

Chapter 12

Thermodynamics



Figure 12.1 Geysers are a dramatic display of thermodynamic principles in nature. Water deep within the underground channels of the geyser is under high pressure and heated to high temperature by magma. When a pocket of water near the surface reaches boiling point and is expelled, the resulting drop in pressure causes larger volumes of water to flash boil, forcefully ejecting steam and water in an impressive eruption. (credit: modification of work by Yellowstone National Park)

Chapter Outline

- 12.1 Spontaneity
- 12.2 Entropy
- 12.3 The Second and Third Laws of Thermodynamics
- 12.4 Free Energy

Introduction

Among the many capabilities of chemistry is its ability to predict if a process will occur under specified conditions. Thermodynamics, the study of relationships between the energy and work associated with chemical and physical processes, provides this predictive ability. Previous chapters in this text have described various applications of thermochemistry, an important aspect of thermodynamics concerned with the heat flow accompanying chemical reactions and phase transitions. This chapter will introduce additional thermodynamic concepts, including those that enable the prediction of any chemical or physical changes under a given set of conditions.

12.1 Spontaneity

By the end of this section, you will be able to:

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally

flow downhill, but uphill flow requires outside intervention such as the use of a pump. Iron exposed to the earth's atmosphere will corrode, but rust is not converted to iron without intentional chemical treatment. A **spontaneous process** is one that occurs naturally under certain conditions. A **nonspontaneous process**, on the other hand, will not take place unless it is “driven” by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (**Figure 12.2**).

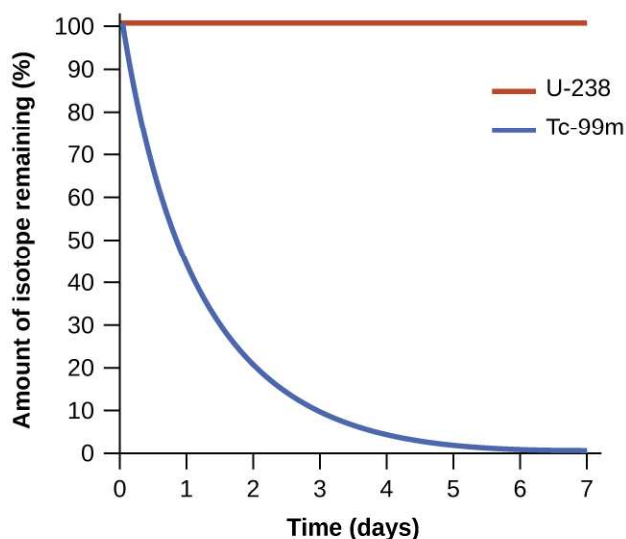
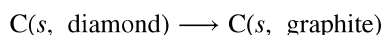


Figure 12.2 Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed.

As another example, consider the conversion of diamond into graphite (**Figure 12.3**).



The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow; so, for all practical purposes diamonds are indeed “forever.” Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

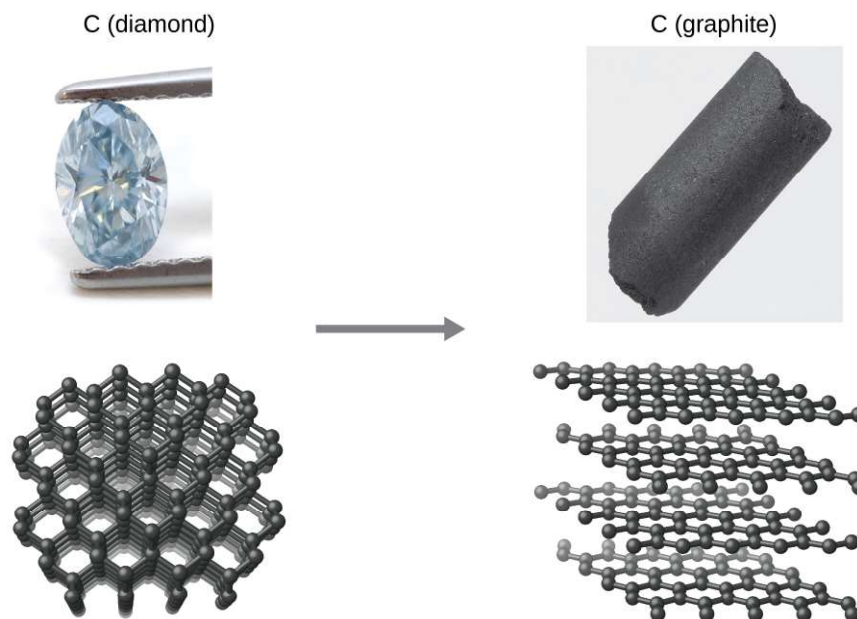


Figure 12.3 The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as *graphitization*, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)

Dispersal of Matter and Energy

Extending the discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas in one flask and the other flask is empty ($P = 0$). (Figure 12.4). When the valve is opened, the gas spontaneously expands to fill both flasks equally. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

$$w = -P\Delta V = 0 \quad (P = 0 \text{ in a vacuum})$$

Note as well that since the system is isolated, no heat has been exchanged with the surroundings ($q = 0$). The *first law of thermodynamics* confirms that there has been no change in the system's internal energy as a result of this process.

$$\Delta U = q + w = 0 + 0 = 0$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the driving force appears to be related to the *greater, more uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous expansion took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

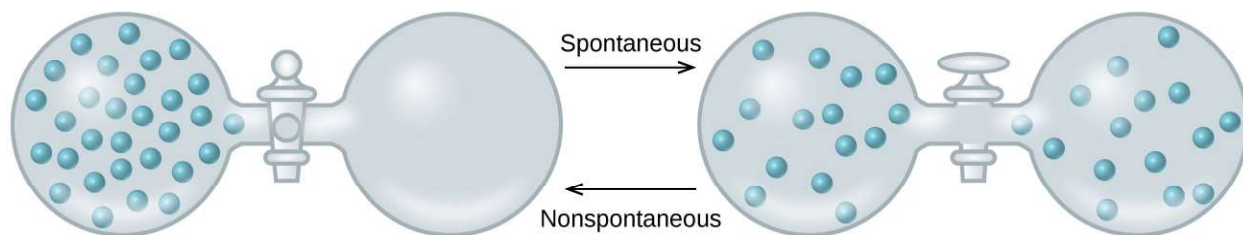


Figure 12.4 An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y , with $T_X > T_Y$ (**Figure 12.5**). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0$$

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.



Figure 12.5 When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

Example 12.1

Redistribution of Matter during a Spontaneous Process

Describe how matter is redistributed when the following spontaneous processes take place:

- A solid sublimates.
- A gas condenses.
- A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution

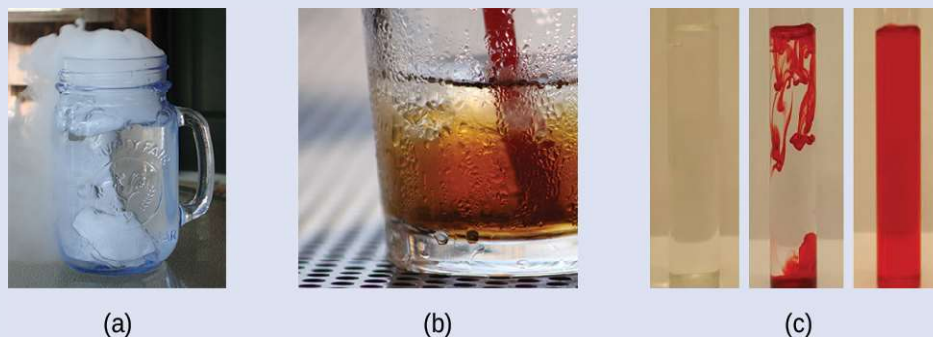


Figure 12.6 (credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Paul A. Flowers)

(a) Sublimation is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition.

