Pearson

18.8: Free Energy Changes in Chemical Reactions: Calculating ΔG^o_{rxn}

In Section 18.6, we saw that the criterion for spontaneity is the change in Gibbs free energy (ΔG). When the reactants and products of a reaction are in their standard states, Gibbs free energy becomes the **standard change in free energy** (ΔG^o_{rxn}). In this section, we examine three methods to calculate the standard change in free energy for a reaction (ΔG^o_{rxn}) .In the first method, we calculate (ΔH^o_{rxn})and ΔS^o_{rxn} from tabulated values of ΔH^o_{rxn} and $S°$, and then use the relationship $\Delta G^o_{\text{rxn}} = \Delta H^o_{\text{rxn}} - T\Delta S^o_{\text{rxn}}$to calculate ΔG^o_{rxn}. In the second method, we use tabulated values of free energies of formation to calculate ΔG^o_{rxn} directly. In the third method, we determine the free energy change for a stepwise reaction from the free energy changes of each step. At the end of this section, we discuss how to make a nonspontaneous process spontaneous and what is "free" about free energy. Remember that ΔG^o_{rxn} is extremely useful because it tells us about the spontaneity of a process at standard conditions. The more negative ΔG^o_{rxn} is, the more spontaneous the process—the further it will go toward products to reach equilibrium.

> Standard conditions represent a very specific reaction mixture. For a reaction mixture with reactants and products in their standard states, $Q = 1$.

Calculating Standard Free Energy Changes with $\Delta G^o_{\text{rxn}} = \Delta H^o_{\text{rxn}} - T\Delta S^o_{\text{rxn}}$

In Chapter 9 (Section 9.10), we learned how to use tabulated values of standard enthalpies of formation to calculate (ΔH^o_{rxn}). In Section 18.7, we learned how to use tabulated values of standard entropies to calculate ΔS^o_{rxn}. We can use these calculated values of ΔH^o_{rxn} and ΔS^o_{rxn} to determine the standard free energy change for a reaction by using the equation:

[18.11]

$$\Delta G^o_{\text{rxn}} = \Delta H^o_{\text{rxn}} - T\Delta S^o_{\text{rxn}}$$

Because tabulated values of standard enthalpies of formation (ΔH^o_{f}) and standard entropies (S^o) are usually applicable at 25 °C, the equation should (strictly speaking) be valid only when T = 298K (25 °C). However, the changes in ΔH^o_{rxn} and ΔS^o_{rxn} over a limited temperature range are small when compared to the changes in the value of the temperature itself. Therefore, we can use Equation 18.11 to estimate changes in free energy at temperatures other than 25 °C.

Example 18.6 Calculating the Standard Change in Free Energy for a Reaction Using $\Delta G^o_{\text{rxn}} = \Delta H^o_{\text{rxn}} - T\Delta S^o_{\text{rxn}}$

One possible initial step in the formation of acid rain is the oxidation of the pollutant SO_2 to SO_3 by the reaction:

$$SO_2\,(g) + \frac{1}{2}O_2\,(g) \rightarrow SO_3\,(g)$$

Calculate ΔG^o_{rxn} at 25 °C and determine whether the reaction is spontaneous.

SOLUTION

Begin by looking up (in Appendix IIB) the standard enthalpy of formation and the standard entropy for each reactant and product.

Reactant or product	ΔH_f° (kJ/mol)	S° (J/mol · K)
$SO_2(g)$	−296.8	248.2
$O_2(g)$	0	205.2
$SO_3(g)$	−395.7	256.8

Calculate ΔH^o_{rxn} using Equation 9.14.

$$\begin{aligned}
\Delta H^o_{\text{rxn}} &= \Sigma_{np}\Delta H^o_{\text{f}}(\text{products}) - \Sigma_{nx}\Delta H^o_{\text{f}}(\text{reactants}) \\
&= \left[\Delta \text{H}^o_{\text{f}},_{\text{so}_3}(g)\right] - \left[\Delta \text{H}^o_{\text{f}},_{\text{so}_2}(g) + \frac{1}{2}\left(\Delta \text{H}^o_{\text{f}},_{\text{o}_{2(g)}}\right)\right] \\
&= -395.7\text{kJ} - (-296.8\text{kJ} + 0.0\text{kJ}) \\
&= -98.9\text{kJ}
\end{aligned}$$

