

## Physics 161: Thermodynamics

### Lecture #8

#### The Second Law of Thermodynamics (continued)

#### Review

In the last lecture we began with the statement of Clausius,

“There is no process possible whose sole result is to transfer heat from a cold body to a hot body.”

Based on this statement, we proved that all reversible heat engines operating between two heat reservoirs have exactly the same efficiency, no matter what the working fluid, and no matter what the cycle. They all have the efficiency of the Carnot engine,

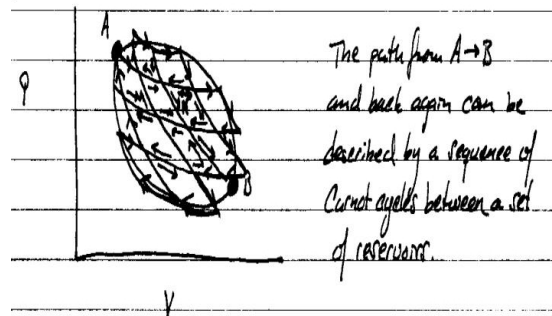
$$\varepsilon_{\text{reversible}} = 1 - \frac{T_C}{T_H}.$$

This efficiency depends only on the ratio of the temperature of the cold reservoir to the temperature of the hot reservoir. As an aside, we were also able to prove that the efficiency of all irreversible heat engines cannot be greater than the Carnot efficiency.

$$\varepsilon_{\text{irreversible heat engine}} \leq 1 - \frac{T_C}{T_H}.$$

This statement is known as Carnot's theorem.

Next, we discussed arbitrary reversible cycles. We reasoned that any reversible cycle can be imagined to be made of an infinite number of reversible adiabatic expansions(or compressions) alternating with an infinite number of reversible isothermal expansions (or compressions), all connected together in a closed loop. Across each isotherm, the system takes on heat (or gives off heat). Across each adiabat, the system lowers (or raises) its temperature. In general, as we travel around a closed loop, the system will have a different temperature for each isotherm. Recall, however, that to carry out the transfer of heat reversibly, the system temperature must be the same as the temperature of the surroundings. Consequently, in order to realize such a cycle in a reversible manner, we would have to have an infinite number of heat reservoirs at our disposal, the  $i$ th reservoir having a temperature  $T_i$  corresponding to the appropriate isotherm.



If you connect all of the isotherms and adiabats and fill out the area in the  $PV$  diagram, you can see that any arbitrary reversible path can be written as a mesh of little Carnot cycles. The internal paths of the adjacent Carnot cycles cancel out, leaving just the external sequence of adiabats and isotherms which takes you around the closed loop of the cycle in question.

We examined the relation between the heat and the temperature for each Carnot cycle in the mesh. Since  $\Delta U = 0$  for any cycle, it follows that, for the  $i$ th Carnot cycle, there is a relation between heat and work,

$$\delta W_{\text{net } i} = \delta Q_{C_i} + \delta Q_{H_i}$$

As usual, we use the  $\delta$  to indicate smallness;  $\delta W$  is a small amount of work, and  $\delta Q$  is a small amount of heat. This means that the efficiency of each Carnot cycle can always be written as

$$\begin{aligned} \varepsilon_i &= \frac{\delta W_{\text{net } i}}{\delta Q_{H_i}} = \frac{\delta Q_{C_i} + \delta Q_{H_i}}{\delta Q_{H_i}} \\ &= 1 + \frac{\delta Q_{C_i}}{\delta Q_{H_i}} \end{aligned}$$

