CHAPTER

1

Thermodynamics

CHAPTER OUTLINE

1.1 PHYSICAL CHEMISTRY

Physical chemistry is the study of the underlying physical principles that govern the properties and behavior of chemical systems.

A chemical system can be studied from either a microscopic or a macroscopic viewpoint. The **microscopic** viewpoint is based on the concept of molecules. The **macroscopic** viewpoint studies large-scale properties of matter without explicit use of the molecule concept. The first half of this book uses mainly a macroscopic viewpoint; the second half uses mainly a microscopic viewpoint.

We can divide physical chemistry into four areas: thermodynamics, quantum chemistry, statistical mechanics, and kinetics (Fig. 1.1). **Thermodynamics** is a macroscopic science that studies the interrelationships of the various equilibrium properties of a system and the changes in equilibrium properties in processes. Thermodynamics is treated in Chapters 1 to 13.

Molecules and the electrons and nuclei that compose them do not obey classical mechanics. Instead, their motions are governed by the laws of quantum mechanics (Chapter 17). Application of quantum mechanics to atomic structure, molecular bonding, and spectroscopy gives us **quantum chemistry** (Chapters 18 to 20).

The macroscopic science of thermodynamics is a consequence of what is happening at a molecular (microscopic) level. The molecular and macroscopic levels are related to each other by the branch of science called **statistical mechanics.** Statistical mechanics gives insight into why the laws of thermodynamics hold and allows calculation of macroscopic thermodynamic properties from molecular properties. We shall study statistical mechanics in Chapters 14, 15, 21, 22, and 23.

Kinetics is the study of rate processes such as chemical reactions, diffusion, and the flow of charge in an electrochemical cell. The theory of rate processes is not as well developed as the theories of thermodynamics, quantum mechanics, and statistical mechanics. Kinetics uses relevant portions of thermodynamics, quantum chemistry, and statistical mechanics. Chapters 15, 16, and 22 deal with kinetics.

The principles of physical chemistry provide a framework for all branches of chemistry.

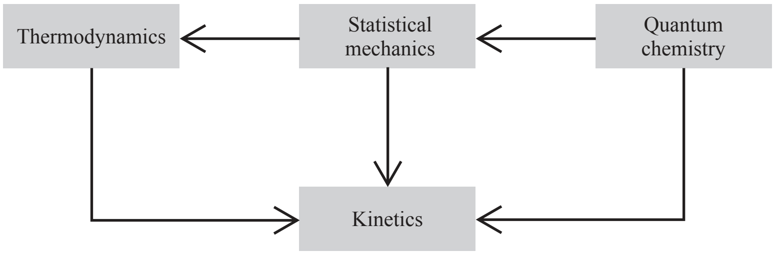


Figure 1.1

The four branches of physical chemistry. Statistical mechanics is the bridge from the microscopic approach of quantum chemistry to the macroscopic approach of thermodynamics. Kinetics uses portions of the other three branches.

Organic chemists use kinetics studies to figure out the mechanisms of reactions, use quantum-chemistry calculations to study the structures and stabilities of reaction intermediates, use symmetry rules deduced from quantum chemistry to predict the course of many reactions, and use nuclear-magnetic-resonance (NMR) and infrared spectroscopy to help determine the structure of compounds. Inorganic chemists use quantum chemistry and spectroscopy to study bonding. Analytical chemists use spectroscopy to analyze samples. Biochemists use kinetics to study rates of enzyme-catalyzed reactions; use thermodynamics to study biological energy transformations, osmosis, and membrane equilibrium, and to determine molecular weights of biological molecules; use spectroscopy to study processes at the molecular level (for example, intramolecular motions in proteins are studied using NMR); and use x-ray diffraction to determine the structures of proteins and nucleic acids.

Environmental chemists use thermodynamics to find the equilibrium composition of lakes and streams, use chemical kinetics to study the reactions of pollutants in the atmosphere, and use physical kinetics to study the rate of dispersion of pollutants in the environment.

Chemical engineers use thermodynamics to predict the equilibrium composition of reaction mixtures, use kinetics to calculate how fast products will be formed, and use principles of thermodynamic phase equilibria to design separation procedures such as fractional distillation. Geochemists use thermodynamic phase diagrams to understand processes in the earth. Polymer chemists use thermodynamics, kinetics, and statistical mechanics to investigate the kinetics of polymerization, the molecular weights of polymers, the flow of polymer solutions, and the distribution of conformations of a polymer molecule.

Widespread recognition of physical chemistry as a discipline began in 1887 with the founding of the journal *Zeitschrift für Physikalische Chemie* by Wilhelm Ostwald with J. H. van't Hoff as coeditor. Ostwald investigated chemical equilibrium, chemical kinetics, and solutions and wrote the first textbook of physical chemistry. He was instrumental in drawing attention to Gibbs' pioneering work in chemical thermodynamics and was the first to nominate Einstein for a Nobel Prize. Surprisingly, Ostwald argued against the atomic theory of matter and did not accept the reality of atoms and molecules until 1908. Ostwald, van't Hoff, Gibbs, and Arrhenius are generally regarded as the founders of physical chemistry. (In Sinclair Lewis's 1925 novel *Arrowsmith,* the character Max Gottlieb, a medical school professor, proclaims that "Physical chemistry is power, it is exactness, it is life.")

In its early years, physical chemistry research was done mainly at the macroscopic level. With the discovery of the laws of quantum mechanics in 1925–1926, emphasis began to shift to the molecular level. (The *Journal of Chemical Physics* was founded in 1933 in reaction to the refusal of the editors of the *Journal of Physical Chemistry* to publish theoretical papers.) Nowadays, the power of physical chemistry has been greatly increased by experimental techniques that study properties and processes at the molecular level and by fast computers that (*a*) process and analyze data of spectroscopy and x-ray crystallography experiments, (*b*) accurately calculate properties of molecules that are not too large, and (*c*) perform simulations of collections of hundreds of molecules.

Nowadays, the prefix *nano* is widely used in such terms as nanoscience, nanotechnology, nanomaterials, nanoscale, etc. A *nanoscale* (or *nanoscopic*) *system* is one with at least one dimension in the range 1 to 100 nm, where 1 nm $= 10^{-9}$ m. (Atomic diameters are typically 0.1 to 0.3 nm.) A nanoscale system typically contains thousands of atoms. The intensive properties of a nanoscale system commonly depend on its size and differ substantially from those of a macroscopic system of the same composition. For example, macroscopic solid gold is yellow, is a good electrical conductor, melts at 1336 K, and is chemically unreactive; however, gold nanoparticles of radius 2.5 nm melt at 930 K, and catalyze many reactions; gold nanoparticles of 100 nm radius are purple-pink, of 20 nm radius are red, and of 1 nm radius are orange; gold particles of 1 nm or smaller radius are electrical insulators. The term *mesoscopic* is sometimes used to refer to systems larger than nanoscopic but smaller than macroscopic. Thus we have the progressively larger size levels: atomic → nanoscopic → mesoscopic → macroscopic.

1.2 THERMODYNAMICS

Thermodynamics

We begin our study of physical chemistry with thermodynamics. **Thermodynamics** (from the Greek words for "heat" and "power") is the study of heat, work, energy, and the changes they produce in the states of systems. In a broader sense, thermodynamics studies the relationships between the macroscopic properties of a system. A key property in thermodynamics is temperature, and thermodynamics is sometimes defined as the study of the relation of temperature to the macroscopic properties of matter.

We shall be studying **equilibrium thermodynamics,** which deals with systems in equilibrium. (**Irreversible thermodynamics** deals with nonequilibrium systems and rate processes.) Equilibrium thermodynamics is a macroscopic science and is independent of any theories of molecular structure. Strictly speaking, the word "molecule" is not part of the vocabulary of thermodynamics. However, we won't adopt a purist attitude but will often use molecular concepts to help us understand thermodynamics. Thermodynamics does not apply to systems that contain only a few molecules; a system must contain a great many molecules for it to be treated thermodynamically. The term "thermodynamics" in this book will always mean equilibrium thermodynamics.

Thermodynamic Systems

The macroscopic part of the universe under study in thermodynamics is called the **system.** The parts of the universe that can interact with the system are called the **surroundings.**

For example, to study the vapor pressure of water as a function of temperature, we might put a sealed container of water (with any air evacuated) in a constant-temperature bath and connect a manometer to the container to measure the pressure (Fig. 1.2). Here, the system consists of the liquid water and the water vapor in the container, and the surroundings are the constant-temperature bath and the mercury in the manometer.

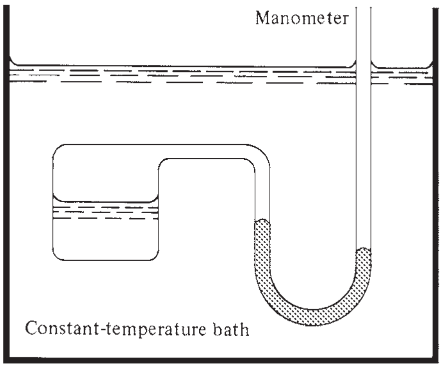


Figure 1.2

A thermodynamic system and its surroundings.

An **open system** is one where transfer of matter between system and surroundings can occur. A **closed system** is one where no transfer of matter can occur between system and surroundings. An **isolated system** is one that does not interact in any way with its surroundings. An isolated system is obviously a closed system, but not every closed system is isolated. For example, in Fig. 1.2, the system of liquid water plus water vapor in the sealed container is closed (since no matter can enter or leave) but not isolated (since it can be warmed or cooled by the surrounding bath and can be compressed or expanded by the mercury). For an isolated system, neither matter nor energy can be transferred between system and surroundings. For a closed system, energy but not matter can be transferred between system and surroundings. For an open system, both matter and energy can be transferred between system and surroundings.

A thermodynamic system is either open or closed and is either isolated or nonisolated. Most commonly, we shall deal with closed systems.

