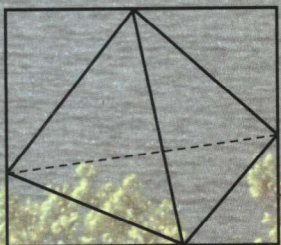


David V. Ragone

# THERMODYNAMICS OF MATERIALS

Volume I

 **WILEY**



THE MIT SERIES  
IN MATERIALS SCIENCE  
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# Thermodynamics of Materials

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## Volume I

**David V. Ragone**

*Massachusetts Institute of Technology*



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# Preface—Vol. I

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Thermodynamics, the study of energy and its transformations, is applicable to all fields of science and engineering. The text for a basic course in thermodynamics need not be directed at students with focused professional aims. But general treatments of thermodynamics tend to be too abstract for engineering and science students who have already committed to a particular area of study. This is especially true of students in materials science and engineering who are interested in how thermodynamics applies to the different classes of materials that are studied as part of a modern curriculum in materials science and engineering.

This volume is a textbook for the first part of a two-course sequence at the undergraduate level on the physical chemistry of materials. The subject matter of the first course, and part of the second, is thermodynamics. The second course, the subject of Volume II, covers the thermodynamics of defects and surfaces, the statistical thermodynamics of molecular motion, and some aspects of solid-state kinetics, such as diffusion, nucleation, reaction kinetics, and nonequilibrium thermodynamics. Together these two courses provide background for a series of other courses that follow, including those devoted to general principles such as physics of materials, and structure of materials, and those devoted to specific classes of materials such as electronic materials, ceramics, polymers, and metals.

In addition to a presentation based on macroscopic thermodynamics, this book includes an introduction to microscopic thermodynamics, or statistical thermodynamics. Macroscopic thermodynamics is an empirical science based on the macroscopic properties of matter, and does not rely on any hypotheses concerning the structure of matter. It predicts many of the relationships among these macroscopic properties, but does not attempt to predict their absolute values. Statistical thermodynamics aims to provide an understanding of the macroscopic thermodynamic properties of materials, and to predict absolute values based on atomic and molecular

structure and motion. It also provides background for the understanding of differences among various classes of materials. The chapter on statistical thermodynamics, for example, deals with the differences in thermodynamic properties of metallic and polymer solutions.

A few words on the sequence of study are in order. The chapter on statistical thermodynamics is placed last, as Chapter 10. It need not be covered last. In fact, the basic sections of Chapter 10 can usefully be studied immediately following Chapter 3, the study of property relations. The same flexibility is true of Chapter 8 on the phase rule. It can, if desired, be presented as part of the background to Chapter 5, the study of chemical reactions. It also fits quite well where it is, as an introduction to phase diagrams, Chapter 9.

The text assumes that students using it will have completed a college-level course in chemistry and a year-long course in physics in addition to a year of calculus.

Those who work in the field of materials, broadly defined, must be multilingual with respect to science and engineering. By this I mean that they must be able to understand and apply the knowledge generated by physicists, chemists, and other scientists, and they must also be able to communicate with, and serve the needs of, engineers from diverse fields. This book intends to provide background for both.

This broad charter influences the text in several ways. The first and second laws of thermodynamics, for example, are presented using an analysis of open systems, as engineers do. Open systems are those in which material may enter, leave, or do both. By the elimination of the flow terms, of course, open system analyses can easily be reduced to closed systems analyses, which are used primarily by scientists. Another influence of the broad charter will be seen in the units used in the statement of problems at the end of each chapter. The text uses the International System of Units (SI), the modern metric system, using joules as a measure of energy, for example. However, the data given in problem statements will use whatever units were attached to the data when they were found in the literature. This approach was adopted as a way of familiarizing students with the variety of units they will encounter in the literature and in the practice of their professions.

I acknowledge, with thanks, the efforts of my colleague, Prof. Gerbrand Ceder, who taught from a draft of this book for three years, and to the student assistants who carefully reviewed the drafts to search out and correct the seemingly endless errors: John Zaroulis, Patrick Tepesch, Gerardo Garbulski, Adrian Kohan, Julie Ngau, and Andrew Kim. Thanks are also due for the helpful and thoughtful suggestions of the reviewers of the manuscript, Profs. John Angus, Robert Auerback, William Bitler, Charles Brooks, Richard Heckel, and George St. Pierre. And finally, I give a special expression of thanks to my wife, Kit, for her patience and constant encouragement during the preparation of this text.

