

4.8: Entropy on a Microscopic Scale

Learning Objectives

By the end of this section you will be able to:

- Interpret the meaning of entropy at a microscopic scale
- Calculate a change in entropy for an irreversible process of a system and contrast with the change in entropy of the universe
- Explain the third law of thermodynamics

We have seen how entropy is related to heat exchange at a particular temperature. In this section, we consider entropy from a statistical viewpoint. Although the details of the argument are beyond the scope of this textbook, it turns out that entropy can be related to how disordered or randomized a system is—the more it is disordered, the higher is its entropy. For example, a new deck of cards is very ordered, as the cards are arranged numerically by suit. In shuffling this new deck, we randomize the arrangement of the cards and therefore increase its entropy (Figure 4.8.1). Thus, by picking one card off the top of the deck, there would be no indication of what the next selected card will be.



Figure 4.8.1: The entropy of a new deck of cards goes up after the dealer shuffles them. (credit: “Rommel SK”/YouTube)

The second law of thermodynamics requires that the entropy of the universe increase in any irreversible process. Thus, in terms of order, the second law may be stated as follows:

In any irreversible process, the universe becomes more disordered. For example, the [irreversible free expansion of an ideal gas](#), results in a larger volume for the gas molecules to occupy. A larger volume means more possible arrangements for the same number of atoms, so disorder is also increased. As a result, the entropy of the gas has gone up. The gas in this case is a closed system, and the process is irreversible. Changes in phase also illustrate the connection between entropy and **disorder**.

✓ Example 4.8.1: Entropy Change of the Universe

Suppose we place 50 g of ice at 0°C in contact with a heat reservoir at 20°C . Heat spontaneously flows from the reservoir to the ice, which melts and eventually reaches a temperature of 20°C . Find the change in entropy of (a) the ice and (b) the universe.

Strategy

Because the entropy of a system is a function of its state, we can imagine two reversible processes for the ice: (1) ice is melted at 0°C (T_A) and (2) melted ice (water) is warmed up from 9°C to 20°C (T_B) under constant pressure. Then, we add the change in entropy of the reservoir when we calculate the change in entropy of the universe.

Solution

1. From $\Delta S = S_B - S_A = \int_A^B \frac{dQ}{T}$, the increase in entropy of the ice is

$$\begin{aligned}
 \Delta S_{ice} &= \Delta S_1 + \Delta S_2 \\
 &= \frac{mL_f}{T_A} + mc \int_A^B \frac{dT}{T} \\
 &= \left(\frac{50 \times 335}{273} + 50 \times 4.19 \times \ln \frac{293}{273} \right) J/K \\
 &= 76.3 J/K.
 \end{aligned}$$

2. During this transition, the reservoir gives the ice an amount of heat equal to

$$\begin{aligned}
 Q &= mL_f + mc(T_B - T_A) \\
 &= 50 \times (335 + 4.19 \times 20) J \\
 &= 2.10 \times 10^4 J.
 \end{aligned}$$

This leads to a change (decrease) in entropy of the reservoir:

$$\Delta S_{reservoir} = \frac{-Q}{T_B} = -71.7 J/K.$$

The increase in entropy of the universe is therefore

$$\Delta S_{universe} = 76.3 J/K - 71.7 J/K = 4.6 J/K > 0.$$

Significance

The entropy of the universe therefore is greater than zero since the ice gains more entropy than the reservoir loses. If we considered only the phase change of the ice into water and not the temperature increase, the entropy change of the ice and reservoir would be the same, resulting in the universe gaining no entropy.

This process also results in a more disordered universe. The ice changes from a solid with molecules located at specific sites to a liquid whose molecules are much freer to move. The molecular arrangement has therefore become more randomized. Although the change in average kinetic energy of the molecules of the heat reservoir is negligible, there is nevertheless a significant decrease in the entropy of the reservoir because it has many more molecules than the melted ice cube. However, the reservoir's decrease in entropy is still not as large as the increase in entropy of the ice. The increased disorder of the ice more than compensates for the increased order of the reservoir, and the entropy of the universe increases by 4.6 J/K.

