

Chapter 19: Thermochemistry II: Entropy and free Energy

Introduction

In Chapter 5, Thermochemistry, we introduced the First Law of Thermodynamics and saw how to use enthalpy to understand energy transfers for heating & cooling, phase changes, and chemical reactions. In this chapter we look more deeply into the laws of thermodynamics to see how they help us to predict the actual direction of change.

What does the word *Thermodynamics* bring to mind ?

Thermo - heat

Dynamics - motion or change

The science of Thermodynamics was developed around the study of steam engines and how to efficiently turn fuel into useful work. So statements of the laws of thermodynamics will often contain this kind of language.

First Law:

For a closed system the change in the internal energy of the system is equal to the sum of the energy in the form of heat exchanged between system and surroundings (q) and the work done on the system (w).

$$\Delta E_{\text{system}} = q + w$$

But the Laws of Thermodynamics are far more profound than simply describing the efficiency of steam engines. They constitute the fundamental principles that govern *all* energy changes. We will see how the concepts of heat and work generalize to the two principle ways that energy can be exchanged between system and surroundings. This will be clearer after we develop the ideas embodied in the Second Law but first, here are other statements of the First Law.

First Law:

The internal energy of an isolated system is constant. $E_{\text{isolated}} = \text{constant}$
Energy is conserved.

The total energy of the universe is constant. $E_{\text{universe}} = \text{constant}$

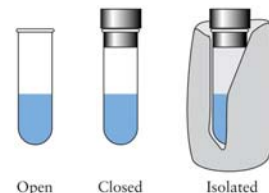
The *change* in the energy of the universe is zero. $\Delta E_{\text{universe}} = 0$

The First Law postulates the concept of internal energy, E , and tells us that while energy may change forms, it is *not created or destroyed*.

Notice that the First Law does not tell us what changes are allowed. To illustrate this, take a look at the following "film clip":

QuickTime™ and a decompressor are needed to see this picture.

FLASHBACK



Open System
Can exchange matter and energy with surroundings.

Closed System
Can exchange energy with surroundings

Isolated System
Cannot exchange matter or energy with surroundings

FLASHBACK

What is internal energy anyway ?

The sum of all the microscopic forms of energy, the kinetic and potential energies of the molecules of a system.

It does not include the translation or rotation of the system as a whole.

Cannot measure E directly. Can only measure the change in

1

2

3

What's wrong with this picture ? If you read left to right you notice that it is backwards. That is, the natural process occurs right to left, a diver leaps off the board into the water. We never observe the opposite happening, the water spontaneously gathering together and the diver flying backward up onto the board. It is no violation of the First Law for this to happen. Either way we view the "film clip", energy is conserved, but we know that there is an *allowed direction* and that we never observe the opposite.

If the Laws of Thermodynamics tell us the fundamental principles that govern *all* energy changes, there must be another law that tells us the *allowed direction* of change.

The Second Law of Thermodynamics summarizes this idea and is one of the most profound laws in nature. Here is a statement of the second law:

Second Law

All physical and chemical changes occur such that at least some energy disperses:
the *total concentrated or organized energy* of the universe *decreases*,
the *total diffuse or disorganized energy* of the universe *increases*.

The Second Law has to do with moving from concentrated energy to dispersed energy in the form of random thermal motion.

Think about this statement in light of the "film clip". The random, disorganized energy of the water and diver (frame 1) won't spontaneously organize itself and propel the diver backward onto the board (frame 3). The natural direction of change is for the concentrated energy of the diver to be changed into a leap with the water absorbing this energy and dissipating it into the pool.

The First Law is about the amount of energy. The Second Law is about the quality of the energy. The First Law postulates the thermodynamic variable *E*, the internal energy. The Second Law postulates a new thermodynamic variable *S*, the *Entropy*, a measure of the dissipated energy within a system at each temperature *that is unavailable to do work*. Entropy has units of:

$$\Delta \text{Energy per degree} = (\text{Joule} / \text{kelvin})$$

There are many different terms used to describe entropy - disorganized, chaotic, random, dispersed, diffuse, unconcentrated, dissipated, delocalized ... In all cases they are referring to the random molecular motion within a system that *cannot be harnessed to do work*. Increasing the temperature increases the random motion and thus increases the entropy.

Entropy tells us the direction of spontaneous change in nature. Change occurs in the direction of increasing total entropy. An isolated system, one that cannot exchange matter or energy with the surroundings (think thermos jar), will never spontaneously decrease in entropy. It will remain unchanged or move to higher entropy. The direction of change is that in which the energy goes from a more concentrated state to a more diffuse state.

Entropy is about the *dispersal* of energy, like the spreading out of water poured onto sand.



OWL Example Problem
19.3a Active Figure: Matter and Energy Dispersal
19.3b Active Figure: Entropy and Dissolving
19.3c Active Figure: Dissolution of NH_4NO_3

Here are some statements of the Second Law using the concept of Entropy:

Second Law

All physical and chemical changes occur such that the **total entropy** the universe *increases*.

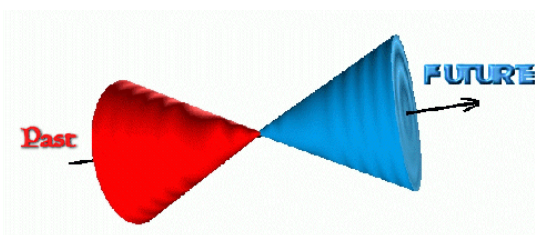
$$S_{\text{universe}} = \text{increases} \quad \text{or} \quad \Delta S_{\text{universe}} > 0$$

The **entropy** of an isolated system never spontaneously *decreases*.

$$\Delta S_{\text{isolated}} \geq 0$$

Time's Arrow and Microstates

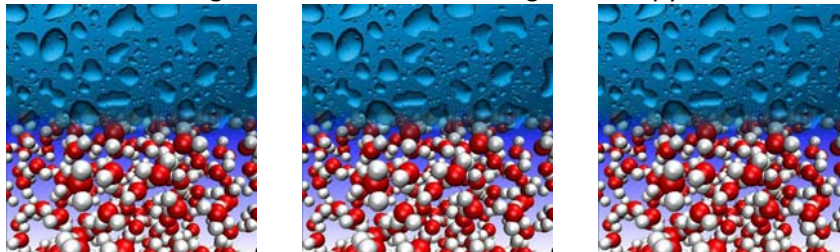
You may hear the statement "*Entropy is time's arrow*". In light of the "film clip" this should make sense, the time axis points to the left, not in the opposite direction. Why is the direction of change toward dissipated energy? Why doesn't the energy dispersed throughout the water spontaneously gather together?



One way to think about this in terms of probability. There are a huge number of ways that the total energy can be distributed into the random motions of the water molecules + diver (FRAME 1). There are a small number of ways to concentrate this same amount of energy in the diver on the board. To go from the state in frame 1, to the state in frame 3, the random thermal energy of the water molecules would have to transfer all of their energy to the diver in the water simultaneously so that he is propelled backwards onto the diving board. This single concentrated state is possible, but it is so unlikely compared to the hundreds of million-million ways to distribute the energy in the water molecules as thermal motion, that the probability of this happening is essentially zero.

Thus at a molecular level we can relate entropy to the number of ways the total energy can be distributed among all of the particles. Each distribution of the energy at the molecular level

characterizes a *microstate* of the system. The entropy is measure of the number of microstates that are accessible at given total energy. The entropy of a system measures the number of ways the system can be different microscopically and still have the same macroscopic state. A high number of microstates (diver in water with energy dispersed in the enormous number of water molecules) corresponds to a high entropy and the natural change in direction is toward higher entropy.



Note: Have a series like this with a slight change in each to help visualize 3 different microstates and the enormous number of ways to distribute the same total E.

This interpretation was developed very elegantly by Austrian physicist, Ludwig Boltzmann and is summarized in the equation:

$$S = k_B \ln W$$

Where k_B = Boltzmann's constant = 1.381×10^{-23} J/K
 W = number of microstates



Notice that Boltzmann's constant has units of entropy (energy/degree) and, as the number of microstates, W , goes up, the entropy, S goes up.

A system can bump itself into any of the " W " accessible microstates, depending upon how much thermal energy is available. The amount of energy available is determined by the temperature. Temperature is a critical factor when considering entropy. You can think about entropy as the amount of diffused energy within a substance at a given temperature. We will come back to this when we discuss the Third Law of Thermodynamics.

Direction of spontaneous change
 Macroscopic view - Dispersal of energy
 Molecular view - Increase in number of accessible microstates.

Spontaneous - What does it really mean ?

