

Gibb's Free Energy

Experience

Matter

Energy

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. 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.

40.1 Spontaneity

Learning Objectives

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

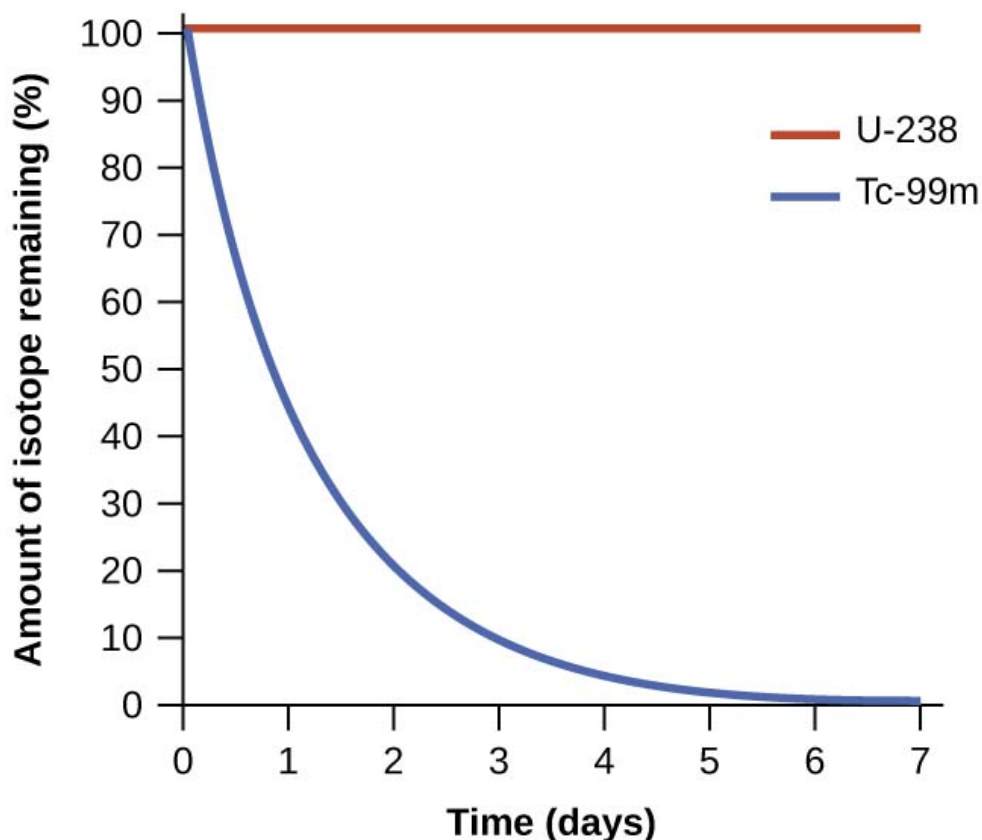
Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. Iron exposed to the earth's atmosphere will corrode, but rust is not converted to iron without intentional 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

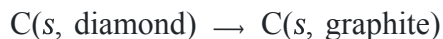
which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years ([Figure 40.1](#)).

Figure 40.1

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 40.2](#)).