(b) Condensation is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition.

(c) The process in question is diffusion. This process yields a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop of dye, zero in the water), and the final state of the system contains a single dye concentration throughout.

Check Your Learning

Describe how energy is redistributed when a spoon at room temperature is placed in a cup of hot coffee.

Answer: Heat will spontaneously flow from the hotter object (coffee) to the colder object (spoon), resulting in a more uniform distribution of thermal energy as the spoon warms and the coffee cools.

12.2 Entropy

By the end of this section, you will be able to:

- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (**Figure 12.7**) published the results of an extensive study regarding the efficiency of steam heat engines. A later review of Carnot’s findings by Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (T). In thermodynamics, a **reversible process** is one that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be “reversed”) by an infinitesimally small change in some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.

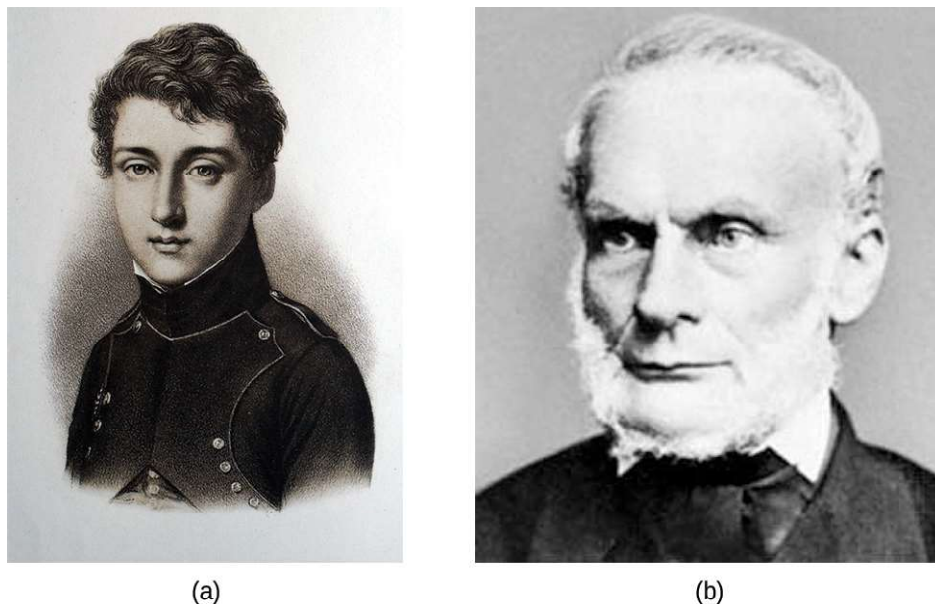


Figure 12.7 (a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property **entropy (S)** and defined its change for any process as the following:

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the *number of microstates* (W) possible for the system. A **microstate** is a specific configuration of all the locations and energies of the atoms or molecules that make up a system. The relation between a system's entropy and the number of possible microstates is

$$S = k \ln W$$

where k is the Boltzmann constant, 1.38×10^{-23} J/K.

As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

$$\Delta S = S_f - S_i = k \ln W_f - k \ln W_i = k \ln \frac{W_f}{W_i}$$

For processes involving an increase in the number of microstates, $W_f > W_i$, the entropy of the system increases and $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $W_f < W_i$, yield a decrease in system entropy, $\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

Consider the general case of a system comprised of N particles distributed among n boxes. The number of microstates possible for such a system is n^N . For example, distributing four particles among two boxes will result in 2^4

= 16 different microstates as illustrated in **Figure 12.8**. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

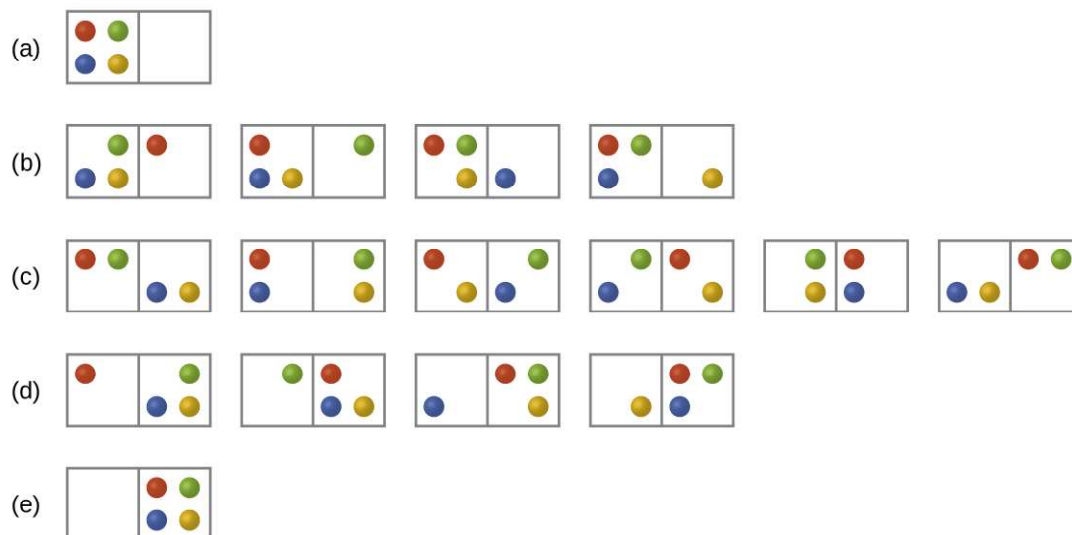


Figure 12.8 The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is $\frac{6}{16}$ or $\frac{3}{8}$. The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of $\frac{1}{16}$. The probability of finding all particles in only one box (either the left box or right box) is then $(\frac{1}{16} + \frac{1}{16}) = \frac{2}{16}$ or $\frac{1}{8}$.

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

This matter dispersal model of entropy is often described qualitatively in terms of the *disorder* of the system. By this description, microstates in which all the particles are in a single box are the most ordered, thus possessing the least entropy. Microstates in which the particles are more evenly distributed among the boxes are more disordered, possessing greater entropy.

The previous description of an ideal gas expanding into a vacuum (**Figure 12.4**) is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. Initially, the gas molecules are confined to just one of the two flasks. Opening the valve between the flasks increases the volume available to the gas molecules and, correspondingly, the number of microstates possible for the system. Since $W_f > W_i$, the expansion process involves an increase in entropy ($\Delta S > 0$) and is spontaneous.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of thermal energy (represented as “*”) in **Figure 12.9**. The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. Thus, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects’ temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

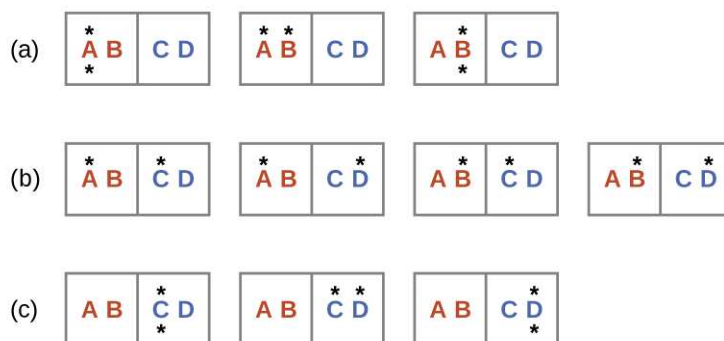
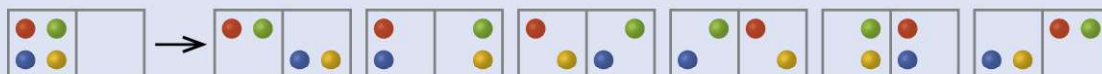


Figure 12.9 This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

Example 12.2

Determination of ΔS

Calculate the change in entropy for the process depicted below.



