Topic 9.1-9.2

Entropy

Learning Objectives

- Describe the entropy of a system and how temperature affects entropy.
- Determine the sign and relative magnitude of the change in entropy for a process.
- Calculate the change in entropy of a reaction using absolute entropies of reactants and products.

Topic Questions

- What is entropy?
- How does temperature affect the entropy of a system?
- How does entropy change as the number of particles within a system changes?
- How does entropy change with phase changes?
- What is the absolute entropy of a compound, and how can it be used to calculate the entropy change of a chemical reaction?

9.1.01 Introduction to Entropy

[ENE-4.A.1 ENE-4.A.2]

Entropy (*S*) is often represented as the level of disorder in a system. The disorder associated with entropy is due to the number of possible arrangements a system can have. A system that has many possible arrangements has a higher entropy (ie, more disorder) than a system with fewer possible arrangements.

Consider a computer system. As shown by Figure 9.1, there are very few ways to arrange the parts of a computer that result in a working system. This means that a working computer is a *highly ordered* system (ie, low entropy). In contrast, there are an almost unlimited number of ways to arrange the parts of a computer that result in a system that *does not* work. Therefore, a nonworking computer is a *highly disordered* system (ie, high entropy).

Highly *ordered* system ⇒ **Low entropy**

Highly *disordered* system ⇒ **High entropy**

There are **very few ways** to put together a working computer.

There are **nearly unlimited ways** to put together a computer that doesn't work.

Figure 9.1 The concept of entropy as it relates to working and nonworking computer systems.

When comparing the entropy of different systems, it is necessary to look at the possible arrangements of *both* matter and energy. A possible arrangement of matter and energy in a system is called a **microstate**. As stated in the computer analogy, a greater number of microstates (ie, arrangements) corresponds to greater entropy. Four important factors that affect the number of microstates in a chemical system are:

- The number of particles in the system
- The volume of the system
- The phases of matter present
- The temperature of the system

In general, more particles, larger volumes, more energetic phases of matter, and higher temperatures each correspond to a greater number of microstates (Figure 9.2).

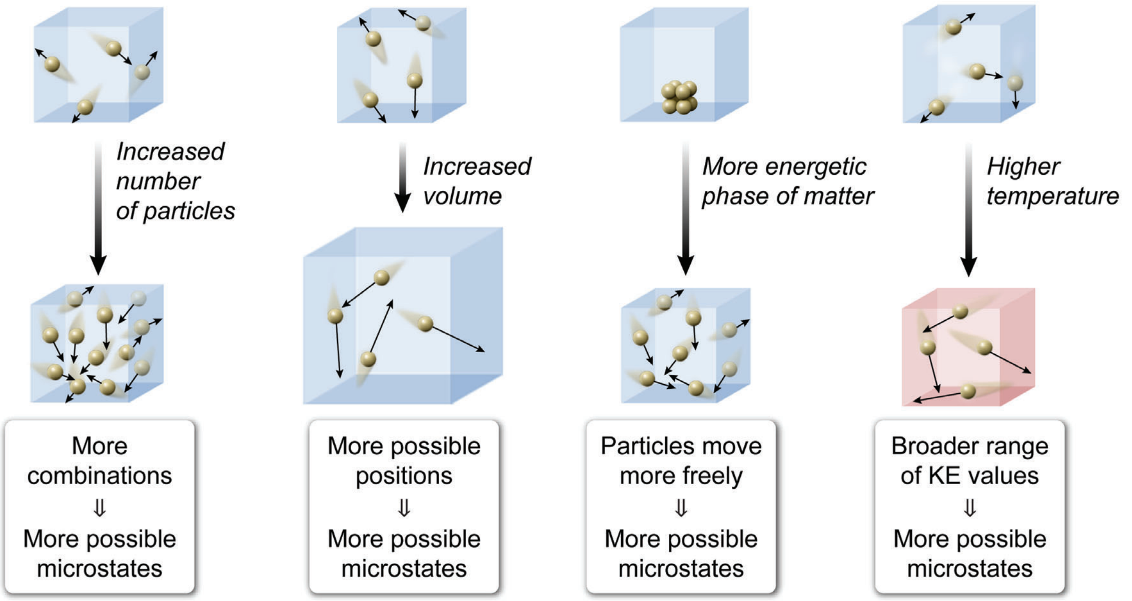


Figure 9.2 Factors that increase entropy.

