

5.7: Gibbs (Free) Energy to the Rescue

We must consider changes in entropy for both the system and its surroundings when we predict which way a change will occur, or in which direction a process is thermodynamically favorable. Because it is almost always easier to look at the system than it is to look at the surroundings (after all, we define the system as that part of the universe we are studying), it would be much more convenient to use criteria for change that refer only to the system. Fortunately, there is a reasonably simple way to do this. Let us return to water freezing again and measure the enthalpy change for this process. The thermal energy change for the system, ΔH freezing, is about -6 kJ/mol . That is, 6 kJ of thermal energy are released into the surroundings for every mole of water that freezes. We can relate this thermal energy release to the entropy change of the surroundings. Entropy is measured in units of J/K (energy/temperature). Because we know how much energy is added to the surroundings, we can calculate the entropy change that this released (enthalpic) energy produces.

Mathematically we can express this as $\Delta S_{\text{surroundings}} = \frac{-\Delta H_{\text{system}}}{T}$. And because we know that $\Delta H_{\text{system}} = -\Delta H_{\text{surroundings}}$, or that the energy lost by the system equals minus (–) the energy gained by the surroundings, we can express the entropy change of the surroundings in terms of measurable variables for the system. That is:

$$\Delta S_{\text{surroundings}} = -\Delta H_{\text{system}}/T \quad (5.7.1)$$

If you recall, we can express the total entropy change (the one relevant for the second law) as $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$. Substituting for the $\Delta S_{\text{surroundings}}$ term, we get $\Delta S_{\text{total}} = \Delta S_{\text{system}} - \Delta H_{\text{system}}/T$. Now we have an equation that involves only variables that relate to the system, which are much easier to measure and calculate. We can rearrange the equation by multiplying throughout by $-T$, which gives us:

$$-T\Delta S_{\text{total}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}} \quad (5.7.2)$$

The quantity $-T\Delta S_{\text{total}}$ has units of energy, and is commonly known as the Gibbs energy change, ΔG (or sometimes as the free energy). The equation is normally written as:

$$\Delta G = \Delta H - T\Delta S. \quad (5.7.3)$$

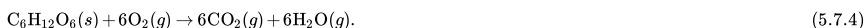
The Gibbs energy change of a reaction is probably the most important thermodynamic term that you will need to learn about. In most biological and biochemical systems, it is ΔG that is commonly used to determine whether reactions are thermodynamically favorable. It is important to remember that ΔG is a proxy for the entropy change of the universe: if it is negative, universal entropy is increasing (and the reaction occurs); if it is positive, universal entropy would decrease if the reaction occurred (and so it does not). It is possible, however, for reactions with a positive ΔG to occur, but only if they are coupled with a reaction with an even greater negative ΔG (see Chapters 8 and 9).

There are numerous tables of thermodynamic data in most texts and on many websites. Because we often want to use thermodynamic data such as ΔH , ΔS , and ΔG , it is useful to have some reference state. This is known as the standard state and is defined as 298 K temperature, 1 atmosphere pressure, 1 M concentrations. When thermodynamic data refer to the standard state they are given the superscript $^\circ$ (nought), so ΔH° , ΔS° , and ΔG° all refer to the standard state. However, we often apply these data at temperatures other than 298 K and although small errors might creep in, the results are usually accurate enough.

What Is Free About Gibbs Free Energy?

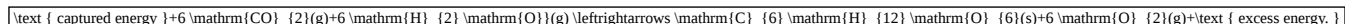
We use ΔG or ΔG° to describe many systems (and especially biological ones) because both the magnitude and sign tell us a lot about how that system behaves. We use ΔG (the Gibbs free energy change) rather than ΔH (the enthalpy change) because ΔG tells us how much energy is actually available to bring about further change (or to do work). In any change some of the energy is lost to the environment as the entropy increases, this dissipated energy cannot be used to do any kind of work and is effectively lost. ΔG differentiates the energy produced from the change from the energy that is lost to the surroundings as increased entropy. As an example, when wood is burned, it is theoretically impossible to use all of the heat released to do work; some of the energy goes to increase the entropy of the system. For any change in the system, some of the energy is always lost in this way to the surroundings. This is why it is impossible to build a machine that is 100% efficient in converting energy from one kind to another (although many have tried—Google “perpetual motion machines” if you don’t believe us). So the term “free energy” doesn’t mean that it is literally free, but rather that it is potentially available to use for further transformations.

