SECTION EXERCISES

13.3.1 Of the following pairs, which has the greater entropy? Explain why in each case. (a) 1 g of dew or 1 g of frost; (b) 1 mol of gaseous hydrogen atoms or 0.5 mol of gaseous hydrogen molecules; (c) "Perfect" diamond or flawed diamond, each $^1/_4$ carat; (d) 5 mL of liquid ethanol at 0 °C or 5 mL of liquid ethanol at 50 °C.

13.3.2 Explain the following differences in entropies in molecular terms (substances at standard conditions unless otherwise noted):
  (a) 1 mol of O_2 has less entropy than 1 mol of O_3.
  (b) 3 mol of O_2 has more entropy than 2 mol of O_3.
  (c) 1 mol of I_2 has less entropy than 1 mol of O_2.
  (d) 1 mol of $HCl_{(aq)}$ in concentrated solution (12 M) has less entropy than 1 mol of $HCl_{(aq)}$ in dilute solution (0.100 M).

13.3.3 Draw molecular pictures to illustrate your answers to part b of Section Exercise 13.3.1 and part b of Section Exercise 13.3.2.

13.3.4 Compute the standard entropy change for the following reaction:

$$12\ NH_{3\ (g)} + 21\ O_{2\ (g)} \rightarrow 8\ HNO_{3\ (g)} + 4\ NO_{(g)} + 12\ H_2O_{(l)}$$

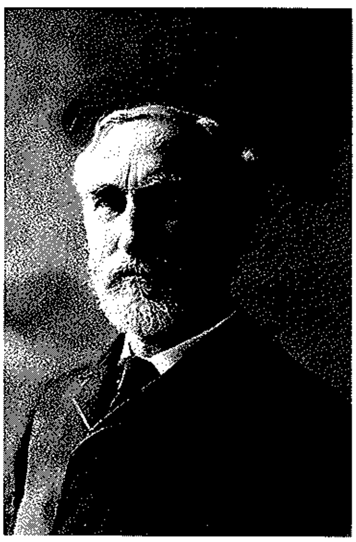
13.4 SPONTANEITY AND FREE ENERGY

The second law of thermodynamics states that the entropy of the universe must increase during a spontaneous process. Consequently, the sign of $\Delta S_{universe}$ must be positive for any chemical process to be spontaneous. To determine whether a particular chemical process is spontaneous, we must calculate the value of $\Delta S_{universe}$ that accompanies the process. Unfortunately, this is not practical for most processes. It is usually possible to calculate the entropy change for a *system*, but the *surroundings* may undergo complicated changes of state for which ΔS cannot be determined easily. The surroundings include virtually all the universe, and keeping track of changes in the universe is a tricky matter. It would be much more convenient if we had some way to determine the direction of spontaneous change using *just the system*, not the surroundings.

No such criterion can be applied to *all* processes. If we restrict the conditions sufficiently, however, there is a state function whose change for the *system* predicts spontaneity. This new state function is called **free energy (*G*)** and is defined by Equation 13-6:

$$\text{Free energy} = G = H - TS \qquad (13\text{-}6)$$

where H is enthalpy, T is temperature, and S is entropy.*



* The American J. Willard Gibbs introduced free energy into chemical thermodynamics. A professor of mathematical physics at Yale University from 1871 until his death in 1903, Gibbs was the first to show how the laws of thermodynamics apply to chemical processes. Because Gibbs published in a little-known American journal at a time when most scientific work was being done in Europe, his outstanding contributions to chemical thermodynamics were not recognized until 13 years after they were first published. In the 1890s, however, his 400 pages of elegant mathematical development of this subject were translated into French and German, and European scientists quickly recognized the greatness of his work. To commemorate Gibbs, free energy is symbolized G and is sometimes called *Gibbs free energy*.

