Chapter 17

Spontaneity, Entropy, and Free Energy

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Solid carbon dioxide (dry ice), when placed in water, causes violent bubbling as gaseous CO2 is released. The “fog” is moisture condensed from the cold air.

The ﬁrst law of thermodynamics is a statement of the law of conservation of energy: Energy can be neither created nor destroyed. In other words, the energy of the universe is constant. Although the total energy is constant, the various forms of energy can be interchanged in physical and chemical processes. For example, if you drop a book, some of the initial potential energy of the book is changed to kinetic energy, which is then transferred to the atoms in the air and the ﬂoor as random motion. The net effect of this process is to change a given quantity of potential energy to exactly the same quantity of thermal energy. Energy has been converted from one form to another, but the same quantity of energy exists before and after the process. Now let’s consider a chemical example. When methane is burned in excess oxygen, the major reaction is

//Chemical Reaction

CR1

This reaction produces a quantity of energy, which is released as heat. This energy ﬂow results from the lowering of the potential energy stored in the bonds of CH4 and O2 as they react to form CO2 and H2O. This is illustrated in Fig. 17.1. Potential energy has been converted to thermal energy, but the energy content of the universe has remained constant in accordance with the ﬁrst law of thermodynamics. The ﬁrst law of thermodynamics is used mainly for energy bookkeeping, that is, to answer such questions as

How much energy is involved in the change?

Does energy ﬂow into or out of the system?

What form does the energy ﬁnally assume?

Although the ﬁrst law of thermodynamics provides the means for accounting for energy, it gives no hint as to why a particular process occurs in a given direction. This is the main question to be considered in this chapter.

//Quote

The ﬁrst law of thermodynamics: The energy of the universe is constant.

//Heading

17.1∆Spontaneous Processes and Entropy

A process is said to be spontaneous if it occurs without outside intervention. Spontaneous processes may be fast or slow. As we will see in this chapter, thermodynamics can tell us the direction in which a process will occur but can say nothing about the speed of the process. As we saw in Chapter 12, the rate of a reaction depends on many factors, such as activation energy, temperature, concentration, and catalysts, and we were able to explain these effects using a simple collision model. In describing a chemical reaction, the discipline of chemical kinetics focuses on the pathway between reactants and products; thermodynamics considers only the initial and ﬁnal states and does not require knowledge of the pathway between reactants and products (see Fig. 17.2).

//Quote

Spontaneous does not mean fast

//Image

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Figure 17.1

When methane and oxygen react to form carbon dioxide and water, the products have lower potential energy than the reactants. This change in potential energy results in energy ﬂow (heat) to the surroundings.

//Image

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Figure 17.2

The rate of a reaction depends on the pathway from reactants to products; this is the domain of kinetics. Thermodynamics tells us whether a reaction is spontaneous based only on the properties of the reactants and products. The predictions of thermodynamics do not require knowledge of the pathway between reactants and products.

In summary, thermodynamics lets us predict whether a process will occur but gives no information about the amount of time required for the process. For example, according to the principles of thermodynamics, a diamond should change spontaneously to graphite. The fact that we do not observe this process does not mean the prediction is wrong; it simply means the process is very slow. Thus we need both thermodynamics and kinetics to describe reactions fully. To explore the idea of spontaneity, consider the following physical and chemical processes:

A ball rolls down a hill but never spontaneously rolls back up the hill.

If exposed to air and moisture, steel rusts spontaneously. However, the iron oxide in rust does not spontaneously change back to iron metal and oxygen gas.

A gas ﬁlls its container uniformly. It never spontaneously collects at one end of the container.

Heat ﬂow always occurs from a hot object to a cooler one. The reverse process never occurs spontaneously.

Wood burns spontaneously in an exothermic reaction to form carbon dioxide and water, but wood is not formed when carbon dioxide and water are heated together.

At temperatures below 00C, water spontaneously freezes, and at temperatures above 00C, ice spontaneously melts.

What thermodynamic principle will provide an explanation of why, under a given set of conditions, each of these diverse processes occurs in one direction and never in the reverse? In searching for an answer, we could explain the behavior of a ball on a hill in terms of gravity. But what does gravity have to do with the rusting of a nail or the freezing of water? Early developers of thermodynamics thought that exothermicity might be the key—that a process would be spontaneous if it were exothermic. Although this factor does appear to be important, since many spontaneous processes are exothermic, it is not the total answer. For example, the melting of ice, which occurs spontaneously at temperatures greater than 00C, is an endothermic process.

//Image

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Iron spontaneously rusts when it comes in contact with water.

What common characteristic causes the processes listed above to be spontaneous in one direction only? After many years of observation, scientists have concluded that the characteristic common to all spontaneous processes is an increase in a property called entropy, denoted by the symbol S. The driving force for a spontaneous process is an increase in the entropy of the universe. What is entropy? Although there is no simple deﬁnition that is completely accurate, entropy can be viewed as a measure of molecular randomness or disorder. The natural progression of things is from order to disorder, from lower entropy to higher entropy. To illustrate the natural tendency toward disorder, you only have to think about the condition of your room. Your room naturally tends to get messy (disordered), because an ordered room requires everything to be in its place. There are simply many more ways for things to be out of place than for them to be in their places.

As another example, suppose you have a deck of playing cards ordered in some particular way. You throw these cards into the air and pick them all up at random. Looking at the new sequence of the cards, you would be very surprised to ﬁnd that it matched the original order. Such an event would be possible, but very improbable. There are billions of ways for the deck to be disordered, but only one way to be ordered according to your deﬁnition. Thus the chances of picking the cards up out of order are much greater than the chance of picking them up in order. It is natural for disorder to increase.

//Image

175

A disordered pile of playing cards.

//Quote

Probability refers to likelihood.

Entropy is a thermodynamic function that describes the number of arrangements (positions and/or energy levels) that are available to a system existing in a given state. Entropy is closely associated with probability. The key concept is that the more ways a particular state can be achieved, the greater is the likelihood (probability) of ﬁnding that state. In other words, nature spontaneously proceeds toward the states that have the highest probabilities of existing. This conclusion is not surprising at all. The difﬁculty comes in connecting this concept to real-life processes. For example, what does the spontaneous rusting of steel have to do with probability? Understanding the connection between entropy and spontaneity will allow us to answer such questions. We will begin to explore this connection by considering a very simple process, the expansion of an ideal gas into a vacuum, as represented in Fig. 17.3. Why is this process spontaneous? The driving force is probability. Because there are more ways of having the gas evenly spread throughout the container than there are ways for it to be in any other possible state, the gas spontaneously attains the uniform distribution.

To understand this conclusion, we will greatly simplify the system and consider the possible arrangements of only four gas molecules in the two-bulbed container (Fig. 17.4). How many ways can each arrangement (state) be achieved? Arrangements I and V can be achieved in only one way—all the molecules must be in one end. Arrangements II and V can be achieved in four ways, as shown in Table 17.1. Each conﬁguration that gives a particular arrangement is called a microstate. Arrangement I has one microstate, and arrangement II has four microstates. Arrangement III can be achieved in six ways (six microstates), as shown in Table 17.1. Which arrangement is most likely to occur? The one that can be achieved in the greatest number of ways. Thus arrangement III is most probable. The relative probabilities of arrangements III, II, and I are 6 : 4 : 1. We have discovered an important principle: The probability of occurrence of a particular arrangement (state) depends on the number of ways (microstates) in which that arrangement can be achieved.

