

Unit 9: *Equilibrium and Advanced Thermodynamics—Balance in Chemical Reactions*



Unit Overview

Some chemical reactions happen spontaneously, like metal rusting. Other reactions are non-spontaneous and need to absorb energy in order to occur. Using the Second Law of Thermodynamics, the principle of entropy, and the calculation of Gibbs free energy, scientists can predict which reactions will occur and vary the conditions to make more of the desired products. In equilibrium reactions, both products and reactants are always present. Equilibrium

reactions in the human body are essential for life and can be exploited in chemical manufacturing as well.

by Thomas van Geel

Sections

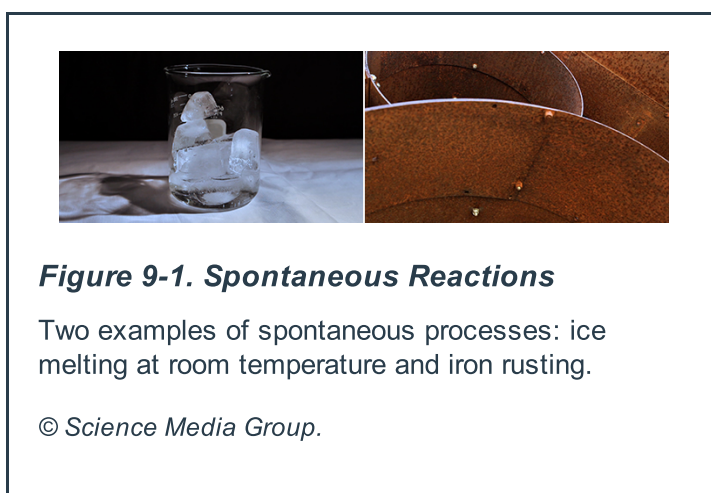
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Unit 9: *Equilibrium and Advanced Thermodynamics—Balance in Chemical Reactions*

Section 1: Introduction

In Unit 7, we discussed thermochemistry (the study of energy in chemical reactions), the First Law of Thermodynamics (the conservation of energy), and exothermic and endothermic reactions (how chemical reactions release or absorb energy). Another goal of thermodynamics is to understand why some reactions occur and others do not. In other words, chemists strive to determine if a reaction will be **spontaneous** or **nonspontaneous**.



A spontaneous process happens without any outside intervention or input of energy. For example, liquids freeze spontaneously at temperatures below their freezing points. A solid melting at a temperature below its freezing point is nonspontaneous; it will not happen, which is why we don't worry about the ice melting in a kitchen freezer. Salt spontaneously dissolves in warm water, and will not spontaneously recrystallize. Iron rusts spontaneously; the process of "unrusting" is nonspontaneous. (Figure 9-1)

Many spontaneous processes release heat; they are exothermic and their ΔH values are negative (see Unit 7, Section 6). A ball spontaneously rolls downhill and loses energy as it goes. A ball does not spontaneously roll uphill; pushing it back uphill requires an input of energy. Many chemical reactions follow the same pattern as that ball. Burning glucose is spontaneous and releases energy:



The reverse reaction is nonspontaneous, and requires an input of energy. In photosynthesis, plants reverse this reaction to create glucose; the energy input comes from sunlight.

It may be tempting, then, to assume that exothermic processes are always spontaneous, and endothermic reactions are nonspontaneous. While this is often true, there are many examples that run counter to this trend. Table salt dissolves spontaneously in water, for instance, and yet this process is endothermic. Steam condensing to water is exothermic; yet at temperatures above 100°C, condensation is nonspontaneous. Clearly, there is more to spontaneity than energy.

Glossary

Nonspontaneous

Referring to the direction of a process that proceeds toward thermodynamic instability.

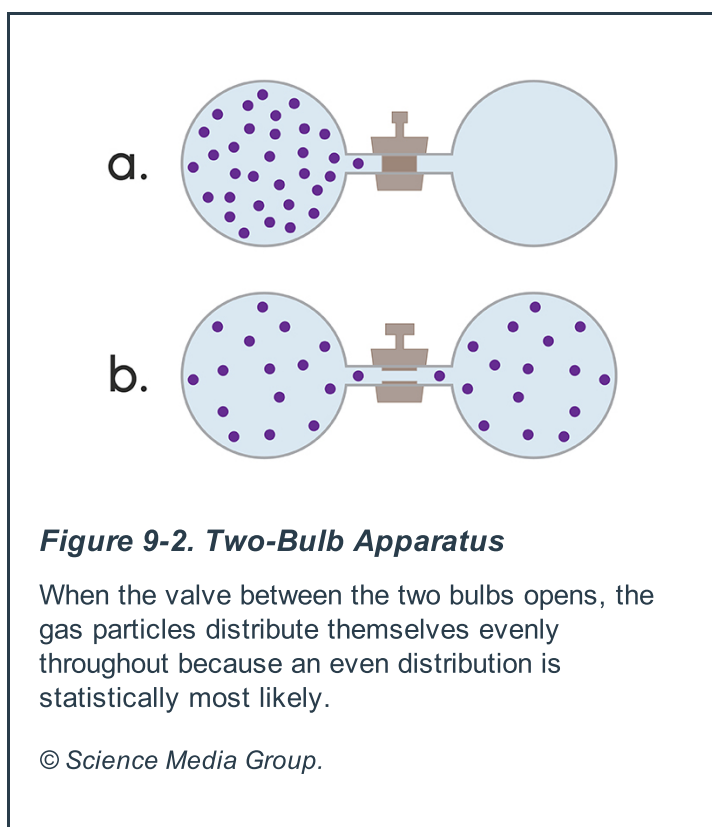
Spontaneous

A process that proceeds toward thermodynamic stability.

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Section 2: Microstates, Macrostates, and Entropy

In 1868, Austrian physicist Ludwig Boltzmann (1844–1906) published the key research that explained spontaneity. Because the numbers of particles involved in chemical reactions are astronomically large, Boltzmann used statistics to describe the positions and energies of the particles. Thus, Boltzmann is the founder of **statistical mechanics**, an approach that revolutionized the study of thermodynamics.



Rather than trying to follow every particle in a reaction at the same time, he just looked at the chances of where the particles were likely to be, and from that, thermodynamics could be explained. Boltzmann's equations showed how particles distribute themselves in predictable ways, despite each particle moving around randomly.

