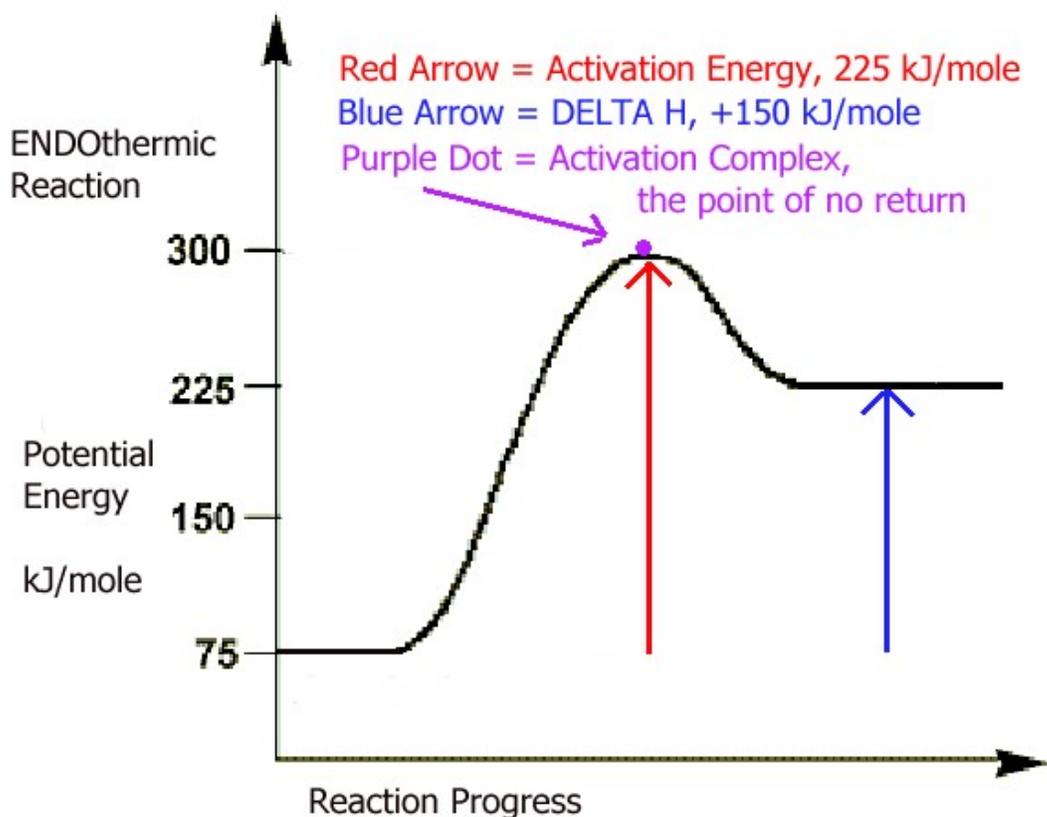
The  $\Delta H$  is always negative in an exothermic reaction, because the products always have less potential energy than the reactants started with. This extra energy is released into the environment.



## 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 literally absorbing energy into the bonds from the surroundings, taking this kinetic energy and converting it into potential energy stored in the products.



Here the reactants start with 75 kJ/mole potential energy at the “beginning of the graph”.

To react they need to absorb the activation energy of 225 kJ/mole (that’s  $300 - 75 = 225$ )

The AC has 300 kJ of energy, but once the products start to form energy is released.

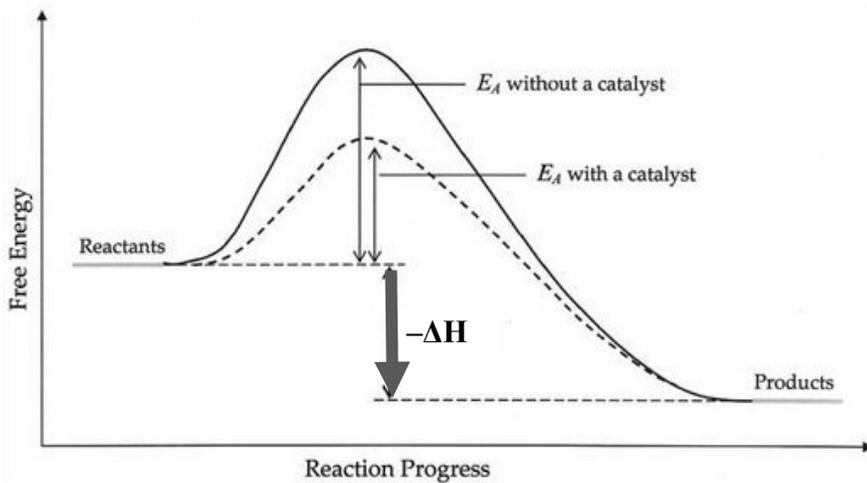
The products finish up with 225 kJ/mole of potential energy.

That’s a difference of (net gain) of 150 kJ/mole.

