Thermodynamics
AP Review Material
Chapter 19

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

Entropy is related to the number of different ways in which a system can arrange the particles within the system and the number of energy levels those particles have available to them. A system that has two particles and three energy states will have less entropy than the same two particles in a system that has five energy levels. Similarly, if we divide the volume of the system into eight units, those two particles can arrange themselves in 64 different ways (8 × 8) If the volume of the system is

doubled, we will have 16 volume units the same size as before. The number of different arrangements of our particles is now 256 (16 × 16). That represents an increase in entropy. These examples must be extrapolated to a very large number of infinitesimally small volume units with extremely large numbers of particles (atoms and molecules) and a correspondingly large number of possible energies to describe real systems. However, the conclusions are relatively straightforward. An increase in the number of particles increases entropy, an increase in volume increases entropy, changing state (e.g., from liquid to gas) increases entropy, and so on. In fact, these definitions are a more precise way to define how randomly the particles in a system can be arranged.

We can visualize that water molecules in ice are constrained to the crystal lattice and have virtually no freedom to move and occupy a different volume unit. A water molecule in a liquid can move from one volume unit to another, but it does so rather slowly and is strongly influenced by other water molecules. Finally, in the gas phase the water molecule rapidly moves from one volume unit to another. Therefore we say that water in ice has the least entropy, whereas water in the gas phase has the most entropy. If a chemical reaction produces a gas such as H_2, the increase in possible positions and kinetic energies compared to that in liquids or solids leads to the conclusion that the entropy increases in such a reaction.

Entropy is assigned the symbol, S, and has units of J °C^{-1}. Standard entropy is based on the mole and is written as $S°$ with units of J °C^{-1} mol^{-1}. Values for $S°$ are tabulated in Appendix 3. It should be noted that standard entropy values for elements are not zero as they are for standard heat of formation, $\Delta H_f°$, and standard free energy, $\Delta G_f°$.

Unlike other thermodynamic quantities, such as energy, E, and enthalpy, H, the actual value for the entropy, S, of a substance can be determined. From fundamental principles, a perfect crystal at absolute zero (0 K or −273.16°C) has zero entropy since all motion ceases and there is perfect order. As the temperature of 1 mole of a chemical is increased from absolute zero, the entropy increases and the standard entropy is defined as

$$S° = \frac{q_{rev}}{T}$$

(12.30)

In this equation T represents the temperature in Kelvins, and q_{rev} is the heat added to raise the temperature very slowly from absolute zero up to T. Heat, q, is not a state function, and it seems that S should not be a state function either. However, if heat is always added in a carefully defined manner, the results will always be the same. This carefully defined path is called a **reversible process,** and the heat added is symbolized as q_{rev}. A reversible process is defined as one that occurs in infinitesimally small steps from the initial to the final state.

Entropy changes due to a chemical process are calculated in the same fashion as the heats of reaction. Just as is done for $\Delta H_f°$ values, the tables list entropies for 1 mole of substance, making entropy an intensive physical property. This can be written as

$$\Delta S° = \sum(S_f° \ 3 \ coeff)_{products} - \sum(S_f° \times coeff)_{reactants}$$

(12.31)

For example, we can calculate the entropy change for the combustion of propane from the data in Appendix 3:

$$CH_3CH_2CH_3(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$
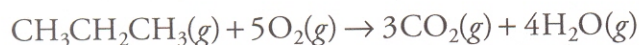
$$\Delta S° = ? \text{ J } °C^{-1}$$

$$\Delta S° = \left[\left(\frac{213.6 \text{ J}}{\text{mol K}} \right)(3 \text{ mol}) + \left(\frac{188.7 \text{ J}}{\text{mol K}} \right)(4 \text{ mol}) \right] -$$

$$\left[\left(\frac{205.0 \text{ J}}{\text{mol K}} \right)(5 \text{ mol}) + \left(\frac{270.2 \text{ J}}{\text{mol K}} \right)(1 \text{ mol}) \right]$$

$$= 1395.6 \text{ J K}^{-1} - 1295.2 \text{ J K}^{-1}.$$

$$= +100.4 \text{ J K}^{-1}$$

This result represents an increase in entropy. We might have predicted an increase for this reaction since there are 7 moles of gaseous products and only 6 moles of gaseous reactants. The increase in the number of moles of gas in this reaction is 1 ($\Delta n_g = 1$), indicating that the entropy change is expected to be positive.