We have used the term *spontaneous* when talking about the Second Law, but what do we really mean by this ? When you think of spontaneous you might think *immediate*, but this is not correct. Spontaneous has a precise thermodynamic definition:

- Any process in which the total entropy of the universe increases.
- Any process that is able to occur without being *driven* by an external source of energy.

Notice that time is not a part of the thermodynamic definition of spontaneous. A spontaneous process may or may not happen immediately. For example, the conversion of diamond to graphite is a spontaneous process at 25°C and a pressure of 1 bar:



C(*diamond*)

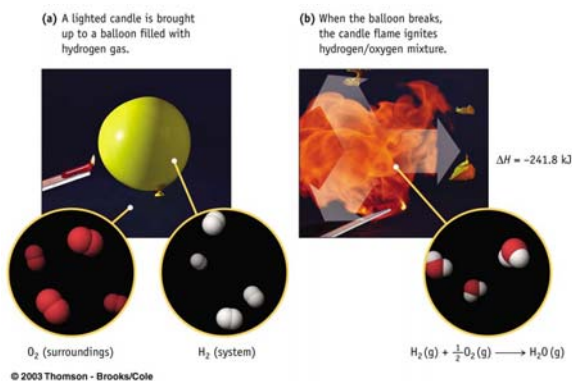
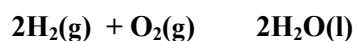
C(*graphite*)

$$\Delta S_{\text{universe}} > 0$$

From a thermodynamic prospective this means that the conversion of carbon in the form of diamond, to carbon in the form of graphite, increases the entropy of the universe. But we know that the reaction is SLOWWWW. So slow that you will not observe it in your lifetime (diamonds are forever). A spontaneous process has nothing to do with time. It merely has to do with the generation of entropy, whether a net amount of energy is dissipated at a given temperature.

An *immediate* process, on the other hand, refers to how fast a process takes place. This is the realm of kinetics, not thermodynamics. If a process happens immediately, it is kinetically favorable. It also has to ultimately generate entropy in order to happen. So an immediate process is both fast and spontaneous.

Another point of confusion, when talking about a spontaneous process is that, although it may require an initial "push" to get it started, it can still be spontaneous. Think about the spontaneous reaction between hydrogen gas and oxygen to create water.




Without an initial spark, these two gases can exist indefinitely undisturbed. The reaction is still spontaneous, whether it happens or not ! The kinetics of this reaction require an initial input of energy (to overcome the energy of activation, a kinetic barrier). Once the reaction begins though, it continues to happen without being driven by an external source of energy.

Contrast this to the reverse reaction, the splitting of water into hydrogen and oxygen gas:

$2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$

NOTE: Get picture with apparatus plugged into wall outlet for discussion below.



Electrolysis of water

For this reaction to proceed a *constant input of energy* must be provided. It must be *driven* by an external source, in this case, electrical energy. Finding cheap ways to "split" water to generate hydrogen gas, a clean-burning fuel, is an important area of chemical research. Electrolysis is very costly but some bacteria are able to do this. Growing bacteria is inexpensive and this idea holds promise for a cheap source of hydrogen in the future.

One final point of confusion about nonspontaneous processes is that you may think that they cannot occur at all. Just as the electrolysis of water shows above, a nonspontaneous process can be made to occur if it is driven by an external source of energy. The overall entropy of the universe must still increase. That is, the production of the energy driving the nonspontaneous process must itself generate more entropy than is consumed. In the case of the electrolysis of water this happens at the power plant where fossil fuels are burned to generate the electricity, throwing off waste heat.



Heat and Work revisited

So now, looking back at the First Law, $\Delta E = q + w$, we can think about heat as a transfer of energy that spreads out in the random motions of the particles. We can think about work as a transfer of energy that is concentrated or localized. In the language of steam engines, heat and work are the terms used to talk about the two ways to transfer energy, through random collisions or concentrated motion.

The Second Law tells us that for a process to happen spontaneously it must create entropy, it must dissipate some energy.

Here are some other statements of the Second Law:

Second Law

It is impossible to completely turn heat into work.

It is impossible to extract thermal energy from a bath at one temperature and turn it completely into work. Some energy must be simultaneously discarded as heat at a lower temperature.

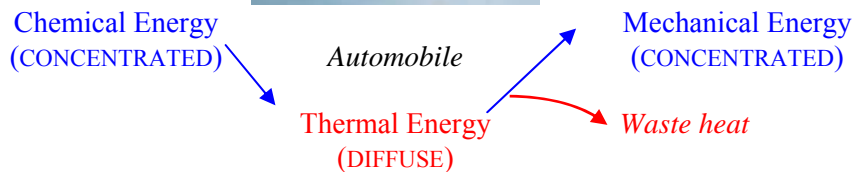
Heat flows from hot to cold - The entropy in the hot area decreases but the entropy in the cold area increases more. For same ΔE , $\Delta S = \Delta E / \text{degree}$, more profound change at low T (inversely proportional).

In all cases the underlying message is that in order for an exchange of energy to occur spontaneously, some of the energy must become more diffuse. Some energy must always be discarded as heat. Otherwise there is no driving force for the change. This is very profound stuff and has inspired lively discussions from how life came about, to the heat death of the universe.



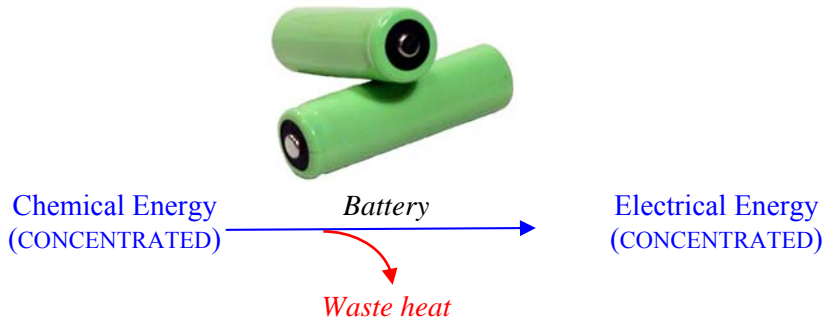
It's really an Entropy crisis.

If the total energy of the universe is constant, how can there be an energy crisis? We aren't losing energy but the Second Law tells us that we are converting it into forms that are not useable. For example in an automobile, concentrated chemical energy in the form of fossil fuel is converted into hot gases (thermal energy) that drive pistons (mechanical energy) and are then spewed out of the tail pipe and cool in the surrounding atmosphere (lower temperature thermal energy).

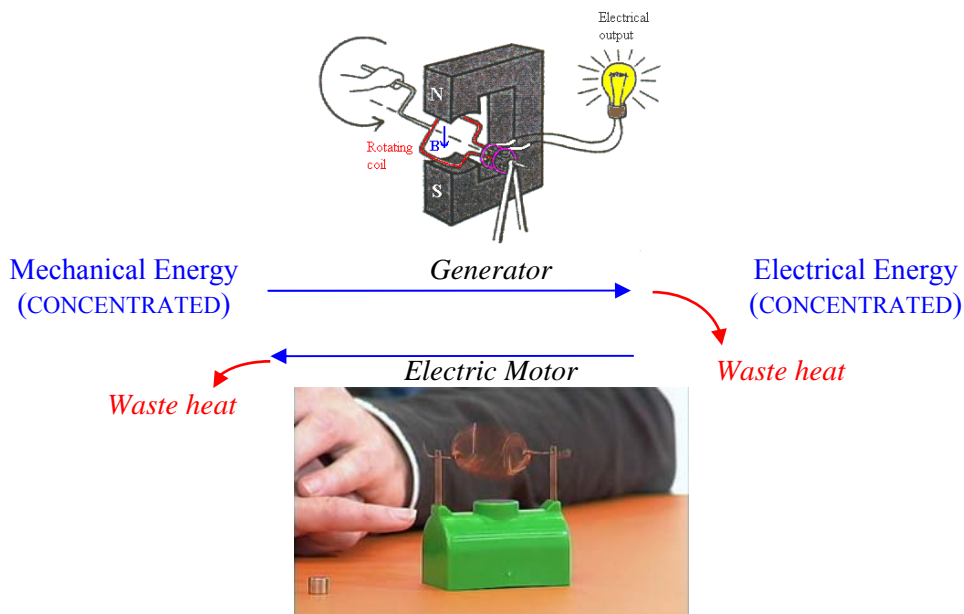


The Second Law tells us that every time an energy exchange occurs some of it must wind up as heat, dissipated energy. In Step 1 it is possible to completely turn concentrated chemical energy into thermal energy. But in order for the diffuse thermal energy of the hot gases to be "reconcentrated" back into mechanical energy some of the energy must be discarded as heat. There cannot be a 100% conversion of heat into work in step 2. And, because we are converting from diffuse energy to concentrated energy, the process is inherently inefficient, ranging from 30% for automobile engines to 85% for a home gas furnace.

