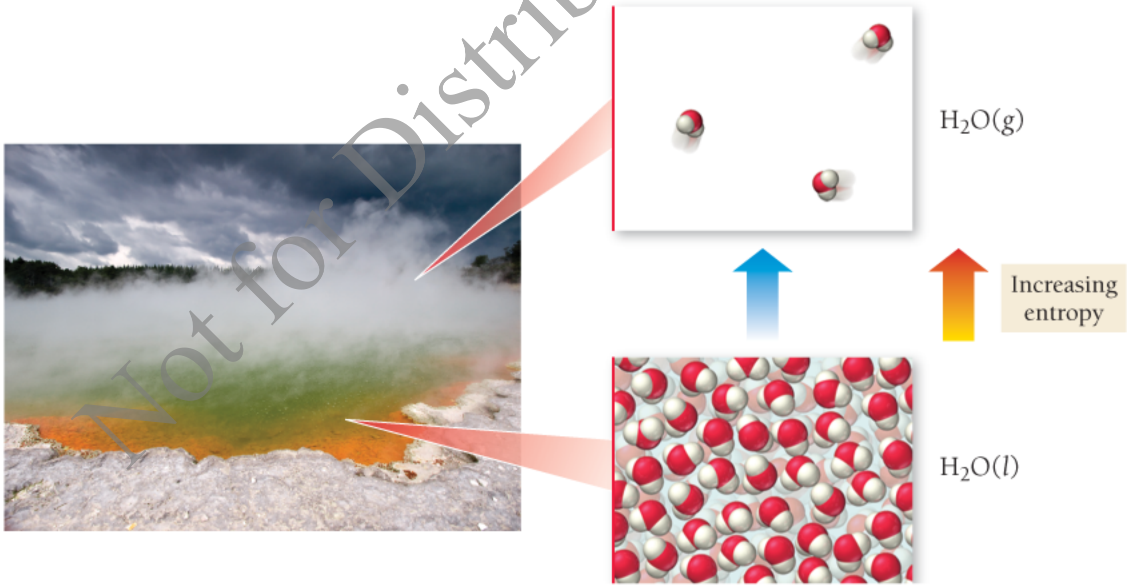
18.3: Entropy and the Second Law of Thermodynamics

Key Concept Video **Entropy and the Second Law of Thermodynamics**

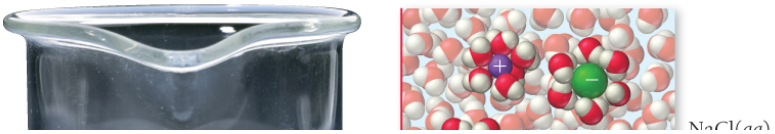
It might initially seem that the way to judge the spontaneity of a chemical process is to examine the change in enthalpy for the process (see Section 9.6). Perhaps, just as a mechanical system proceeds in the direction of lowest potential energy, so a chemical system might proceed in the direction of lowest enthalpy. If this were the case, all exothermic reactions would be spontaneous and all endothermic reactions would not. However, although *most* spontaneous processes are exothermic, some spontaneous processes are *endothermic*. For example, liquid water spilled on the floor at room temperature spontaneously evaporates even though the process is endothermic. Similarly, sodium chloride spontaneously dissolves in water, even though the process is slightly endothermic. These examples indicate that enthalpy is not the sole criterion for spontaneity.

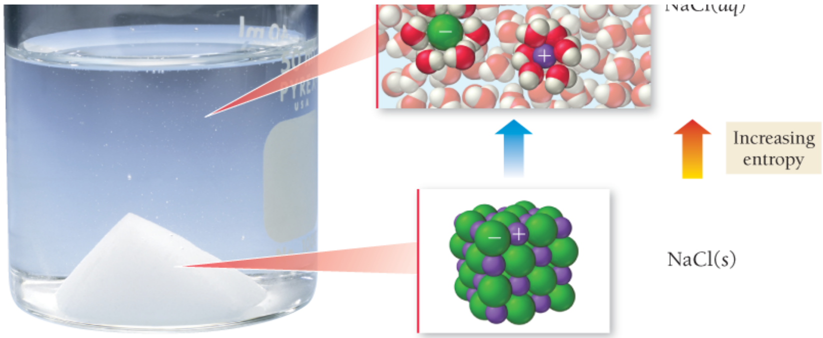
The evaporation of water and the dissolution of sodium chloride in water are both endothermic *and* spontaneous. What drives these processes? In each process, energy spreads out (or disperses) as the process occurs. During the evaporation of water, the thermal energy of the water molecules spreads out from a smaller volume (the volume of the liquid) into a much larger volume (the volume of the gas) as the water evaporates. Recall that a gas occupies a much larger volume than its corresponding liquid because the molecules have much more empty space between them.



