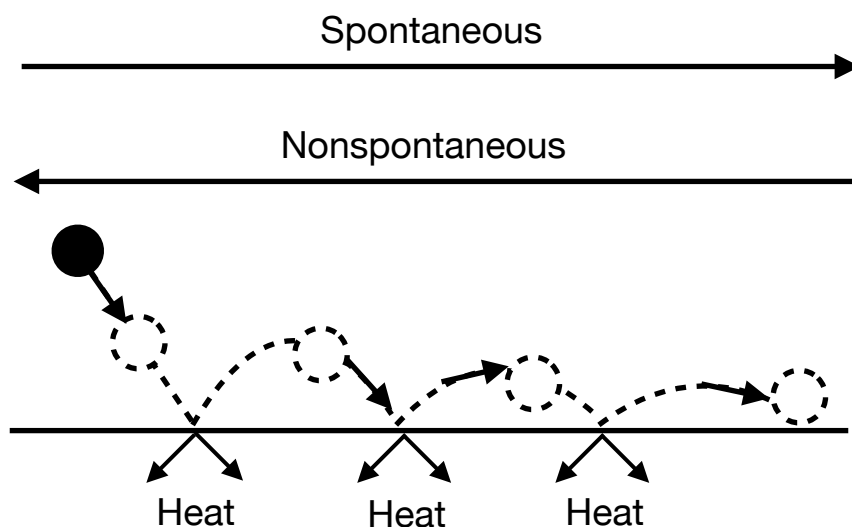
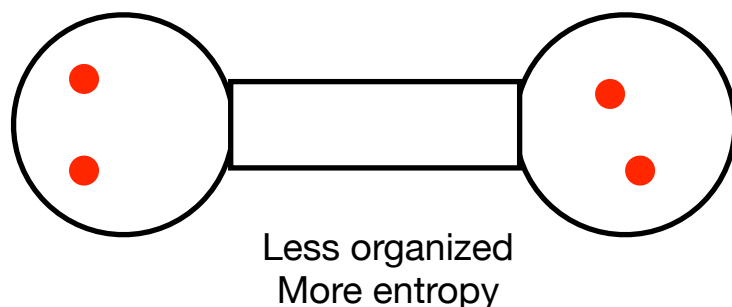
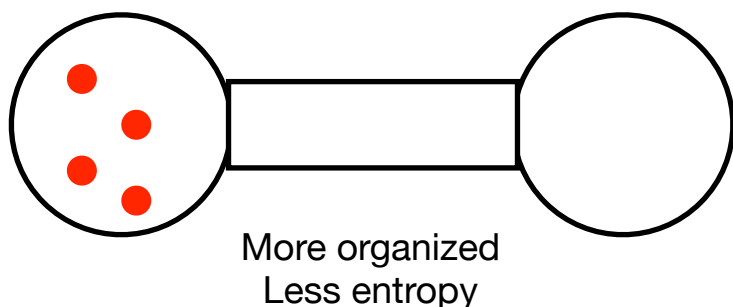