Consider the two-bulb apparatus shown in Figure 9-2. Two glass bulbs connect to each other through a valve. In the top portion of the image, the valve is closed, and the bulb on the left contains a quantity of purple gas; the bulb on the right is empty. Opening the valve allows the gas to travel into the other bulb until the amounts of gas are equal on each side; this process is spontaneous. The reverse process, where the gas gathers together on one side of the apparatus, is nonspontaneous. Another interesting thing about this process is that it is clearly spontaneous for the gas to move, but it doesn't involve a change in enthalpy!

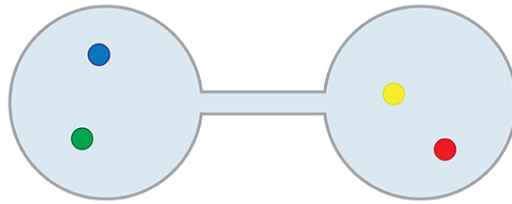


Figure 9-3. A Theoretical Two-Bulb Apparatus Experiment

A theoretical two-bulb apparatus containing four gas particles. The atoms can be in one of 16 possible arrangements at any given time.

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To keep things simple, let's think of a two-bulb apparatus that contains four atoms of gas free to travel between the two bulbs. (Figure 9-3) At any particular point in time, the atoms will be in one of 16 possible arrangements. Each one of these arrangements, such as having all the atoms on the left and none on the right, or having the red, yellow, and blue atoms on the left and the green on the right, is called a "**microstate**." The microstate is a specific description of where the particles are. Counting up the number of atoms on each side gives us the **macrostate**. The macrostate describes the overall distribution of the atoms, for example, four atoms on the left and zero on the right (4:0), or three atoms on the left and one on the right (3:1). Table 9-1 shows all the possible microstates and macrostates for this experiment. With four particles, there are 16 possible microstates divided into five possible macrostates.

Table 9-1. All Possible Microstates and Macrostates of Four Atoms of Gas in a Two-Bulb Apparatus

Arrangement (Microstate)		Distribution (Macrostate)
RYBG	None	4:0
RYB	G	3:1
RYG	B	
RBG	Y	
YBG	R	
RY	BG	2:2
BG	RY	
RB	YG	
YG	RB	
RG	YB	
YB	RG	
G	RYB	2:2
B	RYG	
Y	RBG	
R	YBG	
None	RYBG	0:4

The most common macrostate is the 2:2 distribution; because of the 16 possible microstates, six will create this macrostate. Four microstates make up the 3:1 and 1:3 macrostates, making those less likely to occur. Much less likely to occur are the 4:0 or 0:4 macrostates, because only one in 16 microstates create them.

Even though the atoms are moving randomly, and even though no microstate is more likely than any other, the results show that the most likely macrostate is an equal distribution with two atoms on each side. In the language of physics, the more microstates that make up a macrostate, the more **entropy** the macrostate has. The more entropy a macrostate has, the more likely that macrostate is to occur. In equations, entropy is represented by the symbol **S**. Its units are Joules per mole (J/mol). In more general terms though, entropy is really a measure of the system disorder; the more particles we have, the more possible arrangements we have, and essentially the more mess we can make. Imagine a bedroom: Take out all the clothes and put them on the floor. The more clothes we own, the more of a disordered mess the floor of the room will be. The same is true of molecules.

The distribution of gas particles is just one way to see the effects of entropy. As we will see in the next section, entropy determines not only how particles arrange themselves in space, but also how heat flows between objects.

Glossary

Entropy

The amount of disorder in a system. Statistically, the more microstates that make up a macrostate, the more entropy that macrostate has.

Macrostate

In statistical mechanics, the overall distribution and thermodynamic properties of particles within a given system.

Microstate

In statistical mechanics, the specific distribution and thermodynamic properties of particles within a given system.

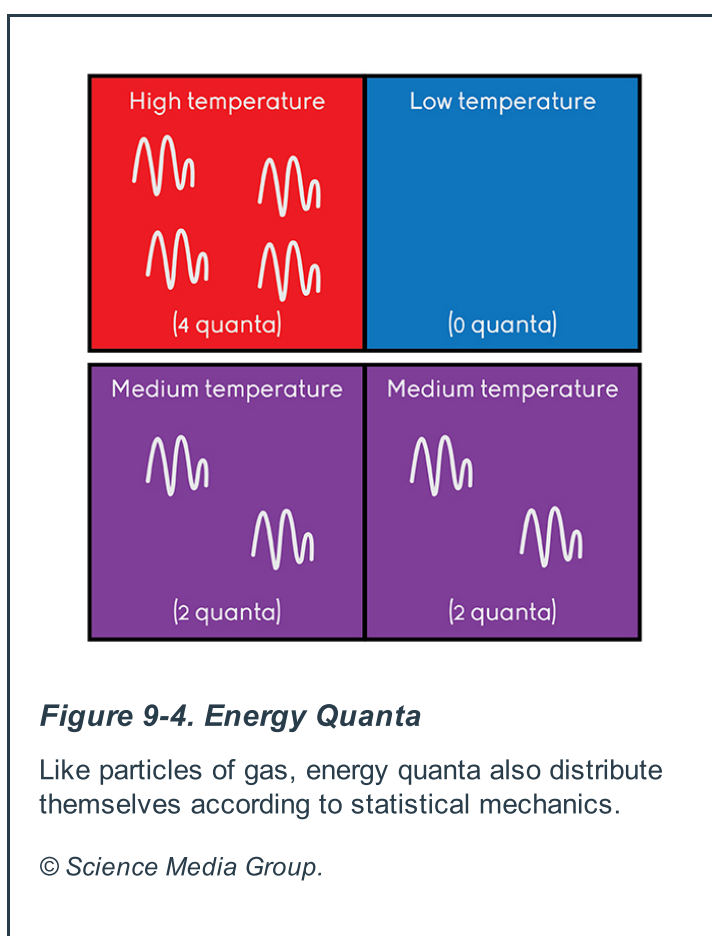
Statistical mechanics

Equations describing how particles distribute themselves in predictable ways, despite each particle moving around randomly.

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Section 3: The Entropy of Energy Quanta

In the previous section, we saw how the random movement of gas particles leads to an even distribution of those particles inside a container. The particles will spontaneously spread out simply because the "spread out" macrostate is the most likely. In other words, the spread-out macrostate has the most entropy.



