# 18. The 2nd & 3rd Laws of Thermodynamics

Introduction and Summary

The oldest statement of the 2nd Law comes from the German physicist and mathematician Rudolf Clausius. He said that "heat can flow spontaneously from a hot object to a cold object; heat does not flow spontaneously from a cold object to a hot object." (P.416 Giancoli and also http://en.wikipedia.org/wiki/Second_law_of _thermodynamics)

At first glance, this appears to be a restatement of the 0th Law but it is in fact a little different. Heat *can* be made to flow from a cold object to a warm object--for example, in a refrigerator or with an air conditioner. However, this does not happen spontaneously--that is, by itself--since work must be done for this to happen. The 2nd Law is a little strange since it is a statement about something that does not happen.

Another statement of the 2nd Law, made by the English physicist Lord Kelvin, is that a quantity of heat Q cannot be converted entirely into work W.
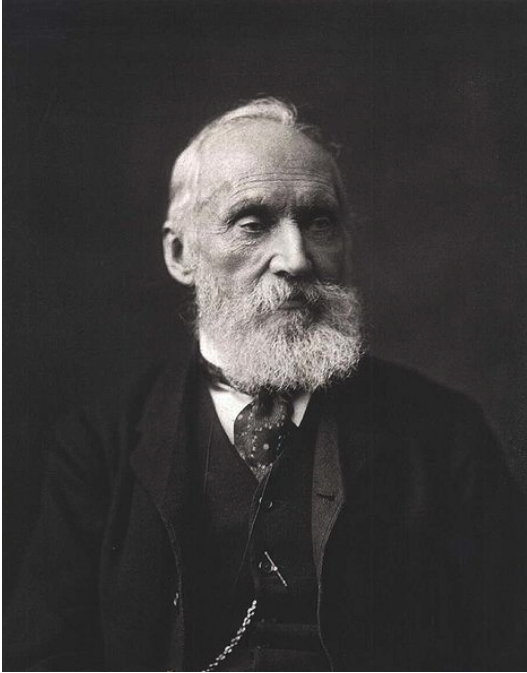
 Some of the heat must leave the engine and be expelled into the environment as waste heat. Since efficiency equals the work done divided by the heat put in, the 2nd Law says a heat engine cannot be 100% efficient. It is perhaps surprising, that if you assume the Clausius statement of the 2nd Law is true, then you can prove that the Kelvin statement is also true and vice-versa. Thus, the Clausius and Kelvin statements are equivalent. See

http://en.wikipedia.org/wiki/William_Thomson,_ 1st_Baron _Kelvin

Later, in the 1860s, Clausius formulated the 2nd Law in terms of Entropy S. "The change in Entropy of an isolated system is greater than or equal to zero for all processes that occur in nature." In other words, $\Delta S \geq 0$ for isolated systems: $\Delta S = 0$ for so-called reversible processes where the system can be returned to its original state by a small change of a parameter like the volume in a heat engine. $\Delta S > 0$ for irreversible processes like the natural flow of heat from a high temperature object to a low temperature object. (More on this later.) The 2nd Law is unusual in that it is a mathematical inequality (instead of the usual equality, like $\Delta U = Q - W$).   Another way of saying the 2nd Law is "the Entropy S of an isolated system never decreases".

Finally, the German physicist Boltzmann (1872) provided a microscopic, kinetic theory formula for the Entropy is given by

$$S = k_B \, Log[\Omega]$$

where Ω is the number of states available to the system. The number of final states is greater than the number of initial state $\Omega_f > \Omega_0$ for irreversible processes and so again $S_f > S_0$. If there were only one state available to the system so $\Omega = 1$ (complete order) then S=0 since Log[1]=0. Another

example, is a gas initially restricted by a partition to only half of a container. If the partition is removed there are more states available to the gas since the gas atoms can now travel anywhere in the container.

