

6.15: State Functions in Systems Undergoing Spontaneous Change

In this chapter, we introduce ideas that underlie classical thermodynamics. Because the development of classical thermodynamics relies on the properties of reversible processes, we have devoted considerable attention to specifying what we mean by a reversible process and to the relationship between reversible processes and the equilibrium states available to a system. In [Section 7.17](#), we develop this theory. The development assumes that we can measure the heat and work exchanged between a system and its surroundings. It assumes that we can measure the state functions volume, pressure, temperature, and the amounts (moles) of chemical substances in a system. We define other state functions, whose values can be computed from these measurable quantities. From observations that we make on systems that are undergoing reversible change, we develop numerous relationships among these state functions.

No real system can change in exactly the manner we have in mind when we talk about a reversible process. Strictly speaking, any process that actually occurs must be spontaneous. The idea of reversible change is clearly an abstraction from reality. Nevertheless, we can determine—to a good approximation—the way in which one variable depends on another in a reversible process. We accomplish this by making measurements on a real system whose behavior approximates the ideal of reversibility as closely as possible. We express the—approximate—result of any such measurement as a number. Normally, we view the approximate character of the number to be a consequence of experimental error. When we say that we make measurements on a system that is undergoing a reversible change, we mean that we are making the measurements on a process that satisfies our definition of reversibility closely enough for the purpose at hand.

There are two reasons for the fact that reversible processes play an essential role in the development of the equations of thermodynamics. The first is that we can measure the entropy change for a process only if the process is reversible. The second and subtler reason is that an intensive variable may not have a unique value in a system that is undergoing a spontaneous change. If the temperature, the pressure, or the concentration of a component varies from point to point within the system, then that state function does not have a unique value, and we cannot use it to model the change. This occurs, for example, when gasoline explodes in a cylinder of a piston engine. The system consists of the contents of the cylinder. At any given instant, the pressure, temperature, and component concentrations vary from place to place within the cylinder. In general, no single value of any of these intensive variables is an adequate approximation for use in the thermodynamic equations that characterize the system as a whole.

To explore this idea further, let us think about measuring changes in extensive state functions during a spontaneous process. Since we are free to define the system as we please, we can choose a definition that makes the volume readily measurable. In the piston-engine example, there is no ambiguity about the volume of the system at any instant. While point-to-point variability means that the concentrations of the chemical components are not defined for the system as a whole, we are confident that there is some specific number of moles of each component present in the system at every instant. We can reach this conclusion by imagining that we can instantaneously freeze the composition by stopping all reactions. We can then find the number of moles of each component at our leisure.

If the system is not too inhomogeneous, we can devise an alternative procedure for making—in concept—such composition measurements. We imagine dividing the system into a large number of macroscopic subsystems. Each of these subsystems has a well-defined volume. We suppose also that each of them has well-defined thermodynamic functions at any given instant; that is, we assume that the pressure, temperature, and concentrations are approximately homogeneous within each of these subsystems. If this condition is satisfied, we can sum up the number of moles of a component in each of the sub-volumes to obtain the number of moles of that component in the whole system.

We can make a similar argument for any extensive thermodynamic function, so it applies to the energy, entropy, enthalpy, and the Helmholtz and Gibbs free energies. As long as the point-to-point variability within the system is small enough so that a division of the system into macroscopic subsystems produces subsystems that are approximately homogeneous, we can find the value for any extensive thermodynamic function in each individual sub-system and for the system as a whole. The measurement we propose has the character of a *gedanken* experiment. We can describe a procedure for making the measurement, whether we can actually perform the procedure or not.

This argument does not work for intensive thermodynamic functions. It is true that we could produce a weighted-average value for the temperature by multiplying the temperature of each subsystem by the subsystem volume, adding up the products, and dividing the sum by the volume of the whole system; however, the result would not be an intensive property of the whole system. For one thing, we could produce a different average temperature for every extensive variable by using it rather than the volume as the weighting factor in the average-temperature computation. Moreover, no such weighted-average temperature can reflect the fact that

different temperatures in different subsystems result in grossly different reaction rates. No single temperature represents the state of the whole system, and we can make the same statement about any other intensive thermodynamic function. For a non-homogeneous system that can be subdivided into approximately homogeneous macroscopic subsystems, we can measure, in principle, the values of the system's extensive state functions; however, its intensive state functions are essentially undefined.