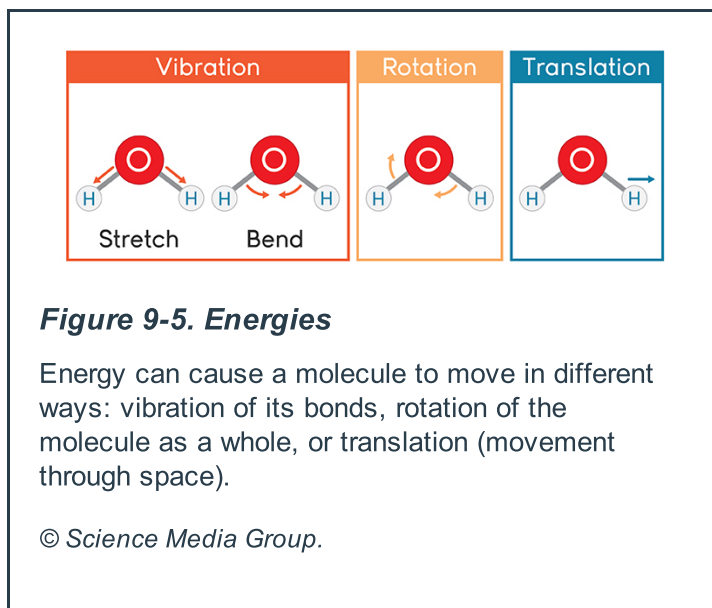
A similar analysis explains why heat flows from hot objects to cold objects. As discussed in Unit 3, energy is quantized; it exists in discrete packets called "quanta." These quanta move randomly between particles as they bump into each other. When two objects of different temperature are brought into contact, the quanta of energy distribute themselves uniformly throughout just like gas particles spreading throughout their container. (Figure 9-4)

Just as the most probable macrostate for the gas particles was 2:2, the most probable macrostate for the energy quanta is 2:2. Boltzmann's statistics not only explain why gas particles spontaneously spread out, but also why energy quanta spontaneously spread out.

As noted in the introduction to this unit, exothermic reactions are often (but not always) spontaneous. The underlying reason for this is that exothermic reactions increase entropy by releasing quanta of energy. The quanta spread out, and entropy increases. Thus, exothermic reactions tend to be spontaneous.

Energy quanta can spread by transferring from one particle to another throughout an object, but they can also spread out in a different sense. Not only can a quantum jump between particles, but it can also cause the particle to move in different ways. (Figure 9-5) A quantum of energy might make a particle move

through space faster; this is called "**translational energy**." It also might cause a molecule to rotate in place; this is called "**rotational energy**." Finally, a quantum of energy might cause the bonds of a molecule to vibrate. This **vibrational energy** causes chemical bonds to stretch and contract, or to bend and straighten.



The more ways a molecule can move, the more ways quanta of energy can be distributed. The water molecules in an ice cube can only vibrate in place. Quanta of energy are restricted to vibrational energy, and therefore ice has a low entropy value. In liquid water, the quanta can spread out to cause vibration and rotation; liquid water has higher entropy. Gaseous water (steam) has the highest amount of entropy because the molecules possess vibrational, rotational, and translational energies.

Glossary

Rotational energy

The energy associated with a spinning object.

Translational energy

The kinetic energy of a particle moving in a straight line.

Vibrational energy

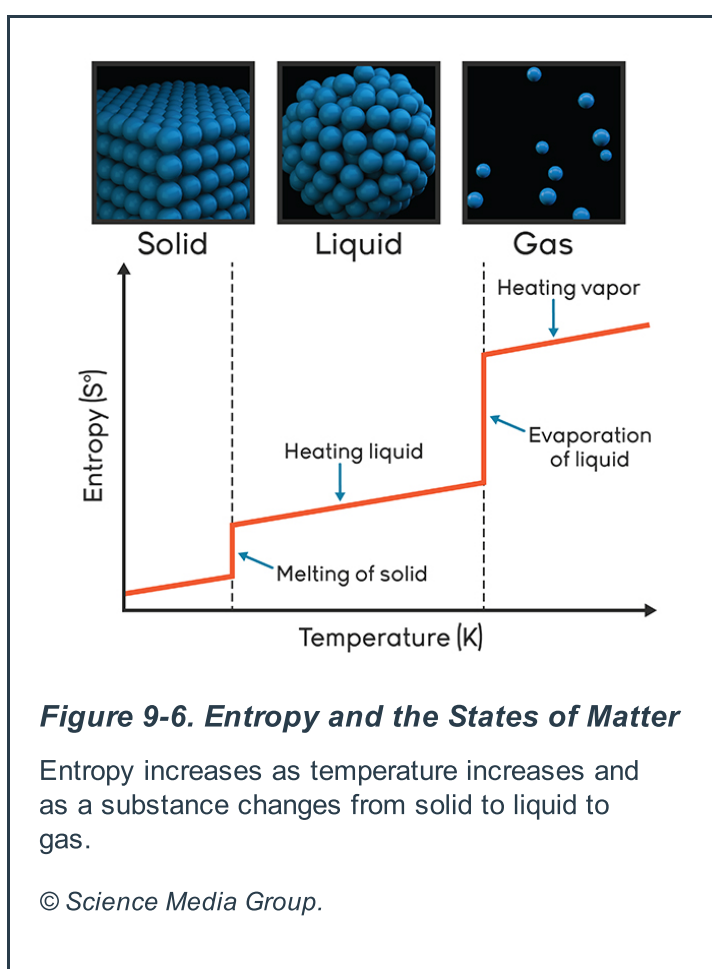
The energy possessed by a substance due to the vibration of chemical bonds.

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Section 4: Entropy and States of Matter

In the previous sections, we saw that high entropy is associated with two things: a wide distribution of particles and a wide distribution of energy quanta. The more particles and energy quanta can spread out, the more entropy there is. (Figure 9-6)

Bearing this in mind, it should make sense that a substance in the solid phase would have relatively low entropy. In a solid, the particles are locked in place and highly ordered, the clear opposite of disorder or entropy. The atoms can hardly move around in a solid's rigid structure and so their opportunities for spreading out are minimal. The quanta of energy in a solid are restricted mainly to vibration, so the distribution of quanta is also minimized.



The entropy of the liquid phase is higher. The particles are no longer locked in place. Because they are now free to move, they can distribute themselves in more ways. The energy quanta can distribute themselves in a greater variety of ways as well. Like a solid, the molecules can vibrate; but because they have more freedom of movement, molecules have rotational and some translational energy, too.

Gases have the highest entropy values because they have the greatest freedom of movement. Gas particles are separate and distribute themselves throughout their container (see Section 2: Microstates, Macrostates, and Matter). And, gases also possess all three types of energy: translational, rotational, and vibrational.