Other types of processes are much more efficient than those based upon combustion reactions because they avoid the intermediate step of converting to diffuse thermal energy. So for example, a battery spontaneously converts chemical energy into electrical energy. Waste heat is generated but the conversion process is much more efficient, on the order of 90% for a dry cell.



Similarly an electric generator converts mechanical energy into electrical energy at efficiencies around 97%. An electric motor does the opposite conversion with efficiencies around 93%.



Thus if we start with a concentrated energy and convert it to another form of concentrated energy, a little heat must be given off to drive the process, but the efficiency is much higher if we choose a converter that avoids an intermediate step using diffuse thermal energy.

The Third Law and Standard Entropies

We have already talked about the fact that as the temperature increases, the random molecular motions of a substance increase and therefore the entropy increases. What happens if you do the opposite, decrease the temperature further and further? The random motions decrease and the entropy goes down. Is there a place where molecular motion essentially stops? If so, the entropy of a substance would become zero. This idea is encompassed in the Third Law of Thermodynamics. As with the First and Second Laws, there are many statements of the Third Law. Here is the one that we will use:

Third Law: The entropy of a pure crystalline substance is zero at absolute zero.

$$\text{As } T \rightarrow 0 \text{ K, } S (\text{pure crystal}) \rightarrow 0 \text{ J/K}$$



A pure crystalline substance is one in which the molecules are in perfect alignment with one another and every molecule is identical. If the molecules do not align themselves perfectly, a substance will have some residual entropy at absolute zero. This is not a violation of the Third Law.

The Third Law of Thermodynamics tells us that there is a zero of entropy. As the temperature is increased, the entropy of a substance increases. The standard entropy of a pure substance, S° , can be determined by careful measurements of the heat capacity as a function of temperature, C_p and by the heat absorbed for each phase change, $\Delta H^{\circ}_{\text{fusion}}$, $\Delta H^{\circ}_{\text{vaporization}}$ and $\Delta H^{\circ}_{\text{sublimation}}$. Recall that heat capacity is the energy required to raise the temperature of a substance by 1° . It has the same units as entropy, Joule/Kelvin.

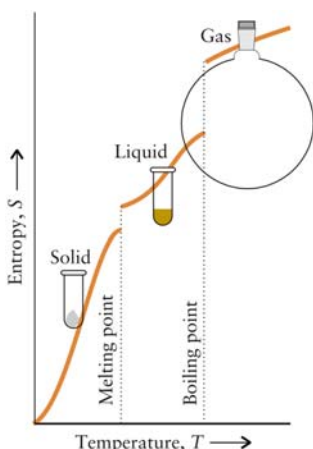


TABLE 7.2 Standard Molar Entropy of Water at Various Temperatures

Phase	Temperature (°C)	S_m° ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)
solid	-273 (0 K)	3.4
	0	43.2
liquid	0	65.2
	20	69.6
	50	75.3
	100	86.8
vapor	100	196.9
	200	204.1

Notice that at each phase change there is a dramatic rise in entropy as the temperature remains fixed.

Standard Entropies for pure substances at 25°C are reported in Table 1.

TABLE 7.3 Standard Molar Entropies at 25°C ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)*					
Gases	S_m°	Liquids	S_m°	Solids	S_m°
ammonia, NH_3	192.4	benzene, C_6H_6	173.3	calcium oxide, CaO	39.8
carbon dioxide, CO_2	213.7	ethanol, $\text{C}_2\text{H}_5\text{OH}$	160.7	calcium carbonate, CaCO_3^{\dagger}	92.9
hydrogen, H_2	130.7	water, H_2O	69.9	diamond, C	2.4
nitrogen, N_2	191.6			graphite, C	5.7
oxygen, O_2	205.1			lead, Pb	64.8

*Additional values are given in Appendix 2A.
[†]Calcite.

FLASHBACK

Standard State
Use same definition as in Chapter 5

Notice in the table that we write S° for a substance, not ΔS° . Because of the Third Law there is an absolute reference point for entropy, $S = 0 \text{ J/K}$ at $T = 0\text{K}$. The standard entropy may also be called the "Third Law entropy" or "absolute entropy".

FLASHBACK

Standard Enthalpy of Formation
Enthalpy change when one mole of a substance is produced from its elements in their standard states.

Use tabulated values to calculate $\Delta H^{\circ}_{\text{rxn}}$ of any reaction:

Contrast this to energy, where there is no temperature at which the internal energy or enthalpy goes to zero. We can only talk about the energy or enthalpy of a substance *relative to* other substances. Thus we must use tabulated values of the enthalpies of formation, ΔH_f^0 (enthalpy of compound *relative to* enthalpy of its elements) to calculate the enthalpy change for a chemical reaction. We do not use absolute enthalpies.

From the Table of Absolute Entropies above a few trends can be observed. The entropy of every substance is greater than zero (recall that for elements $\Delta H_f^0 = 0$, no energy is given off or absorbed in creating an element from itself). At a given temperature, the entropies of gases are, in general, higher than liquids, which are higher than solids. Heavier or more complicated substances tend to have higher entropies than lighter or simpler substances because they have more ways to store thermal energy at a given temperature. The standard entropy of a substance is essentially a measure of the amount of energy distributed within it at 25°C.

Standard Entropy Summary

T = 0 K	S^0 (pure crystal) = 0 J/K
Increase T	S^0 increases
At a specific T	$S^0(\text{gas}) > S^0(\text{liquid}) > S^0(\text{solid})$
At a specific T	$S^0(\text{heavier, more complicated}) > S^0(\text{lighter, simpler})$

Entropy of phase change **Where does this belong. Breaks up the flow here**

When a solid melts it undergoes an increase in entropy (See figure X). The temperature remains constant during this process and at constant pressure the energy change is equal to ΔH_{fusion} . The entropy change for this process is $\Delta H_{\text{fusion}}/T_{\text{fusion}}$. Similar reasoning holds for vaporization and sublimation. We can write a general expression for the change in entropy for any phase change:

$$\Delta S_{\text{phase}} = \Delta H_{\text{phase}}/T_{\text{phase}}$$

TABLE 7.2			TABLE 7.1 Standard Entropy of Vaporization at the Norm	
ENTHALPY CHANGES OF FUSION AND VAPORIZATION†			Liquid	Boiling point (K)
Substance	ΔH_{fus} (kJ mol ⁻¹)	ΔH_{vap} (kJ mol ⁻¹)		
NH ₃	5.65	23.35	acetone	329.4
HCl	1.992	16.15	ammonia	239.7
CO	0.836	6.04	argon	87.3
CCl ₄	2.5	30.0	benzene	353.2
H ₂ O	6.007	40.66	ethanol	351.5
NaCl	28.8	170	helium	4.22
			mercury	629.7
			methane	111.7
			methanol	337.8
			water	373.2

† The enthalpy changes are measured at the normal melting point and the normal boiling point, respectively.

*The normal boiling point is the boiling temperature at 1 atm.

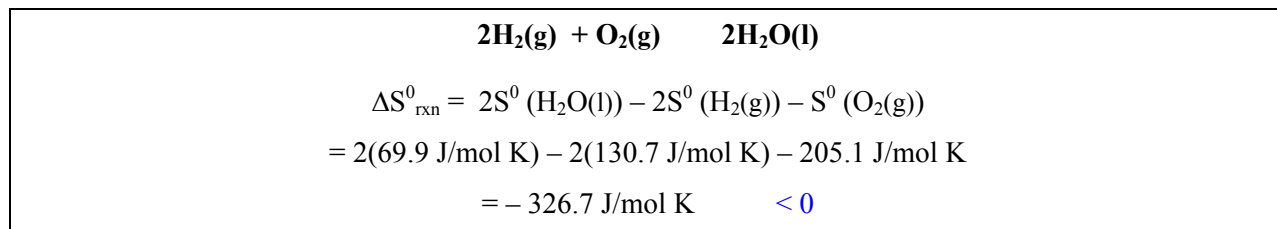
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Standard entropy change of reaction

Similar to calculating ΔH_{rxn}^0 we can use standard entropies to calculate the standard entropy change for a chemical reaction, ΔS_{rxn}^0 at 25°C and 1 atm.

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

The *sign* of $\Delta S_{\text{rxn}}^{\circ}$ can often be estimated by taking into account the phases of reactants and products. For example, when hydrogen and oxygen gas react to form liquid water, 3 moles of gas are converted into 2 moles of liquid. The entropy of the system has clearly gone down in this reaction and you would predict that $\Delta S_{\text{rxn}}^{\circ}$ for this reaction would be negative. A calculation of confirms this.





