

18.7: Entropy Changes in Chemical Reactions: Calculating $\Delta S_{\text{rxn}}^{\circ}$

We now turn our attention to predicting and quantifying entropy and entropy changes in a sample of matter. As we examine this topic, we again encounter the theme of this book: *Structure determines properties*. In this case, the property we are interested in is entropy. In this section, we see how the structure of the particles that compose a particular sample of matter determines the entropy that the sample possesses at a given temperature and pressure.

Defining Standard States and Standard Entropy Changes

In [Chapter 9](#), we learned how to calculate standard changes in enthalpy ($\Delta H_{\text{rxn}}^{\circ}$) for chemical reactions. We now turn to calculating standard changes in *entropy* for chemical reactions. Recall from [Section 9.10](#) that the standard enthalpy change for a reaction ($\Delta H_{\text{rxn}}^{\circ}$) is the change in enthalpy for a process in which all reactants and products are in their standard states. Recall also the definitions of the standard state:

- *For a gas:* The standard state for a gas is the pure gas at a pressure of exactly 1 atm.
- *For a liquid or solid:* The standard state for a liquid or solid is the pure substance in its most stable form at a pressure of 1 atm and at the temperature of interest (often taken to be 25 °C).
- *For a substance in solution:* The standard state for a substance in solution is a concentration of 1 M.

The standard state has recently been changed to a pressure of 1 bar, which is very close to 1 atm (1 atm = 1.013 bar). Both standards are now in common use.

We define the **standard entropy change for a reaction** ($\Delta S_{\text{rxn}}^{\circ}$) as the change in *entropy* for a process in which all reactants and products are in their standard states. Since entropy is a function of state, the standard change in entropy is the standard entropy of the products minus the standard entropy of the reactants:

$$\Delta S_{\text{rxn}}^{\circ} = S_{\text{products}}^{\circ} - S_{\text{reactants}}^{\circ}$$

But how do we determine the standard entropies of the reactants and products? Theoretically, we could use Boltzmann's definition ($S = k \ln W$); however, practically we rely on tables that come from experimental measurements. Recall from [Chapter 9](#) that we defined *standard molar enthalpies of formation* (ΔH_f°) to use in calculating $\Delta H_{\text{rxn}}^{\circ}$. In this chapter, we define **standard molar entropies** (S°) to use in calculating $\Delta S_{\text{rxn}}^{\circ}$.

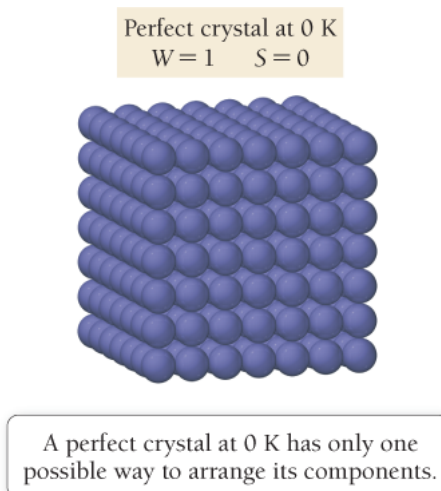
Standard Molar Entropies (S°) and the Third Law of Thermodynamics

Recall that in [Chapter 9](#) we defined a *relative zero* for enthalpy. To do this, we assigned a value of zero to the standard enthalpy of formation for an element in its standard state. This was necessary because absolute values of enthalpy cannot be determined. In other words, for enthalpy, there is no absolute zero against which to measure all other values; therefore, we always have to rely on enthalpy changes from an arbitrarily assigned standard (the elements in their standard states and most stable forms). For entropy, however, *there is an absolute zero*. The absolute zero of entropy is established by the **third law of thermodynamics**, which states:

The entropy of a perfect crystal at absolute zero (0 K) is zero.

A perfect crystal at a temperature of absolute zero has only one possible way ($w = 1$) to arrange its components (Figure 18.5). Based on Boltzmann's definition of entropy ($S = k \ln w$), its entropy is zero ($S = k \ln 1 = 0$).

Figure 18.5 Zero Entropy



We can measure all entropy values against the absolute zero of entropy as defined by the third law. Table 18.2 lists values of standard entropies at 25 °C for selected substances. A more complete list can be found in Appendix IIB. Standard entropy values are listed per mole of substance, in units of joules per mole per kelvin ($\text{J/mol} \cdot \text{K}$). The values are listed per mole because *entropy is an extensive property*—it depends on the amount of the substance.

