

6.2: Thermodynamic Systems and Variables

We characterize the system by specifying the values of enough variables so that the system can be exactly replicated. By “exactly replicated” we mean, of course, that we are not able to distinguish the system from its replicate by any experimental measurement. Any variable that can be used to characterize the system in this way is called a **variable of state**, a **state variable**, or a **state function**.

We can say the same thing in slightly different words by saying that the state of a system is completely specified when the values of all of its state variables are specified. If we initially have a system in some equilibrium state and change one or more of the variables that characterize it, the system will eventually reach a new equilibrium state, in which some state variables will have values different from those that characterized the original state. If we want to return the system to its original state, we must arrange matters so that the value of every state variable is the same as it was originally.

The variables that are associated with a chemical system include **pressure**, **volume**, **temperature**, and the number of **moles** of each substance present. All of these variables can be measured directly; that is, every equilibrium state of a system is associated with a specific value of each of these variables, and this value can be determined without reference to any other state of the system. **Energy** and **entropy** are also variables that are associated with a thermodynamic system. We can only measure changes in energy and entropy; that is, we can only measure energy and entropy for a process in which a system passes from one state to another.

Other important thermodynamic variables are defined as functions of pressure, volume, temperature, energy and entropy. These include **enthalpy**, the **Gibbs free energy**, the **Helmholtz free energy**, **chemical activity**, and the **chemical potential**. Our goals in developing the subject of chemical thermodynamics are to define each of these state functions, learn how to measure each of them, and provide a theory that relates the change that occurs in any one of them to the changes that occur in the others when a chemical system changes from one state to another.

Any interaction through which a chemical system can exchange work with its surroundings can affect its behavior. Work-producing forces can involve many phenomena, including gravitational field, electric field, and magnetic fields; surface properties; and sound (pressure) waves. In [Chapter 17](#), we discuss the work done when an electric current passes through an electrochemical cell. Otherwise, this book focuses on pressure–volume work and gives only passing attention to the job of incorporating other forms of work into the general theory. We include pressure–volume work because it occurs whenever the volume of a system changes. A thermodynamic theory that did not include volume as a variable would be of limited utility.

Thermodynamic variables can be sorted into two classes in another way. Consider the pressure, temperature, and volume of an equilibrium system. We can imagine inserting a barrier that divides this original system into two subsystems—without changing anything else. Each of the subsystems then has the temperature and pressure of the original system; however, the volume of each subsystem is different from the volume of the original system. We say that temperature and pressure are **intensive variables**, by which we mean that the temperature or pressure of an equilibrium system is independent of the size of the system and the same at any location within the system. Intensive variables stand in contrast to **extensive variables**. The magnitude of an extensive variable is directly proportional to the size of the system. Thus, volume is an extensive variable. Energy is an extensive variable. We shall see that entropy, enthalpy, the Helmholtz free energy, and the Gibbs free energy are extensive variables also.

For any extensive variable, we can create a companion intensive variable by dividing by the size of the system. For example, we can convert the mass of a homogeneous system into a companion variable, the density, by dividing by the system’s volume. We will discover that it is useful to define certain **partial molar quantities**, which have units like energy per mole. Partial molar quantities are intensive variables. We will find a partial molar quantity that is particularly important in describing chemical equilibrium. It is called the **chemical potential**, and since it is a partial molar quantity, the chemical potential is an intensive thermodynamic variable.

We think of a system as a specific collection of matter containing specified phases. Our goal is to develop mathematical models (equations) that relate a system’s state functions to one another. A system can be at equilibrium under a great many different circumstances. We say that the system can have many equilibrium positions. A complete description of all of these equilibrium positions requires models that can specify how much of each of the substances that make up the system is present in each phase.

However, if a system is at equilibrium, a half-size copy of it is also at equilibrium; whether a system is at equilibrium can be specified without specifying the sizes of the phases that make it up. This means that we can characterize the equilibrium states of any system that contains specified substances and phases by specifying the values of the system’s intensive variables. In general, not all of these intensive variables will be independent. The number of intensive variables that are independent is called the number

of **degrees of freedom** available to the system. This is also the number of intensive variables that can change independently while a given system remains at equilibrium.

To completely define a particular system we must specify the size and composition of each phase. To do so, we must specify the values of some number of extensive variables. These extensive variables can change while all of the intensive variables remain constant and the system remains at equilibrium. In the next section, we review the phase equilibria of water. A system comprised of liquid and gaseous water in phase equilibrium illustrates these points. Specifying either the pressure or temperature specifies the equilibrium state to within the sizes of the two phases. For a complete description, we must specify the number of moles of water in each phase. By adding or removing heat, while maintaining the original pressure and temperature, we can change the distribution of the water between the two phases.

In 1875, J. Willard Gibbs developed an equation, called **Gibbs' phase rule**, from which we can calculate the number of degrees of freedom available to any particular system. We introduce Gibbs' phase rule in [Section 6.8](#). The perspective and analysis that underlie Gibbs' phase rule have a significance that transcends use of the rule to find the number of degrees of freedom available to a system. In essence, **the conditions assumed in deriving Gibbs' phase rule define what we mean by equilibrium in chemical systems**. From experience, we are usually confident that we know when a system is at equilibrium and when it is not. One of our goals is to relate thermodynamic functions to our experience-based ideas about what equilibrium is and is not. To do so, we need to introduce the idea of a **reversible process**, in which the system undergoes a **reversible change**.

We will see that the states that are accessible to a system that is at equilibrium in terms of Gibbs' phase rule are identically the states that the system can be in while undergoing a reversible change. A principal goal of the remainder of this chapter is to clarify this equivalence between the range of states accessible to the system at equilibrium and the possible paths along which the system can undergo reversible change.

The thermodynamic theory that we develop predicts quantitatively how a system's equilibrium position changes in response to a change that we impose on one or more of its state functions. **The principle of Le Chatelier** makes qualitative predictions about such changes. We introduce the principle of Le Chatelier and its applications later in this chapter. In [Chapter 12](#), we revisit this principle to understand it as a restatement, in qualitative terms, of the thermodynamic criteria for equilibrium.

This page titled [6.2: Thermodynamic Systems and Variables](#) is shared under a [CC BY-SA 4.0](#) license and was authored, remixed, and/or curated by [Paul Ellgen](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.