Finally, a substance that is dissolved in a liquid also has a high level of entropy for reasons similar to gases. Dissolved particles are free to not only move throughout the volume of the liquid, but also to move in all three ways. Generally speaking, the entropy value of a dissolved substance is higher than pure liquids but less than gases. To summarize, the entropy of the phases of matter are:

$$\text{Solid} < \text{Liquid} < \text{Dissolved} < \text{Gas}$$

Using this information, we can make an educated guess about whether entropy is increasing or decreasing when a chemical reaction occurs. Consider the following reaction in which solid table salt dissolves in water:



In this case, a solid (low entropy) is turning into two aqueous ions (higher entropy). We can reasonably assume that entropy increases. When entropy increases, the change in entropy, ΔS , is positive. As we know, this reaction is spontaneous; salt dissolves in water. Consider another spontaneous process, the sublimation of dry ice (solid CO_2):



Here, a solid (low entropy) turns into a gas (high entropy). Again, ΔS is positive.

Both of the above reactions are spontaneous, and both produce products with higher entropy than the reactants. It may be tempting, then, to assume that all such reactions are spontaneous. But consider the burning of hydrogen gas:



In this reaction, gases (high entropy) change into liquid (low entropy); ΔS is negative. Yet, the reaction is spontaneous; hydrogen is highly flammable.

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Section 5: Spontaneity and Gibbs Free Energy

As the previous sections have shown, chemical reactions that increase entropy tend to be spontaneous. Section 3 demonstrated that exothermic reactions increase entropy by allowing a wider distribution of energy quanta. Section 4 illustrated how reactions that create liquids and gases also tend to increase entropy.

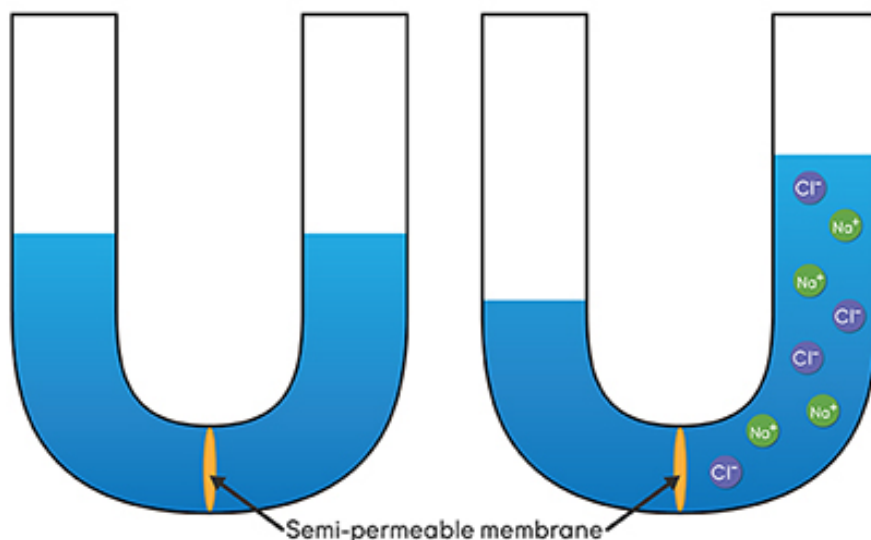
In summary:

- Negative ΔH favors a spontaneous reaction.
- Positive ΔS favors a spontaneous reaction.
- Positive ΔH opposes a spontaneous reaction.
- Negative ΔS opposes a spontaneous reaction.

What now remains is to combine these two factors to create a complete picture—a way to definitively determine if a reaction will be spontaneous. When ΔH and ΔS both favor spontaneity, the reaction is always spontaneous. When they both oppose spontaneity, the reaction is never spontaneous. In other reactions, ΔH and ΔS "disagree," and one favors spontaneity while the other opposes it. In this situation, we must consider the actual values of ΔH and ΔS and perform a simple calculation.

Osmosis and Entropy

The natural progression toward greater entropy sometimes produces surprising results. The diagram below shows a U-shaped tube divided into two halves by a semipermeable membrane. This membrane has tiny pores that allow water molecules to pass freely; larger particles such as Na^+ and Cl^- ions are too big to pass through. When the tube is filled with water, the levels on the right and the left are the same, just as one would expect. However, if salt is added to the left side, a strange thing occurs. Water will pass from the right side to the left side across the membrane, and the two levels will become uneven. This diffusion of water is called "osmosis," and it occurs because of the tendency for things to mix together due to entropy. Greater mixing occurs when water moves toward the side with salt, and therefore the entropy increases.



Osmosis. © Science Media Group.

It may seem that this kind of diffusion due to entropy is a passive process and not important outside of the laboratory. In fact, semipermeable membranes are ubiquitous in living things. The membrane that surrounds all cells is semipermeable; water passes freely but larger molecules do not. The consequences are enormous. Without knowing how it works, humankind has been taking advantage of osmosis for centuries by salting food for preservation. Putting salt on the surface of food pulls moisture out, making it a less hospitable environment for bacteria. A high-salt environment also kills bacteria outright, as osmosis pulls their water out causing the bacteria to shrivel and die. Sugar need not be refrigerated for the same reason; although it is a rich source of energy for microorganisms, such a high concentration of sugar would kill any bacteria attempting to live on it.

Osmosis also plays an important role in some human diseases. The bacterium that causes cholera, *Vibrio cholerae*, secretes a toxin that binds to the surface of cells in the intestine. The toxin stimulates cells to secrete large amounts of Cl^- ions into the intestinal cavity. Na^+ ions and water follow the Cl^- ions via diffusion, and the result is severe diarrhea and dehydration. While too much osmosis is a bad thing, too little can be bad too. Patients suffering from cystic fibrosis have a defect in a chloride channel in the cell membrane. Various mutations in this channel cause it to malfunction, and it does not release enough Cl^- ions onto the membranes lining the pancreas, lungs, sweat glands, salivary glands, and other organs. Because Cl^- ions remain trapped inside the cells, water also remains inside the cell. Thus, the mucus coating these membranes lacks water and becomes too viscous. The symptoms of cystic fibrosis are the result of thick, sticky mucus clogging the channels of the affected organs.

In the 1870s, American mathematician Josiah Willard Gibbs (1839–1903) developed the concept of **Gibbs free energy** (given the variable G) and an equation that determines whether or not a reaction will happen spontaneously. The Gibbs free energy of a system depends on the enthalpy, entropy, and absolute temperature of the system (the derivation of this equation is beyond the scope of this text):

$$G = H - TS$$

The change in Gibbs free energy is calculated as follows:

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

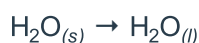
For a spontaneous reaction, ΔG will be negative; for a nonspontaneous reaction, ΔG will be positive. Notice that when both ΔH and ΔS favor a spontaneous reaction (ΔH is negative, ΔS is positive), the sign of ΔG must necessarily be negative, indicating a spontaneous reaction. And when both ΔH and ΔS oppose a spontaneous reaction (ΔH is positive, ΔS is negative), the sign of ΔG must necessarily be positive, indicating a nonspontaneous reaction.