In addition to calculating the entropy change from tabulated data, we can estimate the sign and, to some degree, the magnitude of an entropy change for a chemical process. In making such an estimate, the following principles are important:

1. Formation of a gas increases entropy greatly. The greater the value of Δn_g, the greater the entropy increase. The reverse is true for a decrease in entropy.

2. If $\Delta n_g = 0$, changes from the solid to the liquid phase are the next leading contributors to an increase in entropy. A solid that melts or a solute that dissolves in a solvent both exhibit an increase in entropy. Conversely, the formation of solids always results in a decrease in entropy.

3. An increase in temperature increases the entropy of a system, and a temperature decrease decreases the entropy.

GIBBS FREE-ENERGY, ΔG

This thermodynamic quantity was named in honor of J. Willard Gibbs, a preeminent physical chemist who developed the concept. The **free-energy change,** represented by the symbol $\Delta G°$, is the maximum amount of energy available from any chemical reaction. Two forces drive chemical reactions. The first is the enthalpy, $\Delta H°$, which represents the change in the internal potential energy of the atoms. The second is the drive toward increased randomness, or an increase in the entropy of the system. If the enthalpy is negative, it means that the internal potential energy of the system is decreased, and this favors a spontaneous reaction. If the entropy increases, a spontaneous reaction is also favored. The combination of these two driving forces is represented as

$$\Delta G° = \Delta H° - T\Delta S° \tag{12.32}$$

> **TIP**
>
> Equation 12.32 is given on the AP Exam.

The Gibbs free-energy equation is derived directly from the **second law of thermodynamics,** which states that any physical or chemical change must result in an increase in the entropy of the universe.

Since $\Delta G°$ is a combination of $\Delta H°$ and $\Delta S°$, we can make some generalizations, shown in Table 12.1, based only on the signs of these quantities.

TABLE 12.1

Relationships of the Signs of $\Delta H°$ and $\Delta S°$ to the Sign of $\Delta G°$

$\Delta H°$	$\Delta S°$	$\Delta G°$	Comment
Negative	Positive	Negative	Always spontaneous
Positive	Negative	Positive	Never spontaneous
Negative	Negative	Positive or negative	Decrease temperature to make spontaneous
Positive	Positive	Positive or negative	Increase temperature to make spontaneous

When $\Delta H°$ is negative and $\Delta S°$ is positive, the only value possible for $\Delta G°$ is a negative one. In this case the reaction will be spontaneous at all temperatures. Similarly, when $\Delta H°$ is positive and $\Delta S°$ is negative, $\Delta G°$ must be positive, indicating a nonspontaneous reaction at all temperatures.

When $\Delta H°$ is negative and $\Delta S°$ is negative, $\Delta G°$ may be either negative or positive, depending on the relative magnitudes of $\Delta H°$ and $\Delta S°$. However, the $-T\Delta S°$ term will always be positive. It will have a larger magnitude at high temperatures and a smaller magnitude at low temperatures. This fact suggests that lowering the temperature may make the positive magnitude of $T\Delta S°$ small enough so that, when it is combined with the negative $\Delta H°$, the resulting $\Delta G°$ will be negative and the reaction will be spontaneous.

The reverse is true when $\Delta H°$ is positive and $\Delta S°$ is positive. Again, $\Delta G°$ may be either positive or negative. The same reasoning leads to the conclusion that increasing the temperature will eventually cause the reaction to be spontaneous with a negative $\Delta G°$.