OWL Example Problem
x.x Standard Entropy of Reaction

Entropy change of the surroundings

We said previously that the reaction between hydrogen and oxygen is spontaneous. How can that be possible if $\Delta S_{\text{rxn}}^{\circ}$ is negative? The Second Law states that the entropy of the *universe* must increase.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \quad \text{for spontaneous process}$$

If the system entropy went down but the reaction is spontaneous, the entropy of the surroundings must have gone up, and it must have gone up more than the system entropy went down.

What could contribute to an increase in entropy of the surroundings? Think about what happens when hydrogen and oxygen react. They produce a ball of flames. This reaction is highly exothermic. The flames and heat of this reaction are thrown outward, increasing the thermal energy of the surrounding molecules. The entropy of the surroundings goes up and this more than compensates for the fact that the system entropy goes down.

$$\Delta S_{\text{surroundings}} > -\Delta S_{\text{system}}$$



We have seen how to use standard entropies to calculate the change in entropy of the system. How do we calculate the change in entropy of the surroundings? It must be related to energy given off or absorbed in the reaction. At constant pressure this is equal to the change in *enthalpy* of the system.

The amount of energy that enters the surroundings is $-\Delta H_{\text{system}}$. If we assume that the surroundings is large enough to dissipate the energy without changing temperature, the *entropy* change in the surroundings is:

$$\Delta S_{\text{surroundings}} = -(\Delta H_{\text{system}} / T_{\text{surroundings}})$$

For an exothermic reaction this is a positive quantity, the entropy of the surroundings goes up. Exothermic reactions create entropy in the surroundings and help drive a reaction forward.

For an endothermic reaction this is negative, the entropy of the surroundings goes down. Endothermic reactions decrease entropy in the surroundings and in order for these reactions to be spontaneous the entropy change of the system needs to be high.

Gibbs Free Energy

We can rewrite the Second Law entirely in terms of system variables:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{system}} - (\Delta H_{\text{system}} / T) > 0 \text{ for spontaneous process}$$

Closed system at constant T and P

Note we are careful to say *closed system at constant T and P*. Let's be sure you understand each of these statements:

Closed System

The system and surroundings exchange energy. If they don't, the energy of the reaction would go entirely to changing the temperature of the system. The temperature would increase for an exothermic reaction and decrease for an endothermic one, but the surroundings would not be affected and $\Delta S_{\text{surroundings}}$ would equal 0.



Constant Pressure

The heat absorbed at constant pressure equals ΔH and so $\Delta S_{\text{surroundings}} = -(\Delta H_{\text{system}} / T_{\text{surroundings}})$.

Note: figure above is for constant volume or for a solution rxn.

Constant Temperature

We set $T_{\text{surroundings}} = T_{\text{system}} = T$. If you think about an exothermic reaction like the combustion of hydrogen this can be confusing. The temperature certainly changes during this reaction! In order to be sure that we are measuring a well-defined change we set up the reaction conditions so that the system and surroundings are at the same initial temperature (thermal equilibrium). We allow the reaction to happen and we measure the heat given off. But when do we stop? We let it run until the temperature of the system is back to the initial temperature. This gives a well defined starting and ending point. This is why the temperature is always specified on thermodynamic tables. So "constant temperature" really means $\Delta T = T_{\text{final}} - T_{\text{initial}} = 0$. The actual temperature can, and usually does, change during the course of the reaction, but the final and initial temperatures are always equal.

Equation x above is a statement of the Second Law in terms of entropy, energy per degree. If we multiply by the temperature, we have units of energy (entropy x T = (Joule/K) x K = Joule).

$$T\Delta S_{\text{universe}} = T\Delta S_{\text{system}} - \Delta H_{\text{system}} > 0$$

Now multiply through by -1 (remember the inequality reverses):

$$-T\Delta S_{\text{universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}} < 0$$

This is a statement of the Second Law in terms of energy where $-T\Delta S_{\text{universe}}$ is the change in the Gibbs Free Energy, ΔG . This is a new energy resulting from the Second Law under the special case of constant T and P.

$$-T\Delta S_{\text{universe}} = \Delta G = \Delta H - T\Delta S < 0 \text{ for spontaneous process}$$

Closed system at constant T and P

As we stated previously this equation is entirely in terms of system variables, even though it takes into account ΔS_{system} and $\Delta S_{\text{surroundings}}$. It is common to drop the subscript "system" but remember that this is understood.

$\Delta G = \Delta H - T\Delta S$ is one of the most important equations in chemistry because it tells us the direction of spontaneous change at constant temperature and pressure. If ΔG is less than zero, the reaction is spontaneous in the forward direction. If ΔG is greater than zero the reaction is not spontaneous and must be driven by an external source of energy. It is actually spontaneous in the reverse direction. If $\Delta G = 0$, the reaction is at equilibrium. There is no driving force for change either forward or reverse.

$\Delta G = \Delta H - T\Delta S$	
$\Delta G < 0$	Spontaneous in forward direction.
$\Delta G = 0$	At Equilibrium. No net change will occur.
$\Delta G > 0$	Not Spontaneous forward. Spontaneous in reverse.

Three Thermodynamic Energies

Notice that we have defined three different kinds of thermodynamic energies, ΔE , ΔH and ΔG . It can be a little confusing which is which, so here is summary of how to think about each:

1. The Internal Energy comes directly from the First Law, $\Delta E = q + w$. It is the sum of all the microscopic kinetic and potential energies of all the particles that make up a system.
2. The Enthalpy is a defined energy based upon the internal energy, $H = E + PV$. It is convenient for constant pressure processes common in chemistry because $\Delta H = q_p$, the heat absorbed at constant pressure. Chemists use enthalpy more than internal energy. Think about enthalpy as the internal energy measured at constant pressure.
3. The Gibbs Free Energy, like enthalpy is a defined energy, $G = H + TS$. But it comes from the Second Law, $\Delta S_{\text{universe}} > 0$. At constant temperature and pressure ΔG points the direction of chemical change.

$$\Delta G = -T\Delta S_{\text{universe}} < 0 \quad \text{CONSTANT T AND P.}$$

Internal energy, E , and Enthalpy, H , are First Law energies. They have to do with the *amount* of energy exchanged. The Gibbs Free Energy is a Second Law energy. It has to do with the *direction* of change and the *quality* of the energy, the maximum amount that is available to do work.

Standard Gibbs Free Energy

Similar to the standard enthalpy of reaction, ΔH^0_{rxn} we can define the standard Gibbs Free Energy of reaction, ΔG^0_{rxn} .

$$\Delta G^0_{\text{rxn}} = \Delta H^0_{\text{rxn}} - T\Delta S^0_{\text{rxn}}$$

ΔG^0_{rxn} can be calculated from thermodynamic tables of enthalpies of formation and absolute entropies. It can also be calculated a little more directly from tabulated values of the standard Gibbs Free Energy of formation:

$$\Delta G^0_{\text{rxn}} = \sum \Delta G^0_{\text{f}}(\text{products}) - \sum \Delta G^0_{\text{f}}(\text{reactants})$$

Standard Gibbs Free Energies of formation for pure substances at 25°C are reported in Table 2.

Table 19.3 • Standard Molar Free Energies of Formation of Some Substances at 298 K

Element/Compound	$\Delta G^0_{\text{f}}(\text{kJ} \cdot \text{mol}^{-1})$	Element/Compound	$\Delta G^0_{\text{f}}(\text{kJ} \cdot \text{mol}^{-1})$
H ₂ (g)	0	CO ₂ (g)	-394.4
O ₂ (g)	0	CH ₄ (g)	-50.87
N ₂ (g)	0	H ₂ O(g)	-228.6
C(graphite)	0	H ₂ O(l)	-237.2
C(diamond)	2.900	NH ₃ (g)	-16.4
CO(g)	-137.2	Fe ₂ O ₃ (s)	-742.2

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Once again notice that since ΔG is an energy we tabulate Free Energies of *Formation*, the free energy change *relative* to its elements. Similar to the enthalpy of formation, ΔG^0_{f} for elements in their standard states is zero.