When ΔH and ΔS conflict, plugging in actual values for ΔH , ΔS , and T will determine ΔG and its sign. Let's consider the explosive reaction of sodium metal and chlorine gas to produce table salt:



$$\Delta H = -822.24 \text{ kJ/mol} \quad \Delta S = -181.3 \text{ J/K}\cdot\text{mol} \quad T = 298 \text{ K}$$

The ΔG for this reaction is -768.2 kJ/mol , so this reaction is spontaneous at this temperature. Although the entropy of the system decreases in this reaction, it is more than offset by the heat released to the surroundings. Here's another example:



$$\Delta H = +6.01 \text{ kJ/mol} \quad \Delta S = +22 \text{ J/K}\cdot\text{mol} \quad T = 298 \text{ K}$$

For this simple reaction—the melting of ice—the value of ΔG is -0.546 kJ/mol at 25°C (298 K), which is room temperature. This result comes as no surprise, as the melting point of ice is 0°C (273 K). At room temperature, the increase in the system's entropy outweighs the endothermic nature of the reaction, and the reaction happens spontaneously. Note that dropping the temperature below the melting point changes the sign of ΔG to positive; at -25°C (248 K), $\Delta G = +0.554 \text{ kJ/mol}$. Again, this conforms to experience; below its melting point, a solid will not melt. Indeed, the *reverse* reaction is spontaneous at these lower temperatures; liquid water turns to ice. The value of ΔG for the freezing reaction (at 248 K) is the same but with the sign reversed: -0.554 kJ/mol .

To summarize:

ΔS	ΔH	ΔG	Spontaneous?
+	-	-	Always
-	+	+	Never
-	-	+ at high T, - at low T	At low T
+	+	- at high T, + at low T	At high T

What is ΔG exactly at the melting point? The ΔG when the temperature is 273 K is 0 kJ/mol . Neither the forward nor the reverse reaction is spontaneous. At this particular temperature, the reaction is held in a kind of limbo between the forward and reverse. This state is called "equilibrium," which we will discuss in greater detail in later sections.

Glossary

Gibbs free energy

The value that indicates the thermodynamic stability of a system. All systems spontaneously move toward a minimum in Gibbs free energy.

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Section 6: Coupling Reactions

As mentioned in Section 1 of this unit, the rusting of iron is a spontaneous chemical reaction. Because iron will spontaneously react with oxygen in the air, pure elemental iron is rarely found in the Earth's crust. Iron mines extract various types of iron ore, which consist largely of compounds made of iron and oxygen. To get pure iron metal for use in manufacturing, there must be some way to reverse the spontaneous reaction of iron with oxygen. In other words, the following reaction must occur:



Figure 9-7. Iron Ore Smelting

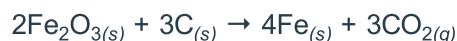
The smelting of iron in a blast furnace requires the coupling of chemical reactions.

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The process of smelting iron ore—processing the ore in a blast furnace—reverses the reaction. (Figure 9-7) In the intense heat of the blast furnace, the reaction is **coupled** to another reaction, the spontaneous reaction of carbon with oxygen:



These reactions are coupled because the O_2 produced by the first reaction is consumed in the second reaction. When two chemical reactions are coupled, the overall ΔG of the reaction determines the spontaneity. Combining the two reactions above, we get:



The ΔG of this combined reaction is negative, so the reaction is spontaneous.

Coupled reactions are not just important in heavy industry; all living things rely on coupled reactions inside their cells. Thousands of nonspontaneous reactions must occur inside an organism to keep it alive, and spontaneous reactions "drive" the nonspontaneous reactions.

For example, the following reaction shows the synthesis of glutamine, an amino acid, from the glutamate ion and ammonia in the form of ammonium:



The ΔG for the reaction is positive, so the reaction is nonspontaneous. Many reactions like this are coupled with the hydrolysis of adenosine triphosphate (ATP):

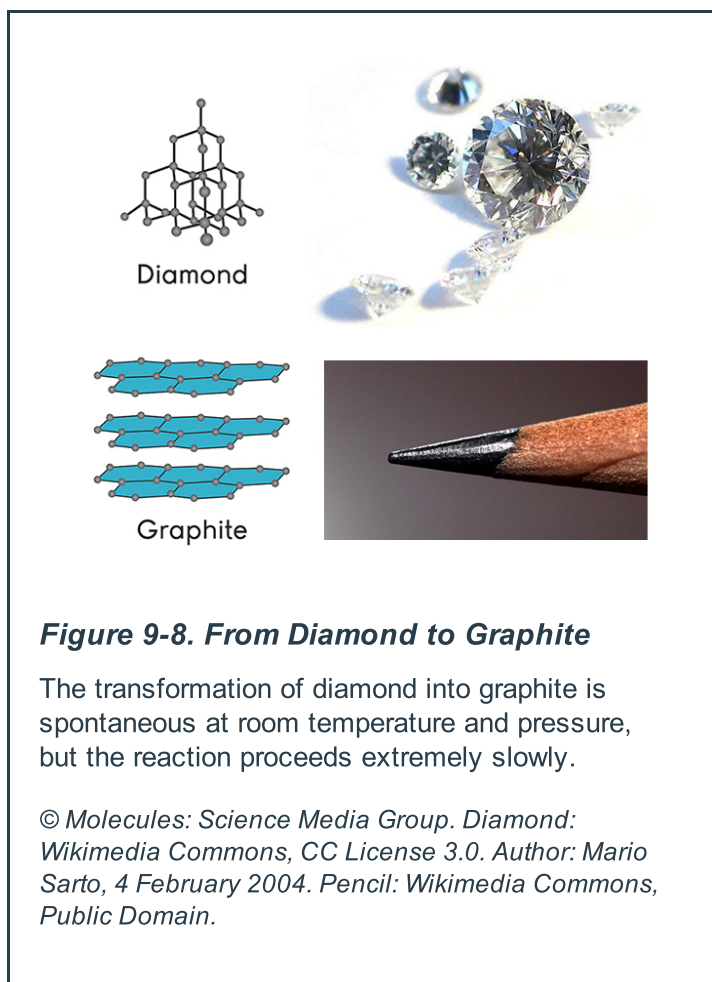


Taken together, the coupled reactions have $\Delta G = 14.2 - 30.5 = -16.3 \text{ kJ/mol}$. So, overall, the process is spontaneous.