But we know that the efficiency depends on the ratio of temperatures between the hot reservoir and the cold reservoir,

$$\varepsilon_i = 1 - \frac{T_{C_i}}{T_{H_i}}$$

Putting these together, we get

$$1 + \frac{\delta Q_{C_i}}{\delta Q_{H_i}} = 1 - \frac{T_{C_i}}{T_{H_i}}$$

Canceling the 1, we end up with

$$\frac{\delta Q_{C_i}}{\delta Q_{H_i}} = -\frac{T_{C_i}}{T_{H_i}}$$

This means that for each Carnot loop,

$$\frac{\delta Q_{C_i}}{T_{C_i}} = -\frac{\delta Q_{H_i}}{T_{H_i}},$$

or that

$$\frac{\delta Q_{C_i}}{T_{C_i}} + \frac{\delta Q_{H_i}}{T_{H_i}} = 0.$$

If this relation is equal to zero for each loop, obviously, summing over all of the loops in the mesh also gives zero;

$$\sum_{i \text{ (all Carnot loops in mesh)}} \left( \frac{\delta Q_{C_i}}{T_{C_i}} + \frac{\delta Q_{H_i}}{T_{H_i}} \right) = 0.$$

But in such a summation, you can see that the cold temperature  $T_C$  for one Carnot loop serves as the hot temperature  $T_H$  for the loop just below. And the heat taken from the hot reservoir  $\delta Q_H$  for one Carnot loop must be the same as the heat dumped into the cold reservoir,  $-\delta Q_C$  for the Carnot loop just above. This means that all of the “shared” internal paths of the little Carnot loops in the mesh cancel out in the sum, leaving only the connected series of adiabats and isotherms which follow along the perimeter. This means that the sum which follows the cycle around the closed loop is equal to zero:

$$\sum_{i \text{ (closed loop)}} \frac{\delta Q_i}{T_i} = 0$$

In the limit of an infinite number of isotherms and adiabats, this can be written as an integral,

$$\int \frac{\delta Q}{T}_{\text{closed loop}} = 0$$

It is also common to indicate the closed loop by the notation

$$\oint \frac{\delta Q}{T} = 0$$

Because this result does not depend on the shape of the loop, it can be shown that the quantity  $\delta Q/T$  for any reversible path must be related to a perfect differential of some state function, some function whose difference only depends on a difference in endpoints, and does not depend on the particular path taken to get from one point to another. This is a new state function that we have not seen before in our discussions of the first law. Clausius called this function “entropy”, and ascribed to it the symbol  $S$ . A small change  $dS$  is equal to  $\delta Q/T$  for reversible heat transfer. To indicate this, we write,

$$dS = \frac{\delta Q_{\text{reversible}}}{T}.$$

This summarizes the *historical* procedure by which Clausius discovered the existence of the property *entropy*.

The Relation Between  $S(T, V)$  and the two equations of state,  $U = U(T, V)$   
and  $P = P(T, V)$

How can it be that all fluids give the same efficiency for a Carnot cycle? We said that it has to be universally true, but doesn't that imply special, *universal* properties of all fluids that cause this to be so? When you take a look back at the calculations we performed to find Carnot efficiency for an ideal gas, you can see that the efficiency hinged on properties of the fluid dictated by both its *physical equation of state*  $P = P(T, V)$  and its *energy equation of state*  $U = U(T, V)$ . For an ideal gas these were  $P = nRT/V$ , and  $U = C_v T$ . Both were established independently by careful measurements of the properties of gases. Yet, since the efficiency of the Carnot cycle combines the properties of both, and since the Carnot efficiency is a universal property of all substances (or else the second law would be violated), you realize that these two equations of state can't be actually be independent relations. When you think about it, for all the fluids that have been discovered in this world (and for all the fluids yet to be discovered), each equation of state  $P = P(T, V)$  must be paired-off with a unique energy equation of state  $U = U(T, V)$  so that all the fluids have the same Carnot efficiency. How do we express the important relationship between  $P(T, V)$  and  $U(T, V)$ ? As we will see below, the two equations of state are linked to one another via the new state function  $S(T, V)$ .