Calculate ΔS^o_{rxn} using Equation 18.1.

$$\begin{aligned}
\Delta S^o_{\text{rxn}} &= \Sigma n_p S^o(\text{products}) - \Sigma n_r S^o(\text{reactants}) \\
&= \left[S^o_{\text{SO}_3(g)}\right] - \left[S^o_{\text{SO}_2(g)} + \tfrac{1}{2}\left(S^o_{\text{O}_2(g)}\right)\right] \\
&= 256.8\text{J/K} - \left[248.2\text{J/K} + \tfrac{1}{2}(205.2\text{J/K})\right] \\
&= -94.0\text{J/K}
\end{aligned}$$

Calculate ΔG^o_{rxn} using the calculated values of $(\Delta H^o_{\text{rxn}})$ and ΔS^o_{rxn} and Equation 18.11. Convert the temperature to kelvins.

$$\begin{aligned}
T &= 25 + 273 = 298\text{K} \\
\Delta G^o_{\text{rxn}} &= \Delta H^o_{\text{rxn}} - T\Delta S^o_{\text{rxn}} \\
&= -98.9 \times 10^3\text{J} - 298\,\cancel{\text{K}}\left(-94.0\text{J}/\,\cancel{\text{K}}\right) \\
&= -70.9 \times 10^3\text{J} \\
&= -70.9\,\text{KJ}
\end{aligned}$$

The reaction is spontaneous at this temperature because ΔG^o_{rxn} is negative.

FOR PRACTICE 18.6 Consider the oxidation of NO to NO_2:

$$\text{NO}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{NO}_2(g)$$

Calculate ΔG^o_{rxn} at 25 °C and determine whether the reaction is spontaneous at standard conditions.

Interactive Worked Example 18.6 **Calculating the Standard Change in Free Energy for a Reaction Using $\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}}$**

Example 18.7 Estimating the Standard Change in Free Energy for a Reaction at a Temperature Other Than 25 °C Using $\Delta G^o_{\text{rxn}} = \Delta H^o_{\text{rxn}} - T\Delta S^o_{\text{rxn}}$

For the reaction in Example 18.5, estimate the value of ΔG^o_{rxn} at 125 °C. Is the reaction more or less spontaneous at this elevated temperature; that is, is the value of ΔG^o_{rxn} more negative (more spontaneous) or more positive (less spontaneous)?

SOLUTION

Estimate ΔG^o_{rxn} at the new temperature using the calculated values of ΔH^o_{rxn} and ΔS^o_{rxn} from Example

18.5. For T, convert the given temperature to kelvins. Make sure to use the same units for $(\Delta H^{o}_{\mathrm{rxn}})$ and $\Delta S^{o}_{\mathrm{rxn}}$ (usually joules).

$$\begin{aligned} T &= 125 + 273 = 398\mathrm{K} \\ \Delta G^{o}_{\mathrm{rxn}} &= \Delta G^{o}_{\mathrm{rxn}} - T\Delta S^{o}_{\mathrm{rxn}} \\ &= -98.9 \times 10^{3}\mathrm{J} - 398\ \cancel{\mathrm{K}} \left(-94.0\mathrm{J}/\ \cancel{\mathrm{K}}\right) \\ &= -61.5 \times 10^{3}\mathrm{J} \\ &= -61.5\mathrm{KJ} \end{aligned}$$

Since the value of $\Delta G^{o}_{\mathrm{rxn}}$ at this elevated temperature is less negative (or more positive) than the value of $\Delta G^{o}_{\mathrm{rxn}}$ at 25 °C (which is $-70.9\mathrm{kJ}$), the reaction is less spontaneous.

FOR PRACTICE 18.7 For the reaction in For Practice 18.5, calculate the value of $\Delta G^{O}_{\mathrm{rxn}}$ at –55 °C. Is the reaction more spontaneous (more negative ΔG^{o}_{rxn} or less spontaneous (more positive ΔG^{o}_{rxn} at the lower temperature?