//Image

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Figure 17.3 The expansion of an ideal gas into an evacuated bulb.

//Image

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Figure 17.4 Possible arrangements (states) of four molecules in a two-bulbed ﬂask.

//Table

T17.1

Table 17.1 The microstates that give a particular Arrangement (State)

//Quote

For two molecules in the ﬂask, there are four possible microstates:

//Image

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//Quote

Thus there is one chance in four of ﬁnding

//Image

179

//Table

T17.2

Table 17.2 Probability of Finding All the Molecules in the Left Bulb as a Function of the Total Number of Molecules

The consequences of this principle are dramatic for large numbers of molecules. One gas molecule in the ﬂask in Fig. 17.4 has one chance in two of being in the left bulb. We say that the probability of ﬁnding the molecule in the left bulb is . For two molecules in the ﬂask, there is one chance in two of ﬁnding each molecule in the left bulb, so there is one chance in four ( ) that both molecules will be in the left bulb. As the number of molecules increases, the relative probability of ﬁnding all of them in the left bulb decreases, as shown in Table 17.2. For 1 mole of gas, the probability of ﬁnding all the molecules in the left bulb is so small that this arrangement would “never” occur.

Thus a gas placed in one end of a container will spontaneously expand to ﬁll the entire vessel evenly because, for a large number of gas molecules, there is a huge number of microstates in which equal numbers of molecules are in both ends. On the other hand, the opposite process,

//Image

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although not impossible, is highly improbable, since only one microstate leads to this arrangement. Therefore, this process does not occur spontaneously.

The type of probability we have been considering in this example is called positional probability because it depends on the number of conﬁgurations in space (positional microstates) that yield a particular state. A gas expands into a vacuum to give a uniform distribution because the expanded state has the highest positional probability, that is, the largest entropy, of the states available to the system.

//Quote

Solid, liquid, and gaseous states were compared in Chapter 10.

Positional probability is also illustrated by changes of state. In general, positional entropy increases in going from solid to liquid to gas. A mole of a substance has a much smaller volume in the solid state than it does in the gaseous state. In the solid state, the molecules are close together, with relatively few positions available to them; in the gaseous state, the molecules are far apart, with many more positions available to them. The liquid state is closer to the solid state than it is to the gaseous state in these terms. We can summarize these comparisons as follows:

//Image

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//Quote

Solids are more ordered than liquids or gases and thus have lower entropy.

Positional entropy is also very important in the formation of solutions. In Chapter 11 we saw that solution formation is favored by the natural tendency for substances to mix. We can now be more precise. The entropy change associated with the mixing of two pure substances is expected to be positive. An increase in entropy is expected because there are many more microstates for the mixed condition than for the separated condition. This effect is due principally to the increased volume available to a given “particle” after mixing occurs. For example, when two liquids are mixed to form a solution, the molecules of each liquid have more available volume and thus more available positions. Therefore, the increase in positional entropy associated with mixing favors the formation of solutions.

//Example

Example 17.1

Positional Entropy

For each of the following pairs, choose the substance with the higher positional entropy (per mole) at a given temperature.

**a**. Solid CO2 and gaseous CO2

**b**. N2 gas at 1 atm and N2 gas at 1.0 x 10-2 atm

//Solution

**a.** Since a mole of gaseous CO2 has the greater volume by far, the molecules have many more available positions than in a mole of solid CO2. Thus gaseous CO2 has the higher positional entropy.

**b.** A mole of N2 gas at 1 x 10-2 atm has a volume 100 times that (at a given temperature) of a mole of N2 gas at 1 atm. Thus N2 gas at 1 x 10-2 atm has the higher positional entropy.

//Example

Example 17.2 Predicting Entropy Changes

Predict the sign of the entropy change for each of the following processes.

**a**. Solid sugar is added to water to form a solution.

**b.** Iodine vapor condenses on a cold surface to form crystals

//Solution

1. The sugar molecules become randomly dispersed in the water when the solution forms and thus have access to a larger volume and a larger number of possible positions. The positional disorder is increased, and there will be an increase in entropy. ∆S is positive, since the ﬁnal state has a larger entropy than the initial state, and ∆S = ∆S ﬁnal - ∆S initial.
2. Gaseous iodine is forming a solid. This process involves a change from a relatively large volume to a much smaller volume, which results in lower positional disorder. For this process ∆S is negative (the entropy decreases).

//Headline

17.2 ∆Entropy and the Second Law of Thermodynamics

We have seen that processes are spontaneous when they result in an increase in disorder. Nature always moves toward the most probable state available to it. We can state this principle in terms of entropy: In any spontaneous process there is always an increase in the entropy of the universe. This is the second law of thermodynamics. Contrast this with the ﬁrst law of thermodynamics, which tells us that the energy of the universe is constant. Energy is conserved in the universe, but entropy is not. In fact, the second law can be paraphrased as follows: The entropy of the universe is increasing.

As in Chapter 6, we ﬁnd it convenient to divide the universe into a system and the surroundings. Thus we can represent the change in the entropy of the universe as

//Chemical Reaction

CR2

where ∆Ssys and ∆Ssurr represent the changes in entropy that occur in the system and surroundings, respectively. To predict whether a given process will be spontaneous, we must know the sign of ∆Suniv. If ∆Suniv is positive, the entropy of the universe increases, and the process is spontaneous in the direction written. If ∆Suniv is negative, the process is spontaneous in the opposite direction. If ∆Suniv is zero, the process has no tendency to occur, and the system is at equilibrium. To predict whether a process is spontaneous, we must consider the entropy changes that occur both in the system and in the surroundings and then take their sum.

//Quote

The total energy of the universe is constant, but the entropy is increasing.

//Example

Example 17.2∆Entropy and the Second Law of Thermodynamics

We have seen that processes are spontaneous when they result in an increase in disorder. Nature always moves toward the most probable state available to it. We can state this principle in terms of entropy: In any spontaneous process there is always an increase in the entropy of the universe. This is the second law of thermodynamics. Contrast this with the ﬁrst law of thermodynamics, which tells us that the energy of the universe is constant. Energy is conserved in the universe, but entropy is not. In fact, the second law can be paraphrased as follows: The entropy of the universe is increasing. As in Chapter 6, we ﬁnd it convenient to divide the universe into a system and the surroundings. Thus we can represent the change in the entropy of the universe as

//Chemical Reaction

CR3

where ∆Ssys and ∆Ssurr represent the changes in entropy that occur in the system and surroundings, respectively. To predict whether a given process will be spontaneous, we must know the sign of ∆Suniv. If ∆Suniv is positive, the entropy of the universe increases, and the process is spontaneous in the direction written. If ∆Suniv is negative, the process is spontaneous in the opposite direction. If ∆Suniv is zero, the process has no tendency to occur, and the system is at equilibrium. To predict whether a process is spontaneous, we must consider the entropy changes that occur both in the system and in the surroundings and then take their sum.

//Example

Example 17.3

In a living cell, large molecules are assembled from simple ones. Is this process consistent with the second law of thermodynamics?

//Solution

To reconcile the operation of an order-producing cell with the second law of thermodynamics, we must remember that ∆Suniv, not ∆Ssys, must be positive for a process to be spontaneous. A process for which ∆Ssys is negative can be spontaneous if the associated ∆Ssurr is both larger and positive. The operation of a cell is such a process.

//chemical connections

Entropy: An Organizing Force?

