Introduction to Physical Chemistry – Lecture 8

I. LECTURE OVERVIEW

In this lecture we will discuss heat engines. The study of heat engines is what originally led to the emergence of thermodynamics as a branch of science. We will study a particular heat engine known as the Carnot cycle, from which it is possible to deduce the existence of entropy as a state function. This is the way that entropy was actually discovered. Because this approach to entropy is not obtained directly from the laws of probability, it suggests a number of apparent ways to violate the Second Law of Thermodynamics. We will discuss these paradoxes, and how they may be resolved.

II. HEAT ENGINES

A heat engine is a device that absorbs heat energy from a high temperature region, uses some of that heat energy to do work, and then expels heat energy to a region of lower temperature. This concept is illustrated in Figure 1.

The steam engine is a good example of a heat engine (see Figure 2). The way it works is that a heat source, say a fire, is used to heat water to boil. The steam then pushes on a piston, which generates work that can be used to produce motion. As the steam expands, it cools. It is then recycled back to the heat source, where the cycle can begin again.

The early steam engines were highly inefficient, converting only a few percent of the heat absorbed into useful work. The drive to improve the efficiency of steam engines led to general studies of heat engines, which eventually gave birth to the science of thermodynamics.

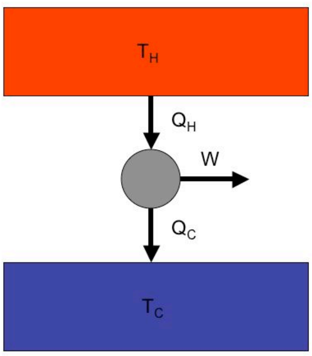

FIG. 1: A schematic of a heat engine operating between a heat source at temperature T_H, and a heat sink at temperature T_C. The heat engine takes in heat from the heat source, converts some of that heat into work, and then dumps the remaining energy into the heat sink.

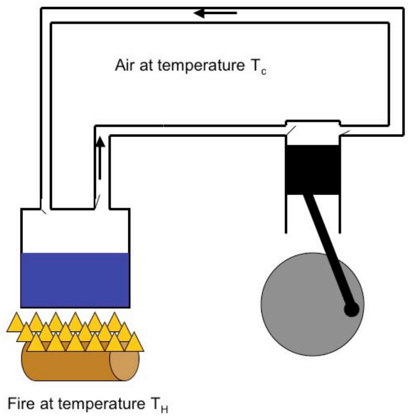

FIG. 2: The steam engine as a heat engine. A heat source, say a fire, is used to heat up a gas (boil water to create steam). The heated gas expands and does work on a piston. The gas cools as it does work. It then cools further while in contact with a low temperature system (the surrounding air). The gas returns to its original state (liquid water), and the cycle begins again.

In 1824, Sadi Carnot published a seminal paper, entitled “Reflections on the motive power of fire,” in which he constructed an idealized heat engine that is capable of extracting the maximum amount of useful work from a given amount of heat. This heat engine is known as a *Carnot cycle*, and we will focus our attention on it next.

III. THE CARNOT CYCLE

The motivation behind the Carnot heat engine is as follows: Given a heat source at a temperature T_H, and a heat sink at a temperature T_C, where $T_H > T_C$, what is the maximum amount of useful work that can be performed by an engine that extracts heat from the heat source at temperature T_H, and dumps any unused energy as heat to the heat sink at the lower temperature T_C?

A. Reversibility as the key to maximizing engine efficiency

Carnot’s central hypothesis is that *the engine must operate in a reversible manner at all times.* To understand this physically, consider a quantity Q of heat absorbed by the engine. If the engine is at a lower temperature than the heat source, the the engine will get hotter. But this means that some of the heat energy is wasted in heating up the engine, rather than doing any kind of useful work. Furthermore, during any expansion of the piston, if the pressure of the gas pushing on the piston is greater than the external pressure, then work is not being extracted optimally from the gas. The reason for this is that, during a change in volume dV, if the gas pressure is P_{gas}, and the pressure of the surroundings is $P_{surround}$, then the work done on the surroundings is $\delta W = P_{surround}dV$. If $P_{gas} > P_{surround}$, then the maximum amount of work that could be extracted is $\delta W_{max} = P_{gas}dV > P_{surround}dV = \delta W$. Therefore, the amount of work actually extracted is less than optimal.