Walls

A system may be separated from its surroundings by various kinds of walls. (In Fig. 1.2, the system is separated from the bath by the container walls.) A wall can be either **rigid** or **nonrigid** (movable). A wall may be **permeable** or **impermeable,** where by "impermeable" we mean that it allows no matter to pass through it. Finally, a wall may be **adiabatic** or **nonadiabatic.** In plain language, an adiabatic wall is one that does not conduct heat at all, whereas a nonadiabatic wall does conduct heat. However, we have not yet defined heat, and hence to have a logically correct development of thermodynamics, adiabatic and nonadiabatic walls must be defined without reference to heat. This is done as follows.

Suppose we have two separate systems A and B, each of whose properties are observed to be constant with time. We then bring A and B into contact via a rigid, impermeable wall (Fig. 1.3). If, no matter what the initial values of the properties of A and B are, we observe no change in the values of these properties (for example, pressures, volumes) with time, then the wall separating A and B is said to be **adiabatic.** If we generally observe changes in the properties of A and B with time when they are brought in contact via a rigid, impermeable wall, then this wall is called **nonadiabatic** or **thermally conducting.** (As an aside, when two systems at different temperatures are brought in contact through a thermally conducting wall, heat flows from the hotter to the colder system, thereby changing the temperatures and other properties of the two systems; with an adiabatic wall, any temperature difference is maintained. Since heat and temperature are still undefined, these remarks are logically out of place, but they have been included to clarify the definitions of adiabatic and thermally conducting walls.) An adiabatic wall is an idealization, but it can be approximated, for example, by the double walls of a Dewar flask or thermos bottle, which are separated by a near vacuum.

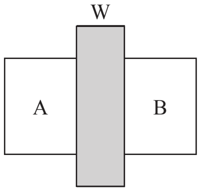


Figure 1.3

Systems A and B are separated by a wall W.

In Fig. 1.2, the container walls are impermeable (to keep the system closed) and are thermally conducting (to allow the system's temperature to be adjusted to that of the surrounding bath). The container walls are essentially rigid, but if the interface between the water vapor and the mercury in the manometer is considered to be a "wall," then this wall is movable. We shall often deal with a system separated from its surroundings by a piston, which acts as a movable wall.

A system surrounded by a rigid, impermeable, adiabatic wall cannot interact with the surroundings and is isolated.

Equilibrium

Equilibrium thermodynamics deals with systems in **equilibrium.** An isolated system is in equilibrium when its macroscopic properties remain constant with time. A nonisolated system is in equilibrium when the following two conditions hold: (*a*) The system's macroscopic properties remain constant with time; (*b*) removal of the system from contact with its surroundings causes no change in the properties of the system. If condition (*a*) holds but (*b*) does not hold, the system is in a *steady state.* An example of a steady state is a metal rod in contact at one end with a large body at 50°C and in contact at the other end with a large body at 40°C. After enough time has elapsed, the metal rod satisfies condition (*a*); a uniform temperature gradient is set up along the rod. However, if we remove the rod from contact with its surroundings, the temperatures of its parts change until the whole rod is at 45°C.

The equilibrium concept can be divided into the following three kinds of equilibrium. For **mechanical equilibrium,** no unbalanced forces act on or within the system; hence the system undergoes no acceleration, and there is no turbulence within the system. For **material equilibrium,** no net chemical reactions are occurring in the system, nor is there any net transfer of matter from one part of the system to another or between the system and its surroundings; the concentrations of the chemical species in the various parts of the system are constant in time. For **thermal equilibrium** between a system and its surroundings, there must be no change in the properties of the system or surroundings when they are separated by a thermally conducting wall. Likewise, we can insert a thermally conducting wall between two parts of a system to test whether the parts are in thermal equilibrium with each other. For thermodynamic equilibrium, all three kinds of equilibrium must be present.

Thermodynamic Properties

What properties does thermodynamics use to characterize a system in equilibrium? Clearly, the **composition** must be specified. This can be done by stating the mass of each chemical species that is present in each phase. The **volume** V is a property of the system. The pressure P is another thermodynamic variable. **Pressure** is defined as the magnitude of the perpendicular force per unit area exerted by the system on its surroundings:

$$P \equiv F/A \qquad \textbf{(1.1)*}$$

where F is the magnitude of the perpendicular force exerted on a boundary wall of area A. The symbol $\equiv$ indicates a definition. *An equation with a star after its number should be memorized.* Pressure is a scalar, not a vector. For a system in mechanical equilibrium, the pressure throughout the system is uniform and equal to the pressure of the surroundings. (We are ignoring the effect of the earth's gravitational field, which causes a slight increase in pressure as one goes from the top to the bottom of the system.) If external electric or magnetic fields act on the system, the field strengths are thermodynamic variables; we won't consider systems with such fields. Later, further thermodynamic properties (for example, temperature, internal energy, entropy) will be defined.

An **extensive** thermodynamic property is one whose value is equal to the sum of its values for the parts of the system. Thus, if we divide a system into parts, the mass of the system is the sum of the masses of the parts; mass is an extensive property. So is volume. An **intensive** thermodynamic property is one whose value does not depend on the size of the system, provided the system remains of macroscopic size—recall nanoscopic systems (Sec. 1.1). Density and pressure are examples of intensive properties. We can take a drop of water or a swimming pool full of water, and both systems will have the same density.

If each intensive macroscopic property is constant throughout a system, the system is **homogeneous.** If a system is not homogeneous, it may consist of a number of homogeneous parts. A homogeneous part of a system is called a **phase.** For example, if the system consists of a crystal of AgBr in equilibrium with an aqueous solution of AgBr, the system has two phases: the solid AgBr and the solution. A phase can consist of several disconnected pieces. For example, in a system composed of several

AgBr crystals in equilibrium with an aqueous solution, all the crystals are part of the same phase. Note that the definition of a phase does not mention solids, liquids, or gases. A system can be entirely liquid (or entirely solid) and still have more than one phase. For example, a system composed of the nearly immiscible liquids H_2O and CCl_4 has two phases. A system composed of the solids diamond and graphite has two phases.

A system composed of two or more phases is **heterogeneous.**

The **density** ρ (rho) of a phase of mass m and volume V is

$$\rho \equiv m/V \tag{1.2}*$$

Figure 1.4 plots some densities at room temperature and pressure. The symbols *s*, *l*, and *g* stand for solid, liquid, and gas.

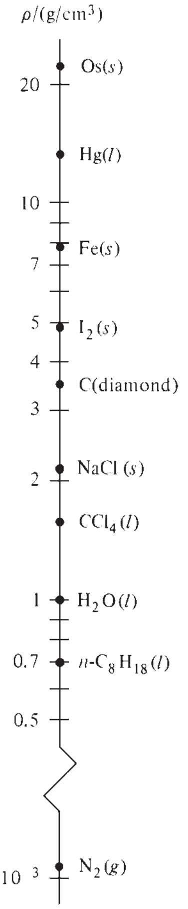


Figure 1.4

Densities at 25°C and 1 atm. The scale is logarithmic.

Suppose that the value of every thermodynamic property in a certain thermodynamic system equals the value of the corresponding property in a second system. The systems are then said to be in the same **thermodynamic state.** The state of a thermodynamic system is defined by specifying the values of its thermodynamic properties. However, it is not necessary to specify all the properties to define the state. Specification of a certain minimum number of properties will fix the values of all other properties. For example, suppose we take 8.66 g of pure H_2O at 1 atm (atmosphere) pressure and 24°C. It is found that in the absence of external fields all the remaining properties (volume, heat capacity, index of refraction, etc.) are fixed. (This statement ignores the possibility of surface effects, which are considered in Chapter 7.) Two thermodynamic systems each consisting of 8.66 g of H_2O at 24°C and 1 atm are in the same thermodynamic state. Experiments show that, for a single-phase system containing specified fixed amounts of nonreacting substances, specification of two additional thermodynamic properties is generally sufficient to determine the thermodynamic state, provided external fields are absent and surface effects are negligible.

A thermodynamic system in a given equilibrium state has a particular value for each thermodynamic property. These properties are therefore also called **state functions,** since their values are functions of the system's state. The value of a state function depends only on the present state of a system and not on its past history. It doesn't matter whether we got the 8.66 g of water at 1 atm and 24°C by melting ice and warming the water or by condensing steam and cooling the water.

1.3 TEMPERATURE

Suppose two systems separated by a movable wall are in mechanical equilibrium with each other. Because we have mechanical equilibrium, no unbalanced forces act and each system exerts an equal and opposite force on the separating wall. Therefore each system exerts an equal pressure on this wall. Systems in mechanical equilibrium with each other have the same pressure. What about systems that are in thermal equilibrium (Sec. 1.2) with each other?

Just as systems in *mechanical* equilibrium have a common *pressure,* it seems plausible that there is some thermodynamic property common to systems in *thermal* equilibrium. This property is what we *define* as the **temperature,** symbolized by θ (theta). By definition, *two systems in thermal equilibrium with each other have the same temperature; two systems not in thermal equilibrium have different temperatures.*

Although we have asserted the existence of temperature as a thermodynamic state function that determines whether or not thermal equilibrium exists between systems, we need experimental evidence that there really is such a state function. Suppose that we find systems A and B to be in thermal equilibrium with each other when brought in contact via a thermally conducting wall. Further suppose that we find systems B and

C to be in thermal equilibrium with each other. By our definition of temperature, we would assign the same temperature to A and B ($\theta_A = \theta_B$) and the same temperature to B and C ($\theta_B = \theta_C$). Therefore, systems A and C would have the same temperature ($\theta_A = \theta_C$), and we would expect to find A and C in thermal equilibrium when they are brought in contact via a thermally conducting wall. If A and C were not found to be in thermal equilibrium with each other, then our definition of temperature would be invalid. It is an experimental fact that:

Two systems that are each found to be in thermal equilibrium with a third system will be found to be in thermal equilibrium with each other.