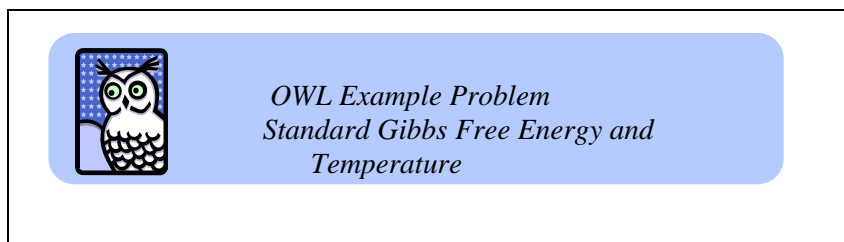


OWL Example Problem
x.x Standard Gibbs Free Energy

Can we give these numbers some meaning? For most compounds ΔG^0_{f} is negative. This says that under standard state conditions, compounds are, in general, more stable than their elements. They are *lower* in free energy and could form spontaneously from their elements. It is fairly rare to find pure elements in nature. For the most part you will find them combined. Another way to say this is that elements are higher in free energy and there is a driving force for them to combine chemically. This energy can be harnessed to do something useful (think about H₂ + O₂).

Standard Gibbs Free Energy and Temperature

We can use Equation X to determine how ΔG^0_{rxn} changes with temperature. Experimentally we find that ΔH^0_{rxn} and $T\Delta S^0_{\text{rxn}}$ remain fairly constant over a reasonable temperature range. Thus as the temperature increases, the entropy change for a reaction plays a larger and larger role in the magnitude of ΔG^0_{rxn} .



Standard Free Energy vs Nonstandard: ΔG^0 vs ΔG

We have seen how to calculate the standard free energy change for a chemical reaction. What if we are not at standard state? How is ΔG^0 related to ΔG ? What does each tell us about a chemical reaction?

We will develop these ideas using the equilibrium concepts presented in Chapter 15. From the Second Law statement at constant T and P we know that:

$\Delta G < 0$ tells us the reaction is spontaneous in the forward direction

$\Delta G = 0$ tells us the reaction is at equilibrium

$\Delta G > 0$ tells us the reaction is spontaneous in the reverse direction.

FLASHBACK

Reaction Quotient
Use same definition as
in Chapter 15

Does this sound familiar to the ideas of Chapter 15? Recall the concept of comparing the reaction quotient, Q, to the equilibrium constant, K:

$Q < K$	Reaction runs in the forward direction to reach equilibrium. \longrightarrow	
$Q = K$	Reaction is at equilibrium. \longleftrightarrow	
$Q > K$	Reaction runs in the reverse direction to reach equilibrium. \longleftarrow	

Comparing these ideas should lead you to the conclusion that ΔG is somehow related to the reaction quotient, Q. We will not derive this relationship but merely state it (if you continue on in chemistry you will see this derivation):

$$\Delta G = \Delta G^0 + RT \ln Q$$

In words, this equation says that the Gibbs Free energy change for a reaction is equal to the Gibbs Free energy change under standard state conditions plus a correction factor for being away from standard state. We use standard state as our reference state and characterize the state of the reaction relative to this. The value of Q tells us how far away from standard state we are.

Let's look more deeply into this equation. At standard state the pressure of all gases = 1 bar, the concentration of all ions in solution = 1 M, and $Q = 1$. The natural log of 1 = 0, so at standard state $\Delta G = \Delta G^0$, just as it should.


What if, instead, we are at equilibrium? In that case $Q = K$ and $\Delta G = 0$. Equation x becomes:

$$0 = \Delta G^0 + RT \ln K$$

We can rearrange this to:

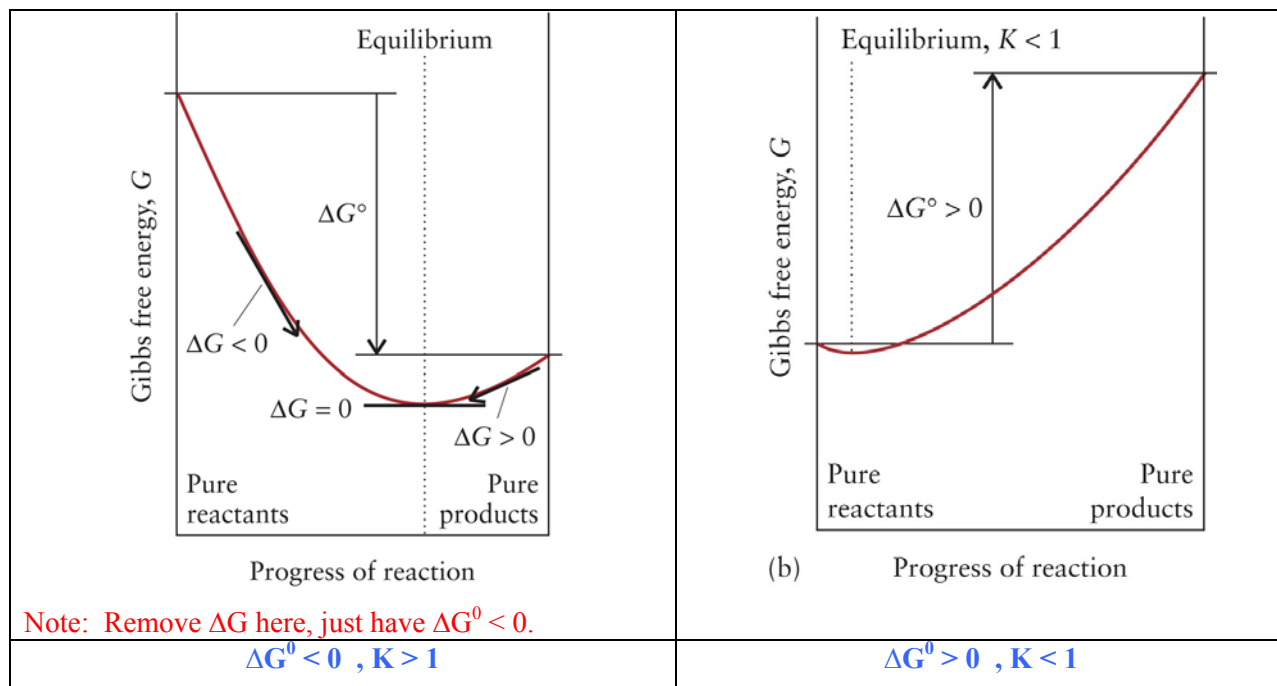
$$\Delta G^0 = -RT \ln K$$

We have just derived a very important relationship. Since R and K are constants, the Standard Gibbs Free energy change is also constant at a given temperature. Like the equilibrium constant, ΔG^0 is a constant that characterizes a chemical reaction. If we know K we can calculate ΔG^0 , or if we know ΔG^0 we can calculate K .



OWL Example Problem
x.x *Gibbs Free Energy and the Equilibrium Constant*

From Chapter 15 we already know that if $K < 1$, reactants are favored at equilibrium. In this case $\ln K$ is negative and $\Delta G^0 > 0$. Another way to say this is that the reaction does not have to go very far to reach equilibrium. If $K > 1$, products are favored at equilibrium and $\Delta G^0 < 0$.



<i>Product favored at equilibrium</i>	<i>Reactant favored at equilibrium</i>
Like K, ΔG^0 tells us about the <i>position</i> of equilibrium - reactant or product favored.	

How is this related to what ΔG tells us? If we put equations X and XX together and use the logarithmic relation $\ln a - \ln b = \ln(a/b)$ we obtain:

$$\Delta G = -RT \ln K + RT \ln Q$$

or

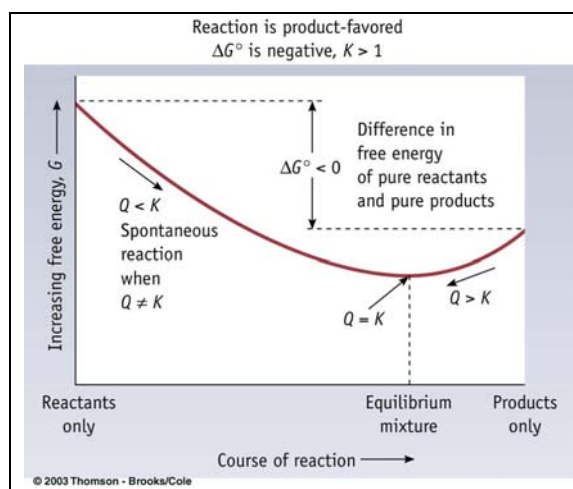
$$\Delta G = RT \ln (Q/K)$$

Let's examine this equation in more detail.

If $Q < K$ then $(Q/K) < 1$ and $\Delta G < 0$.
The reaction must run in the forward direction to reach equilibrium.

If $Q = K$ then $(Q/K) = 1$ and $\Delta G = 0$.
The reaction is at equilibrium.

If $Q > K$ then $(Q/K) > 1$ and $\Delta G > 0$.
The reaction must run in the reverse direction to reach equilibrium.



Like Q, ΔG tells us the *direction* the reaction must run in order to reach equilibrium - forward or reverse.