Calculating ΔG^{o}_{rxn} with Tabulated Values of Free Energies of Formation

Because $\Delta G^{o}_{\mathrm{rxn}}$ is the *change* in free energy for a chemical reaction—the difference in free energy between the products and the reactants—and because free energy is a state function, we can calculate $\Delta G^{o}_{\mathrm{rxn}}$ by subtracting the free energies of the reactants of the reaction from the free energies of the products. Also, since we are interested only in *changes* in free energy (and not in absolute values of free energy), we are free to define the *zero* of free energy as conveniently as possible. By analogy with our definition of enthalpies of formation, we define the **free energy of formation** $(\Delta G^{o}_{\mathrm{f}})$ as follows:

> **The free energy of formation $(\Delta G^{o}_{\mathrm{f}})$ is the change in free energy when 1 mol of a compound in its standard state forms from its constituent elements in their standard states. The free energy of formation of pure elements in their standard states is zero.**

We can measure all changes in free energy relative to pure elements in their standard states. To calculate $\Delta G^{o}_{\mathrm{rxn}}$, we subtract the free energies of formation of the reactants multiplied by their stoichiometric coefficients from the free energies of formation of the products multiplied by their stoichiometric coefficients. In the form of an equation:

[18.12]

$$\Delta G^{o}_{\mathrm{rxn}} = \Sigma n_{p}\Delta G^{o}_{\mathrm{f}}(\text{products}) - \Sigma n_{r}\Delta G^{o}_{\mathrm{f}}(\text{reactants})$$

In Equation 18.12, n_{p} represents the stoichiometric coefficients of the products, n_{r} represents the stoichiometric coefficients of the reactants, and $\Delta G^{o}_{\mathrm{f}}$ represents the standard free energies of formation. Table 18.3 lists $\Delta G^{o}_{\mathrm{f}}$ values for selected substances. You can find a more complete list in Appendix IIB. Notice that, by definition, *elements* have standard free energies of formation of zero. Notice also that most *compounds* have negative standard free energies of formation. This means that those compounds spontaneously form from their elements in their standard states. Compounds with positive free energies of formation do not spontaneously form from their elements and are therefore less common.

Table 18.3 **Standard Molar Free Energies of Formation $(\Delta G^{o}_{\mathrm{f}})$ for Selected Substances at 298 K**

Substance	$\Delta G^{o}_{\mathrm{f}}$ (kJ/mol)	Substance	$\Delta G^{o}_{\mathrm{f}}$ (kJ/mol)
$H_2(g)$	0	$CH_4(g)$	−50.5
$O_2(g)$	0	$H_2O(g)$	−228.6

$N_2(g)$	0	$H_2O(l)$	−237.1
C(*s*, graphite)	0	$NH_3(g)$	−16.4
C(*s*, diamond)	2.900	NO(*g*)	+87.6
CO(*g*)	−137.2	$NO_2(g)$	+51.3
$CO_2(g)$	−394.4	NaCl(*s*)	−384.1

Example 18.8 demonstrates the calculation of ΔG^o_{rxn} from ΔG^o_f values. This method of calculating ΔG^o_{rxn} works only at the temperature for which the free energies of formation are tabulated, namely, 25 °C. To estimate ΔG^o_{rxn} at other temperatures, we must use $\Delta G^o_{rxn} = \Delta H^o_{rxn} - T\Delta S^o_{rxn}$ as demonstrated previously.

Example 18.8 Calculating ΔG^o_{rxn} from Standard Free Energies of Formation

Ozone in the lower atmosphere is a pollutant that can form by the following reaction involving the oxidation of unburned hydrocarbons:

$$CH_4(g) + 8O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + 4O_3(g)$$

Use the standard free energies of formation to determine ΔG^o_{rxn} for this reaction at 25 °C.

SOLUTION

Begin by looking up (in Appendix IIB) the standard free energies of formation for each reactant and product. Remember that the standard free energy of formation of a pure element in its standard state is zero.

Reactant/product	ΔG°_f (in kJ/mol)
$CH_4(g)$	−50.5
$O_2(g)$	0.0
$CO_2(g)$	−394.4
$H_2O(g)$	−228.6
$O_3(g)$	163.2

Calculate ΔG°_{rxn} by substituting into Equation 18.12.

$$\begin{aligned}
\Delta G^\circ_{rxn} &= \Sigma n_p \Delta G^\circ_f(\text{products}) - \Sigma n_r \Delta G^\circ_f(\text{reactants}) \\
&= [\Delta G^\circ_{f,\,CO_2(g)} + 2(\Delta G^\circ_{f,\,H_2O(g)}) + 4(\Delta G^\circ_{f,\,O_3(g)})] - [\Delta G^\circ_{f,\,CH_4(g)} + 8(\Delta G^\circ_{f,\,O_2(g)})] \\
&= [-394.4\text{ kJ} + 2(-228.6\text{ kJ}) + 4(163.2\text{ kJ})] - [-50.5\text{ kJ} + 8(0.0\text{ kJ})] \\
&= -198.8\text{ kJ} + 50.5\text{ kJ} \\
&= -148.3\text{ kJ}
\end{aligned}$$

