2.4: The State of the System

The thermodynamic **state** of the system is an important and subtle concept. At each instant of time, the system is in some definite state that we may describe with values of the macroscopic properties we consider to be relevant for our purposes. The values of these properties at any given instant define the state at that instant. Whenever the value of any of these properties changes, the state has changed. If we subsequently find that each of the relevant properties has the value it had at a certain previous instant, then the system has returned to its previous state.

> Do not confuse the *state* of the system with the kind of *physical state* or state of aggregation of a phase discussed in Sec. 2.2.1. A *change of state* refers to a change in the state of the system, not necessarily to a phase transition.

2.4.1 State functions and independent variables

The properties whose values at each instant depend only on the state of the system at that instant, and not on the past or future history of the system, are called **state functions** (or state variables or state parameters). There may be other system properties that we consider to be irrelevant to the state, such as the shape of the system, and these are *not* state functions.

Various conditions determine what states of a system are physically possible. If a uniform phase has an equation of state, property values must be consistent with this equation. The system may have certain built-in or externally-imposed conditions or constraints that keep some properties from changing with time. For instance, a closed system has constant mass; a system with a rigid boundary has constant volume. We may know about other conditions that affect the properties during the time the system is under observation.

We can define the state of the system with the values of a certain minimum number of state functions which we treat as the **independent variables**. Once we have selected a set of independent variables, consistent with the physical nature of the system and any conditions or constraints, we can treat all other state functions as **dependent variables** whose values depend on the independent variables.

Whenever we adjust the independent variables to particular values, every other state function is a dependent variable that can have only one definite, reproducible value. For example, in a single-phase system of a pure substance with T, p, and n as the independent variables, the volume is determined by an equation of state in terms of T, p, and n; the mass is equal to nM; the molar volume is given by $V_{\mathrm{m}} = V/n$; and the density is given by $\rho = nM/V$.

2.4.2 An example: state functions of a mixture

The heat-conducting metal rod shown in Fig. 2.8 is a system in such a steady state. Each end of the rod is in thermal contact with a **heat reservoir** (or **thermal reservoir**), which is a body or external system whose temperature remains constant and uniform when there is heat transfer to or from it.

A heat reservoir can be a body that is so large that its temperature changes only imperceptibly during heat transfer; a thermostat bath whose temperature can be controlled; or an external system of coexisting phases of a pure substance (e.g., ice and water) at constant pressure.

The two heat reservoirs in the figure have different temperatures, causing a temperature gradient to form along the length of the rod and energy to be transferred by heat from the warmer reservoir to the rod and from the rod to the cooler reservoir. Although the properties of the steady state of the rod remain constant, the rod is clearly not in an equilibrium state because the temperature gradient will quickly disappear when we isolate the rod by removing it from contact with the heat reservoirs.