6.9: Reversible vs. Irreversible Processes

When we think about a physical system that is undergoing a reversible change, we imagine that the system passes through a series of states. In each of these states, every thermodynamic variable has a well-defined value in every phase of the system. We suppose that successive states of the changing system are arbitrarily close to one another in the sense that the successive values of every thermodynamic are arbitrarily close to one another. These suppositions are equivalent to assuming that the state of the system and the value of every thermodynamic variable are continuous functions of time. Then every thermodynamic variable is either constant or a continuous function of other thermodynamic variables. When we talk about a reversible process, we have in mind a physical system that behaves in this way and in which an arbitrarily small change in one of the thermodynamic variables can reverse the direction in which other thermodynamic variables change.

A process that is not reversible is said to be ***irreversible***. We distinguish between two kinds of irreversible processes. A process that cannot occur under a given set of conditions is said to be an ***impossible*** process. A process that can occur, but does not do so reversibly, is called a ***possible*** process or a ***spontaneous*** process.

Another essential characteristic of a reversible process is that changes in the system are driven by conditions that are imposed on the system by the surroundings. In our discussion of the phase equilibria of water, we note that the surroundings can transfer heat to the system only when the temperature of the surroundings is greater than that of the system. However, if the process is to be reversible, this temperature difference must be arbitrarily small, so that heat can be made to flow from the system to the surroundings by an arbitrarily small decrease in the temperature of the surroundings.

Similar considerations apply when the process involves the exchange of work between system and surroundings. We focus on changes in which the work exchanged between system and surroundings is pressure–volume work. A process can occur reversibly only if the pressure of the system and the pressure applied to the system by the surroundings differ by an arbitrarily small amount. To abbreviate these statements, we customarily introduce a figure of speech and say that, for a reversible process, $T_{system} = T_{surroundings}$ (or $T = \hat{T}$) and that $P_{system} = P_{surroundings}$ (or $P = P_{applied}$).

Since a reversible process involves a complementary exchange of energy increments between system and surroundings, it is evident that an isolated system cannot undergo a reversible change. Any change that occurs in an isolated system must be spontaneous. By the contrapositive, an isolated system that cannot undergo change must be at equilibrium.

While $T = \hat{T}$ and $P = P_{applied}$ are necessary conditions for a reversible process, they are not sufficient. A spontaneous process can occur under conditions in which the system temperature is arbitrarily close to the temperature of the surroundings and the system pressure is arbitrarily close to the applied pressure. Consider a mixture of hydrogen and oxygen in a cylinder closed by a frictionless piston. We suppose that the surroundings are maintained at a constant temperature and that the surroundings apply a constant pressure to the piston. We suppose that the system contains a small quantity of a poorly effective catalyst. By controlling the activity of the catalyst, we can arrange for the formation of water to occur at an arbitrarily slow rate—a rate so slow that the temperature and pressure gradients that occur in the neighborhood of the catalyst are arbitrarily small. Nevertheless, the reaction is a spontaneous process, not a reversible one. If the process were reversible, an arbitrarily small increase in the applied pressure would be sufficient to reverse the direction of reaction, causing water to decompose to hydrogen and oxygen.