*David V. Ragone*  
*Cambridge, Massachusetts*  
*March 1994*

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# Chapter 1

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## The First Law

The science of thermodynamics is concerned with heat and work, and transformations between the two. It is based on two laws of nature, the first and second laws of thermodynamics. By logical reasoning and skillful manipulation of these laws, it is possible to correlate many of the properties of materials and to gain insight into the many chemical and physical changes that materials undergo.

The first law of thermodynamics is simply the principle of conservation of energy; that is, energy can be neither created nor destroyed. To derive the practical benefits of knowing this principle, we must construct an accounting system for energy, sometimes called an energy balance. This system must handle flows of energy, such as heat and work, as well as the various forms of energy that matter possesses. To operate this accounting system, we will need to understand a series of basic notions and definitions.

### 1.1 SYSTEM AND SURROUNDINGS

As the word is used in thermodynamics, a *system* is any portion of space or matter set aside for study. A system can be open or closed. An open system is one in which matter is allowed to enter, leave the system, or do both. In a closed system no matter enters or leaves.

Whether a system is open or closed does not depend on any particular physical configuration of the apparatus being studied. It depends on how the system chosen for study is defined. Consider, for example, a fluid flowing through a pipe. A specific portion of the pipe may be considered to be the system. In this case we have defined an open system. Fluid enters and leaves the system. Alternatively, one can define the system as a particular piece of fluid traveling through the pipe. In this case, we have defined a closed system. Although the system moves, matter neither enters nor leaves the system as we have defined it. Note that if the fluid is a compressible fluid, such as a gas, its boundaries, in addition to moving through space, may expand or contract. Its physical volume may change. However, as long as no matter enters or leaves the system as defined, it is a closed system.

Having thus defined a *system*, we say that *the surroundings* is everything else: that is, the universe outside the system.

## 1.2 ENERGY TRANSFER

For the purposes of thermodynamics, energy transferred between system and surroundings is divided into two categories, heat and work. The reason for this division may seem arbitrary at this point. The importance of the distinction will become apparent when we discuss the second law of thermodynamics, which deals with restrictions on the conversion of heat into work.

Heat ( $Q$ ) is energy transferred between the system and surroundings *because of a temperature difference*. Take, for example, a cold piece of iron placed in a high temperature furnace. Energy flows into the iron to heat it. If one defines the iron as the system, then the energy that flows into the system is called heat. The algebraic sign of the heat term is positive when heat flows from the surroundings into the system. The increase in temperature of the iron (the system) is caused by an increase in the *thermal energy* of the system. The system, by our definition, may not possess heat. Heat is a flow quantity. *Heat is energy in transit*.

Work ( $W$ ) is defined as all other forms of energy transferred between the system and its surroundings. Thermodynamic work can take many forms (mechanical, electrical, magnetic, etc.). To examine one form of mechanical work, consider the compression of a gas in a cylinder of an automobile engine. If we consider the gas to be the system, then work is done on the system by the face of the piston. The magnitude of the work done is the force  $F$ , multiplied by the distance  $\Delta l$  through which the piston moved (Figure 1.1).

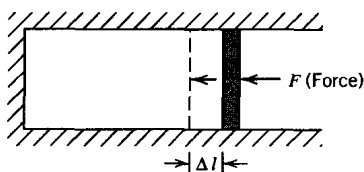
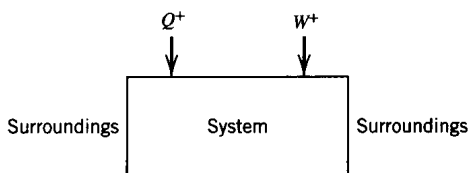


Figure 1.1 Mechanical work.



**Figure 1.2** The sign convention for heat and work.

If the cross-sectional area of the piston is taken as  $A$ , this work term can be converted into:

$$W = F \Delta l = \frac{F}{A} A \Delta l = P \Delta V \quad (1.1)$$

The work done is, thus, the resisting pressure  $P$  multiplied by  $\Delta V$ , the change in volume of the system. The work term is expressed in Joules (J) when the pressure is expressed in newtons per square meter [ $\text{N/m}^2$ , or pascals (Pa)], and the volume change is expressed in cubic meters.

The direction of force and the distance moved establishes the algebraic sign of the work term (Figure 1.2). The magnitude of the work term is considered *positive* when work is done *on* a system by the surroundings. Work is *negative* when the system does work *on* the surroundings.<sup>1</sup> The sign convention is the same for both heat and work; that is, these terms are considered to be positive when they add energy to the system.