Solution

The initial number of microstates is one, the final six:

$$\Delta S = k \ln \frac{W_c}{W_a} = 1.38 \times 10^{-23} \text{ J/K} \times \ln \frac{6}{1} = 2.47 \times 10^{-23} \text{ J/K}$$

The sign of this result is consistent with expectation; since there are more microstates possible for the final state than for the initial state, the change in entropy should be positive.

Check Your Learning

Consider the system shown in **Figure 12.9**. What is the change in entropy for the process where *all* the

energy is transferred from the hot object (AB) to the cold object (CD)?

Answer: 0 J/K

Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in **Figure 12.10**. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{\text{liquid}} > S_{\text{solid}}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

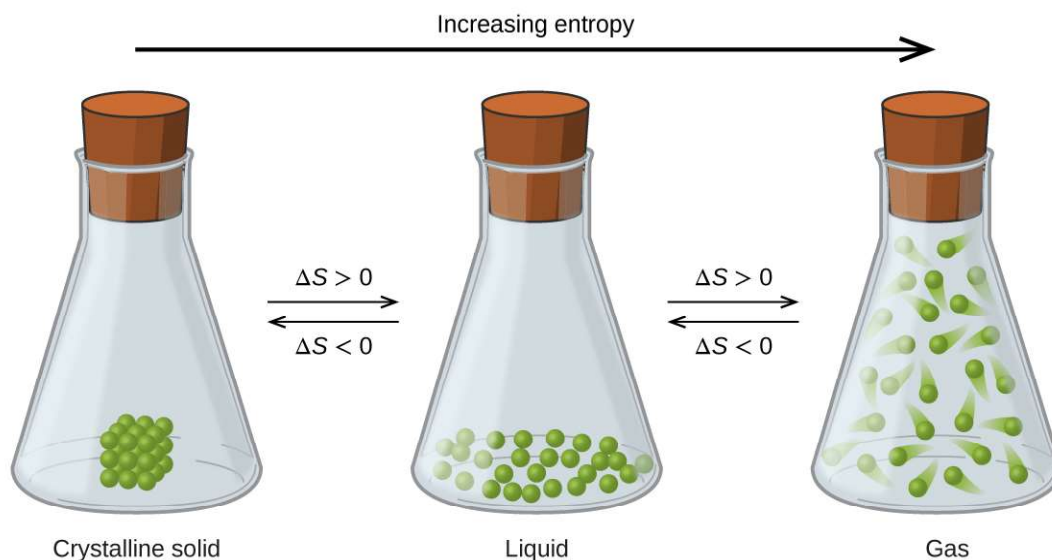


Figure 12.10 The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the gaseous phase, in which a given number of atoms or molecules occupy a *much* greater volume than in the liquid phase. Each atom or molecule can be found in many more locations, corresponding to a much greater number of microstates. Consequently, for any substance, $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (**Figure 12.11**).

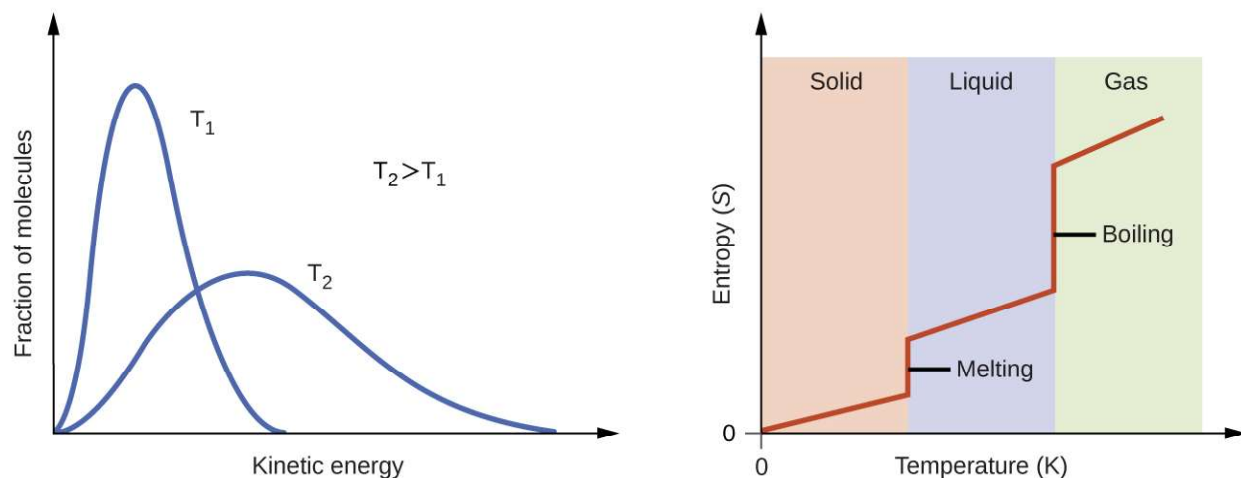


Figure 12.11 Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance undergoes a phase transition, its entropy changes significantly.

Link to Learning

Try this [simulator \(http://openstaxcollege.org//16freemotion\)](http://openstaxcollege.org//16freemotion) with interactive visualization of the dependence of particle location and freedom of motion on physical state and temperature.

The entropy of a substance is influenced by the structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle's mass and the spacing of quantized translational energy levels (a topic beyond the scope of this text). For molecules, greater numbers of atoms increase the number of ways in which the molecules can vibrate and thus the number of possible microstates and the entropy of the system.

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

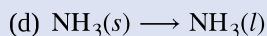
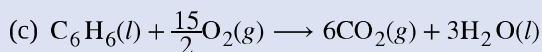
Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in **Example 12.3**.

Example 12.3

Predicting the Sign of ΔS

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

- One mole liquid water at room temperature \longrightarrow one mole liquid water at 50 °C
- $\text{Ag}^+(aq) + \text{Cl}^-(aq) \longrightarrow \text{AgCl}(s)$



Solution

(a) positive, temperature increases

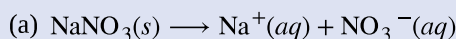
(b) negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter

(c) negative, net decrease in the amount of gaseous species

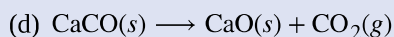
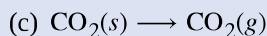
(d) positive, phase transition from solid to liquid, net increase in dispersal of matter

Check Your Learning

Predict the sign of the entropy change for the following processes. Give a reason for your prediction.



(b) the freezing of liquid water



Answer: (a) Positive; The solid dissolves to give an increase of mobile ions in solution. (b) Negative; The liquid becomes a more ordered solid. (c) Positive; The relatively ordered solid becomes a gas. (d) Positive; There is a net increase in the amount of gaseous species.

12.3 The Second and Third Laws of Thermodynamics

By the end of this section, you will be able to:

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

The Second Law of Thermodynamics

In the quest to identify a property that may reliably predict the spontaneity of a process, a promising candidate has been identified: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}}$$

The magnitudes of $-q_{\text{rev}}$ and q_{rev} are equal, their opposite arithmetic signs denoting loss of heat by the system and gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the entropy *decrease* of the system will be less than the entropy *increase* of the surroundings, and so *the entropy of the universe will increase*:

$$|\Delta S_{\text{sys}}| < |\Delta S_{\text{surr}}|$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}}$$

The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes (that is, *the direction of the heat flow*) will yield a negative value for ΔS_{univ} . *This process involves a decrease in the entropy of the universe.*

3. The objects are at essentially the same temperature, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the magnitudes of the entropy changes are essentially the same for both the system and the surroundings. In this case, the entropy change of the universe is zero, and the system is *at equilibrium*.

$$|\Delta S_{\text{sys}}| \approx |\Delta S_{\text{surr}}|$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the **second law of thermodynamics**: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in **Table 12.1**.