In this way, ATP drives thousands of biological reactions. Instead of making more ATP from scratch, organisms simply reverse the breakdown of ATP in the nonspontaneous reaction:



This regeneration is driven, in turn, by the breakdown of nutrients such as glucose:



What about spontaneous reactions: *Must* they occur? While many reactions are technically spontaneous according to their ΔG values, this tells us nothing about the rate at which the chemical reaction will occur. For example, pure carbon in the form of a diamond will spontaneously turn into carbon's cheap graphite form; the ΔG of this reaction is -2.87 kJ/mol at room temperature. (Figure 9-8) The reaction is so slow, however, that it is not noticeable over human scales of time. However, if we accidentally lost a diamond ring in the batter while baking a cake, the temperatures in the oven would speed up the process and turn the diamond into worthless graphite.

Glossary

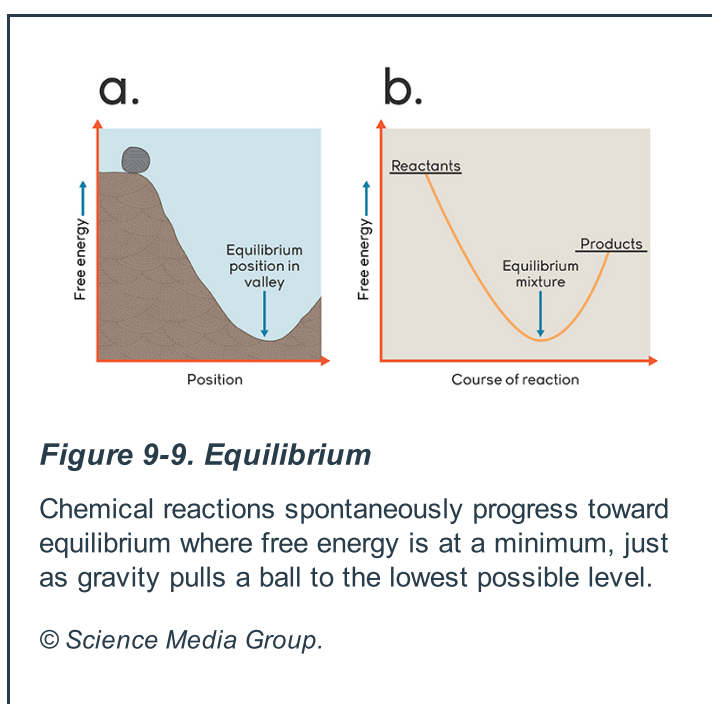
Coupled reactions

When a spontaneous reaction drives a nonspontaneous reaction.

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Section 7: Equilibrium

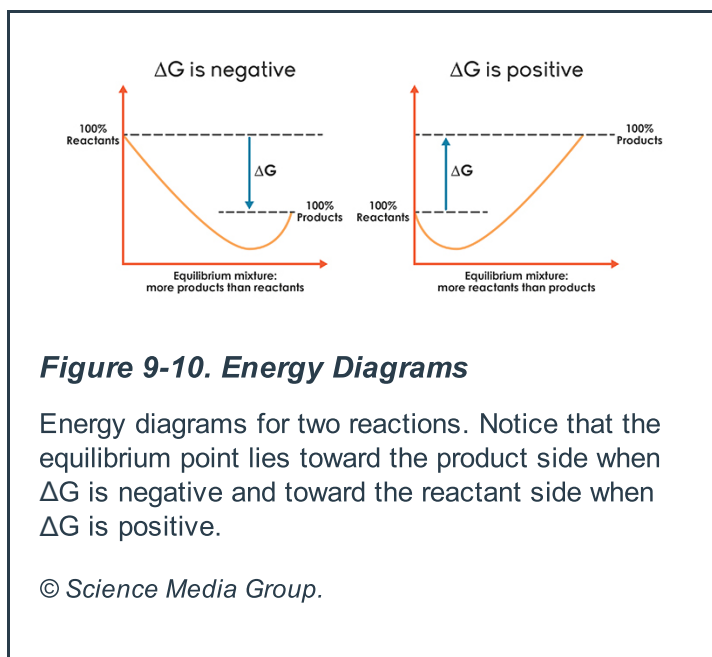
The ΔG value of a chemical equation only tells us if the reactants are more stable than the products, or vice versa. If ΔG is negative, the products are more stable than the reactants; if ΔG is positive, the reactants are more stable than the products. If the products are more stable than the reactants, this does *not* mean that the reaction will continue until *all* of the reactants have changed into products. Some of the time, the most stable situation is when there is a *mixture* of reactants and products. The reaction will continue until it reaches this state of maximum thermodynamic stability (lowest Gibbs free energy).



The situation is analogous to a ball rolling into a valley, as shown in Figure 9-9. When the ball sits at the top of the hill at position A, the reaction vessel contains 100% reactants, and the system has high free energy. When the ball is at position B, the reaction vessel contains 100% products. Note that position B is more stable than A because it is lower. The most stable position is in the valley between A and B. At this point, the system has reached minimum free energy—maximum thermodynamic stability.

This position is called "**equilibrium**." At equilibrium, the reaction appears to have stopped, because the amounts of reactants and products are constant. They are constant not because the reactions have stopped, but because the forward and reverse reactions are happening at the same rate. At equilibrium, products are formed via the forward reaction and destroyed by the reverse reaction. Because the rates of formation and destruction are equal, the amount of products remains constant. The same is true for the reactants; the forward reaction destroys the reactants, and the reverse reaction creates them, but the amount remains constant.

When the value of ΔG is negative, we say that the reactants are "favored" in the reaction. When ΔG is a positive number, the products are favored. When the products are favored, the mixture of chemicals at equilibrium will have a high percentage of products and a low percentage of reactants, and chemists will say that the equilibrium position "lies to the right." If the reactants are favored, the equilibrium state has a high percentage of reactants and a low percentage of products, and the equilibrium position "lies to the left." (Figure 9-10)



To quantify exactly where the equilibrium lies, we can calculate the ratio of products to reactants in a very specific way. The next section will describe how this is done.

Glossary

Equilibrium

The state of maximum thermodynamic stability of a chemical reaction. While the reaction is still occurring in the forward and the reverse directions, there is no macroscopic evidence of changing amounts of products or reactants.

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Section 8: The Equilibrium Constant Expression

For a particular reaction, the ratio of products to reactants at equilibrium will always be the same; the ratio is called the "**equilibrium constant**" or K.