Table 18.2 Standard Molar Entropy Values (S°) for Selected Substances at 298 K

Substance	$S^\circ (\text{J/mol} \cdot \text{K})$	Substance	$S^\circ (\text{J/mol} \cdot \text{K})$	Substance	$S^\circ (\text{J/mol} \cdot \text{K})$
Gases		Liquids		Solids	
$\text{H}_2(g)$	130.7	$\text{H}_2\text{O}(l)$	70.0	$\text{MgO}(s)$	27.0
$\text{Ar}(g)$	154.8	$\text{CH}_3\text{OH}(l)$	126.8	$\text{Fe}(s)$	27.3
$\text{CH}_4(g)$	186.3	$\text{Br}_2(l)$	152.2	$\text{Li}(s)$	29.1
$\text{H}_2\text{O}(g)$	188.8	$\text{C}_6\text{H}_6(l)$	173.4	$\text{Cu}(s)$	33.2
$\text{N}_2(g)$	191.6			$\text{Na}(s)$	51.3
$\text{NH}_3(g)$	192.8			$\text{K}(s)$	64.7
$\text{F}_2(g)$	202.8			$\text{NaCl}(s)$	72.1
$\text{O}_2(g)$	205.2			$\text{CaCO}_3(s)$	91.7
$\text{Cl}_2(g)$	223.1			$\text{FeCl}_3(s)$	142.3
$\text{C}_2\text{H}_4(g)$	219.3				

At 25 °C the standard entropy of any substance is the energy dispersed into one mole of that substance at 25 °C, which depends on the number of “places” to put energy within the substance. The number of “places” to put energy depends on the structure of the substance. In particular, the state of the substance, the molar mass of the substance, the particular allotrope, the molecular complexity of the substance, and its extent of dissolution each affect the entropy contained in the substance (at a given temperature). Let's examine each of these separately.

Some elements exist in two or more forms, called *allotropes*, within the same state.

Relative Standard Entropies: States of Matter






As we saw earlier in [Section 18.3](#), the entropy of a gas is generally greater than the entropy of a liquid, which is in turn greater than the entropy of a solid. We can see these trends in the tabulated values of standard entropies. For example, consider the relative standard entropies of liquid water and gaseous water at 25 °C:

	S° (J/mol · K)
$\text{H}_2\text{O}(l)$	70.0
$\text{H}_2\text{O}(g)$	188.8

Gaseous water has a much greater standard entropy than liquid water because a gas has more energetically equivalent ways to arrange its components, which in turn results in greater energy dispersal at 25 °C.

Relative Standard Entropies: Molar Masses


Consider the standard entropies of the noble gases at 25 °C:

	S° (J/mol · K)	
He(g)	126.2	
Ne(g)	146.1	
Ar(g)	154.8	
Kr(g)	163.8	
Xe(g)	169.4	

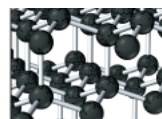
The more massive the noble gas, the greater its entropy at 25 °C. A complete explanation of why entropy increases with increasing molar mass is beyond the scope of this book. Briefly, the energy states associated with the motion of heavy atoms are more closely spaced than those of lighter atoms. The more closely spaced energy states allow for greater dispersal of energy at a given temperature and therefore greater entropy. This trend holds only for elements in the same physical state. (The effect of a physical state change—from a liquid to a gas, for example—is far greater than the effect of molar mass.)

Relative Standard Entropies: Allotropes

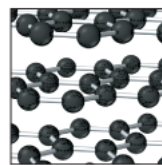
Recall from [Chapter 12](#) that some elements can exist in two or more forms with different structures—called **allotropes**—in the same state of matter. For example, the allotropes of carbon include diamond and graphite—both solid forms of carbon. Since the arrangement of atoms within these forms is different, their standard molar entropies are different:

S° (J/mol · K)


C(s, diamond) 2.4



C(s, graphite) 5.7



In diamond, the atoms are constrained by chemical bonds in a highly restricted three-dimensional crystal structure. In graphite, the atoms bond together in sheets, but the sheets have freedom to slide past each other. The less constrained structure of graphite results in more “places” to put energy and therefore greater entropy compared to diamond.

Relative Standard Entropies: Molecular Complexity

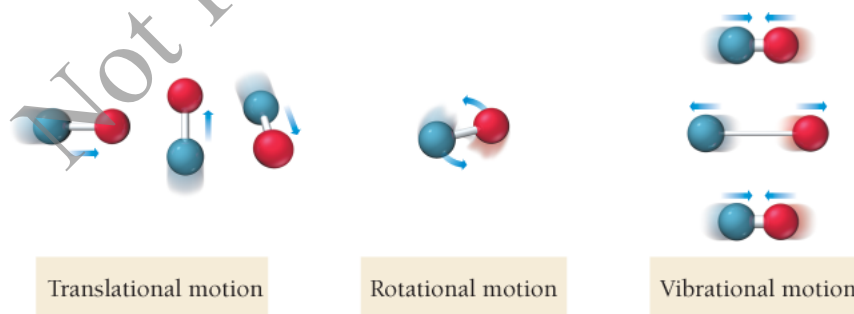
For a given state of matter, entropy generally increases with increasing molecular complexity. For example, consider the standard entropies of gaseous argon and nitrogen monoxide:

	Molar Mass (g/mol)	S° (J/mol · K)
Ar(g)	39.948	154.8
NO(g)	30.006	210.8

Ar has a greater molar mass than NO, yet it has less entropy at 25 °C. Why? Molecules generally have more “places” to put energy than do atoms. In a gaseous sample of argon, the only form that energy can take is the translational motion of the atoms. In a gaseous sample of NO, on the other hand, energy can take the form of translational motion, rotational motion, and (at high enough temperatures) vibrational motions of the molecules (Figure 18.6). Therefore, for a given state, molecules generally have a greater entropy than free atoms.