The Second Law of Thermodynamics

$\Delta S_{\text{univ}} > 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{\text{univ}} = 0$	at equilibrium

Table 12.1

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev} , and the second law may be stated as the following:

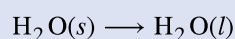
$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$$

We may use this equation to predict the spontaneity of a process as illustrated in **Example 12.4**.

Example 12.4

Will Ice Spontaneously Melt?

The entropy change for the process



is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at -10.00°C ? Is it spontaneous at $+10.00^\circ\text{C}$?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, $\Delta S_{\text{sys}} = 22.1 \text{ J/K}$ and $q_{\text{surr}} = -6.00 \text{ kJ}$.

At $-10.00 \text{ }^\circ\text{C}$ (263.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1 \text{ J/K} + \frac{-6.00 \times 10^3 \text{ J}}{263.15 \text{ K}} = -0.7 \text{ J/K}\end{aligned}$$

$S_{\text{univ}} < 0$, so melting is nonspontaneous (*not* spontaneous) at $-10.0 \text{ }^\circ\text{C}$.

At $10.00 \text{ }^\circ\text{C}$ (283.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1 \text{ J/K} + \frac{-6.00 \times 10^3 \text{ J}}{283.15 \text{ K}} = +0.9 \text{ J/K}\end{aligned}$$

$S_{\text{univ}} > 0$, so melting *is* spontaneous at $10.00 \text{ }^\circ\text{C}$.

Check Your Learning

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of S_{univ} ?

Answer: Entropy is a state function, so $\Delta S_{\text{freezing}} = -\Delta S_{\text{melting}} = -22.1 \text{ J/K}$ and $q_{\text{surr}} = +6.00 \text{ kJ}$. At $-10.00 \text{ }^\circ\text{C}$ spontaneous, $+0.7 \text{ J/K}$; at $+10.00 \text{ }^\circ\text{C}$ nonspontaneous, -0.9 J/K .

The Third Law of Thermodynamics

The previous section described the various contributions of matter and energy dispersal that contribute to the entropy of a system. With these contributions in mind, consider the entropy of a pure, perfectly crystalline solid possessing no kinetic energy (that is, at a temperature of absolute zero, 0 K). This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion means there is but one possible location for each identical atom or molecule comprising the crystal ($W = 1$). According to the Boltzmann equation, the entropy of this system is zero.

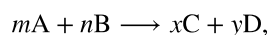
$$S = k \ln W = k \ln(1) = 0$$

This limiting condition for a system's entropy represents the **third law of thermodynamics**: *the entropy of a pure, perfect crystalline substance at 0 K is zero.*

Careful calorimetric measurements can be made to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. **Standard entropies (S°)** are for one mole of substance under standard conditions (a pressure of 1 bar and a temperature of 298.15 K; see details regarding standard conditions in the thermochemistry chapter of this text). The **standard entropy change (ΔS°)** for a reaction may be computed using standard entropies as shown below:

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

where ν represents stoichiometric coefficients in the balanced equation representing the process. For example, ΔS° for the following reaction at room temperature



is computed as:

$$= [xS^\circ(\text{C}) + yS^\circ(\text{D})] - [mS^\circ(\text{A}) + nS^\circ(\text{B})]$$

A partial listing of standard entropies is provided in **Table 12.2**, and additional values are provided in **Appendix G**. The example exercises that follow demonstrate the use of S° values in calculating standard entropy changes for physical and chemical processes.

Substance	S° (J mol ⁻¹ K ⁻¹)
carbon	
C(s, graphite)	5.740
C(s, diamond)	2.38
CO(g)	197.7
CO ₂ (g)	213.8
CH ₄ (g)	186.3
C ₂ H ₄ (g)	219.5
C ₂ H ₆ (g)	229.5
CH ₃ OH(l)	126.8
C ₂ H ₅ OH(l)	160.7
hydrogen	
H ₂ (g)	130.57
H(g)	114.6
H ₂ O(g)	188.71
H ₂ O(l)	69.91
HCl(g)	186.8
H ₂ S(g)	205.7
oxygen	
O ₂ (g)	205.03

Table 12.2 Standard entropies for selected substances measured at 1 atm and 298.15 K. (Values are approximately equal to those measured at 1 bar, the currently accepted standard state pressure.)

Example 12.5

Determination of ΔS°

Calculate the standard entropy change for the following process:



Solution

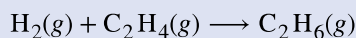
Calculate the entropy change using standard entropies as shown above:

$$\Delta S^\circ = (1 \text{ mol})(70.0 \text{ J mol}^{-1} \text{ K}^{-1}) - (1 \text{ mol})(188.8 \text{ J mol}^{-1} \text{ K}^{-1}) = -118.8 \text{ J/K}$$

The value for ΔS° is negative, as expected for this phase transition (condensation), which the previous section discussed.

Check Your Learning

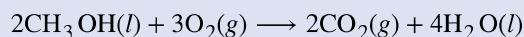
Calculate the standard entropy change for the following process:



Answer: -120.6 J/K

Example 12.6**Determination of ΔS°**

Calculate the standard entropy change for the combustion of methanol, CH_3OH :

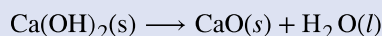
**Solution**

Calculate the entropy change using standard entropies as shown above:

$$\begin{aligned} \Delta S^\circ &= \sum \nu S^\circ(\text{products}) - \sum \nu S^\circ(\text{reactants}) \\ &= [2 \text{ mol} \times S^\circ(\text{CO}_2(\text{g})) + 4 \text{ mol} \times S^\circ(\text{H}_2\text{O}(\text{l}))] - [2 \text{ mol} \times S^\circ(\text{CH}_3\text{OH}(\text{l})) + 3 \text{ mol} \times S^\circ(\text{O}_2(\text{g}))] \\ &= \{ [2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.03)] \} = -161.1 \text{ J/K} \end{aligned}$$

Check Your Learning

Calculate the standard entropy change for the following reaction:



Answer: 24.7 J/K

12.4 Free Energy

One of the challenges of using the second law of thermodynamics to determine if a process is spontaneous is that it requires measurements of the entropy change for the system *and* the entropy change for the surroundings. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the **Gibbs free energy (G)** (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS$$

Free energy is a state function, and at constant temperature and pressure, the **free energy change (ΔG)** may be expressed as the following:

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

(For simplicity's sake, the subscript "sys" will be omitted henceforth.)

The relationship between this system property and the spontaneity of a process may be understood by recalling the previously derived second law expression:

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T}$$

The first law requires that $q_{\text{surr}} = -q_{\text{sys}}$, and at constant pressure $q_{\text{sys}} = \Delta H$, so this expression may be rewritten as:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T}$$

Multiplying both sides of this equation by $-T$, and rearranging yields the following:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$$

Comparing this equation to the previous one for free energy change shows the following relation:

$$\Delta G = -T\Delta S_{\text{univ}}$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ} . **Table 12.3** summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Relation between Process Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{\text{univ}} > 0$	$\Delta G < 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	$\Delta G > 0$	nonspontaneous
$\Delta S_{\text{univ}} = 0$	$\Delta G = 0$	at equilibrium

Table 12.3

What's “Free” about ΔG ?