he definition of free energy gives us an equation that relates the change in free gy for any system to other thermodynamic changes:

$$\Delta G_{sys} = \Delta H_{sys} - \Delta(TS)_{sys}$$

se ΔG_{sys} to predict spontaneity, we must relate this equation to the total entropy ge of the universe. This cannot be done unless some restrictions are placed on onditions. First, the process must occur at *constant temperature*. This lets us e $\Delta(TS)_{sys}$ to ΔS_{sys}:

$$\Delta(TS) = (TS)_{final} - (TS)_{initial} = T(S_f - S_i) = T\Delta S_{sys}$$

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} \qquad \text{(constant } T\text{)} \qquad \textbf{(13-7)}$$

ext, the *enthalpy* change for the system can be related to the *entropy* change for urroundings by restricting the conditions to *constant pressure*. Recall that quals q when P is constant:

$$\Delta H_{sys} = q_{sys} \qquad \text{(constant } P\text{)}$$

ember also that the heat flow for a system is always equal in magnitude but site in sign to the heat flow of the surroundings:

$$q_{sys} = -q_{surr} \quad \textit{and} \quad \Delta H_{sys} = -q_{surr}$$

ermore, we have already restricted the process to constant temperature, so eat flow of the surroundings measures the entropy change of the surroundings. is:

$$\frac{q_{surr}}{T} = \Delta S_{surr} \quad \textit{and} \quad q_{surr} = T\Delta S_{surr}$$

bining these equalities gives an equation that relates ΔH_{sys} and ΔS_{surr}:

$$\Delta H_{sys} = -T\Delta S_{surr} \text{ (constant } P \text{ and } T\text{)}$$

we substitute this result into Equation 13-7:

$$\Delta G_{sys} = -T\Delta S_{surr} - T\Delta S_{sys} = -T(\Delta S_{surr} + \Delta S_{sys})$$

ly, because $\Delta S_{surr} + \Delta S_{sys} = \Delta S_{universe}$:

$$\Delta G_{sys} = -T\Delta S_{universe} \qquad \text{(constant } T \text{ and } P\text{)}$$

is a powerful result because it states that the free energy of the *system* changes way that mirrors the entropy change of the *universe* in any process that occurs at tant T and P. By defining a new function and imposing some restrictions, we found a way to use properties of a system to determine whether a process is aneous. Because T is always positive, and $\Delta S_{universe}$ is positive for any sponta- s process, ΔG_{sys} is *negative* for spontaneous processes under constant T and P tions. Although the restrictions of constant T and P are stringent, they are met any important chemical processes. For example, the human body has a constant 37 °C. Any biochemical reaction that occurs in the body occurs under conditions hich the immediate surroundings are at constant T and P.

Because free energy is a state function, its values can be tabulated for use in chemical calculations. As with standard heats of formation, the **standard molar free energy of formation** (**$\Delta G°_f$**) for any substance is defined to be the change of free energy when 1 mol of that substance is formed from elements in their standard states. Following the same reasoning we used for enthalpy changes, we obtain an equation for calculating the free energy change for any chemical reaction:

$$\Delta G°_{\text{reaction}} = \Sigma \text{ coeff}_p \, \Delta G°_f(\text{products}) - \Sigma \text{ coeff}_r \, \Delta G°_f(\text{reactants}) \quad (13\text{-}8)$$

The form of Equation 13-8 should be familiar because it is analogous to Equation 12-11 for reaction enthalpies and Equation 13-5 for reaction entropies.

The standard free energy change for a reaction can also be calculated from $\Delta H°$ and $\Delta S°$ for the reaction by making use of Equation 13-7 under standard conditions:

$$\Delta G° = \Delta H° - T\Delta S° \quad (13\text{-}9)$$

Either of these equations can be used to find standard free energy changes. Which equation we use depends on the available data. Sample Problem 13-6 illustrates both types of calculations.

SAMPLE PROBLEM 13-6 FREE ENERGY OF REACTION

Find the standard free energy change for the acrylonitrile synthesis discussed in Sample Problem 13-5.

