

Introduction

THERMODYNAMICS is mainly concerned with the transformations of heat into mechanical work and the opposite transformations of mechanical work into heat.

Only in comparatively recent times have physicists recognized that heat is a form of energy that can be changed into other forms of energy. Formerly, scientists had thought that heat was some sort of fluid whose total amount was invariable, and had simply interpreted the heating of a body and analogous processes as consisting of the transfer of this fluid from one body to another. It is, therefore, noteworthy that on the basis of this heat-fluid theory Carnot was able, in the year 1824, to arrive at a comparatively clear understanding of the limitations involved in the transformation of heat into work, that is, of essentially what is now called the second law of thermodynamics (see Chapter III).

In 1842, only eighteen years later, R. J. Mayer discovered the equivalence of heat and mechanical work, and made the first announcement of the principle of the conservation of energy (the first law of thermodynamics).

We know today that the actual basis for the equivalence of heat and dynamical energy is to be sought in the kinetic interpretation, which reduces all thermal phenomena to the disordered motions of atoms and molecules. From this point of view, the study of heat must be considered as a special branch of mechanics: the mechanics of an ensemble of such an enormous number of particles (atoms or molecules) that the detailed description of the state and the motion loses importance and only average properties of large numbers of particles are to be considered. This branch of mechanics, called *statistical mechanics*, which has been developed mainly through the work of Maxwell, Boltzmann, and Gibbs, has led to a very satisfactory understanding of the fundamental thermodynamical laws.

But the approach in pure thermodynamics is different. Here the fundamental laws are assumed as postulates based on experimental evidence, and conclusions are drawn from them without entering into the kinetic mechanism of the phenomena. This procedure has the advantage of being independent, to a great extent, of the simplifying assumptions that are often made in statistical mechanical considerations. Thus, thermodynamical results are generally highly accurate. On the other hand, it is sometimes rather unsatisfactory to obtain results without being able to see in detail how things really work, so that in many respects it is very often convenient to complete a thermodynamical result with at least a rough kinetic interpretation.

The first and second laws of thermodynamics have their statistical foundation in classical mechanics. In recent years Nernst has added a third law which can be interpreted statistically only in terms of quantum mechanical concepts. The last chapter of this book will concern itself with the consequences of the third law.

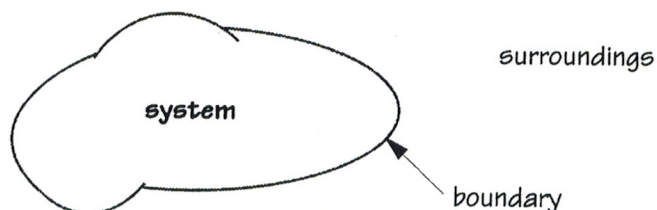
Why do we need an understanding of thermodynamics to study the atmosphere, ocean, and solid earth? Some of the reasons include:

- a) The forces that drive the motions of the atmosphere and ocean are created by differential heating of the Earth's surface and atmosphere by the sun. Because of the Earth's spherical shape and axial tilt, the tropics receive more energy than the poles. Furthermore, the heat capacities of water, land, and air are very different, as are the efficiencies at which they absorb solar radiation. Differential heating spanning a wide range of spatial scales creates thermodynamic imbalances, which in turn create winds and ocean currents as the atmosphere/ocean system attempts to return to thermodynamical equilibrium. Within the solid Earth, the mantle acts as a heat engine, producing mechanical power in the process of transferring heat from the hot interior to the cool surface, resulting in plate tectonics.
- b) Changes of phase of water in the atmosphere result in the formation of clouds and precipitation. Associated with the formation of clouds and precipitation are the release of latent heat and modifications to atmospheric radiative transfer. Freezing and melting of seawater in high latitudes influences profoundly the manner in which heat is exchanged between the atmosphere and ocean. Complex phase changes also occur in the "solid" Earth, owing to the high pressures and temperatures.
- c) Accounting for heat exchanges is essential in any predictive model of the in the atmosphere, ocean and solid earth, for any space or time scale that is considered.

Although other motivations can be provided, these motivations determine the focus of this course.

2.1 System, Boundary, Surroundings

In thermodynamics, we formally identify that part of the universe to which we intend to apply an analysis; we call that part the *system*. The system may be anything we choose, though in particular situations one choice may simplify an analysis more than other choices. The system may be a single homogeneous chunk of matter (one liter of water) or it may contain any number of diverse, discrete objects (all the equipment in Figure 1.1).



Beyond the system lies another part of the universe, which we call the *surroundings*. The surroundings contains all the ways by which we can observe and manipulate the system. That is, as engineers, we always stand in the surroundings and try to extract data from the system or impose changes on the system or both. The surroundings is necessarily larger than the system, but it is usually of finite size.

The system and the surroundings are separated by a *boundary*. The boundary may be real (the wall of a holding tank) or imaginary (a dotted line on a flow sheet); it may have finite mass or its mass may be negligible compared to that of the system. What is important is that different boundaries have different characteristics; that is, a boundary may limit the kinds of observations or manipulations that we can make on the system. Hence, it is always important to know the location of the boundary and what limitations it imposes.

