Pearson

18.5: Heat Transfer and Entropy Changes of the Surroundings

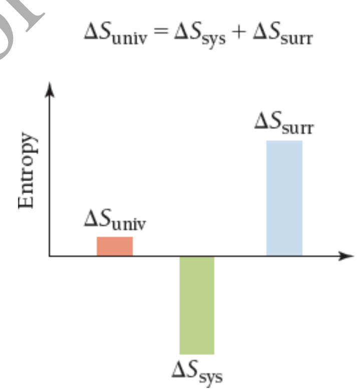
In Section 18.3, we observed that the criterion for spontaneity is an increase in the entropy of the universe. In Section 18.4, we saw how we can calculate the entropy change for a state change. But some of these state changes seem to happen spontaneously and correspond to a decrease in entropy. For example, when water freezes at temperatures below 0 °C, the entropy of the water decreases, yet the process is spontaneous. Similarly, when water vapor in air condenses into fog on a cold night, the entropy of the water also decreases. Why are these processes spontaneous?

To answer this question, we must return to the second law: for any spontaneous process, the entropy *of the universe* increases ($\Delta S_{\text{univ}} > 0$). Even though the entropy *of the water* decreases during freezing and condensation, the entropy *of the universe* must somehow increase in order for these processes to be spontaneous. If we define the water as the system, then ΔS_{sys} is the entropy change for the water itself, ΔS_{surr} is the entropy change for the surroundings, and ΔS_{univ} is the entropy change for the universe. The entropy change for the universe is the sum of the entropy changes for the system and the surroundings:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

The second law states that the entropy of the universe must increase ($\Delta S_{\text{univ}} > 0$) for a process to be spontaneous. The entropy of the *system* can decrease ($\Delta S_{\text{sys}} < 0$) as long as the entropy of the *surroundings* increases by a greater amount ($\Delta S_{\text{surr}} > -\Delta S_{\text{sys}}$), so that the overall entropy of the *universe* undergoes a net increase.

For liquid water freezing or water vapor condensing, we know that the change in entropy for the system ΔS_{sys} is negative (because state changes from liquid to solid and from gas to liquid both result in less entropy). For ΔS_{univ} to be positive, therefore, ΔS_{surr} must be positive and greater in absolute value (or magnitude) than ΔS_{sys}, as shown graphically here:



But why does the freezing of ice or the condensation of water increase the entropy of the surroundings? Because both processes are *exothermic:* they give off heat to the surroundings. Because entropy is the dispersal or randomization of energy, *the release of heat energy by the system disperses that energy into the surroundings, increasing the entropy of the surroundings*. The freezing of water below 0 °C and the condensation of water vapor on a cold night both increase the entropy of the universe because the heat given off to the surroundings increases the entropy of the surroundings to a sufficient degree to overcome the entropy decrease in the system.

> Even though (as we saw earlier) enthalpy by itself cannot determine spontaneity, the increase in the entropy of the surroundings caused by the release of heat explains why exothermic processes are

so *often* spontaneous.

Summarizing Entropy Changes in the Surroundings:

- An exothermic process increases the entropy of the surroundings.
- An endothermic process decreases the entropy of the surroundings.

The Temperature Dependence of ΔS_{surr}

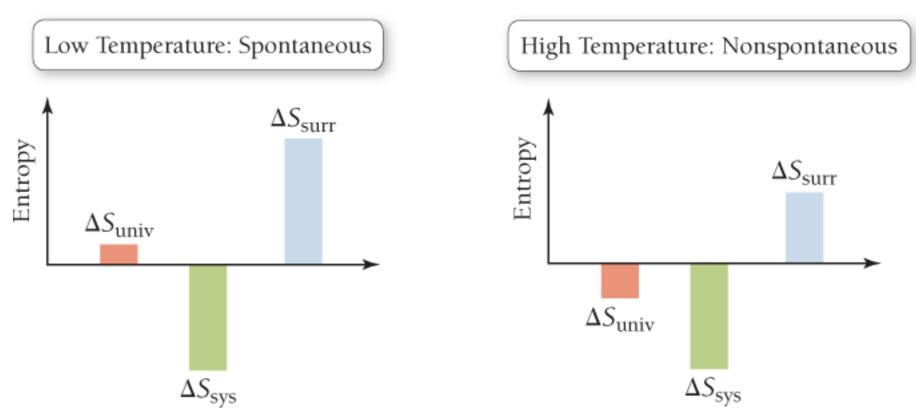
We just discussed how the freezing of water increases the entropy of the surroundings by dispersing heat energy into the surroundings. Yet we know that the freezing of water is not spontaneous at all temperatures. The freezing of water becomes *nonspontaneous* above 0 °C. Why? Because entropy represents the energy dispersed into a sample of matter *per unit temperature*—it has the units of joules per kelvin (J/K). The magnitude of the increase in entropy of the surroundings due to the dispersal of energy into the surroundings is *temperature dependent*.

The greater the temperature, the smaller the increase in entropy for a given amount of energy dispersed into the surroundings. The higher the temperature, the lower the amount of entropy for a given amount of energy dispersed. You can understand the temperature dependence of entropy changes due to heat flow with a simple analogy. Imagine that you have $1000 to give away. If you gave the $1000 to a rich man, the impact on his net worth would be negligible (because he already has so much money). If you gave the same $1000 to a poor man, however, his net worth would change substantially (because he has so little money). Similarly, if you disperse 1000 J of energy into surroundings that are hot, the entropy increase is small (because the impact of the 1000 J is small on surroundings that already contain a lot of energy). If you disperse the same 1000 J of energy into surroundings that are cold, however, the entropy increase is large (because the impact of the 1000 J is great on surroundings that contain little energy). For this same reason, the impact of the heat released to the surroundings by the freezing of water depends on the temperature of the surroundings—the higher the temperature, the smaller the impact.