So if $\Omega_f > \Omega_0$ then $S_f > S_0$ which is the same as the Clausius form of the 2nd Law.

See http://en.wikipedia.org/wiki/Ludwig_Boltzmann and there is even a picture of his tombstone at the top of which is his formula.

The natural scheme of things is that isolated systems go from order to disorder and so entropy increases. Natural processes act to increase the amount of disorder in a system, but if a system

consists of two subsystems then the entropy can decrease in one subsystem while increasing in the other subsystem provided the overall entropy increases for the total system. The 2nd Law is consistent with the biological phenomena of life (and that is a good thing!) An organism represents a more order state than a lifeless state so the entropy of an organism would be less than the entropy of the random state of the constituent molecules which makeup the organism. The organism is not be isolated and it interacts with the world for food, fuel, etc. The entropy of the world increases to compensate for the decrease in entropy of the organism.

The 3rd Law of Thermodynamics is also a statement of something that is not feasible: "It is not possible to achieve the absolute zero of temperature in a finite number of steps." The Dutch physicist, Kamerlingh Onnes and other scientists engaged in a race to liquefy all the gases, including oxygen, nitrogen, and helium, by a series of steps of alternately compressing a gas and then evaporating a bit of it to take off some of the heat. Onnes was in 1908, the first to liquefy Helium which was the last elemental gas to be liquefied.

Incidentally, Helium was discovered on the Sun before it was found on the Earth!) See for example, http://en.wikipedia.org/wiki/Heike_Kamerlingh_Onnes   Experimentally, it became apparent that the closer to 0°K Onnes got, the harder it became to lower the temperature, and this difficulty was formulated as the 3rd Law. Today physicists have gotten to within 10^{-9} °K of absolute zero and they are trying to go still closer to absolute 0°K but they do not expect they will be able to get all the way there. See for example the report of the work of some MIT researcher as of May 10, 2010. http://web.mit.edu/newsoffice/2003/cooling.html

Heat Engines: The Carnot Cycle

A heat engine is an ideal machine that is so simplified that none of the details like the gears, source of heat, etc. are important. Only what is produced and used in the engine is important. In order to keep things as simple as possible we focus only on what is most important. The king of France gave Carnot the task of determining how to improve the efficiency of heat engines like the steam engine.

Below is a picture of Carnot (about 1824) and he was in the military at the time.

A heat engine takes in heat Q_{IN} from a higher temperature source (which is called a heat "reservoir" because it is so large that its temperature T_H is a constant). You can think of the high temperature T_H as being maintained by burning fuel and to be specific, take T_H as 373°K, the boiling point of water. After taking in the heat Q_{IN}, the engine produces some usable work W_{OUT} and also outputs some waste heat Q_{OUT} that usually goes into the environment (the atmosphere, a stream of water, the ocean, etc.) which is called a low temperature T_L reservoir. Ideally, this reservoir is so large that dumping the heat Q_{OUT} does not change the temperature of the T_L reservoir. Schematically, a heat engine appears as:
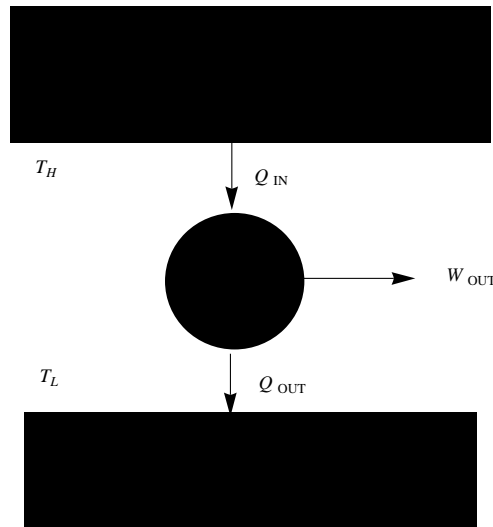
(By the way, just connecting the two reservoirs with a metal rod made of something like copper would cause heat to flow naturally from the high temperature T_H reservoir to the low temperature