SPONTANEITY OF REACTIONS

When $\Delta G°$ is negative, a reaction is spontaneous. When $\Delta G°$ is positive, a reaction is nonspontaneous.
When the signs of $\Delta S°$ and $\Delta H°$ are different, the reaction will **always** be either sponaneous or nonspontaneous.
When the signs of $\Delta S°$ and $\Delta H°$ are the same, the reaction may be either spontaneous or nonspontaneous, depending on the Kelvin temperature.

As is true of $\Delta H°$ and $\Delta S°$ calculations, we can calculate the value of $\Delta G°$ for a reaction from tabulated values of free energies of formation. These values are listed in a table in Appendix 3. Since temperature is an important variable that affects the value of the free energy, the temperature must be specified. It is most common to list $\Delta G°$ values for room temperature of 25°C or 298 K. The symbol for free energy

incorporates the temperature, as in ΔG°_{298}. In using the free-energy table, we subtract the ΔG°_{298} of the reactants from the ΔG°_{298} values of the products in the equation:

$$\Delta G^\circ_{298} = \sum(\Delta G^\circ_{298} \times \text{coeff})_{\text{products}} - \sum(\Delta G^\circ_{298} \times \text{coeff})_{\text{reactants}} \quad (12.33)$$

For the combustion of propane (Equation 12.16) we obtain

$$\Delta G^\circ_{298} = \left[\left(\frac{-394.4 \text{ kJ}}{\text{mol}}\right)(3 \text{ mol}) + \left(\frac{-228.6 \text{ kJ}}{\text{mol}}\right)(4 \text{ mol})\right] - \left[\left(\frac{-23.5 \text{ kJ}}{\text{mol}}\right)(1 \text{ mol})\right]$$

$$= (-1183.2 \text{ kJ} - 914.4 \text{ kJ}) - (-23.5 \text{ kJ})$$

$$= -2074.1 \text{ kJ}$$

The negative value indicates that the reaction is spontaneous, as anyone who has used a barbecue grill or propane torch already knows.

We have calculated ΔH° and ΔS° for this reaction in preceding sections of this chapter. Using those values, along with a temperature of 298 K, we have a second way to determine the value of ΔG°_{298}:

$$\Delta G^\circ_{298} = \Delta H^\circ - T\Delta S^\circ$$

$$= -2044 \text{ kJ} - (298 \text{ K})(100.4 \text{ J K}^{-1})$$

$$= -2044 \text{ kJ} - 29.9 \text{ kJ}$$

$$= -2074 \text{ kJ}$$

Free Energy at Temperatures Other Than 298 K

Using the table of standard free energies of formation in Appendix 3, we can calculate the free-energy change at 298 K. Standard free-energy changes at other temperatures can also be calculated. For this purpose we need to know the standard heat of reaction, $\Delta H^\circ_{\text{react}}$, and the standard entropy change, $\Delta S^\circ_{\text{react}}$, for the reaction. These values are correct for 298 K, but we may assume that they do not change significantly with temperature. Using these values in the free-energy equation with a temperature other than 298 K gives the free-energy change at that different temperature.

EXERCISE 12.6

For a certain reaction, $\Delta H^\circ = +2.98$ kJ and $\Delta S^\circ = +12.3$ J K^{-1}. What is G° at 298 K, 200 K, and 400 K?

Solution

The equation to be solved is

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

Substituting the values given in the problem yields

$$\Delta G^{\circ}_{298} = 2.98\,\text{kJ} - 298\,(12.3\,\text{J K}^{-1})$$
$$= 2.98\,\text{kJ} - 3665\,\text{J}$$

To complete the solution, -3665 J must be converted to -3.67 kJ. Then

$$\Delta G^{\circ} = -0.69\,\text{kJ}\ \ (\text{a spontaneous reaction})$$

At 200 K and 400 K the answers are

$$\Delta G^{\circ}_{200} = 2.98\,\text{kJ} - 200\,\text{K}\,(12.3\,\text{J K}^{-1}) = +0.52\,\text{kJ}$$

and

$$\Delta G^{\circ}_{400} = 2.98\,\text{kJ} - 400\,\text{K}\,(12.3\,\text{J K}^{-1}) = -1.94\,\text{kJ}$$

In this exercise we see that the reaction is not spontaneous at 200 K but is spontaneous at 298 K and 400 K.