In this text we have emphasized the meaning of the second law of thermodynamics— that the entropy of the universe is always increasing. Although the results of all our experiments support this conclusion, this does not mean that order cannot appear spontaneously in a given part of the universe. The best example of this phenomenon involves the assembly of cells in living organisms. Of course, when a process that creates an ordered system is examined in detail, it is found that other parts of the process involve an increase in disorder such that the sum of all the entropy changes is positive. In fact, scientists are now ﬁnding that the search for maximum entropy in one part of a system can be a powerful force for organization in another part of the system.

To understand how entropy can be an organizing force, look at the accompanying ﬁgure. In a system containing large and small “balls” as shown in the ﬁgure, the small balls can “herd” the large balls into clumps in the corners and near the walls. This clears out the maximum space for the small balls so that they can move more freely, thus maximizing the entropy of the system, as demanded by the second law of thermodynamics.

In essence, the ability to maximize entropy by sorting different-sized objects creates a kind of attractive force, called a depletion, or excluded-volume, force. These “entropic forces” operate for objects in the size range of approximately 10-8 to approximately 10-6 m. For entropy-induced ordering to occur, the particles must be constantly jostling each other and must be constantly agitated by solvent molecules, thus making gravity unimportant.

There is increasing evidence that entropic ordering is important in many biological systems. For example, this phenomenon seems to be responsible for the clumping of sickle-cell hemoglobin in the presence of much smaller proteins that act as the “smaller balls.” Entropic forces also have been linked to the clustering of DNA in cells without nuclei, and Allen Minton of the National Institutes of Health in Bethesda, Maryland, is studying the role of entropic forces in the binding of proteins to cell membranes.

Entropic ordering also appears in nonbiological settings, especially in the ways polymer molecules clump together. For example, polymers added to paint to improve the ﬂow characteristics of the paint actually caused it to coagulate because of depletion forces.

Thus, as you probably have concluded already, entropy is a complex issue. As entropy drives the universe to its ultimate death of maximum chaos, it provides some order along the way.

//Image

182

//Heading

17.3∆The Effect of Temperature on Spontaneity

To explore the interplay of ∆Ssys and ∆Ssurr in determining the sign of ∆Suniv, we will ﬁrst discuss the change of state for one mole of water from liquid to gas,∆

//Chemical Reaction

CR4

considering the water to be the system and everything else the surroundings.

What happens to the entropy of water in this process? A mole of liquid water (18 grams) has a volume of approximately 18 mL. A mole of gaseous water at 1 atmosphere and 1000C occupies a volume of approximately 31 liters. Clearly, there are many more positions available to the water molecules in a volume of 31 L than in 18 mL, and the vaporization of water is favored by this increase in positional probability. That is, for this process the entropy of the system increases; ∆Ssys has a positive sign. What about the entropy change in the surroundings? Although we will not prove it here, entropy changes in the surroundings are determined primarily by the ﬂow of energy into or out of the system as heat. To understand this, suppose an exothermic process transfers 50 J of energy as heat to the surroundings, where it becomes thermal energy, that is, kinetic energy associated with the random motions of atoms. Thus this ﬂow of energy into the surroundings increases the random motions of atoms there and thereby increases the entropy of the surroundings. The sign of ∆ Ssurr is positive. When an endothermic process occurs in the system, it produces the opposite effect. Heat ﬂows from the surroundings to the system, and the random motions of the atoms in the surroundings decrease, decreasing the entropy of the surroundings. The vaporization of water is an endothermic process. Thus, for this change of state, ∆Ssurr is negative.

Remember it is the sign of ∆Suniv that tells us whether the vaporization of water is spontaneous. We have seen that ∆Ssys is positive and favors the process and that ∆Ssurr is negative and unfavorable. Thus the components of Suniv are in opposition. Which one controls the situation? The answer depends on the temperature. We know that at a pressure of 1 atmosphere, water changes spontaneously from liquid to gas at all temperatures above 1000C. Below 1000C, the opposite process (condensation) is spontaneous.

//Image

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Boiling water to form steam increases its volume and thus its entropy.

Since ∆Ssys and ∆Ssurr are in opposition for the vaporization of water, the temperature must have an effect on the relative importance of these two terms. To understand why this is so, we must discuss in more detail the factors that control the entropy changes in the surroundings. The central idea is that the entropy changes in the surroundings are primarily determined by heat ﬂow. An exothermic process in the system increases the entropy of the surroundings, because the resulting energy ﬂow increases the random motions in the surroundings. This means that exothermicity is an important driving force for spontaneity. In earlier chapters we have seen that a system tends to undergo changes that lower its energy. We now understand the reason for this tendency. When a system at constant temperature moves to a lower energy, the energy it gives up is transferred to the surroundings, leading to an increase in entropy there.

The signiﬁcance of exothermicity as a driving force depends on the temperature at which the process occurs. That is, the magnitude of ∆Ssurr depends on the temperature at which the heat is transferred. We will not attempt to prove this fact here. Instead, we offer an analogy. Suppose that you have $50 to give away. Giving it to a millionaire would not create much of an impression—a millionaire has money to spare. However, to a poor college student, $50 would represent a signiﬁcant sum and would be received with considerable joy. The same principle can be applied to energy transfer via the ﬂow of heat. If 50 J of energy is transferred to the surroundings, the impact of that event depends greatly on the temperature. If the temperature of the surroundings is very high, the atoms there are in rapid motion. The 50 J of energy will not make a large percent change in these motions. On the other hand, if 50 J of energy is transferred to the surroundings at a very low temperature, where atomic motion is slow, the energy will cause a large percent change in these motions. The impact of the transfer of a given quantity of energy as heat to or from the surroundings will be greater at lower temperatures.

For our purposes, there are two important characteristics of the entropy changes that occur in the surroundings:

1. The sign of ∆Ssurr depends on the direction of the heat ﬂow. At constant temperature, an exothermic process in the system causes heat to ﬂow into the surroundings, increasing the random motions and thus the entropy of the surroundings. For this case, ∆Ssurr is positive. The opposite is true for an endothermic process in a system at constant temperature. Note that although the driving force described here really results from the change in entropy, it is often described in terms of energy: Nature tends to seek the lowest possible energy.

2. The magnitude of ∆Ssurr depends on the temperature. The transfer of a given quantity of energy as heat produces a much greater percent change in the randomness of the surroundings at a low temperature than it does at a high temperature. Thus ∆Ssurr depends directly on the quantity of heat transferred and inversely on temperature.

//Quote

In a process occurring at constant temperature, the tendency for the system to lower its energy results from the positive value of ∆ S surr.

//Chemical Reaction

CR5

We can express ∆Ssurr in terms of the change in enthalpy ∆H for a process occurring at constant pressure, since

//Chemical Reaction

CR6

Recall that ∆H consists of two parts: a sign and a number. The sign indicates the direction of ﬂow, where a plus sign means into the system (endothermic) and a minus sign means out of the system (exothermic). The number indicates the quantity of energy. Combining all these concepts produces the following deﬁnition of ∆Ssurr for a reaction that takes place under conditions of constant temperature (in kelvins) and pressure:

//Chemical Reaction

CR7

The minus sign is necessary because the sign of ∆H is determined with respect to the reaction system, and this equation expresses a property of the surroundings. This means that if the reaction is exothermic, ∆H has a negative sign, but since heat ﬂows into the surroundings, ∆Ssurr is positive.

