

Answer to Essential Question 15.6: We can immediately fill in the following values: $Q_{1\rightarrow 2} = 0$ because there is no heat in an adiabatic process; $\Delta E_{\text{int},2\rightarrow 3} = +800 \text{ J}$ so the $2 \rightarrow 3$ process satisfies the first law; and $\Delta E_{\text{int,cycle}} = 0$ because that is always true (the system returns to its initial state, with no change in temperature). With those three values in the table it is straightforward to fill in the remaining values by (a) making sure that each row satisfies the first law ($Q = W + \Delta E_{\text{int}}$) and, (b) that in every column the sum of the values for the individual processes is equal to the value for the entire cycle. The completed table is shown in Table 15.4.

Process	Q (J)	W (J)	ΔE_{int} (J)
1 \rightarrow 2	0	+300	-300
2 \rightarrow 3	+800	0	+800
3 \rightarrow 1	-1000	-500	-500
Entire Cycle	-200	-200	0

Table 15.4: The completed table.

15-7 Entropy and the Second Law of Thermodynamics

A system of ideal gas in a particular state has an entropy, just as it has a pressure, a volume, and a temperature. Unlike pressure, volume, and temperature, which are easy to determine, the entropy of a system can be difficult to find. On the other hand, changes in entropy can be quite straightforward to calculate.

Entropy: Entropy is in some sense a measure of disorder. The symbol for entropy is S , and the units are J/K.

Change in entropy: In certain cases the change in entropy, ΔS , is easy to determine. An example is in an isothermal process in which an amount of heat Q is transferred to a system:

$$\Delta S = \frac{Q}{T} \quad \text{(Equation 15.12: Change in entropy for an isothermal process)}$$

In cases where heat is transferred while the temperature changes, the change in entropy can be approximated if the temperature change is small compared to the absolute temperature. In this case:

$$\Delta S \approx \frac{Q}{T_{\text{av}}}, \quad \text{(Equation 15.13: Approximate change in entropy)}$$

where T_{av} is the average temperature of the system while the heat is being transferred.

EXAMPLE 15.7 – Mixing water

You have two containers of water. In one container there is 1.0 kg of water at 17°C, while in the second container there is 1.0 kg of water at 37°C. You then pour the water in one container into the other container and allow the system to come to equilibrium. Assuming no heat is transferred from the water to the container or the surroundings, determine the change in entropy for (a) the water that is initially cooler, (b) the water that is initially warmer, and (c) the system.

SOLUTION

Because the two samples of water have equal mass the equilibrium temperature will be 27°C, halfway between the initial temperatures of the two samples. Thus, while heat is being transferred from the warmer water to the cooler water the average temperature of the cooler water will be 22°C, or 295K, and the average temperature of the warmer water will be 32°C (305K).

(a) Because a temperature change of 10° is small compared to the absolute temperature of about 300K, we can use Equation 15.13 to find the change in entropy. To find the heat, use:

$$Q = mc\Delta T = (1.0 \text{ kg})(4186 \text{ J/kg } ^\circ\text{C})(10^\circ\text{C}) = 41860 \text{ J} .$$

This heat is added to the cooler water, so the heat is a positive quantity. Thus:

$$\Delta S_1 \approx \frac{Q}{T_{av}} = \frac{+41860 \text{ J}}{295\text{K}} = +141.90 \text{ J/K} .$$

(b) The heat added to the cooler water comes from the warmer water, so the heat involved for the warmer water is also 41860 J, but negative because it is removed. Thus:

$$\Delta S_2 \approx \frac{Q}{T_{av}} = \frac{-41860 \text{ J}}{305\text{K}} = -137.25 \text{ J/K} .$$

(c) Although the entropy of the warmer water decreases, on the whole, the system's entropy increases by an amount:

$$\Delta S = \Delta S_1 + \Delta S_2 = +141.90 \text{ J/K} - 137.25 \text{ J/K} = +4.7 \text{ J/K} .$$

The situation above is an example of an irreversible process. Even though energy in the 2.0 kg of water at 27°C after mixing is equal to the total energy in the two separate containers before mixing, the entropy of the mixture at one temperature is larger than that of the system of two separate containers at different temperatures. The mixture will not spontaneously separate back into two halves with a 20°C difference, making the process irreversible. This leads us to the second law of thermodynamics.

The Second Law of Thermodynamics: The entropy of a closed system never decreases as time goes by. Reversible processes do not change the entropy of a system, while irreversible processes increase a system's entropy.
 $\Delta S \geq 0$. (Equation 15.14: **The Second Law of Thermodynamics**)

Entropy is sometimes referred to as time's arrow – time proceeds in the direction of increasing entropy. Imagine watching a science fiction movie in which a spacecraft in deep space explodes into a million pieces. Then you play the film backwards, and see the million pieces magically come together to form the spacecraft. You know without a doubt that the film is running backwards – what is it that gives it away? Both momentum and energy are conserved in the explosion, whether you view it forwards or backwards. What gives it away that you are viewing the film backwards is that the process of the million pieces coming together to form the spacecraft decreases the entropy of the system. Our experience is that systems obey the second law of thermodynamics, and proceed in a direction that tends to increase entropy.

What if you view a film forwards and backwards and you can not tell which direction corresponds to time moving forwards? An example would be an elastic collision between two objects. In such a case, the process on film is most likely reversible, with no change (or negligible change) in entropy, giving us nothing to go by to determine the direction of increasing time.

Related End-of-Chapter Exercises: 39, 40, and 57.

Essential Question 15.7: When you were younger, you were probably asked to clean up your room. Let's say that you cleaned your room up on Saturday, and over the course of the next week it gradually got messy again – the second law of thermodynamics at work! The next Saturday you had to clean your room again. What happened to the entropy of your room when you cleaned it up? Does this violate the second law of thermodynamics? Explain.