We have proved above that there is a new state function  $S$ , called entropy, that is related to the reversible heat transfer, i.e.

$$\delta Q_{\text{reversible}} = TdS$$

This has been shown to be a consequence of the second law, the assertion that heat will not spontaneously flow from a cold body to a hot body. Recall now the first law of thermodynamics,

$$dU = \delta Q - \delta W$$

which asserts in part that the energy  $U$  is a function of state. This means that for any process that gives rise to a change in state, we can always calculate a change  $\Delta U$  by following a hypothetical reversible path for which the same change in state is achieved. As we have discussed, for a reversible process, the work

$$\delta W_{\text{reversible}} = PdV$$

is connected to the state functions  $P$  and  $V$ . Moreover, we have just established that, for a reversible process, the heat

$$\delta Q_{\text{reversible}} = TdS$$

is connected to the state functions  $T$  and  $S$ . Substituting these two quantities into the first law establishes an important connection between changes in the state functions  $U$ ,  $S$ , and  $V$ :

$$dU = TdS - PdV. \tag{1}$$

This is the celebrated equation that establishes the relation between  $U(T, V)$  and  $P(T, V)$  so that all fluids have the same Carnot efficiency. Alternatively, it can be regarded as the *definition* of the state function  $S$ . By rearranging terms in (1) we can write

$$dS = \frac{1}{T}dU + \frac{P}{T}dV \quad (2)$$

Comparing this to a formal expansion of a state function  $S(U, V)$ ,

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV, \quad (3)$$

we see by comparing the expansion coefficients that multiply  $dU$  and  $dV$  that the entropy  $S(U, V)$  must be such that

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}, \text{ and} \quad (4)$$

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}. \quad (5)$$

These two relations define entropy.

As a definition of the entropy, it is probably best to remember relation (2), and then compare this with relations (3)-(5). But most people find it easier to remember equation (1) because it is written in the same form as the first law for a reversible process. Indeed, equation (1) looks like the first law, and yet, as the definition of  $S$ , it is actually a statement of the second law!

Along the same lines, the second law establishes a connection between changes in the state functions  $H$ ,  $S$ , and  $P$ . Starting with  $dH = dU + d(PV)$ , and substituting the expression above for  $dU$ , we have

$$\begin{aligned} dH &= TdS - PdV + d(PV) \\ &= TdS - PdV + PdV + VdP \end{aligned}$$

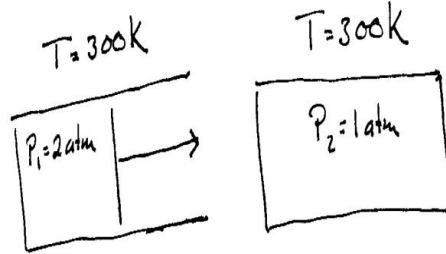
$$\therefore dH = TdS + VdP$$

### Examples of Calculations of $\Delta S$

In order to become more familiar with entropy, let us calculate  $\Delta S$  for various physical processes.

Example 1:

One mole of ideal gas is confined in a piston at a pressure of 2 atm and a temperature of  $T = 300$  K. The gas is allowed to expand reversibly and isothermally, to a final pressure that is half of the initial pressure (1 atm). Calculate  $Q$  and  $\Delta S$  for this process.



First of all,  $\Delta U = \Delta H = 0$  for an ideal gas at constant temperature. This implies that  $Q = W$ . Second, we recall that for a reversible isothermal expansion, the work is given by

$$\begin{aligned}
 W &= \int_1^2 P dV = \int_1^2 nRT \frac{dV}{V} \\
 &= nRT \int_1^2 \frac{dV}{V} \\
 &= nRT \ln V \Big|_1^2 \\
 &= nRT (\ln V_1 - \ln V_2) \\
 &= nRT \ln \frac{V_2}{V_1}
 \end{aligned}$$

For constant temperature, we know that the volume ratio

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} = \frac{2 \text{ atm}}{1 \text{ atm}} = 2$$

is the reciprocal of the pressure ratio.

$$\therefore W = nRT \ln 2$$

$$\begin{aligned}
 \therefore Q &= nRT \ln 2 \\
 &= 1 \text{ mole} \times 8.314 \frac{\text{J}}{\text{mole K}} \times 300 \text{ K} \times \ln 2 \\
 &= 1.7 \text{ kJ}
 \end{aligned}$$