//Example

Example 17.2 Determinin∆G ∆Ssurr

In the metallurgy of antimony, the pure metal is recovered via different reactions, depending on the composition of the ore. For example, iron is used to reduce antimony in sulﬁde ores:

//Chemical Reaction

CR8

Calculate ∆Ssurr for each of these reactions at 250C and 1 atm.

//Solution

//Chemical Reaction

CR9

//image

184

The mineral stibnite contains Sb2S3.

//Table

T17.3

Note that ∆Ssurr is positive, as it should be, since this reaction is exothermic and heat ﬂow occurs to the surroundings, increasing the randomness of the surroundings. For the oxide ore reaction,

//Chemical Reaction

CR10

In this case ∆Ssurr is negative because heat ﬂow occurs from the surroundings to the system.

We have seen that the spontaneity of a process is determined by the entropy change it produces in the universe. We also have seen that ∆Suniv has two components, ∆Ssys and ∆Ssurr. If for some process both ∆Ssys and ∆Ssurr are positive, then ∆Suniv is positive, and the process is spontaneous. If, on the other hand, both ∆Ssys and ∆Ssurr are negative, the process does not occur in the direction indicated but is spontaneous in the opposite direction. Finally, if ∆Ssys and ∆Ssurr have opposite signs, the spontaneity of the process depends on the sizes of the opposing terms. These cases are summarized in Table 17.3. We can now understand why spontaneity is often dependent on temperature and thus why water spontaneously freezes below 00C and melts above 00C. The term ∆Ssurr is temperature-dependent. Since

//Chemical Reaction

CR11

at constant pressure, the value of ∆Ssurr changes markedly with temperature. The magnitude of ∆Ssurr will be very small at high temperatures and will increase as the temperature decreases. That is, exothermicity is most important as a driving force at low temperatures.

//Heading

17.4 Free Energy

So far we have used ∆Suniv to predict the spontaneity of a process. However, another thermodynamic function is also related to spontaneity and is especially useful in dealing with the temperature dependence of spontaneity. This function is called the free energy, which is symbolized by G and deﬁned by the relationship

//Chemical Reaction

CR12

where H is the enthalpy, T is the Kelvin temperature, and S is the entropy.

For a process that occurs at constant temperature, the change in free energy (G) is given by the equation

//Chemical Reaction

CR13

Note that all quantities here refer to the system. From this point on we will follow the usual convention that when no subscript is included, the quantity refers to the system. To see how this equation relates to spontaneity, we divide both sides of the equation by - T to produce

//Chemical Reaction

//Image

CR14

This result is very important. It means that a process carried out at constant temperature and pressure will be spontaneous only if G is negative. A process (at constant T and P) is spontaneous in the direction in which the free energy decreases (-∆G means ∆Suniv). Now we have two functions that can be used to predict spontaneity: the entropy of the universe, which applies to all processes, and free energy, which can be used for processes carried out at constant temperature and pressure. Since so many chemical reactions occur under the latter conditions, free energy is the more useful to chemists. Let’s use the free energy equation to predict the spontaneity of the melting of ice:

//Chemical Reaction

CR15

Results of the calculations of ∆Suniv and ∆G0 at -100C, 00C, and 100C are shown in Table 17.4. These data predict that the process is spontaneous at 100C; that is, ice melts at this temperature because ∆Suniv is positive and G is negative. The opposite is true at 10C, where water freezes spontaneously.

Why is this so? The answer lies in the fact that ∆Ssys (∆S0) and ∆Ssurr oppose each other. The term S favors the melting of ice because of the increase in positional entropy, and ∆Ssurr favors the freezing of water because it is an exothermic process. At temperatures below 00C, the change of state occurs in the exothermic direction because ∆Ssurr is larger in magnitude than ∆Ssys. But above 00C the change occurs in the direction in which ∆Ssys is favorable, since in this case ∆Ssys is larger in magnitude than ∆Ssurr. At 00C the opposing tendencies just balance, and the two states coexist; there is no driving force in either direction. An equilibrium exists between the two states of water. Note that ∆Suniv is equal to 0 at 00C.

//Quote

The superscript degree symbol (0) indicates all substances are in their standard states.

To review the deﬁnitions of standard state

//Table

T17.4

Table 17.4

We can reach the same conclusions by examining ∆G0. At 10, ∆G0 is positive because the ∆H0 term is larger than the TS term. The opposite is true at 100C. At 00C, H is equal to TS and ∆G is equal to 0. This means that solid H2O and liquid H2O have the same free energy at 0C (∆G0= GGliquid - Gsolid), and the system is at equilibrium. We can understand the temperature dependence of spontaneity by examining the behavior of ∆G. For a process occurring at constant temperature and pressure,

//Chemical Reaction

CR16

If ∆H and ∆S favor opposite processes, spontaneity will depend on temperature in such a way that the exothermic direction will be favored at low temperatures. For example, for the process

//Chemical Reaction

CR17

∆H is positive and ∆S is positive. The natural tendency for this system to lower its energy is in opposition to its natural tendency to increase its positional randomness. At low temperatures, ∆H dominates, and at high temperatures, ∆S dominates. The various possible cases are summarized in Table 17.5.

//Example

Example 17.5 Free Energy and Spontaneity

At what temperatures is the following process spontaneous at 1 atm?

//Chemical Reaction

CR18

What is the normal boiling point of liquid Br2?

//Solution

The vaporization process will be spontaneous at all temperatures where ∆G is0 negative. Note that ∆S0 favors the vaporization process because of the increase in positional entropy, and ∆H0 favors the opposite process, which is exothermic. These opposite tendencies will exactly balance at the boiling point of liquid Br2, since at this temperature liquid and gaseous Br2 are in equilibrium (∆G0=0). We can ﬁnd this temperature by setting ∆G0=0 in the equation

//Chemical Reaction

CR19

//Table

T17.5

Table 17.5

//Quote

Note that although ∆H0 and ∆S0 are somewhat temperature-dependent, it is a good approximation to assume they are constant over a relatively small temperature range.

//Chemical Reaction

CR20

At temperatures above 333 K, T∆S0 has a larger magnitude than ∆H0, and ∆G0 (or ∆H0 - T∆S0) is negative. Above 333 K, the vaporization process is spontaneous; the opposite process occurs spontaneously below this temperature. At 333 K, liquid and gaseous Br2 coexist in equilibrium. These observations can be summarized as follows (the pressure is 1 atm in each case):

1. T > 333 K. The term S controls. The increase in entropy when liquid Br2 is vaporized is dominant.

2. T<333 K. The process is spontaneous in the direction in which it is exothermic. The term H controls.

3. T = 333 K. The opposing driving forces are just balanced (∆G0=0), and the liquid and gaseous phases of bromine coexist. This is the normal boiling point.

//Heading

17.5 Entropy Changes in Chemical Reactions

The second law of thermodynamics tells us that a process will be spontaneous if the entropy of the universe increases when the process occurs. We saw in Section 17.4 that for a process at constant temperature and pressure, we can use the change in free energy of the system to predict the sign of ∆Suniv and thus the direction in which it is spontaneous. So far we have applied these ideas only to physical processes, such as changes of state and the formation of solutions. However, the main business of chemistry is studying chemical reactions, and, therefore, we want to apply the second law to reactions.

First, we will consider the entropy changes accompanying chemical reactions that occur under conditions of constant temperature and pressure. As for the other types of processes we have considered, the entropy changes in the surroundings are determined by the heat ﬂow that occurs as the reaction takes place. However, the entropy changes in the system (the reactants and products of the reaction) are determined by positional probability.