The  $\Delta H$  is +150 kJ/mole (that’s  $225 - 75 = 150$ )

## Catalysts in Potential Energy Diagrams

A catalyst lowers the activation energy of the reaction. It takes less energy to get to the “top” of the hill, so the reaction happens faster. We show the effect of a catalyst with a dotted line. The catalyst must lower the AE, but the reaction “pathway” needs still to go both “up and down” inside the middle of the graph.

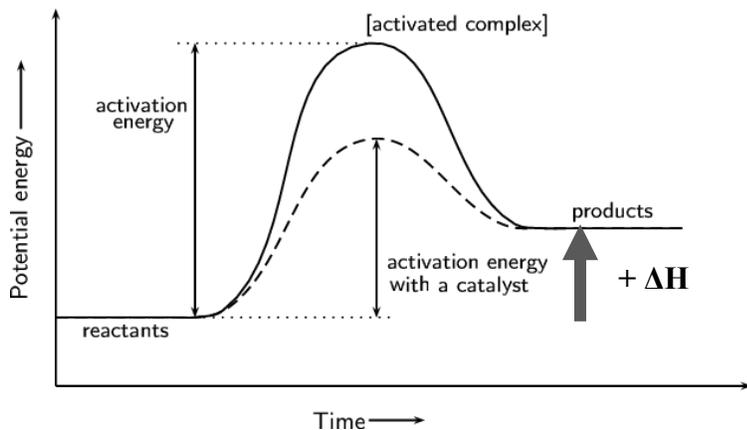


Here  $E_A$  means energy of activation. Normally this reaction follows the solid line to the “top” of the hill.

With a catalyst the reaction can follow an alternate path (a shortcut so to speak) which is the dotted line.

The  $\Delta H$  does not change, the catalyst does not change the start or end points.  $\Delta H$  is this difference.

Since this graph goes “DOWN”, the  $\Delta H$  is negative.



Here the catalyst affect (dotted line) still goes “up and down” inside the dome of the graph, which lowers the AE but not changing the  $\Delta H$ . Since the graph goes “UP”, the  $\Delta H$  is POSITIVE.

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 stopping the reaction.

## 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. In equilibrium the forward reaction keeps happening at same rate as the reverse reaction. Constantly changing and constantly staying the same.

The symbol is this:  $\rightleftharpoons$

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

The forward reaction below is the synthesis of AB. The forward reaction is endothermic as energy is a reactant. The reverse reaction is the decomposition of AB and it's exothermic as the reverse reaction releases energy as a product. The double arrows mean that the synthesis happens at a certain rate, which is matched by the decomposition.



The  $\Delta H$  for the forward reaction is unknown exactly, but it has a  $+\Delta H$   
The reverse reaction has a  $-\Delta H$ , unknown but equal to it's

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)
- adding or removing stuff (reactants or products)

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

Equilibrium is a state that can exist depending upon the current conditions. When these conditions are altered (change temp, pressure, or adding/removing stuff), this equilibrium accommodates the stress, and creates a new dynamic equilibrium at the new conditions. Every time you adjust the conditions, the dynamic equilibrium will adjust to relieve the stress you have applied, and another new equilibrium forms.

This seems basic when you think about it, but it was proposed first by the French chemist named Henry Louis LeChatelier in the early 1880's. The famous “LeChatelier's Principle is this:

“A dynamic equilibrium will stay in equilibrium. If a stress is added to a chemical equilibrium, the system will adjust to relieve the 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 amounts of reactants, and you can then predict which way the equilibrium will shift FORWARD or REVERSE to accommodate that stress, and then a new equilibrium can form.

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

$\text{N}_{2(\text{G})} + 3\text{H}_{2(\text{G})} \rightleftharpoons 2\text{NH}_{3(\text{G})} + \text{energy}$	The stress will cause this to happen because...
Add $\text{N}_2 \rightarrow$	Forward shift, causes more collisions to speed up synthesis, until a new dynamic equilibrium is reached.
Add $\text{H}_2 \rightarrow$	Forward shift, causes more collisions to speed up synthesis, until a new dynamic equilibrium is reached.
$\leftarrow$ Add $\text{NH}_3$	Reverse shift, more ammonia can only decompose quicker, until a new dynamic equilibrium is reached.
$\leftarrow$ Add heat	Reverse shift, more heat will cause faster decomp, until a new dynamic equilibrium is reached.
Increase Pressure $\rightarrow$	This is special. Higher pressure favors less moles of gas. There are less moles of gas going forward, so, Forward shift until a new dynamic equilibrium is reached.
$\leftarrow$ Decrease pressure	This is special. Lower pressure favors more moles of gas. There are more moles of gas going reverse, so, Reverse shift until a new dynamic equilibrium is reached.
X Add a Catalyst X	Catalysts do not favor forward or reverse, but they do get to equilibrium faster. We indicate this will a "double X" instead of two arrows.
$\leftarrow$ Remove $\text{H}_2$	Removing $\text{H}_2$ makes the forward reaction slow down. With less $\text{H}_2$ we get less collisions. Reverse shift, until a new dynamic equilibrium is reached.
Remove $\text{NH}_3 \rightarrow$	Less decomp can happen so we get a forward shift, until a new dynamic equilibrium is reached.
Remove heat $\rightarrow$	Less heat slows the reverse reaction while the forward reaction keeps going. Here we get a forward shift, until a new dynamic equilibrium is reached.