In addition to indicating spontaneity, the free energy change also provides information regarding the amount of useful work (w) that may be accomplished by a spontaneous process. Although a rigorous treatment of this subject is beyond the scope of an introductory chemistry text, a brief discussion is helpful for gaining a better perspective on this important thermodynamic property.

For this purpose, consider a spontaneous, exothermic process that involves a decrease in entropy. The free energy, as defined by

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

may be interpreted as representing the difference between the energy produced by the process, ΔH , and the energy lost to the surroundings, $T\Delta S$. The difference between the energy produced and the energy lost is the energy available (or “free”) to do useful work by the process, ΔG . If the process somehow could be made to take place under conditions of thermodynamic reversibility, the amount of work that could be done would be maximal:

$$\Delta G = w_{\text{max}}$$

However, as noted previously in this chapter, such conditions are not realistic. In addition, the technologies used to extract work from a spontaneous process (e.g., automobile engine, steam turbine) are never 100% efficient, and so the work done by these processes is always less than the theoretical maximum. Similar reasoning may be applied to a nonspontaneous process, for which the free energy change represents the *minimum* amount of work that must be done on the system to carry out the process.

Calculating Free Energy Change

Free energy is a state function, so its value depends only on the conditions of the initial and final states of the system. A convenient and common approach to the calculation of free energy changes for physical and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute **standard free energy changes, ΔG°** , according to the following relation:

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

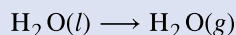
Example 12.7

Using Standard Enthalpy and Entropy Changes to Calculate ΔG°

Use standard enthalpy and entropy data from **Appendix G** to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for ΔG° say about the spontaneity of this process?

Solution

The process of interest is the following:



The standard change in free energy may be calculated using the following equation:

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

From **Appendix G**:

Substance	ΔH_f° (kJ/mol)	S° (J/K·mol)
$\text{H}_2\text{O}(l)$	-286.83	70.0
$\text{H}_2\text{O}(g)$	-241.82	188.8

Using the appendix data to calculate the standard enthalpy and entropy changes yields:

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\text{H}_2\text{O}(g)) - \Delta H_f^\circ(\text{H}_2\text{O}(l)) \\ &= [-241.82 \text{ kJ/mol} - (-286.83)] \text{ kJ/mol} = 45.01 \text{ kJ} \\ \Delta S^\circ &= 1 \text{ mol} \times S^\circ(\text{H}_2\text{O}(g)) - 1 \text{ mol} \times S^\circ(\text{H}_2\text{O}(l)) \\ &= (1 \text{ mol})188.8 \text{ J/mol}\cdot\text{K} - (1 \text{ mol})70.0 \text{ J/mol}\cdot\text{K} = 118.8 \text{ J/mol}\cdot\text{K} \\ \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ\end{aligned}$$

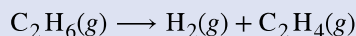
Substitution into the standard free energy equation yields:

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 45.01 \text{ kJ} - (298 \text{ K} \times 118.8 \text{ J/K}) \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\ &= 45.01 \text{ kJ} - 35.4 \text{ kJ} = 9.6 \text{ kJ}\end{aligned}$$

At 298 K (25 °C) $\Delta G^\circ > 0$, so boiling is nonspontaneous (*not* spontaneous).

Check Your Learning

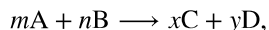
Use standard enthalpy and entropy data from **Appendix G** to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for ΔG° say about the spontaneity of this process?



Answer: $\Delta G^\circ = 102.0 \text{ kJ/mol}$; the reaction is nonspontaneous (*not* spontaneous) at 25 °C.

The standard free energy change for a reaction may also be calculated from **standard free energy of formation** ΔG_f° values of the reactants and products involved in the reaction. The standard free energy of formation is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpy of formation, ΔG_f° is by definition zero for elemental substances under standard state conditions. The approach used to calculate ΔG° for a reaction from ΔG_f° values is the same as that demonstrated

previously for enthalpy and entropy changes. For the reaction



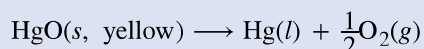
the standard free energy change at room temperature may be calculated as

$$\begin{aligned}\Delta G^\circ &= \sum \nu \Delta G^\circ(\text{products}) - \sum \nu \Delta G^\circ(\text{reactants}) \\ &= [x\Delta G_f^\circ(\text{C}) + y\Delta G_f^\circ(\text{D})] - [m\Delta G_f^\circ(\text{A}) + n\Delta G_f^\circ(\text{B})].\end{aligned}$$

Example 12.8

Using Standard Free Energies of Formation to Calculate ΔG°

Consider the decomposition of yellow mercury(II) oxide.



Calculate the standard free energy change at room temperature, ΔG° , using (a) standard free energies of formation and (b) standard enthalpies of formation and standard entropies. Do the results indicate the reaction to be spontaneous or nonspontaneous under standard conditions?

Solution

The required data are available in **Appendix G** and are shown here.

Compound	ΔG_f° (kJ/mol)	ΔH_f° (kJ/mol)	S° (J/K·mol)
HgO (s, yellow)	-58.43	-90.46	71.13
Hg(l)	0	0	75.9
O ₂ (g)	0	0	205.2

(a) Using free energies of formation:

$$\begin{aligned}\Delta G^\circ &= \sum \nu \Delta G_f^\circ(\text{products}) - \sum \nu \Delta G_f^\circ(\text{reactants}) \\ &= [1\Delta G_f^\circ(\text{Hg}(l)) + \frac{1}{2}\Delta G_f^\circ(\text{O}_2(g))] - 1\Delta G_f^\circ(\text{HgO}(s, \text{yellow})) \\ &= \left[1 \text{ mol}(0 \text{ kJ/mol}) + \frac{1}{2} \text{ mol}(0 \text{ kJ/mol})\right] - 1 \text{ mol}(-58.43 \text{ kJ/mol}) = 58.43 \text{ kJ/mol}\end{aligned}$$

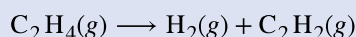
(b) Using enthalpies and entropies of formation:

$$\begin{aligned}
 \Delta H^\circ &= \sum \nu \Delta H_f^\circ (\text{products}) - \sum \nu \Delta H_f^\circ (\text{reactants}) \\
 &= \left[1 \Delta H_f^\circ \text{ Hg}(l) + \frac{1}{2} \Delta H_f^\circ \text{ O}_2(g) \right] - 1 \Delta H_f^\circ \text{ HgO}(s, \text{ yellow}) \\
 &= \left[1 \text{ mol}(0 \text{ kJ/mol}) + \frac{1}{2} \text{ mol}(0 \text{ kJ/mol}) \right] - 1 \text{ mol}(-90.46 \text{ kJ/mol}) = 90.46 \text{ kJ/mol} \\
 \Delta S^\circ &= \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants}) \\
 &= \left[1 \Delta S^\circ \text{ Hg}(l) + \frac{1}{2} \Delta S^\circ \text{ O}_2(g) \right] - 1 \Delta S^\circ \text{ HgO}(s, \text{ yellow}) \\
 &= \left[1 \text{ mol}(75.9 \text{ J/mol K}) + \frac{1}{2} \text{ mol}(205.2 \text{ J/mol K}) \right] - 1 \text{ mol}(71.13 \text{ J/mol K}) = 107.4 \text{ J/mol K} \\
 \Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ = 90.46 \text{ kJ} - 298.15 \text{ K} \times 107.4 \text{ J/K} \cdot \text{mol} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\
 \Delta G^\circ &= (90.46 - 32.01) \text{ kJ/mol} = 58.45 \text{ kJ/mol}
 \end{aligned}$$

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is nonspontaneous (*not* spontaneous) at room temperature.