Because the process was carried out reversibly, there is a direct connection between the entropy and the heat.

$$\begin{aligned}
 \Delta S &= \frac{Q_{\text{reversible}}}{T} \\
 &= \frac{nRT \ln 2}{T}
 \end{aligned}$$

$$\begin{aligned}
\therefore \Delta S &= nR \ln 2 \\
&= 1 \text{ mole} \times 8.314 \frac{\text{J}}{\text{mole K}} \times \ln 2 \\
&= 5.8 \text{ J/K}
\end{aligned}$$

It is also useful to note the change in entropy of the surroundings. As we mentioned before, owing to its enormous extent, heat is always taken on reversibly by the surroundings, so we have

$$\Delta S_{\text{surroundings}} = \frac{Q_{\text{surroundings}}}{T}$$

If the system gains an amount of heat  $Q$ , then the surroundings loses an amount of heat  $Q$ .

$$\begin{aligned}
\therefore Q_{\text{surroundings}} &= -Q \\
&= -nRT \ln 2
\end{aligned}$$

$$\begin{aligned}
\therefore \Delta S_{\text{surroundings}} &= -nR \ln 2 \\
&= -5.8 \text{ J/K}
\end{aligned}$$

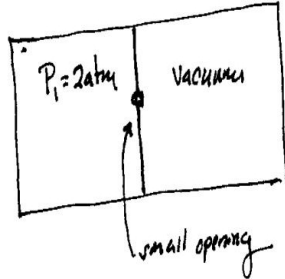
The entropy change of the surroundings is just the negative of the entropy change of the system. Thus the entropy change of the system plus the surroundings (the universe) is

$$\begin{aligned}
\Delta S_{\text{universe}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\
&= nR \ln 2 - nR \ln 2 = 0.
\end{aligned}$$

Example 2:

One mole of ideal gas is confined in one half of a cylinder at a pressure of 2 atm, and is in equilibrium with the surroundings at temperature of  $T = 300$  K. The other half of the cylinder is initially evacuated. The two halves of the chamber are separated by a baffle, but connected to one another by a small opening which is initially sealed with a cork. When the cork is withdrawn, the gas expands to fill the entire cylinder, and again comes to equilibrium with the surroundings at  $T = 300$  K. Calculate  $Q$  and  $\Delta S$  for this process. Calculate  $\Delta S_{\text{universe}}$ . Compare your results to those of Example 1.

Because the temperature is constant, after the volume doubles, the pressure drops to one half of its initial value. So the initial pressure  $P_1 = 2$  atm, and the final pressure  $P_2 = 1$  atm. Therefore the initial and final states of the system are identical to the initial and final states of Example 1. The only difference in the two examples is that this isothermal process clearly takes place irreversibly; the gas is no longer in equilibrium as it rushes to fill both halves of the cylinder.



Again we will take advantage of the fact that  $\Delta U = 0$  for an ideal gas at constant temperature, and consequently  $Q = W$ . In this case there is no piston, and so the gas does no work on the surroundings.  $W = 0$ , and therefore

$$Q = 0.$$

Now, doesn't the fact that  $Q = 0$  imply that

$$\Delta S = 0?$$

In this case, the answer is no. We must remember that heat is only connected to the change in entropy for a reversible process, i.e.,

$$dS = \frac{dQ_{\text{reversible}}}{T}.$$

As this process is irreversible, the fact that  $Q = 0$  does not necessarily mean that  $\Delta S = 0$ . How then do we calculate  $\Delta S$ ? We will take advantage of the fact that  $S$  is a state function, so that the change in  $S$  only depends on the initial and final states, and not on the path taken to go from one to the other. To facilitate a calculation, let us try to imagine a reversible path which will connect these same two states, and then calculate the change in  $S$  as we integrate along this path. We need not stretch ourselves on this point; the expansion carried out in Example 1 is, after all, an example of a reversible process which connects these same two states. Indeed, let us imagine that we achieve a doubling of the volume of the cylinder by, say, slowly sliding the baffle to the right, allowing the gas to do reversible work against the baffle until the volume is doubled. The change in  $S$  can be calculated by considering the first law relation

$$dU = TdS - PdV$$

The energy  $U$  does not change because the process is isothermal and the gas is ideal. Therefore, we have

$$0 = TdS - PdV$$



or

$$\begin{aligned}dS &= \frac{P}{T}dV \\ &= \frac{\left(\frac{nRT}{V}\right)}{T}dV \\ &= nR\frac{dV}{V}.\end{aligned}$$

