

Chapter 16 - Thermodynamics

In Chapter 5, we examined the relationship between heat and reactions. In Chapter 12, we saw that the rate and extent of reactions depend on energy considerations. In this chapter we will examine energy relationships again and begin to show the interconnectedness of these topics.

At this point it would be a very good idea for you to review the enthalpy sections of Chapter 5.

This chapter attempts to be as correct as possible about some difficult topics. We will be skipping over some of that material because the purpose here is to give you a basic introduction to chemical thermodynamics. In some places the notes expressly say that you won't be responsible for certain material. If you have any questions about topics I don't go over in class, make sure you ask me about them.

16.1 Spontaneity

Many processes in nature appear to always proceed in the same direction. The book offers iron rusting or melting ice at room temperature as examples. Another process would be a fire burning. It would be shocking for you to observe any of these processes occurring in reverse.

Processes that occur without outside intervention are called spontaneous. Processes that are spontaneous in one direction are nonspontaneous in the reverse direction. They require the input of energy to proceed, if they do proceed. (Remember activation energy from Chapter 12. In the reverse direction that energy might lead to other reactions.)

NB: Spontaneity says nothing about rate. Some spontaneous processes occur quite readily and rapidly, for example a brick falls immediately and rapidly when you let go. Others occur quite slowly. A container filled with hydrogen and oxygen will remain essentially unchanged for

centuries unless a spark is added to start the reaction. Both are spontaneous, however. (The former example has no activation energy, while the latter example has a high activation energy.)

Two factors affect reaction spontaneity within a system. The first you have already encountered, enthalpy. As you know from both experience (e.g. fire) and Chapter 5, exothermic processes tend to be spontaneous. There is a second major factor, entropy, which we will discuss shortly.

The book makes an interesting and valuable point at the bottom of p. 862. Some processes are “thermodynamically unstable, but kinetically stable.” These processes are uncommon, but are real. Basically, what is being said is that the reaction should occur, but there is a barrier that stops the reaction from occurring. The water behind a dam is thermodynamically unstable, but kinetically stable, for example. The book’s diamond example is a chemical one.

Dispersal of Matter and Energy

Consider two identical bulbs that are connected by a valve, one containing a gas, the other under a vacuum. What happens if the valve opens? Of course, some of the gas moves to the side with no gas. I say "of course" because no one ever guesses that the gas just stays in its original bulb (for that matter, no one would guess that gas in two bulbs would spontaneously move into just one of them). This happens even if the bulbs are kept at constant temperature, so heat evolution can't be the answer. Nor can work, because the gases expand into a vacuum. Yet the gas **always** moves into the vacuum. Why?

Likewise, if two iron blocks at different temperatures, isolated from the environment, are put into contact with one another, the hot block will transfer heat energy to the cool block. Why?

In each case, the answer is the energy in the system is more dispersed than in the second case. It's easier to see this in the block example. If the blocks are equal in size and one starts at 0 °C

and the other at 100 °C, they equilibrate at 50 °C. That the energy is more dispersed is simply a function of the now larger size/mass of the combined blocks. The case of the gases is similar, but not as apparent. Going back to the blocks, when the heat flows from the hot block to the cold block the heat is now distributed among twice as many iron atoms. In the gas example, the number of gas molecules is fixed, but their possible locations doubles when the gas expands into the second flask. Thus, the number of locations where the energy could be located doubles and the energy is therefore more dispersed.

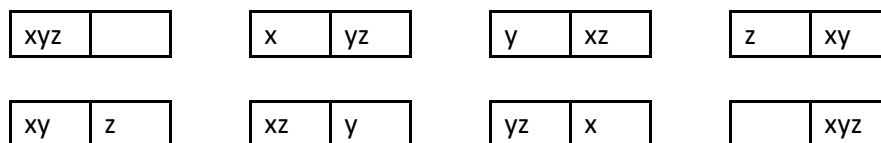
If this doesn't make sense, think about the reverse processes, which **never** happen. You never have two flasks and all of the gas moves into one of them from the other. You never have two spoons in a drawer spontaneously have one get hot and the other cold by exactly the same number of degrees. If you saw either of these things happen you'd think it was a magic trick or that you were losing your mind.

