

thermodynamics

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preface

This book is intended as the first course in thermodynamics taken by students in all branches of engineering. It contains more material than can normally be covered in a one-semester course. I intended this in order to enable the instructor to vary his emphasis depending on the role of the course in the students' program and possible follow-on coursework in the thermal sciences.

The presentation is fairly well balanced among three general areas:

1. Macroscopic or classical thermodynamics
2. Microscopic or statistical thermodynamics
3. Engineering applications, including direct-energy-conversion schemes

An attempt has been made to show how macroscopic and microscopic thermodynamics complement each other in achieving an understanding of thermal behavior of substances. The degree to which various chapters and sections are linked together as well as the sequence of presentation is motivated by the desire to give the student an overall picture of the power and utility of thermodynamic analysis. The interests of the individual student will provide a natural motivation toward further study in particular phases of the subject. The student interested in solid-state electronics will find the sections on applications of statistical thermodynamics useful in later work, but, hopefully, he will recognize the importance of

classical thermodynamics in developing a proper foundation for the microscopic models of substances. The student interested in power cycles and energy conversion will find the application sections on these subjects to his liking, but, again hopefully, will see how an understanding of microscopic thermodynamics can be useful, particularly in direct-energy-conversion schemes and in the calculation of high-temperature gas properties.

To achieve this balanced presentation within a book of modest length, exposition in some areas has been necessarily compressed. The technique of "teaching by example" has been employed in several of the sections on energy analysis as well as in those portions of the book devoted to power cycles.

It is impossible for me to single out previous thermodynamics texts which have motivated and contributed to the writing of this book. All the books published in the last 25 years have contributed, in one way or another, to my understanding of the subject. I hope that a blanket note of acknowledgment to all these previous authors will be sufficient thanks. Many individuals have contributed to my thoughts on the subject of thermodynamics over the years. C. A. Besio was an early mentor, and the clarity of his lectures will never be forgotten. J. H. Boggs provided further stimulation, and many lively discussions with Erich Soehngen contributed to a physical understanding of the subject. Finally, the engaging questions of many students provided pedagogical motivation for the combined macroscopic-microscopic approach represented by this book, and the typing efforts of my wife Katherine and Mrs. Jacquelyn Newbury made the final manuscript possible.

j. p. holman

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chapter one
introduction

1-1 the nature of thermodynamics

Thermodynamics is the study of energy and its transformation. At first, this statement may seem rather aspiring, since it could easily be interpreted to mean that thermodynamics is the one science that is basic to all others. It is not difficult to imagine many different types of energy: the frictional work of a block sliding on a plane, electric energy, magnetic energy, nuclear energy, the energy stored in a spring, the energy stored in a battery, the energy of a quantum of light, and others. All of these types of energy can fall in the province of thermodynamics, although they are not always discussed in an elementary treatment of the subject. We shall take the approach of recognizing the applicability of thermodynamics to some rather unusual processes, but we shall not necessarily go into an extensive analysis.

Generally speaking, most studies of thermodynamics are primarily concerned with two forms of energy: heat and work. The principal objectives of the study are to develop basic principles describing these types of energy and to become conversant with the language surrounding these basic principles. As in all such studies the first step is to build a vocabulary of definitions and terms which may be used to conserve thought as the development becomes more complex. To
1 define rigorously the various concepts of thermodynamics requires considerable

space and effort, and will, of course, form a large part of the discussion in this book. In this introductory chapter we seek to give a brief qualitative picture of the broad subject of thermodynamics to achieve a perspective for detailed studies in subsequent chapters. In this respect it is well to note that many of the qualitative discussions are offered on the basis of physical reasonableness and should be accepted with the view that more rigorous definitions and developments will be presented later. The objective of this chapter is to achieve an overall picture of the scope of thermodynamics.