Summary

As a chemical reaction proceeds, the amounts of reactants and products change. The value of Q, a ratio of the product and reactant concentrations, changes throughout the reaction. Because of this, the value of ΔG changes throughout the reaction.

Reactions proceed until the composition of the reaction mixture corresponds to a minimum in the Gibbs Free Energy, equilibrium. At this point the composition of the reaction mixture ceases to change and is characterized by K.

ΔG^0 Summary	
Equations	$\Delta G^0_{\text{rxn}} = \Delta H^0_{\text{rxn}} - T\Delta S^0_{\text{rxn}}$
	$\Delta G^0_{\text{rxn}} = \sum \Delta G^0_f(\text{products}) - \sum \Delta G^0_f(\text{reactants})$
	$\Delta G^0_{\text{rxn}} = -RT \ln K$

Interpretation	Tells <i>position</i> of equilibrium. Constant throughout reaction (like K). $\Delta G^0_{\text{rxn}} < 0$ $K > 1$ Products favored at equilibrium $\Delta G^0_{\text{rxn}} > 0$ $K < 1$ Reactants favored at equilibrium
IF at Standard State:	$\Delta G^0_{\text{rxn}} < 0$ Rxn spontaneous in forward direction $\Delta G^0_{\text{rxn}} > 0$ Rxn spontaneous in reverse direction

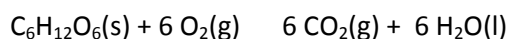
ΔG Summary	
Equations	$\Delta G = -(\Delta S_{\text{universe}} / T)$ CONSTANT T AND P $\Delta G = \Delta H - T\Delta S$ $\Delta G = \Delta G^0 + RT \ln Q$ $\Delta G = RT \ln (Q/K)$
Interpretation	Tells <i>direction</i> to reach equilibrium Changes throughout reaction (like Q). $\Delta G < 0$ $Q < K$ Rxn spontaneous in forward direction $\Delta G = 0$ $Q = K$ Rxn at equilibrium $\Delta G > 0$ $Q > K$ Rxn spontaneous in reverse direction

Apply to chemical reactions

Now that we have developed the principles of spontaneous, reactant/product favored, and equilibrium, in terms of ΔG and ΔG^0 , let's see how they help us understand 4 different kinds of chemical reactions. Remember that in order to use ΔG or ΔG^0 as a predictor of direction or position of equilibrium, we must be at constant T and P (that is $T_{\text{final}} = T_{\text{initial}}$ and $P = 1$ bar).

1. Combustion of sugar, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$.

Can we predict the sign of ΔH^0 , ΔS^0 and therefore ΔG^0 for this reaction? First write the balanced chemical equation. Combustion means combine with oxygen to form the oxides of the elements. The oxide of carbon is carbon dioxide. The oxide of hydrogen is water.



The burning of hydrocarbons and carbohydrates is exothermic, $\Delta H^0 < 0$. Six moles of CO_2 gas + six moles of liquid are produced from six moles of O_2 gas (lighter, lower entropy) + 1 mole of solid (lower entropy), so $\Delta S^0 > 0$. We can see that at any temperature:

$$\Delta G^0 = \begin{array}{ccc} \Delta H^0 & - & T\Delta S^0 \\ & - & - (+) \end{array} < 0$$

Interpretation:

- This reaction is product-favored ($K > 1$) at any temperature.
- We can also say that *if we start from standard state conditions*, the reaction is *spontaneous* at any temperature.

2. Freeze a liquid.

We'll use water for this example but the conclusions apply to the freezing of any pure liquid. We will again try to predict the sign of ΔH^0 , ΔS^0 and therefore ΔG^0 for this reaction.



As we discussed in Chapter 5, energy is released when liquids freeze, $\Delta H = -\Delta H^0_{\text{fusion}}$ (this may seem strange but remember that you must put energy in to melt a solid). Freezing is an exothermic process. At a fixed temperature the entropy of a solid is less than a liquid so $\Delta S^0 < 0$.

$$\Delta G^0 = \begin{array}{ccc} \Delta H^0 & - & T\Delta S^0 \\ & - & - (-) \end{array} = ?$$

In this case we see that the negative ΔH^0 contributes to a product-favored reaction ($\Delta S_{\text{surroundings}} > 0$). But the entropy of the system goes down, working against this. If the entropy term, $T\Delta S$, is smaller than ΔH^0 , the reaction will be product-favored and spontaneous if we start from standard state conditions. If the entropy term is large, it will overpower the enthalpy and the reaction will be reactant-favored and non-spontaneous under standard state conditions. What could change to influence this? The temperature is the important factor here. At low temperature the exothermicity of the reaction, dissipating heat into the surroundings, dominates, and the reaction is product favored.

$$\Delta G^0 = \begin{array}{ccc} \Delta H^0 & - & T\Delta S^0 \\ & - & - (-) \end{array} \begin{array}{l} < 0 \text{ Low T} & \text{Enthalpy dominates - FAVORABLE} \\ > 0 \text{ High T} & \text{Entropy dominates - UNFAVORABLE} \end{array}$$

The temperature factor should make physical sense to you. You must reduce the temperature of a liquid in order for it to freeze. Liquids do not freeze at high temperature.

We refer to reactions that have favorable enthalpy but unfavorable entropy as "enthalpy driven". These reactions must be run at a temperature low enough to keep the unfavorable entropy term from overcoming the favorable enthalpy term.

Interpretation:

- This reaction is product-favored ($K > 1$) at low temperature. It is reactant-favored ($K < 1$) at high temperature.

- We can also say that *if we start from standard state conditions*, the reaction is *spontaneous* at low temperature and *nonspontaneous* at high temperature.

3. Boil a liquid. Use dissolving of NH_4NO_3 instead ? Easy to rewrite

We'll again use water for this example but the conclusions apply to the boiling of any pure liquid.



Boiling is an endothermic process, $\Delta H = \Delta H_{\text{vaporization}}^0$. At a fixed temperature the entropy of a gas is greater than a liquid so $\Delta S^0 > 0$.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = ?$$

+ - (+)

In this case we see that the positive ΔS^0 contributes to a product-favored reaction but the enthalpy works against this ($\Delta S_{\text{surroundings}} < 0$). If the entropy term, $T\Delta S$, is larger than ΔH^0 , the reaction will be product-favored and spontaneous if we start from standard state conditions. If the enthalpy term is large, it will overpower the entropy and the reaction will be reactant-favored and non-spontaneous under standard state conditions. Again the temperature is the important factor here. At high temperature the entropy change in going to the gas phase dominates, and the reaction is product favored.

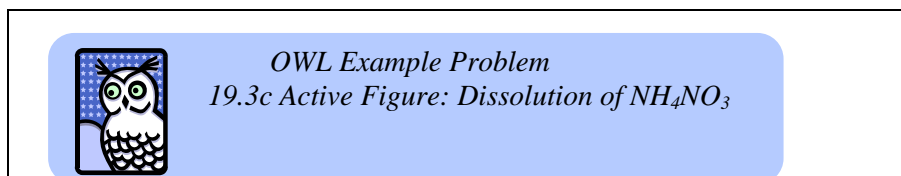
$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

+ - (+)

> 0 Low T Enthalpy dominates - UNFAVORABLE
< 0 High T Entropy dominates - FAVORABLE

A liquid does not boil at any temperature. You must increase the temperature in order for it to boil.

This reaction is "entropy driven". Reaction which are favorable in terms of the entropy but unfavorable in terms of the enthalpy must be run at temperatures high enough to keep the enthalpy term from overcoming the entropy term.



Interpretation:

- This reaction is product-favored ($K > 1$) at high temperature. It is reactant-favored ($K < 1$) at low temperature.
- We can also say that *if we start from standard state conditions*, the reaction is *spontaneous* at high temperature and *nonspontaneous* at low temperature.

4. Unburn sugar ?

So far we have seen examples of three different combinations of ΔH and ΔS : negative + positive, negative + negative, and positive + positive. Here is the last combination. Notice it is just the reverse of the first reaction.



If the burning of sugar is exothermic, the "unburning" of sugar is endothermic, $\Delta H^\circ > 0$. Similarly the sign of the entropy change of the system reverses, $\Delta S^\circ < 0$. We can see that at any temperature:

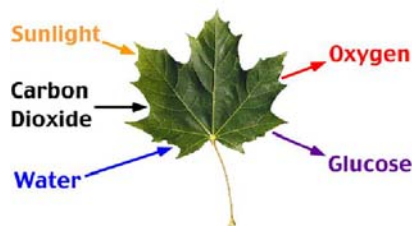
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ > 0$$

+ - (-)

Interpretation:

- This reaction is reactant-favored ($K < 1$) at any temperature.
- We can also say that *if we start from standard state conditions*, the reaction is *nonspontaneous* at any temperature.