When water evaporates, the thermal energy contained in the water molecules spreads out over a larger volume.

In the dissolution of a salt into water, the thermal energy contained in the salt crystals spreads out over the entire volume of the solution as the salt dissolves. In both of these processes, a quantity called *entropy*—related to the spreading out of energy—increases.





When salt dissolves in water, entropy increases.

Entropy

Entropy is the criterion for spontaneity in all systems, including chemical systems. Formally, **entropy**, abbreviated by the symbol *S*, has the following definition:

> **Entropy (*S*) is a thermodynamic function that increases with the number of *energetically equivalent* ways to arrange the components of a system to achieve a particular state.**

Austrian physicist Ludwig Boltzmann (1844–1906) expressed this definition mathematically in the 1870s as

$$S = k \ln W$$

where *k* is the Boltzmann constant (the gas constant divided by Avogadro's number, $R/N_{\text{A}} = 1.38 \times 10^{-23} \text{J/K}$) and *W* is the number of energetically equivalent ways to arrange the components of the system. Since *W* is unitless (it is simply a number), the units of entropy are joules per kelvin (J/k). We discuss the significance of the units shortly. As we can see from the equation, as *W* increases, entropy increases.

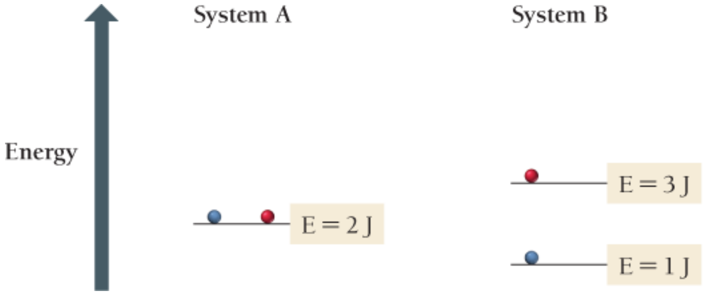
Boltzmann's equation is engraved on his tombstone.

The key to understanding entropy is the quantity *W*. What does *W*—the number of energetically equivalent ways to arrange the components of the system—signify? In order to answer this question, we must first understand how the energy of a system can distribute itself among the system's particles.

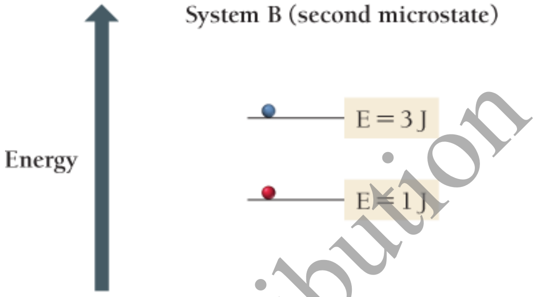
Imagine a system of particles such as a fixed amount of an ideal gas in a container. The particles have kinetic energy and are colliding with each other and the walls of their container. *A given set of conditions* (*P*, *V*, *and T*) *defines the* **macrostate** (or state) *of the system*. The overall energy of a macrostate is constant as long as the conditions remain constant. However, the exact distribution of that energy is anything but constant.

At any one instant, a particular gas particle may have lots of kinetic energy, but at the next instant, it may have very little (because it lost its energy through collisions with other particles). *We call the exact internal energy distribution among the particles at any one instant a* **microstate**. We can think of a microstate as a snapshot of the system at a given instant in time. The next instant, the snapshot (the microstate) changes. However, the *macrostate*—defined by *P*, *V*, and *T*—remains constant. Many different microstates can give rise to a particular macrostate. In fact, the microstate (or snapshot) of a given macrostate is generally different from one moment to the next as the energy of the system constantly redistributes itself among the particles of the system.