1-2 relation between classical mechanics and thermodynamics

The study of classical mechanics involves concepts of force, mass, distance, and time. A force has a physical meaning of a “push or pull” which may be represented mathematically as a vector with a point of application. Mechanics is developed through the application of Newton’s laws of motion and, particularly, the second law which states that the summation of forces acting on a particle is proportional to the time rate of change of momentum,

$$\Sigma F = \frac{d}{dt}(mv)$$

For purposes of analyzing mechanical systems a *free body* is used whereby a definite portion of a mechanism is broken away and all forces acting on this mechanism are specified for use with Newton’s second law. It is important to realize that the mechanical *system* is specified in terms of its coordinates of space and velocity. The behavior of the mechanical system is further described in terms of its interaction with its surroundings through the application of various forces. We say that the *state* of the system may be specified with its space and velocity coordinates and its *behavior*, i.e., its change from one state to another, is described in terms of its interactions with adjoining mechanisms or surroundings. It may be observed that the mechanical system will not change its state, i.e., its position in space and/or its velocity, unless it is acted upon by some net external force. The important point of this brief reference to classical mechanics is that the concept of a system (free body) and specification of the *state* of a system through the use of space or velocity coordinates are already familiar to those readers with experience in classical mechanics.

Although we are concerned with dynamical quantities in mechanics, the analysis of thermodynamic systems is concerned with energy quantities. A system is described in thermodynamics by breaking away a certain quantity of matter similar to the free-body technique in mechanics. The matter outside this system is termed the *surroundings* and the separation between the system and surroundings is called the *boundary* of the system. As an example of a thermodynamic system consider a mass of air contained under pressure in a steel tank. The

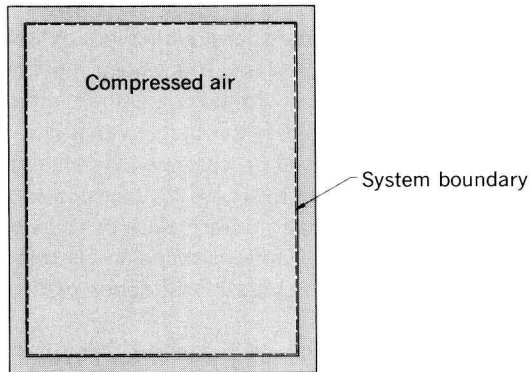


figure 1-1 compressed air in a tank as a thermodynamic system.

boundary of the system would be the inside surface of the tank and the surroundings would consist of the tank and the medium outside the tank. It is well to mention that the boundary of a system may be either a real or imaginary surface. The air-tank system is shown in Fig. 1-1.

In mechanics the state of a system is specified by its space and velocity coordinates. The state of a thermodynamic system is described by specifying its thermodynamic coordinates. We cannot describe all thermodynamic coordinates at this point but may note that temperature, pressure, chemical energy content, etc., are typical examples. These coordinates are usually denoted as *properties* of the system. In mechanics we noted that a system will not change its state unless there is some interaction with its surroundings to change its spatial position and/or velocity. This interaction usually takes the form of an energy transfer into or out of the system.

When a thermodynamic system changes from one state to another, it is said to execute a *process*.

In the study of thermodynamics we are interested in the changes which a system may undergo as it executes various processes. Clearly, we must be able to define the state of the system or its thermodynamic coordinates if we are to meet with success in describing processes which the system may undergo. For, if we are to describe the process, we must say what is happening each step of the way. The state of the system must be described at each point in the process. To do this, a very fundamental concept must be introduced—the concept of equilibrium.

A system is said to be in equilibrium when its pressure, temperature, and density are uniform (we shall employ a more rigorous definition of *equilibrium* later on). The system consisting of a mass of air in a tank would be in equilibrium if its pressure, temperature, and density were uniform throughout; however, if heat is applied to the tank such that the temperature at one end is higher than at

the other end, the system will not be in equilibrium. When a system is in equilibrium, its thermodynamic coordinates are related in a definite way. Notice the importance of the concept of equilibrium. The system must be in equilibrium if we are to define its thermodynamic coordinates and their interrelationships.

Obviously we are interested in the process that is a succession of equilibrium states, because in this type of process we can define the state of the system each step along the way. We call this type of process *reversible*. The meaning of this term will be demonstrated later; nevertheless this type of process is physically described as a succession of equilibrium states and is sometimes called a *quasistatic* process because it is composed of a series of nearly static equilibrium states.

