between thermodynamics and information theory, and the study of chaotic behavior in thermodynamic systems, attract a great deal of attention. Modern ideas, furthermore, have been shown to be applicable to a wider variety of phenomena than hitherto suspected.

Thermodynamics has captured the imagination of many of the greatest minds of science. Einstein, who was captivated by the subject, wrote: "A theory is the more impressive the greater the simplicity of its premises, and the more extended its area of applicability. Therefore, the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the applicability of its basic concepts, it will never be overthrown." That is quite a statement, indeed!

1.2 DEFINITIONS

In developing the basic ideas of thermodynamics the originators of the theory were careful not to be so concise as to render definitions sterile. The following brief definitions will be illustrated by examples in future sections.

Thermodynamics can be described as the study of *equilibrium properties* in which *temperature* is an important variable. All of the words in italics need to be defined.

In thermodynamics we are concerned with a *system,* some portion of the physical world. The system could be a container of gas, a piece of metal, a magnet. The system must not interact chemically with the vessel that contains it. (The behavior of a liquid must not be influenced by the test tube that holds it.) A system may exchange energy with other systems, which constitute the *surroundings* of the given system. The system, together with its surroundings, comprise a *universe.*

We classify systems as to whether they are open, closed, or isolated. An *open* system can exchange mass and energy with its surroundings. A *closed* system cannot exchange mass with its surroundings, but can exchange energy in other forms. An *isolated* system cannot exchange mass or energy in any form with its surroundings; it is completely cut off from other systems.

The quantities we use to describe the macroscopic behavior of a system are called *properties,* observable characteristics of a system. Other names are thermodynamic variables or thermodynamic coordinates. An extremely important concept is that of a *state variable,* a property whose differential is exact.

Properties are extensive or intensive. An *extensive* property is proportional to the mass. An example is the volume V; if the mass is doubled, the volume is doubled (assuming that the density remains constant). An *intensive* property is independent of the mass. Temperature T is an intensive property; its value is not affected by a change of mass. Pressure P and density ρ are further examples of intensive properties.

Inherently extensive properties are given by capital letters. Inherently intensive properties are denoted by lowercase letters. There are two important exceptions: The temperature T is always capitalized to avoid confusion with the time t; and the pressure P is capitalized to distinguish it from the probability p.

An extensive property can be converted to an intensive property by dividing by the mass. This is called a *specific value:*

$$\text{Specific value} \equiv \frac{\text{value of the extensive property}}{\text{mass of the system}}.$$

In this text, we will go back and forth between extensive properties and their corresponding specific values.

1.3 THE KILOMOLE

The kilomole is a unit of mass defined as follows:

$$1 \text{ kilomole} \equiv \text{mass } m \text{ in kilograms equal to the molecular weight.}$$

Thus one kilomole of oxygen gas (O_2) is equal to 32 kg. (The mole is a unit of mass more familiar to chemists; one mole is equal to the mass in grams. Thus a mole of oxygen gas is 32 g.)

1.4 LIMITS OF THE CONTINUUM

We tacitly assume that classical thermodynamics is a continuum theory, that properties vary smoothly from point to point in the system. But if all systems are made up of atoms and molecules (as our definition of the kilomole implies), it is reasonable to ask: how small a volume can we be concerned with and still have confidence that our continuum theory is valid?

We can obtain an approximate answer to this question by invoking Avogadro's law, which states that at standard temperature and pressure (0°C and atmospheric pressure), one kilomole of gas occupies 22.4 m^3 and contains 6.02×10^{26} molecules. (The latter is called Avogadro's number, N_A.) Then

$$\frac{6.02 \times 10^{26} \text{ molecules kilomole}^{-1}}{22.4 \text{ m}^3 \text{ kilomole}^{-1}} = 2.69 \times 10^{25} \frac{\text{molecules}}{\text{m}^3}.$$

This molecular density is sometimes called Loschmidt's number. Using it we can easily show that a cube one millimeter on each side contains roughly 10^{16} molecules, whereas a cube one nanometer (10^{-9} m) on a side has a very small probability of containing even one molecule. We can therefore be reasonably certain that classical thermodynamics is applicable down to very small macroscopic (and even microscopic) volumes, but ultimately a limit is reached where our theory will break down.