In thermodynamics, a distinction is made between reversible and irreversible processes. In general, a process is called reversible if the initial state of the system can be restored with no observable effects in the system or the surroundings. As an example of irreversible work, consider a gas expanding into a vacuum chamber. If the gas is taken as the system (imagine it to be enclosed in a very flexible balloon), then the resisting force (and pressure) is zero. To restore the system and surroundings to their original conditions, the gas must be compressed by a steadily increasing force. Work will be done on the system. This will result in an energy increase in the system. Clearly there will be an observable effect on the system and on the surroundings; therefore the process is irreversible. If, however, the forces at the boundary of the system are balanced such that the resisting force at the boundary differs from the force inside the system by only an infinitesimal amount, the work is reversible. The direction of the movement of the boundary could be reversed by just an infinitesimal change in the forces. In the case of  $P$ - $V$  work, if the pressure resisting an expansion differs only infinitesimally from the pressure of the gas in the system, the work is considered to be reversible. If there is a finite pressure difference between the system and the surroundings in which the movement is taking place, the work is irreversible.

<sup>1</sup>According to the opposite sign convention for work, used in some texts on thermodynamics, work done *on* the system is considered negative. The effect of this on the statement of the energy balance is discussed later as footnote 4.

## 4 Chapter 1/The First Law

The examples of reversible and irreversible processes just cited refer to mechanical work. The same basic idea applies to other forms of work as well. If a battery whose open circuit voltage is 1.5 V is charged using a source of electrical energy at 2.0 V, we say that the process is irreversible. When the battery tries to return to its original uncharged state, it will discharge the electrical energy at 1.5 V or less. As we will see later, the irreversible work done during the charging process will end up as heat, which must be dissipated from the battery.

### 1.3 ENERGY OF A SYSTEM

For our purposes, the energy of a system can be divided into three categories: internal energy, potential energy, and kinetic energy. To take them in reverse order, kinetic energy refers to the energy possessed by the system because of its *overall* motion, either translational or rotational. The word “overall” is italicized because the kinetic energy to which we refer is the kinetic energy of the entire system, not the kinetic energy of the molecules in the system. If the system is a gas, the kinetic energy is the energy due to the macroscopic flow of the gas, not the motion of individual molecules. A familiar form of kinetic energy is the translational energy  $\frac{1}{2}mv^2$  possessed by a body of mass  $m$  moving at a velocity  $v$ .

The potential energy of a system is the sum of the gravitational, centrifugal, electrical, and magnetic potential energies. To illustrate using gravitational potential energy, a one-kilogram mass, 10 m above the ground, clearly has a greater potential energy than the same kilogram mass on the ground. That potential energy can be converted into other forms of energy, such as kinetic energy, if the mass is allowed to fall freely. Kinetic and potential energy depend on the environment in which the system exists. In particular, the potential energy of a system depends on the choice of a zero level. In our example, if the ground level is considered to be at zero potential energy, then the potential energy of the mass at 10 m above the ground will have a positive potential energy equal to the mass (1 kg) multiplied by the gravitational constant ( $g = 9.807 \text{ m/s}^2$ ) and the height above the ground (10 m). Its potential energy will be  $98.07 \text{ (kg}\cdot\text{m}^2\text{)/s}^2$ , or  $98.07 \text{ newton-meters (N}\cdot\text{m)}$ , that is,  $98.07 \text{ J}$ . The datum plane for potential energy can be chosen arbitrarily. If it had been chosen at 10 m above the ground level, the potential energy of the mass would have been zero. Of course, the *difference* in potential energy between the mass at 10 m and the mass at ground level is the same independent of the datum plane.

The internal energy of a system depends on the inherent qualities, or properties, of the materials in the system, such as composition and physical form, as well as the environmental variables (temperature, pressure, electric field, magnetic field, etc.). Internal energy can have many forms, including mechanical, chemical, electrical, magnetic, surface, and thermal.<sup>2</sup> To consider some examples, a spring that is

---

<sup>2</sup>In addition to the forms of internal energy already mentioned, the mass of the system itself can be considered a form of energy according to Einstein's relationship,  $E = mc^2$ , where  $c$  is the speed of light. Such a term must be introduced when the mass of a system changes, as in nuclear reactor fuel.

compressed has a higher internal energy (mechanical energy) than a spring that is not compressed, because the compressed spring can do some work on changing (expanding) to the uncompressed state. As an example of chemical energy, consider two identical vessels, each containing hydrogen and oxygen. In the first, the gases are contained in the elemental form, pure hydrogen and pure oxygen in a ratio of 2:1. In the second, the identical number of atoms is contained, but in the form of water. One can appreciate that the internal energy of the first is different from the second. A spark set off in the first container will result in a violent release of energy. The same will not be true in the second. Clearly, the internal energy present differs in these two situations. Any energy balance will have to take this difference into account.