This generalization from experience is *the zeroth law of thermodynamics.* It is so called because only after the first, second, and third laws of thermodynamics had been formulated was it realized that the zeroth law is needed for the development of thermodynamics. Moreover, a statement of the zeroth law logically precedes the other three. The zeroth law allows us to assert the existence of temperature as a state function.

Having defined temperature, how do we measure it? Of course, you are familiar with the process of putting a liquid-mercury thermometer in contact with a system, waiting until the volume change of the mercury has ceased (indicating that thermal equilibrium between the thermometer and the system has been reached), and reading the thermometer scale. Let us analyze what is being done here.

To set up a temperature scale, we pick a reference system r, which we call the **thermometer.** For simplicity, we choose r to be homogeneous with a fixed composition and a fixed pressure. Furthermore, we require that the substance of the thermometer must always expand when heated. This requirement ensures that at fixed pressure the volume of the thermometer r will define the state of system r uniquely—two states of r with different volumes at fixed pressure will not be in thermal equilibrium and must be assigned different temperatures. Liquid water is unsuitable for a thermometer since when heated at 1 atm, it contracts at temperatures below 4°C and expands above 4°C (Fig. 1.5). Water at 1 atm and 3°C has the same volume as water at 1 atm and 5°C, so the volume of water cannot be used to measure temperature. Liquid mercury always expands when heated, so let us choose a fixed amount of liquid mercury at 1 atm pressure as our thermometer.

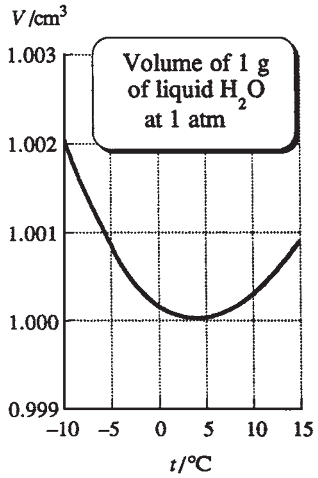


Figure 1.5

Volume of 1 g of water at 1 atm versus temperature. Below 0°C, the water is supercooled (Sec. 7.4).

We now assign a different numerical value of the temperature θ to each different volume V_r of the thermometer r. The way we do this is arbitrary. The simplest approach is to take θ as a linear function of V_r. We therefore *define* the temperature to be $\theta \equiv aV_r + b$, where V_r is the volume of a fixed amount of liquid mercury at 1 atm pressure and a and b are constants, with a being positive (so that states which are experienced physiologically as being hotter will have larger θ values). Once a and b are specified, a measurement of the thermometer's volume V_r gives its temperature θ.

The mercury for our thermometer is placed in a glass container that consists of a bulb connected to a narrow tube. Let the cross-sectional area of the tube be A, and let the mercury rise to a length l in the tube. The mercury volume equals the sum of the mercury volumes in the bulb and the tube, so

$$\theta \equiv aV_r + b = a(V_{\text{bulb}} + Al) + b = aAl + (aV_{\text{bulb}} + b) \equiv cl + d \qquad (1.3)$$

where c and d are constants defined as $c \equiv aA$ and $d \equiv aV_{\text{bulb}} + b$.

To fix c and d, we define the temperature of equilibrium between pure ice and liquid water saturated with dissolved air at 1 atm pressure as 0°C (for centigrade), and we define the temperature of equilibrium between pure liquid water and water vapor at 1 atm pressure (the normal boiling point of water) as 100°C. These points are called the *ice point* and the *steam point.* Since our scale is linear with the length of the mercury column, we mark off 100 equal intervals between 0°C and 100°C and extend the marks above and below these temperatures.

Having armed ourselves with a thermometer, we can now find the temperature of any system B. To do so, we put system B in contact with the thermometer, wait until thermal equilibrium is achieved, and then read the thermometer's temperature from the graduated scale. Since B is in thermal equilibrium with the thermometer, B's temperature equals that of the thermometer.

Note the arbitrary way we defined our scale. This scale depends on the expansion properties of a particular substance, liquid mercury. If we had chosen ethanol instead of mercury as the thermometric fluid, temperatures on the ethanol scale would differ slightly from those on the mercury scale. Moreover, there is at this point no reason, apart from simplicity, for choosing a linear relation between temperature and mercury volume. We could just as well have chosen θ to vary as $aV_r^2 + b$. Temperature is a fundamental concept of thermodynamics, and one naturally feels that it should be formulated less arbitrarily. Some of the arbitrariness will be removed in Sec. 1.5, where the ideal-gas temperature scale is defined. Finally, in Sec. 3.6 we shall define the most fundamental temperature scale, the thermodynamic scale. The mercury centigrade scale defined in this section is not in current scientific use, but we shall use it until we define a better scale in Sec. 1.5.

Let systems A and B have the same temperature ($\theta_A = \theta_B$), and let systems B and C have different temperatures ($\theta_B \neq \theta_C$). Suppose we set up a second temperature scale using a different fluid for our thermometer and assigning temperature values in a different manner. Although the numerical values of the temperatures of systems A, B, and C on the second scale will differ from those on the first temperature scale, it follows from the zeroth law that on the second scale systems A and B will still have the same temperature, and systems B and C will have different temperatures. Thus, although numerical values on any temperature scale are arbitrary, the zeroth law assures us that the temperature scale will fulfill its function of telling whether or not two systems are in thermal equilibrium.

Since virtually all physical properties change with temperature, properties other than volume can be used to measure temperature. With a *resistance thermometer,* one measures the electrical resistance of a metal wire. A *thermistor* (which is used in a digital fever thermometer) is based on the temperature-dependent electrical resistance of a semiconducting metal oxide. A *thermocouple* involves the temperature dependence of the electric potential difference between two different metals in contact (Fig. 13.4). Very high temperatures can be measured with an *optical pyrometer,* which examines the light emitted by a hot solid. The intensity and frequency distribution of this light depend on the temperature (Fig. 17.1*b*), and this allows the solid's temperature to be found (see *Quinn,* chap. 7; references with the author's name italicized are listed in the Bibliography).

Temperature is an abstract property that is not measured directly. Instead, we measure some other property (for example, volume, electrical resistance, emitted radiation) whose value depends on temperature and (using the definition of the temperature scale and calibration of the measured property to that scale) we deduce a temperature value from the measured property.

Thermodynamics is a macroscopic science and does not explain the molecular meaning of temperature. We shall see in Sec. 14.3 that increasing temperature corresponds to increasing average molecular kinetic energy, provided the temperature scale is chosen to give higher temperatures to hotter states.

The concept of temperature does not apply to a single atom, and the minimum-size system for which a temperature can be assigned is not clear. A statistical-mechanical calculation on a very simple model system indicated that temperature might not be a meaningful concept for some nanoscopic systems [M. Hartmann, *Contemporary Physics,* **47,** 89 (2006); X. Wang et al., *Am. J. Phys.,* **75,** 431 (2007)].

1.4 THE MOLE

We now review the concept of the mole, which is used in chemical thermodynamics.

The ratio of the average mass of an atom of an element to the mass of some chosen standard is called the **atomic weight** or **relative atomic mass** A_r of that element (the r stands for "relative"). The standard used since 1961 is $\frac{1}{12}$ times the mass of the isotope ^{12}C. The atomic weight of ^{12}C is thus exactly 12, by definition. The ratio of the average mass of a molecule of a substance to $\frac{1}{12}$ times the mass of a ^{12}C atom is called the **molecular weight** or **relative molecular mass** M_r of that substance. The statement that the molecular weight of H_2O is 18.015 means that a water molecule has on the average a mass that is 18.015/12 times the mass of a ^{12}C atom. We say "on the average" to acknowledge the existence of naturally occurring isotopes of H and O. Since atomic and molecular weights are *relative* masses, these "weights" are dimensionless numbers. For an ionic compound, the mass of one formula unit replaces the mass of one molecule in the definition of the molecular weight. Thus, we say that the molecular weight of NaCl is 58.443, even though there are no individual NaCl molecules in an NaCl crystal.

The number of ^{12}C atoms in exactly 12 g of ^{12}C is called **Avogadro's number.** Experiment (Sec. 18.2) gives 6.02×10^{23} as the value of Avogadro's number. Avogadro's number of ^{12}C atoms has a mass of 12 g, exactly. What is the mass of Avogadro's number of hydrogen atoms? The atomic weight of hydrogen is 1.0079, so each H atom has a mass 1.0079/12 times the mass of a ^{12}C atom. Since we have equal numbers of H and ^{12}C atoms, the total mass of hydrogen is 1.0079/12 times the total mass of the ^{12}C atoms, which is (1.0079/12) (12 g) = 1.0079 g; this mass in grams is numerically equal to the atomic weight of hydrogen. The same reasoning shows that Avogadro's number of atoms of any element has a mass of A_r grams, where A_r is the atomic weight of the element. Similarly, Avogadro's number of molecules of a substance whose molecular weight is M_r will have a mass of M_r grams.

The average mass of an atom or molecule is called the **atomic mass** or the **molecular mass.** Molecular masses are commonly expressed in units of **atomic mass units** (amu), where 1 amu is one-twelfth the mass of a ^{12}C atom. With this definition, the atomic mass of C is 12.011 amu and the molecular mass of H_2O is 18.015 amu. Since 12 g of ^{12}C contains 6.02×10^{23} atoms, the mass of a ^{12}C atom is $(12\text{ g})/(6.02 \times 10^{23})$ and $1\text{ amu} = (1\text{ g})/(6.02 \times 10^{23}) = 1.66 \times 10^{-24}$ g. The quantity 1 amu is called 1 dalton by biochemists, who express molecular masses in units of daltons.