Entropy can also be thought of as the degree to which matter and energy are spread out within a system. The **second law of thermodynamics** states that the universe is moving constantly toward a greater dispersion (ie, spreading out) of matter and energy. As matter and energy spread out in the universe, the number of microstates for the universe increases. As a result, the entropy of the universe is always increasing.

Entropy and Phase Changes

The change in entropy resulting from phase changes can be more easily understood by looking at the structure of the different states of matter. A solid crystal has *low entropy* because its atoms occupy a limited volume and are aligned and spaced evenly within an orderly crystal structure. As a result, solids have a relatively small number of microstates. In contrast, a gas has *high entropy* because its individual molecules are widely spread out within a relatively large volume and are randomly spaced and oriented. This results in a far greater number of microstates.

Like a solid, a liquid is limited in its volume due to the intermolecular forces holding the particles together. However, the particles in a liquid are free to move around and slide past one another. Therefore, a liquid has more microstates (greater entropy) than a solid but fewer microstates (lower entropy) than a gas (Figure 9.3).

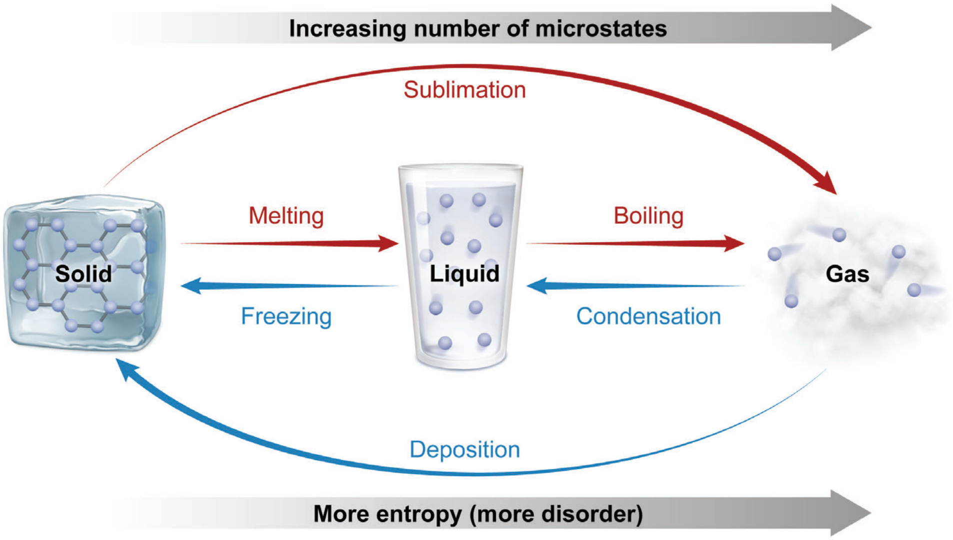
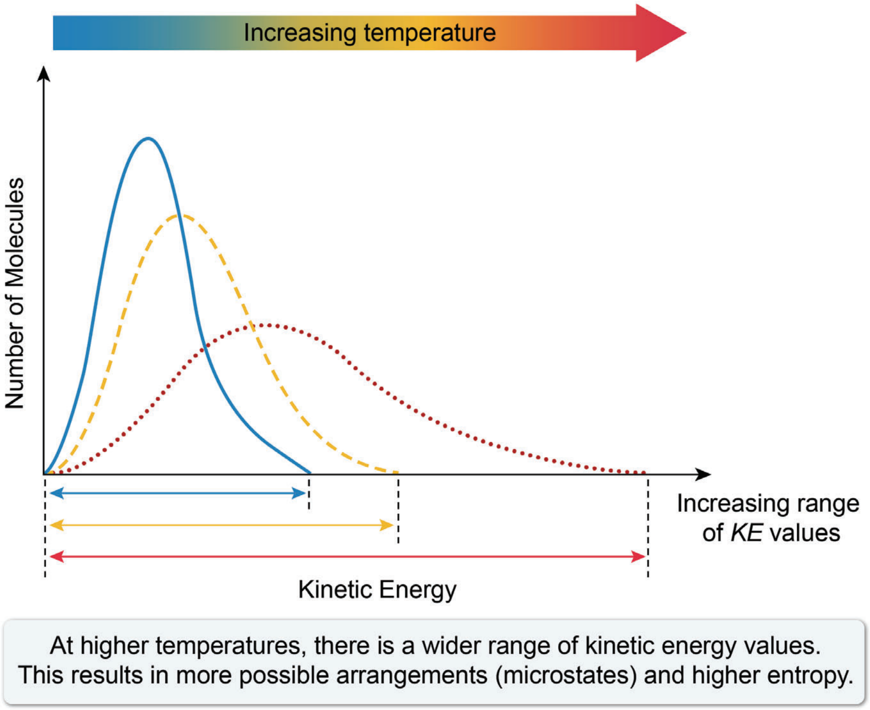


