Some Concepts and Definitions

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One excellent definition of thermodynamics is that it is the science of energy and entropy. Since we have not yet defined these terms, an alternate definition in already familiar terms is: Thermodynamics is the science that deals with heat and work and those properties of substances that bear a relation to heat and work. As with all sciences, the basis of thermodynamics is experimental observation. In thermodynamics these findings have been formalized into certain basic laws, which are known as the *first*, *second*, and *third laws of thermodynamics*. In addition to these laws, the *zeroth law of thermodynamics*, which in the logical development of thermodynamics precedes the first law, has been set forth.

In the chapters that follow, we will present these laws and the thermodynamic properties related to these laws and apply them to a number of representative examples. The objective of the student should be to gain both a thorough understanding of the fundamentals and an ability to apply them to thermodynamic problems. The examples and problems further this twofold objective. It is not necessary for the student to memorize numerous equations, for problems are best solved by the application of the definitions and laws of thermodynamics. In this chapter, some concepts and definitions basic to thermodynamics are presented.

2.1 A THERMODYNAMIC SYSTEM AND THE CONTROL VOLUME

A thermodynamic system is a device or combination of devices containing a quantity of matter that is being studied. To define this more precisely, a control volume is chosen so that it contains the matter and devices inside a control surface. Everything external to the control volume is the surroundings, with the separation provided by the control surface. The surface may be open or closed to mass flows, and it may have flows of energy in terms of heat transfer and work across it. The boundaries may be movable or stationary. In the case of a control surface that is closed to mass flow, so that no mass can escape or enter the control volume, it is called a control mass containing the same amount of matter at all times.

Selecting the gas in the cylinder of Fig. 2.1 as a control volume by placing a control surface around it, we recognize this as a control mass. If a Bunsen burner is placed under the cylinder, the temperature of the gas will increase and the piston will rise. As the piston rises, the boundary of the control mass moves. As we will see later, heat and work cross the boundary of the control mass during this process, but the matter that composes the control mass can always be identified and remains the same.

An isolated system is one that is not influenced in any way by the surroundings. This means that no mass, heat, or work cross the boundary of the system. In many cases, a
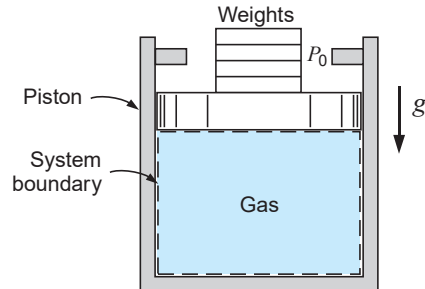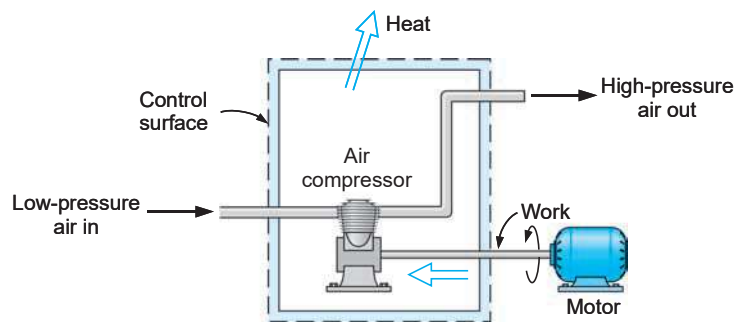
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FIGURE 2.1 Example of a control mass.

FIGURE 2.2 Example of a control volume.

thermodynamic analysis must be made of a device, such as an air compressor, which has a flow of mass into it, out of it, or both, as shown schematically in Fig. 2.2. The procedure followed in such an analysis is to specify a control volume that surrounds the device under consideration. The surface of this control volume is the control surface, which may be crossed by mass momentum, as well as heat and work.