On the question of thermal energy, it is intuitive that the internal energy of a system increases as its temperature is increased. We know that we have to add energy to a bar of iron to raise its temperature. The form of internal energy of a material that is related to its temperature is called *thermal energy*. To be precise, we should not call it heat. Heat is the energy *in transfer* between a system and the surroundings. Thermal energy is *possessed* by the system.

## 1.4 ENERGY AS A STATE FUNCTION

The entire structure of the science of thermodynamics is built on the concept of equilibrium states and the postulate that the change in the value of thermodynamic quantities, such as internal energy, between two equilibrium states of a system does not depend on the thermodynamic path the system took to get between the two states. The change is defined by the final and beginning equilibrium states of that system.<sup>3</sup>

This means that the internal energy *change* of a system is determined by a knowledge of all the parameters that specify the system in its final state and in its initial state. The parameters are pressure, temperature, magnetic field, surface area, mass, and so on. If a system changes from a state labeled 1 to a state labeled 2, the change in internal energy ( $\Delta U$ ) will be  $U_2 - U_1$ , the internal energy in the final state less the internal energy in the initial state. The difference does not depend on how the system got from state 1 to state 2. The internal energy thus is referred to as a state function, or a point function, that is, a function of the *state* of the system only, and not its history.

$$\Delta U = U_2 - U_1 \quad (1.2)$$

## 1.5 WORK

In contrast to internal energy, the work done on or by the system as it progresses from state 1 to state 2 is a function of the path taken.

---

<sup>3</sup>At this point in our study of thermodynamics, it is sufficient to state that a system is in equilibrium if its temperature, pressure, density, and other physical properties are uniform throughout. For a more general definition of equilibrium, see Chapters 4 and 5.



## 6 Chapter 1/The First Law

To illustrate, let us define a system consisting of a gas that will proceed from state 1 to state 2 as indicated in Figure 1.3a. The pressure on the system is plotted on the vertical axis, the volume of the system on the horizontal axis. The work done by the system, which is the resisting pressure multiplied by the change in volume, is negative because the system does work on the surroundings. For the purposes of this example, let us assume that the process took place reversibly. The pressure inside the gas is equal to the resisting pressure (i.e., differs from the resisting pressure by only an infinitesimal amount). Path 1 proceeds by an isobaric (constant pressure) expansion from point 1 to intermediate point A, followed by an isochoric (constant volume) increase in pressure from A to point 2. No work was done during the second part of the process because there was no motion. The total work done is:

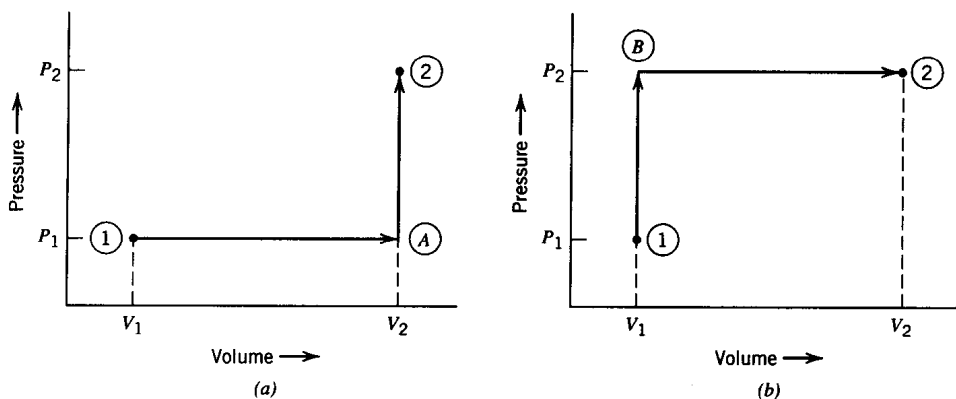
$$W = -P_1(V_2 - V_1) \quad (1.3)$$

The system could, of course, have proceeded from point 1 to point 2 by a variety of paths. Path 2, shown in Figure 1.3b, is one such path. The system moves from point 1 to B on an isochoric path (no work done), and then from B to 2 on an isobaric path. The work done by the system in this process (1 to B to 2) is:

$$W = -P_2(V_2 - V_1) \quad (1.4)$$

By comparing Eqs. 1.3 and 1.4, one can see that the work done via the two different paths is indeed different. The work done on path 1-B-2 is larger than 1-A-2 because  $P_2$  is greater than  $P_1$ .

The different pressure-volume paths of the gas in the system just described were controlled by changing the temperature of the gas (i.e., by adding or subtracting heat). Note that the system could be operated in a cyclical fashion, that is, by pro-



**Figure 1.3** Work is a function of path: less work is done in (a) than in (b).