For example, in the ammonia synthesis reaction

//Chemical Reaction

CR21

four reactant molecules become two product molecules, lowering the number of independent units in the system, which leads to less positional disorder.

//Image

Fewer molecules mean fewer possible conﬁgurations. To help clarify this idea, consider a special container with a million compartments, each large enough to hold a hydrogen molecule. Thus there are a million ways one H2 molecule can be placed in this container. But suppose we break the H-H bond and place the two independent H atoms in the same container. A little thought will convince you that there are many more than a million ways to place the two separate atoms. The number of arrangements possible for the two independent atoms is much greater than the number for the molecule. Thus for the process

//Chemical Reaction

CR22

positional entropy increases. Does positional entropy increase or decrease when the following reaction takes place?

//Chemical Reaction

CR23

In this case 9 gaseous molecules are changed to 10 gaseous molecules, and the positional entropy increases. There are more independent units as products than as reactants. In general, when a reaction involves gaseous molecules, the change in positional entropy is dominated by the relative numbers of molecules of gaseous reactants and products. If the number of molecules of the gaseous products is greater than the number of molecules of the gaseous reactants, positional entropy typically increases, and S will be positive for the reaction.

//Example

Example 17.6 Predicting the Sign of ∆S0

Predict the sign of ∆S0 for each of the following reactions.

1. The thermal decomposition of solid calcium carbonate:

//Chemical Reaction

CR24

The oxidation of SO2 in air:

//Chemical Reaction

CR25

//Solution

a. Since in this reaction a gas is produced from a solid reactant, the positional entropy increases, and ∆S0 is positive.

b. Here three molecules of gaseous reactants become two molecules of gaseous products. Since the number of gas molecules decreases, positional entropy decreases, and ∆S0 is negative.

In thermodynamics it is the change in a certain function that is usually important. The change in enthalpy determines if a reaction is exothermic or endothermic at constant pressure. The change in free energy determines if a process is spontaneous at constant temperature and pressure. It is fortunate that changes in thermodynamic functions are sufﬁcient for most purposes, since absolute values for many thermodynamic characteristics of a system, such as enthalpy or free energy, cannot be determined. However, we can assign absolute entropy values. Consider a solid at 0 K, where molecular motion virtually ceases. If the substance is a perfect crystal, its internal arrangement is absolutely regular [see Fig. 17.5(a)]. There is only one way to achieve this perfect order: Every particle must be in its place. For example, with N coins there is only

//Image

186

one way to achieve the state of all heads. Thus a perfect crystal represents the lowest possible entropy; that is, the entropy of a perfect crystal at 0 K is zero. This is a statement of the third law of thermodynamics.

As the temperature of a perfect crystal is increased, the random vibrational motions increase, and disorder increases within the crystal [see Fig. 17.5(b)]. Thus the entropy of a substance increases with temperature. Since S is zero for a perfect crystal at 0 K, the entropy value for a substance at a particular temperature can be calculated by knowing the temperature dependence of entropy. (We will not show such calculations here.)

The standard entropy values S0 of many common substances at 298 K and 1 atm are listed in Appendix 4. From these values you will see that the entropy of a substance does indeed increase in going from solid to liquid to gas. One especially interesting feature of this table is the very low S value for diamond. The structure of diamond is highly ordered, with each carbon strongly bound to a tetrahedral arrangement of four other carbon atoms (see Section 10.5, Fig. 10.22). This type of structure allows very little disorder and has a very low entropy, even at 298 K. Graphite has a slightly higher entropy because its layered structure allows for a little more disorder.

Because entropy is a state function of the system (it is not pathway-dependent), the entropy change for a given chemical reaction can be calculated by taking the difference between the standard entropy values of products and those of the reactants:

//Chemical Reaction

CR26

where, as usual, represents the sum of the terms. It is important to note that entropy is an extensive property (it depends on the amount of substance present). This means that the number of moles of a given reactant (nr) or product (np) must be taken into account.

//Example

Example 17.5

//Chemical Reaction

CR27

//Solution

//Chemical Reaction

CR28

We would expect ∆S0 to be negative because the number of gaseous molecules decreases in this reaction.

//Example

Example 17.8

//Chemical Reaction

CR29

//Solution

//Chemical Reaction

CR30

The reaction considered in Example 17.8 involves 3 moles of hydrogen gas on the reactant side and 3 moles of water vapor on the product side. Would you expect ∆S0 to be large or small for such a case? We have assumed that ∆S0 depends on the relative numbers of molecules of gaseous reactants and products. Based on this assumption, ∆S0 should be near zero for this reaction. However, S is large and positive. Why is this so? The large value for S results from the difference in the entropy values for hydrogen gas and water vapor. The reason for this difference can be traced to the difference in molecular structure. Because it is a nonlinear, triatomic molecule, H2O has more rotational and vibrational motions (see Fig. 17.6) than does the diatomic H2 molecule. Thus the standard entropy value for H2O(g) is greater than that for H2(g). Generally, the more complex the molecule, the higher the standard entropy value.

//Heading

For chemical reactions we are often interested in the standard free energy change (∆G0), the change in free energy that will occur if the reactants in their standard states are converted to the products in their standard states. For example, for the ammonia synthesis reaction at 250C,

//Chemical Reaction

CR31

This ∆G0 value represents the change in free energy when 1 mol nitrogen gas at 1 atm reacts with 3 mol hydrogen gas at 1 atm to produce 2 mol gaseous NH3 at 1 atm.

It is important to recognize that the standard free energy change for a reaction is not measured directly. For example, we can measure heat ﬂow in a calorimeter to determine H, but we cannot measure ∆G0 this way. The value of ∆G0 for the ammonia synthesis in Equation (17.1) was not obtained by mixing 1 mol N2 and 3 mol H2 in a ﬂask and measuring the change in free energy as 2 mol NH3 formed. For one thing, if we mixed 1 mol N2 and 3 mol H2 in a ﬂask, the system would go to equilibrium rather than to completion. Also, we have no instrument that measures free energy. However, while we cannot directly measure ∆G0 for a reaction, we can calculate it from other measured quantities, as we will see later in this section.

//Image

187

Figure 17.6 The H2O molecule can vibrate and rotate in several ways, some of which are shown here. This freedom of motion leads to a higher entropy for water than for a substance like hydrogen, a simple diatomic molecule with fewer possible motions.

Why is it useful to know ∆G0 for a reaction? As we will see in more detail later in this chapter, knowing the ∆G0 values for several reactions allows us to compare the relative tendency of these reactions to occur. The more negative the value of ∆G0, the further a reaction will go to the right to reach equilibrium. We must use standard-state free energies to make this comparison because free energy varies with pressure or concentration. Thus, to get an accurate comparison of reaction tendencies, we must compare all reactions under the same pressure or concentration conditions. We will have more to say about the signiﬁcance of ∆G0 later. There are several ways to calculate ∆G0. One common method uses the equation

//Chemical Reaction

CR32

which applies to a reaction carried out at constant temperature. For example, for the reaction

//Chemical Reaction

CR33

//Chemical Reaction

CR34

//Quote

The value of ∆G0 tells us nothing about the rate of a reaction, only its eventual equilibrium position.