2.4 Processes

We change the state of our system by applying a *process* using the available interactions. This is the standard thermodynamic problem: we have a system in an initial state, then we apply a process to move the system to a final state; see Figure 2.4. Often, we want to know the following about a pro-

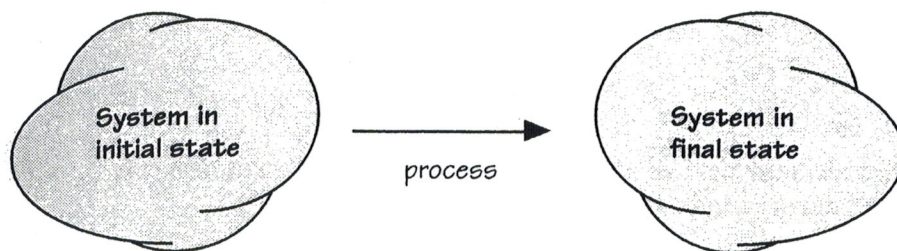


Figure 2.4 The standard thermodynamic problem: a process transforms the initial state of a system into a final state.

cess: What kinds of mass and energy transfers will be involved? What will be the costs of those transfers? What is the most efficient way to perform the process? Are other processes more efficient?

Just as a system has a set of properties for identifying its state, so too does a process have a set of quantities for monitoring its progress and characterizing its behavior. These quantities are called *process variables*; examples include the external pressure P_{ext} and the work. We emphasize that the jargon here is very precise: a property applies to the system and is a function of state. But a process variable is *not* a property nor a state function.

The nature of a system's boundary limits the kinds of processes that we can apply. For example, if the boundary is rigid, then there is no work mode for changing the system volume. Table 2.1 provides a list of common boundaries and the corresponding processes. Note that an isolated system has a boundary that is closed, rigid, and insulated.

Table 2.1

Examples of System Boundaries and the Corresponding Constraints on Interactions between the System and Its Surroundings.

Boundary	Process
open	any mass and energy transfer is possible
insulated	adiabatic (no thermal interaction)
rigid	isometric (no volume change)
closed	no bulk or diffusional mass transfer
isolated	no mass or energy interaction

A thermodynamic state variable is a quantity that specifies the thermodynamic state of a substance (*e.g.*, temperature). For a closed system, the mass and chemical composition define the system itself; the rest of the properties define its *state*. For a homogeneous system of constant composition, there are three variables that describe the state of the substance, only two of which are independent. These variables are the pressure p , the volume V , and the temperature T . If any two of the three thermodynamic variables are known, the value of the third will be fixed, because the variables are related in a definite way. Thus for a homogeneous system we have the following *equation of state* relating the three variables:

$$f(p,V,T) = 0$$

For an ideal gas, we have the familiar equation of state,

$$pV = nR^* T$$

where n is the number of moles and $R^* = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ is the universal gas constant.

Thermodynamic variables and the functions derived from these variables are called *extensive* if they depend on mass (*e.g.*, volume, internal energy), and *intensive* if they do not depend on mass and can be defined for every point of the system (*e.g.*, temperature, density). We shall, with some exceptions (such as temperature), use capital letters for extensive properties and lower case letters for intensive variables. Intensive variables are particularly advantageous in studying atmospheres and oceans since they make keeping track of the number of moles, mass, etc. unnecessary in these large thermodynamic systems.

Central to the description of a thermodynamic system is its chemical composition and physical state. In the remainder of this chapter the composition, structure, and state of the atmosphere and ocean are described.

2.1.2 Extensive and intensive properties

A quantitative property of a system describes some macroscopic feature that, although it may vary with time, has a particular value at any given instant of time. Most of the properties studied by thermodynamics may be classified as either extensive or intensive. We can distinguish these two types of properties by the following considerations.

If we imagine the system to be divided by an imaginary surface into two parts, any property of the system that is the sum of the property for the two parts is an **extensive property**. That is, an additive property is extensive. Examples are mass, volume, amount, energy, and the surface area of a solid.

Sometimes a more restricted definition of an extensive property is used: The property must be not only additive, but also proportional to the mass or the amount when intensive properties remain constant. According to this definition, mass, volume, amount, and energy are extensive, but surface area is not.

If we imagine a homogeneous region of space to be divided into two or more parts of arbitrary size, any property that has the same value in each part and the whole is an **intensive property**; for example density, concentration, pressure (in a fluid), and temperature. The value of an intensive property is the same everywhere in a homogeneous region but may vary from point to point in a heterogeneous region.

Since classical thermodynamics treats matter as a continuous medium, whereas matter actually contains discrete microscopic particles, the value of an intensive property at a point is a statistical average of the behavior of many particles. For instance, the density of a gas at one point in space is the average mass of a small volume element at that point, large enough to contain many molecules, divided by the volume of that element.

Some properties are defined as the ratio of two extensive quantities. If both extensive quantities refer to a homogeneous region of the system or to a small volume element, the ratio is an *intensive* property; for example, concentration = amount/volume. A mathematical derivative of one such extensive quantity with respect to another is also intensive. A special case is an extensive quantity divided by the mass, giving an intensive **specific quantity**; for example

$$\text{Specific volume} = \frac{\text{volume}}{\text{mass}}$$

Another special case that we encounter frequently in this book is an extensive quantity for a pure, homogeneous substance divided by the amount n ; the resulting intensive quantity is called, in general, a **molar quantity**. To symbolize a molar quantity, this book follows the recommendation of the IUPAC: The symbol of the extensive quantity is followed by subscript m , and optionally the identity of the substance is indicated either by a subscript or a formula in parentheses. Examples are

$$\text{Molar volume} = \frac{V}{n} = V_m \quad (2.1.1)$$

$$\text{Molar volume of substance } i = \frac{V}{n_i} = V_{m,i}$$