Richard Feynman on entropy….

With regard to the conservation of energy, we should note that *available* energy is another matter—there is a lot of jiggling around in the atoms of the water of the sea, because the sea has a certain temperature, but it is impossible to get them herded into a definite motion without taking energy from somewhere else. That is, although we know for a fact that energy is conserved, the energy available for human utility is not conserved so easily. The laws which govern how much energy is available are called the *laws of thermodynamics* and involve a concept called entropy for irreversible thermodynamic processes.

44–2 The second law

Now, what about the second law of thermodynamics? We know that if we do work against friction, say, the work lost to us is equal to the heat produced. If we do work in a room at temperature T, and we do the work slowly enough, the room temperature does not change much, and we have converted work into heat at a given temperature. What about the reverse possibility? Is it possible to convert the heat back into work at a given temperature? The second law of thermodynamics asserts that it is not. It would be very convenient to be able to convert heat into work merely by reversing a process like friction. If we consider only the conservation of energy, we might think that heat energy, such as that in the vibrational motions of molecules, might provide a goodly supply of useful energy. But Carnot assumed that it is impossible to extract the energy of heat at a single temperature. In other words, if the whole world were at the same temperature, one could not convert any of its heat energy into work: while the process of making work go into heat can take place at a given temperature, one cannot reverse it to get the work back again. Specifically, Carnot assumed that heat cannot be taken in at a certain temperature and converted into work *with no other change* in the system or the surroundings.

That last phrase is very important. Suppose we have a can of compressed air at a certain temperature, and we let the air expand. It can do work; it can make hammers go, for example. It cools off a little in the expansion, but if we had a big sea, like the ocean, at a given temperature—a heat reservoir—we could warm it up again. So we have taken the heat out of the sea, and we have done work with the compressed air. But Carnot was not wrong, because *we did not leave everything as it was*. If we recompress the air that we let expand, we will find we are doing extra work, and when we are finished we will discover that we not only got no work out of the system at temperature T, but we actually put some in. We must talk only about situations in which the *net result* of the whole process is to take heat away and convert it into work, just as the net result of the process of doing work against friction is to take work and convert it into heat. If we move in a circle, we can bring the system back precisely to its starting point, with the net result that we did work against friction and produced heat. Can we reverse the process? Turn a switch, so that everything goes backwards, so the friction does work against us, and cools the sea? According to Carnot: no! So let us suppose that this is impossible.

than much detail for special applications.

The two laws of thermodynamics are often stated this way:

First law: the energy of the universe is always constant.

Second law: the entropy of the universe is always increasing.

That is not a very good statement of the second law; it does not say, for example, that in a reversible cycle the entropy stays the same, and it does not say exactly what the entropy is. It is just a clever way of remembering the two laws, but it does not really tell us exactly where we stand. We have summarized the laws discussed in this chapter in Table 44–1. In the next chapter we shall apply these laws to discover the relationship between the heat generated in the expansion of a rubber band, and the extra tension when it is heated.

45–3 The Clausius-Clapeyron equation

The vaporization of a liquid is another application of the results we have derived. Suppose we have some liquid in a cylinder, such that we can compress it by pushing on the piston, and we ask ourselves, "If we keep the temperature constant, how does the pressure vary with volume?" In other words, we want to draw an isothermal line on the P-V diagram. The substance in the cylinder is not the ideal gas that we considered earlier; now it may be in the liquid or the vapor phase, or both may be present. If we apply sufficient pressure, the substance will condense to a liquid. Now if we squeeze still harder, the volume changes very little, and our isothermal line rises rapidly with decreasing volume, as shown at the left in Fig. 45–3.

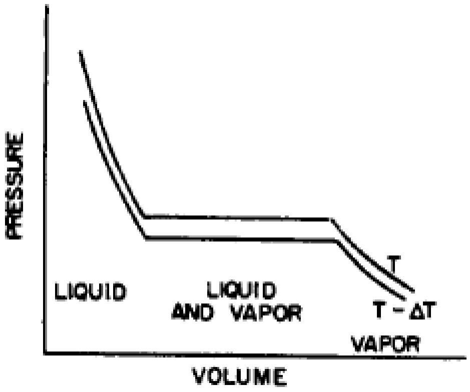

Fig. 45–3. Isothermal lines for a condensable vapor compressed in a cylinder. At the left, the substance is in the liquid phase. At the right, the substance is vaporized. In the center, both liquid and vapor are present in the cylinder.