//Example

Example 17.9 Calculating ∆H0, ∆S0, and ∆G0

Consider the reaction

//Chemical Reaction

CR35

//Solution

The value of ∆H0 can be calculated from the enthalpies of formation using the equation we discussed in Section 6.4:

//Chemical Reaction

CR36

A second method for calculating ∆G0 for a reaction takes advantage of the fact that, like enthalpy, free energy is a state function. Therefore, we can use procedures for ﬁnding ∆G0 that are similar to those for ﬁnding ∆H0 using Hess’s law.

To illustrate this method for calculating the free energy change, we will obtain ∆G0 for the reaction

//Chemical Reaction

CR37

//Chemical Reaction

CR38

Note that CO(g) is a reactant in Equation (17.2). This means that Equation (17.3) must be reversed, since CO(g) is a product in that reaction as written. When a reaction is reversed, the sign of ∆G0 is also reversed. In Equation (17.4), CO2(g) is a product, as it is in Equation (17.2), but only one molecule of CO2 is formed. Thus Equation (17.4) must be multiplied by 2, which means the ∆G0 value for Equation (17.4) also must be multiplied by 2. Free energy is an extensive property, since it is deﬁned by two extensive properties, ∆H0 and ∆S0.

//Chemical Reaction

CR39

This example shows that the ∆G0 values for reactions are manipulated in exactly the same way as the ∆H0 values.

//Example

Example 17.10 Calculating ∆G0

Using the following data (at 250C)

//Chemical Reaction

CR40

//Solution

We reverse Equation (17.6) to make graphite a product, as required, and then add the new equation to Equation (17.5):

//Chemical Reaction

CR41

Since ∆G0 is negative for this process, diamond should spontaneously change to graphite at 250C and 1 atm. However, the reaction is so slow under these conditions that we do not observe the process. This is another example of kinetic rather than thermodynamic control of a reaction. We can say that diamond is kinetically stable with respect to graphite even though it is thermodynamically unstable.

//Image

188

//Image

189

In Example 17.10 we saw that the proces

//Chemical Reaction

CR42

is spontaneous but very slow at 250C and 1 atm. The reverse process can be made to occur at high temperatures and pressures. Diamond has a more compact structure and thus a higher density than graphite, so exerting very high pressure causes it to become thermodynamically favored. If high temperatures are also used to make the process fast enough to be feasible, diamonds can be made from graphite. The conditions typically used involve temperatures greater than 10000C and pressures of about 105 atm. About half of all industrial diamonds are made this way.

A third method for calculating the free energy change for a reaction uses standard free energies of formation. The standard free energy of formation (∆G f) of a substance is deﬁned as the change in free energy that accompanies the formation of 1 mole of that substance from its constituent elements with all reactants and products in their standard states. For the formation of glucose (C6H12O6), the appropriate reaction is

//Chemical Reaction

CR43

….

The standard free energy associated with this process is called the free energy of formation of glucose. Values of the standard free energy of formation are useful in calculating ∆G0 for speciﬁc chemical reactions using the equation.

//Chemical Reaction

CR44

…

Values of Gf for many common substances are listed in Appendix 4. Note that, analogous to the enthalpy of formation, the standard free energy of formation of an element in its standard state is zero. Also note that the number of moles of each reactant (nr) and product (np) must be used when calculating G for a reaction

//Quote

The standard state of an element is its most stable state of 25°C and 1 atm.

Calculating ∆G0 is very similar to calculating ∆H0

//Example

Example 17.11 Calculating ∆G0

Methanol is a high-octane fuel used in high-performance racing engines. Calculate ∆G0 for the reaction

//Chemical Reaction

CR45

//Solution

We use the equation

//Chemical Reaction

CR46

The large magnitude and the negative sign of ∆G0 indicate that this reaction is very favorable thermodynamically.

//Example

Example 17.12 Free Energy and Spontaneity

A chemical engineer wants to determine the feasibility of making ethanol (C2H5OH) by reacting water with ethylene (C2H4) according to the equation

//Chemical Reaction

CR47

Is this reaction spontaneous under standard conditions?

//Solution

To determine the spontaneity of this reaction under standard conditions, we must determine ∆G0 for the reaction. We can do this using standard free energies of formation at 25C from Appendix 4:

//Chemical Reaction

CR48

Thus the process is spontaneous under standard conditions at 250C

//Image

190

Although the reaction considered in Example 17.12 is spontaneous, other features of the reaction must be studied to see if the process is feasible. For example, the chemical engineer will need to study the kinetics of the reaction to determine whether it is fast enough to be useful and, if it is not, whether a catalyst can be found to enhance the rate. In doing these studies, the engineer must remember that ∆G0 depends on temperature:.

//Chemical Reaction

CR49

Thus, if the process must be carried out at high temperatures to be fast enough to be feasible, ∆G0 must be recalculated at that temperature from the ∆H0 and ∆S0 values for the reaction

Heading

17.7 The Dependence of Free Energy on Pressure

In this chapter we have seen that a system at constant temperature and pressure will proceed spontaneously in the direction that lowers its free energy. This is why reactions proceed until they reach equilibrium. The equilibrium position represents the lowest free energy value available to a particular reaction system. The free energy of a reaction system changes as the reaction proceeds, because free energy is dependent on the pressure of a gas or on the concentration of species in solution. We will deal only with the pressure dependence of the free energy of an ideal gas. The dependence of free energy on concentration can be developed using similar reasoning. To understand the pressure dependence of free energy, we need to know how pressure affects the thermodynamic functions that comprise free energy, that is, enthalpy and entropy (recall that G = H- TS). For an ideal gas, enthalpy is not pressure-dependent. However, entropy does depend on pressure because of its dependence on volume. Consider 1 mole of an ideal gas at a given temperature. At a volume of 10.0 L, the gas has many more positions available for its molecules than if its volume is 1.0 L. The positional entropy is greater in the larger volume. In summary, at a given temperature for 1 mole of ideal gas.

//Chemical Reaction

CR50

..

or, since pressure and volume are inversely related,

//Chemical Reaction

CR51

We have shown qualitatively that the entropy and therefore the free energy of an ideal gas depend on its pressure. Using a more detailed argument, which we will not consider here, it can be shown tha

//Chemical Reaction

CR52

where G is the free energy of the gas at a pressure of 1 atm, ∆G0 is the free energy of the gas at a pressure of P atm, R is the universal gas constant, and T is the Kelvin temperature. To see how the change in free energy for a reaction depends on pressure, we will consider the ammonia synthesis reaction

//Chemical Reaction

CR53

//Chemical Reaction

CR54

….

where Q is the reaction quotient (from the law of mass action), T is the temperature (K), R is the gas law constant and is equal to 8.3145 J/K mol, ∆G0 is the free energy change for the reaction with all reactants and products at a pressure of 1 atm, and G is the free energy change for the reaction for the speciﬁed pressures of reactants and products.

//Quote

See Appendix 1.2 to review logarithms.

//Example

Example 17.13 Calculating ∆G0

One method for synthesizing methanol (CH3OH) involves reacting carbon monoxide and hydrogen gases:

//Chemical Reaction

CR55

..

Calculate ∆G0 at 25C for this reaction where carbon monoxide gas at 5.0 atm and hydrogen gas at 3.0 atm are converted to liquid methanol.

//Solution

//Chemical Reaction

CR56

..