T_L reservoir. Just doing that would produce no work, however.) Carnot showed that for an ideal heat engine, the ratio of the heats out and in is proportional to the ratio of the temperatures of the reservoirs:

$$\frac{Q_{OUT}}{Q_{IN}} = \frac{T_L}{T_H} \qquad \text{Equation \#1}$$

(Keep this equation in mind as it figures into the 2nd Law.) While we will not prove this result, it is none-the-less plausible and is important to the argument below.   The heat Q_{OUT} is taken out of the heat engine during an isothermal process at temperature T_L. In the Carnot engine, since the gas is in thermal contact with the heat reservoir, the Carnot engine itself is at temperature T_L.   The heat Q_{IN} is put into the engine during an isothermal process at temperature T_H. Again, since the gas is in thermal contact with the heat reservoir, the Carnot engine itself is at temperature T_H. The Carnot engine is an ideal engine having no gears etc. to heat up when it is in motion so the only heat involved is due to the heat reservoirs. Carnot's engine can be reversed, in which case you have a refrigerator or an air conditioner. See below.

Carnot Engine Efficiency:

Recall that the efficiency of a heat engine Eff is "what you get" divided by "what you pay"--that is,

$$\text{Eff} = \frac{W_{CYCLE}}{Q_{IN}} \qquad \text{Equation \#2}$$

Q_{IN} is considered a cost since it is from a high temperature reservoir which is maintained at the high temperature T_H by burning fuel etc. which is obviously a "cost". Q_{OUT} the "waste" that is dumped in the lower temperature reservoir is not considered a cost since we depend on Mother

Nature to maintain the temperature T_L. (Perhaps Q_{OUT} should be considered a cost (BUT Q_{OUT} HAS NOT BEEN TRADITIONALLY A COST) since Q_{OUT} heats up the atmosphere, heats of the stream, heats up the ocean used in cooling the heat engine.) Also recall the 1st Law written for a complete cycle is

$$\Delta U_{cycle} = Q_{cycle} - W_{cycle}$$

For a complete cycle, $\Delta U_{cycle} = 0$, which is OK if you think of the internal energy as $U = N\left(\frac{3}{2} k_B T\right)$ and recognize that in a cycle the beginning temperature, T, is the same as the endpoint T. So the 1st Law results in

$$W_{cycle} = Q_{cycle}$$

W_{cycle} is the net work done. The heat for the cycle $Q_{cycle} = Q_{IN} - Q_{OUT}$, so the 1st Law appears as

$$W_{CYCLE} = Q_{IN} - Q_{OUT}$$

Using this in the formula for efficiency, we get

$$Eff = \frac{Q_{IN} - Q_{OUT}}{Q_{IN}} = 1 - \frac{Q_{OUT}}{Q_{IN}}$$

and finally equation #1 yields Carnot's formula for the efficient

$$Eff = 1 - \frac{T_L}{T_H} \qquad \text{Equation \#3}$$

The way to maximize efficiency is to have T_L as small as possible--which would ideally be 0°K-- and/or have T_H as large as possible--ideally, $T_H \to \infty$ (which is not going to happen). As a (somewhat) more practical example, take T_L as 273°K, the freezing point of water, and T_H as

373°K, the boiling point of water. This results in an efficiency of Eff=0.23 (or 23%).