Thus the more general control surface defines a control volume, where mass may flow in or out, with a control mass as the special case of no mass flow in or out. Hence the control mass contains a fixed mass at all times, which explains its name. The difference in the formulation of the analysis is considered in detail in Chapter 6. The terms closed system (fixed mass) and open system (involving a flow of mass) are sometimes used to make this distinction. Here, we use the term system as a more general and loose description for a mass, device, or combination of devices that then is more precisely defined when a control volume is selected. The procedure that will be followed in presenting the first and second laws of thermodynamics is first to present these laws for a control mass and then to extend the analysis to the more general control volume.

2.2 MACROSCOPIC VERSUS MICROSCOPIC POINTS OF VIEW

The behavior of a system may be investigated from either a microscopic or macroscopic point of view. Let us briefly describe a system from a microscopic point of view. Consider a system consisting of a cube 25 mm on a side and containing a monatomic gas at atmospheric pressure and temperature. This volume contains approximately 10^{20} atoms. To describe the position of each atom, we need to specify three coordinates; to describe the velocity of each atom, we specify three velocity components.

Thus, to describe completely the behavior of this system from a microscopic point of view, we must deal with at least 6×10^{20} equations. Even with a large digital computer, this is a hopeless computational task. However, there are two approaches to this problem that reduce the number of equations and variables to a few that can be computed relatively easily. One is the statistical approach, in which, on the basis of statistical considerations and probability theory, we deal with average values for all particles under consideration. This is usually done in connection with a model of the atom under consideration. This is the approach used in the disciplines of kinetic theory and statistical mechanics.

The other approach to reducing the number of variables to a few that can be handled is the macroscopic point of view of classical thermodynamics. As the word *macroscopic* implies, we are concerned with the gross or average effects of many molecules. These effects can be perceived by our senses and measured by instruments. However, what we really perceive and measure is the time-averaged influence of many molecules. For example, consider the pressure a gas exerts on the walls of its container. This pressure results from the change in momentum of the molecules as they collide with the wall. From a macroscopic point of view, however, we are concerned not with the action of the individual molecules but with the time-averaged force on a given area, which can be measured by a pressure gauge. In fact, these macroscopic observations are completely independent of our assumptions regarding the nature of matter.

Although the theory and development in this book are presented from a macroscopic point of view, a few supplementary remarks regarding the significance of the microscopic perspective are included as an aid to understanding the physical processes involved. Another book in this series, *Introduction to Thermodynamics: Classical and Statistical*, by R. E. Sonntag and G. J. Van Wylen, includes thermodynamics from the microscopic and statistical point of view.

A few remarks should be made regarding the continuum. From the macroscopic point of view, we are always concerned with volumes that are very large compared to molecular dimensions and, therefore, with systems that contain many molecules. Because we are not concerned with the behavior of individual molecules, we can treat the substance as being continuous, disregarding the action of individual molecules. This continuum concept, of course, is only a convenient assumption that loses validity when the mean free path of the molecules approaches the order of magnitude of the dimensions of the vessel, as, for example, in high-vacuum technology. In much engineering work the assumption of a continuum is valid and convenient, going hand in hand with the macroscopic point of view.

2.3 PROPERTIES AND STATE OF A SUBSTANCE

If we consider a given mass of water, we recognize that this water can exist in various forms. If it is a liquid initially, it may become a vapor when it is heated or a solid when it is cooled. Thus, we speak of the different phases of a substance. A phase is defined as a quantity of matter that is homogeneous throughout. When more than one phase is present, the phases are separated from each other by the phase boundaries. In each phase the substance may exist at various pressures and temperatures or, to use the thermodynamic term, in various states. The state may be identified or described by certain observable, macroscopic properties; some familiar ones are temperature, pressure, and density. In later chapters, other properties will be introduced. Each of the properties of a substance in a given state has only one definite value, and these properties always have the same value for a given state, regardless of how the

substance arrived at the state. In fact, a property can be defined as any quantity that depends on the state of the system and is independent of the path (that is, the prior history) by which the system arrived at the given state. Conversely, the state is specified or described by the properties. Later we will consider the number of independent properties a substance can have, that is, the minimum number of properties that must be specified to fix the state of the substance.