A **mole** of some substance is defined as an amount of that substance which contains Avogadro's number of elementary entities. For example, a mole of hydrogen atoms contains 6.02×10^{23} H atoms; a mole of water molecules contains 6.02×10^{23} H_2O molecules. We showed earlier in this section that, if $M_{r,i}$ is the molecular weight of species i, then the mass of 1 mole of species i equals $M_{r,i}$ grams. The mass per mole of a pure substance is called its **molar mass** M. For example, for H_2O, $M =$ 18.015 g/mole. The molar mass of substance i is

$$M_i \equiv \frac{m_i}{n_i} \qquad \textbf{(1.4)*}$$

where m_i is the mass of substance i in a sample and n_i is the number of moles of i in the sample. The molar mass M_i and the molecular weight $M_{r,i}$ of i are related by $M_i = M_{r,i} \times 1$ g/mole, where $M_{r,i}$ is a dimensionless number.

After Eq. (1.4), n_i was called "the number of moles" of species i. Strictly speaking, this is incorrect. In the officially recommended SI units (Sec. 2.1), the **amount of substance** (also called the **chemical amount**) is taken as one of the fundamental physical quantities (along with mass, length, time, etc.), and the unit of this physical quantity is the mole, abbreviated mol. Just as the SI unit of mass is the kilogram, the SI unit of amount of substance is the mole. Just as the symbol m_i stands for the mass of substance i, the symbol n_i stands for the amount of substance i. The quantity m_i is not a pure number but is a number times a unit of mass; for example, m_i might be 4.18 kg (4.18 kilograms). Likewise, n_i is not a pure number but is a number times a unit of amount of substance; for example, n_i might be 1.26 mol (1.26 moles). Thus the correct statement is that n_i is the amount of substance i. The number of moles of i is a pure number and equals n_i/mol, since n_i has a factor of 1 mol included in itself.

Since Avogadro's number is the number of molecules in one mole, the number of molecules N_i of species i in a system is

$$N_i = (n_i/\text{mol}) \cdot (\text{Avogadro's number})$$

where n_i/mol is the number of moles of species i in the system. The quantity (Avogadro's number)/mol is called the **Avogadro constant** N_A. We have

$$N_i = n_i N_A \qquad \text{where } N_A = 6.02 \times 10^{23}\ \text{mol}^{-1} \tag{1.5}*$$

Avogadro's number is a pure number, whereas the Avogadro constant N_A has units of mole^{-1}.

Equation (1.5) applies to any collection of elementary entities, whether they are atoms, molecules, ions, radicals, electrons, photons, etc. Written in the form $n_i = N_i/N_A$, Eq. (1.5) gives the definition of the amount of substance n_i of species i. In this equation, N_i is the number of elementary entities of species i.

If a system contains n_i moles of chemical species i and if n_{tot} is the total number of moles of all species present, then the **mole fraction** x_i of species i is

$$x_i \equiv n_i/n_{\text{tot}} \tag{1.6}*$$

The sum of the mole fractions of all species equals 1; $x_1 + x_2 + \cdots = n_1/n_{\text{tot}} + n_2/n_{\text{tot}} + \cdots = (n_1 + n_2 + \cdots)/n_{\text{tot}} = n_{\text{tot}}/n_{\text{tot}} = 1$.

1.5 IDEAL GASES

The laws of thermodynamics are general and do not refer to the specific nature of the system under study. Before studying these laws, we shall describe the properties of a particular kind of system, namely, an ideal gas. We shall then be able to illustrate the application of thermodynamic laws to an ideal-gas system. Ideal gases also provide the basis for a more fundamental temperature scale than the liquid-mercury scale of Sec. 1.3.

Boyle's Law

Boyle investigated the relation between the pressure and volume of gases in 1662 and found that, for a fixed amount of gas kept at a fixed temperature, P and V are inversely proportional:

$$PV = k \qquad \text{constant } \theta, m \tag{1.7}$$

where k is a constant and m is the gas mass. Careful investigation shows that Boyle's law holds only approximately for real gases, with deviations from the law approaching zero in the limit of zero pressure. Figure 1.6*a* shows some observed P-versus-V curves for 28 g of N_2 at two temperatures. Figure 1.6*b* shows plots of PV versus P for 28 g of N_2. Note the near constancy of PV at low pressures (below 10 atm) and the significant deviations from Boyle's law at high pressures.

Note how the axes in Fig. 1.6 are labeled. The quantity P equals a pure number times a unit; for example, P might be 4.0 atm $= 4.0 \times 1$ atm. Therefore, P/atm (where

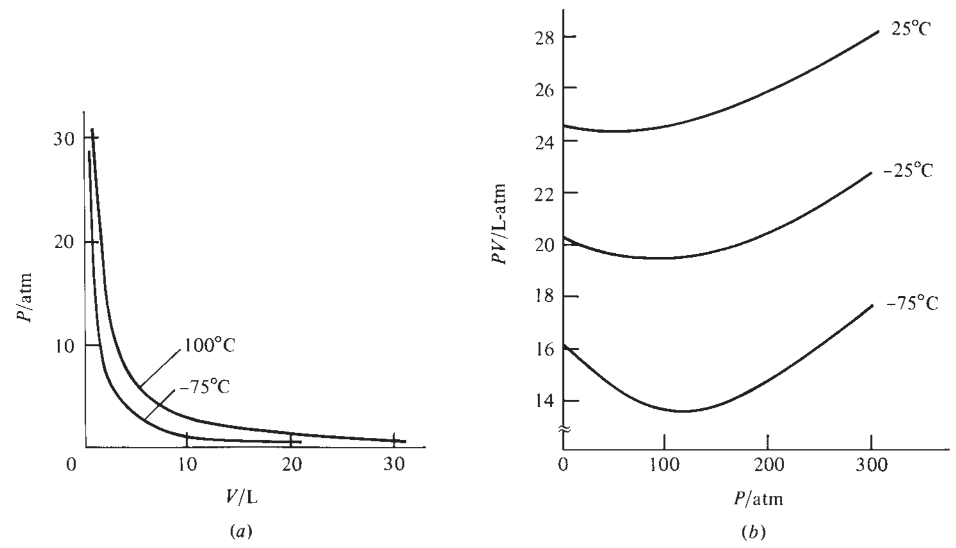


Figure 1.6

Plots of (*a*) *P* versus *V* and (*b*) *PV* versus *P* for 1 mole of N_2 gas at constant temperature.

the slash means "divided by") is a pure number, and the scales on the axes are marked with pure numbers. If $P = 4.0$ atm, then $P/\text{atm} = 4.0$. (If a column in a table is labeled $10^3P/\text{atm}$, then an entry of 5.65 in this column would mean that $10^3P/\text{atm} = 5.65$ and simple algebra gives $P = 5.65 \times 10^{-3}$ atm.)

Boyle's law is understandable from the picture of a gas as consisting of a huge number of molecules moving essentially independently of one another. The pressure exerted by the gas is due to the impacts of the molecules on the walls. A decrease in volume causes the molecules to hit the walls more often, thereby increasing the pressure. We shall derive Boyle's law from the molecular picture in Chapter 14, starting from a model of the gas as composed of noninteracting point particles. In actuality, the molecules of a gas exert forces on one another, so Boyle's law does not hold exactly. In the limit of zero density (reached as the pressure goes to zero or as the temperature goes to infinity), the gas molecules are infinitely far apart from one another, forces between molecules become zero, and Boyle's law is obeyed exactly. We say the gas becomes **ideal** in the zero-density limit.

Pressure and Volume Units

From the definition $P \equiv F/A$ [Eq. (1.1)], pressure has dimensions of force divided by area. In the SI system (Sec. 2.1), its units are newtons per square meter (N/m^2), also called **pascals** (Pa):

$$1 \text{ Pa} \equiv 1 \text{ N/m}^2 \qquad \textbf{(1.8)*}$$

Because 1 m^2 is a large area, the pascal is an inconveniently small unit of pressure, and its multiples the kilopascal (kPa) and megapascal (MPa) are often used: 1 kPa $\equiv 10^3$ Pa and 1 MPa $= 10^6$ Pa.

Chemists customarily use other units. One **torr** (or 1 mmHg) is the pressure exerted at 0°C by a column of mercury one millimeter high when the gravitational acceleration has the standard value $g = 980.665 \text{ cm/s}^2$. The downward force exerted by the mercury equals its mass *m* times *g*. Thus a mercury column of height *h*, mass *m*, cross-sectional area *A*, volume *V*, and density ρ exerts a pressure *P* given by

$$P = F/A = mg/A = \rho Vg/A = \rho Ahg/A = \rho gh \qquad (1.9)$$

The density of mercury at 0°C and 1 atm is 13.5951 g/cm^3. Converting this density to kg/m^3 and using (1.9) with $h = 1$ mm, we have

$$1 \text{ torr} = \left(13.5951 \frac{\text{g}}{\text{cm}^3}\right)\left(\frac{1 \text{ kg}}{10^3 \text{ g}}\right)\left(\frac{10^2 \text{ cm}}{1 \text{ m}}\right)^3 (9.80665 \text{ m/s}^2)(10^{-3} \text{ m})$$

$$1 \text{ torr} = 133.322 \text{ kg m}^{-1} \text{ s}^{-2} = 133.322 \text{ N/m}^2 = 133.322 \text{ Pa}$$

since 1 N = 1 kg m s^{-2} [Eq. (2.7)]. One **atmosphere** (atm) is defined as exactly 760 torr:

$$1 \text{ atm} \equiv 760 \text{ torr} = 1.01325 \times 10^5 \text{ Pa} \tag{1.10}$$

Another widely used pressure unit is the **bar:**

$$1 \text{ bar} \equiv 10^5 \text{ Pa} = 0.986923 \text{ atm} = 750.062 \text{ torr} \tag{1.11}$$

The bar is slightly less than 1 atm. The approximation

$$1 \text{ bar} \approx 750 \text{ torr} \qquad \textbf{(1.12)*}$$

will usually be accurate enough for our purposes. See Fig. 1.7.