METHOD: There are two ways to calculate $\Delta G°_{rxn}$. The first method uses standard free energies of formation and Equation 13-8. The second method uses Equation 13-9 and the values of $\Delta H°$ and $\Delta S°$ calculated earlier. We perform both calculations to show they give the same result. First, recall the balanced equation for the acrylonitrile synthesis:

$$2\,C_3H_{6\,(g)} + 2\,NH_{3\,(g)} + 3\,O_{2\,(g)} \rightarrow 2\,C_3H_3N_{\,(l)} + 6\,H_2O_{\,(l)}$$

(a) Using $\Delta G°_f$ values from Appendix E:

$$\Delta G°_{rxn} = [(6\text{ mol})(-237.13\text{ kJ/mol}) + (2\text{ mol})(208.6\text{ kJ/mol})] -$$
$$[(3\text{ mol})(0\text{ kJ/mol}) + (2\text{ mol})(-16.45\text{ kJ/mol}) + (2\text{ mol})(74.62\text{ kJ/mol})]$$
$$\Delta G°_{rxn} = -1122\text{ kJ}$$

(b) Using the results of Sample Problem 13-5:

$$\Delta G°_{rxn} = \Delta H° - T\Delta S°$$
$$\Delta G°_{rxn} = [-1318\text{ kJ}] - [(298\text{ K})(-659\text{ J/K})(10^{-3}\text{ kJ/J})] = -1122\text{ kJ}$$

The large negative $\Delta G°_{rxn}$ found in this problem indicates that the production of acrylonitrile is highly spontaneous under standard conditions.

Pay close attention to units when using Equation 13-9. The values of $\Delta H°$ and $\Delta G°$ are usually given in kJ or kJ/mol, but entropies are usually expressed in J/K or J/mol K. Thus entropies must be multiplied by 10^{-3} kJ/J before adding the two terms.

CHANGE IN FREE ENERGY UNDER NONSTANDARD CONDITIONS

Standard conditions refer to unit concentrations and 298 K, but chemical reactions occur at many different concentrations and temperatures. To use ΔG as a measure of spontaneity under nonstandard conditions, we must understand how free energy depends on temperature and concentration. First, Equation 13-9 is valid at any temperature as long as the temperature is *constant*. However, to apply the equation to a temperature different from 298 K, we must have the appropriate values for ΔH_{rxn} and ΔS_{rxn}.

Chemical substances become more disordered as temperature increases. These changes in entropy as a function of temperature can be calculated, but the techniques require calculus. Fortunately, temperature affects the entropies of reactants and products in the same way. In other words, changes in the disorder of the reactants are often almost the same as changes in the disorder of the products. As a result, the temperature effect on the *net* entropy change of a reaction is usually small. In fact, in most cases we can assume that ΔS_{rxn} is independent of temperature.

The temperature variation of the change in entropy during a reaction (ΔS_{rxn}) can often be neglected, but temperature variations in *absolute* entropies of individual substances (S_{molar}) are *never* negligible.

Recall that ΔH_{rxn} also does not change rapidly with temperature. As a result, we can estimate free energy changes at temperatures other than 298 K by assuming that standard enthalpies and entropies at 298 K also apply at any other temperature:

$$\Delta G^\circ_{rxn,T} \cong \Delta H^\circ_{rxn,298} - T\Delta S^\circ_{rxn,298} \qquad \textbf{(13-10)}$$

In Equation 13-10 we use the superscript "o" to denote standard *concentrations* (1 atm, 1 M) of all reagents, even though *temperature* is nonstandard ($T \neq$ 298 K). When the temperature is not specified, "o" means 298 K and standard concentrations. Therefore ΔG° means "free energy change at 298 K, all reagents at unit concentration," whereas ΔG°_{500} means "free energy change at 500 K, all reagents at unit concentration."

An immediate consequence of Equation 13-10 is that any reaction with a large ΔS° is very sensitive to temperature. Sample Problem 13-7 shows a simple example.

SAMPLE PROBLEM 13-7 TEMPERATURE AND SPONTANEITY

Dinitrogen tetroxide can decompose into two molecules of nitrogen dioxide:

$$N_2O_{4\,(g)} \rightarrow 2\ NO_{2\,(g)}$$

(a) Show that this reaction is not spontaneous under standard conditions.
(b) Find the temperature at which the reaction becomes spontaneous at standard pressures.

METHOD: The key word here is *spontaneous,* which suggests that we need to work with free energies to solve this problem. Recall that the criterion for spontaneity is $\Delta G_{rxn} < 0$. We must find this free energy change at standard temperature. Then, using Equation 13-10, we can calculate the temperature that makes $\Delta G_{rxn} < 0$.

