The Oil Drum: Canada
DISCUSSIONS ABOUT ENERGY AND OUR FUTURE

In this house, we obey the laws of thermodynamics!

Posted by Libelle on December 30, 2008 - 11:11am in The Oil Drum: Canada
Topic: Miscellaneous
Tags: energy, entropy, heat, original, thermodynamics, work [list all tags]

When you use energy, the rules are very well defined. The first and second laws of thermodynamics have been well understood for well over a century, and the third for just over a century, but the subject is still viewed by most as being pretty arcane. This is a pity, both because these laws are of such importance, and because almost everyone has a fair understanding of the first and second laws, even if they think they don't. Understanding the implications of the laws is another matter.

There are many facetious versions of the laws. The set I like best goes:

(zeroth law) You must play the game.
(first law) You can't win.
(second law) You can only break even on a very cold day.
(third law) It doesn't get that cold.

These are surprisingly accurate.

The actual laws are, it should be remembered, experimental in origin. The world has been found to work this way.

Zeroth Law

The zeroth law actually states that if two systems A and B are in equilibrium with each other, and systems B and C are also in equilibrium with each other, then systems A and C are also in equilibrium with each other. Another way of putting it is that situations like Escher's "Waterfall" don't occur in real life.

You must play the game.

First Law

The first law is the law of conservation of energy. It includes the equivalence of heat and work, but is more general than that, in that there are many forms of energy that are interconvertible, but with the total for an isolated system remaining constant over time. One point that is often misunderstood is the role of the equation $E = mc^2$. This is usually taken to refer to a conversion of matter into energy, but the reality is simpler. Energy has mass, and the equation tells you how

much. No matter what conversions take place in a isolated system, its total energy (and hence mass) remains constant.

You can't win.

Second Law

The second law is the one that results from the observation that hot things lose heat to colder ones. It's a one-way process. Mechanical work can be turned into heat. Heat can be turned into mechanical work, but there are limitations. The implications of this are far-reaching, and a surprising amount can be deduced (and defined) from just this and a thought experiment.

If we have two reservoirs of heat (both conveniently infinite in capacity) at different temperatures, then devices can be constructed that take heat from the hotter reservoir, turn some of it into mechanical work and reject the rest to the colder reservoir. The rejection of part of the heat has been found to be unavoidable, but the amount of rejected heat becomes less as the temperature of the heat source is raised. Without at this stage defining what we mean by the numerical value of a temperature, let us suppose that the maximum possible efficiency of conversion is a definite function of the two temperatures. Engine efficiencies are usually defined as [work out/heat in], but in this case, I'll look at [heat out/heat in] or [1 - efficiency]. If the temperatures of the two reservoirs are T_1 and T_2 and the heat taken from the hotter is q_1, and the heat released to the colder is q_2, then we will say that:

$q_2/q_1 = F(T_2,T_1)$ F is some as yet unknown function (an algebraic expression) of the two temperatures.

Maximum efficiency implies reversibility of the process. An example of this is that heat transfer from the hotter reservoir to the engine must be achieved without any temperature difference between the reservoir and the part of the engine that absorbs the heat. If there were any difference, the heat engine would operate at a lower efficiency (smaller temperature difference between hot and cold), and it would not be possible to run the process backwards (heat won't flow "uphill"). There can't be any friction either. The engine with maximum efficiency is thus reversible and can be used as a heat pump, pumping heat from the cooler reservoir to the hotter, and requiring mechanical work to do it. The values of q_1 and q_2 are the same as in the case of the engine, but the direction of flow is reversed and work is put into the system rather than being taken out. The absence of temperature differences between the engine/heat pump and its heat reservoirs also means that the processes will be infinitely slow, but that is the case for all these ideal machines.