Notice that we have eliminated both  $P$  and  $T$  by substituting the equation of state. Integrating from the initial volume to the final volume, we have

$$\begin{aligned}\int_1^2 dS &= nR \int_1^2 \frac{dV}{V} \\ S|_1^2 &= nR \ln V|_1^2 \\ S_2 - S_1 &= nR \ln \frac{V_2}{V_1}\end{aligned}$$

$$\begin{aligned}\therefore \Delta S &= nR \ln 2 \\ &= 5.8 \text{ J/K}\end{aligned}$$

Note that the entropy change is exactly the same as it was for Example 1, even though  $Q = 0$  whereas 1.7 kJ for Example 1.

Was it obvious from the start that  $\Delta S$  would again be 5.8 J/K? Indeed, since  $S$  is a state variable, we should have known that  $\Delta S$  would be the same for the two processes as soon as we realized that the initial and final states of the gas were the same.

Let us look now at  $\Delta S_{\text{surroundings}}$ . Because  $Q = 0$ , we see that

$$\Delta S_{\text{surroundings}} = 0$$

It follows, therefore, that in this case the entropy change of the universe,

$$\begin{aligned}\Delta S_{\text{universe}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ &= nR \ln 2 \\ &= 5.8 \text{ J/K}.\end{aligned}$$

Note that for the reversible expansion carried out in Example 1, we found that the entropy change of the universe was zero. For the irreversible expansion we now find that the entropy change of the universe is positive. We will see that this is just an illustration of a general result; for a reversible process the entropy of the universe will remain constant; for an irreversible process, the entropy of the universe will always increase.

Example 3:

A cup holding 100 gms of water at a temperature of 100 C comes to equilibrium with the surroundings at a temperature of 25 C, at constant pressure. Calculate  $Q$  and  $\Delta S$  for the system,  $\Delta S$  for the surroundings, and  $\Delta S$  for the universe. Take the heat capacity  $\bar{C}_P = 1 \text{ cal}/(\text{g K})$  to be independent of temperature.

Recall that the heat added at constant pressure is given by the change in enthalpy, which is given by

$$\Delta H = C_P \Delta T$$

in the case of a constant heat capacity. -----

If the expression above is unfamiliar, you should recall that the change in enthalpy can be found by integrating  $dH$  between the initial and final states. It is wise to expand  $H$  in terms of the two variables  $T$  and  $P$ ,

$$dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP,$$

so that one can take advantage of the fact that  $P$  is held constant so  $dP = 0$ , and therefore,

$$dH = \left( \frac{\partial H}{\partial T} \right)_P dT.$$

Integrating both sides, we have

$$\begin{aligned} \Delta H &= \int_1^2 \left( \frac{\partial H}{\partial T} \right)_P dT \\ &= \int_1^2 C_P dT \end{aligned}$$

Taking  $C_P$  to be constant, it can be removed from the integration, giving the advertised result,

$$\Delta H = C_P \Delta T.$$

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 $Q = \Delta H$  at constant pressure, it follows that

$$\begin{aligned} Q &= C_P \Delta T \\ &= 1 \frac{\text{cal}}{\text{g K}} \times 100 \text{ gm} \times (298 \text{ K} - 373 \text{ K}) \\ &= -7.5 \text{ kcal}. \end{aligned}$$

Because  $Q_{\text{surroundings}} = -Q_{\text{system}}$ , we see the change in entropy of the surroundings will be positive;

$$\begin{aligned} \Delta S_{\text{surroundings}} &= \frac{7.5 \text{ kcal}}{T_{\text{surroundings}}} \\ &= \frac{7.5 \text{ kcal}}{298 \text{ K}} \\ &= 25 \text{ cal/K}. \end{aligned}$$