16.2 Entropy

Summarizing the last section: energy never spontaneously concentrates. Entropy, S , is a measure of how much energy is dispersed as a function of temperature. The book provides a nice, detailed explanation which is summarized here. The question that comes out of this is “why is dispersal the naturally preferred progression?” Consider two boxes: one with two compartments (**A**), one with three compartments (**B**). If you throw a ball into box A, you have a 1-in-2 chance of having the ball land in either of the compartments, while in box **B** you have a 1-in-3 chance. If you throw a second ball in the boxes there are 4 arrangements for **A** and 9 for **B**. The arrangements for box **A** are shown here, where the balls are labeled x and y.



Since the balls are identical, this simplifies to 3 arrangements, 1 with two balls in compartment 1, 1 with two balls in compartment 2, and two with two balls in compartment 3. Thus, doubling the number of balls, doubles the number of possible arrangements. With 3 balls, the number of arrangements increases again:



For this particular example, it's an exponential function, but that isn't the case for every situation. The point here is that, if you have identical balls and boxes, as the number of either increases, the number of possible arrangements (microstates) also increases. Since everything is identical, the particular arrangement that is observed is completely random, but some are more likely (probable) than others. In the case of 3 balls, the odds of having all three balls in the first compartment are 1 in 8, while having 2 in the first compartment are 3 in 8. Here, the entropy of the 3-ball example is higher than the entropy of the 2-ball example.

How does this tie into a physically real situation? We return to the first example in the "Dispersal of Energy and Matter" section (p. 2 of notes). Imagine a box, with a divider cutting it exactly in half. On one side are some gas molecules, on the other a vacuum (no gas molecules). We start by looking only at the side with gas molecules. Since it's a gas, the molecules are widely separated and so there are many different locations for them to occupy, but the exact number doesn't matter for this discussion. We know that if we remove the divider, the gas will flow into the vacuum until half of the molecules are on each side of where the divider was. Since the sides are equal in size, we know the number of locations for the molecules to reside has doubled. The molecules possess energy and the spontaneous movement of the gas from the area of high pressure to low disperses that energy, thus increasing the entropy of the system. This is a purely statistical

argument.

Another example that is easy to see (and that we'll return to in a bit) is that of a liquid and gas of the same substance at the same temperature (e.g. water/steam at 100°). The gas can both hold more energy internally and, because it is more mobile, carry it away from a source more readily. For this reason, the entropy of the gas would be higher than that of the liquid. Another way to look at this is by examining a gas at two different temperatures. Figure 9.33 (p. 501) shows the range of velocities of nitrogen gas molecules at several temperatures. (There is also a generic graph on p. 870.) You can see that the molecules at the higher temperature are spread out over a much wider range of speeds. If each velocity is viewed as a state, then there is a wider range of states available to the higher temperature molecules.

Here is one final example: when ice melts, heat must be added (an endothermic process). Yet the temperature remains at 0 °C until the last of the solid liquifies. Why? In ice the water molecules are held in a rigid lattice unable to move. On melting to liquid water, the molecules are free to move about. In the liquid the molecules are also able to spin (or tumble) with much greater freedom than they could in the solid state. Thus, liquid water can spread energy out within itself more effectively (e.g. by spinning faster) or by moving around to other locations (i.e. carrying the energy away from its source).

Entropy increases as dispersal of energy increases. Although absolute entropies can be determined, the difference in entropy between initial and final conditions is usually of greater interest to us.

$$\Delta S = S_f - S_i$$

Hence, $\Delta S > 0$ indicates that the final state has spread out energy relative to the initial state. There are some generalities that come out of this. For example, $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$ for the same substance

at the same temperature.

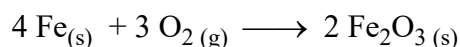
The term “disorder” is usually associated with entropy and you’ll notice that the book goes to some lengths to avoid using it. In fact, it is only used once, p. 867, one paragraph from the bottom of the page and that is to explain the origin of using the word. This is because the casual/common use of “disorder” has been misleading. Also, you should read Section 18.2’s description of the statistical mechanical description of entropy. The book does a very nice job of explaining it.