The quantity, *W*, is the number of *possible* microstates that can result in a given macrostate. For example, suppose that we have two systems (call them System A and System B) and that each is composed of two particles (one blue and one red). Both systems have a total energy of 4 J, but System A has only one energy level and System B has two:



Each system has the same total energy (4 J), but System A has only one possible microstate (the red and the blue particles both occupying the 2 J energy level), while System B has a second possible microstate:



In this second microstate for System B, the blue particle has 3 J and the red one has 1 J (as opposed to System B's first microstate, where the energy of the particles is switched). This second microstate is not possible for System A because System A has only one energy level. For System A, $W = 1$, but for System B, $W = 2$. In other words, System B has more microstates in the same 4 J macrostate than System A. Since *W* is larger for System B than for System A, System B has greater *entropy*; it has more *energetically equivalent ways to arrange the components of the system*.

We can best understand entropy by turning our attention to energy for a moment. The entropy of a macrostate of a system increases with the number of *energetically equivalent* ways to arrange the components of the system to achieve that particular macrostate. This implies that *the state with the highest entropy also has the greatest dispersal of energy*. Returning to our previous example, we find that the energy of System B is dispersed over two energy levels instead of being confined to just one. At the heart of entropy, therefore, is the concept of energy dispersal or energy randomization. *A state in which a given amount of energy is more highly dispersed (or more highly randomized) has more entropy than a state in which the same energy is more highly concentrated*.

The Second Law of Thermodynamics

We have already alluded to the **second law of thermodynamics**, and now we can formally define it:

> **For any spontaneous process, the entropy of the *universe* increases** ($\Delta S_{\text{univ}} > 0$).

The criterion for spontaneity is the entropy of the universe. Processes that increase the entropy of the universe—those that result in greater dispersal or randomization of energy—occur spontaneously. Processes that decrease the entropy of the universe do not occur spontaneously.

Entropy, like enthalpy, is a *state function*—its value depends only on the state of the system, not on how the system arrived at that state. Therefore, for any process, *the change in entropy is the entropy of the final state minus the entropy of the initial state*.

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

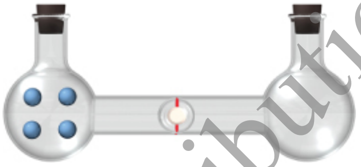
> See the discussion of state functions in Section 9.3.

Entropy determines the direction of chemical and physical change. *A chemical system proceeds in a direction that increases the entropy of the universe*—it proceeds in a direction that has the largest number of *energetically equivalent* ways to arrange its components.

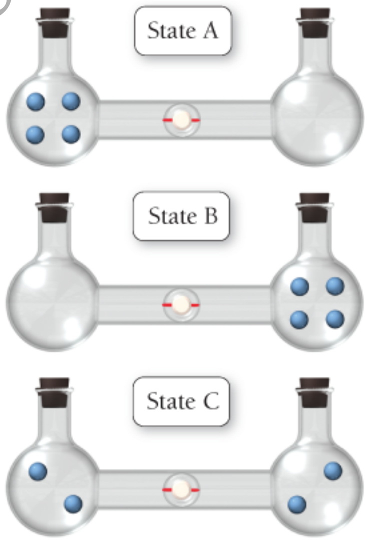
The Entropy Change upon the Expansion of an Ideal Gas

To better understand the second law, let us examine the expansion of an ideal gas into a vacuum (a spontaneous process with no associated change in enthalpy). Consider a flask containing an ideal gas that is connected to an evacuated flask by a tube equipped with a stopcock. When the stopcock is opened, the gas spontaneously expands into the evacuated flask. Since the gas is expanding into a vacuum, the pressure against which it expands is zero, and therefore the work ($w = -P_{\text{ext}}\Delta V$) is also zero (see Section 9.4).

However, even though the total energy of the gas does not change during the expansion, the entropy does change. As an illustration, consider a simplified system containing only four gas atoms.