(a) Use Equation 13-8 and values for ΔG°_f from Appendix E to show that the decomposition reaction is not spontaneous under standard conditions:

$$\Delta G^\circ = (2\ \text{mol})(51.31\ \text{kJ/mol}) - (1\ \text{mol})(97.89\ \text{kJ/mol}) = 4.73\ \text{kJ}$$

The positive value for ΔG° indicates that this reaction is *not* spontaneous under standard conditions. In fact, the calculation tells us that the reaction will be spontaneous in the opposite direction. Under standard conditions, NO_2 reacts to form N_2O_4:

$$2\ NO_{2\,(g)} \rightarrow N_2O_{4\,(g)} \qquad \Delta G^\circ = -4.73\ \text{kJ}$$

(b) Use Equation 13-10 to find the temperature at which N_2O_4 decomposition becomes spontaneous when the partial pressures of both gases are 1 atm:

$$\Delta G^\circ_{rxn,T} \cong \Delta H^\circ_{rxn,298} - T\Delta S^\circ_{rxn,298}$$

As temperature changes, ΔG must become zero before it becomes negative. We must find the temperature at which $\Delta G = 0$. Begin by calculating ΔH° and ΔS° using tabulated data:

$$\Delta H^\circ = (2\ \text{mol})(33.18\ \text{kJ/mol}) - (1\ \text{mol})(9.16\ \text{kJ/mol}) = 57.2\ \text{kJ}$$

$$\Delta S^\circ = (2\ \text{mol})(240.1\ \text{J/mol K}) - (1\ \text{mol})(304.3\ \text{J/mol K}) = 175.9\ \text{J/K}$$

$$\Delta S^\circ = 0.1759\ \text{kJ/K} \qquad \Delta H^\circ = 57.2\ \text{kJ}$$

Set ΔG equal to zero and rearrange the equation to solve for temperature:

$$\Delta G = \Delta H^\circ - T\Delta S^\circ = 0 \quad or \quad T\Delta S^\circ = \Delta H^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{57.2\ \text{kJ}}{0.1759\ \text{kJ/K}} = 325\ \text{K}$$

At 325 K, $\Delta G^\circ = 0$. Therefore at all temperatures greater than 325 K, ΔG° is negative, and decomposition of N_2O_4 is spontaneous at 1 atm partial pressures.

CHANGING CONCENTRATION

The substances participating in a chemical reaction typically are at concentrations different from 1 M or pressures different from 1 atm. For example, a biochemist who wants to know what processes are spontaneous under physiological conditions will find that the substances dissolved in biological fluids are rarely at 1 M concentration. How does change in free energy vary with changes in molarity and pressure? Recall that enthalpy is virtually independent of concentration but that entropy obeys Equation 13-4.

To see how entropy affects ΔG, consider the synthesis of ammonia carried out in a pressurized reactor containing N_2, H_2, and NH_3 at partial pressures *(p)* different from 1 atm:

$$N_{2\,(g)} + 3\,H_{2\,(g)} \rightarrow 2\,NH_{3\,(g)}$$

Equation 13-4 gives the molar entropy of each gas as a function of its partial pressure:

$$S = S° - R\,ln\,c = S° - R\,\;ln\,p$$

$$\textit{For example, } S(N_2) = S°(N_2) - R\,ln\{p(N_2)\}$$

The entropy change for the reaction is the difference in entropy between products and reactants, obtained by multiplying each corrected entropy by the appropriate stoichiometric coefficient:

$$\Delta S_{rxn} = 2\,S(NH_3) - 3\,S(H_2) - S(N_2)$$

Now we substitute each of the corrected entropies:

$$\Delta S_{rxn} = 2[S°(NH_3) - R\,ln\{p(NH_3)\}] - 3[S°(H_2) - R\,ln\{p(H_2)\}] - [S°(N_2) - R\,ln\{p(N_2)\}]$$

Next, rearrange the equation so that all the logarithmic terms are together:

$$\Delta S_{rxn} = 2\,S°(NH_3) - 3\,S°(H_2) - S°(N_2) - 2\,R\,ln\{p(NH_3)\} + 3\,R\,ln\{p(H_2)\} + R\,ln\{p(N_2)\}$$