Check Your Learning

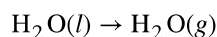
Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies (**Appendix G**). Do the results indicate the reaction to be spontaneous or nonspontaneous at 25 °C?



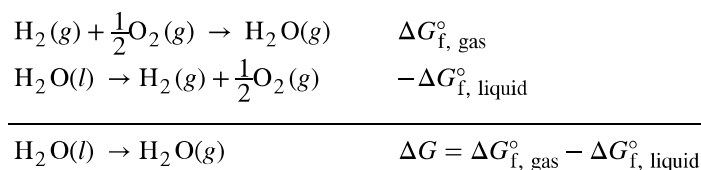
Answer: 141.5 kJ/mol, nonspontaneous

Free Energy Changes for Coupled Reactions

The use of free energies of formation to compute free energy changes for reactions as described above is possible because ΔG is a state function, and the approach is analogous to the use of Hess' Law in computing enthalpy changes (see the chapter on thermochemistry). Consider the vaporization of water as an example:



An equation representing this process may be derived by adding the formation reactions for the two phases of water (necessarily reversing the reaction for the liquid phase). The free energy change for the sum reaction is the sum of free energy changes for the two added reactions:



This approach may also be used in cases where a nonspontaneous reaction is enabled by coupling it to a spontaneous reaction. For example, the production of elemental zinc from zinc sulfide is thermodynamically unfavorable, as indicated by a positive value for ΔG° :



The industrial process for production of zinc from sulfidic ores involves coupling this decomposition reaction to the thermodynamically favorable oxidation of sulfur:



The coupled reaction exhibits a negative free energy change and is spontaneous:



This process is typically carried out at elevated temperatures, so this result obtained using standard free energy values

is just an estimate. The gist of the calculation, however, holds true.

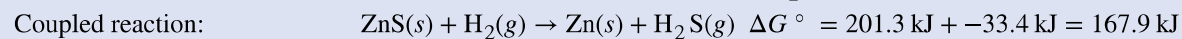
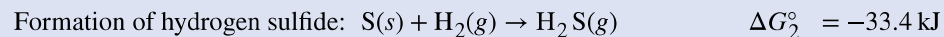
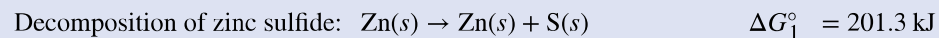
Example 12.9

Calculating Free Energy Change for a Coupled Reaction

Is a reaction coupling the decomposition of ZnS to the formation of H₂S expected to be spontaneous under standard conditions?

Solution

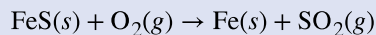
Following the approach outlined above and using free energy values from **Appendix G**:



The coupled reaction exhibits a positive free energy change and is thus nonspontaneous.

Check Your Learning

What is the standard free energy change for the reaction below? Is the reaction expected to be spontaneous under standard conditions?



Answer: -199.7 kJ ; spontaneous

Key Terms

entropy (S) state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates; often described as a measure of the disorder of the system

Gibbs free energy change (G) thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in G

microstate possible configuration or arrangement of matter and energy within a system

nonspontaneous process process that requires continual input of energy from an external source

reversible process process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes

second law of thermodynamics all spontaneous processes involve an increase in the entropy of the universe

spontaneous change process that takes place without a continuous input of energy from an external source

standard entropy (S°) entropy for one mole of a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K

standard entropy change (ΔS°) change in entropy for a reaction calculated using the standard entropies

standard free energy change (ΔG°) change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

standard free energy of formation (ΔG_f°) change in free energy accompanying the formation of one mole of substance from its elements in their standard states

third law of thermodynamics entropy of a perfect crystal at absolute zero (0 K) is zero

Key Equations

- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $S = k \ln W$
- $\Delta S = k \ln \frac{W_f}{W_i}$
- $\Delta S^\circ = \sum \nu S^\circ(\text{products}) - \sum \nu S^\circ(\text{reactants})$
- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$
- $\Delta G = \Delta H - T\Delta S$
- $\Delta G = \Delta G^\circ + RT \ln Q$
- $\Delta G^\circ = -RT \ln K$

Summary

12.1 Spontaneity

Chemical and physical processes have a natural tendency to occur in one direction under certain conditions. A spontaneous process occurs without the need for a continual input of energy from some external source, while a nonspontaneous process requires such. Systems undergoing a spontaneous process may or may not experience a gain or loss of energy, but they will experience a change in the way matter and/or energy is distributed within the system.

12.2 Entropy

Entropy (S) is a state function that can be related to the number of microstates for a system (the number of ways the system can be arranged) and to the ratio of reversible heat to kelvin temperature. It may be interpreted as a measure of the dispersal or distribution of matter and/or energy in a system, and it is often described as representing the “disorder” of the system.

For a given substance, entropy depends on phase with $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$. For different substances in the same physical state at a given temperature, entropy is typically greater for heavier atoms or more complex molecules. Entropy increases when a system is heated and when solutions form. Using these guidelines, the sign of entropy changes for some chemical reactions and physical changes may be reliably predicted.

12.3 The Second and Third Laws of Thermodynamics

The second law of thermodynamics states that a spontaneous process increases the entropy of the universe, $S_{\text{univ}} > 0$. If $\Delta S_{\text{univ}} < 0$, the process is nonspontaneous, and if $\Delta S_{\text{univ}} = 0$, the system is at equilibrium. The third law of thermodynamics establishes the zero for entropy as that of a perfect, pure crystalline solid at 0 K. With only one possible microstate, the entropy is zero. We may compute the standard entropy change for a process by using standard entropy values for the reactants and products involved in the process.

12.4 Free Energy

Gibbs free energy (G) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A number of approaches to the computation of free energy changes are possible.

Exercises

12.1 Spontaneity

1. What is a spontaneous reaction?
2. What is a nonspontaneous reaction?
3. Indicate whether the following processes are spontaneous or nonspontaneous.
 - (a) Liquid water freezing at a temperature below its freezing point
 - (b) Liquid water freezing at a temperature above its freezing point
 - (c) The combustion of gasoline
 - (d) A ball thrown into the air
 - (e) A raindrop falling to the ground
 - (f) Iron rusting in a moist atmosphere
4. A helium-filled balloon spontaneously deflates overnight as He atoms diffuse through the wall of the balloon. Describe the redistribution of matter and/or energy that accompanies this process.
5. Many plastic materials are organic polymers that contain carbon and hydrogen. The oxidation of these plastics in air to form carbon dioxide and water is a spontaneous process; however, plastic materials tend to persist in the environment. Explain.

12.2 Entropy

6. In **Figure 12.8** all possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS , if the particles are initially evenly distributed between the two boxes, but upon redistribution all end up in Box (b).

7. In **Figure 12.8** all of the possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS , for the system when it is converted from distribution (b) to distribution (d).

8. How does the process described in the previous item relate to the system shown in **Figure 12.4**?

9. Consider a system similar to the one in **Figure 12.8**, except that it contains six particles instead of four. What is the probability of having all the particles in only one of the two boxes in the case? Compare this with the similar probability for the system of four particles that we have derived to be equal to $\frac{1}{8}$. What does this comparison tell us about even larger systems?

10. Consider the system shown in **Figure 12.9**. What is the change in entropy for the process where the energy is initially associated only with particle A, but in the final state the energy is distributed between two different particles?

11. Consider the system shown in **Figure 12.9**. What is the change in entropy for the process where the energy is initially associated with particles A and B, and the energy is distributed between two particles in different boxes (one in A-B, the other in C-D)?

12. Arrange the following sets of systems in order of increasing entropy. Assume one mole of each substance and the same temperature for each member of a set.