We can now see why water spontaneously freezes at low temperature but not at high temperature. For the freezing of liquid water into ice, the change in entropy of the system is negative at all temperatures.

$$\Delta S_{\text{univ}} = \underbrace{\Delta S_{\text{sys}}}_{\text{Negative}} + \underbrace{\Delta S_{\text{surr}}}_{\substack{\text{Positive and large at low temperature} \\ \text{Positive and small at high temperature}}}$$

At low temperatures, the decrease in entropy of the system is overcome by the large increase in the entropy of the surroundings (a positive quantity), resulting in a positive ΔS_{univ} and a spontaneous process. At high temperatures, on the other hand, the decrease in entropy of the system is not overcome by the increase in entropy of the surroundings (because the magnitude of the positive ΔS_{surr} is smaller at higher temperatures), resulting in a negative ΔS_{univ}; therefore, the freezing of water is not spontaneous at high temperature as shown graphically here:



$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \quad \text{(for water freezing)}$$

Quantifying Entropy Changes in the Surroundings

We have seen that when a system exchanges heat with the surroundings, it changes the entropy of the surroundings. In Section 18.4, we saw that, at constant temperature, we can use Equation 18.1 ($\Delta S = q_{rev}/T$) to quantify the entropy change in the system. We can use the same expression to quantify entropy changes in the surroundings. In other words, the change in entropy of the surroundings depends on: (1) the amount of heat transferred into or out of the surroundings; and (2) the temperature of the surroundings.

Since the surroundings are usually an infinitely large bath at constant temperature, the heat transferred into or out of that bath under conditions of constant pressure (where only *PV* work is allowed) is simply $-\Delta H_{sys}$. The negative sign reflects that, according to the first law of thermodynamics, any heat leaving the system must go into the surroundings and vice versa $(q_{sys} = -q_{surr})$. If we incorporate this idea into Equation 18.1, we get the following expression:

[18.2]

$$\Delta S_{surr} = -\frac{\Delta H_{sys}}{T} (\text{constant } P, T)$$

For any chemical or physical process occurring at constant temperature and pressure, the entropy change of the surroundings is equal to the heat dispersed into or out of the surroundings ($-\Delta H_{sys}$) divided by the temperature of the surroundings in kelvins. Notice that:

- A process that emits heat into the surroundings (ΔH_{sys} negative) *increases* the entropy of the surroundings (positive ΔS_{surr}).
- A process that absorbs heat from the surroundings (ΔH_{sys} positive) *decreases* the entropy of the surroundings (negative ΔS_{surr}).
- The magnitude of the change in entropy of the surroundings is proportional to the magnitude of ΔH_{sys}.

Equation 18.1 gives us insight into why exothermic processes have a tendency to be spontaneous at low temperatures—they increase the entropy of the surroundings. As temperature increases, however, a given negative $-\Delta H_{sys}$ produces a smaller positive ΔS_{surr}; for this reason, exothermicity becomes less of a determining factor for spontaneity as temperature increases.

Example 18.3 Calculating Entropy Changes in the Surroundings

Consider the combustion of propane gas:

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g) \quad \Delta H_{rxn} = -2044 \text{kJ}$$

a. Calculate the entropy change in the surroundings associated with this reaction occurring at 25 °C.
b. Determine the sign of the entropy change for the system.
c. Determine the sign of the entropy change for the universe. Is the reaction spontaneous?

SOLUTION

a. The entropy change of the surroundings is given by Equation 18.2. Substitute the value of ΔH_{rxn} and the temperature in kelvins and calculate ΔS_{surr}.

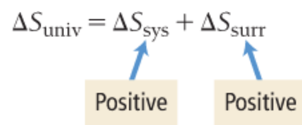
$$T = 273 + 25 = 298\text{K}$$
$$\Delta S_{surr} = \frac{-\Delta H_{rxn}}{T} = \frac{-(-2044\text{kJ})}{298\text{K}}$$
$$= +6.86 \text{ kJ/K}$$
$$= +6.86 \times 10^{-3} \text{ J/K}$$

b. Determine the number of moles of gas on each side of the reaction. An increase in the number of moles of gas implies a positive ΔS_{sys} .

$$\underbrace{C_3H_8\,(g) + 5O_2\,(g)}_{\text{6mol gas}} \rightarrow \underbrace{3CO_2\,(g) + 4H_2O\,(g)}_{\text{7mol gas}}$$

ΔS_{sys} is positive.

c. The change in entropy of the universe is the sum of the entropy changes of the system and the surroundings. If the entropy changes of the system and surroundings are both the same sign, the entropy change for the universe also has the same sign.



Therefore, ΔS_{univ} is positive and the reaction is spontaneous.

FOR PRACTICE 18.3 Consider the reaction between nitrogen and oxygen gas to form dinitrogen monoxide:

$$2\,N_2\,(g) + O_2g \rightarrow 2\,N_2O\,(g) \quad \Delta H_{\text{rxn}} = +163.2\text{ kJ}$$

a. Calculate the entropy change in the surroundings associated with this reaction occurring at 25 °C.
b. Determine the sign of the entropy change for the system.
c. Determine the sign of the entropy change for the universe. Is the reaction spontaneous?

FOR MORE PRACTICE 18.3 A reaction has $\Delta H_{\text{rxn}} = -107$ kJ and $\Delta S_{\text{rxn}} = 285$ J/K. At what temperature is the change in entropy for the reaction equal to the change in entropy for the surroundings?

Conceptual Connection 18.2 **Entropy and Biological Systems**

Interactive