Note that this is the value of \_*G*\_ for the reaction of 1 mol CO with 2 mol H2 to produce

1 mol CH3OH. We might call this the value of \_*G*\_ for one “round” of the reaction

or for one mole of the reaction. Thus the \_*G*\_ value might better be written as \_2.9 \_

104 J/mol of reaction, or \_2.9 \_ 104 J/mol rxn.

//Chemical Reaction

CR57

Note that ∆G is signiﬁcantly more negative than ∆G0, implying that the reaction is more spontaneous at reactant pressures greater than 1 atm. We might expect this result from Le Châtelier’s principle.

//Quote

Note in this case that ∆G0 is deﬁned for “one mole of the reaction,” that is, for 1 mol CO( g ) reacting with 2 mol H2( g ) to form 1 mol CH3OH( l ).Thus ∆G , ∆G0 , and RT ln( Q ) all have units of J/mol of reaction. In this case the units of R are actually J/K mol of reaction, although they are usually not written this way.

The Meaning of ∆G for a Chemical Reaction

In this section we have learned to calculate G for chemical reactions under various conditions. For example, in Example 17.13 the calculations show that the formation of CH3OH(l) from CO(g) at 5.0 atm reacting with H2(g) at 3.0 atm is spontaneous. What does this result mean? Does it mean that if we mixed 1.0 mol CO(g) and 2.0 mol H2(g) together at pressures of 5.0 and 3.0 atm, respectively, that 1.0 mol CH3OH(l) would form in the reaction ﬂask? The answer is no. This answer may surprise you in view of what has been said in this section. It is true that 1.0 mol CH3OH(l) has a lower free energy than 1.0 mol CO(g) at 5.0 atm plus 2.0 mol H2(g) at 3.0 atm. However, when CO(g) and H2(g) are mixed under these conditions, there is an even lower free energy available to this system than 1.0 mol pure CH3OH(l). For reasons we will discuss shortly, the system can achieve the lowest possible free energy by going to equilibrium, not by going to completion. At the equilibrium position, some of the CO(g) and H2(g) will remain in the reaction ﬂask. So even though 1.0 mol pure CH3OH(l) is at a lower free energy than 1.0 mol CO(g) and 2.0 mol H2(g) at 5.0 and 3.0 atm, respectively, the reaction system will stop short of forming 1.0 mol CH3OH(l). The reaction stops short of completion because the equilibrium mixture of CH3OH(l), CO(g), and H2(g) exists at the lowest possible free energy available to the system.

To illustrate this point, we will explore a mechanical example. Consider balls rolling down the two hills shown in Fig. 17.7. Note that in both cases point B has a lower potential energy than point A.

In Fig. 17.7(a) the ball will roll to point B. This diagram is analogous to a phase change. For example, at 250C ice will spontaneously change completely to liquid water, because the latter has the lowest free energy.

In this case liquid water is the only choice. There is no intermediate mixture of ice and water with lower free energy. The situation is different for a chemical reaction system, as illustrated in Fig. 17.7(b). In Fig. 17.7(b) the ball will not get to point B because there is a lower potential energy at point C. Like the ball, a chemical system will seek the lowest possible free energy, which, for reasons we will discuss below, is the equilibrium position.

Therefore, although the value of G for a given reaction system tells us whether the products or reactants are favored under a given set of conditions, it does not mean that the system will proceed to pure products (if G is negative) or remain at pure reactants (if G is positive). Instead, the system will spontaneously go to the equilibrium position,

//Image

191

...

the lowest possible free energy available to it. In the next section we will see that the value of G for a particular reaction tells us exactly where this position will be.

//Heading

17.8 Free Energy and Equilibrium

When the components of a given chemical reaction are mixed, they will proceed, rapidly or slowly depending on the kinetics of the process, to the equilibrium position. In Chapter 13 we deﬁned the equilibrium position as the point at which the forward and reverse reaction rates are equal. In this chapter we look at equilibrium from a thermodynamic point of view, and we ﬁnd that the equilibrium point occurs at the lowest value of free energy available to the reaction system. As it turns out, the two deﬁnitions give the same equilibrium state, which must be the case for both the kinetic and thermodynamic models to be valid.

To understand the relationship of free energy to equilibrium, let’s consider the following simple hypothetical reaction

//Chemical Reaction

CR58

…

where 1.0 mole of gaseous A is initially placed in a reaction vessel at a pressure of 2.0 atm. The free energies for A and B are diagrammed as shown in Fig. 17.8(a). As A reacts to form B, the total free energy of the system changes, yielding the following results

//Chemical Reaction

CR59

..

As A changes to B, GA will decrease because PA is decreasing [Fig. 17.8(b)]. In contrast, GB will increase because PB is increasing. The reaction will proceed to the right as long as the total free energy of the system decreases (as long as GB is less than GA). At some point the pressures of A and B reach the values Pe A and Pe B that make GA equal to GB. The system has reached equilibrium [Fig. 17.8(c)]. Since A at pressure Pe A and B at pressure Pe B have the same free energy (GA equals GB), G is zero for A at pressure P e A changing to B at pressure P e B. The system has reached minimum free energy. There is no longer any driving force to change A to B or B to A, so the system remains at this position (the pressures of A and B remain constant).

//Image

192

(a) The initial free energies of A and B. (b) As A(g) changes to B(g), the free energy of A decreases and that of B increases. (c) Eventually, pressures of A and B are achieved such that GA = GB, the equilibrium position

Suppose that for the experiment described above, the plot of free energy versus the mole fraction of A reacted is deﬁned as shown in Fig. 17.9(a). In this experiment, minimum free energy is reached when 75% of A has been changed to B. At this point, the pressure of A is 0.25 times the original pressure, or

//Chemical Reaction

CR60

…

//Image

193

Since this is the equilibrium position, we can use the equilibrium pressures to calculate a value for K for the reaction in which A is converted to B at this temperature:

//Chemical Reaction

CR61

Exactly the same equilibrium point would be achieved if we placed 1.0 mol pure B(g) in the ﬂask at a pressure of 2.0 atm. In this case B would change to A until equilibrium (GB= GA) is reached. This is shown in Fig. 17.9(b). The overall free energy curve for this system is shown in Fig. 17.9(c). Note that any mixture of A(g) and B(g) containing 1.0 mol (A plus B) at a total pressure of 2.0 atm will react until it reaches the minimum in the curve. In summary, when substances undergo a chemical reaction, the reaction proceeds to the minimum free energy (equilibrium), which corresponds to the point where

//Chemical Reaction

CR62

…

We must note the following characteristics of this very important equation.

Case 1: ∆G=0. When ∆G0 equals zero for a particular reaction, the free energies of the reactants and products are equal when all components are in the standard states (1 atm for gases). The system is at equilibrium when the pressures of all reactants and products are 1 atm, which means that K equals 1.

Case 2: G<0. In this case G (G0products - G0reactants) is negative, which means that

//Chemical Reaction

CR63

If a ﬂask contains the reactants and products, all at 1 atm, the system will not be at equilibrium. Since Gproducts is less than Greactants, the system will adjust to the right to reach equilibrium. In this case K will be greater than 1, since the pressures of the products at equilibrium will be greater than 1 atm and the pressures of the reactants at equilibrium will be less than 1 atm.

//Chemical Reaction

CR64

…

If a ﬂask contains the reactants and products, all at 1 atm, the system will not be at equilibrium. In this case the system will adjust to the left (toward the reactants, which have a lower free energy) to reach equilibrium. The value of K will be less than 1, since at equilibrium the pressures of the reactants will be greater than 1 atm and the pressures of the products will be less than 1 atm.

These results are summarized in Table 17.6 and Figure 17.10. The value of K for a speciﬁc reaction can be calculated from the equation

//Chemical Reaction

CR65

…

as is shown in Examples 17.14 and 17.15.