EXERCISE 12.7

For a certain reaction, $\Delta H^{\circ} = -13.65$ kJ and a $\Delta S^{\circ} = -75.8$ J K^{-1}. (a) What is ΔG°_{298} at 298 K? (b) Will increasing or decreasing the temperature make the reaction spontaneous? If so, at what temperature will the reaction become spontaneous?

Solution

(a) At 298 K the free energy is

$$\Delta G^{\circ}_{298} = -13.65\,\text{kJ} - 298\,\text{K}\,(-75.8\,\text{J K}^{-1}) = +8.94\,\text{kJ}$$

(b) The reaction is not spontaneous at 298 K. Since ΔH° and ΔS° both have the same sign, the free energy will change from positive to negative at some temperature. Since the number zero divides the positive numbers from the negative numbers, we may conclude that $\Delta G^{\circ} = 0.00$ kJ is the dividing line between spontaneous and nonspontaneous reactions. Consequently, the free-energy equation is set up as

$$\Delta G^{\circ}_{\text{react}} = \Delta H^{\circ}_{\text{react}} - T\Delta S^{\circ}_{\text{react}}$$

$$0.00\,\text{kJ} = -13.65\,\text{kJ} - T(-75.8\,\text{J K}^{-1})$$

$$T = \frac{13.65\,\text{kJ}}{0.0758\,\text{kJ K}^{-1}} = 180\,\text{K}$$

From this result we predict that the reaction will be spontaneous below 180 K and nonspontaneous above 180 K.

The condensation of a gas and the crystallization of a liquid are two physical processes that are spontaneous at low temperatures and nonspontaneous at higher temperatures.

Free Energy and Equilibrium

When a system is not at standard state, the free-energy change is represented by ΔG, not $\Delta G°$. Equation 12.34 shows the relationship between ΔG and $\Delta G°$:

$$\Delta G = \Delta G° + RT \ln Q \qquad (12.34)$$

From Chapter 10 we recall that Q is the reaction quotient. If the value of Q is not equal to the equilibrium constant, further reaction occurs until the system reaches equilibrium.

Using Equation 12.34, we find that when a system is at standard state all concentrations are equal to 1 and $Q = 1$. The natural logarithm of 1 is zero ($\ln 1 = 0$), and consequently $\Delta G = \Delta G°$.

The value of ΔG (without the superscript) tells us whether the reaction will continue and, if so, in which direction it will go. When ΔG is negative, the reaction will proceed in the forward direction. When ΔG is positive, the reaction proceeds in the reverse direction. If ΔG is zero, the reaction is at equilibrium and no further reaction occurs. For the equilibrium condition we find that

$$\Delta G° = -RT \ln K \qquad (12.35)$$

by setting $\Delta G = 0$, substituting the equilibrium constant, K, for the reaction quotient, Q, in Equation 12.34, and rearranging.

The relationships between ΔG and $\Delta G°$ are diagrammed in Figure 12.3. The standard free energies, $\Delta G°$, are shown for the reactants on the left side and for the products on the right side of each graph. The difference between the two is $\Delta G°$ for the reaction. In each diagram the curved line connecting the two $G°$ values represents the value of G for the reaction mixture. The slope of the curved line is ΔG, and at the minimum, where the slope $= 0$, the reaction is in equilibrium.