Figure 9.3 Relative entropy comparisons of different phases of matter and associated phase changes.

Entropy and Temperature

Recall that temperature is a measure of the *average* kinetic energy *KE* (energy of motion) of the particles in a sample. At any given temperature, some particles have more kinetic energy than others. This range of kinetic energies can be represented graphically by the Maxwell-Boltzmann distribution, as shown in Figure 9.4.



At higher temperatures, there is a wider range of kinetic energy values. This results in more possible arrangements (microstates) and higher entropy.

Figure 9.4 Effects of temperature on the range of kinetic energy values and entropy of a system.

As temperature increases, the average *KE* of a sample increases. In the graph, this is shown by higher temperature peaks being shifted farther to the right. In addition, the peaks for higher temperatures are wider than those for lower temperatures. These wider peaks show that higher temperatures result in a much broader range of *KE* values for the particles of a system. A system with more possible *KE* values has more microstates (greater entropy). Therefore, the entropy of a system increases as temperature increases.

Entropy Change of Physical and Chemical Processes

During a process, whether a physical change or a chemical reaction, the entropy S of a system changes. This change in entropy is expressed as ΔS, where

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

The exact ΔS of a process must be measured experimentally. However, a qualitative evaluation of ΔS for a process can be made by considering the factors summarized in Table 9.1.

Table 9.1 Factors affecting the entropy of a system.

Factor	Trend	Reason
Number of particles	More particles ⇒ greater entropy	More particles allow for more possible arrangements (ie, microstates).
Volume (V)	Increased $V \Rightarrow$ greater entropy	More positions are possible, which increases the number of microstates.
Phase(s) of matter present	$S_{\text{solid}} < S_{\text{liquid}} \approx S_{\text{aqueous}} < S_{\text{gas}}$	Higher energy phases of matter allow more possible positions and energies.
Temperature (T)	Increased $T \Rightarrow$ greater entropy	A wider range of kinetic energy values at high T results in more microstates.

Sometimes, the only information that is given for a process is its chemical equation. In these cases, a quick evaluation of ΔS can be made by focusing on the number of particles and the phases of matter present, as Figure 9.5 shows.