When ΔG is negative, we know that the reaction will be thermodynamically favored.^[25] The best-case scenario is when ΔH is negative (an exothermic change in which the system is losing energy to the surroundings and becoming more stable), and ΔS is positive (the system is increasing in entropy). Because T is always greater than 0 (in Kelvins), $T\Delta S$ is also positive and when we subtract this value from ΔH , we get an even larger negative ΔG value. A good example of such a process is the reaction (combustion) of sugar ($\text{C}_6\text{H}_{12}\text{O}_6$) with molecular oxygen (O_2):



This is an exothermic process and, as you can see from the reaction equation, it results in the production of more molecules than we started with (often a sign that entropy has increased, particularly if the molecules are of a gas).

A process such as this ($-\Delta H$ and $+\Delta S$) is thermodynamically favored at all temperatures. On the other hand, an endothermic process ($+\Delta H$) and a decrease in entropy ($-\Delta S$) will never occur as an isolated reaction (but in the real world few reactions are actually isolated from the rest of the universe). For example, a reaction that combined CO_2 and H_2O to form sugar (the reverse reaction to the combustion reaction above) is never thermodynamically favored because ΔH is positive and ΔS is negative, making ΔG positive at all temperatures. Now you may again find yourself shaking your head. Everyone knows that the formation of sugars from carbon dioxide and water goes on all over the world right now (in plants)! The key here is that plants use energy from the sun, so the reaction is actually:



Just because a process is thermodynamically unfavorable doesn’t mean that it can never occur. What it does mean is that that process cannot occur in isolation; it must be “coupled” to other reactions or processes.

Free Energy and Temperature

So we have two very clear-cut cases that allow us to predict whether a process will occur: where the enthalpy and entropy predict the same outcome. But there are two possible situations where the enthalpy change and the entropy term ($T\Delta S$) “point” in different directions. When ΔH is positive and ΔS is positive, and when ΔH is negative while ΔS is negative. When this happens, we need to use the fact that the free energy change is temperature-dependent in order to predict the outcome. Recall that the expression $\Delta G = \Delta H - T\Delta S$ depends upon temperature. For a system where the entropy change is positive ($+\Delta S$), an increase in temperature will lead to an increasingly negative contribution to ΔG . In other words, as the temperature rises, a process that involves an increase in entropy becomes more favorable. Conversely, if the system change involves a decrease in entropy, (ΔS is negative), ΔG becomes more positive (and less favorable) as the temperature increases.

ΔH	ΔS	ΔG
Negative (exothermic)	Positive (entropy increases)	Negative at all temperatures (always thermodynamically favored)
Positive (endothermic)	Negative (entropy decreases)	Positive at all temperatures (never thermodynamically favored)
Negative (exothermic)	Negative (entropy decreases)	Temperature dependent: as the temperature increases ΔG will become more positive and the reaction will become less favored (go backwards)

ΔH	ΔS	ΔG
Positive (endothermic)	Positive (entropy increases)	Temperature dependent: as the temperature increases ΔG will become more negative and the reaction will become favored (go forwards)

The idea that temperature affects the direction of some processes is perhaps a little disconcerting. It goes against common-sense that if you heat something up a reaction might actually stop and go backwards (rest assured we will come back to this point later). But in fact there are a number of common processes where we can apply this kind of reasoning and find that they make perfect sense.