Q, the Reaction Quotient

When a chemical reaction is not at equilibrium, it naturally reacts until equilibrium is reached. With too much product, the reaction will "shift to the left" to reach equilibrium. With too much reactant, the reaction will "shift to the right" to reach equilibrium. It's not always easy to determine which way a certain combination of products and reactants will shift; it depends on their specific concentrations and the value of K. Fortunately, it's easy to predict mathematically with the reaction quotient, or Q. Q has the same formula as K, only the concentrations plugged in are the actual current concentrations, not the concentrations that will exist at equilibrium. For example:



Let's say we make a solution so that:

$$[\text{HC}_2\text{H}_3\text{O}_2] = 0.5 \text{ M} \quad [\text{H}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = 0.3 \text{ M}$$

Which direction will this reaction go, if these are the starting concentrations?

First, calculate Q:

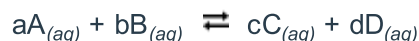
$$Q = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{0.3(0.3)}{0.5} = 0.18$$

Because this value is higher than the K value, we conclude that the current concentration of the products is too high; thus, the reaction will shift to the left to attain equilibrium. The rules are:

- If $Q > K$, the reaction shifts to the left.
- If $Q < K$, the reaction shifts to the right.
- If $Q = K$, the reaction is already at equilibrium; no shift occurs.

For example, in the unsaturated solution, Q would be less than K; more solute needs to dissolve to reach equilibrium. When the solution is saturated, equilibrium has been achieved and Q equals K. If the solution becomes supersaturated, Q is greater than K, and some of the solute would need to precipitate out to get back to equilibrium.

The value of K is calculated by dividing the amounts of products at equilibrium by the amounts of reactants at equilibrium. For example, let's look at the generic reaction:



In this reaction, the capital letters are the chemical formulas, and the lowercase letters are the coefficients that balance the equation. The equilibrium is calculated by setting up the following equation, which is called the "equilibrium constant expression":

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

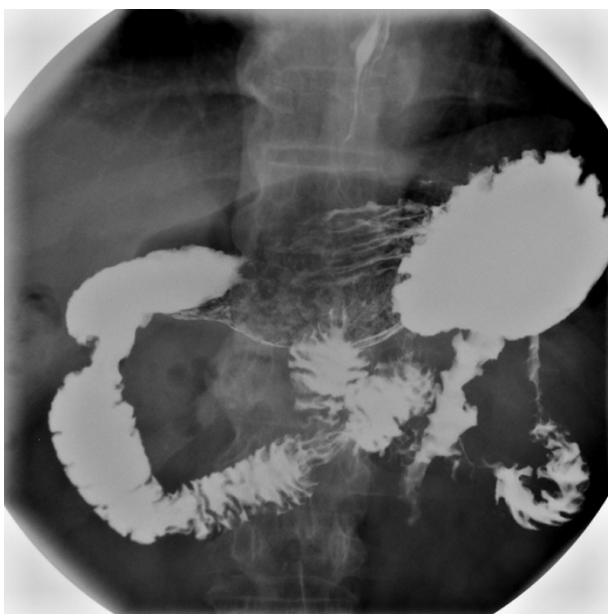


Figure 9-11. Barium Sulfate Meal

Barium sulfate enhances an X-ray of a patient's colon. Barium sulfate is not toxic due to its low K value.

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The chemical symbols in brackets mean molarity: "[C]" means "the molarity of chemical C." Note that the coefficients in the chemical equation have become exponents in the equilibrium constant expression.

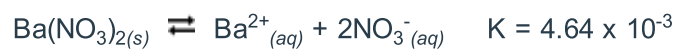
The values of K have a huge range: K can be less than 1×10^{-20} and more than 1×10^{20} . If K is very high, the equilibrium concentration of products is much higher than the concentration of reactants; the reaction favors the products (ΔG is negative). If K is very low, the equilibrium concentration of reactants is much higher than the concentration of products; the reaction favors the reactants (ΔG is positive).

The value of K has a huge impact on the properties of a substance. The K value for dissolving a solid indicates how soluble the solid is. When barium sulfate dissolves, the reaction is:



Barium ions are extremely toxic. The low K value for the above reaction means that barium sulfate hardly dissolves at all; it is so low, in fact, that barium sulfate is safe to use inside the body for medical imaging as a contrast agent (barium blocks X-rays well). There is no danger when a patient swallows a suspension of barium sulfate because the barium ions remain bound to sulfate and are therefore harmless. (Figure 9-11)

Barium nitrate, on the other hand, dissociates much more:



Due to the higher K value, barium nitrate is highly toxic, and the lethal dose is between 1 and 15 grams. One of the recommended treatments for barium nitrate poisoning is sodium or magnesium sulfate; because the K value for barium sulfate is so low, the sulfate ions will combine with the toxic barium ions and precipitate out as the harmless, insoluble barium sulfate.

Glossary

Equilibrium constant

A mathematical expression of the relative amounts of products and reactants when a reaction is at equilibrium.

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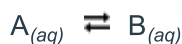
Section 9: Le Chatelier's Principle

When a chemical system reaches equilibrium, it is in its most stable state. If something disturbs the equilibrium—for example, the concentration of a chemical is changed—the system will return to equilibrium just as a ball pushed up a hill will roll back down. As it returns to equilibrium, it counteracts the original disturbance. For example, if the concentration of a reactant increases, the reaction will lower its concentration. If a product is removed, it will be restored. If heat is added, the reaction will cool back down, etc. In 1888, French chemist Henri Louis Le Chatelier (1850–1936) described this phenomenon that bears his name:

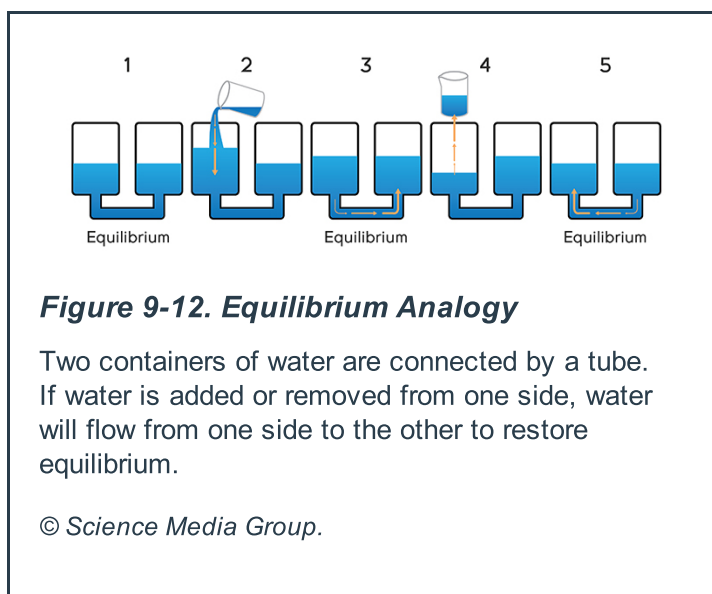
Every change of one of the factors of an equilibrium occasions a rearrangement of the system in such a direction that the factor in question experiences a change in a sense opposite to the original change.