Thermodynamic properties can be divided into two general classes: intensive and extensive. An intensive property is independent of the mass; the value of an extensive property varies directly with the mass. Thus, if a quantity of matter in a given state is divided into two equal parts, each part will have the same value of intensive properties as the original and half the value of the extensive properties. Pressure, temperature, and density are examples of intensive properties. Mass and total volume are examples of extensive properties. Extensive properties per unit mass, such as specific volume, are intensive properties.

Frequently we will refer not only to the properties of a substance but also to the properties of a system. When we do so, we necessarily imply that the value of the property has significance for the entire system, and this implies equilibrium. For example, if the gas that composes the system (control mass) in Fig. 2.1 is in thermal equilibrium, the temperature will be the same throughout the entire system, and we may speak of the temperature as a property of the system. We may also consider mechanical equilibrium, which is related to pressure. If a system is in mechanical equilibrium, there is no tendency for the pressure at any point to change with time as long as the system is isolated from the surroundings. There will be variation in pressure with elevation because of the influence of gravitational forces, although under equilibrium conditions there will be no tendency for the pressure at any location to change. However, in many thermodynamic problems, this variation in pressure with elevation is so small that it can be neglected. Chemical equilibrium is also important and will be considered in Chapter 16. When a system is in equilibrium regarding all possible changes of state, we say that the system is in thermodynamic equilibrium.

2.4 | PROCESSES AND CYCLES

Whenever one or more of the properties of a system change, we say that a change in state has occurred. For example, when one of the weights on the piston in Fig. 2.3 is removed, the piston rises and a change in state occurs, for the pressure decreases and the specific volume increases. The path of the succession of states through which the system passes is called the process.

Let us consider the equilibrium of a system as it undergoes a change in state. The moment the weight is removed from the piston in Fig. 2.3, mechanical equilibrium does not exist; as a result, the piston is moved upward until mechanical equilibrium is restored.
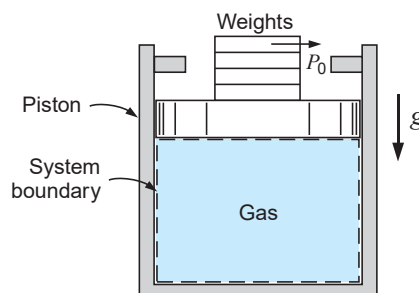

FIGURE 2.3 Example of a system that may undergo a quasi-equilibrium process.

The question is this: Since the properties describe the state of a system only when it is in equilibrium, how can we describe the states of a system during a process if the actual process occurs only when equilibrium does not exist? One step in finding the answer to this question concerns the definition of an ideal process, which we call a *quasi-equilibrium* process. A quasi-equilibrium process is one in which the deviation from thermodynamic equilibrium is infinitesimal, and all the states the system passes through during a quasi-equilibrium process may be considered equilibrium states. Many actual processes closely approach a quasi-equilibrium process and may be so treated with essentially no error. If the weights on the piston in Fig. 2.3 are small and are taken off one by one, the process could be considered quasi-equilibrium. However, if all the weights are removed at once, the piston will rise rapidly until it hits the stops. This would be a nonequilibrium process, and the system would not be in equilibrium at any time during this change of state.

For nonequilibrium processes, we are limited to a description of the system before the process occurs and after the process is completed and equilibrium is restored. We are unable to specify each state through which the system passes or the rate at which the process occurs. However, as we will see later, we are able to describe certain overall effects that occur during the process.

Several processes are described by the fact that one property remains constant. The prefix *iso-* is used to describe such a process. An isothermal process is a constant-temperature process, an isobaric (sometimes called *isopiestic*) process is a constant-pressure process, and an isochoric process is a constant-volume process.