Up to this point, we have been considering physical changes to a system—populations of molecules going from solid to liquid or liquid to gaseous states (and back). Not really what one commonly thinks of as chemistry, but the fact is that these transformations involve the making and breaking of interactions between molecules. We can therefore consider phase transitions as analogous to chemical reactions, and because they are somewhat simpler, develop a logic that applies to both processes. So let us begin by considering the phase change/reaction system



We use a double arrow \rightleftharpoons to indicate that, depending upon the conditions the reaction could go either to the right (boiling) or to the left (condensing). So, let us assume for the moment that we do not already know that water boils (changes from liquid to gas) at 100°C . What factors would determine whether the reaction $\text{H}_2\text{O (liquid)} \rightleftharpoons \text{H}_2\text{O (gas)}$ favors the liquid or the gaseous state at a particular temperature? As we have seen, the criterion for whether a process will “go” at a particular temperature is ΔG . We also know that the free energy change for a reaction going in one direction is the negative of the ΔG for the reaction going in the opposite direction. So that the ΔG for the reaction: $\text{H}_2\text{O (liquid)} \rightleftharpoons \text{H}_2\text{O (gas)}$ is $-\Delta G$ for the reaction $\text{H}_2\text{O (gas)} \rightleftharpoons \text{H}_2\text{O (liquid)}$.

When water boils, all the intermolecular attractions between the water molecules must be overcome, allowing the water molecules to fly off into the gaseous phase. Therefore, the process of water boiling is endothermic ($\Delta H_{\text{vaporization}} = +40.65 \text{ kJ/mol}$); it requires an energy input from the surroundings (when you put a pot of water on the stove you have to turn on the burner for it to boil). When the water boils, the entropy change is quite large ($\Delta S_{\text{vaporization}} = 109 \text{ J/molK}$), as the molecules go from being relatively constrained in the liquid to gas molecules that can fly around. At temperatures lower than the boiling point, the enthalpy term predominates and ΔG is positive. As you increase the temperature in your pan of water, eventually it reaches a point where the contributions to ΔG of ΔH and $T\Delta S$ are equal. That is, ΔG goes from being positive to negative and the process becomes favorable. At the temperature where this crossover occurs $\Delta G = 0$ and $\Delta H = T\Delta S$. At this temperature (373 K , 100°C) water boils (at 1 atmosphere). At temperatures above the boiling point, ΔG is always negative and water exists predominantly in the gas phase. If we let the temperature drop below the boiling point, the enthalpy term becomes predominant again and ΔG for boiling is positive. Water does not boil at temperatures below 100°C at one atmosphere.^[26]

Let us now consider a different phase change, such as water freezing. When water freezes, the molecules in the liquid start to aggregate and form hydrogen bonding interactions with each other, and energy is released to the surroundings (remember it is this energy that is responsible for increasing the entropy of the surroundings). Therefore ΔH is negative: freezing is an exothermic process ($\Delta H_{\text{fusion}} = -6 \text{ kJ/mol}$).^[27] Freezing is also a process that reduces the system's entropy. When water molecules are constrained, as in ice, their positional entropy is reduced. So, water freezing is a process that is favored by the change in enthalpy and disfavored by the change in entropy. As the temperature falls, the entropy term contributes less to ΔG , and eventually (at the crossover point) ΔG_{fusion} goes to zero and then becomes negative. The process becomes thermodynamically favored. Water freezes at temperatures below 0°C . At temperatures where phase changes take place (boiling point, melting point), $\Delta G = 0$. Furthermore, if the temperature were kept constant, there would be no observable change in the system. We say that the system is at equilibrium; for any system at equilibrium, $\Delta G = 0$.

? Question

Questions to Answer

- For each of these processes, give the change in entropy of the system, the direction of thermal energy transfer (the sign of ΔH), the change in entropy of the surroundings, and the change in entropy of the universe:
- Water freezing at -10°C
- Water boiling at 110°C
- For each of these processes predict the sign of change in entropy (ΔS) of the system, the direction of thermal energy transfer (the sign of ΔH), and the sign of the Gibbs free energy change, ΔG . What does the sign of ΔG tell you?
- Water freezing at -10°C ; Water boiling at 110°C
 - Water boiling at -10°C ; Water freezing at 110°C

Questions to Ponder

- Why do we denote excess energy as a product of this equation?

$$\text{captured energy} + 6 \text{ kJ/mol CO}_2(\text{g}) + 6 \text{ kJ/mol H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \text{ kJ/mol O}_2(\text{g}) + \text{excess energy.}$$
- What other processes do you know that must be coupled to external energy sources to make them go?

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