

18.2: Spontaneous and Nonspontaneous Processes

The study of thermodynamics helps us to understand and predict whether a particular process occurs spontaneously. For example, does rust spontaneously form when iron comes into contact with oxygen? Does water spontaneously decompose into hydrogen and oxygen? A **spontaneous process** is one that occurs without ongoing outside intervention (such as the performance of work by some external force). For example, when we drop a book in a gravitational field, it spontaneously drops to the floor. When we place a ball on a slope, it spontaneously rolls down the slope. Both of these processes are spontaneous.



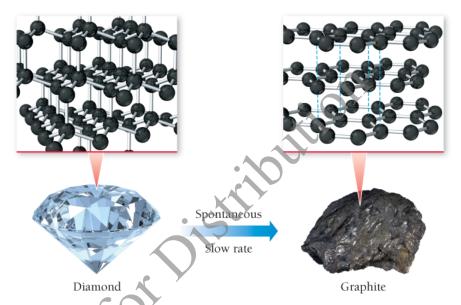
Iron spontaneously rusts when it comes in contact with oxygen.

For chemical processes, we must be careful not to confuse the *spontaneity* of the process with its *speed*. In chemical thermodynamics, we study the *spontaneity* of a reaction—the direction in which and the extent to which a chemical reaction proceeds. In kinetics, we study the *speed* of the reaction—how fast it takes place (Figure 18.1.). A reaction may be thermodynamically spontaneous but kinetically slow at a given temperature. For example, the conversion of diamond to graphite is thermodynamically spontaneous. But your diamonds will not become worthless anytime soon because the process is extremely slow kinetically. Although the rate of a spontaneous process can be increased by using a catalyst, a catalyst cannot make a nonspontaneous process spontaneous. Catalysts affect only the rate of a reaction, not the spontaneity.

Figure 18.1 Thermodynamics and Kinetics

Thermodynamics deals with the relative chemical potentials of the reactants and products. It enables us to predict whether a reaction will be spontaneous and to calculate how much work it can do. Kinetics involves the chemical potential of intermediate states and enables us to determine why a reaction is slow or fast.

One last word about nonspontaneity—a nonspontaneous process is not *impossible*. For example, the extraction of iron metal from iron ore is a nonspontaneous process; it does not happen if the iron ore is left to itself, but that does not mean it is impossible. As we will see later in this chapter, a nonspontaneous process can be made spontaneous by coupling it to another process that is spontaneous or by supplying energy from an external source. Iron can be separated from its ore if external energy is supplied, usually by means of another reaction (that is highly spontaneous).



Even though graphite is thermodynamically more stable than diamond, the conversion of diamond to graphite is kinetically so slow that it does not occur at any measurable rate.