The first three terms are the standard entropy change for the reaction, allowing us to simplify:

$$\Delta S_{rxn} = \Delta S°_{rxn} - 2\,R\,ln\{p(NH_3)\} + 3\,R\,ln\{p(H_2)\} + R\,ln\{p(N_2)\}$$

The properties of logarithms can be used to combine the *ln* terms. First, $x\,ln\,y = ln\,y^x$, giving:

$$2\,R\,ln\{p(NH_3)\} = R\,ln\{p^2(NH_3)\} \quad \text{and} \quad 3\,R\,ln\{p(H_2)\} = R\,ln\{p^3(H_2)\}$$

With these changes, the equation becomes:

$$\Delta S_{rxn} = \Delta S°_{rxn} - R\,[ln\{p^2(NH_3)\} - ln\{p^3(H_2)\} - ln\{p(NH_3)\}]$$

A second logarithmic property, $(ln\,x - ln\,y) = ln(x/y)$, lets us put all the logarithmic terms into a single ratio:

$$\Delta S_{rxn} = \Delta S^{\circ}_{rxn} - R\, ln\left[\frac{p^2(NH_3)}{p(N_2)\, p^3(H_2)}\right]$$

Note that the pressure ratio has product concentrations raised to their stoichiometric coefficients in the numerator and reactant concentrations raised to their stoichiometric coefficients in the denominator. The form of this equation applies to all reactions, not just the synthesis of ammonia. Thus for the general reaction,

$$aA + bB \rightarrow cC + dD$$

the entropy change is:

$$\Delta S_{rxn} = \Delta S^{\circ}_{rxn} - R\, ln\left[\frac{[C]^c[D]^d}{[A]^a[B]^b}\right]$$

The ratio in the logarithmic term is called the **concentration quotient *(Q)*:**

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = Q \qquad \textbf{(13-11)}$$

A concentration quotient always contains the concentrations that are variable, that is, those of gases and solutes. The concentrations must be expressed relative to standard conditions, so gas concentrations are in atm, whereas solute concentrations are in mol/L.

The entropy change for a reaction under nonstandard concentrations can be expressed in terms of the standard entropy change and Q:

$$\Delta S_{rxn} = \Delta S^{\circ}_{rxn} - R\, ln\, Q$$

This allows us to write an equation for the free energy change when concentrations are nonstandard:

$$\Delta G_{rxn} = \Delta H^{\circ}_{rxn} - T(\Delta S^{\circ}_{rxn} - R\, ln\, Q)$$

Notice that $\Delta H^{\circ} - T\Delta S^{\circ}$ is just ΔG°, so this equation reduces to Equation 13-12:

$$\Delta G_{rxn} = \Delta G^{\circ}_{rxn} + RT\, ln\, Q \qquad \textbf{(13-12)}$$

An immediate consequence of Equation 13-12 is that the direction of spontaneity of a reaction depends heavily on the concentrations of reactants and products. Product concentrations appear in the numerator of Q, so when the concentration of a product increases, $ln\, Q$ increases, as well. Increasing the $ln\, Q$ term makes ΔG less negative, so a reaction becomes less spontaneous as product concentrations increase. Conversely, reactant concentrations appear in the denominator of Q, so increasing the concentration of a reactant also increases $ln\, Q$, which in turn makes ΔG more negative. Thus a reaction becomes more spontaneous as reactant concentrations increase.

If we have a reaction that is not spontaneous at unit concentrations, we can try to force it to go forward by increasing the concentrations of reactants or by removing products as quickly as they form. If a reaction has a very positive ΔG°_{rxn}, however, it may not be possible to change the value of Q sufficiently to make $\Delta G_{rxn} < 0$. Remember that the term $ln\, Q$ changes much more slowly than Q itself. A 10-fold change in Q, for instance, only changes $ln\, Q$ by a factor of 2.3. Nonetheless, reactions that are almost spontaneous under standard conditions can be driven forward by making appropriate changes in concentration. Sample Problem 13-8 shows how this is done.

SAMPLE PROBLEM 13-8 EFFECT OF CONCENTRATION ON SPONTANEITY

The decomposition of dinitrogen tetroxide follows:

$$N_2O_{4\,(g)} \rightarrow 2\ NO_{2\,(g)}$$

(a) Find the minimum partial pressure of N_2O_4 at which the reaction is spontaneous if $p(NO_2) = 1$ atm and $T = 298$ K.