Similarly, during any compression of the piston, if the pressure of the surroundings pushing on the piston is greater than the gas pressure, then an excess amount of work is lost in compressing the gas. If the change in the volume of the gas is given by $-dV$, then $\delta W = -P_{surround}dV$. If $P_{surround} > P_{gas}$, then $\delta W < -P_{gas}dV$, so that the surroundings loses more energy than necessary to compress the gas. Again, this leads to a less than optimal amount of work extracted from the system.

B. Definition of the Carnot cycle

We consider a heat engine containing an ideal gas that can push on a piston (Figure 3 will be helpful here). In the first step, the engine starts at the temperature T_H of the heat source, and is contacted with the heat source. We assume that this heat source is massive, so that heat flow to the engine does not effect the temperature of the source (think of going to the "tayelet" in Tel-Aviv and throwing a piece of ice into the Mediterranean. The heat transferred from the sea water to melt the ice will negligibly affect the temperature of the sea). We reversibly transfer a quantity Q_H of heat to the engine. As the gas absorbs heat energy, it will expand and do work on the surroundings. This expansion is isothermal, because the heat source is so massive that it keeps the engine temperature at T_H (such a heat source is known as a *thermal bath*). As mentioned previously, we assume that, in addition to being isothermal, this expansion is also reversible.

In the second step, the heat source is removed. The engine must now be cooled to the temperature of the heat sink. So, from T_H, the gas is allowed to undergo a reversible, adiabatic expansion, until it reaches a temperature T_C.

In the third step, the piston must be compressed (after all, we want to bring the engine back to its starting state). So, we extract an amount Q_C of heat from the working fluid, resulting in a reversible, isothermal compression of the fluid.

We are not quite done. The gas has been compressed, but it is still at a temperature T_C. So, after extracting the amount Q_C of heat, the heat sink is removed, and the gas undergoes a reversible, adiabatic compression until it reaches a temperature T_H and its original volume.

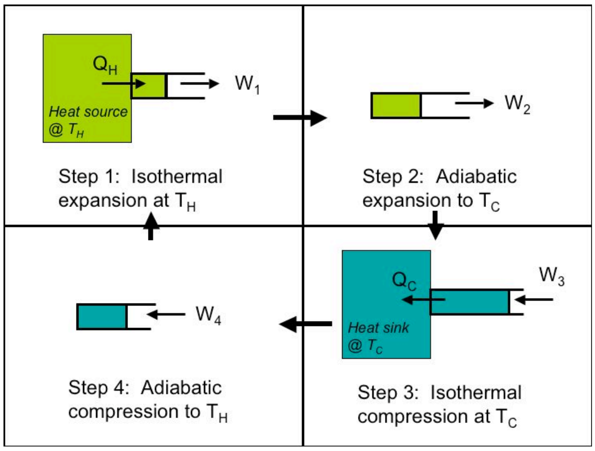

FIG. 3: The four steps of the Carnot heat engine.

This completes the Carnot cycle, which can now begin again.

In summary, the Carnot cycle is a four step process:

1. Isothermal expansion at T_H.
2. Adiabatic expansion from T_H to T_C.
3. Isothermal compression at T_C.
4. Adiabatic compression from T_C to T_H.

C. Efficiency of the Carnot cycle

To compute the efficiency of the Carnot cycle, let us assume that there are n moles of ideal gas driving the piston.