The preceding paragraphs have linked the analysis methods of mechanics with those of thermodynamics; in particular, it has been implied that the free body and thermodynamic system represent similar analysis techniques. They are similar in that in both cases certain quantities of matter are broken away and a study is made of the interactions with the surroundings. There is one important difference, however. In the free body of mechanics we are always careful to study the forces which act on the free body. In thermodynamic system analysis we study the effect of the forces as they interact with the system and its surroundings and focus our attention on energy quantities. The two kinds of interaction energies, i.e., energies which leave or enter the system, are work and heat. We shall see that there are forms of energy "contained" within the system which must also be considered.

1-3 temperature and heat

The terms *temperature* and *heat* are normally used with the implication that the reader understands the meaning of these concepts. The contrary is more likely, however, because a precise understanding of heat and temperature is one of the objectives of the study of thermodynamics. Intuitively, the physical meaning of temperature is that it describes whether a body is "hot or cold." For example, we touch a block of metal at 120°F and conclude that it is hotter than a block of ice. The reason for this conclusion is that the hot block of metal gives up heat energy to the hand whereas the cold block of ice extracts energy. Notice that this intuitive concept of temperature is based upon an energy-transfer process which we might simply describe as *heat exchange*. It might therefore be possible to conclude that if two bodies at the same temperature are brought into contact no heat will be exchanged between the two. This serves to define *equality of temperature* but cannot establish an absolute scale of temperature which may only be accomplished with the second law of thermodynamics to be discussed in subsequent chapters. The concept of equality of temperature may be stated in the form:

*quasistatic
process*

*work and heat
interact*

temperature

zeroth law of
thermodynamics

Two bodies, each in thermal equilibrium with a third body, are in thermal equilibrium with each other. This statement is sometimes referred to as the *zeroth law of thermodynamics*.

It may be noted that for two bodies to be in complete equilibrium it is necessary to specify that more than the temperature of the two bodies must be equal, i.e., the pressure must also be equal and the two bodies must be so constituted that chemical change does not take place when they are brought into contact.

temperature
measurement

Insofar as everyday observations are concerned, we usually take as an indication of the temperature of a system the effect on some easily observable property of a measuring device. Thus a mercury-in-glass thermometer identifies temperature level with the relative expansion of the mercury and glass, an electrical resistance thermometer identifies temperature level with the electrical resistance of some particular metal (usually platinum), a thermocouple identifies temperature with the electromotive force generated at the junction of two dissimilar metals, and so on. In all these cases temperature, a thermodynamic property (or thermodynamic coordinate), is expressed in terms of other properties of either a liquid or metallic substance.

heat and
temperature
related

In accordance with this brief discussion we may tentatively conclude that heat is a form of energy which flows from one body to another as a result of a temperature difference. Note the almost circular definitions: equality of temperature is related to a condition of zero heat flow—heat is related to temperature difference. We shall clarify this matter later on.

1-4 temperature scales

The two temperature scales normally employed for measurement purposes are the Fahrenheit and Celsius scales. These scales are based on a specification of the number of increments between the freezing point and boiling point of water at standard atmospheric pressure. The Celsius scale has 100 units between these points, whereas the Fahrenheit scale has 180 units. The zero points on the scales are arbitrary.

absolute
thermodynamic
temperature

It will be shown that the second law of thermodynamics serves to define an absolute *thermodynamic* temperature scale having only positive values. The absolute Celsius scale is called the *Kelvin scale*, and the absolute Fahrenheit scale is termed the *Rankine scale*. The zero points on both *absolute* scales represent the same physical state, and the ratio of two values is the same regardless of the scale used, i.e.,

$$\left(\frac{T_2}{T_1}\right)_{\text{Rankine}} = \left(\frac{T_2}{T_1}\right)_{\text{Kelvin}} \quad (1-1)$$

The boiling point of water is arbitrarily taken as 100° on the Celsius scale and