(b) Find the maximum partial pressure of NO_2 at which the reaction is spontaneous if $p(N_2O_4) = 1$ atm and $T = 298$ K.

METHOD: This is a two-part problem, so each part should be solved independently. Both parts require us to relate change in free energy to concentrations, so we must use Equation 13-12:

$$\Delta G = \Delta G^\circ + RT\, ln\, Q = \Delta G^\circ + RT\, ln\left[\frac{p^2(NO_2)}{p(N_2O_4)}\right]$$

(a) We are asked to find the partial pressure of N_2O_4 that will make the decomposition spontaneous when $T = 298$ K and p of $NO_2 = 1$ atm. The value of ΔG must be zero before it can become negative. Therefore to find the threshold pressure of N_2O_4 that makes the decomposition spontaneous, we set $\Delta G = 0$ and $p(NO_2) = 1$ atm, and then rearrange to solve for the partial pressure of N_2O_4:

The mol unit in the value of ΔG° refers to "per mole of reaction" and comes from the concept of the *reaction unit*. The mol unit in ΔG° is included in the calculation to cancel the mol unit in *R*. For a review of the reaction unit, see Section 12.4.

$$0 = \Delta G^\circ + RT\, ln\left[\frac{(1\ \text{atm})^2}{p(N_2O_4)}\right]$$

$$ln\left[\frac{(1\ \text{atm})^2}{p(N_2O_4)}\right] = -\frac{\Delta G^\circ}{RT} = \frac{4.73 \times 10^3\ \text{J/mol}}{(8.314\ \text{J/mol K})(298\ \text{K})} = -1.909$$

$$\frac{(1\ \text{atm})^2}{p(N_2O_4)} = e^{-1.909} = 0.1482 \quad and \quad p(N_2O_4) = 1/0.1482 = 6.75\ \text{atm}$$

Recall that when $y = lnx$, $x = e^y$, where e is the basis for natural logarithms.

This decomposition is spontaneous as long as the pressure of N_2O_4 is greater than 6.75 atm. As always, we have to be careful about units. Standard free energy was converted to joules to use the appropriate value of the gas constant *(R)* in J/mol K. Our final number is an antilogarithm, which has no dimensions, but the pressure must have the same units as the standard state for gases, which is atmospheres.

(b) We are asked to find the maximum partial pressure of NO_2 below which the decomposition is spontaneous when $T = 298$ K and p of $N_2O_4 = 1$ atm. The procedure is analogous to the one we just developed. You should be able to show that the desired pressure is 0.385 atm.

This problem shows that a reaction with a small positive ΔG° can be made spontaneous by relatively small changes in concentrations.

If neither temperature nor concentrations are at their standard values, free energy calculations must be done in two steps. First, correct for temperature to obtain ΔG°_T using Equation 13-10. Second, use that result in Equation 13-12 to complete the calculation of ΔG.

INFLUENCING SPONTANEITY

Suppose we want to design a particular chemical synthesis, but we find that the reaction has a positive value for ΔG°. The thermodynamic calculation indicates that the reaction is spontaneous in the wrong direction under *standard* conditions, but this does not prevent it from occurring under *all* conditions. What can we do to make the reaction go in the desired direction?

Sample Problem 13-8 illustrates that changing the concentration quotient changes the entropy change of the system. In particular, reducing the pressure of NO_2 below 0.386 atm or increasing the pressure of N_2O_4 above 6.71 atm would cause spontaneous decomposition of N_2O_4, even though this reaction is not spontaneous under standard conditions. As with this gas-phase reaction, a reaction in liquid solution may be induced to proceed spontaneously by increasing the concentrations of reactants or by reducing the concentrations of products.

Changing the temperature of the system is another way to influence the spontaneity of a reaction. The equation for ΔG has two parts, ΔH and $T\Delta S$, which can work together or in opposition:

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

A *positive* ΔS° promotes spontaneity because it makes ΔG° more negative. This reflects the fact that a positive ΔS° means the system becomes more disordered during the reaction. A *negative* ΔH° promotes spontaneity, as well, because it also makes ΔG° more negative. This reflects the fact that the surroundings become more disordered when a reaction releases energy. Thus a reaction that has a positive ΔS° and a negative ΔH° is spontaneous at any T.