At the beginning of the first step, the gas is at temperature $T_1 = T_H$, and volume V_1. The gas absorbs a quantity Q_H of heat as part of an isothermal expansion. Because $\Delta U = 0$ for this step (why?), we have that the amount of work performed on the surroundings is $W_1 = Q_H$. However, if V_2 denotes the final volume of the gas, then,

$$\begin{aligned} Q_H = W_1 &= \int_{V_1}^{V_2} PdV \\ &= \int_{V_1}^{V_2} \frac{nRT_H}{V} dV \\ &= nRT_H \ln \frac{V_2}{V_1} \end{aligned} \tag{1}$$

In the second step, the gas adiabatically expands from V_2 to some volume V_3, such that its temperature is now T_C. If W_2 denotes the amount of work performed on the surroundings during this step, then from the First Law we have $W_2 = -\Delta U = n\bar{C}_V(T_H - T_C)$ for this process. The relationship between V_2 and V_3 is given by,

$$\frac{T_C}{T_H} = (\frac{V_2}{V_3})^{R/\bar{C}_V} \Rightarrow V_3 = V_2(\frac{T_H}{T_C})^{\bar{C}_V/R} \tag{2}$$

In the third step, the gas is isothermally compressed to some volume V_4, during which a quantity Q_C is extracted and dumped into the heat sink. If W_3 denotes the amount of work performed on the surroundings during this process, then we have from the First Law that $W_3 = -Q_C$ (because Q_C refers to the amount of heat transferred to the heat sink. Therefore, since in the statement of the First Law, a positive Q refers to heat being transferred to the system, we need to put a "-" sign in front of Q_C).

Arguing similarly to the case for the isothermal expansion, we have,

$$W_3 = nRT_C \ln \frac{V_4}{V_3} \Rightarrow Q_C = nRT_C \ln \frac{V_3}{V_4} \tag{3}$$

In the final step, the gas returns to a volume V_1 and temperature T_H, via an adiabatic compression. If W_4 denotes the amount of work performed on the surroundings during this process, then arguing as with the second step we have $W_4 = -\Delta U = -n\bar{C}_V(T_H - T_C)$. The relationship between V_4 and V_1 is given by,

$$V_4 = V_1 (\frac{T_H}{T_C})^{\bar{C}_V/R} \tag{4}$$

The total amount of work done during this cycle is,

$$\begin{aligned}
W_{total} &= W_1 + W_2 + W_3 + W_4 \\
&= Q_H - Q_C \\
&= nR(T_H \ln \frac{V_2}{V_1} - T_C \ln \frac{V_3}{V_4}) \\
&= nR(T_H \ln V_2 - T_C \ln V_3 - T_H \ln V_1 + T_C \ln V_4) \\
&= nR(T_H \ln V_2 - T_C \ln V_2 - \frac{\bar{C}_V T_C}{R} \ln \frac{T_H}{T_C} \\
&\quad -T_H \ln V_1 + T_C \ln V_1 + \frac{\bar{C}_V T_C}{R} \ln \frac{T_H}{T_C}) \\
&= nR(T_H - T_C) \ln \frac{V_2}{V_1} \\
&= nRT_H (1 - \frac{T_C}{T_H}) \ln \frac{V_2}{V_1} \\
&= (1 - \frac{T_C}{T_H}) Q_H
\end{aligned} \tag{5}$$

where in the last two lines we used the fact that $Q_H = W_1 = nRT_H \ln V_2/V_1$.