When a system in a given initial state goes through a number of different changes of state or processes and finally returns to its initial state, the system has undergone a cycle. Therefore, at the conclusion of a cycle, all the properties have the same value they had at the beginning. Steam (water) that circulates through a steam power plant undergoes a cycle.

A distinction should be made between a thermodynamic cycle, which has just been described, and a mechanical cycle. A four-stroke-cycle internal-combustion engine goes through a mechanical cycle once every two revolutions. However, the working fluid does not go through a thermodynamic cycle in the engine, since air and fuel are burned and changed to products of combustion that are exhausted to the atmosphere. In this book, the term *cycle* will refer to a thermodynamic cycle unless otherwise designated.

2.5 | UNITS FOR MASS, LENGTH, TIME, AND FORCE

Since we are considering thermodynamic properties from a macroscopic perspective, we are dealing with quantities that can, either directly or indirectly, be measured and counted. Therefore, the matter of units becomes an important consideration. In the remaining sections of this chapter we will define certain thermodynamic properties and the basic units. Because the relation between force and mass is often difficult for students to understand, it is considered in this section in some detail.

Force, mass, length, and time are related by Newton's second law of motion, which states that the force acting on a body is proportional to the product of the mass and the acceleration in the direction of the force:

$$F \propto ma$$

The concept of time is well established. The basic unit of time is the second (s), which in the past was defined in terms of the solar day, the time interval for one complete revolution of the earth relative to the sun. Since this period varies with the season of the year, an

TABLE 2.1
Unit Prefixes

Factor	Prefix	Symbol	Factor	Prefix	Symbol
10^{12}	tera	T	10^{-3}	milli	m
10^{9}	giga	G	10^{-6}	micro	μ
10^{6}	mega	M	10^{-9}	nano	n
10^{3}	kilo	k	10^{-12}	pico	p

average value over a 1-year period is called the *mean solar day*, and the mean solar second is 1/86 400 of the mean solar day. (The earth's rotation is sometimes measured relative to a fixed star, in which case the period is called a *sidereal day*.) In 1967, the General Conference of Weights and Measures (CGPM) adopted a definition of the second as the time required for a beam of cesium-133 atoms to resonate 9 192 631 770 cycles in a cesium resonator.

For periods of time less than 1 s, the prefixes *milli*, *micro*, *nano*, or *pico*, as listed in Table 2.1, are commonly used. For longer periods of time, the units minute (min), hour (h), or day (day) are frequently used. It should be pointed out that the prefixes in Table 2.1 are used with many other units as well.

The concept of length is also well established. The basic unit of length is the meter (m). For many years the accepted standard was the International Prototype Meter, the distance between two marks on a platinum–iridium bar under certain prescribed conditions. This bar is maintained at the International Bureau of Weights and Measures in Sevres, France. In 1960, the CGPM adopted a definition of the meter as a length equal to 1 650 763.73 wavelengths in a vacuum of the orange-red line of krypton-86. Then in 1983, the CGPM adopted a more precise definition of the meter in terms of the speed of light (which is now a fixed constant): The meter is the length of the path traveled by light in a vacuum during a time interval of 1/299 792 458 of a second.

The fundamental unit of mass is the kilogram (kg). As adopted by the first CGPM in 1889 and restated in 1901, it is the mass of a certain platinum–iridium cylinder maintained under prescribed conditions at the International Bureau of Weights and Measures. A related unit that is used frequently in thermodynamics is the mole (mol), defined as an amount of substance containing as many elementary entities as there are atoms in 0.012 kg of carbon-12. These elementary entities must be specified; they may be atoms, molecules, electrons, ions, or other particles or specific groups. For example, one mole of diatomic oxygen, having a molecular mass of 32 (compared to 12 for carbon), has a mass of 0.032 kg. The mole is often termed a *gram mole*, since it is an amount of substance in grams numerically equal to the molecular mass. In this book, when using the metric SI system, we will find it preferable to use the kilomole (kmol), the amount of substance in kilograms numerically equal to the molecular mass, rather than the mole.