16.3 The Second and Third Laws of Thermodynamics

Second Law

What you have just seen for these examples is generally true. Processes that result in an increase in entropy tend to be favored over those in which entropy decreases. There are two ironclad rules regarding entropy, however. The first is the Second Law of Thermodynamics: **For any spontaneous process, the entropy of the universe increases.** Recall that the "universe" refers to the combination of the system and surroundings ($\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$). Also, for systems at equilibrium, $\Delta S_{\text{univ}} = 0$. What the second law means is that if the energy within your system becomes less dispersed (e.g. freezing water to ice), the surroundings must become even more dispersed.

Here is a chemical example: iron rusts according to the reaction:



The entropy change here is negative. First, 7 species combine to form 2, but more important, the reaction converts 3 gas molecules to the solid state. How is the entropy of the surroundings increased? By the heat released in the reaction ($\Delta H_{\text{rxn}} \approx 1645 \text{ kJ}$). That heat makes molecules in the surroundings move faster. Those in the solid state vibrate more rapidly and liquid and gas

molecules move about at a higher velocity. The spreading out of energy in the surroundings more than offsets the loss in the system when the gas molecules are moved into the solid state. (You don't feel the heat given off when iron rusts because the process is so slow.) We shall see shortly that this exothermicity is what makes the reaction spontaneous.

This description is a manifestation of what your book discusses on pp. 871-872. Although you can't feel it, rusting iron is warmer than the surroundings and the heat spontaneously flows from the system to the surroundings.

Third Law

There is a third, and final, law of thermodynamics: **The entropy of a perfect crystal of any substance at absolute zero is zero.** A perfect crystal is one that is 100% pure and has no defects.

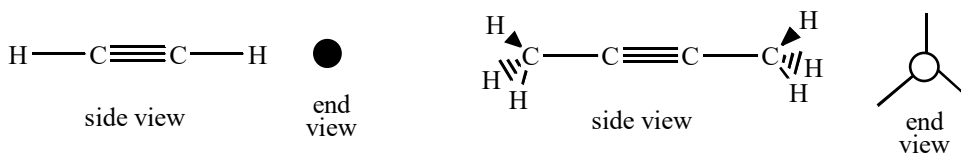
Entropy has been described in terms of molecular motion. For example, gas molecules move about more than molecules in the solid state and so have more entropy. Likewise, for equal numbers of molecules in different volumes, the molecules in the larger volume possess higher entropy because they can move into more locations.

It is relatively easy to see that a solid is more ordered than a gas. And not too difficult to see that liquids are more ordered than gases. (The molecules move more slowly in liquids (i.e. there is a smaller range of velocities), so entropy is lower in liquids.) But why should entropy change in the solid state as temperature changes?

To understand how energy is dispersed by molecules, we need to look at the different types of motions molecules undergo. The motion discussed exclusively to this point is translational motion. This is motion that results in movement between different locations (i.e. moving from here to there). Translational motion in gases is high, moderate-to-low in liquids, and very near-to-exactly zero in solids. When solids crystallize, they inevitably have defects. One such defect

is a missing molecule at a site. As a solid warms to near its melting point, it is possible for a molecule to hop from its existing site to an adjacent hole. Nevertheless, this does not happen often and translational motion does not generally contribute significantly to the entropy of solids. Translational motion disperses energy by carrying it to another site and through the range of velocities available to the molecule.

When a molecule spins about an internal axis, it undergoes rotational motion. Like all motions, rotational motion decreases with decreasing temperature. Small, highly symmetrical molecules frequently have significant rotational motion. Consider a sphere (e.g. a noble gas atom). As it spins about any internal axis, there is nothing to bump into a nearby atom to slow its rotation. Likewise, linear $\text{H-C}\equiv\text{C-H}$, could spin in place much easier than $\text{H}_3\text{C-C}\equiv\text{C-CH}_3$ because the latter has C-H bonds that project out of the molecular axis that could easily bump into a neighboring molecule. Replacing the hydrogens in the latter molecule with $-\text{CH}_3$ groups would slow rotation



even more at a given temperature.

Finally, all atoms in molecules engage in vibrational motion. The location of atoms in molecules is not static. Bound atoms vibrate much like balls connected by a spring. At higher temperatures there is more vibration. Both bond vibration and rotation allow the dispersal of energy within a molecule. We'll spend some time in class discussing this concept.