Therefore, the total amount of useful work extracted from a Carnot cycle is given by $(1 - T_C/T_H)$ times the amount of heat input. And so, the efficiency ϵ_{Carnot} of the Carnot engine is given by,

$$\epsilon_{Carnot} = \frac{W_{total}}{Q_H} = 1 - \frac{T_C}{T_H} \tag{6}$$

We will soon prove that this is the maximal possible efficiency of any heat engine. Note in particular that if $T_C > 0$, then the engine efficiency will be less than 1. Therefore, *it is impossible for any heat engine that operates between temperatures greater than absolute zero to convert all of the heat energy into useful work. Some of the energy will invariably be lost as heat.*

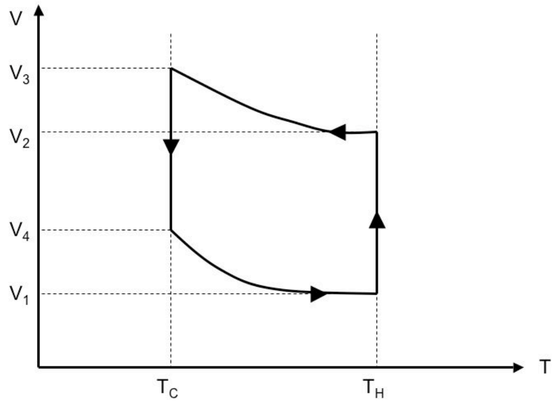

FIG. 4: A plot of temperature T and volume V of the ideal gas as it moves through a Carnot cycle.

For convenience sake, we show a (T, V) diagram illustrating the path that the gas in the Carnot engine traces during the course of the Carnot cycle.

D. The Carnot cycle in reverse

We should also point out that the Carnot engine may be run in reverse. That is, the Carnot engine can remove heat from a cold source at temperature T_C, and with a work input from the surroundings, it can dump the heat into a higher temperature bath. A device that functions in this way is known as a *heat pump*.

An air conditioner is nothing more than a heat pump, since it extracts heat from a room that we want to keep cool and dumps it to the outside air. If the air conditioner can extract heat at a rate equal to the rate at which heat flows into the room from the outside, then the room will remain at its cool temperature.

For a Carnot engine, note that $Q_H = W_{total} + Q_C$. Since $W_{total} = (1 - T_C/T_H)Q_H$, we have $Q_H = W_{total}/(1 - T_C/T_H)$, so that,

$$\begin{aligned}
&\frac{W_{total}}{1 - T_C/T_H} - W_{total} = Q_C \Rightarrow \\
&W_{total} = \frac{Q_C}{\frac{1}{1-\frac{T_C}{T_H}} - 1} \Rightarrow \\
&W_{total} = \frac{Q_C}{\frac{T_H}{T_H - T_C} - \frac{T_H - T_C}{T_H - T_C}} \Rightarrow \\
&W_{total} = Q_C(\frac{T_H}{T_C} - 1)
\end{aligned} \tag{7}$$

and so, the Carnot heat pump must perform $T_H/T_C - 1$ units of work for every unit of heat energy removed from the cool temperature region.

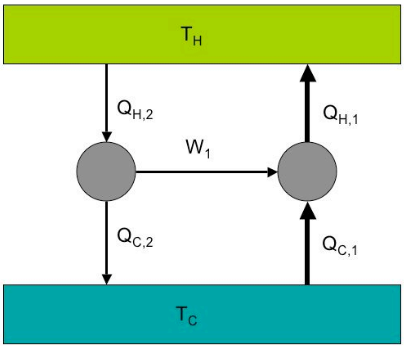

FIG. 5: Illustration of how two reversible heat engines with differing efficiencies leads to a device that facilitates the spontaneous flow of heat from a region of low temperature to a region of high temperature.

Note that the greater the discrepancy between T_H and T_C, the harder the heat pump has to work per unit of heat extracted.

E. The Carnot cycle and engine efficiency

We can prove that the efficiency of the Carnot heat engine is maximal. That is, given any other heat engine that extracts heat from a temperature source T_H and deposits heat to a temperature source T_C, the efficiency ϵ of this engine must satisfy $\epsilon \leq 1 - T_C/T_H$.

To show this, let us consider two reversible heat engines, with efficiencies ϵ_1 and ϵ_2 (we can assume reversibility, since an irreversible heat engine will operate below optimal efficiency). We claim that $\epsilon_1 = \epsilon_2$.