1.5 MORE DEFINITIONS

The *state* of a system is defined as a condition uniquely specified by a set of properties. Examples of such properties are pressure, volume, and temperature. The question arises: how many properties are required to specify the state of a thermodynamic system? By "required number" we mean that every time a system with the given properties is subjected to a particular environment, every feature of its subsequent behavior is identical. In classical mechanics, if the displacement and velocity of a system are known at some instant of time, as well as the forces acting on it, the behavior of the system is predicted for all times. Most frequently, the thermodynamic state of a single component system is also specified by two independent variables.

An *equilibrium state* is one in which the properties of the system are uniform throughout and do not change with time unless the system is acted upon by external influences. A *non-equilibrium state* characterizes a system in which gradients exist and whose properties vary with time (the atmosphere and the oceans are examples). *State variables* are properties that describe equilibrium states. An *equation of state* is a functional relationship among the state variables for a system in equilibrium. A *path* is a series of states through which a system passes.

In introductory physics, a "change of state" is frequently used to denote a transition from a liquid to a gas, or from a solid to a liquid, etc. In thermodynamics, such a change is referred to as a *change of phase* or *phase transformation.*

If the pressure P, the volume V, and the temperature T are the state variables of the system, the equation of state takes the form

$$f(P, V, T) = 0. \tag{1.1}$$

This relationship reduces the number of independent variables of the system from three to two. The function f is assumed to be given as part of the specification of the system. It is customary to represent the state of such a system by a point in three-dimensional P-V-T space. The equation of state then defines a surface in this space (Figure 1.2). Any point lying on this surface represents a state in equilibrium. In thermodynamics a state automatically means a state in equilibrium unless otherwise specified.

The boundary between a system and its surroundings through which changes may be imposed is called a *system wall.* An *adiabatic wall* is a boundary that permits no heat interaction with the surroundings. The word comes from

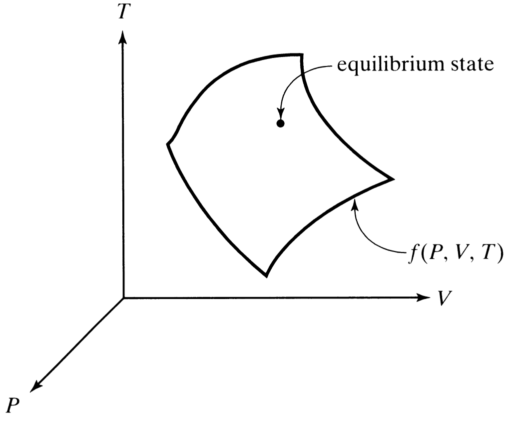

Figure 1.2 Surface in P-V-T space. Points on the surface represent equilibrium states of the system whose equation of state is $f(P, V, T) = 0$.

the Greek *adiabatos,* meaning "not going through." An isolated system is adiabatically contained. However, a system with an adiabatic wall is not necessarily isolated. Mechanical interactions can take place through adiabatic walls. For example, material can be removed or added, the volume can change, a magnetic field can be applied, etc. A *diathermal wall* is a boundary that freely allows heat to be exchanged. The Greek word *diathermos* means "heat through."

If a system strongly interacts with its walls, the problem becomes complicated. Think of pancake batter sticking to the griddle, or sulfuric acid in an iron vessel!

A *process* is a change of state expressed in terms of a path along the equation of state surface in Figure 1.2. In a *cyclical process,* the initial and final states are the same. A *quasi-static process* is a process in which, at each instant, the system departs only infinitesimally from an equilibrium state. That is, changes of state are described in terms of differentials. An example is the gradual compression of a gas.

A *reversible process* is a process whose direction can be reversed by an infinitesimal change in some property. It is a quasi-static process in which no dissipative forces such as friction are present. All reversible processes are quasi-static, but a quasi-static process is not necessarily reversible. For example, a slow leak in a tire is quasi-static but not reversible. A reversible process is an idealization; friction is always present. An *irreversible process* involves a finite change in a property in a given step and includes dissipation (energy loss). All natural processes are irreversible.

In many processes, some property of the system remains constant. An *isobaric process* is a process in which the pressure is constant. If the volume is constant, the process is *isochoric.* And if the temperature doesn't change, the process is called *isothermal.*

Suppose a piston enclosing a gas is immersed in a heat bath, so that the gas is kept at constant temperature. The gas is slowly compressed (Figure 1.3).