The combustion of propane is an example of a reaction that is spontaneous at all temperatures:

$$C_3H_{8\,(g)} + 5\ O_{2\,(g)} \rightarrow 3\ CO_{2\,(g)} + 4\ H_2O_{\,(g)}$$

$$\Delta H^\circ = -897\ \text{kJ} \qquad \Delta S^\circ = +145\ \text{J/K}$$

The products of this reaction are more disordered than the reactants, and the reaction releases energy. Consequently, ΔG° is negative at all T, so the reverse reaction cannot be made spontaneous by altering T.

By the same reasoning, a *negative* ΔS° and a *positive* ΔH° oppose spontaneity, so a reaction that meets these criteria is nonspontaneous regardless of T. The system and its surroundings would experience decreases in entropy if such a process were to occur, and this would violate the second law of thermodynamics.

A reaction that has the same sign for ΔS° and ΔH° will be spontaneous at some temperatures but nonspontaneous at others. At low temperature, ΔS° is multiplied by a small value for T, so at sufficiently low temperature, ΔH° contributes more to ΔG° than $T\Delta S^\circ$. At high temperature, ΔS° is multiplied by a large value for T, so at sufficiently high temperature, ΔS° contributes more to ΔG° than ΔH°.

Reactions with positive ΔH° and positive ΔS° are favored by entropy but disfavored by enthalpy. Such reactions are spontaneous at high T, where the $T\Delta S^\circ$ term dominates ΔG°. The reactions are nonspontaneous at low T, where the ΔH° term dominates ΔG°. These reactions are spontaneous at high temperature by virtue of the increased disorder in the system.

The opposite situation holds for reactions that have negative values for ΔH° and ΔS°. These reactions are spontaneous at low T by virtue of the increased disorder in the surroundings. The favorable ΔH° dominates ΔG° as long as T does not become too large. At high T, however, the unfavorable ΔS° dominates ΔG°, and the reaction is no longer spontaneous. The effects of temperature on spontaneity are summarized in Table 13-3.

TABLE 13-3 THE INFLUENCE OF TEMPERATURE ON SPONTANEITY

ΔH°	ΔS°	ΔG° (HIGH T)	ΔG° (LOW T)	SPONTANEOUS
−	+	−	−	All T
+	−	+	+	No T
+	+	−	+	High T
−	−	+	−	Low T

ΔH°, Standard enthalpy change; ΔS°, standard entropy change; ΔG°, standard change in free energy.

Calcium sulfate, the solid used to absorb water in desiccators, provides an example of this sensitivity to temperature. Anhydrous calcium sulfate absorbs water vapor from the atmosphere to give the hydrated salt. The reaction has a negative ΔS° because the system becomes more ordered when gaseous water molecules move into the solid state. The reaction also has a negative ΔH° because of the coulombic forces of attraction between the ions of the salt and the polar water molecules.

$$CaSO_{4\,(s)} + 2\,H_2O_{\,(g)} \rightarrow CaSO_4{\cdot}2H_2O_{\,(s)}$$

$$\Delta H^\circ = -104.9\ \text{kJ} \qquad \Delta S^\circ = -290.2\ \text{J/K}$$

At 300 K, the favorable ΔH° contributes more to ΔG° than the unfavorable ΔS°:

$$\Delta G^\circ_{300\,K} = (-104.9\ \text{kJ}) - (300\ \text{K})(-290.2\ \text{J/K})(10^{-3}\ \text{kJ/J}) = -17.8\ \text{kJ}$$

Thus at room temperature, anhydrous calcium sulfate acts as a "chemical sponge," trapping water vapor spontaneously to form calcium sulfate dihydrate.