To show this, let us run the engine with efficiency ϵ_1 in reverse, so that it operates as a heat pump (see Figure 5). If we extract an amount of energy $Q_{C,1}$ from the cold source, then we need to input a quantity $W_1 = \epsilon_1/(1-\epsilon_1)Q_{C,1}$ of work. We also dump a quantity $Q_{H,1} = Q_{C,1}/(1-\epsilon_1)$ of heat to the hot source.

Now, we transfer this heat to the hot source of the second engine, and use some of the heat to extract work. If we want the work extracted to equal the work input to the first engine, then we have that the heat input must be,

$$Q_{H,2} = \frac{W_1}{\epsilon_2} = \frac{\epsilon_1}{\epsilon_2}\frac{1}{1-\epsilon_1}Q_{C,1} \tag{8}$$

and the amount of heat dumped to the cold source is,

$$Q_{C,2} = (1-\epsilon_2)Q_{H,2} = \frac{\epsilon_1}{\epsilon_2}\frac{1-\epsilon_2}{1-\epsilon_1}Q_{C,1} \tag{9}$$

Therefore, the net amount of heat extracted from the cold source is,

$$Q_{C,1} - Q_{C,2} = Q_{C,1}\frac{\epsilon_2 - \epsilon_1}{\epsilon_2(1-\epsilon_1)} \tag{10}$$

while the net amount of heat deposited to the hot source is,

$$Q_{H,1} - Q_{H,2} = Q_{C,1}\frac{\epsilon_2 - \epsilon_1}{\epsilon_2(1-\epsilon_1)} \tag{11}$$

Note then that if $\epsilon_2 > \epsilon_1$, the two engines combined will, without any net input or output of work, transfer heat from a cold source to a hot source. The combined engines will essentially result in the spontaneous flow of heat energy from a cold region to a hot region, which contradicts the definition of temperature.

Therefore, $\epsilon_1 = \epsilon_2$, which means that all reversible heat engines operating between a given heat source and a given heat sink must have the same efficiency. Since we have computed the efficiency for one such engine as $1 - T_C/T_H$, it follows that the maximal efficiency of any engine operating between temperatures T_H and T_C must be $1 - T_C/T_H$.

IV. THE CARNOT CYCLE AND ENTROPY

We can use the Carnot cycle and the fact that all reversible heat engines have the same efficiency to arrive at the existence of a state function defined by $dS = (\delta Q/T)_{rev}$. We will do this in several steps:

A. Step 1: Proof that $\oint (\delta Q/T)_{rev} = 0$

We first wish to show that, given a closed system, the integral of $\delta Q/T$ over any cyclic, reversible process is 0. By a cyclic process we mean a process that has the same starting and ending points.

To prove this, consider a system undergoing a cyclic process. For convenience, we can represent the state of the system at any time by its temperature T and volume V. Therefore, as the system undergoes a cyclic process, it traces out a closed curve in T,V-space (see Figure 6).

Now, this closed curve encloses a region of space, denoted R, which we can divide into lots of smaller subregions. Let us label these regions $R_1, R_2, \dots, R_N$. For each region R_i, we let ∂R_i denote the boundary of region R_i. If ∂R denotes the boundary of R, then we claim that,

$$\oint_{\partial R} (\delta Q/T)_{rev} = \sum_{i=1}^{N} \oint_{\partial R_i} (\delta Q/T)_{rev} \tag{12}$$

Figure 7 may be helpful in seeing this. The central point is that, where two regions touch each other, the integral over the boundary of each region is traced out in opposite directions, so that the contributions to the total integral cancel. Carrying through these cancellations, we

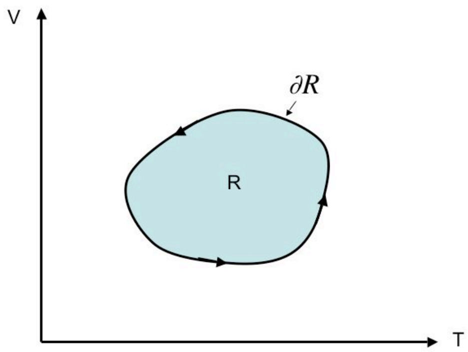

FIG. 6: Illustration of a cyclic reversible path in T,V-space.