Figure 18.6 “Places” for Energy in Gaseous NO

Energy can be contained in translational motion, rotational motion, and (at high enough temperatures) vibrational motion.



Similarly, more complex molecules generally have more entropy than simpler ones. For example, consider the standard entropies of carbon monoxide and ethene gas:

	Molar Mass (g/mol)	S° (J/mol · K)
CO(g)	28.01	197.7
C ₂ H ₄ (g)	28.05	219.3

These two substances have nearly the same molar mass, but the greater complexity of C_2H_4 results in a greater molar entropy.

When molecular complexity and molar mass both increase (as is often the case), molar entropy also increases, as demonstrated by the oxides of nitrogen:

	S° (J/mol · K)
NO(g)	210.8
NO ₂ (g)	240.1
N ₂ O ₄ (g)	304.4

The increasing molecular complexity as we move down this list, as well as the increasing molar mass, results in more “places” to put energy and therefore greater entropy.

Relative Standard Entropies: Dissolution

The dissolution of a crystalline solid into solution usually results in an increase in entropy. For example, consider the standard entropies of solid and aqueous potassium chlorate:

	S° (J/mol · K)
KClO ₃ (s)	143.1
KClO ₃ (aq)	265.7

The standard entropies for aqueous solutions are for the solution in its standard state, which is defined as having a concentration of 1 M.

When solid potassium chlorate dissolves in water, the thermal energy that was concentrated within the crystal becomes dispersed throughout the entire solution. The greater energy dispersal results in greater entropy.

Conceptual Connection 18.4 Standard Entropies

Calculating the Standard Entropy Change ($\Delta S^\circ_{\text{rxn}}$) for a Reaction

Since entropy is a state function and since standard entropies for many common substances are tabulated, we can calculate the standard entropy change for a chemical reaction by calculating the difference in entropy between the products and the reactants. More specifically:

To calculate $\Delta S^\circ_{\text{rxn}}$, subtract the standard entropies of the reactants multiplied by their stoichiometric coefficients from the standard entropies of the products multiplied by their stoichiometric coefficients. In the form of an equation:

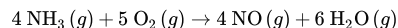
[18.10]

$$\Delta S^\circ_{\text{rxn}} = \sum n_p S^\circ (\text{products}) - \sum n_r S^\circ (\text{reactants})$$

In Equation 18.10, n_p represents the stoichiometric coefficients of the products, n_r represents the stoichiometric coefficients of the reactants, and S° represents the standard entropies. Keep in mind when using this equation that, unlike enthalpies of formation, which are zero for elements in their standard states, standard entropies are always nonzero at 25 °C. Example 18.5 demonstrates the application of Equation 18.10.

Example 18.5 Calculating Standard Entropy Changes ($\Delta S_{\text{rxn}}^{\circ}$)

Calculate $\Delta S_{\text{rxn}}^{\circ}$ for this balanced chemical equation.

**SOLUTION**

Begin by looking up the standard entropy for each reactant and product in Appendix IIB. Always note the correct state—(g), (l), (aq), or (s)—for each reactant and product.

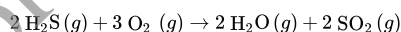
Reactant or product	S° (J/mol · K)
$\text{NH}_3(g)$	192.8
$\text{O}_2(g)$	205.2
$\text{NO}(g)$	210.8
$\text{H}_2\text{O}(g)$	188.8

Calculate $\Delta S_{\text{rxn}}^{\circ}$ by substituting the appropriate values into Equation 18.10. Remember to include the stoichiometric coefficients in your calculation. (The units of S° become J/K when multiplied by the stoichiometric coefficients in moles.)

$$\begin{aligned}
 \Delta S_{\text{rxn}}^{\circ} &= \Sigma n_p S^{\circ}(\text{products}) - \Sigma n_r S^{\circ}(\text{reactants}) \\
 &= [4(S_{\text{NO}(g)}^{\circ}) + 6(S_{\text{H}_2\text{O}(g)}^{\circ})] - [4(S_{\text{NH}_3(g)}^{\circ}) + 5(S_{\text{O}_2(g)}^{\circ})] \\
 &= [4(210.8 \text{ J/K}) + 6(188.8 \text{ J/K})] - [4(192.8 \text{ J/K}) + 5(205.2 \text{ J/K})] \\
 &= 1976.0 \text{ J/K} - 1797.2 \text{ J/K} \\
 &= 178.8 \text{ J/K}
 \end{aligned}$$

CHECK Notice that $\Delta S_{\text{rxn}}^{\circ}$ is positive, as you would expect for a reaction in which the number of moles of gas increases.

FOR PRACTICE 18.5 Calculate $\Delta S_{\text{rxn}}^{\circ}$ for this balanced chemical equation.



Interactive Worked Example 18.5 Calculating Standard Entropy Changes ($\Delta S_{\text{rxn}}^{\circ}$)

Not for Distribution

Not for Distribution