//Table

T17.6

Table 17.16

//Image

194

Figure 17.10 The relationship of ∆G0 for a reaction to its eventual equilibrium position.

//Example

Example 17.14 Free Energy and Equilibrium

Consider the ammonia synthesis reaction

//Chemical Reaction

CR66

..

where ∆G033.3 kJ per mole of N2 consumed at 250C. For each of the following mixtures of reactants and products at 250C, predict the direction in which the system will shift to reach equilibrium.

//Chemical Reaction

CR67

..

//Solution

a. We can predict the direction of reaction to equilibrium by calculating the value of ∆G0 using the equation.

//Chemical Reaction

CR68

…

Since ∆G0 = 0, the reactants and products have the same free energies at these partial pressures. The system is already at equilibrium, and no shift will occur.

1. The partial pressures given here are all 1.00 atm, which means that the system is in the standard state. That is,

//Chemical Reaction

CR69

..

For this reaction at 250C,

//Chemical Reaction

CR70

The negative value for ∆G0 means that in their standard states the products have a lower free energy than the reactants. Thus the system will move to the right to reach equilibrium. That is, K is greater than 1.

//Example

Example 17.15

Free Energy and Equilibrium II

//Chemical Reaction

CR71

The overall reaction for the corrosion (rusting) of iron by oxygen is

Using the following data, calculate the equilibrium constant for this reaction at 250C.

//Solution

//Chemical Reaction

CR72

This is a very large equilibrium constant. The rusting of iron is clearly very favourable from a thermodynamic point of view.

//Image

195

Formation of rust on bare steel is a spontaneous process.

The Temperature Dependence of K

In Chapter 13 we used Le Châtelier’s principle to predict qualitatively how the value of K for a given reaction would change with a change in temperature. Now we can specify the quantitative dependence of the equilibrium constant on temperature from the relationship

//Chemical Reaction

CR73

Note that this is a linear equation of the form y= mx+ b, where y = ln(K), m =-∆ H0/R slope, x 1/T, and b =∆S0R= intercept. This means that if values of K for a given reaction are determined at various temperatures, a plot of ln(K) versus 1T will be linear, with slope HR and intercept SR. This result assumes that both ∆H0 and ∆S0 are independent of temperature over the temperature range considered. This assumption is a good approximation over a relatively small temperature range.

//Heading

17.9 Free Energy and Work

One of the main reasons we are interested in physical and chemical processes is that we want to use them to do work for us, and we want this work done as efﬁciently and economically as possible. We have already seen that at constant temperature and pressure, the sign of the change in free energy tells us whether a given process is spontaneous. This is very useful information because it prevents us from wasting effort on a process that has no inherent tendency to occur. Although a thermodynamically favorable chemical reaction may not occur to any appreciable extent because it is too slow, it makes sense in this case to try to ﬁnd a catalyst to speed up the reaction. On the other hand, if the reaction is prevented from occurring by its thermodynamic characteristics, we would be wasting our time looking for a catalyst.

In addition to its qualitative usefulness (telling us whether a process is spontaneous), the change in free energy is important quantitatively because it can tell us how much work can be done with a given process. The maximum possible useful work obtainable from a process at constant temperature and pressure is equal to the change in free energy:

//Chemical Reaction

CR74

This relationship explains why this function is called the free energy. Under certain conditions, ∆G0 for a spontaneous process represents the energy that is free to do useful work. On the other hand, for a process that is not spontaneous, the value of ∆G0 tells us the minimum amount of work that must be expended to make the process occur. Knowing the value of ∆G0 for a process thus gives us valuable information about how close the process is to 100% efﬁciency. For example, when gasoline is burned in a car’s engine, the work produced is about 20% of the maximum work available. For reasons we will only brieﬂy introduce in this book, the amount of work we actually obtain from a spontaneous process is always less than the maximum possible amount.

//Quote

Note that “ PV work” is not counted as useful work here.

//Image

196

A battery can do work by sending current to a starter motor. The battery can then be recharged by forcing current through it in the opposite direction. If the current ﬂow in both processes is inﬁnitesimally small, w1 = w2. This is a reversible process. But if the current ﬂow is ﬁnite, as it would be in any real case, w2 > w1. This is an irreversible process (the universe is different after the cyclic process occurs). All real processes are irreversible

To explore this idea more fully, let’s consider an electric current ﬂowing through the starter motor of a car. The current is generated from a chemical change in a battery, and we can calculate G for the battery reaction and so determine the energy available to do work. Can we use all this energy to do work? No, because a current ﬂowing through a wire causes frictional heating, and the greater the current, the greater the heat. This heat represents wasted energy—it is not useful for running the starter motor. We can minimize this energy waste by running very low currents through the motor circuit. However, zero current ﬂow would be necessary to eliminate frictional heating entirely, and we cannot derive any work from the motor if no current ﬂows. This represents the difﬁculty in which nature places us. Using a process to do work requires that some of the energy be wasted, and usually the faster we run the process, the more energy we waste.

Achieving the maximum work available from a spontaneous process can occur only via a hypothetical pathway. Any real pathway wastes energy. If we could discharge the battery inﬁnitely slowly by an inﬁnitesimal current ﬂow, we would achieve the maximum useful work. Also, if we could then recharge the battery using an inﬁnitesimally small current, exactly the same amount of energy would be used to return the battery to its original state. After we cycle the battery in this way, the universe (the system and surroundings) is exactly the same as it was before the cyclic process. This is a reversible process (see Fig. 17.11).

However, if the battery is discharged to run the starter motor and then recharged using a ﬁnite current ﬂow, as is the case in reality, more work will always be required to recharge the battery than the battery produces as it discharges. This means that even though the battery (the system) has returned to its original state, the surroundings have not, because the surroundings had to furnish a net amount of work as the battery was cycled. The universe is different after this cyclic process is performed, and this function is called an irreversible process. All real processes are irreversible. In general, after any real cyclic process is carried out in a system, the surroundings have less ability to do work and contain more thermal energy. In any real cyclic process in the system, work is changed to heat in the surroundings, and the entropy of the universe increases. This is another way of stating the second law of thermodynamics. Thus thermodynamics tells us the work potential of a process and then tells us that we can never achieve this potential. In this spirit, thermodynamicist Henry Bent has paraphrased the ﬁrst two laws of thermodynamics as follows:

First law: You can’t win, you can only break even.

Second law: You can’t break even.

The ideas we have discussed in this section are applicable to the energy crisis that will probably increase in severity over the next 25 years. The crisis is obviously not one of supply; the ﬁrst law tells us that the universe contains a constant supply of energy. The problem is the availability of useful energy. As we use energy, we degrade its usefulness. For example, when gasoline reacts with oxygen in the combustion reaction, the change in potential energy results in heat ﬂow. Thus the energy concentrated in the bonds of the gasoline and oxygen molecules ends up spread over the surroundings as thermal energy, where it is much more difﬁcult to harness for useful work. This is a way in which the entropy of the universe increases: Concentrated energy becomes spread out—more disordered and less useful. Thus the crux of the energy problem is that we are rapidly consuming the concentrated energy found in fossil fuels. It took millions of years to concentrate the sun’s energy in these fuels, and we will consume these same fuels in a few hundred years. Thus we must use these energy sources as wisely as possible.

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When energy is used to do work, it becomes less organized and less concentrated and thus less useful.