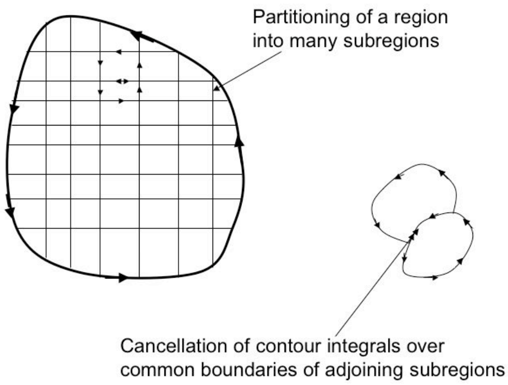

FIG. 7: Partitioning of a closed region and the cancellation of integrals over adjoining boundaries of the various subregions.

get that the only portions of the boundaries of the various regions that actually contribute to the sum are the boundaries that lie on the boundary of the whole region. And so, summing up the integrals over the boundaries of the various subregions, we get the integral over the boundary of the whole region.

The trick is to now fill the region R with appropriate subregions R_i. So, we choose to fill R with lots of infinitesimally small subregions whose boundaries are defined by a Carnot process (depending on the direction of our original cycle, our Carnot processes may need to be either heat engines or heat pumps). That is, the boundaries of each of these subregions is given by a vertical line going from some temperature T_h and volume V_1 to the same temperature T_h and some volume $V_2 > V_1$ (isothermal expansion), another curve going from T_h and V_2 to T_c and $V_3 > V_2$ (adiabatic expansion), another vertical line going from T_c and V_3 to T_c and $V_4 < V_3$ (isothermal compression), and finally a curve going from T_c and V_4 to T_h and $V_1 < V_4$ (adiabatic compression).

By making each of these regions infinitesimally small, so that $T_h - T_c,\ V_2 - V_1,\ V_3 - V_2,\ V_4 - V_3,\ V_1 - V_4$ are all small, we can fill up our region with lots of these little "Carnot" subregions. Denoting such a subregion by $R_{i,Carnot}$, all we need to do is show that $\oint_{R_{i,Carnot}} (\delta Q/T)_{rev} = 0$ to prove our claim.

Now, for a Carnot cycle, note that,

$$\oint (\delta Q/T)_{rev} = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} \tag{13}$$

Since the efficiency of a Carnot engine is $1 - T_C/T_H$, we have $Q_C = (T_C/T_H)Q_H$, giving,

$$\oint (\delta Q/T)_{rev} = 0 \tag{14}$$

Therefore, $\oint_{\partial R} (\delta Q/T)_{rev} = 0$, as we wished to show.

B. Step 2: Construction of S

We may use the result of the previous section to construct a new state function, the entropy. As with energy, we do not need to define an absolute value for entropy (although the Third Law provides us with a convenient reference point), rather, we only need a way to compute entropy differences.

So, given two states, labelled 1 and 2, of a system, with entropies S_1 and S_2 respectively, we define the entropy difference $S_2 - S_1$ via,

$$S_2 - S_1 = \int_{State1}^{State2} (\frac{\delta Q}{T})_{rev} \tag{15}$$

In order for this integral to be well-defined, however, the path from State 1 to State 2 must not be important. Therefore, we need to show that the integral of $(\delta Q/T)_{rev}$ is independent of path.