If we increase the volume by pulling the piston out, the pressure drops until we reach the point at which the liquid starts to boil, and then vapor starts to form. If we pull the piston out farther, all that happens is that more liquid vaporizes. When there is part liquid and part vapor in the cylinder, the two phases are in equilibrium—liquid is evaporating and vapor is condensing at the same rate. If we make more room for the vapor, more vapor is needed to maintain the pressure, so a little more liquid evaporates, but the pressure remains constant. On the flat part of the curve in Fig. 45–3 the pressure does not change, and the value of the pressure here is called the *vapor pressure at temperature T.* As we continue to increase the volume, there comes a time when there is no more liquid to evaporate. At this juncture, if we expand the volume further, the pressure will fall as for an ordinary gas, as shown at the right of the P-V diagram. The lower curve in Fig. 45–3 is the isothermal line at a slightly lower temperature $T - \Delta T$. The pressure in the liquid phase is slightly reduced because liquid expands with an increase in temperature (for most substances, but not for water near the freezing point) and, of course, the vapor pressure is lower at the lower temperature.

We will now make a cycle out of the two isothermal lines by connecting them (say by adiabatic lines) at the ends of the flat sections, as shown in Fig. 45–4. The little jiggle in the lower right-hand corner of the figure will make little difference and we will neglect it. We are going to use the argument of Carnot, which tells us that the heat added to the substance in changing it from a liquid to a vapor is related to the work done by the substance as it goes around the cycle. Let us call L the heat needed to vaporize the substance in the cylinder. As in the argument immediately preceding Eq. (45.5), we know that $L(\Delta T/T) =$ work done by the substance. As before, the work done by the substance is the shaded area, which is approximately $\Delta P(V_G - V_L)$, where ΔP is the difference in vapor pressure at the two temperatures T and $T - \Delta T$, V_G is the volume of the gas, and V_L is the volume of the liquid, both volumes measured at the vapor pressure. Setting these two expressions for the area equal, we get $L\Delta T/T = \Delta P(V_G - V_L)$, or

$$\frac{L}{T(V_G - V_L)} = (\partial P_{\text{vap}}/\partial T). \tag{45.14}$$

Equation (45.14) gives the relationship between the rate of change of vapor pressure with temperature and the amount of heat required to evaporate the liquid. This relationship was deduced by Carnot, but it is called the Clausius-Clapeyron equation.

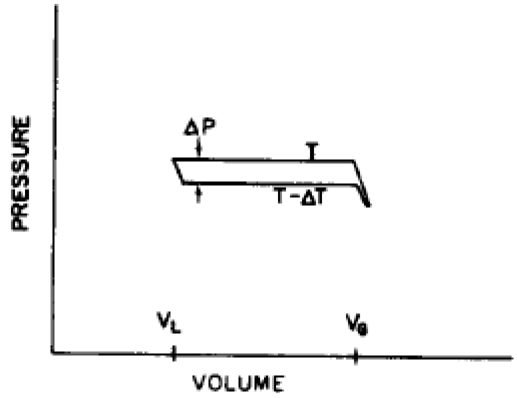

Fig. 45–4. Pressure-volume diagram for a Carnot cycle with a condensable vapor in the cylinder. At the left, the substance is in the liquid state. A quantity of heat *L* is added at temperature *T* to vaporize the liquid. The vapor expands adiabatically as *T* changes to *T* − Δ*T*.

Table 44–1

Summary of the laws of thermodynamics

First law:

Heat put into a system + Work done on a system = Increase in internal energy of the system:

$$dQ + dW = dU.$$

Second law:

A process whose *only* net result is to take heat from a reservoir and convert it to work is impossible.

No heat engine taking heat Q_1 from T_1 and delivering heat Q_2 at T_2 can do more work than a reversible engine, for which

$$W = Q_1 - Q_2 = Q_1\left(\frac{T_1 - T_2}{T_1}\right).$$

The entropy of a system is defined this way:

(a) If heat ΔQ is added reversibly to a system at temperature T, the increase in entropy of the system is $\Delta S = \Delta Q/T$.

(b) At $T = 0$, $S = 0$ (*third law*).

In a *reversible change*, the total entropy of all parts of the system (including reservoirs) does not change.

In *irreversible change*, the total entropy of the system always increases.