Does this mean that the reaction can never happen? Take a close look at the reaction and see if you recognize it. This is the reaction carried out by green plants, photosynthesis. So we know that it can happen and it does indeed happen every day. But it must be driven by sunlight.



Summary Table

Example	ΔH°	ΔS°	ΔG°	
1. Burn Sugar	-	+	< 0	All T Enthalpy & Entropy - FAVORABLE
2. Freeze Liquid	-	-	< 0	Low T Enthalpy dominates - FAVORABLE
			> 0	High T Entropy dominates - UNFAVORABLE
3. Boil Liquid	+	+	> 0	Low T Enthalpy dominates - UNFAVORABLE
			< 0	High T Entropy dominates - FAVORABLE
4. Photosynthesis	+	-	> 0	All T Enthalpy & Entropy - UNFAVORABLE <i>REACTION MUST BE DRIVEN BY EXTERNAL SOURCE OF ENERGY</i>



OWL Example Problem
x.x Gibbs Free Energy

EXAMPLE PROBLEM 19.1.1: Predict which substances have higher entropy.

Predict which substance in each pair has the higher entropy. Assume there is one mole of each substance at 25°C and 1 bar.

- (a) Hg(l) or CO(g)
- (b) CH₃OH(l) or CH₃CH₂OH(l)
- (c) KI(s) or CaS(s)

SOLUTION:

You are asked to choose the substance with the higher entropy.

You are given two substances and their states.

- (a) At 25°C carbon monoxide gas has a higher entropy than liquid mercury because the motion of the gas molecules is much more random than the motion of the mercury atoms in the liquid state.
- (b) Ethanol liquid, CH₃CH₂OH(l), has a higher entropy than liquid methanol, CH₃OH(l) because it is a larger, more complex molecule and therefore has a larger number of ways to distribute energy at a given temperature.
- (c) Potassium iodide, composed of K⁺ and I⁻ ions, has a higher entropy than calcium sulfide, composed of Ca²⁺ and S²⁻ ions. The entropy of ionic solids tends to increase as the attractive forces between the ions decrease because vibrational motion between the ions is easier.

EXAMPLE PROBLEM 19.2.1: Calculate the entropy change when a gas condenses at its boiling point

Calculate the entropy change when 2 moles of carbon monoxide condenses at its boiling point of -191.4°C. The heat of vaporization of CO is 6.04 kJ/mol.

SOLUTION:

You are asked to calculate ΔS for the condensation of CO(g) at its boiling point.

You are given:

$$n = 2 \text{ mol CO}$$

$$T_{\text{boil}} = (-191.4^{\circ}\text{C} + 273.15) = 81.75 \text{ K}$$

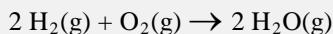
$$\Delta H_{\text{vaporization}} = 6.04 \text{ kJ/mol}$$

Use equation 19.2 to calculate ΔS for this process. Remember that the gas condenses, the opposite of vaporization, so the sign of $\Delta H_{\text{vaporization}}$ is reversed.

$$\Delta S_{\text{condense}} = -\Delta H_{\text{vaporization}}/T_{\text{boil}} = -(6.04 \text{ kJ/mol})(2 \text{ mol})/81.75 \text{ K} = -(0.1478 \text{ kJ/K})(1000 \text{ J/kJ}) = -148 \text{ J/K}$$

EXAMPLE PROBLEM 19.2.2: Predict the sign and calculate ΔS° for a reaction.

Hydrogen and oxygen react to form water vapor in a spontaneous reaction.



Predict the sign of the entropy change for this reaction and using Table 19.2 calculate $\Delta S^\circ_{\text{rxn}}$ at 25°C .

SOLUTION:

You are asked to predict the sign of $\Delta S^\circ_{\text{rxn}}$ and then to calculate this value.

You are given the balanced chemical equation and the standard molar entropies for water vapor, and hydrogen and oxygen gas.

When hydrogen and oxygen gas react to form water vapor, 3 moles of gas are converted into 2 moles of gas, for every mole of reaction. The total number of moles of gas decreases, so ΔS° for this reaction should be negative.

Use standard molar entropy values and equation 19.3b to calculate the standard entropy change.

$$\begin{aligned} \Delta S^\circ_{\text{rxn}} &= \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}} \\ &= (2 \text{ mol})(S^\circ[\text{H}_2\text{O}(\text{g})]) - \{(2 \text{ mol})(S^\circ[\text{H}_2(\text{g})]) + (1 \text{ mol})(S^\circ[\text{O}_2(\text{g})])\} \\ &= (2 \text{ mol})(188.8 \text{ J/K}\cdot\text{mol}) - \{(2 \text{ mol})(130.7 \text{ J/K}\cdot\text{mol}) + (1 \text{ mol})(205.1 \text{ J/K}\cdot\text{mol})\} \\ &= -88.9 \text{ J/K} \end{aligned}$$

The entropy change for this reaction is negative, as predicted based on the reaction stoichiometry.

EXAMPLE PROBLEM 19.2.3: Calculate ΔS_{surr} and $\Delta S_{\text{universe}}$ for a reaction.

Hydrogen and oxygen react to form water vapor in a spontaneous reaction with a negative standard entropy change.



Calculate the entropy change of the surroundings and the universe at 25°C .

SOLUTION:

You are asked to calculate $\Delta S_{\text{surroundings}}$ and $\Delta S_{\text{universe}}$ at 25°C for the reaction above.

You are given the balanced chemical equation and $\Delta S^\circ_{\text{rxn}}$.

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{rxn}}}{T}$$

Use standard heats of formation to calculate the enthalpy change for this reaction under standard state conditions. Recall that the standard heat of formation for an element in its standard state is equal to zero.

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \\ &= (2 \text{ mol})(\Delta H_f^\circ[\text{H}_2\text{O}(\text{g})]) - (2 \text{ mol})(\Delta H_f^\circ[\text{H}_2(\text{g})]) - \Delta H_f^\circ[\text{O}_2(\text{g})] \\ &= (2 \text{ mol})(-241.8 \text{ kJ/mol}) - 0 - 0 \\ &= -483.6 \text{ kJ} \end{aligned}$$

At 25°C

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{rxn}}}{T} = \frac{-(-483.6 \text{ kJ})}{298 \text{ K}} = 1.62 \text{ kJ/K}$$

The reaction is exothermic, so ΔS_{surr} is positive (the entropy of the surroundings increases).

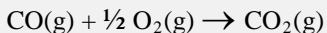
To calculate the entropy change of the universe, add the entropy changes for the system and surroundings, converting the system entropy change units to kJ/K.

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} = (-88.9 \times 10^{-3} \text{ kJ/K}) + 1.62 \text{ kJ/K} = 1.53 \text{ kJ/K}$$

The reaction is spontaneous ($\Delta S_{\text{univ}} > 0$).

EXAMPLE PROBLEM 19.3.1: Calculate standard free energy change using ΔH_f° and S° values.

Carbon monoxide and oxygen gas react to form carbon dioxide.



Calculate the standard free energy change for this reaction at 25°C from $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$.

SOLUTION:

You are asked to calculate $\Delta G_{\text{rxn}}^\circ$ from $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$ at 25°C for the reaction above.

You are given the balanced chemical equation and ΔH_f° and S° data for each substance (in the thermodynamic tables).

Step 1: Use standard heats of formation to calculate the enthalpy change for this reaction under standard state conditions.

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \Sigma \Delta H_f^\circ(\text{products}) - \Sigma \Delta H_f^\circ(\text{reactants}) \\ &= \Delta H_f^\circ[\text{CO}_2(\text{g})] - \Delta H_f^\circ[\text{CO}(\text{g})] - \frac{1}{2} \Delta H_f^\circ[\text{O}_2(\text{g})] \\ &= -393.5 \text{ kJ/mol} - (-110.5 \text{ kJ/mol}) - 0 \\ &= -283.0 \text{ kJ/mol}\end{aligned}$$

Step 2: Use standard entropy values to calculate the entropy change for this reaction under standard state conditions.

$$\begin{aligned}\Delta S_{\text{rxn}}^\circ &= \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants}) \\ &= S^\circ[\text{CO}_2(\text{g})] - \Delta S^\circ[\text{CO}(\text{g})] - \frac{1}{2} S^\circ[\text{O}_2(\text{g})] \\ &= 213.7 \text{ J/mol K} - (197.7 \text{ J/mol K}) - (\frac{1}{2})(205.1 \text{ J/mol K}) \\ &= -86.6 \text{ J/mol K}\end{aligned}$$

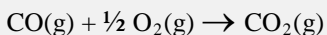
Note $\Delta S_{\text{rxn}}^\circ$ is negative as predicted by the stoichiometry: 1.5 moles of gas goes to form 1 mole of gas.