The calcium sulfate in a desiccator is effective at removing water vapor only as long as some anhydrous salt remains. When all the anhydrous salt has been converted to the dihydrate, the desiccator can no longer maintain a dry atmosphere. Fortunately, the thermodynamics of this reaction makes it possible to regenerate the drying agent. At 450 K, ΔS° contributes more to ΔG° than does ΔH°:

$$\Delta G^\circ_{450\,K} = (-104.9\ \text{kJ}) - (450\ \text{K})(-290.2\ \text{J/K})(10^{-3}\ \text{kJ/J}) = +25.7\ \text{kJ}$$

At this T, the reverse reaction is spontaneous. Calcium sulfate dihydrate can be converted to anhydrous calcium sulfate by placing it in a drying oven at 450 K. Then it can be cooled and returned to a desiccator, ready once more to act as a chemical sponge for water.

SECTION EXERCISES

13.4.1 Estimate ΔG° for the formation of gaseous water at $T = 373$ K.

13.4.2 Using Sample Problem 13-8, find the minimum partial pressure of N_2O_4 at which decomposition of N_2O_4 occurs, if T is 400 K and p of $NO_2 = 0.50$ atm.

13.4.3 Does a temperature exist at which the water formation reaction becomes nonspontaneous under standard pressure? If so, compute this T. If not, explain why in molecular terms.

13.5 SOME APPLICATIONS OF THERMODYNAMICS

NITROGEN FIXATION

The distribution of nitrogen between the Earth's crust and the atmosphere is very uneven. In the crust, nitrogen is present at the level of 19 parts per million (ppm) by mass, four orders of magnitude less than oxygen (4.55×10^5 ppm) and silicon (2.72×10^5 ppm). In contrast, 80% of the atmosphere is molecular nitrogen. Paradoxically, nitrogen is absolutely essential for all life, but the sea of atmospheric nitrogen is virtually inaccessible to higher life forms. Most biochemical systems lack the ability to break the strong triple bond between the nitrogen atoms in N_2. Molecular nitrogen must be converted to some other form, usually ammonia (NH_3) or nitrate (NO_3^-), before most life forms can incorporate nitrogen atoms into their biochemical molecules. This process, known as **nitrogen fixation,** is accomplished by various algae and bacteria, including a special group of bacteria that live in the roots of certain leguminous plants.

:N≡N:
Bond energy = 940 kJ/mol

The thermodynamics of nitrogen chemistry helps explain why nitrogen is so abundant in our atmosphere and yet remains inaccessible to most life forms. Table 13-4 shows that most of the abundant elements react with molecular oxygen under standard conditions. This is why many of the elements are encountered in the Earth's crust as their oxides. Nitrogen, however, is resistant to oxidation, as shown by the positive $\Delta G°_f$ for NO_2.

Because of their resistance to chemical attack, nitrogen atoms are not "locked up" in any solid or liquid substances as are other elements, such as Si, Al, Fe, and H. On the Earth the most stable form of the element nitrogen is a gaseous diatomic molecule. Therefore the element nitrogen is concentrated in the Earth's gaseous atmosphere even though it is only a trace element in overall abundance.

Every breath of air we take is 80% nitrogen, but our bodies must rely on the nitrogen found in the proteins we eat to supply the elemental nitrogen required for biosynthesis. In the plant kingdom, the most important sources of nitrogen are NH_3 and the ammonium cation (NH_4^+).

TABLE 13-4 SURFACE-ABUNDANT ELEMENTS AND THEIR OXIDES

ELEMENT	% BY MASS	OXIDE	$\Delta G°_f$ (kJ/mol)
O	49.1	O_2	0
Si	26.1	SiO_2	−856
Al	7.5	Al_2O_3	−1376
Fe	4.7	Fe_3O_4	−1013
Ca	3.4	CaO	−604
Na	2.6	Na_2O	−377
K	2.4	KO_2	−239
Mg	1.9	MgO	−570
H	0.88	H_2O	−237
Ti	0.58	TiO_2	−885
Cl	0.19	Cl_2O	+98
C	0.09	CO_2	−394
N	**<0.1**	**NO_2***	**+51**

*Several other oxides of nitrogen exist. All have even more positive free energies of formation than NO_2.

According to Table 13-4, chlorine (Cl) is also resistant to oxidation. Unlike nitrogen, however, chlorine reacts spontaneously with metals to generate such salts as NaCl and $MgCl_2$. Thus among abundant elements on Earth, nitrogen is uniquely stable in its elemental form.