On the other hand, we may be able to assume that an effectively homogeneous subsystem of macroscopic proportions does have well-defined extensive and intensive state functions, even if it is not in an equilibrium state. While a spontaneously changing system need not be homogenous, we commonly encounter systems that are homogeneous to within some arbitrarily small deviation. Consider a closed and well-stirred system in which some chemical reaction is occurring slowly. We immerse this system in a constant-temperature bath, and arrange for the applied pressure to be constant. From experience, we know that the temperature and pressure within such a system will be essentially constant, equal to the bath temperature and the applied pressure, respectively, and homogeneous throughout the system. In such a system, the temperature and the pressure of the system are at equilibrium with those imposed by the surroundings. The chemical process is not at equilibrium, but the component concentrations are homogeneous.

An important question now arises: Are all of the equations of equilibrium thermodynamics applicable to a system in which some processes occur spontaneously? That they are not is evident from the fact that we can calculate an entropy change from its defining equation, $dS = dq^{rev}/T$, only if the behavior of the system is reversible.

Nevertheless, we will find that the relationships among state functions that we derive for reversible processes can be augmented to describe spontaneous processes that occur in homogeneous systems. The necessary augmentation consists of the addition of terms that express the effects of changing composition. (In [Section 9.14](#), we develop the **fundamental equation**,

$$dE = TdS - PdV + dw_{NPV}$$

which applies to any reversible process in a closed system. In [Section 14.1](#), we infer that the fundamental equation becomes

$$dE = TdS - PdV + dw_{NPV} + \sum_i \mu_i dn_i$$

for a spontaneous process in which μ_i and dn_i are the chemical potential and the change in the number of moles of component i , respectively.)

The distinction between reversible process and spontaneous processes plays a central role in our theory. We find a group of relationships that express this distinction, and we call these relationships **criteria for change**. (In [Section 9.19](#), we find that $(dE)_{SV} = dw_{NPV}$ if and only if the process is reversible, while $(dE)_{SV} < dw_{npv}$ if and only if the process is spontaneous. We find a close connection between the criteria for change and the composition-dependent terms that are needed to model the thermodynamic functions during spontaneous processes. We find that $\sum_i \mu_i dn_i = 0$ if and only if the process is reversible, while $\sum_i \mu_i dn_i < 0$ if and only if the process is spontaneous.)

In thinking about spontaneous processes, we should also keep in mind that the validity of our general relationships among state functions does not depend on our ability to measure the state functions of any particular state of a system. For example, we can find relationships among the molar volume and other thermodynamic properties of liquid water. Liquid water does not exist at 200 C and 1 bar, so we cannot undertake to measure its thermodynamic properties. However, by using our relationships among state functions and properties that we measure for liquid water where it does exist, we can estimate the thermodynamic properties of liquid water at 200 C and 1 bar. The results are two steps removed from reality; they are the estimated properties of a hypothetical substance. Nevertheless, they have predictive value; for example, we can use them to predict that liquid water at 200 C and 1 bar will spontaneously vaporize to form gaseous water at 1 bar. The equations of thermodynamics are creatures of theory. We should not expect every circumstance that is described by the theory to exist in reality. What we require is that the theory accurately describe every circumstance that actually occurs.

To develop the equations of classical thermodynamics, we consider reversible processes. We then find general criteria for change that apply to any sort of change in any system. Later, we devise criteria based on the changes that occur in the composition of the system. In this book, we consider such composition-based criteria only for homogeneous systems. An extensive theory^{4,5} has been developed to model spontaneous processes in systems that are not necessarily homogeneous. This theory is often called **irreversible thermodynamics** or **non-equilibrium thermodynamics**. Development of this theory has led to a wide variety of useful insights about various molecular processes. However, much of what we are calling classical thermodynamics also describes irreversible

processes. Even as we develop our theory of reversible thermodynamics, we use arguments that apply the equations we infer from reversible processes to describe closely related systems that are not at equilibrium.

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