Step 3: Calculate $\Delta G_{\text{rxn}}^\circ$ using equation 19.9

$$\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T\Delta S_{\text{rxn}}^\circ = -283.0 \text{ kJ/mol} - (298 \text{ K})(-86.6 \text{ J/mol K})(1 \text{ kJ}/1000 \text{ J}) = -257 \text{ kJ/mol}$$

EXAMPLE PROBLEM 19.3.2 CALCULATE FREE ENERGY CHANGE USING STANDARD FREE ENERGIES OF FORMATION

Use standard free energies of formation to calculate the standard free energy change for the formation of carbon dioxide from carbon monoxide and oxygen gas at 25°C.

**SOLUTION:**

You are asked to calculate $\Delta G_{\text{rxn}}^\circ$ using ΔG_f° values.

You are given the balanced chemical equation and ΔG_f° data for each substance (in the thermodynamic tables).

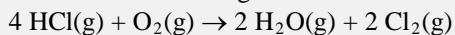
Use 19.10 and ΔG_f° data to calculate the standard free energy change for this reaction.

$$\begin{aligned}\Delta G_{\text{rxn}}^\circ &= \Sigma \Delta G_f^\circ(\text{products}) - \Sigma \Delta G_f^\circ(\text{reactants}) \\ &= \Delta G_f^\circ[\text{CO}_2(\text{g})] - \Delta G_f^\circ[\text{CO}(\text{g})] - \frac{1}{2} \Delta G_f^\circ[\text{O}_2(\text{g})] \\ &= -394.4 \text{ kJ/mol} - (-137.2 \text{ kJ/mol}) - 0 \\ &= -257.2 \text{ kJ/mol}\end{aligned}$$

Note that this agrees with the result obtained in the previous example using ΔH_f° and S° data, as it should.

EXAMPLE PROBLEM 19.3.3: Calculate free energy change under nonstandard state conditions.

Using standard thermodynamic data to calculate ΔG at 298.15 K for the reaction below, assuming that all gases have a pressure of 22.51 mm Hg.

**SOLUTION:**

You are asked to calculate ΔG_{rxn} at 298.15 K.

You are given the balanced chemical equation, the pressure of each gas, and ΔG_f° data for each substance (in the thermodynamic tables).

Use equation 19.11 to calculate the free energy change under nonstandard state conditions. First, calculate ΔG° using ΔG_f° values.

$$\begin{aligned}\Delta G^\circ &= \Sigma \Delta G_f^\circ(\text{products}) - \Sigma \Delta G_f^\circ(\text{reactants}) \\ &= (2 \text{ mol})(\Delta G_f^\circ[\text{H}_2\text{O(g)}]) - (4 \text{ mol})(\Delta G_f^\circ[\text{HCl(g)}]) \\ &= (2 \text{ mol})(-228.6 \text{ kJ/mol}) - (4 \text{ mol})(-95.3 \text{ kJ/mol}) \\ &= -76.0 \text{ kJ}\end{aligned}$$

For a gas phase reaction, Q is expressed in terms of partial pressures (atm).

$$22.51 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 0.02962 \text{ atm}$$
$$Q = \frac{P_{\text{H}_2\text{O}}^2 \cdot P_{\text{Cl}_2}^2}{P_{\text{HCl}}^4 \cdot P_{\text{O}_2}} = \frac{(0.02962)^2 (0.02962)^2}{(0.02962)^4 (0.02962)} = 33.76$$

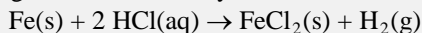
Finally, substitute these values, along with temperature and the ideal gas constant, into equation 19.11 and calculate ΔG . We will use units of “kJ/mol” for the calculated ΔG° value to indicate the standard free energy change is for the reaction as written above.

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q = (-76.0 \text{ kJ/mol}) + (8.3145 \times 10^{-3} \text{ kJ/K}\cdot\text{mol})(298.15 \text{ K})[\ln(33.76)] \\ &= -76.0 \text{ kJ/mol} + 8.72 \text{ kJ/mol} \\ &= -67.3 \text{ kJ/mol}\end{aligned}$$

The negative ΔG value tells us that the reaction is not at equilibrium and must react in the forward direction to reach equilibrium.

EXAMPLE PROBLEM 19.3.4: Calculate equilibrium constant from free energy change.

Using standard thermodynamic data, calculate the equilibrium constant at 298.15 K for the reaction shown below.

**SOLUTION:**

You are asked to calculate the equilibrium constant at 298.15 K.

You are given the balanced chemical equation and ΔG_f° data for each substance (in the thermodynamic tables).

Use equation 19.12 to calculate the equilibrium constant at this temperature. First, calculate ΔG° using ΔG_f° values.

$$\begin{aligned}\Delta G^\circ &= \Sigma \Delta G_f^\circ(\text{products}) - \Sigma \Delta G_f^\circ(\text{reactants}) \\ &= (1 \text{ mol})(\Delta G_f^\circ[\text{FeCl}_2\text{(s)}]) - (2 \text{ mol})(\Delta G_f^\circ[\text{HCl(aq)}]) \\ &= (1 \text{ mol})(-302.3 \text{ kJ/mol}) - (2 \text{ mol})(-131.2 \text{ kJ/mol}) \\ &= -39.9 \text{ kJ}\end{aligned}$$

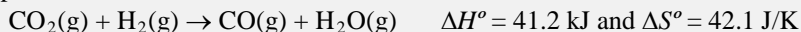
Substitute this value, along with temperature and the ideal gas constant, into equation 19.12 and calculate K .

$$\begin{aligned}\Delta G^\circ &= -RT \ln K \\ \ln K &= \frac{-\Delta G^\circ}{RT} = \frac{-(-39.9 \text{ kJ/mol})}{(8.3145 \times 10^{-3} \text{ kJ/K} \cdot \text{mol})(298.15 \text{ K})} = 16.1 \\ K &= e^{16.1} = 9.78 \times 10^6\end{aligned}$$

The large negative ΔG° value tells us that the position of equilibrium for this reaction lies very far toward products.

EXAMPLE PROBLEM 19.3.5: Calculate temperature at which ΔG° changes sign.

Calculate the temperature (in kelvin) at which the sign of ΔG° changes from positive to negative. This corresponds to the temperature at which $K < 1$ changes to $K > 1$. Assume that ΔH° and ΔS° are constant and do not change with temperature.

**SOLUTION:**

You are asked to calculate the temperature at which $\Delta G^\circ_{\text{rxn}}$ changes sign.

You are given the balanced chemical equation, ΔH° and ΔS° for the reaction.

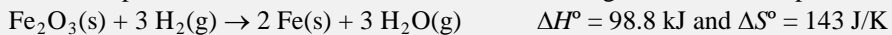
Use equation 19.8 to calculate the temperature at which ΔG° changes from a positive to a negative value. At this crossover point, ΔG° is equal to zero. Note that entropy change is converted to units of kJ/K in the calculation.

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = 0 \\ \Delta H^\circ &= T\Delta S^\circ \text{ and } T = \frac{\Delta H^\circ}{\Delta S^\circ} \text{ at the crossover point} \\ T &= \frac{41.2 \text{ kJ}}{42.1 \times 10^{-3} \text{ kJ/K}} = 979 \text{ K}\end{aligned}$$

At temperatures above 979 K, the $(-T\Delta S^\circ)$ term is greater than ΔH° , and the standard free energy change for this reaction will be negative. The reaction becomes product favored above 979 K.

EXAMPLE PROBLEM 19.3.6: Predict the temperature-dependence for a chemical or physical change.

Predict the temperature conditions under which the following reaction will be product-favored.

**SOLUTION:**

You are asked to predict the temperature conditions under which the reaction will be product-favored.

You are given the balanced chemical equation, ΔH° and ΔS° for the reaction.

For a reaction to be product-favored ΔG° must be less than zero. The dependence of ΔG° on temperature is given by the following equation, assuming that ΔH° and ΔS° are independent of temperature.

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

For this reaction, $\Delta H^\circ = 98.8 \text{ kJ}$ and $\Delta S^\circ = 143 \text{ J/K}$. Because both ΔH° and ΔS° are positive, temperature will control the position of the equilibrium. At high temperatures, the term $(-T\Delta S^\circ)$ has a large, negative value, resulting in a negative free energy change ($\Delta G^\circ < 0$).

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

$$? \quad (+) \quad (+)(+)$$

The reaction is product-favored at high temperatures and reactant-favored at low temperatures. It is an entropy-driven reaction.