You might suspect that the growth of different forms of life might be a net ordering process and therefore a violation of the second law. After all, a single cell gathers molecules and eventually becomes a highly structured organism, such as a human being. However, this ordering process is more than compensated for by the disordering of the rest of the universe. The net result is an increase in entropy and an increase in the disorder of the universe.

? Exercise 4.8.1

In Example 4.8.1, the spontaneous flow of heat from a hot object to a cold object results in a net increase in entropy of the universe. Discuss how this result can be related to an increase in disorder of the system.

Solution

When heat flows from the reservoir to the ice, the internal (mainly kinetic) energy of the ice goes up, resulting in a higher average speed and thus an average greater position variance of the molecules in the ice. The reservoir does become more ordered, but due to its much larger amount of molecules, it does not offset the change in entropy in the system.

The second law of thermodynamics makes clear that the entropy of the universe never decreases during any thermodynamic process. For any other thermodynamic system, when the process is reversible, the change of the entropy is given by $\Delta S = Q/T$. But what happens if the temperature goes to zero, $T \rightarrow 0$? It turns out this is not a question that can be answered by the second law.

A fundamental issue still remains: Is it possible to cool a system all the way down to zero kelvin? We understand that the system must be at its lowest energy state because lowering temperature reduces the kinetic energy of the constituents in the system. What happens to the entropy of a system at the absolute zero temperature? It turns out the absolute zero temperature is not reachable—at

least, not through a finite number of cooling steps. This is a statement of the **third law of thermodynamics**, whose proof requires quantum mechanics that we do not present here. In actual experiments, physicists have continuously pushed that limit downward, with the lowest temperature achieved at about $1 \times 10^{-10} \text{ K}$ in a low-temperature lab at the Helsinki University of Technology in 2008.

Like the second law of thermodynamics, the third law of thermodynamics can be stated in different ways. One of the common statements of the third law of thermodynamics is:

The absolute zero temperature cannot be reached through any finite number of cooling steps.

In other words, the temperature of any given physical system must be finite, that is, $T > 0$. This produces a very interesting question in physics: Do we know how a system would behave if it were at the absolute zero temperature?

The reason a system is unable to reach 0 K is fundamental and requires quantum mechanics to fully understand its origin. But we can certainly ask what happens to the entropy of a system when we try to cool it down to 0 K. Because the amount of heat that can be removed from the system becomes vanishingly small, we expect that the change in entropy of the system along an isotherm approaches zero, that is

$$\lim_{T \rightarrow 0} (\Delta S)_T = 0$$

This can be viewed as another statement of the third law, with all the isotherms becoming **isentropic**, or into a reversible ideal adiabat. We can put this expression in words:

A system becomes perfectly ordered when its temperature approaches absolute zero and its entropy approaches its absolute minimum.

The third law of thermodynamics puts another limit on what can be done when we look for energy resources. If there could be a reservoir at the absolute zero temperature, we could have engines with efficiency of 100%, which would, of course, violate the second law of thermodynamics.

✓ Example 4.8.2: Entropy Change of an Ideal Gas in Free Expansion

An ideal gas occupies a partitioned volume V_1 inside a box whose walls are thermally insulating, as shown in Figure 4.8.2a. When the partition is removed, the gas expands and fills the entire volume V_2 of the box, as shown in Figure 4.8.2b. What is the entropy change of the universe (the system plus its environment)?

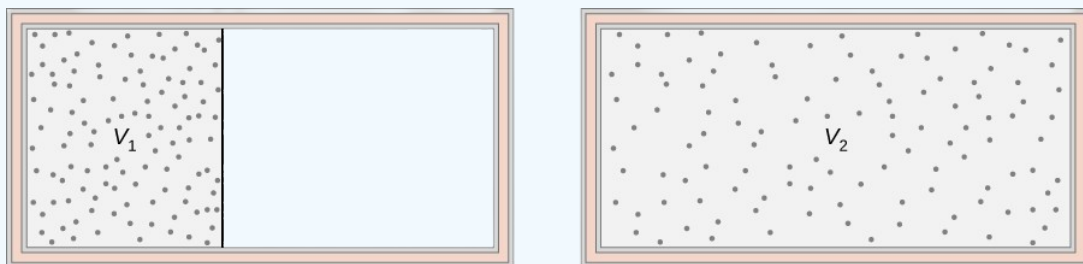


Figure 4.8.2: The adiabatic free expansion of an ideal gas from volume V_1 to volume V_2 .