FOR PRACTICE 18.8 One reaction that occurs within a catalytic converter in the exhaust pipe of a car is the simultaneous oxidation of carbon monoxide and reduction of nitrogen monoxide (both of which are harmful pollutants).

$$2\,CO(g) + 2\,NO(g) \rightarrow 2\,CO_2(g) + N_2(g)$$

Use standard free energies of formation to determine ΔG^o_{rxn} for this reaction at 25 °C. Is the reaction spontaneous at standard conditions?

FOR MORE PRACTICE 18.8 In For Practice 18.7, you calculated ΔG^o_{rxn} for the simultaneous oxidation of carbon monoxide and reduction of nitrogen monoxide using standard free energies of formation. Calculate ΔG^o_{rxn} for that reaction again at 25 °C, only this time use. $\Delta G^o_{rxn} = \Delta H^o_{rxn} - T\Delta S^o_{rxn}$ How do the two values compare? Use your results to calculate ΔG^o_{rxn} at 500.0 K and explain why you could not calculate ΔG^o_{rxn} at 500.0 K using tabulated standard free energies of formation.

Calculating ΔG^o_{rxn} for a Stepwise Reaction from the Changes in Free Energy for Each of the Steps

Recall from Section 9.6 that since enthalpy is a state function, we can calculate ΔH^o_{rxn} for a stepwise reaction from the sum of the changes in enthalpy for each step (according to Hess's law). Since free energy is also a state function, the same relationships that we covered in Chapter 9 for enthalpy also apply to free energy:

1. If a chemical equation is multiplied by some factor, ΔG_{rxn} is also multiplied by the same factor.
2. If a chemical equation is reversed, ΔG_{rxn} changes sign.
3. If a chemical equation can be expressed as the sum of a series of steps, ΔG_{rxn} for the overall equation is the sum of the free energies of reactions for each step.

Example 18.9 illustrates the use of these relationships to calculate ΔG^o_{rxn} for a stepwise reaction.

Example 18.9 Calculating ΔG^o_{rxn} for a Stepwise Reaction

Find ΔG^o_{rxn} for the reaction:

$$3\ \mathrm{C}(s) + 4\mathrm{H_2}\,(g) \rightarrow \mathrm{C_3H_8}\,(g)$$

Use the following reactions with known values of ΔG^o:

$$\begin{aligned} \mathrm{C_3H_8}(g) + 5\mathrm{O_2}\,(g) &\rightarrow 3\mathrm{CO_2}\,(g) + 4\mathrm{H_2O}\,(g) & \Delta G^o_{rxn} &= -2074\mathrm{kJ} \\ C\,(s) + \mathrm{O_2}\,(g) &\rightarrow \mathrm{CO_2}\,(g) & \Delta G^o_{rxn} &= -394.4\mathrm{kJ} \\ 2\mathrm{H_2}\,(g) + \mathrm{O_2}\,(g) &\rightarrow 2\mathrm{H_2O}\,(g) & \Delta G^o_{rxn} &= -457.1\mathrm{kJ} \end{aligned}$$

SOLUTION

To work this problem, manipulate the reactions with known values of ΔG^o_{rxn} in such a way as to get the reactants of interest on the left, the products of interest on the right, and other species to cancel.

Since the first reaction has $\mathrm{C_3H_8}$ as a reactant, and the reaction of interest has $\mathrm{C_3H_8}$ as a product, reverse the first reaction and change the sign of ΔG^o_{rxn}.

$$3\mathrm{CO_2}\,(g) + 4\mathrm{H_2O}\,(g) \rightarrow \mathrm{C_3H_8}\,(g) + 5\mathrm{O_2}\,(g) \quad \Delta G^o_{rxn} = +2074\mathrm{kJ}$$

The second reaction has C as a reactant and $\mathrm{CO_2}$ as a product, as required in the reaction of interest. However, the coefficient for C is 1, and in the reaction of interest, the coefficient for C is 3. Therefore, multiply this equation and its ΔG^o_{rxn} by 3.