The system of units in use presently throughout most of the world is the metric International System, commonly referred to as *SI units* (from Le Système International d'Unités). In this system, the second, meter, and kilogram are the basic units for time, length, and mass, respectively, as just defined, and the unit of force is defined directly from Newton's second law.

Therefore, a proportionality constant is unnecessary, and we may write that law as an equality:

$$F = ma \hspace{4cm} (2.1)$$

The unit of force is the newton (N), which by definition is the force required to accelerate a mass of one kilogram at the rate of one meter per second per second:

$$1\,\text{N} = 1\,\text{kg m/s}^2$$

It is worth noting that SI units derived from proper nouns use capital letters for symbols; others use lowercase letters. The liter, with the symbol L, is an exception.

The traditional system of units used in the United States is the English Engineering System. In this system the unit of time is the second, which was discussed earlier. The basic unit of length is the foot (ft), which at present is defined in terms of the meter as

$$1\,\text{ft} = 0.3048\,\text{m}$$

The inch (in.) is defined in terms of the foot:

$$12\,\text{in.} = 1\,\text{ft}$$

The unit of mass in this system is the pound mass (lbm). It was originally defined as the mass of a certain platinum cylinder kept in the Tower of London, but now it is defined in terms of the kilogram as

$$1\,\text{lbm} = 0.453\,592\,37\,\text{kg}$$

A related unit is the pound mole (lb mol), which is an amount of substance in pounds mass numerically equal to the molecular mass of that substance. It is important to distinguish between a pound mole and a mole (gram mole).

In the English Engineering System of Units, the unit of force is the pound force (lbf), defined as the force with which the standard pound mass is attracted to the earth under conditions of standard acceleration of gravity, which is that at $45°$ latitude and sea level elevation, $9.806\,65\,\text{m/s}^2$ or $32.1740\,\text{ft/s}^2$. Thus, it follows from Newton's second law that

$$1\,\text{lbf} = 32.174\,\text{lbm ft/s}^2$$

which is a necessary factor for the purpose of units conversion and consistency. Note that we must be careful to distinguish between a lbm and a lbf, and we do not use the term *pound* alone.

The term *weight* is often used with respect to a body and is sometimes confused with mass. Weight is really correctly used only as a force. When we say that a body weighs so much, we mean that this is the force with which it is attracted to the earth (or some other body), that is, the product of its mass and the local gravitational acceleration. The mass of a substance remains constant with elevation, but its weight varies with elevation.

EXAMPLE 2.1   What is the weight of a 1 kg mass at an altitude where the local acceleration of gravity is $9.75\,\text{m/s}^2$?

Solution

Weight is the force acting on the mass, which from Newton's second law is

$$F = mg = 1\,\text{kg} \times 9.75\,\text{m/s}^2 \times [1\,\text{N s}^2/\text{kg m}] = 9.75\,\text{N}$$

EXAMPLE 2.1E What is the weight of a 1 lbm mass at an altitude where the local acceleration of gravity is 32.0 ft/s²?

Solution

Weight is the force acting on the mass, which from Newton's second law is

$$F = mg = 1 \text{ lbm} \times 32.0 \text{ ft/s}^2 \times [\text{lbf s}^2/32.174 \text{ lbm ft}] = 0.9946 \text{ lbf}$$

2.6 ENERGY

One very important concept in a study of thermodynamics is energy. Energy is a fundamental concept, such as mass or force, and, as is often the case with such concepts, it is very difficult to define. Energy has been defined as the capability to produce an effect. Fortunately the word energy and the basic concept that this word represents are familiar to us in everyday usage, and a precise definition is not essential at this point.

Energy can be stored within a system and can be transferred (as heat, for example) from one system to another. In a study of statistical thermodynamics we would examine, from a molecular point of view, the ways in which energy can be stored. Because it is helpful in a study of classical thermodynamics to have some notion of how this energy is stored, a brief introduction is presented here.