To calculate the change in entropy of the system, we can take advantage of the relation between enthalpy and entropy,

$$dH = TdS + VdP.$$

Pressure is constant, so  $dP = 0$ , and as we have noted above,  $dH = C_P dT$ . Therefore, this implies that

$$C_P dT = TdS$$

or that

$$dS = C_P \frac{dT}{T}$$

Integrating both sides of this equation, find that the change in entropy of the system is negative;

$$\begin{aligned} \Delta S &= C_P \ln \frac{T_2}{T_1} \\ &= 1 \frac{\text{cal}}{\text{g K}} \times 100 \text{ gm} \times \ln \frac{298}{373} \\ &= -22 \text{ cal/K.} \end{aligned}$$

The change in entropy of the universe is positive,

$$\begin{aligned} \Delta S_{\text{universe}} &= -22 \text{ cal/K} + 25 \text{ cal/K} \\ &= 3 \text{ cal/K.} \end{aligned}$$

Example 4:

100 gms of water in a beaker on the window sill is supercooled to  $-10^\circ\text{C}$  on a chilly NM night. A Snow flake settles into the supercooled water and initiates crystallization. The liquid is completely crystallized, and the heat liberated is absorbed into the ambient surroundings at  $-10^\circ\text{C}$ . Calculate  $\Delta S$  for the water, and for the surroundings. Take  $C_P(\text{liquid}) = 4.184 \text{ J}/(\text{gm K})$ ,  $C_P(\text{solid}) = 2.092 \text{ J}/(\text{gm K})$ , and the latent heat of fusion  $\Delta H_{\text{fusion}} = 333.3 \text{ J}/\text{gm}$ .

To calculate  $\Delta S$  let us imagine following a reversible path from the initial state of supercooled water at  $-10^\circ\text{C}$  to the final state consisting of ice at  $-10^\circ\text{C}$ . Let us take the following steps:

1. Imagine first that we slowly warm the water from  $-10^\circ\text{C}$  up to  $0^\circ\text{C}$ . For this step,

$$\begin{aligned} \Delta S_1 &= C_P(\text{liquid}) \int \frac{dT}{T} \\ &= 100 \text{ gm} \times 4.184 \text{ J}/(\text{gmK}) \times \ln \frac{273}{263} \\ &= 15.61 \text{ J/K} \end{aligned}$$

2. Imagine the second step is to put the water at  $0^\circ\text{C}$  in contact with a cold reservoir at nearly  $0^\circ\text{C}$ , and let the water freeze reversibly. The amount of heat

taken out of the water to freeze it is given by the latent heat of fusion. The system loses heat reversibly, so for this step,

$$\begin{aligned}\Delta S_2 &= \frac{Q_{\text{reversible}}}{T} \\ &= \frac{-\Delta H_{\text{fusion}}}{T} \\ &= 100 \text{ gm} \times \frac{-333.3\text{J/gm}}{273\text{K}} = -122.1 \text{ J/K}\end{aligned}$$

3. Imagine a third step in which the ice at 0 C is now slowly cooled back down to -10 C. The change in entropy for this step is

$$\begin{aligned}\Delta S_3 &= C_{P(\text{solid})} \int \frac{dT}{T} \\ &= 100 \text{ gm} \times 2.092\text{J}/(\text{gmK}) \times \ln \frac{263}{273} \\ &= -7.807 \text{ J/K}\end{aligned}$$

Adding up the entropy changes for all three reversible stages gives the total entropy change,

$$\begin{aligned}\Delta S &= 15.61 \text{ J/K} - 122.1 \text{ J/K} - 7.807 \text{ J/K} \\ &= -114.30 \text{ J/K},\end{aligned}$$

which is negative.