# Thermodynamics

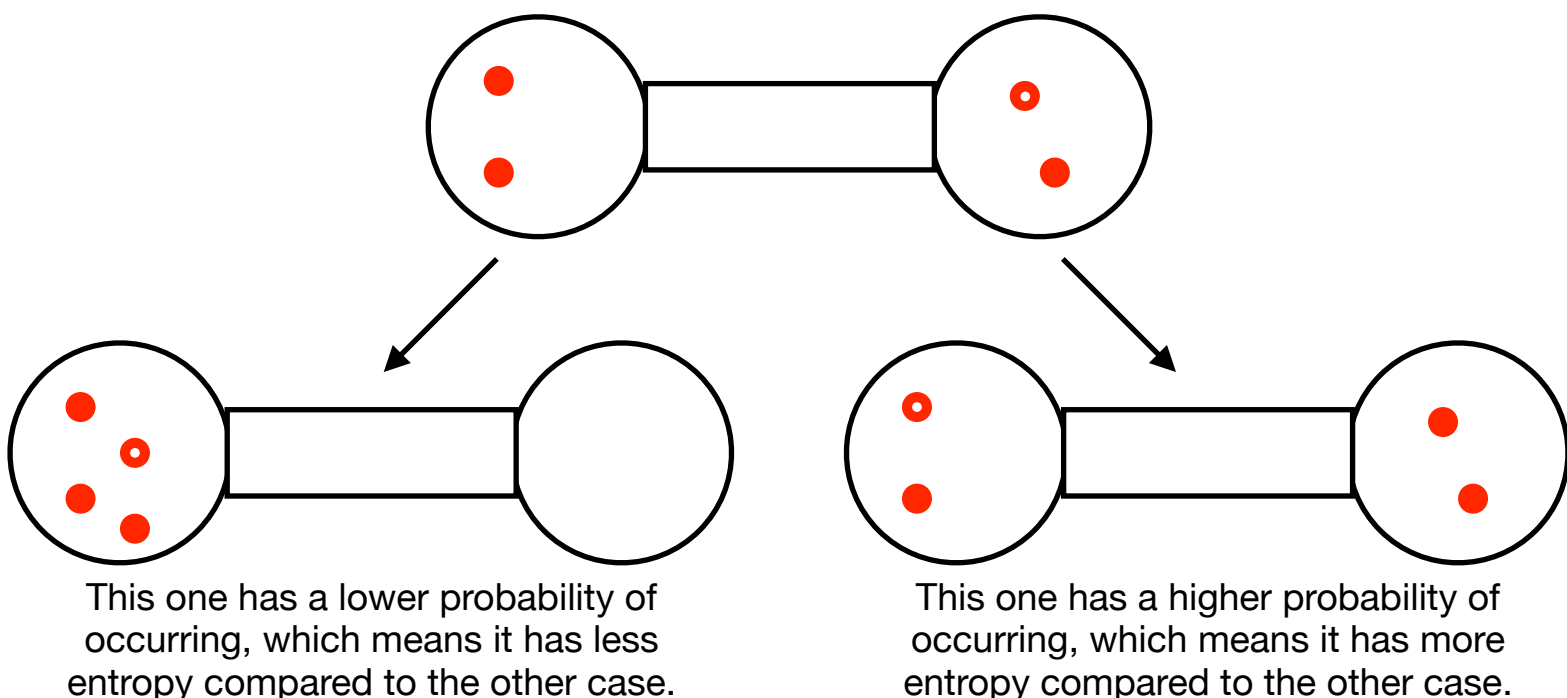
- Thermodynamics is the study of chemistry that will determine if a reaction will take place. One of the values in thermodynamics is the concept of entropy. Entropy can be loosely defined as the amount of disorder a system has. Consider a ball that is falling



- The ball will never spontaneously go in the reverse direction. Before the ball is dropped the energy of the system is highly organized. After the ball is dropped the energy of the system is highly disorganized.
- After the ball falls and comes to rest the energy gets transferred into heat and sound. Heat is the transfer of motion of the molecules in a random motion. Because this motion is random we classify the transfer of energy as becoming more disorganized.
- What does it mean for a system to become more “disorganized” or a system that is increasing in entropy? There is a connection between entropy (or disorder) with probability. For example consider a container that has two bulbs (a left side and a right side) and we put 4 red balls in it. Each ball can either be found on the left side or right side.



- From looking at the two pictures above the left picture has more “order” or has less entropy. But who is to say that when all of the balls are on one side that it has less entropy? Because there are only two places each ball can appear and the amount of entropy is related to a probability we can think of the appearance of the balls on each side as a coin flip where the left side represents heads and the right side represents tails.
- If we flip a coin 4 times it is more likely that we will get 2 heads and 2 tails vs getting all 4 heads. Therefore, because there is a higher probability for getting 2 heads and 2 tails (or 2 balls on the left side and 2 balls on the right side) that one will have more entropy and is considered less organized. One way that we could ensure that we get each of the balls on the left side is that we could place them there, but that would require us to put in energy. There is also a connection between how much energy is put in and entropy that we will discuss later.
- Let's imagine we have a bulb with 2 balls on the left side and 2 balls on the right side. Which path is more likely to occur if each ball represents one coin flip and each ball is allowed a “do-over” coin flip. To relate this back to chemistry this would be if the molecules are allowed to move within the container.



- The difference between the start for where the balls are in the container and the right scenario is that the ball label with the white dot has switched places. If a change were to take place it is more likely that the change will look more like the right scenario than the left, which means the left scenario has more entropy than the right.
- Now let's imagine that we have a dice with 16 sides and we have a table with 16 boxes where each box represents one side of the dice. If we roll the dice it is more likely that we will get two numbers that are not right next to each other on the grid than to get two numbers are next to each other.
- For example, let's say that we roll a 1 on the first roll. The probability that we will roll a 2, 5, or 6 on the next roll is not as likely as getting a 3, 4, 7, 8, 9, 10, 11, 12, 13, 14, 15, or 16 simply because there are more of the second set of numbers.