$$3 \times [\mathrm{C}\,(s) + \mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g)] \quad \begin{aligned} \Delta G^o_{rxn} &= 3 \times (-394.\mathrm{kJ}) \\ &= -1183\mathrm{kJ} \end{aligned}$$

The third reaction has $\mathrm{H_2}\,(g)$ as a reactant, as required. However, the coefficient for $\mathrm{H_2}$ is 2, and in the reaction of interest, the coefficient for $\mathrm{H_2}$ is 4. Multiply this reaction and its ΔG^o_{rxn} by 2.

$$2 \times [2\mathrm{H_2}\,(g) + \mathrm{O_2}(g) \rightarrow 2\mathrm{H_2O}\,(g)] \quad \begin{aligned} \Delta G^o_{rxn} &= 2 \times (-457.1\mathrm{kJ}) \\ &= -914.2 \end{aligned}$$

Lastly, rewrite the three reactions after multiplying by the indicated factors and show how they sum to the reaction of interest. $\Delta G^{o}_{\text{rxn}}$ for the reaction of interest is then the sum of the ΔG^{o} values for the steps.

$$\begin{array}{rcll}
\cancel{3\,CO_2}(g) + \cancel{4\,H_2O}(g) & \longrightarrow & C_3H_8(g) + \cancel{5\,O_2}(g) & \Delta G^{\circ}_{\text{rxn}} = +2074\text{ kJ} \\
3\,C(s) + \cancel{3\,O_2}(g) & \longrightarrow & \cancel{3\,CO_2}(g) & \Delta G^{\circ}_{\text{rxn}} = -1183\text{ kJ} \\
4\,H_2(g) + \cancel{2\,O_2}(g) & \longrightarrow & \cancel{4\,H_2O}(g) & \Delta G^{\circ}_{\text{rxn}} = -914.2\text{ kJ} \\
\hline
3\,C(s) + 4\,H_2(g) & \longrightarrow & C_3H_8(g) & \Delta G^{\circ}_{\text{rxn}} = -23\text{ kJ}
\end{array}$$

FOR PRACTICE 18.9 Find $\Delta G^{o}_{\text{rxn}}$ for the reaction:

$$N_2O\,(g) + NO_2\,(g) \rightarrow 3NO\,(g)$$

Use the following reactions with known ΔG values:

$$\begin{array}{rcllcl}
2NO\,(g) + O_2 & \rightarrow & 2NO_2\,(g) & \Delta G^{o}_{\text{rxn}} & = & -71.2\text{kJ} \\
N_2\,(g) + O_2\,(g) & \rightarrow & 2NO\,(g) & \Delta G^{o}_{\text{rxn}} & = & +175.2\text{kJ} \\
2N_2O\,(g) & \rightarrow & 2N_2\,(g) + O_2\,(g) & \Delta G^{o}_{\text{rxn}} & = & -207.4\text{kJ}
\end{array}$$

Making a Nonspontaneous Process Spontaneous

As we mentioned in Section 18.2, a process that is nonspontaneous can be made spontaneous by coupling it with another process that is highly spontaneous. For example, hydrogen gas is a potential future fuel because it can be used in a fuel cell (a type of battery in which the reactants are constantly supplied—see Chapter 19) to generate electricity. The main problem with switching to hydrogen is securing a source. Where can we get the huge amounts of hydrogen gas that we need to meet our world's energy demands? Earth's oceans and lakes contain vast amounts of hydrogen. But that hydrogen is locked up in water molecules, and the decomposition of water into hydrogen and oxygen has a positive $\Delta G^{o}_{\text{rxn}}$ and is therefore nonspontaneous:

$$H_2O\,(g) \rightarrow H_2\,(g) + \frac{1}{2}O_2\,(g) \quad \Delta G^{o}_{\text{rxn}} = +228.6\text{kJ}$$

To obtain hydrogen from water, we need to find another reaction with a highly negative $\Delta G^{o}_{\text{rxn}}$ that can couple with the decomposition reaction to give an overall reaction with a negative $\Delta G^{o}_{\text{rxn}}$. For example, the oxidation of carbon monoxide to carbon dioxide has a large negative $\Delta G^{o}_{\text{rxn}}$ and is highly spontaneous:

$$CO\,(g) + \frac{1}{2}O_2\,(g) \rightarrow CO_2\,(g) \quad \Delta G^{o}_{\text{rxn}} = -257.2\text{kJ}$$