To prove this, consider two paths, denoted Γ_1 and Γ_2, from State 1 to State 2. If Γ_2^{-1} denotes the reverse of Γ_2, then the path given by Γ_1 followed by Γ_2^{-1} is a path that starts and ends at State 1. If we denote this path by $\Gamma_1\Gamma_2^{-1}$, then we have,

$$\oint_{\Gamma_1\Gamma_2^{-1}} (\frac{\delta Q}{T})_{rev} = 0 \tag{16}$$

But, we then have,

$$\begin{aligned} 0 &= \oint_{\Gamma_1\Gamma_2^{-1}} (\frac{\delta Q}{T})_{rev} \\ &= \int_{\Gamma_1} (\frac{\delta Q}{T})_{rev} + \int_{\Gamma_2^{-1}} (\frac{\delta Q}{T})_{rev} \\ &= \int_{\Gamma_1} (\frac{\delta Q}{T})_{rev} - \int_{\Gamma_2} (\frac{\delta Q}{T})_{rev} \\ &\Rightarrow \int_{\Gamma_1} (\frac{\delta Q}{T})_{rev} = \int_{\Gamma_2} (\frac{\delta Q}{T})_{rev} \end{aligned} \tag{17}$$

and so the difference in entropy is well-defined.

Note then that without knowing about statistical mechanics, we were able to deduce the existence of entropy from certain basic postulates regarding heat flows.

V. PERPETUAL MOTION MACHINES AND MAXWELL'S DEMON

Notice that the way that we developed entropy in this lecture relied on the idea that heat has a preferred direction of flow, and that there is a quantity called temperature that can be used to define the direction of this flow. Without the statistical-mechanical basis of temperature, however, it is not clear why a property such as temperature should even exist for a material, and it is not immediately clear why heat should have a preferred direction of flow.

Therefore, before the advent of statistical mechanics, the concept of entropy was obtained by relying on reasonable hypotheses obtained through extensive observations of physical systems. However, there was no proof that these assumptions should always hold, and therefore led people to come up with devices that could seemingly violate the Laws of Thermodynamics. Such devices are known as perpetual motion machines.

A *perpetual motion machine* is a device that can run forever. There are two kinds of perpetual motion machines that violate the laws of thermodynamics:

A perpetual motion machine of the *first kind* violates the law of conservation of energy. That is, it is a machine that essentially runs spontaneously, without any external input of energy.

A perpetual motion machine of the *second kind* violates the principle that heat can only flow from a region of high temperature to a region of low temperature. This type of machine takes in energy from a low temperature source, uses the energy to perform work, and then dumps the excess heat to a high temperature source.

A highly problematic construct for thermodynamics, which in principle could form the basis for constructing a perpetual motion machine of the second kind, is a device known as *Maxwell's Demon.*

Imagine a box filled with an ideal gas at some temperature, and imagine that we now place a dividing wall in the center of the box. Maxwell's Demon is a little machine attached to a door covering a hole in the wall. The Demon detects when a particle from one side of the box approaches the hole, and, if there is no particle coming from the other side, will open the door and allow the particle to cross to the other side. If we set the operational parameters of the Demon to be such that only particles from the left side of the box can cross to the right side of the box, then Maxwell's Demon will eventually bring all of the gas to one side of the box, in apparent violation of the Second Law.

Until the advent of Statistical Mechanics, and later Information Theory, there was no concrete refutation of Maxwell's Demon. It was simply assumed that such a device could not be constructed in such a way as to violate the Second Law of Thermodynamics.

With the probabilistic interpretation of entropy provided by Statistical Mechanics and then Information Theory, the answer that finally emerged is this: For Maxwell's Demon to function properly, it has to *know* when a particle from one side of the box is approaching, and when a particle from the other side is not. To know this, the Demon needs a way to detect the presence or absence of particles in some way. This can be accomplished by bouncing a radar signal, etc. The central point is that the Demon must consume energy, because the Demon must make use of a medium with which to acquire the information it requires to function. It turns out that the minimal amount of energy that Maxwell's Demon consumes is such that the Second Law of Thermodynamics is not violated.