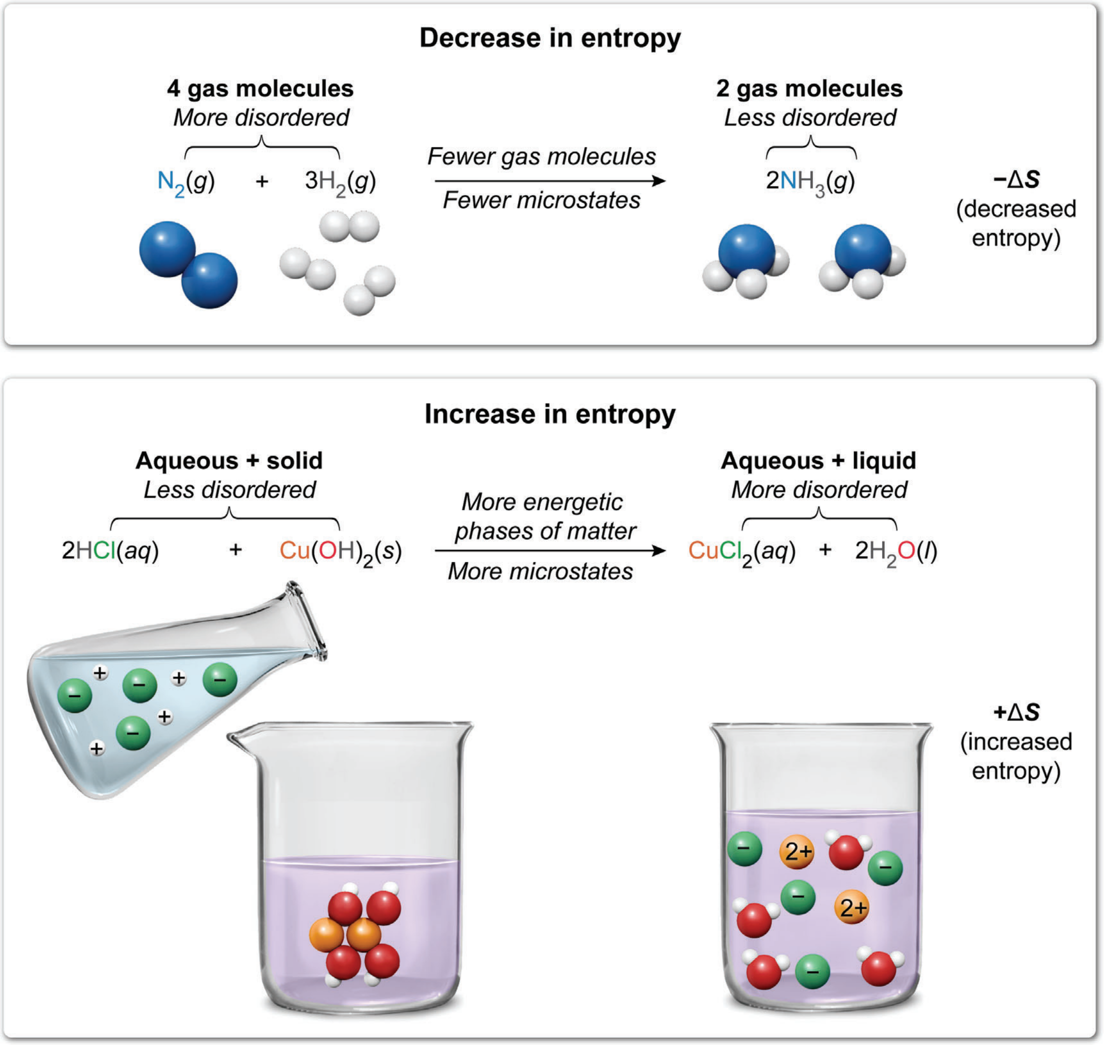


Figure 9.5 Qualitative evaluations of entropy change.

In general, processes that result in more particles and more energetic phases of matter have a positive Δ*S*.

9.2.01 Absolute Entropy and Entropy Change

[ENE-4.B.1]

At a temperature of absolute zero (ie, 0 K), a substance should (in theory) be a crystalline solid with no motion. This means that a substance at 0 K has only one microstate and zero entropy (assuming a perfect crystal structure). Using a temperature of 0 K as a starting point, the **absolute molar entropy *S*** of a chemical substance can be determined using experimental methods.