Not as likely

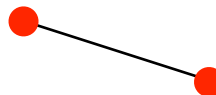
● 1	2	3	4
● 5	6	7	8
9	10	11	12
13	14	15	16

More likely

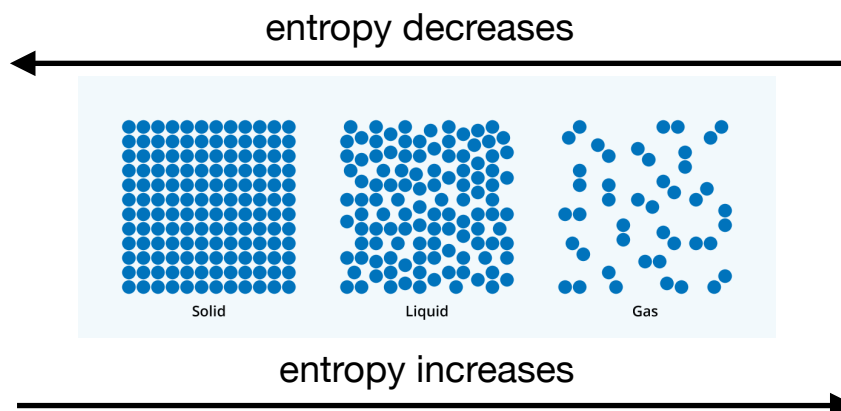
● 1	2	3	4
5	6	7	● 8
9	10	11	12
13	14	15	16



- If we make a connection between the two dots of 1 and 5 it would look similar to what a solid would look like (if the connection was a bond) and if we make a connection between dots 1 and 8 it would look more like a gas or liquid molecule.



- The following picture shows what the atoms/molecules look like for a solid, liquid, and gas.



- Solids have the most order, then liquids, then aqueous, the gases. Gasses have a much greater amount of disorder or entropy than any other phase. You can use the following chart to determine if entropy is increasing or decreasing:

Entropy of the System	
Highest Priority	Creating more moles of a gas creates more disorder
	The phases below show an increase in disorder from left to right:  s → l → aq → g
Second Highest Priority	As heat is added to the system the amount of disorder will increase.
Third Highest Priority	As the volume of the system increases the amount of disorder will increase.

**BEWARE:** Entropy is a measure of disorder. Something that has a high amount of order will have a low entropy value and something that has a high amount of disorder will have a high amount of entropy.

*Example -1:*

Determine the sign of entropy for each of the following:

1. A cube of sugar dissolves in hot coffee.
2. A lake freezes in the winter.
3. Rainwater on the pavement evaporates.
4.  $\text{Pb (s)} + 1/2 \text{ O}_2 \text{ (g)} \rightarrow \text{PbO}_2 \text{ (g)}$
5.  $\text{C}_2\text{H}_2 \text{ (g)} + 2\text{H}_2 \text{ (g)} \rightarrow \text{C}_2\text{H}_6 \text{ (g)}$
6.  $\text{CuCl}_2 \text{ (s)} \rightarrow \text{Cu}^{2+} \text{ (aq)} + 2\text{Cl}^- \text{ (aq)}$

—To determine the sign of the entropy you need to look at what phase transitioning is happening. For the first example a cube of sugar, which is a solid, becomes aqueous. A solid is the highest amount of order (lowest entropy) so if a reaction produces something that is not a solid is an increase in entropy so **the change in entropy is positive**.

For number 2 when a lake freezes a liquid becomes a solid and because a solid has the most order **entropy is decreasing**.

For number 3 a rain puddle, which is a liquid, becomes a gas when it evaporates. A gas has a lot of disorder so **entropy is increasing**, which has a positive delta S.

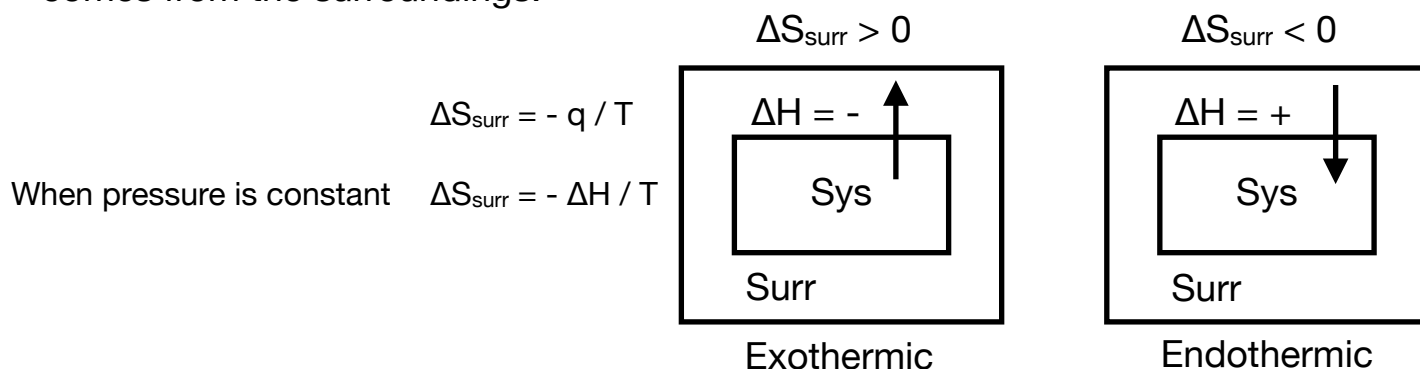
For number 4 we have a solid a gas creating only a single solid. If the reaction is making the gas disappear by making a solid then **the change in entropy is negative** because more order is being made.