Let's now suppose that we have a third heat reservoir at a still lower temperature, T_3, and that a second engine operates between the second and third reservoirs. If the heat taken from the second reservoir is q_2 (same as rejected by the first engine), and that rejected to the third is q_3, then:

$q_3/q_2 = F(T_3,T_2)$

But we could instead have used one engine directly between the first and third reservoirs. This engine must have the same overall efficiency as the combination of the other two, because if it didn't, then heat could be run continuously around the cycle of three engines, using the power from one or two engines to drive the other(s) backwards, leaving a net work output with heat being taken from one reservoir only. This would not be consistent with the way things work. So:

$q_3/q_1 = F(T_3, T_1)$

But: $q_3/q_1 = (q_3/q_2) \times (q_2/q_1)$

So: $F(T_3, T_1) = F(T_3, T_2) \times F(T_2/T_1)$

If you didn't switch off at the beginning of the algebra, it should be evident that this places a very severe restriction on the nature of the function F. In the last equation, T_2 disappears from the right hand side, simply as a result of the multiplication. This means that $F(T_1, T_2)$ must be of the form $f(T_1)/f(T_2)$, where f is some other function.

So: $q_2/q_1 = f(T_2)/f(T_1)$

You may remember that I started this argument without defining what exactly was meant by a temperature. This equation gives us an opportunity to *define* a temperature scale, by choosing the function f. This is what [William Thomson](#) (later Lord Kelvin) did in 1848. He chose f(T) to be as simple as possible:

$f(T) = T$

So: $F(T_2, T_1) = T_2/T_1$ and $q_2/q_1 = T_2/T_1$

In other words, an absolute temperature scale can be defined in terms of the behaviour of heat engines, independent of the properties of any particular substance. If an ideal heat engine has a conversion efficiency of 50% (half the input heat is turned into work and half to rejected heat), then the ratio of the heat source temperature to the heat sink temperature is 2 - by definition.

To complete the definition of such an absolute temperature scale, we need to set the size of a degree. If we set the degree size such that the difference between the freezing and boiling points of water is 100 degrees, we have a scale that can match the Celsius scale, but with an offset corresponding to the freezing point of water on the absolute scale. That offset turns out to be 273.15 degrees and we now have the Kelvin scale.

Entropy

The idea of entropy is associated in most people's minds with the ideas of order and disorder (higher entropy = more disorder). This is correct, but the origin of the idea comes from the movement of heat. If an amount of heat q enters a system at (absolute) temperature T, then the entropy of the system increases by q/T. This is the definition of entropy. If we look at the first heat engine above, the entropy of the hotter reservoir decreases by q_1/T_1, and that of the cooler increases by q_2/T_2. If the engine is reversible, $q_2/q_1 = T_2/T_1$, so the overall change in entropy is zero. This is a characteristic of reversible processes. In real processes, the change in total entropy is always positive. One example is the flow of heat from a hot body to a cooler one - the hot body loses entropy, but the cooler one gains more than the hotter one lost, since the T in the q/T expression is smaller and the q is the same.

Available work, or Exergy

The maximum amount of work that could possibly be extracted as a process proceeds (i.e., if it proceeds reversibly) can readily be calculated from energy and entropy changes between the starting and finishing states of the process. This is sometimes referred to as the exergy available at the start. Just how it may be derived may be the subject for another posting. Exergy, unlike energy, may be destroyed. The ideal amount of work is never realised of course, but it is

reasonably straightforward to show that the exergy irretrievably lost when an *irreversible* change takes place is equal to the entropy increase associated with the irreversible change multiplied by the temperature of the environment in which the process takes place. That is the lowest temperature at which heat can be rejected by the process. It follows that if the temperature of the environment is absolute zero, there is no loss in exergy or available work, whatever happens.

You can only break even on a very cold day.

Third Law

There are two ways of stating the third law:

The entropy of every pure substance at absolute zero is zero.
It impossible to reach absolute zero in a finite number of steps.

The reason the second follows from the first is that any process that reduces the temperature of a substance must entail a step in which the entropy changes. If the entropy of everything is zero, then no changes of entropy are possible and there is no means of doing any cooling. In fact, the observed law is that the *change* in entropy is always zero. It is then convenient to declare all entropies zero at absolute zero and this matches the statistical interpretation of entropy. One can get very close (in degrees) to absolute zero - the current record is about 10^{-10}K, but the closer one gets, the more difficult it becomes to cool further.

It doesn't get that cold.