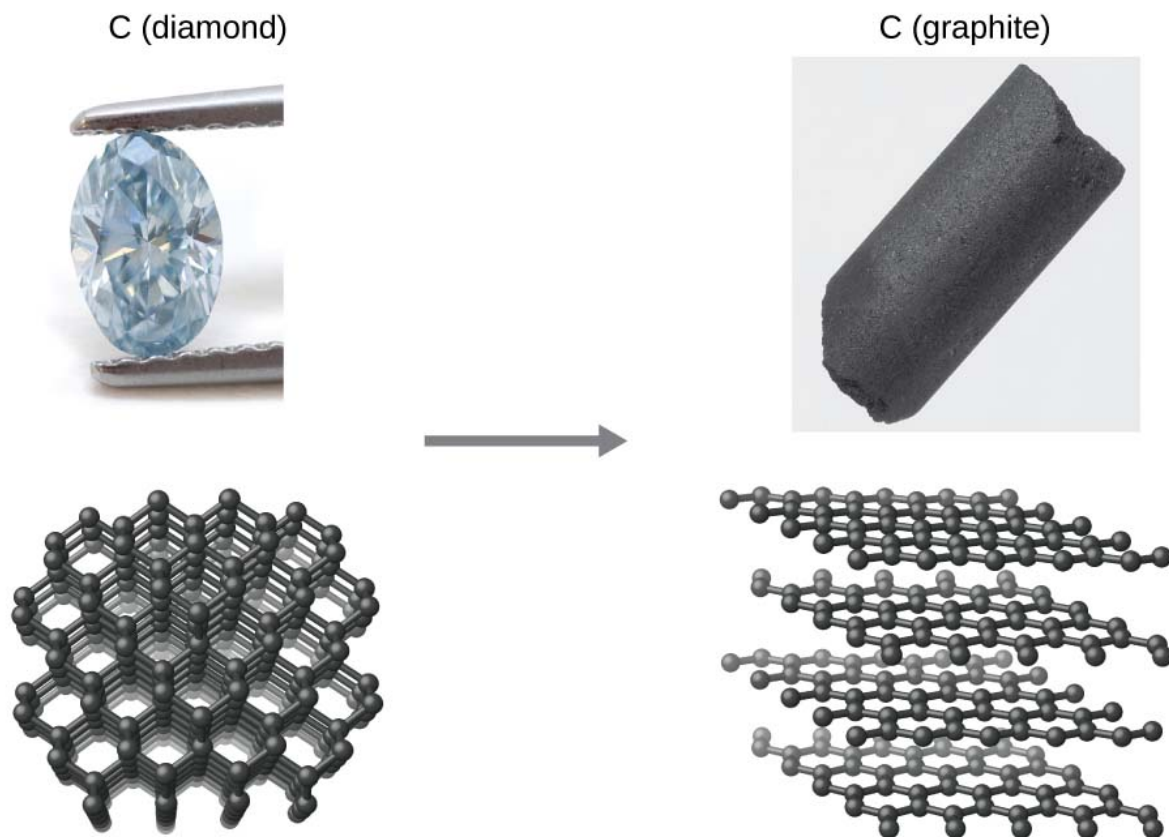


The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section 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 40.2

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 40.3](#)). 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.

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

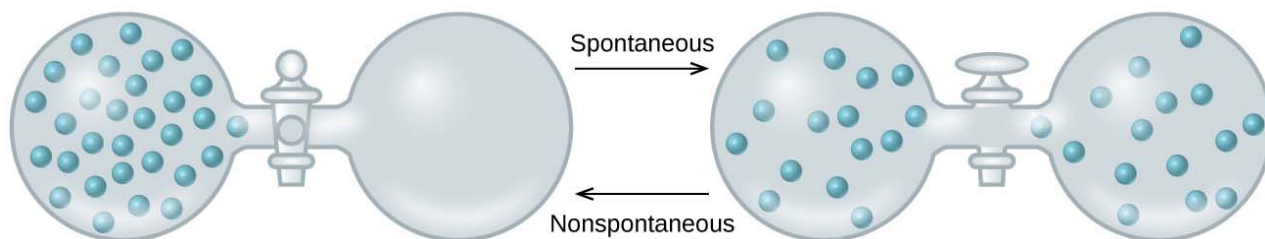
Note as well that since the system is isolated, no heat has been exchanged with the surroundings ($q = 0$). The *first law of thermodynamics* confirms that there has been no change in the system's internal energy as a result of this process.

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

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 40.3

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 40.4). 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 40.4

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 40.1

Redistribution of Matter during a Spontaneous Process

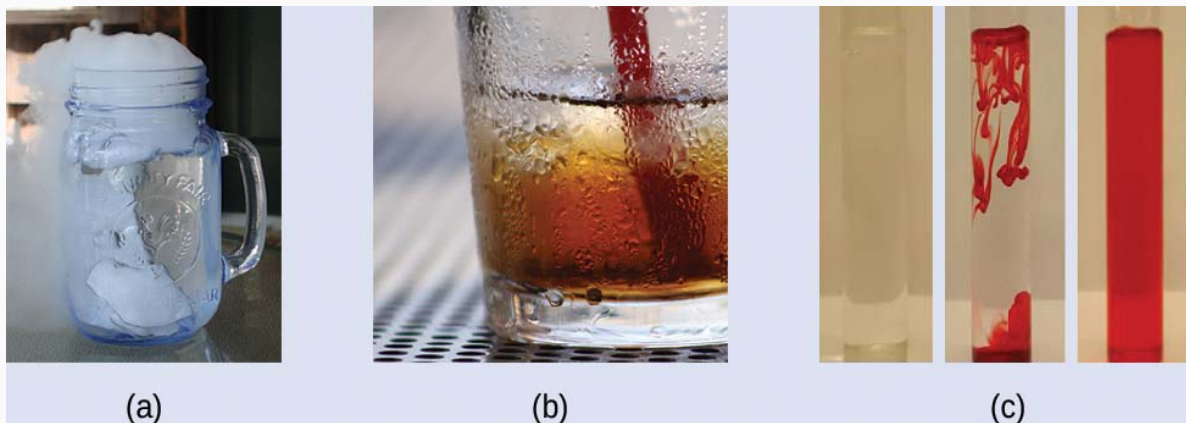
Describe how matter is redistributed when the following spontaneous processes take place:

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

Solution

Figure 40.5

(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.

Link to Supplemental Exercises

[Supplemental exercises](#) are available if you would like more practice with these concepts.