If we add the two reactions together, we get a negative $\Delta G^{o}_{\text{rxn}}$:

Nonspontaneous

$$\begin{array}{rcll}
H_2O(g) & \longrightarrow & H_2(g) + \cancel{\tfrac{1}{2}O_2}(g) & \Delta G^{\circ}_{\text{rxn}} = +228.6\text{ kJ} \\
CO(g) + \cancel{\tfrac{1}{2}O_2}(g) & \longrightarrow & CO_2(g) & \Delta G^{\circ}_{\text{rxn}} = -257.2\text{ kJ} \\
\hline
H_2O(g) + CO(g) & \longrightarrow & H_2(g) + CO_2(g) & \Delta G^{\circ}_{\text{rxn}} = -28.6\text{ kJ}
\end{array}$$

Spontaneous

The reaction between water and carbon monoxide is thus a spontaneous way to generate hydrogen gas.

The coupling of nonspontaneous reactions with highly spontaneous ones is also important in biological systems. The synthesis reactions that create the complex biological molecules (such as proteins and DNA) needed by living organisms, for example, are themselves nonspontaneous. Living systems grow and reproduce by coupling these nonspontaneous reactions to highly spontaneous ones. The main spontaneous reaction that ultimately drives the nonspontaneous ones is the metabolism of food. The oxidation of glucose, for example, is highly spontaneous:

$$C_6H_{12}O_6\,(s) + 6O_2\,(g) \rightarrow 6CO_2\,(g) + 6H_2O\,(l) \quad \Delta G^o_{\mathrm{rxn}} = -2880\ \mathrm{kJ}$$

Spontaneous reactions such as these ultimately drive the nonspontaneous reactions necessary to sustain life.

Why Free Energy Is “Free”

We often want to use the energy released by a chemical reaction to do work. For example, in an automobile, we use the energy released by the combustion of gasoline to move the car forward. The change in free energy of a chemical reaction represents the maximum amount of energy available, or *free*, to do work (if $\Delta G^o_{\mathrm{rxn}}$ is negative). For many reactions, the amount of free energy change is less than the change in enthalpy for the reaction.

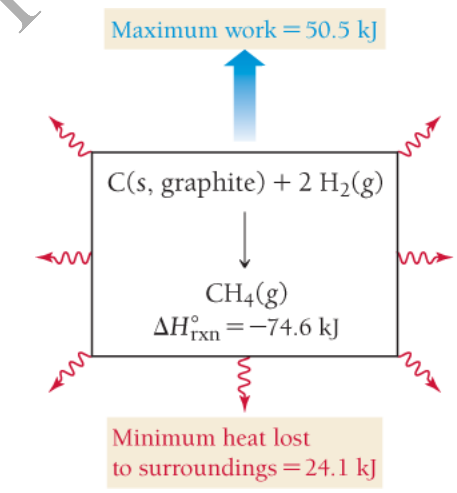
Consider the reaction between carbon and hydrogen occurring at 25 °C:

$$\begin{aligned} &C(s,\mathrm{graphite}) + 2H_2\,(g) \rightarrow CH_4\,(g) \\ \Delta H^o_{\mathrm{rxn}} &= -74.6\mathrm{kJ} \\ \Delta S^o_{\mathrm{rxn}} &= -80.8\mathrm{J/K} \\ \Delta G^o_{\mathrm{rxn}} &= -50.5\mathrm{kJ} \end{aligned}$$

The reaction is exothermic and gives off 74.6 kJ of heat energy. However, the maximum amount of energy available for useful work is only 50.5 kJ (Figure 18.7). Why? We can see that the change in entropy of the *system* is negative. Nevertheless, the reaction is spontaneous. This is possible only if some of the emitted heat goes to increase the entropy of the surroundings by an amount sufficient to make the change in entropy of the *universe* positive. The amount of energy available to do work (the free energy) is what remains after accounting for the heat that must be lost to the surroundings.