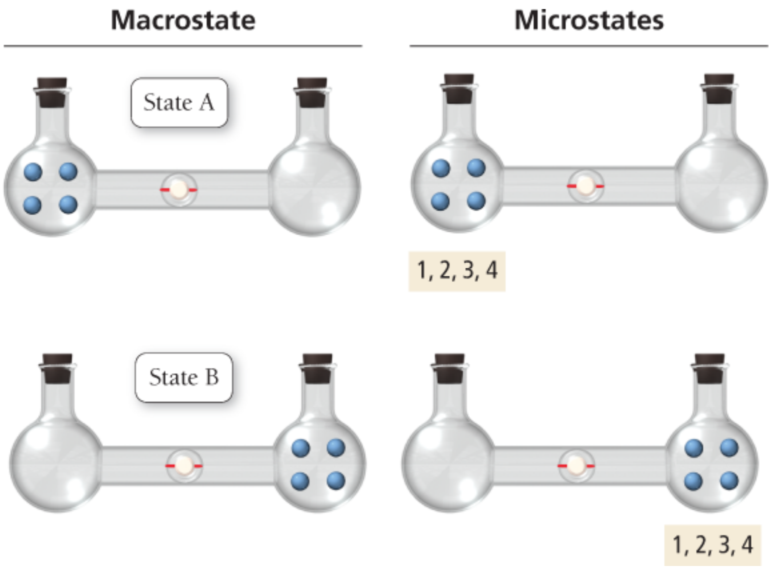


When the stopcock is opened, several possible energetically equivalent final states may result, each with the four atoms distributed in a different way. For example, there could be three atoms in the flask on the left and one in the flask on the right, or vice versa. For simplicity, we consider only the possibilities shown below: state A, state B, and state C. Since the energy of any one atom is the same in either flask and the atoms do not interact, states A, B, and C are energetically equivalent.



> Other states, such as those in which three atoms are in one flask and one atom is in the other, are omitted here to simplify the discussion.

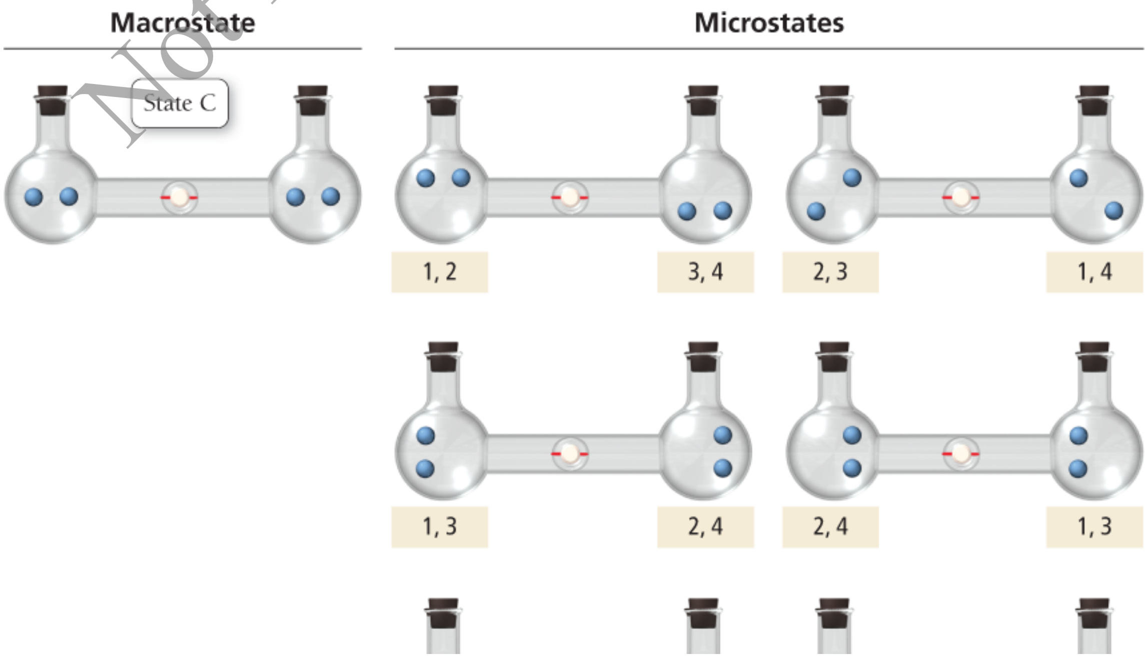
Now we ask the following question for each state: How many microstates give rise to the same macrostate? To keep track of the microstates, we label the atoms 1–4. However, even though the atoms have different numbered labels, they are all identical. For states A and B, only one microstate results in the specified macrostate—atoms 1–4 on the left side or the right side, respectively.