The entropy of a crystal is zero when it has no defects and all of the atoms and molecules cease to engage in translational and rotational motions, and are limited to a single set of vibrations.

A few generalizations are:

a) For a collection of substances at the same temperature, the gases will usually possess greater

entropy than the solids or liquids regardless of chemical make-up.

- b) For a single substance, $S_{(g)} > S_{(\ell)} > S_{(s)}$, always.
- c) In a given physical state, entropy increases with temperature.
- d) In a chemical reaction, entropy will increase if the number of gas molecules increases.

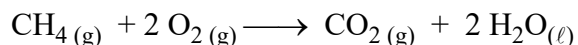
Calculation of Entropy Changes

The entropy change associated with reactions or physical changes is calculated much like enthalpy changes are calculated. The generic equation one uses is:

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

where n are the stoichiometric coefficients from the reaction. Remember they have units (moles) and that the superscript “ \circ ” means the entropy value was determined under standard conditions (25 °C, 1 atm (for gases), pure liquids and solids, 1 M concentration (if in liquid solution)). An important difference between enthalpies and entropies, is that while elemental enthalpies are defined as zero, all entropies have non-zero values. Also note from their units ($\text{J/mol}\cdot\text{K}$) that entropies are temperature dependent.

Example: What is the entropy change associated with burning one mole of ethane?



$$\begin{aligned} \Delta S^{\circ} &= [(1 \text{ mol}_{\text{CO}_2})(213.8 \text{ J/mol}\cdot\text{K}) + (2 \text{ mol}_{\text{H}_2\text{O}})(69.91 \text{ J/mol}\cdot\text{K})] \\ &\quad - [(1 \text{ mol}_{\text{CH}_4})(186.3 \text{ J/mol}\cdot\text{K}) + (2 \text{ mol}_{\text{O}_2})(205.0 \text{ J/mol}\cdot\text{K})] \\ &= -242.4 \text{ J/K} \end{aligned}$$

16.4 Gibbs Free Energy

If enthalpy and entropy independently tend to cause reactions to proceed spontaneously, then, as you might expect, there is a relationship between them that always predicts spontaneity. We

know that enthalpy is favorable when it is negative and entropy is favorable when it is positive. Furthermore, we know entropy increases with increasing temperature. We can combine these observations to yield a new quantity: Gibbs free energy, ΔG , where:

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

For any process,

If $\Delta G < 0$, the process is spontaneous as written

$\Delta G > 0$, the process is spontaneous in the reverse direction

$\Delta G = 0$, the process is at equilibrium.

Standard Free Energy Changes

To make free energy easier to use, we will employ the same standard conditions used in enthalpy. That is: 25 °C, 1 atm (for gases), pure liquids and solids, and 1 M (for solutions). Elements are defined as having $\Delta G^\circ = 0$. (Remember the superscript “°” means standard state.)

Just as for ΔH and ΔS :

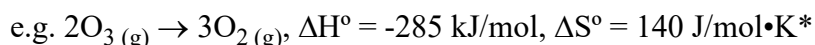
$$\Delta G^\circ_{\text{rxn}} = \sum n\Delta G_f^\circ(\text{products}) - \sum n\Delta G_f^\circ(\text{reactants})$$

Using Appendix G, we can determine whether or not a reaction is spontaneous or not at a particular temperature. It is important to state again that ΔG° tells us nothing about reaction rate.

Temperature Dependence of Spontaneity

The temperature dependence of ΔG can be significant. Your experience tells you that reactions accelerate when the temperature increases. What may surprise you is that whether the reactions occurs or not (Is it spontaneous or not?) may depend on temperature. There are four possible enthalpy/entropy pairs.

$\Delta H < 0$ & $\Delta S > 0$: ΔG is always negative, so the reaction is always spontaneous.



$\Delta H > 0$ & $\Delta S < 0$: ΔG is always positive, so the reaction is never spontaneous.

e.g. The reverse of the previous reaction

$\Delta H < 0$ & $\Delta S < 0$: $\Delta G < 0$ only at “low” temperatures. Low temperatures make the entropy term smaller and less important.

e.g. $\text{CaO}_{(s)} + \text{CO}_{2(g)} \rightarrow \text{CaCO}_{3(s)}$, high temperature drives the CO_2 off the product.

