7.11: Other Statements of the First Law

The first law has been stated in many ways. Some are intended to be humorous or evocative rather than precise statements; for example, “You can’t get something (useful work in some system) for nothing (no decrease in the energy of some other system).” Others are potentially ambiguous, because we construct them to be as terse as possible. To make them terse, we omit ideas that we deem to be implicit.

A compact and often used statement is, “$E=q+w$, and E is a state function.” In this statement, the fact that energy is conserved is taken to be implicit in the operational definition, $E=q+w$. We can give an equally valid statement by saying, “Energy is conserved ($E_{universe}=E+\hat{E}=0$) in all processes.” In making this statement, we assume that the definition of energy ($E=q+w$) is understood and that the state-function postulate is implicit in this definition.

To see that the postulate that energy is conserved and the postulate that energy is a state function are logically independent, let us consider a system that undergoes a particular cyclic process, which we call “Cycle A.” In Cycle A, the final state of the system is the same as its initial state; the postulate that energy is a state function is then equivalent to the statement that $E_{Cycle\ A}=0$. The postulate that energy is conserved is equivalent to the statement that $E_{Cycle\ A}+\hat{E}_{Cycle\ A}=0$. Now, what can we say about $\hat{E}_{Cycle\ A}$? Obviously, if we combine the information from the two postulates, it follows that $\hat{E}_{Cycle\ A}=0$. The essential point, however, is that $\hat{E}_{Cycle\ A}=0$ is not required by either postulate alone.

- $\hat{E}_{Cycle\ A}=0$ is not required by the postulate that energy is a state function, because the surroundings do not necessarily traverse a cycle whenever the system does.
- $\hat{E}_{Cycle\ A}=0$ is not required by conservation of energy, which merely requires $\hat{E}_{Cycle\ A}=-E_{Cycle\ A}$, and absent the requirement that E be a state function, $E_{Cycle\ A}$ could be anything.

In Chapter 9, we explore a statement of the second law that denies the possibility of constructing a “perpetual motion machine of the second kind.” Such a perpetual motion machine converts heat from a constant-temperature reservoir into work. This statement is: “It is impossible to construct a machine that operates in a cycle, exchanges heat with its surroundings at only one temperature, and produces work in the surroundings.”

A parallel statement is sometimes taken as a statement of the first law. This statement denies the possibility of constructing a “perpetual motion machine of the first kind.” This statement is, “It is impossible to construct a machine that operates in a cycle and converts heat into a greater amount of work.” The shared perspective and phrasing of these statements is esthetically pleasing. Let us consider the relationship between this statement of the first law and the statement given in §10. (For brevity, let us denote this impossibility statement as the “machine-based” statement of the first law and refer to it as proposition “MFL.” We refer to the statement of the first law given in §10 as proposition “FL.”)

In the machine-based statement (MFL), we mean by “a machine” a system that accepts heat from its surroundings and produces a greater amount of work, which appears in the surroundings. If such a machine exists, the machine-based statement of the first law is false, and proposition ∼MFL is true. For one cycle of this first-law violating machine, we have $\hat{w}>q>0$. Since $q=-\hat{q}$, we have $\hat{w}>-\hat{q}>0$. It follows that $\hat{E}=\hat{q}+\hat{w}>0$. Our statement of the principle of conservation of energy ($E+\hat{E}=0$) then requires that, for one cycle of this perpetual motion machine, $E<0$. Our statement of the first law, FL, requires that, since energy is a state function, $E=0$. Since this is a contradiction, the existence of a perpetual motion machine of the first kind (proposition ∼MFL) implies that the first law (energy is a state function, proposition FL) is false (∼MFL ⇒ ∼FL).

From this result, we can validly conclude: If the first law is true, the existence of a perpetual motion machine of the first kind is impossible:

$$(\sim\text{MFL} \Rightarrow \sim\text{FL}) \Rightarrow(\sim\sim\text{FL}\Rightarrow\sim\sim\text{MFL})\Rightarrow(\text{FL}\Rightarrow\text{MFL})$$

We cannot conclude that the impossibility of perpetual motion of the first kind implies that energy is a state function

$$(\sim\text{MFL} \Rightarrow \sim\text{FL}) \text{ does not imply } (\text{MFL}\Rightarrow\text{FL})$$

That is, the impossibility of perpetual motion of the first kind, as we have interpreted it, is not shown (by this argument) to be equivalent to the first law, as we have stated it. (It remains possible, of course, that this equivalence could be proved by some other argument.)

Evidently, when we take the impossibility of constructing a perpetual motion machine of the first kind as a statement of the first law, we have a different interpretation in mind. The difference is this: When we specify a machine that operates in a cycle, we intend that everything about the machine shall be the same at the end of the cycle as at the beginning—including its energy. That is, we intend the statement to be understood as requiring that, for one cycle of the perpetual motion machine $E=0$. Equivalently, we intend the statement to be understood to include the stipulation that energy is a state function.

Now, for one cycle of the perpetual motion machine, we have $E=0$ and $\hat{E}>0$. Given the basic idea that energy is additive, so that $E_{universe}=E+\hat{E}$, we have that $E_{universe}>0$. The impossibility statement asserts that this is false; equivalently, the impossibility statement asserts that energy cannot be created. This conclusion is a weak form of the principle of conservation of energy; it says less than we want the first law to say. We postulate that energy can be neither created nor destroyed. That is, $E_{universe}>0$ and $E_{universe}<0$ are both false. When we consider the impossibility statement to assert the principle of energy conservation, we implicitly stipulate that the machine can also be run in reverse. (See problem 10.)

We intend the first law to assert the existence of energy and to summarize its properties. However we express the first law, we recognize that the concept of energy encompasses several closely interrelated ideas.