The **standard molar entropy *S*°** of a substance is the absolute molar entropy of that substance under standard state conditions. During a reaction, the *S*° of a system changes, and the **overall change in standard entropy $\Delta S^\circ_{\text{reaction}}$** for 1 mole of reaction can be calculated by:

$$\Delta S^\circ_{\text{reaction}} = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

where $\sum S^\circ_{\text{products}}$ and $\sum S^\circ_{\text{reactants}}$ are the sums of the absolute molar entropies of the products and reactants, respectively, with each species multiplied by its stoichiometric coefficient. A positive $\Delta S^\circ_{\text{reaction}}$ indicates that products have more possible arrangements (more disorder) than the reactants, and a negative $\Delta S^\circ_{\text{reaction}}$ indicates fewer possible arrangements (less disorder).

For example, consider the following reaction:

$$4\ \mathrm{Fe}(s) + 3\ \mathrm{O_2}(g) \rightarrow 2\ \mathrm{Fe_2O_3}(s)$$

$\Delta S°$ for this reaction can be calculated by using the standard molar entropies given in Table 9.2.

Table 9.2 Entropy values for selected substances.

Substance	**$S°$ (J/mol·K)**
$\mathrm{Fe}(s)$	27.3
$\mathrm{Fe_2O_3}(s)$	87.4
$\mathrm{O_2}(g)$	205.0

Using the $S°$ values in Table 9.2, $\sum S°_{\text{products}}$ is calculated by multiplying the coefficient of the product by its molar entropy:

$$\sum S^\circ_{\text{products}} = (2\ \cancel{\text{mol}})\left(87.4\ \frac{\text{J}}{\cancel{\text{mol}}\cdot\text{K}}\right) = 174.8\ \frac{\text{J}}{\text{K}}$$

Similarly, $\sum S°_{\text{reactants}}$ is calculated by multiplying the coefficient of each reactant by its molar entropy and adding the results:

$$\sum S^\circ_{\text{reactants}} = (4\ \cancel{\text{mol}})\left(27.3\ \frac{\text{J}}{\cancel{\text{mol}}\cdot\text{K}}\right) + (3\ \cancel{\text{mol}})\left(205.0\ \frac{\text{J}}{\cancel{\text{mol}}\cdot\text{K}}\right) = 724.2\ \frac{\text{J}}{\text{K}}$$

Substituting these two values into the $\Delta S°_{\text{reaction}}$ equation gives:

$$\Delta S^\circ_{\text{reaction}} = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}} \quad \Longrightarrow \quad \Delta S^\circ_{\text{reaction}} = 174.8\ \frac{\text{J}}{\text{K}} - 724.2\ \frac{\text{J}}{\text{K}} = -549.4\ \frac{\text{J}}{\text{K}}$$

Topic 9.1-9.2 Entropy

Check for Understanding Quiz

1. Which of the following processes has a positive change in entropy Δ*S*?
   - A. Water vapor condensing into rain
   - B. Red-hot steel cooling to room temperature
   - C. Iodine gas crystalizing on a flat surface
   - D. NaCl(*s*) breaking into ions when dissolved in water

2. Consider the reaction between iron and oxygen.

$$4\ \mathrm{Fe}(s) + 3\ \mathrm{O_2}(g) \rightarrow 2\ \mathrm{Fe_2O_3}(s)$$

   Which of the following best describes the change in entropy Δ*S*° for this reaction?
   - A. Δ*S*° is positive because there are fewer total moles of product than reactants.
   - B. Δ*S*° is negative because a gaseous reactant becomes part of a solid product.
   - C. Δ*S*° is positive because there are more moles of solid reactants than solid products.
   - D. Δ*S*° is negative because there are more total moles of product than reactants.

3. Under certain conditions, molecular nitrogen and molecular oxygen can react to produce nitrogen monoxide, according to the following reaction:

$$\mathrm{N_2}(g) + \mathrm{O_2}(g) \rightarrow 2\ \mathrm{NO}(g)$$

   Using the absolute molar entropy values provided in the table below, what is Δ*S*° for the reaction?

Substance	*S*° (J/K·mol)
N_2(*g*)	191.6
O_2(*g*)	205.2
NO(*g*)	210.8

   - A. 408.1 J/(K·mol)
   - B. 24.8 J/(K·mol)
   - C. −24.8 J/(K·mol)
   - D. −185.8 J/(K·mol)

Note: Answers to this quiz are in the back of the book (appendix).