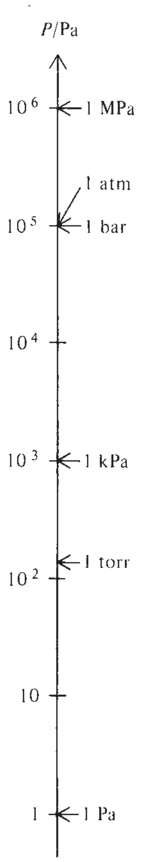


Figure 1.7

Units of pressure. The scale is logarithmic.

Common units of volume are cubic centimeters (cm^3), cubic decimeters (dm^3), cubic meters (m^3), and liters (L or l). The **liter** is defined as exactly 1000 cm^3. One liter equals $10^3 \text{ cm}^3 = 10^3(10^{-2} \text{ m})^3 = 10^{-3} \text{ m}^3 = (10^{-1} \text{ m})^3 = 1 \text{ dm}^3$, where one decimeter (dm) equals 0.1 m.

$$1 \text{ liter} = 1 \text{ dm}^3 = 1000 \text{ cm}^3 \qquad \textbf{(1.13)*}$$

Charles' Law

Charles (1787) and Gay-Lussac (1802) measured the thermal expansion of gases and found a linear increase in volume with temperature (measured on the mercury centigrade scale) at constant pressure and fixed amount of gas:

$$V = a_1 + a_2\theta \qquad \text{const. } P, m \tag{1.14}$$

where a_1 and a_2 are constants. For example, Fig. 1.8 shows the observed relation between V and θ for 28 g of N_2 at a few pressures. Note the near linearity of the curves, which are at low pressures. The content of Charles' law is simply that the thermal expansions of gases and of liquid mercury are quite similar. The molecular explanation for Charles' law lies in the fact that an increase in temperature means the molecules are moving faster and hitting the walls harder and more often. Therefore, the volume must increase if the pressure is to remain constant.

The Ideal-Gas Absolute Temperature Scale

Charles' law (1.14) is obeyed most accurately in the limit of zero pressure; but even in this limit, gases still show small deviations from Eq. (1.14). These deviations are due to small differences between the thermal-expansion behavior of ideal gases and

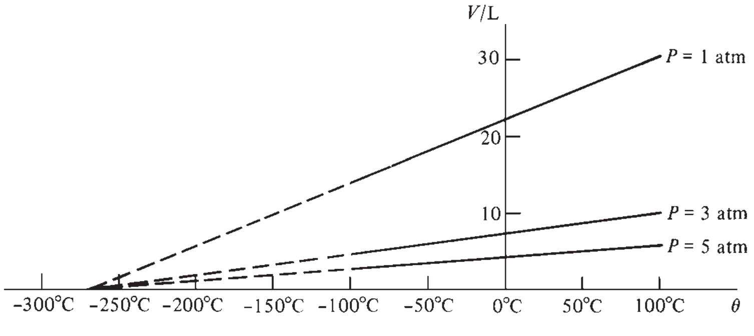


Figure 1.8

Plots of volume versus centigrade temperature for 1 mole of N_2 gas at constant pressure.

that of liquid mercury, which is the basis for the θ temperature scale. However, in the zero-pressure limit, the deviations from Charles' law are the *same* for different gases. In the limit of zero pressure, all gases show the same temperature-versus-volume behavior at constant pressure.

Extrapolation of the N_2 low-pressure V-versus-θ curves in Fig. 1.8 to low temperatures shows that they all intersect the θ axis at the same point, approximately $-273°$ on the mercury centigrade scale. Moreover, extrapolation of such curves for any gas, not just N_2, shows they intersect the θ axis at $-273°$. At this temperature, any ideal gas is predicted to have zero volume. (Of course, the gas will liquefy before this temperature is reached, and Charles' law will no longer be obeyed.)

As noted, all gases have the same temperature-versus-volume behavior in the zero-pressure limit. Therefore, to get a temperature scale that is independent of the properties of any one substance, we shall define an ideal-gas temperature scale T by the requirement that the T-versus-V behavior of a gas be exactly linear (that is, obey Charles' law exactly) in the limit of zero pressure. Moreover, because it seems likely that the temperature at which an ideal gas is predicted to have zero volume might well have fundamental significance, we shall take the zero of our ideal-gas temperature scale to coincide with the zero-volume temperature. We therefore define the **absolute ideal-gas temperature** T by the requirement that the relation $T \equiv BV$ shall hold exactly in the zero-pressure limit, where B is a constant for a fixed amount of gas at constant P, and where V is the gas volume. Any gas can be used.

To complete the definition, we specify B by picking a fixed reference point and assigning its temperature. In 1954 it was internationally agreed to use the triple point (tr) of water as the reference point and to define the absolute temperature T_{tr} at this triple point as exactly 273.16 K. The K stands for the unit of absolute temperature, the **kelvin,** formerly called the degree Kelvin (°K). (The water *triple point* is the temperature at which pure liquid water, ice, and water vapor are in mutual equilibrium.) At the water triple point, we have $273.16\text{ K} \equiv T_{\text{tr}} = BV_{\text{tr}}$, and $B = (273.16\text{ K})/V_{\text{tr}}$, where V_{tr} is the gas volume at T_{tr}. Therefore the equation $T \equiv BV$ defining the absolute ideal-gas temperature scale becomes

$$T \equiv (273.16\text{ K}) \lim_{P \to 0} \frac{V}{V_{\text{tr}}} \qquad \text{const. } P, m \tag{1.15}$$

How is the limit $P \to 0$ taken in (1.15)? One takes a fixed quantity of gas at some pressure P, say 200 torr. This gas is put in thermal equilibrium with the body whose temperature T is to be measured, keeping P constant at 200 torr and measuring the volume V of the gas. The gas thermometer is then put in thermal equilibrium with a water triple-point cell at 273.16 K, keeping P of the gas at 200 torr and measuring V_{tr}. The ratio V/V_{tr} is then calculated for $P = 200$ torr. Next, the gas pressure is reduced to, say, 150 torr, and the gas volume at this pressure is measured at temperature T and at 273.16 K; this gives the ratio V/V_{tr} at $P = 150$ torr. The operations are repeated at successively lower pressures to give further ratios V/V_{tr}. These ratios are then plotted against P, and the curve is extrapolated to $P = 0$ to give the limit of V/V_{tr} (see Fig. 1.9). Multiplication of this limit by 273.16 K then gives the ideal-gas absolute temperature T of the body. In practice, a constant-volume gas thermometer is easier to use than a constant-pressure one; here, V/V_{tr} at constant P in (1.15) is replaced by P/P_{tr} at constant V.

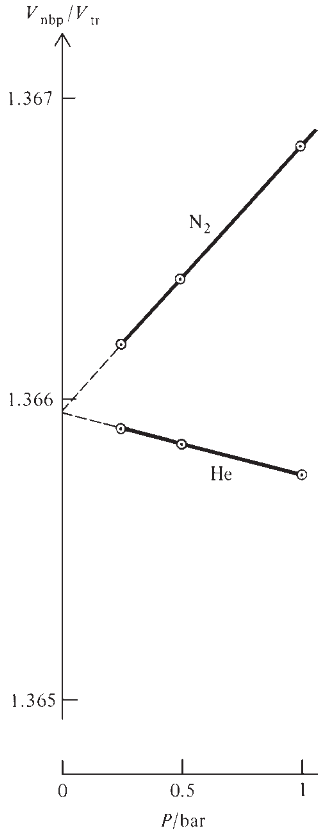


Figure 1.9

Constant-pressure gas thermometer plots to measure the normal boiling point (nbp) of H_2O. Extrapolation gives $V_{\text{nbp}}/V_{\text{tr}} = 1.36595_5$, so $T_{\text{nbp}} = 1.36595_5(273.16\text{ K}) = 373.124\text{ K} = 99.974°\text{C}$.

Accurate measurement of a body's temperature with an ideal-gas thermometer is tedious, and this thermometer is not useful for day-to-day laboratory work. What is done instead is to use an ideal-gas thermometer to determine accurate values for several fixed points that cover a wide temperature range. The fixed points are triple points and normal melting points of certain pure substances (for example, O_2, Ar, Zn, Ag). The specified values for these fixed points, together with specified interpolation formulas that use platinum resistance thermometers for temperatures between the fixed points, constitute the International Temperature Scale of 1990 (ITS-90). The ITS-90 scale is designed to reproduce the ideal-gas absolute scale within experimental error and is used to calibrate laboratory thermometers. Details of ITS-90 are given in B. W. Mangum, *J. Res. Natl. Inst. Stand. Technol.,* **95,** 69 (1990); *Quinn,* sec. 2-12 and appendix II.

Since the ideal-gas temperature scale is independent of the properties of any one substance, it is superior to the mercury centigrade scale defined in Sec. 1.3. However, the ideal-gas scale still depends on the limiting properties of *gases.* The thermodynamic temperature scale, defined in Sec. 3.6, is independent of the properties of any particular kind of matter. For now we shall use the ideal-gas scale.

The present definition of the **Celsius** (centigrade) **scale** t is in terms of the ideal-gas absolute temperature scale T as follows:

$$t/°\mathrm{C} \equiv T/\mathrm{K} - 273.15 \qquad \textbf{(1.16)}^*$$

For the water triple-point Celsius temperature t_{tr}, we have $t_{\mathrm{tr}}/°\mathrm{C} = (273.16\ \mathrm{K})/\mathrm{K} - 273.15 = 0.01$, so t_{tr} is exactly 0.01°C. On the present Celsius and Kelvin scales, the ice and steam points (Sec. 1.3) are not fixed but are determined by experiment, and there is no guarantee that these points will be at 0°C and 100°C. However, the value 273.16 K for the water triple point and the number 273.15 in (1.16) were chosen to give good agreement with the old centigrade scale, so we expect the ice and steam points to be little changed from their old values. Experiment gives 0.00009°C for the ice point and for the steam point gives 99.984°C on the thermodynamic scale and 99.974°C on the ITS-90 scale.