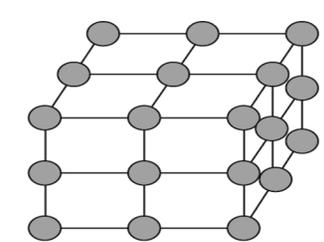
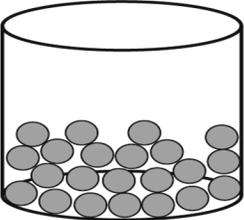
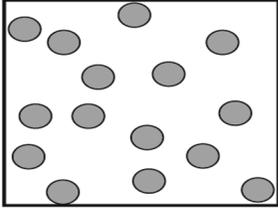
This reaction is technically NOT a real dynamic equilibrium, the forward reaction is very exothermic ( $\Delta H = -3351 \text{ kJ}$ ), but if the double arrow are present, we will use this more as a thinking exercise. This is more of an exercise on LeChatelier's Principle than actual chemistry. It's practice, and the shifting rules will be followed because of the double arrows.

$4\text{Al}_{(s)} + 3\text{O}_{2(g)} \rightleftharpoons 2\text{Al}_2\text{O}_{3(s)} + \text{energy}$	The stress will cause this to happen because...
$\leftarrow$ Add $\text{Al}_2\text{O}_3$	Reverse shift, more $\text{Al}_2\text{O}_3$ causes more decomposition, until a new dynamic equilibrium is reached.
Add $\text{O}_2 \rightarrow$	Forward shift, causes more collisions to speed up synthesis, until a new dynamic equilibrium is reached.
Add $\text{Al} \rightarrow$	Forward shift, causes more collisions to speed up synthesis, until a new dynamic equilibrium is reached.
$\leftarrow$ Decrease pressure	Lower pressure favors more moles of gas. There are 3 moles of gas on the left, and NO moles of gas on the right. Reverse shift until a new dynamic equilibrium is reached.
$\leftarrow$ Add heat	Reverse shift, more heat will cause faster decomp, until a new dynamic equilibrium is reached.
Increase Pressure $\rightarrow$	Higher pressure favors less moles of gas. There are NO moles of gas on the right, so this will favor a forward shift until a new dynamic equilibrium is reached.
<b>X</b> Add a Catalyst <b>X</b>	Catalysts do not favor forward or reverse, but they do get to equilibrium faster. We indicate this will a "double X" instead of two arrows.
$\leftarrow$ Remove $\text{Al}$	Removing $\text{Al}$ makes the forward reaction slow down. With less $\text{Al}$ we get less collisions. Reverse shift, until a new dynamic equilibrium is reached.
Remove $\text{Al}_2\text{O}_3 \rightarrow$	By removing $\text{Al}_2\text{O}_3$ there will be forward reaction but much less of the reverse, so we will get a forward shift, until a new dynamic equilibrium is reached.
Remove heat $\rightarrow$	Less heat slows the reverse reaction while the forward reaction keeps going. Here we get a forward shift, until a new dynamic equilibrium is reached.

## ENTROPY

Entropy is the measure of disorder, or chaos, in a chemical system. Technically it is quantifiable, with a complex math, but that is outside the scope of our class. Entropy for us is just going to be comparable.

We can compare entropy by PHASE water in its three phases.

 <p><b>Solid</b></p>	 <p><b>Liquid</b></p>	 <p><b>Gas</b></p>
<p><b>Lowest Entropy</b> Ice has the lowest entropy because the molecules are all stuck in place. They can “hum” but they don’t really move around. They are well organized, and not chaotic.</p>	<p><b>Medium Entropy</b> Water has medium entropy. Liquids stay within the beaker, but the molecules are in constant motion.</p>	<p><b>Highest Entropy</b> Steam has the highest entropy. Gas molecules move the fastest and are not likely to stay contained. They have high chaos compared to the other two phases.</p>

Another way to compare different substances and entropy is by particle size. Larger particles have a lower entropy than smaller particles when they are at the same conditions of pressure and temperature.

These three gases are all at the same Temperature and Pressure

octane $C_8H_{18}$	propane $C_3H_8$	methane $CH_4$
26 atoms bonded together LOWEST ENTROPY	11 atoms bonded together MEDIUM ENTROPY	5 atoms bonded together HIGHEST ENTROPY

A final way to compare entropy is by temperature.

1.5 M $NaCl_{(AQ)}$ at $10^\circ C$	1.5 M $NaCl_{(AQ)}$ at $40^\circ C$	1.5 M $NaCl_{(AQ)}$ at $85^\circ C$
COLDEST has the LOWEST ENTROPY	Medium temperature has MEDIUM ENTROPY	HOTTEST has the HIGHEST ENTROPY

**The Universe is tending towards higher entropy and lower energy.**  
Things are breaking down into smaller particles, the Universe is falling apart. Energy dissipates.

The end. ☺