Now let us calculate the entropy change of the surroundings. This is related to the heat added to the system as follows:

$$\begin{aligned}\Delta S_{\text{surroundings}} &= \frac{Q_{\text{surroundings}}}{T_{\text{surroundings}}} \\ &= \frac{-Q_{\text{system}}}{263 \text{ K}}.\end{aligned}$$

The heat added to the system,  $Q_{\text{system}}$  is given by  $\Delta H$  for the process. This can be calculated by following the same three stages:

$$\begin{aligned}\Delta H_1 &= \int_{263}^{273} C_{P(\text{liquid})} dT \\ &= 100 \text{ gm} \times 4.184\text{J}/(\text{gmK}) \times (273 - 263) \text{ K} \\ &= 4184 \text{ J}.\end{aligned}$$

$$\begin{aligned}\Delta H_2 &= 100 \text{ gm} \times -333.3\text{J/gm} \\ &= -33,330 \text{ J}\end{aligned}$$

$$\begin{aligned}\Delta H_3 &= \int_{273}^{263} C_{P(\text{solid})} dT \\ &= 100 \text{ gm} \times 2.092\text{J}/(\text{gmK}) \times (263 - 273) \text{ K} \\ &= -2092 \text{ J}\end{aligned}$$

Therefore

$$\begin{aligned} Q &= \Delta H = 4184 \text{ J} - 33,330 \text{ J} - 2092 \text{ J} \\ &= -31,241 \text{ J} \end{aligned}$$

It follows that

$$\begin{aligned} \Delta S_{\text{surroundings}} &= \frac{31,241 \text{ J}}{263 \text{ K}} \\ &= 118.79 \text{ J/K} \end{aligned}$$

The change in entropy of the universe for this process is positive;

$$\begin{aligned} \Delta S_{\text{universe}} &= 118.79 \text{ J/K} - 114.30 \text{ J/K} \\ &= 4.49 \text{ J/K}. \end{aligned}$$

#### Direction of Change

For the four processes described above, the entropy of the system was found to be zero, negative, positive, and positive, respectively. There doesn't seem to be a pattern here. But there is a trend if you focus instead on the change in entropy of the universe. For the three irreversible processes examined in Examples 2, 3, and 4, the change in entropy of the universe was found to be positive. These examples represent processes which obviously occur in nature. It is interesting to think about what we would have found had we had accidentally chosen processes which are impossible. Suppose, for example, that we had posed each of these processes in reverse:

Example 1: Initially gas occupies a cylinder which is partitioned by a baffle which divides the cylinder in half. The pressure is 1 atm, and the temperature is 300 K. When a small opening is made in the baffle, all of the gas moves over to the left chamber, leaving a vacuum in the right chamber. What is the change in entropy of the universe for this process?

Clearly, we would follow the same procedure as above, but since the process is backwards, we would find that

$$\Delta S_{\text{universe}} = -5.8 \text{ J/K}.$$

Example 2: Initially a cup containing 100 gms of hot water is at a temperature of 25 C, which is the same as the temperature of the surroundings. The water is observed to spontaneously warm up, to a temperature of 100 C. What is the change in entropy of the universe for this process?

$$\Delta S_{\text{universe}} = -3 \text{ cal/K}.$$

Example 3: Initially ice is sitting on the window sill at the ambient temperature of -10 C. The ice changes spontaneously to supercooled water at -10 C. What is the change in entropy of the universe for this process?

$$\Delta S_{\text{universe}} = -4.49 \text{ J/K}$$

For all three of these proposed “reverse” irreversible processes, the change in entropy of the universe is negative. This is rather obvious, because the answer must be just the opposite of what we found when examining the processes in the “forward” direction, and in the forward direction we found the entropy change of the universe to be positive. Still, this is very interesting because if there is a general rule that the entropy of the universe always increases for possible irreversible processes, then the entropy of the universe must always decrease for impossible irreversible processes. This would then give us a rule of thumb, allowing us to figure out beforehand whether or not something is possible! If someone suggests a process and we are dubious as to whether or not it could actually happen, we could simply sit down and calculate the change in entropy of the universe.