Since the absolute ideal-gas temperature scale is based on the properties of a general class of substances (gases in the zero-pressure limit, where intermolecular forces vanish), one might suspect that this scale has fundamental significance. This is true, and we shall see in Eqs. (14.14) and (14.15) that the average kinetic energy of motion of molecules through space in a gas is directly proportional to the absolute temperature T. Moreover, the absolute temperature T appears in a simple way in the law that governs the distribution of molecules among energy levels; see Eq. (21.69), the Boltzmann distribution law.

From Eq. (1.15), at constant P and m we have $V/T = V_{\mathrm{tr}}/T_{\mathrm{tr}}$. This equation holds exactly only in the limit of zero pressure but is pretty accurate provided the pressure is not too high. Since $V_{\mathrm{tr}}/T_{\mathrm{tr}}$ is a constant for a fixed amount of gas at fixed P, we have

$$V/T = K \qquad \text{const. } P, m$$

where K is a constant. This is Charles' law. However, logically speaking, this equation is not a law of nature but simply embodies the *definition* of the ideal-gas absolute temperature scale T. After defining the thermodynamic temperature scale, we can once again view $V/T = K$ as a law of nature.

The General Ideal-Gas Equation

Boyle's and Charles' laws apply when T and m or P and m are held fixed. Now consider a more general change in state of an ideal gas, in which the pressure, volume, and temperature all change, going from P_1, V_1, T_1 to P_2, V_2, T_2, with m unchanged. To apply Boyle's and Charles' laws, we imagine this process to be carried out in two steps:

$$P_1,\ V_1,\ T_1 \xrightarrow{(a)} P_2,\ V_a,\ T_1 \xrightarrow{(b)} P_2,\ V_2,\ T_2$$

Since T and m are constant in step (*a*), Boyle's law applies and $P_1V_1 = k = P_2V_a$; hence $V_a = P_1V_1/P_2$. Use of Charles' law for step (*b*) gives $V_a/T_1 = V_2/T_2$. Substitution of $V_a = P_1V_1/P_2$ into this equation gives $P_1V_1/P_2T_1 = V_2/T_2$, and

$$P_1V_1/T_1 = P_2V_2/T_2 \qquad \text{const. } m, \text{ ideal gas} \qquad (1.17)$$

What happens if we vary the mass m of ideal gas while keeping P and T constant? Volume is an extensive quantity, so V is directly proportional to m for any one-phase, one-component system at constant T and P. Thus V/m is constant at constant T and P. Combining this fact with the constancy of PV/T at constant m, we readily find (Prob. 1.24) that PV/mT remains constant for any variation in P, V, T, and m of any pure ideal gas: $PV/mT = c$, where c is a constant. There is no reason for c to be the same for different ideal gases, and in fact it is not. To obtain a form of the ideal-gas law that has the same constant for every ideal gas, we need another experimental observation.

In 1808 Gay-Lussac noted that the ratios of volumes of gases that react with one another involve small whole numbers when these volumes are measured at the same temperature and pressure. For example, one finds that two liters of hydrogen gas react with one liter of oxygen gas to form water. This reaction is $2H_2 + O_2 \rightarrow 2H_2O$, so the number of hydrogen molecules reacting is twice the number of oxygen molecules reacting. The two liters of hydrogen must then contain twice the number of molecules as does the one liter of oxygen, and therefore one liter of hydrogen will have the same number of molecules as one liter of oxygen at the same temperature and pressure. The same result is obtained for other gas-phase reactions. We conclude that equal volumes of different gases at the same temperature and pressure contain equal numbers of molecules. This idea was first recognized by Avogadro in 1811. (Gay-Lussac's law of combining volumes and Avogadro's hypothesis are strictly true for real gases only in the limit $P \rightarrow 0$.) Since the number of molecules is proportional to the number of moles, Avogadro's hypothesis states that equal volumes of different gases at the same T and P have equal numbers of moles.

Since the mass of a pure gas is proportional to the number of moles, the ideal-gas law $PV/mT = c$ can be rewritten as $PV/nT = R$ or $n = PV/RT$, where n is the number of moles of gas and R is some other constant. Avogadro's hypothesis says that, if P, V, and T are the same for two different gases, then n must be the same. But this can hold true only if R has the same value for every gas. R is therefore a universal constant, called the **gas constant.** The final form of the ideal-gas law is

$$PV = nRT \qquad \text{ideal gas} \qquad \textbf{(1.18)*}$$

Equation (1.18) incorporates Boyle's law, Charles' law (more accurately, the definition of T), and Avogadro's hypothesis.

An **ideal gas** is a gas that obeys $PV = nRT$. Real gases obey this law only in the limit of zero density, where intermolecular forces are negligible.

Using $M \equiv m/n$ [Eq. (1.4)] to introduce the molar mass M of the gas, we can write the ideal-gas law as

$$PV = mRT/M \qquad \text{ideal gas}$$

This form enables us to find the molecular weight of a gas by measuring the volume occupied by a known mass at a known T and P. For accurate results, one does a series of measurements at different pressures and extrapolates the results to zero pressure (see Prob. 1.21). We can also write the ideal-gas law in terms of the density $\rho = m/V$ as

$$P = \rho RT/M \qquad \text{ideal gas}$$

The only form worth remembering is $PV = nRT$, since all other forms are easily derived from this one.

The gas constant R can be evaluated by taking a known number of moles of some gas held at a known temperature and carrying out a series of pressure–volume measurements at successively lower pressures. Evaluation of the zero-pressure limit of PV/nT then gives R (Prob. 1.20). The experimental result is

$$R = 82.06\ (\text{cm}^3\ \text{atm})/(\text{mol K}) \qquad \textbf{(1.19)*}$$

Since 1 atm = 101325 N/m^2 [Eq. (1.10)], we have 1 cm^3 atm = $(10^{-2}\text{ m})^3 \times 101325$ N/m^2 = 0.101325 m^3 N/m^2 = 0.101325 J. [One newton-meter = one joule (J); see Sec. 2.1.] Hence $R = 82.06 \times 0.101325$ J/(mol K), or

$$R = 8.314_5 \text{ J/(mol K)} = 8.314_5 \text{ (m}^3\text{ Pa)/(mol K)} \qquad \textbf{(1.20)*}$$

Using 1 atm = 760 torr and 1 bar ≈ 750 torr, we find from (1.19) that $R = 83.14_5$ (cm^3 bar)/(mol K). Using 1 calorie (cal) = 4.184 J [Eq. (2.44)], we find

$$R = 1.987 \text{ cal/(mol K)} \qquad \textbf{(1.21)*}$$

Accurate values of physical constants are listed inside the back cover.

Ideal Gas Mixtures

So far, we have considered only a pure ideal gas. In 1810 Dalton found that the pressure of a mixture of gases equals the sum of the pressures each gas would exert if placed alone in the container. (This law is exact only in the limit of zero pressure.) If n_1 moles of gas 1 is placed alone in the container, it would exert a pressure n_1RT/V (where we assume the pressure low enough for the gas to behave essentially ideally). Dalton's law asserts that the pressure in the gas mixture is $P = n_1RT/V + n_2RT/V + \cdots = (n_1 + n_2 + \cdots)RT/V = n_{\text{tot}}RT/V$, so

$$PV = n_{\text{tot}}RT \qquad \text{ideal gas mixture} \qquad \textbf{(1.22)*}$$

Dalton's law makes sense from the molecular picture of gases. Ideal-gas molecules do not interact with one another, so the presence of gases 2, 3, . . . has no effect on gas 1, and its contribution to the pressure is the same as if it alone were present. Each gas acts independently, and the pressure is the sum of the individual contributions. For real gases, the intermolecular interactions in a mixture differ from those in a pure gas, and Dalton's law does not hold accurately.

The **partial pressure** P_i of gas i in a gas mixture (ideal or nonideal) is defined as

$$P_i \equiv x_iP \qquad \text{any gas mixture} \qquad \textbf{(1.23)*}$$

where $x_i = n_i/n_{\text{tot}}$ is the mole fraction of i in the mixture and P is the mixture's pressure. For an ideal gas mixture, $P_i = x_iP = (n_i/n_{\text{tot}})(n_{\text{tot}}RT/V)$ and

$$P_i = n_iRT/V \qquad \text{ideal gas mixture} \qquad \textbf{(1.24)*}$$

The quantity n_iRT/V is the pressure that gas i of the mixture would exert if it alone were present in the container. However, for a nonideal gas mixture, the partial pressure P_i as defined by (1.23) is not necessarily equal to the pressure that gas i would exert if it alone were present.

EXAMPLE 1.1 Density of an ideal gas

Find the density of F_2 gas at 20.0°C and 188 torr.

The unknown is the density ρ, and it is often a good idea to start by writing the definition of what we want to find: $\rho \equiv m/V$. Neither m nor V is given, so we seek to relate these quantities to the given information. The system is a gas at a relatively low pressure, and it is a good approximation to treat it as an ideal gas. For an ideal gas, we know that $V = nRT/P$. Substitution of $V = nRT/P$ into $\rho = m/V$ gives $\rho = mP/nRT$. In this expression for ρ, we know P and T but not m or n. However, we recognize that the ratio m/n is the mass per mole, that is, the molar mass M. Thus $\rho = MP/RT$. This expression contains only known quantities, so we are ready to substitute in numbers. The molecular weight of F_2 is 38.0, and its molar mass is $M = 38.0$ g/mol. The absolute temperature is $T = 20.0° + 273.15° = 293.2$ K. Since we know a value of R involving atmospheres, we convert P to atmospheres: $P = (188 \text{ torr}) (1 \text{ atm}/760 \text{ torr}) = 0.247$ atm. Then

$$\rho = \frac{MP}{RT} = \frac{(38.0 \text{ g mol}^{-1})(0.247 \text{ atm})}{(82.06 \text{ cm}^3 \text{ atm mol}^{-1} \text{ K}^{-1})(293.2 \text{ K})} = 3.90 \times 10^{-4} \text{ g/cm}^3$$

Note that the units of temperature, pressure, and amount of substance (moles) canceled. The fact that we ended up with units of grams per cubic centimeter, which is a correct unit for density, provides a check on our work. *It is strongly recommended that the units of every physical quantity be written down when doing calculations.*

Exercise

Find the molar mass of a gas whose density is 1.80 g/L at 25.0°C and 880 torr. (*Answer:* 38.0 g/mol.)