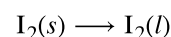
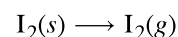
(a) $\text{H}_2(g)$, $\text{HBrO}_4(g)$, $\text{HBr}(g)$

(b) $\text{H}_2\text{O}(l)$, $\text{H}_2\text{O}(g)$, $\text{H}_2\text{O}(s)$

(c) $\text{He}(g)$, $\text{Cl}_2(g)$, $\text{P}_4(g)$

13. At room temperature, the entropy of the halogens increases from I_2 to Br_2 to Cl_2 . Explain.

14. Consider two processes: sublimation of $\text{I}_2(s)$ and melting of $\text{I}_2(s)$ (Note: the latter process can occur at the same temperature but somewhat higher pressure).



Is ΔS positive or negative in these processes? In which of the processes will the magnitude of the entropy change be greater?

15. Indicate which substance in the given pairs has the higher entropy value. Explain your choices.

(a) $\text{C}_2\text{H}_5\text{OH}(l)$ or $\text{C}_3\text{H}_7\text{OH}(l)$

(b) $\text{C}_2\text{H}_5\text{OH}(l)$ or $\text{C}_2\text{H}_5\text{OH}(g)$

(c) $2\text{H}(g)$ or $\text{H}(g)$

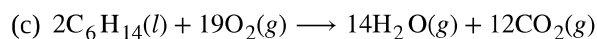
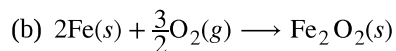
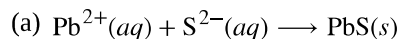
16. Predict the sign of the entropy change for the following processes.

(a) An ice cube is warmed to near its melting point.

(b) Exhaled breath forms fog on a cold morning.

(c) Snow melts.

17. Predict the sign of the entropy change for the following processes. Give a reason for your prediction.



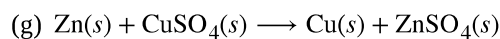
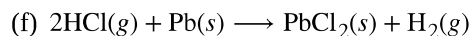
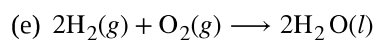
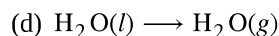
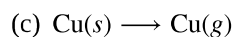
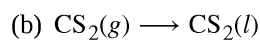
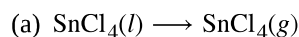
18. Write the balanced chemical equation for the combustion of methane, $\text{CH}_4(\text{g})$, to give carbon dioxide and water vapor. Explain why it is difficult to predict whether ΔS is positive or negative for this chemical reaction.

19. Write the balanced chemical equation for the combustion of benzene, $\text{C}_6\text{H}_6(\text{l})$, to give carbon dioxide and water vapor. Would you expect ΔS to be positive or negative in this process?

12.3 The Second and Third Laws of Thermodynamics

20. What is the difference between ΔS and ΔS° for a chemical change?

21. Calculate ΔS° for the following changes.

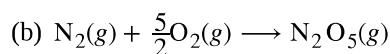
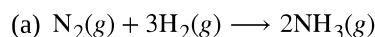


22. Determine the entropy change for the combustion of liquid ethanol, $\text{C}_2\text{H}_5\text{OH}$, under the standard conditions to give gaseous carbon dioxide and liquid water.

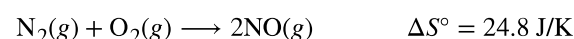
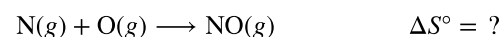
23. Determine the entropy change for the combustion of gaseous propane, C_3H_8 , under the standard conditions to give gaseous carbon dioxide and water.

24. “Thermite” reactions have been used for welding metal parts such as railway rails and in metal refining. One such thermite reaction is $\text{Fe}_2\text{O}_3(\text{s}) + 2\text{Al}(\text{s}) \longrightarrow \text{Al}_2\text{O}_3(\text{s}) + 2\text{Fe}(\text{s})$. Is the reaction spontaneous at room temperature under standard conditions? During the reaction, the surroundings absorb 851.8 kJ/mol of heat.

25. Using the relevant S° values listed in **Appendix G**, calculate ΔS° for the following changes:



26. From the following information, determine ΔS° for the following:



27. By calculating ΔS_{univ} at each temperature, determine if the melting of 1 mole of $\text{NaCl}(\text{s})$ is spontaneous at 500 °C and at 700 °C.

$$S_{\text{NaCl}(\text{s})}^\circ = 72.11 \frac{\text{J}}{\text{mol}\cdot\text{K}} \quad S_{\text{NaCl}(\text{l})}^\circ = 95.06 \frac{\text{J}}{\text{mol}\cdot\text{K}} \quad \Delta H_{\text{fusion}}^\circ = 27.95 \text{ kJ/mol}$$

What assumptions are made about the thermodynamic information (entropy and enthalpy values) used to solve this problem?

28. Use the standard entropy data in **Appendix G** to determine the change in entropy for each of the following reactions. All the processes occur at the standard conditions and 25 °C.

- (a) $\text{MnO}_2(s) \longrightarrow \text{Mn}(s) + \text{O}_2(g)$
 (b) $\text{H}_2(g) + \text{Br}_2(l) \longrightarrow 2\text{HBr}(g)$
 (c) $\text{Cu}(s) + \text{S}(g) \longrightarrow \text{CuS}(s)$
 (d) $2\text{LiOH}(s) + \text{CO}_2(g) \longrightarrow \text{Li}_2\text{CO}_3(s) + \text{H}_2\text{O}(g)$
 (e) $\text{CH}_4(g) + \text{O}_2(g) \longrightarrow \text{C}(s, \text{ graphite}) + 2\text{H}_2\text{O}(g)$
 (f) $\text{CS}_2(g) + 3\text{Cl}_2(g) \longrightarrow \text{CCl}_4(g) + \text{S}_2\text{Cl}_2(g)$

29. Use the standard entropy data in **Appendix G** to determine the change in entropy for each of the reactions listed in **Exercise 12.28**. All the processes occur at the standard conditions and 25 °C.

12.4 Free Energy

30. What is the difference between ΔG and ΔG° for a chemical change?

31. A reaction has $\Delta H^\circ = 100 \text{ kJ/mol}$ and $\Delta S^\circ = 250 \text{ J/mol}\cdot\text{K}$. Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

32. Explain what happens as a reaction starts with $\Delta G < 0$ (negative) and reaches the point where $\Delta G = 0$.

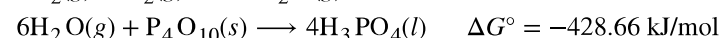
33. Use the standard free energy of formation data in **Appendix G** to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

- (a) $\text{MnO}_2(s) \longrightarrow \text{Mn}(s) + \text{O}_2(g)$
 (b) $\text{H}_2(g) + \text{Br}_2(l) \longrightarrow 2\text{HBr}(g)$
 (c) $\text{Cu}(s) + \text{S}(g) \longrightarrow \text{CuS}(s)$
 (d) $2\text{LiOH}(s) + \text{CO}_2(g) \longrightarrow \text{Li}_2\text{CO}_3(s) + \text{H}_2\text{O}(g)$
 (e) $\text{CH}_4(g) + \text{O}_2(g) \longrightarrow \text{C}(s, \text{ graphite}) + 2\text{H}_2\text{O}(g)$
 (f) $\text{CS}_2(g) + 3\text{Cl}_2(g) \longrightarrow \text{CCl}_4(g) + \text{S}_2\text{Cl}_2(g)$

34. Use the standard free energy data in **Appendix G** to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

- (a) $\text{C}(s, \text{ graphite}) + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$
 (b) $\text{O}_2(g) + \text{N}_2(g) \longrightarrow 2\text{NO}(g)$
 (c) $2\text{Cu}(s) + \text{S}(g) \longrightarrow \text{Cu}_2\text{S}(s)$
 (d) $\text{CaO}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{Ca(OH)}_2(s)$
 (e) $\text{Fe}_2\text{O}_3(s) + 3\text{CO}(g) \longrightarrow 2\text{Fe}(s) + 3\text{CO}_2(g)$
 (f) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(s) \longrightarrow \text{CaSO}_4(s) + 2\text{H}_2\text{O}(g)$

35. Given:

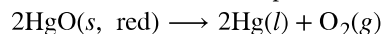


(a) Determine the standard free energy of formation, ΔG_f° , for phosphoric acid.