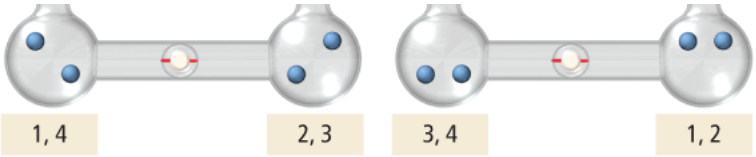


For state C, however, six different possible microstates all result in the same macrostate (two atoms on each side).

This means that the statistical probability of finding the atoms in state C is six times greater than the probability of finding the atoms in state A or state B. Consequently, even for a simple system consisting of only four atoms, the atoms are most likely to be found in state C. State C has the greatest entropy—it has the greatest number of energetically equivalent ways to distribute its components.

As the number of atoms increases, the number of microstates that leads to the atoms being equally distributed between the two flasks increases dramatically. For example, with 10 atoms, the number of microstates leading to an equal distribution of atoms between two flasks is 252 and with 20 atoms the number of microstates is 184,756. Yet, the number of microstates that leads to all of the atoms being only in the left flask (or all only in the right flask) does not increase—it is always only 1. In other words, the arrangement in which the atoms are equally distributed between the two flasks has a much larger number of possible microstates and therefore much greater entropy. The system thus tends toward that state.





> In these drawings, the exact location of an atom within a flask is insignificant. The significant aspect is whether the atom is in the left flask or the right flask.

The *change in entropy* in transitioning from a state in which all of the atoms are in the left flask to the state in which the atoms are evenly distributed between both flasks is *positive* because the final state has greater entropy than the initial state:

$$\Delta S = \underset{\substack{\uparrow \\ \text{Entropy of state in} \\ \text{which atoms are} \\ \text{distributed between} \\ \text{both flasks}}}{S_{\text{final}}} - \underset{\substack{\uparrow \\ \text{Entropy of state in} \\ \text{which atoms are all} \\ \text{in one flask}}}{S_{\text{initial}}}$$

> For n particles, the number of ways to put r particles in one flask and $n - r$ particles in the other flask is $n!/[(n-r)!r!]$. For 10 atoms, $n = 10$ and $r = 5$.

Since S_{final} is greater than S_{initial}, ΔS is positive and the process is spontaneous according to the second law. Notice that when the atoms are confined to one flask, their energy is also confined to that one flask; however, when the atoms are evenly distributed between both flasks, their energy is spread out over a greater volume. As the gas expands into the empty flask, energy is dispersed.

The second law explains many phenomena not explained by the first law of thermodynamics. In Section 9.4, we saw that heat travels from a substance at higher temperature (such as a hot cup of coffee) to one at lower temperature (such as the surrounding cooler air). Why? The first law of thermodynamics would not prohibit some heat from flowing the other way—from the surrounding cooler air into the hot cup of coffee. The surroundings could lose 100 J of heat (cooling even more), and the coffee could gain 100 J of heat (warming even more). The first law would not be violated by such a heat transfer. Imagine having your cup of coffee get warmer as it absorbed thermal energy from the surroundings! It will never happen because heat transfer from cold to hot violates the second law of thermodynamics. According to the second law, energy is dispersed, not concentrated. The transfer of heat from a substance of higher temperature to one of lower temperature results in greater energy randomization—the energy that was concentrated in the hot substance becomes dispersed into the surroundings. The second law accounts for this pervasive tendency.

Thermal energy always travels from hot to cold.

Conceptual Connection 18.1 **Entropy**

Interactive