1.6 DIFFERENTIAL CALCULUS

Physical chemistry uses calculus extensively. We therefore review some ideas of differential calculus. (In the novel *Arrowsmith,* Max Gottlieb asks Martin Arrowsmith, "How can you know physical chemistry without much mathematics?")

Functions and Limits

To say that the variable y is a **function** of the variable x means that for any given value of x there is specified a value of y; we write $y = f(x)$. For example, the area of a circle is a function of its radius r, since the area can be calculated from r by the expression πr^2. The variable x is called the *independent variable* or the *argument* of the function f, and y is the *dependent variable.* Since we can solve for x in terms of y to get $x = g(y)$, it is a matter of convenience which variable is considered to be the independent one. Instead of $y = f(x)$, one often writes $y = y(x)$.

To say that the **limit** of the function $f(x)$ as x approaches the value a is equal to c [which is written as $\lim_{x\to a} f(x) = c$] means that for all values of x sufficiently close to a (but *not* necessarily equal to a) the difference between $f(x)$ and c can be made as small as we please. For example, suppose we want the limit of $(\sin x)/x$ as x goes to zero. Note that $(\sin x)/x$ is undefined at $x = 0$, since 0/0 is undefined. However, this fact is irrelevant to determining the limit. To find the limit, we calculate the following values of $(\sin x)/x$, where x is in radians: 0.99833 for $x = \pm 0.1$, 0.99958 for $x = \pm 0.05$, 0.99998 for $x = \pm 0.01$, etc. Therefore

$$\lim_{x\to 0} \frac{\sin x}{x} = 1$$

Of course, this isn't a rigorous proof. Note the resemblance to taking the limit as $P \to 0$ in Eq. (1.15); in this limit both V and V_{tr} become infinite as P goes to zero, but the limit has a well-defined value even though ∞/∞ is undefined.

Slope

The **slope** of a straight-line graph, where y is plotted on the vertical axis and x on the horizontal axis, is defined as $(y_2 - y_1)/(x_2 - x_1) = \Delta y/\Delta x$, where (x_1, y_1) and (x_2, y_2) are the coordinates of any two points on the graph, and Δ (capital delta) denotes the change in a variable. If we write the equation of the straight line in the form $y = mx + b$, it follows from this definition that the line's slope equals m. The **intercept** of the line on the y axis equals b, since $y = b$ when $x = 0$.

The **slope** of any curve at some point P is defined to be the slope of the straight line tangent to the curve at P. For an example of finding a slope, see Fig. 9.3. Students sometimes err in finding a slope by trying to evaluate $\Delta y/\Delta x$ by counting boxes on the graph paper, forgetting that the scale of the y axis usually differs from that of the x axis in physical applications.

In physical chemistry, one often wants to define new variables to convert an equation to the form of a straight line. One then plots the experimental data using the new variables and uses the slope or intercept of the line to determine some quantity.

EXAMPLE 1.2 Converting an equation to linear form

According to the Arrhenius equation (16.66), the rate coefficient k of a chemical reaction varies with absolute temperature according to the equation $k = Ae^{-E_a/RT}$, where A and E_a are constants and R is the gas constant. Suppose we have measured values of k at several temperatures. Transform the Arrhenius equation to the form of a straight-line equation whose slope and intercept will enable A and E_a to be found.

The variable T appears as part of an exponent. By taking the logs of both sides, we eliminate the exponential. Taking the natural logarithm of each side of $k = Ae^{-E_a/RT}$, we get $\ln k = \ln(Ae^{-E_a/RT}) = \ln A + \ln(e^{-E_a/RT}) = \ln A - E_a/RT$, where Eq. (1.67) was used. To convert the equation $\ln k = \ln A - E_a/RT$ to a straight-line form, we define new variables in terms of the original variables k and T as follows: $y \equiv \ln k$ and $x \equiv 1/T$. This gives $y = (-E_a/R)x + \ln A$. Comparison with $y = mx + b$ shows that a plot of $\ln k$ on the y axis versus $1/T$ on the x axis will have slope $-E_a/R$ and intercept $\ln A$. From the slope and intercept of such a graph, E_a and A can be calculated.

Exercise

The moles n of a gas adsorbed divided by the mass m of a solid adsorbent often varies with gas pressure P according to $n/m = aP/(1 + bP)$, where a and b are constants. Convert this equation to a straight-line form, state what should be plotted versus what, and state how the slope and intercept are related to a and b. (*Hint:* Take the reciprocal of each side.)

Derivatives

Let $y = f(x)$. Let the independent variable change its value from x to $x + h$; this will change y from $f(x)$ to $f(x + h)$. The average rate of change of y with x over this interval equals the change in y divided by the change in x and is

$$\frac{\Delta y}{\Delta x} = \frac{f(x+h) - f(x)}{(x+h) - x} = \frac{f(x+h) - f(x)}{h}$$

The *instantaneous* rate of change of y with x is the limit of this average rate of change taken as the change in x goes to zero. The instantaneous rate of change is called the **derivative** of the function f and is symbolized by f':

$$f'(x) \equiv \lim_{h\to 0} \frac{f(x+h) - f(x)}{h} = \lim_{\Delta x \to 0} \frac{\Delta y}{\Delta x} \qquad \textbf{(1.25)*}$$

Figure 1.10 shows that *the derivative of the function $y = f(x)$ at a given point is equal to the slope of the curve of y versus x at that point.*

As a simple example, let $y = x^2$. Then

$$f'(x) = \lim_{h\to 0} \frac{(x+h)^2 - x^2}{h} = \lim_{h\to 0} \frac{2xh + h^2}{h} = \lim_{h\to 0} (2x + h) = 2x$$

The derivative of x^2 is $2x$.

A function that has a sudden jump in value at a certain point is said to be **discontinuous** at that point. An example is shown in Fig. 1.11*a*. Consider the function $y = |x|$, whose graph is shown in Fig. 1.11*b*. This function has no jumps in value anywhere and so is everywhere **continuous.** However, the slope of the curve changes suddenly at $x = 0$. Therefore, the derivative y' is discontinuous at this point; for negative x the function y equals $-x$ and y' equals -1, whereas for positive x the function y equals x and y' equals $+1$.

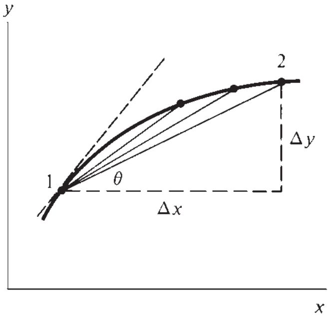


Figure 1.10

As point 2 approaches point 1, the quantity $\Delta y/\Delta x = \tan\theta$ approaches the slope of the tangent to the curve at point 1.

Since $f'(x)$ is defined as the limit of $\Delta y/\Delta x$ as Δx goes to zero, we know that, for small changes in x and y, the derivative $f'(x)$ will be approximately equal to $\Delta y/\Delta x$. Thus $\Delta y \approx f'(x)\,\Delta x$ for Δx small. This equation becomes more and more accurate as Δx gets smaller. We can conceive of an infinitesimally small change in x, which we symbolize by dx. Denoting the corresponding infinitesimally small change in y by dy, we have $dy = f'(x)\,dx$, or

$$dy = y'(x)\,dx \qquad \textbf{(1.26)*}$$

The quantities dy and dx are called **differentials.** Equation (1.26) gives the alternative notation dy/dx for a derivative. Actually, the rigorous mathematical definition of dx and dy does not require these quantities to be infinitesimally small; instead they can be of any magnitude. (See any calculus text.) However, in our applications of calculus to thermodynamics, we shall always conceive of dy and dx as infinitesimal changes.

Let a and n be constants, and let u and v be functions of x; $u = u(x)$ and $v = v(x)$. Using the definition (1.25), one finds the following derivatives:

$$\frac{da}{dx} = 0, \qquad \frac{d(au)}{dx} = a\frac{du}{dx}, \qquad \frac{d(x^n)}{dx} = nx^{n-1}, \qquad \frac{d(e^{ax})}{dx} = ae^{ax}$$

$$\frac{d\ln ax}{dx} = \frac{1}{x}, \qquad \frac{d\sin ax}{dx} = a\cos ax, \qquad \frac{d\cos ax}{dx} = -a\sin ax$$

$$\frac{d(u+v)}{dx} = \frac{du}{dx} + \frac{dv}{dx}, \qquad \frac{d(uv)}{dx} = u\frac{dv}{dx} + v\frac{du}{dx} \qquad \textbf{(1.27)*}$$

$$\frac{d(u/v)}{dx} = \frac{d(uv^{-1})}{dx} = -uv^{-2}\frac{dv}{dx} + v^{-1}\frac{du}{dx}$$

The chain rule is often used to find derivatives. Let z be a function of x, where x is a function of r; $z = z(x)$, where $x = x(r)$. Then z can be expressed as a function of r; $z = z(x) = z[x(r)] = g(r)$, where g is some function. The *chain rule* states that $dz/dr = (dz/dx)\,(dx/dr)$. For example, suppose we want $(d/dr)\sin 3r^2$. Let $z = \sin x$ and $x = 3r^2$. Then $z = \sin 3r^2$, and the chain rule gives $dz/dr = (\cos x)\,(6r) = 6r\cos 3r^2$.