40.2 Free Energy

Learning Objectives

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

- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate free energy change for a process using free energies of formation for its reactants and products
- Calculate free energy change for a process using enthalpies of formation and the entropies for its reactants and products

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 40.1](#) summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Table 40.1

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

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 40.2

Using Standard Enthalpy and Entropy Changes to Calculate ΔG°

Use standard enthalpy and entropy data from OpenStax's [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 OpenStax's [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:

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\text{H}_2\text{O}(g)) - \Delta H_f^\circ(\text{H}_2\text{O}(l)) \\ &= [-241.82 \text{ kJ/mol} - (-286.83)] \text{ kJ/mol} = 45.01 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= 1 \text{ mol} \times S^\circ(\text{H}_2\text{O}(g)) - 1 \text{ mol} \times S^\circ(\text{H}_2\text{O}(l)) \\ &= (1 \text{ mol})188.8 \text{ J/mol}\cdot\text{K} - (1 \text{ mol})70.0 \text{ J/mol}\cdot\text{K} = 118.8 \text{ J/mol}\cdot\text{K}\end{aligned}$$

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

Substitution into the standard free energy equation yields:

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

$$45.01 \text{ kJ} - 35.4 \text{ kJ} = 9.6 \text{ kJ}$$

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 OpenStax's [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,

$$\Delta G_f^\circ$$

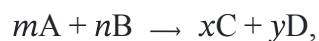
is by definition zero for elemental substances in their standard states. The approach used to calculate

$$\Delta G^\circ$$

for a reaction from

$$\Delta G_f^\circ$$

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

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

Example 40.3

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 OpenStax's [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:

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

(b) Using enthalpies and entropies of formation:

$$\begin{aligned}\Delta H^\circ &= \sum \nu \Delta H_f^\circ(\text{products}) - \sum \nu \Delta H_f^\circ(\text{reactants}) \\&= [1\Delta H_f^\circ \text{Hg}(l) + \frac{1}{2}\Delta H_f^\circ \text{O}_2(g)] - 1\Delta H_f^\circ \text{HgO}(s, \text{yellow}) \\&= [1 \text{ mol}(0 \text{ kJ/mol}) + \frac{1}{2} \text{ mol}(0 \text{ kJ/mol})] - 1 \text{ mol}(-90.46 \text{ kJ/mol}) = 90.46 \text{ kJ/mol}\end{aligned}$$

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

$$= [1\Delta S^\circ\text{Hg}(l) + \frac{1}{2}\Delta S^\circ\text{O}_2(g)] - 1\Delta S^\circ\text{HgO}(s, \text{ yellow})$$

$$= [1 \text{ mol} (75.9 \text{ J/mol K}) + \frac{1}{2} \text{ mol}(205.2 \text{ J/mol K})] - 1 \text{ mol}(71.13 \text{ J/mol K}) = 107.4 \text{ J/mol K}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 90.46 \text{ kJ} - 298.15 \text{ K} \times 107.4 \text{ J/K}\cdot\text{mol} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta G^\circ = (90.46 - 32.01) \text{ kJ/mol} = 58.45 \text{ kJ/mol}$$

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 (reference OpenStax's [Appendix G](#)). Do the results indicate the reaction to be spontaneous or nonspontaneous at 25 °C?



Answer

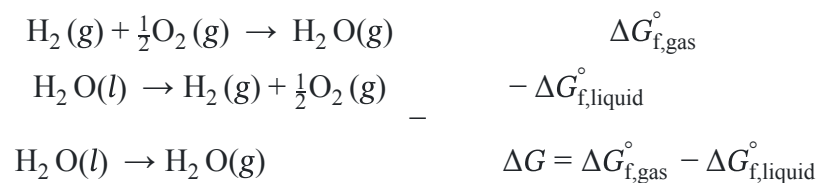
- (a) 140.8 kJ/mol, nonspontaneous
- (b) 141.5 kJ/mol, nonspontaneous

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.

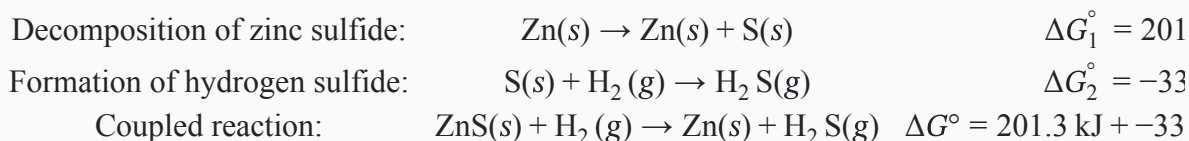
Example 40.4

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

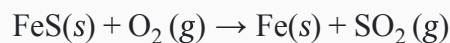
Following the approach outlined above and using free energy values from [Appendix G](#):



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

Link to Supplemental Exercises

[Supplemental exercises](#) are available if you would like more practice with these concepts.

Files

[Open in Google Drive](#)

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