Figure 18.7 Free Energy

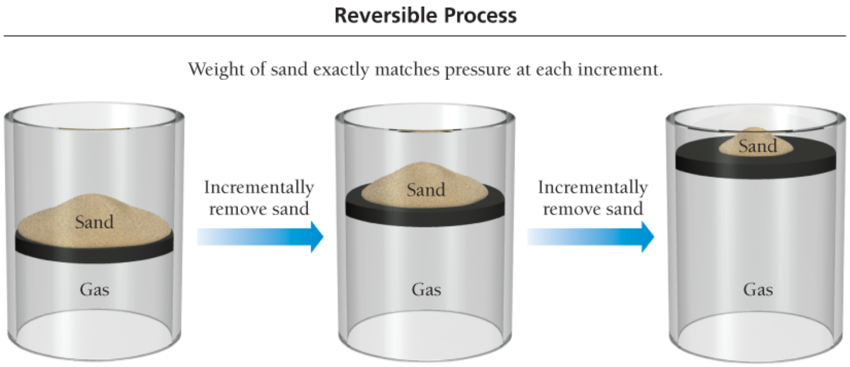
Although the reaction produces 74.6 kJ of heat, only a maximum of 50.5 kJ is available to do work. The rest of the energy is lost to the surroundings.



The change in free energy for a chemical reaction represents a *theoretical limit* as to how much work can be done by the reaction. In a *real* reaction, the amount of energy available to do work is even *less* than $\Delta G^o_{\mathrm{rxn}}$ because additional energy is lost to the surroundings as heat. The only reactions that reach the theoretical limit are reversible reactions (see Section 18.4 for the definition of reversible processes). A reversible chemical reaction occurs infinitesimally slowly, and the free energy is drawn out in infinitesimally small increments that exactly match the amount of energy that the reaction is producing during that increment (Figure 18.8).

Figure 18.8 A Reversible Process

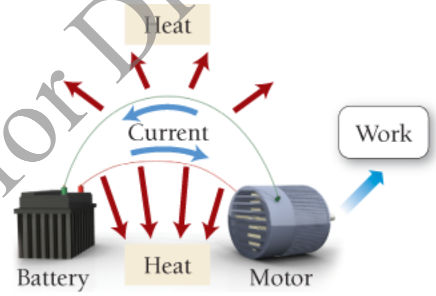
In a reversible process, the free energy is drawn out in infinitesimally small increments that exactly match the amount of energy that the process is producing in that increment. In this case, grains of sand are removed one at a time, resulting in a series of small expansions in which the weight of sand exactly matches the pressure of the expanding gas. This process is close to reversible—each sand grain would need to have an infinitesimally small mass for the process to be fully reversible.


Reversible Process
Weight of sand exactly matches pressure at each increment.
Sand
Gas
Incrementally remove sand
Sand
Gas
Incrementally remove sand
Sand
Gas

All real reactions are irreversible and therefore do not achieve the theoretical limit of available free energy. Let's return to the discharging battery from the opening section of this chapter as an example of this concept. A battery contains chemical reactants configured in such a way that, upon spontaneous reaction, they produce an electrical current. We can harness the free energy released by the reaction to do work. For example, an electric motor can be wired to the battery. Flowing electrical current makes the motor turn (Figure 18.9).

Figure 18.9 Energy Loss in a Battery

When current is drawn from a battery to do work, some energy is lost as heat due to resistance in the wire. Consequently, the quantity of energy required to recharge the battery is more than the quantity of work done.



Because of the resistance in the wire, the flowing electrical current also produces some heat, which is lost to the surroundings and is not available to do work. The amount of free energy lost as heat can be decreased by slowing down the rate of current flow. The slower the rate of current flow, the less free energy is lost as heat and the more is available to do work. However, only in the theoretical case of infinitesimally slow current flow is the maximum amount of work (equal to ΔG^o_{rxn}) done. Any real rate of current flow results in some loss of energy as heat. This lost energy is the "heat tax" that we discussed in the opening section of this chapter. Recharging the battery necessarily requires more energy than was obtained as work because some of the energy was lost as heat. In other words, during discharging and recharging, the battery has gone through a cycle in which it returns to its original (charged) state. However, the surroundings have gained some heat during the process, and the entropy of the surroundings has increased (which makes the process spontaneous). Any real (or irreversible) cyclical process such as this suffers the same fate—the system may return to its original state, but the surroundings do not, resulting in the permanent dispersal of energy to the surroundings.

If the change in free energy of a chemical reaction is positive, then ΔG^o_{rxn} represents *the minimum amount of* *energy required to make the reaction occur*. Again, $\Delta G^{\circ}_{\mathrm{rxn}}$ represents a theoretical limit. Making a real nonspontaneous reaction occur always requires more energy than the theoretical limit.