Running a Heat Engine in Reverse: A Refrigerator

A diagram of the heat engine running in reverse (a refrigerator) is below. You do NOT get work from a refrigerator. Instead, you have to put work in--usually through an electric motor running a gas compressor. The function of a refrigerator is to take heat Q_{IN} from inside of the refrigerator, which is at a lower temperature T_L than the outside room, and dump some heat Q_{OUT} into the surrounding room which is at a higher temperature T_H. Heat does NOT flow in this direction naturally without some work done. However, if you run a Carnot engine (an ideal engine), one complete cycle in the forward direction AND THEN run the Carnot engine in reverse one complete cycle as a refrigerator, then nothing in the world has changed. No work is done and no heat is used up. Such a heat engine is called reversible. Real engines are NOT reversible because, for example, they burn up fuel in the forward direction and fuel is of course NOT unburned in the reverse direction. By the way, the 2nd Law tells us that the heat output Q_{OUT} cannot be converted completely (i.e. 100%) into work and this work used to run the engine in reverse as a refrigerator.
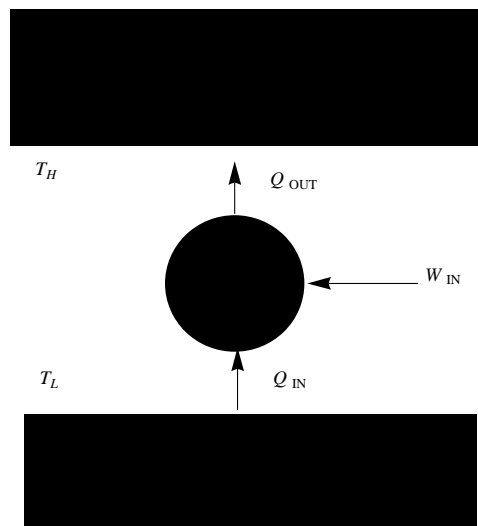
The 2nd Law: Clausius Form

The change in entropy ΔS during a reversible and isothermal process at temperature T is given by

$$\Delta S = \frac{Q}{T} \quad \text{Equation \#4}$$

where Q is the heat absorbed.

Application: Carnot Engine which is a reversible process

The entropy change for the case of the Carnot Engine using equation #4 is

$$\Delta S = \frac{Q_{IN}}{T_H} - \frac{Q_{OUT}}{T_L}$$

Recall equation #1

$$\frac{Q_{OUT}}{Q_{IN}} = \frac{T_L}{T_H} \quad \text{or} \quad \frac{Q_{IN}}{T_H} = \frac{Q_{OUT}}{T_L}$$

Combining this with the previous equation we get ΔS=0 for the Carnot engine which is a reversible

process.

The Entropy Change During an Irreversible Process is ΔS > 0

As an example of an irreversible process, suppose an amount of heat Q flows from a high

temperature T_H reservoir to a low temperature T_L reservoir as indicated below.

T_H

Q OUT

Q

T_L
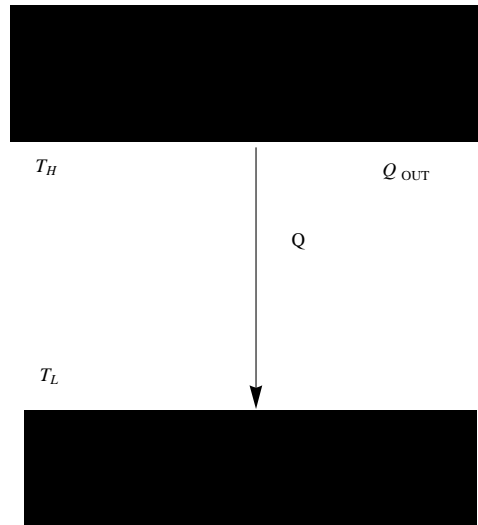
No work is produced in this case of spontaneous heat flow which occurs all the time in nature. The entropy change in this case is

$$\Delta S = -\frac{Q}{T_H} + \frac{Q}{T_L} = Q\left(\frac{-1}{T_H} + \frac{1}{T_L}\right) > 0$$

So using the definition of entropy as $\Delta S = Q/T$ it has been shown that for the Carnot reversible process $\Delta S = 0$ while for spontaneous heat flow irreversible processes $\Delta S > 0$. It is natural to assert these conditions on ΔS 0 hold for general reversible and irreversible processes.