When a reaction at equilibrium is disturbed, it will *shift* to the right or the left to return to equilibrium. Shifting to the right means some reactants are consumed and more products are made. Shifting to the left means some products are consumed and more reactants are made. There are a number of ways in which an equilibrium can be disturbed:

Adding or Removing a Product or Reactant



If more A is added, the reaction will shift to the right to restore the equilibrium ratio. Adding B will shift the reaction left. Removing A shifts the reaction left; removing B shifts it right.

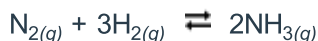


To remember how an equilibrium shifts when chemicals are added or removed, consider the analogy in Figure 9-12. Two containers of water represent the reactants and products of a chemical reaction. A tube allows water to flow from one to the other. The system starts out at equilibrium, and the water levels are

even. If extra water is added to the container on the left, the water flows from left to right until the levels equalize and equilibrium is reached again.

Likewise, if water is removed from the reactant (left) side, the flow from right to left will restore the equilibrium.

In chemical syntheses, the goal is to maximize the amount of product. In this case, equilibrium is not a desirable state; once equilibrium is reached, the product ceases to accumulate. The Haber-Bosch process for synthesizing ammonia from atmosphere nitrogen (discussed in Unit 7 and illustrated in the *Control the Haber-Bosch Ammonia Plant* interactive) faces this problem. The reaction reaches equilibrium:



To prevent the reaction from stopping, the ammonia is continually removed from the reaction apparatus. Keeping the amount of NH_3 low forces the reaction to shift to the right until the reactants are used up.

Change in Pressure

Pressure only affects reactions involving gases; it does not affect reactions where no gases are present. When pressure on the system increases, the reaction will shift to counteract the increase in pressure; it does this by shifting *toward the side of the reaction with fewer moles of gas*. For example:



In this reaction, there is one mole of gas on the left and three moles of gas on the right. If the pressure increases, the reaction will try to decrease the pressure by decreasing the amount of gas—it will shift to the left. Conversely, if the pressure decreases, the reaction will try to increase the pressure by increasing the amount of gas—it will shift to the right.

The shifting due to pressure is also used to maximize yield in the Haber-Bosch process. There are four moles of gas on the reactant side of the equation and two moles on the product side. To shift the reaction toward the product side, the reaction mixture is kept under high pressure.

Catalysts

In Unit 12, we will explore how catalysts speed up reactions. At equilibrium, both the forward and reverse reactions are happening at the same rate. Adding a catalyst speeds up *both* reactions, and therefore the equilibrium balance is maintained, but a reaction can reach equilibrium faster. *Catalysts do not cause shifts in equilibrium.*

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Section 10: Temperature and Equilibrium

As discussed in Unit 7, Section 6, exothermic reactions release energy and endothermic reactions absorb energy. Because exothermic reactions give off heat, we can consider heat a product of the reaction, and we can even include it in the chemical equation for convenience:



If the reaction is endothermic, we consider heat a reactant:



It is now possible to predict the direction of shift when the reaction is heated or cooled. If an exothermic reaction is heated, the reaction shifts left; if cooled, it shifts right. If an endothermic reaction is heated, the reaction shifts right; if the reaction is cooled, it shifts to the left. It is important to remember that heat isn't really a product or a reactant of the reaction; this is just a way to understand how temperature affects equilibrium. So, we can pretend it is like Le Châtelier's Principle from Section 9 of this unit to get an idea of which way the reaction will shift. However, what really happens when the temperature changes is that the value of the equilibrium constant (K) changes, and the reaction has to move to shift to that new ratio. Whether K goes up or down is a function of whether the reaction is endothermic or exothermic.

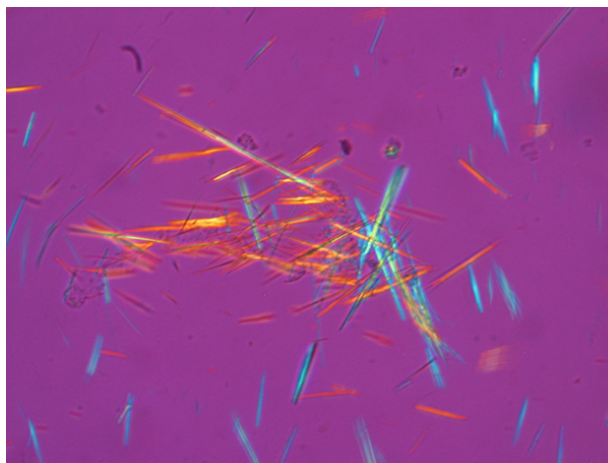


Figure 9-13. Uric Acid Crystals

Gout is a painful condition that occurs when crystals of uric acid precipitate out inside the joints. This image shows these crystals photographed under polarized light.

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These equilibrium shifts explain why some substances are more or less soluble at higher temperatures. Dissolving CO_2 in water is exothermic; cooling the water shifts the reaction to the right, allowing more gas to dissolve. Warming the solution causes a shift to the left, and CO_2 comes out of the solution; this explains why soda goes flat as it comes to room temperature.

Conversely, dissolving uric acid (a waste product in the bloodstream) is endothermic. It dissolves more at higher temperatures, and less at lower temperatures. In parts of the body that become cold such as the feet, the solubility of uric acid can decrease so much that it precipitates out as tiny needle-shaped crystals. (Figure 9-13) This leads to an extremely painful form of arthritis called "gout." Attacks of gout also occur more often at night because the ambient temperature is lower.

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Section 11: Conclusion

The research on entropy pioneered by Boltzmann led to a radical new understanding of the physical world. All spontaneous processes increase the entropy of the universe; the driving force of the universe is statistical. All chemical reactions, from dissolving the sugar in coffee to the synthesis of DNA, occur because atoms and energy follow the path of increasing entropy.

In this unit, we saw that when a chemical system reaches a point of maximum entropy, it has reached equilibrium. Understanding and influencing equilibria are vital to many aspects of chemistry, including the chemistry of acids and bases, which we will discuss in the next unit.



Unit 9: *Equilibrium and Advanced Thermodynamics—Balance in Chemical Reactions*

Section 12: Further Reading

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