4.5: Refrigeration

The flow of heat from a hot source to a cold sink is spontaneous, which you now know means that the total entropy increases. To demonstrate, let's imagine that a hot metal block is placed next to a cold one. Initially the hot block loses $-\partial q$ of thermal energy of which $+\partial q$ is gained by the cold one. If we assume this occurs over a short period of time and the magnitude of the initial heat transaction is small, then the relative temperatures are assumed to remain constant. The absolute values of the entropy changes for each system have the following relationship:

$$\left|\frac{+\partial q}{T_{cold}}\right| > \left|\frac{-\partial q}{T_{hot}}\right|$$

due to the fact that $T_{hot} > T_{cold}$. As a result:

$$\Delta S_{total} = \Delta S_{cold} + \Delta S_{hot} = \frac{\partial q}{T_{cold}} - \frac{\partial q}{T_{hot}} > 0\ J/K$$

and the process is spontaneous; this is summarized in Figure 4.7.

Next we move on to your refrigerator, which is a freak of nature because heat flows the wrong way. As shown in Figure 4.7, energy must flow out of the cold reservoir (the refrigerator interior) to the hot exterior. Thus, the ∂q's from our derivation above switch signs and the process is non-spontaneous: $\Delta S_{total} = \Delta S_{cold} + \Delta S_{hot} = \frac{\partial q}{T_{hot}} - \frac{\partial q}{T_{cold}} < 0\ J/K$. Since it is impossible for any process to decreases total entropy, we just proved refrigerators don't exist.

Since you obey the laws of thermodynamics in your household, there is in fact a mechanism by which your refrigerator can transfer heat from cold to hot yet still generate a net positive change in total entropy. Shown in Figure 4.8 is a diagram of a refrigerator, where a cool gas flows in a continuous loop. The compressor liquefies the coolant, generating heat which is expelled out into the exterior. The liquid then flows past an expansion valve that causes the liquid to become gas, which is a phase change requiring an input of heat from interior of the system. For the remaining discussion, we assume that the closed loop is the system that experiences a positive input of heat ∂q_{cold} at T_{cold} and expels a negative quantity of heat ∂q_{hot} at T_{hot}.

To see how the system generates a net positive (or 0 J/K at a minimum) of total entropy, we first note that there is an input of work (the gas compression) that is turned into heat, the energy of which is fed into the flow from cold to hot as shown in Figure 4.8. As a result, the warmer exterior experiences a greater (+)heat exchange compared to the losses of (-)heat energy by the refrigerator interior. This means $|\partial q_{cold}| < \partial q_{hot}$ (recall that ∂q_{cold} is negative and ∂q_{hot} is positive, so we have to make comparisons to the absolute value of $|\partial q_{cold}|$), and thus the total entropy change is:

$$\Delta S_{total} = \Delta S_{cold} + \Delta S_{hot} = \frac{\partial q_{cold}}{T_{cold}} + \frac{\partial q_{hot}}{T_{hot}} \geq 0\ J/K$$

To summarize, refrigerators work because the heat flow to the exterior is increased to offset the effect of dividing by a larger value of temperature when calculating the entropy change.

4.5.1 Coefficient of performance

In a refrigerator the compressor is responsible for the input of work, which contributes to the relative efficiency of the system as defined by the coefficient of performance (COP):

$$COP = \frac{-\Delta q_{cold}}{\Delta w}$$

The COP defined as a positive quantity (hence -Δq_{cold} in the numerator, and Δw is positive), and is not quite the same thing as efficiency because it can be $>$100%. Of course a COP is desirable, and typical values are $\sim$2$\rightarrow$3. To derive the COP from these metrics of a refrigerator, we first note that conservation of energy requires:

$$\Delta w = \Delta q_{hot} - \Delta q_{cold}$$

as is obvious from Figure 4.8, and as a result $COP = \frac{-\Delta q_{cold}}{\Delta q_{hot} - \Delta q_{cold}}$. To understand the COP better, we need to demonstrate a relationship between the two heat transactions (Δq_{hot} andΔq_{cold}) with the refrigerator "cold" and exterior "hot" temperatures. To do so we will assume that the closed loop of coolant is as efficient as a Carnot engine, and that the 1st Carnot step is the input of heat into the cooling coil inside the refrigerator and the 3rd leg of the Carnot cycle represents the expulsion of heat into the exterior. From Figure 4.5 we see:

$$\frac{\Delta q_{cold}}{\Delta q_{hot}} = \frac{-\Delta w_1}{-\Delta w_3} = \frac{nRT_{cold} \cdot \ln\left(\frac{V_2}{V_1}\right)}{nRT_{hot} \cdot \ln\left(\frac{V_4}{V_3}\right)}$$

Since we showed in the previous section that: $\ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{V_3}{V_4}\right)$ then: $\frac{\Delta q_{cold}}{\Delta q_{hot}} = -\frac{T_{cold}}{T_{hot}}$, or:

$$\Delta q_{cold} = -\frac{T_{cold}}{T_{hot}} \Delta q_{hot}$$

Plugging the above into the equation for the COP yields:

COP=\frac{\frac{T_{cold}}{T_{hot}}\Delta q_{hot}}{\Delta q_{hot}+\frac{T_{cold}}{T_{hot}}\Delta q_{hot}}=\frac{\frac{T_{cold}}{T_{hot}}}{1+\frac{T_{cold}}{T_{hot}}}=\frac{T_{cold}}{T_{hot}-T_{cold}}

We can see that a higher COP can be achieved by minimizing the exterior and interior temperature differences. Too bad, as trying to cool a refrigerator more inherently makes it less efficient.

4.5.2 Thermoelectric Cooling

You may have heard of thermoelectric cooling devices, which are based on the Peltier effect that converts current directly into a temperature gradient. This effect occurs when two different materials are conjoined and current is forced through it, causing one side of the device to warm and the other to cool. While these solid-state devices may seem desirable for cooling as they have no moving parts, are small and lightweight, unfortunately, they are $\sim$1/4th as efficient (or worse) compared to conventional refrigerators. This is because the efficiency of the thermoelectric effect necessitates the use of materials that are highly electrically conductive yet minimally thermally conductive, which are two properties that are usually correlated. Researching new materials with a high thermoelectric efficiency is a current topic of research.