9.12: Entropy and Predicting Change

The entropy-based criteria that we develop in Section 9.2 through Section 9.8 are of central importance. If we are able to evaluate the change in the entropy of the universe for a prospective process and find that it is greater than zero, we can conclude that the process can occur spontaneously. The reverse of a spontaneous process cannot occur; it is an impossible process and the change in the entropy of the universe for such a process must be less than zero. Since an equilibrium process is a reversible process, the entropy of the universe must remain unchanged when a system goes from an initial state to a final state along a path whose every point is an equilibrium state. Using another figure of speech, we often say that a change that occurs along a reversible path is a change that "occurs at equilibrium."

These conclusions are what make the entropy function useful: If we can calculate $\Delta S_{universe}$ for a prospective process, we know whether the system is at equilibrium with respect to that process; whether the process is possible; or whether the process cannot occur. If we find $\Delta S_{universe} > 0$ for a process, we can conclude that the process is possible; however, we cannot conclude that the process will occur. Indeed, many processes can occur spontaneously but do not do so. For example, hydrocarbons can react spontaneously with oxygen; most do so only at elevated temperatures or in the presence of a catalyst.

The criteria $\Delta S_{universe} = \Delta S + \Delta \hat{S} \geq 0$ are completely general. They apply to any process occurring under any conditions. To apply them we must determine both ΔS and $\Delta \hat{S}$. By definition, the system comprises the part of the universe that is of interest to us; the need to determine $\Delta \hat{S}$ would appear to be a nuisance. This proves not to be the case. So long as the surroundings have a well-defined temperature, we can develop additional criteria for equilibrium and spontaneous change in which $\Delta \hat{S}$ does not occur explicitly. In §14, we develop criteria that apply to reversible processes. In §15, we find a general relationship for $\Delta \hat{S}$ that enables us to develop criteria for spontaneous processes.

To develop the criteria for spontaneous change, we must define what we mean by spontaneous change more precisely. To define a spontaneous process in an isolated system as one that can take place on its own is reasonably unambiguous. However, when a system is in contact with its surroundings, the properties of the surroundings affect the change that occurs in the system. To specify a particular spontaneous process we must specify some properties of the surroundings or—more precisely—properties of the system that the surroundings act to establish. The ideas that we develop in §15 lead to criteria for changes that occur while one or more thermodynamic functions remain constant. These criteria supplement the second-law criteria $\Delta S + \Delta \hat{S} \geq 0$. In using these criteria, we can say that the change occurs subject to one or more constraints.

Some of these criteria depend on the magnitudes of ΔE and ΔH in the prospective process. We also find criteria that are expressed using new state functions that we call the Helmholtz and Gibbs free energies. In the next section, we introduce these functions.