Strategy

The adiabatic free expansion of an ideal gas is an irreversible process. There is no change in the internal energy (and hence temperature) of the gas in such an expansion because no work or heat transfer has happened. Thus, a convenient reversible path connecting the same two equilibrium states is a slow, isothermal expansion from V_1 to V_2 . In this process, the gas could be expanding against a piston while in thermal contact with a heat reservoir, as in step 1 of the Carnot cycle.

Solution

Since the temperature is constant, the entropy change is given by $\Delta S = Q/T$, where

$$Q = W = \int_{V_1}^{V_2} p dV$$

because $\Delta E_{int} = 0$. Now, with the help of the ideal gas law, we have

$$\Delta S = \frac{Q}{T} = nR \ln \frac{V_2}{V_1}.$$

Because $V_2 > V_1$, ΔS is positive, and the entropy of the gas has gone up during the free expansion.

Significance

What about the environment? The walls of the container are thermally insulating, so no heat exchange takes place between the gas and its surroundings. The entropy of the environment is therefore constant during the expansion. The net entropy change of the universe is then simply the entropy change of the gas. Since this is positive, the entropy of the universe increases in the free expansion of the gas.

✓ Example 4.8.3: Entropy Change during Heat Transfer

Heat flows from a steel object of mass 4.00 kg whose temperature is 400 K to an identical object at 300 K. Assuming that the objects are thermally isolated from the environment, what is the net entropy change of the universe after thermal equilibrium has been reached?

Strategy

Since the objects are identical, their common temperature at equilibrium is 350 K. To calculate the entropy changes associated with their transitions, we substitute the irreversible process of the heat transfer by two isobaric, reversible processes, one for each of the two objects. The entropy change for each object is then given by $\Delta S = mc \ln(T_B/T_A)$.

Solution

Using $c = 450 \text{ J/kg} \cdot \text{K}$, the specific heat of steel, we have for the hotter object

$$\begin{aligned} \Delta S_h &= \int_{T_1}^{T_2} \frac{mc dT}{T} \\ &= mc \ln\left(\frac{T_2}{T_1}\right) \\ &= (4.00 \text{ kg})(450 \text{ J/kg} \cdot \text{K}) \ln \frac{350 \text{ K}}{400 \text{ K}} = -240 \text{ J/K}. \end{aligned}$$

Similarly, the entropy change of the cooler object is

$$\Delta S_c = (4.00 \text{ kg})(450 \text{ J/kg} \cdot \text{K}) \ln \frac{350 \text{ K}}{300 \text{ K}} = 277 \text{ J/K}.$$

The net entropy change of the two objects during the heat transfer is then

$$\Delta S_h + \Delta S_c = 37 \text{ J/K}.$$

Significance

The objects are thermally isolated from the environment, so its entropy must remain constant. Thus, the entropy of the universe also increases by 37 J/K.

? Exercise 4.8.1

A quantity of heat Q is absorbed from a reservoir at a temperature T_h by a cooler reservoir at a temperature T_c . What is the entropy change of the hot reservoir, the cold reservoir, and the universe?

Answer

$$-Q/T_h; Q/T_c; \text{ and } Q(T_h - T_c)/(T_h T_c)$$

? Exercise 4.8.2

A 50-g copper piece at a temperature of 20°C is placed into a large insulated vat of water at 100°C .

- What is the entropy change of the copper piece when it reaches thermal equilibrium with the water?
- What is the entropy change of the water?
- What is the entropy change of the universe?

Answer

a. 4.71 J/K ; b. -4.18 J/K ; c. 0.53 J/K

View this [site](#) to learn about entropy and microstates. Start with a large barrier in the middle and 1000 molecules in only the left chamber. What is the total entropy of the system? Now remove the barrier and let the molecules travel from the left to the right hand side? What is the total entropy of the system now? Lastly, add heat and note what happens to the temperature. Did this increase entropy of the system?

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