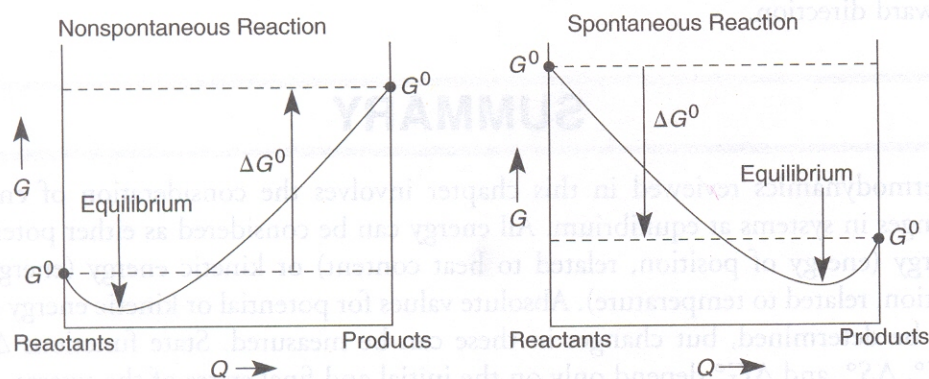**FIGURE 12.3.** Free-energy diagrams for a nonspontaneous reaction and a spontaneous reaction. The difference between the $G°$ points is $\Delta G°$. The slope of the curved line is ΔG, and the equilibrium point is at the minimum of the curve.

The curves in Figure 12.3 illustrate that in a nonspontaneous reaction a small amount of reactants is converted into products at equilibrium (minimum of curved line). A spontaneous reaction, on the other hand, has most of the reactants converted into products because the minimum is closer toward the product side. The slope of the curved line is negative to the left of the equilibrium point, so that ΔG is negative and the reaction moves toward the products and also toward the minimum. On the right-hand side of the equilibrium point, the slope and ΔG are positive. The reaction proceeds toward the reactants and also toward the minimum.

EXERCISE 12.8

The value of the equilibrium constant is 45 at 298 K. At the same temperature $Q = 35$. Determine the value of $\Delta G°$ for the reaction at 298 K, and show that the value of G indicates the same direction for the reaction as Q predicts.

Solution

The value of $\Delta G°$ is calculated as

$$\Delta G° = -RT \ln K$$
$$= -(8.314 \text{ J mol}^{-1} \text{K}^{-1}) (298 \text{ K}) [\ln (45)]$$
$$= -9.43 \text{ kJ mol}^{-1}$$

The value of ΔG is calculated as

$$\Delta G = \Delta G° + RT \ln K$$
$$= -9.43 \text{ kJ mol}^{-1} + (8.314 \text{ J mol}^{-1} \text{K}^{-1}) (298 \text{ K}) [\ln (35)]$$
$$= -9.43 \text{ kJ mol}^{-1} + 8.81 \text{ kJ mol}^{-1}$$
$$= -0.62 \text{ kJ mol}^{-1}$$

The value of ΔG predicts that the reaction will proceed in the forward direction. The fact that Q is less than K also indicates that the reaction will proceed in the forward direction.

SUMMARY

Thermodynamics reviewed in this chapter involves the consideration of energy changes in systems at equilibrium. All energy can be considered as either potential energy (energy of position, related to heat content) or kinetic energy (energy of motion, related to temperature). Absolute values for potential or kinetic energy cannot be determined, but changes in these can be measured. State functions $\Delta E°$, $\Delta H°$, $\Delta S°$, and $\Delta G°$ depend only on the initial and final states of the system. The maximum work available from a system is equal to $\Delta G° = \Delta H° - T \Delta S°$. $\Delta E°$ is the change in total internal energy and is measured with a bomb calorimeter. Enthalpy, the heat of a reaction, $\Delta E°$, is measured in a calorimeter at ambient pressure. The standard free energy change is related to the equilibrium constant, and either may be used to determine if a reaction is spontaneous. A spontaneous reac-

tion is generally one where the amount of product is greater than the amount of reactants at equilibrium. This means that $\Delta E°$ is negative and $K_{eq} > 1$.

Important Concepts

Forms of energy
Law of conservation of energy
Hess's law
Standard state
Gibbs free energy, entropy, and enthalpy
Spontaneous and nonspontaneous reactions

Important Equations

$q = $ (SPECIFIC HEAT) (MASS) (TEMPERATURE CHANGE)

$\Delta E = q + w$

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° - RT \ln Q$

$\Delta G° = -RT \ln K$