$\Delta H > 0$ & $\Delta S > 0$: $\Delta G < 0$ only at “high” temperatures. High temperatures make the entropy term larger and more important. Think of it as the extra energy required to drive endothermic reactions.

*This is a chemical example of kinetic vs. thermodynamic stability. As you can see, ozone is always unstable relative to dioxygen, but it does exist and can be isolated. In the long run, however, ozone always decomposes to normal oxygen.

The words low and high in the preceding sentences appeared in quotation marks. Why? Because they are relative terms. For example, assume the ΔH for two different reactions is -10 kJ/mol. Reaction 1 has a ΔS of -10 J/mol•K, while ΔS for reaction 2 is -100 J/mol•K. In the first case, the reaction isn't spontaneous until 1000 K (727 °C), a high temperature indeed. However, the second reaction is spontaneous over 100 K (-173 °C); a temperature that no one would consider toasty. Thus, “high temperature” means that if one begins warming a reaction mixture from 1 K, the reaction is initially nonspontaneous and at some temperature will become spontaneous. Low temperature means that warming will eventually cause a spontaneous reaction to become nonspontaneous. The following example will show how such a calculation proceeds.

Ex: Is the reaction $2 \text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow 2 \text{H}_2\text{O}_{(\ell)}$ spontaneous at 25 °C? At what temperature does it become spontaneous?

$$\Delta H_{\text{rxn}}^{\circ} = [(2 \text{ mol}_{\text{H}_2\text{O}})(-285.83 \frac{\text{J}}{\text{mol}\cdot\text{K}})] - [(2 \text{ mol}_{\text{H}_2})(0 \frac{\text{J}}{\text{mol}\cdot\text{K}}) + (1 \text{ mol}_{\text{O}_2})(0 \frac{\text{J}}{\text{mol}\cdot\text{K}})]$$

$$= -571.66 \text{ kJ}$$

$$\Delta S_{\text{rxn}}^{\circ} = [(2 \text{ mol}_{\text{H}_2\text{O}})(70.0 \frac{\text{J}}{\text{mol}\cdot\text{K}})] - [(2 \text{ mol}_{\text{H}_2})(130.7 \frac{\text{J}}{\text{mol}\cdot\text{K}}) + (1 \text{ mol}_{\text{O}_2})(205.2 \frac{\text{J}}{\text{mol}\cdot\text{K}})]$$

$$= -326.6 \text{ J/K}$$

$$\Delta G_{\text{rxn}}^{\circ} = -571.66 \text{ kJ} - (298 \text{ K})(-326.6 \text{ J/K})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

$$= -474 \text{ kJ}$$

$\Delta G < 0$ so the reaction is spontaneous at 25 °C.

Since $\Delta H_{\text{rxn}}^{\circ} < 0$ and $\Delta S_{\text{rxn}}^{\circ} < 0$, the reaction is favored at low temperatures. The crossover point for spontaneity is when $\Delta G_{\text{rxn}}^{\circ} = 0$. Below this temperature the reaction is spontaneous, above it nonspontaneous. In this calculation, we assume ΔH and ΔS don't change with temperature. They actually do, but not very much.

$$0 \text{ kJ} = -571.66 \text{ kJ} - (T)(-326.6 \text{ J/K})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

$$T = 1750 \text{ K (or } 1480 \text{ °C)}$$

Free Energy and Equilibrium

The book derives a very useful equation, but all you need to do is to remember it.

$$\Delta G^{\circ} = -RT \ln K_{\text{eq}}$$

where $R = 8.314 \text{ J/mol}\cdot\text{K}$ and $K_{\text{eq}} = K_{\text{C}}$ for solutions, K_{P} for gases (use atm), and χ for liquid mixtures. Thus, the free energy of an equilibrium can simply be determined by measuring the amount of each substance present. Not surprisingly, if K_{eq} is greater than one (the equilibrium lies to the right), then ΔG is negative.

Also, when an equilibrium is stressed (e.g. addition of a reactant, temperature/pressure are changed), the free energy of the system changes according to the equation

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

where Q is the reaction quotient. You can use this to determine the spontaneity of the reaction if you don't know K_{eq} .

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