Number 5 has 3 moles of gas part of the reactants and 1 mole of gas as the product. Therefore, fewer moles of gas are being created which means more order is being created. This means that the **change in entropy will be negative**.

Number 6 has a solid that makes an aqueous solution. This means that a solid is being put into a liquid and the ionic bond breaks apart. Because a solid has the least amount of entropy and an aqueous has more entropy than a solid the **change in entropy will be positive**. —

## Second Law of Thermodynamic

- Some reactions (or processes) occur by themselves without us having to put in energy and other reactions require us to add energy to get them to proceed. For example if we go back to the first example on page 1 of the ball falling, the ball will fall all by itself and it will create more disorder as it proceeds to fall. This process is spontaneous and entropy increases. If we consider water becoming ice at -5C and at 1 atm that process is also occurring by itself, but instead it is creating order so entropy is decreasing.
- In order to make a chemical go from a solid to a liquid to a gas we have to put energy into the system in the form of heat, which at constant pressure is the change in enthalpy but where does this heat come from when reactions occur by themselves? The answer is that this heat comes from the surroundings.



- The second law of thermodynamics states that all spontaneous process increase the disorder of the universe. When a reaction does not occur by itself it is called nonspontaneous. The direction of spontaneity is determined by the change in the quantity of energy.

$$\Delta S_{\text{uni}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}} > 0$$

- For spontaneous process the energy becomes more dispersed in a more disordered way. Think back to the example of water freezing to make ice at -5C and at 1 atm. That process at that temperature and pressure is spontaneous but order is being created. How is that possible if all spontaneous processes increase the disorder of the universe? The answer is that the entropy of the surroundings must also be taking into account. The system includes what we are interested in and the surroundings includes everything else and together those make up the entropy of the universe.
- Some reactions are reversible and for those reaction the change in entropy of the universe is equal to zero. For example consider ice melting. Ice melts and freezes at the same temperature and liquid can become and solid and a solid can become a liquid at 0C. So if you are given a chemical at the melting/freezing point or the boiling point the change in entropy of the universe will be equal to zero.

$$\Delta S_{\text{uni}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}} = 0$$

- There is a connection between if a reaction will occur all by itself, the entropy of the system, the enthalpy of the system, and the temperature. When a reaction is able to proceed all by itself it is called spontaneous, meaning we do not have to put energy into the system for the reaction to take place and the reaction will happen all on it's own.

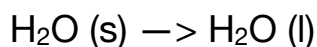
$$\Delta G = \Delta H - T\Delta S$$

- The  $\Delta G$  is the amount of energy in a system that is available to do work, which is called "Gibbs free energy". Many reactions have to generate heat in order to make the process spontaneous. Gibbs free energy is a measure of the remaining energy that is available to do work. The value determines which direction a reaction will proceed. When this number is negative the reaction will be spontaneous (Reactants will make Product), when the number is positive this reaction will be nonspontaneous (Products will make Reactants), and when this number is zero the reaction will be at equilibrium.

**BEWARE:** Gibbs free energy only tells you if a reaction will take place. It does not tell you how fast it will take place or what will be left over or in excess. It does not tell you how much of each reactant or product you have.

*Example -2:*

Determine the sign of  $\Delta S_{\text{uni}}$ ,  $\Delta S_{\text{surr}}$ , and  $\Delta S_{\text{sys}}$  for the process at 25C and 1 atm.