Consider as a system a certain gas at a given pressure and temperature contained within a tank or pressure vessel. Using the molecular point of view, we identify three general forms of energy:

1. Intermolecular potential energy, which is associated with the forces between molecules
2. Molecular kinetic energy, which is associated with the translational velocity of individual molecules
3. Intramolecular energy (that within the individual molecules), which is associated with the molecular and atomic structure and related forces

The first of these forms of energy, intermolecular potential energy, depends on the magnitude of the intermolecular forces and the position of the molecules relative to each other at any instant of time. It is impossible to determine accurately the magnitude of this energy because we do not know either the exact configuration and orientation of the molecules at any time or the exact intermolecular potential function. However, there are two situations for which we can make good approximations. The first situation is at low or moderate densities. In this case the molecules are relatively widely spaced, so that only two-molecule or two- and three-molecule interactions contribute to the potential energy. At these low and moderate densities, techniques are available for determining, with reasonable accuracy, the potential energy of a system composed of fairly simple molecules. The second situation is at very low densities; under these conditions, the average intermolecular distance between molecules is so large that the potential energy may be assumed to be zero. Consequently, we have in this case a system of independent particles (an ideal gas) and, therefore, from a statistical point of view, we are able to concentrate our efforts on evaluating the molecular translational and internal energies.

FIGURE 2.4 The coordinate system for a diatomic molecule.
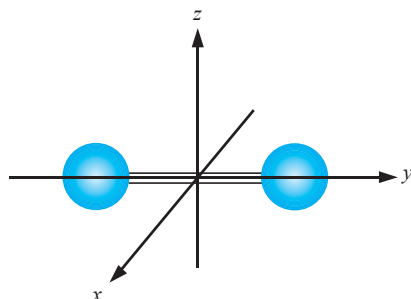
The translational energy, which depends only on the mass and velocities of the molecules, is determined by using the equations of mechanics—either quantum or classical.

The intramolecular internal energy is more difficult to evaluate because, in general, it may result from a number of contributions. Consider a simple monatomic gas such as helium. Each molecule consists of a helium atom. Such an atom possesses electronic energy as a result of both orbital angular momentum of the electrons about the nucleus and angular momentum of the electrons spinning on their axes. The electronic energy is commonly very small compared with the translational energies. (Atoms also possess nuclear energy, which, except in the case of nuclear reactions, is constant. We are not concerned with nuclear energy at this time.) When we consider more complex molecules, such as those composed of two or three atoms, additional factors must be considered. In addition to having electronic energy, a molecule can rotate about its center of gravity and thus have rotational energy. Furthermore, the atoms may vibrate with respect to each other and have vibrational energy. In some situations there may be an interaction between the rotational and vibrational modes of energy.

In evaluating the energy of a molecule, we often refer to the degree of freedom, f, of these energy modes. For a monatomic molecule such as helium, $f = 3$, which represents the three directions x, y, and z in which the molecule can move. For a diatomic molecule, such as oxygen, $f = 6$. Three of these are the translation of the molecule as a whole in the x, y, and z directions, and two are for rotation. The reason why there are only two modes of rotational energy is evident from Fig. 2.4, where we take the origin of the coordinate system at the center of gravity of the molecule, and the y-axis along the molecule's internuclear axis. The molecule will then have an appreciable moment of inertia about the x-axis and the z-axis but not about the y-axis. The sixth degree of freedom of the molecule is vibration, which relates to stretching of the bond joining the atoms.

For a more complex molecule such as H_2O, there are additional vibrational degrees of freedom. Figure 2.5 shows a model of the H_2O molecule. From this diagram, it is evident that there are three vibrational degrees of freedom. It is also possible to have rotational energy about all three axes. Thus, for the H_2O molecule, there are nine degrees of freedom ($f = 9$): three translational, three rotational, and three vibrational.

FIGURE 2.5 The three principal vibrational modes for the H_2O molecule.