3.2: Spontaneous, Reversible, and Irreversible Processes

A **spontaneous process** is a process that can actually occur in a finite time period under the existing conditions. Any change over time in the state of a system that we observe experimentally is a spontaneous process.

A spontaneous process is sometimes called a natural process, feasible process, possible process, allowed process, or real process.

3.2.1 Reversible processes

A **reversible process** is an important concept in thermodynamics. This concept is needed for the chain of reasoning that will allow us to define entropy changes in the next chapter, and will then lead on to the establishment of criteria for spontaneity and for various kinds of equilibria.

Before reversible processes can be discussed, it is necessary to explain the meaning of the *reverse* of a process. If a particular process takes the system from an initial state A through a continuous sequence of intermediate states to a final state B, then the reverse of this process is a change over time from state B to state A with the same intermediate states occurring in the reverse time sequence. To visualize the reverse of any process, imagine making a movie film of the events of the process. Each frame of the film is a "snapshot" picture of the state at one instant. If you run the film backward through a movie projector, you see the reverse process: the values of system properties such as p and V appear to change in reverse chronological order, and each velocity changes sign.

The concept of a reversible process is not easy to describe or to grasp. Perhaps the most confusing aspect is that a reversible process is not a process that ever actually occurs, but is only approached as a hypothetical limit. During a reversible process the system passes through a continuous sequence of equilibrium states. These states are ones that can be approached, as closely as desired, by the states of a spontaneous process carried out sufficiently slowly. As the spontaneous process is carried out more and more slowly, it approaches the reversible limit. Thus, a reversible process is an *idealized* process with a sequence of equilibrium states that are those of a spontaneous process in the *limit* of infinite slowness.

This e-book has many equations expressing relations among heat, work, and state functions during various kinds of reversible processes. What is the use of an equation for a process that can never actually occur? The point is that the equation can describe a spontaneous process to a high degree of accuracy, if the process is carried out slowly enough for the intermediate states to depart only slightly from exact equilibrium states. For example, for many important spontaneous processes we will assume the temperature and pressure are uniform throughout the system, which strictly speaking is an approximation.

A reversible process of a closed system, as used in this e-book, has all of the following characteristics:

- We must imagine the reversible process to proceed at a finite rate, otherwise there would be no change of state over time. The precise rate of the change is not important. Imagine a gas whose volume, temperature, and pressure are changing at some finite rate while the temperature and pressure magically stay perfectly uniform throughout the system. This is an entirely imaginary process, because there is no temperature or pressure gradient—no physical "driving force"—that would make the change tend to occur in a particular direction. This imaginary process is a reversible process—one whose states of uniform temperature and pressure are approached by the states of a real process as the real process takes place more and more slowly.

  It is a good idea, whenever you see the word "reversible," to think "in the reversible limit." Thus a *reversible process* is a process in the reversible limit, *reversible work* is work in the reversible limit, and so on.

3.2.2 Irreversible processes

An **irreversible** process is a spontaneous process whose reverse is neither spontaneous nor reversible. That is, the reverse of an irreversible process can never actually occur and is *impossible*. If a movie is made of a spontaneous process, and the time sequence of the events depicted by the film when it is run backward could not occur in reality, the spontaneous process is irreversible.

A good example of a spontaneous, irreversible process is experiment 1 in Section 3.1.3, in which the sinking of an external weight immersed in water causes a paddle wheel to rotate and the temperature of the water to increase. During this experiment mechanical energy is dissipated into thermal energy. Suppose you insert a thermometer in the water and make a movie film of the experiment. Then when you run the film backward in a projector, you will see the paddle wheel rotating in the direction that raises the weight, and the water becoming cooler according to the thermometer. Clearly, this reverse process is impossible in the real physical world, and the process occurring during the experiment is irreversible. It is not difficult to understand why it is

irreversible when we consider events on the microscopic level: it is extremely unlikely that the H_2O molecules next to the paddles would happen to move simultaneously over a period of time in the concerted motion needed to raise the weight.

3.2.3 Purely mechanical processes

There is a class of spontaneous processes that are also spontaneous in reverse; that is, spontaneous but not irreversible. These are *purely mechanical* processes involving the motion of perfectly-elastic macroscopic bodies without friction, temperature gradients, viscous flow, or other irreversible changes.

A simple example of a purely mechanical process and its reverse is shown in Fig. 3.2. The ball can move spontaneously in either direction. Another example is a flywheel with frictionless bearings rotating in a vacuum.

A purely mechanical process proceeding at a finite rate is not reversible, for its states are not equilibrium states. Such a process is an idealization, of a different kind than a reversible process, and is of little interest in chemistry. Later chapters of this e-book will ignore such processes and will treat the terms *spontaneous* and *irreversible* as synonyms.