— To determine if the  $\Delta S_{\text{sys}}$  for the reaction is positive or negative you need to ask the question: Is the reaction creating order or disorder? If we go from a solid to a liquid that is creating more disorder and because entropy is a measure of disorder the  $\Delta S_{\text{sys}}$  for the reaction will be positive. —

— To determine if  $\Delta S_{\text{surr}}$  for the reaction is positive or negative you need to ask the question: Is heat entering or exiting the reaction? To get ice to melt heat from the surroundings must enter the system to turn the ice to water, so  $\Delta H$  must be positive and the  $\Delta S_{\text{surr}}$  has to be negative. —

— To determine if  $\Delta S_{\text{uni}}$  or  $\Delta S_{\text{tot}}$  for the reaction is positive or negative you need to ask the question: Will this reaction happen on its own? If we have a piece of ice at 25C and 1 atm it will melt because the normal melting point is 0C. Therefore, the  $\Delta S_{\text{uni}}$  for the reaction is positive. —

— You can use the following chart to determine which questions to ask when trying to figure out  $\Delta S_{\text{uni}}$ ,  $\Delta S_{\text{surr}}$ , and  $\Delta S_{\text{sys}}$ . —

$\Delta S_{\text{sys}}$	$\Delta S_{\text{surr}}$	$\Delta S_{\text{uni}}$
Is the reaction creating order or disorder?	Is heat entering or exiting the reaction?	Will this reaction happen on its own?
If order is being created $\Delta S_{\text{sys}}$ will be negative	If heat is entering the system $\Delta S_{\text{surr}}$ will be negative	If the reaction is nonspont $\Delta S_{\text{uni}}$ will be negative
If disorder is being created $\Delta S_{\text{sys}}$ will be positive	If heat is exiting the system $\Delta S_{\text{surr}}$ will be positive	If the reaction is spont $\Delta S_{\text{uni}}$ will be positive

• You can use the following chart to determine if a reaction will be spontaneous or not.

$\Delta H$	$\Delta S$	Result
-	+	Favored at all temps
+	+	Favored at high temps
-	-	Favored at low temps
+	-	Not favored at any temp

- You do not need to memorize the following table. When the temperature is low you can cover up the  $-T\Delta S$  in the equation  $\Delta G = \Delta H - T\Delta S$  and the equation become  $\Delta G = \Delta H$  at low temperatures. When the temperature is high the equation becomes  $\Delta G = -T\Delta S$ .

Low Temperature	High Temperature
$\Delta G = \Delta H$	$\Delta G = -T\Delta S$
When $\Delta H$ is negative the reaction is spont.	When $\Delta S$ is negative the reaction is nonspont.
When $\Delta H$ is positive the reaction is nonspont.	When $\Delta S$ is positive the reaction is spont.

- When we use the term “low temperature” and “high temperature” we are referring to the critical temperature for a particular reaction that needs to be reach for a reaction to be considered a “high” or “low” temperature. For example, some reaction will only be spontaneous at certain temperatures, but other will be spontaneous at all temperatures.

*Example -3:*

If the normal molar heat of fusion of  $H_2O$  is 6.01 kJ/mol what is the amount of entropy?

— If we are referring to the amount of heat that is released when water becomes ice or the amount of heat that is absorbed when ice becomes water then the temperature must be 0C. At the freezing point you are at equilibrium, which means you are at the temperature at which water can become ice and ice can become water. This means that the change in Gibbs free energy is equal to zero.

If we know the change in Gibbs free energy, the amount of enthalpy, and the temperature we can solve for the change in entropy.—

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

$$0 = 6.01 - 298.15 (\Delta S)$$

$$\Delta S = 0.02 \text{ kJ/mol}$$



- Just like when we used the formation enthalpy equation shown below

$$\Delta H_{\text{rxn}}^{\circ} = \sum (n \Delta H_{\text{f products}}^{\circ}) - \sum (n \Delta H_{\text{f reactants}}^{\circ})$$

We can also use a similar equation for  $\Delta S$  and  $\Delta G$ .

$$\Delta S_{\text{rxn}}^{\circ} = \sum (n \Delta S_{\text{f products}}^{\circ}) - \sum (n \Delta S_{\text{f reactants}}^{\circ})$$

$$\Delta G_{\text{rxn}}^{\circ} = \sum (n \Delta G_{\text{f products}}^{\circ}) - \sum (n \Delta G_{\text{f reactants}}^{\circ})$$

- Keep in mind that when we use these equations the concentrations must all be 1M at 0C and the pressure must 1 atm. As soon as the reaction starts the concentrations will no longer be 1M and the value we find for  $\Delta S$  and  $\Delta G$  will no longer apply. However, if the when all of the chemicals are at 1M finding  $\Delta S$  or  $\Delta G$  this way will give us some insight for which way the reaction will progress and if order will be created.