Defining Temperature and Entropy

In "Kinetic Theory: A Brief Review," a unit in the Classical Concept Review also on this Web site, we derived the result that the pressure exerted by a gas is proportional to the number of molecules per unit volume n and to their average kinetic energy. That is, for a container enclosing a single kind of monoatomic molecules,

$$P = \frac{2}{3} n \langle mv^2/2 \rangle$$

We were then able to show that, in equilibrium (i.e., after waiting a very long time), the average kinetic energy of the molecules was proportional to the absolute temperature:

$$\langle mv^2/2 \rangle = 3kT/2 \propto T \qquad \textbf{8-4}\boldsymbol{a}$$

Thus, the average (translational) kinetic energy of the gas in the container is a property of the absolute temperature and not of the particular kind of gas or any of its other properties. We could then use the average kinetic energy to define a simple temperature scale that would be independent of any substance by making the average kinetic energy equal to the absolute temperature. Of course, that was not done, but we did the next-best thing and defined a scale where the average kinetic energy is proportional to the absolute temperature, as in Equation 8-4*a*, the constant of proportionality, or conversion factor, being the Boltzmann constant.

Shifting our attention a bit to reversible thermodynamic engines and following an example developed by Feynman, we define a standard, or reference temperature to be 1 K. Heat delivered by an engine at this standard temperature we will call Q_s. This means that when an engine absorbs heat Q at temperature T, it will deliver to a sink at our standard temperature an amount of heat Q_s. The heat Q is (1) a function of the temperature, increasing as T increases (since work is required to run an engine backward), and (2) Q is proportional to Q_s. We can express this as

$$Q = f(T) Q_s \qquad \textbf{8-4}\boldsymbol{b}$$

where f is an increasing function of T. Since the efficiency of reversible engines is independent of the working substance, $f(T)$ is similarly independent and we can define the function itself as the temperature, measured in units of our standard:

$$Q = ST \qquad \textbf{8-4}\boldsymbol{c}$$

where

$$Q_s = S \times 1\ \mathrm{K}$$

This temperature T we call the *absolute temperature*. (It can be shown that this temperature and that defined earlier in terms of the average kinetic energy of the molecules are equivalent.)

Thus, if we have two engines, one operating between T_1 and 1 K and the other between T_2 and 1 K, then the heats absorbed are related by

$$\frac{Q_1}{T_1} = S = \frac{Q_2}{T_2} \qquad \textbf{8-4}\boldsymbol{d}$$

For an engine operating between T_1 and T_2, then $(Q_1/T_1)_{\text{absorbed}} = (Q_2/T_2)_{\text{delivered}}$ and there is no net gain or loss of (Q/T). This quantity $Q/T = S$ is called the *entropy*. The SI units of entropy are joules/kelvin (J/K). This is the result (from thermodynamics) that there is no net change in entropy in a reversible cycle. Extending this discussion to irreversible cycles, we can show in thermodynamics that for reversible cycles, the entropy *always* increases; that is, $\Delta S > 0$. Since there are no truly reversible cycles in nature, we conclude that the entropy of the universe always increases.