(b) How does your calculated result compare to the value in **Appendix G**? Explain.

36. Is the formation of ozone ($\text{O}_3(g)$) from oxygen ($\text{O}_2(g)$) spontaneous at room temperature under standard state conditions?

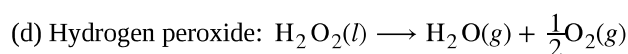
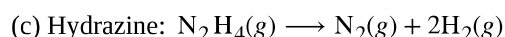
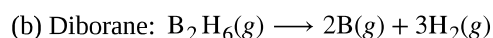
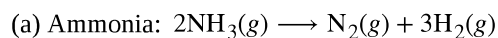
37. Consider the decomposition of red mercury(II) oxide under standard state conditions.



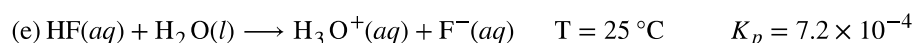
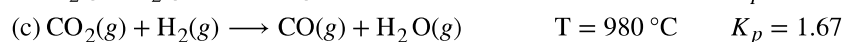
(a) Is the decomposition spontaneous under standard state conditions?

(b) Above what temperature does the reaction become spontaneous?

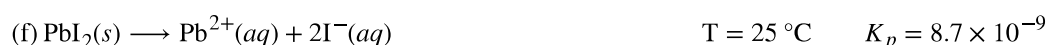
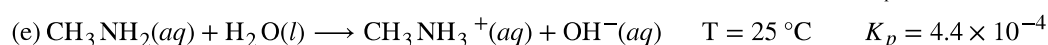
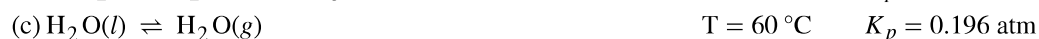
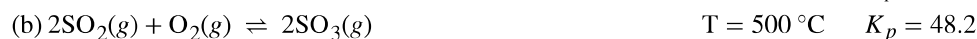
38. Among other things, an ideal fuel for the control thrusters of a space vehicle should decompose in a spontaneous exothermic reaction when exposed to the appropriate catalyst. Evaluate the following substances under standard state conditions as suitable candidates for fuels.



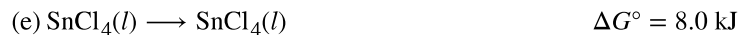
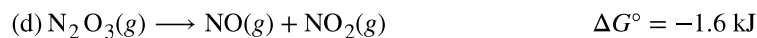
39. Calculate ΔG° for each of the following reactions from the equilibrium constant at the temperature given.



40. Calculate ΔG° for each of the following reactions from the equilibrium constant at the temperature given.



41. Calculate the equilibrium constant at 25°C for each of the following reactions from the value of ΔG° given.



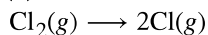
42. Determine ΔG° for the following reactions.

(a) Antimony pentachloride decomposes at 448 °C. The reaction is:



An equilibrium mixture in a 5.00 L flask at 448 °C contains 3.85 g of SbCl_5 , 9.14 g of SbCl_3 , and 2.84 g of Cl_2 .

(b) Chlorine molecules dissociate according to this reaction:



1.00% of Cl_2 molecules dissociate at 975 K and a pressure of 1.00 atm.

43. Given that the ΔG_f° for $\text{Pb}^{2+}(aq)$ and $\text{Cl}^-(aq)$ is -24.3 kJ/mole and -131.2 kJ/mole respectively, determine the solubility product, K_{sp} , for $\text{PbCl}_2(s)$.

44. Determine the standard free energy change, ΔG_f° , for the formation of $\text{S}^{2-}(aq)$ given that the ΔG_f° for $\text{Ag}^+(aq)$ and $\text{Ag}_2\text{S}(s)$ are 77.1 kJ/mole and -39.5 kJ/mole respectively, and the solubility product for $\text{Ag}_2\text{S}(s)$ is 8×10^{-51} .

45. Determine the standard enthalpy change, entropy change, and free energy change for the conversion of diamond to graphite. Discuss the spontaneity of the conversion with respect to the enthalpy and entropy changes. Explain why diamond spontaneously changing into graphite is not observed.

46. The evaporation of one mole of water at 298 K has a standard free energy change of 8.58 kJ.



(a) Is the evaporation of water under standard thermodynamic conditions spontaneous?

(b) Determine the equilibrium constant, K_p , for this physical process.

(c) By calculating ΔG , determine if the evaporation of water at 298 K is spontaneous when the partial pressure of water, $P_{\text{H}_2\text{O}}$, is 0.011 atm.

(d) If the evaporation of water were always nonspontaneous at room temperature, wet laundry would never dry when placed outside. In order for laundry to dry, what must be the value of $P_{\text{H}_2\text{O}}$ in the air?

47. In glycolysis, the reaction of glucose (Glu) to form glucose-6-phosphate (G6P) requires ATP to be present as described by the following equation:



In this process, ATP becomes ADP summarized by the following equation:



Determine the standard free energy change for the following reaction, and explain why ATP is necessary to drive this process:



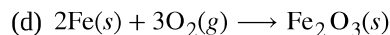
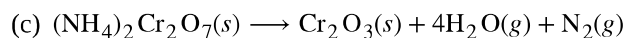
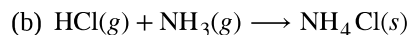
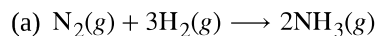
48. One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):



(a) Is the reaction spontaneous or nonspontaneous under standard thermodynamic conditions?

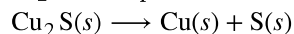
(b) Standard thermodynamic conditions imply the concentrations of G6P and F6P to be 1 M, however, in a typical cell, they are not even close to these values. Calculate ΔG when the concentrations of G6P and F6P are 120 μM and 28 μM respectively, and discuss the spontaneity of the forward reaction under these conditions. Assume the temperature is 37 °C.

49. Without doing a numerical calculation, determine which of the following will reduce the free energy change for the reaction, that is, make it less positive or more negative, when the temperature is increased. Explain.



50. When ammonium chloride is added to water and stirred, it dissolves spontaneously and the resulting solution feels cold. Without doing any calculations, deduce the signs of ΔG , ΔH , and ΔS for this process, and justify your choices.

51. An important source of copper is from the copper ore, chalcocite, a form of copper(I) sulfide. When heated, the Cu_2S decomposes to form copper and sulfur described by the following equation:



(a) Determine ΔG° for the decomposition of $\text{Cu}_2\text{S}(s)$.

(b) The reaction of sulfur with oxygen yields sulfur dioxide as the only product. Write an equation that describes this reaction, and determine ΔG° for the process.

(c) The production of copper from chalcocite is performed by roasting the Cu_2S in air to produce the Cu. By combining the equations from Parts (a) and (b), write the equation that describes the roasting of the chalcocite, and explain why coupling these reactions together makes for a more efficient process for the production of the copper.

52. What happens to ΔG° (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?