Equations (1.26) and (1.27) give the following formulas for differentials:

$$d(x^n) = nx^{n-1}\,dx, \qquad d(e^{ax}) = ae^{ax}\,dx$$

$$d(au) = a\,du, \qquad d(u+v) = du + dv, \qquad d(uv) = u\,dv + v\,du \qquad \textbf{(1.28)*}$$

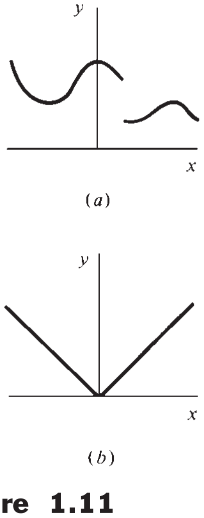


Figure 1.11

(*a*) A discontinuous function.
(*b*) The function $y = |x|$.

We often want to find a maximum or minimum of some function $y(x)$. For a function with a continuous derivative, the slope of the curve is zero at a maximum or minimum point (Fig. 1.12). Hence to locate an extremum, we look for the points where $dy/dx = 0$.

The function dy/dx is the first derivative of y. The **second derivative** d^2y/dx^2 is defined as the derivative of the first derivative: $d^2y/dx^2 \equiv d(dy/dx)/dx$.

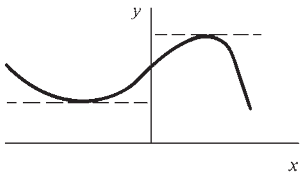


Figure 1.12

Horizontal tangent at maximum and minimum points.

Partial Derivatives

In thermodynamics we usually deal with functions of two or more variables. Let z be a function of x and y; $z = f(x, y)$. We define the **partial derivative** of z with respect to x as

$$\left(\frac{\partial z}{\partial x}\right)_y \equiv \lim_{\Delta x \to 0} \frac{f(x + \Delta x, y) - f(x, y)}{\Delta x} \tag{1.29}$$

This definition is analogous to the definition (1.25) of the ordinary derivative, in that if y were a constant instead of a variable, the partial derivative $(\partial z/\partial x)_y$ would become just the ordinary derivative dz/dx. The variable being held constant in a partial derivative is often omitted and $(\partial z/\partial x)_y$ written simply as $\partial z/\partial x$. In thermodynamics there are many possible variables, and to avoid confusion it is essential to show which variables are being held constant in a partial derivative. The partial derivative of z with respect to y at constant x is defined similarly to (1.29):

$$\left(\frac{\partial z}{\partial y}\right)_x \equiv \lim_{\Delta y \to 0} \frac{f(x, y + \Delta y) - f(x, y)}{\Delta y}$$

There may be more than two independent variables. For example, let $z = g(w, x, y)$. The partial derivative of z with respect to x at constant w and y is

$$\left(\frac{\partial z}{\partial x}\right)_{w,y} \equiv \lim_{\Delta x \to 0} \frac{g(w, x + \Delta x, y) - g(w, x, y)}{\Delta x}$$

How are partial derivatives found? To find $(\partial z/\partial x)_y$ we take the ordinary derivative of z with respect to x while regarding y as a constant. For example, if $z = x^2y^3 + e^{yx}$, then $(\partial z/\partial x)_y = 2xy^3 + ye^{yx}$; also, $(\partial z/\partial y)_x = 3x^2y^2 + xe^{yx}$.

Let $z = f(x, y)$. Suppose x changes by an infinitesimal amount dx while y remains constant. What is the infinitesimal change dz in z brought about by the infinitesimal change in x? If z were a function of x only, then [Eq. (1.26)] we would have $dz = (dz/dx)\,dx$. Because z depends on y also, the infinitesimal change in z at constant y is given by the analogous equation $dz = (\partial z/\partial x)_y\,dx$. Similarly, if y were to undergo an infinitesimal change dy while x were held constant, we would have $dz = (\partial z/\partial y)_x\,dy$. If now both x and y undergo infinitesimal changes, the infinitesimal change in z is the sum of the infinitesimal changes due to dx and dy:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag*{\textbf{(1.30)*}}$$

In this equation, dz is called the **total differential** of $z(x, y)$. Equation (1.30) is often used in thermodynamics. An analogous equation holds for the total differential of a function of more than two variables. For example, if $z = z(r, s, t)$, then

$$dz = \left(\frac{\partial z}{\partial r}\right)_{s,t} dr + \left(\frac{\partial z}{\partial s}\right)_{r,t} ds + \left(\frac{\partial z}{\partial t}\right)_{r,s} dt$$

Three useful partial-derivative identities can be derived from (1.30). For an infinitesimal process in which y does not change, the infinitesimal change dy is 0, and (1.30) becomes

$$dz_y = \left(\frac{\partial z}{\partial x}\right)_y dx_y \tag{1.31}$$

where the y subscripts on dz and dx indicate that these infinitesimal changes occur at constant y. Division by dz_y gives

$$1 = \left(\frac{\partial z}{\partial x}\right)_y \frac{dx_y}{dz_y} = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y$$

since from the definition of the partial derivative, the ratio of infinitesimals dx_y/dz_y equals $(\partial x/\partial z)_y$. Therefore

$$\left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{(\partial x/\partial z)_y} \qquad \textbf{(1.32)*}$$

Note that the same variable, y, is being held constant in both partial derivatives in (1.32). When y is held constant, there are only two variables, x and z, and you will probably recall that $dz/dx = 1/(dx/dz)$.

For an infinitesimal process in which z stays constant, Eq. (1.30) becomes

$$0 = \left(\frac{\partial z}{\partial x}\right)_y dx_z + \left(\frac{\partial z}{\partial y}\right)_x dy_z \qquad (1.33)$$

Dividing by dy_z and recognizing that dx_z/dy_z equals $(\partial x/\partial y)_z$, we get

$$0 = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x \quad \text{and} \quad \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x = -\frac{1}{(\partial y/\partial z)_x}$$

where (1.32) with x and y interchanged was used. Multiplication by $(\partial y/\partial z)_x$ gives

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \qquad \textbf{(1.34)*}$$

Equation (1.34) looks intimidating but is actually easy to remember because of the simple pattern of variables: $\partial x/\partial y$, $\partial y/\partial z$, $\partial z/\partial x$; the variable held constant in each partial derivative is the one that doesn't appear in that derivative.

Sometimes students wonder why the ∂y's, ∂z's, and ∂x's in (1.34) don't cancel to give $+1$ instead of -1. One can cancel ∂y's etc. only when the same variable is held constant in each partial derivative. The infinitesimal change dy_z in y with z held constant while x varies is not the same as the infinitesimal change dy_x in y with x held constant while z varies. [Note that (1.32) can be written as $(\partial z/\partial x)_y(\partial x/\partial z)_y = 1$; here, cancellation occurs.]

Finally, let dy in (1.30) be zero so that (1.31) holds. Let u be some other variable. Division of (1.31) by du_y gives

$$\frac{dz_y}{du_y} = \left(\frac{\partial z}{\partial x}\right)_y \frac{dx_y}{du_y}$$

$$\left(\frac{\partial z}{\partial u}\right)_y = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial u}\right)_y \qquad \textbf{(1.35)*}$$

The ∂x's in (1.35) can be canceled because the same variable is held constant in each partial derivative.

A function of two independent variables $z(x, y)$ has the following four second partial derivatives:

$$\left(\frac{\partial^2 z}{\partial x^2}\right)_y \equiv \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial x}\right)_y\right]_y, \qquad \left(\frac{\partial^2 z}{\partial y^2}\right)_x \equiv \left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial y}\right)_x\right]_x$$

$$\frac{\partial^2 z}{\partial x\, \partial y} \equiv \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y, \qquad \frac{\partial^2 z}{\partial y\, \partial x} \equiv \left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x$$

Provided $\partial^2 z/(\partial x\,\partial y)$ and $\partial^2 z/(\partial y\,\partial x)$ are continuous, as is generally true in physical applications, one can show that they are equal (see any calculus text):

$$\frac{\partial^2 z}{\partial x\,\partial y} = \frac{\partial^2 z}{\partial y\,\partial x} \qquad \textbf{(1.36)*}$$

The order of partial differentiation is immaterial.

Fractions are sometimes written with a slant line. The convention is that

$$a/bc + d \equiv \frac{a}{bc} + d$$

1.7 EQUATIONS OF STATE

Experiment generally shows the thermodynamic state of a homogeneous system with a fixed composition to be specified when the two variables P and T are specified. If the thermodynamic state is specified, this means the volume V of the system is specified. Given values of P and T of a fixed-composition system, the value of V is determined. But this is exactly what is meant by the statement that V is a function of P and T. Therefore, $V = u(P, T)$, where u is a function that depends on the nature of the system. If the restriction of fixed composition is dropped, the state of the system will depend on its composition as well as on P and T. We then have

$$V = f(P, T, n_1, n_2, \ldots) \qquad (1.37)$$

where $n_1, n_2, \ldots$ are the numbers of moles of substances 1, 2, . . . in the homogeneous system and f is some function. This relation between P, T, $n_1, n_2, \ldots$, and V is called a **volumetric equation of state,** or, more simply, an **equation of state.** If the system is heterogeneous, each phase will have its own equation of state.

For a one-phase system composed of n moles of a single pure substance, the equation of state (1.37) becomes $V = f(P, T, n)$, where the function f depends on the nature of the system; f for liquid water differs from f for ice and from f for liquid benzene. Of course, we can solve the equation of state for P or for T to get the alternative form $P = g(V, T, n)$ or $T = h(P, V, n)$, where g and h are certain functions. The laws of thermodynamics are general and cannot be used to deduce equations of state for particular systems. Equations of state must be determined experimentally. One can also use statistical mechanics to deduce an approximate equation of state starting from some assumed form for the intermolecular interactions in the system.

An example of an equation of state is $PV = nRT$, the equation of state of an ideal gas. In reality, no gas obeys this equation of state.

The volume of a one-phase, one-component system is clearly proportional to the number of moles n present at any given T and P. Therefore the equation of state for any pure one-phase system can be written in the form

$$V = nk(T, P)$$

where the function k depends on what substance is being considered. Since we usually deal with closed systems (n fixed), it is convenient to eliminate n and write the equation of state using only intensive variables. To this end, we define the **molar volume** V_m of any pure, one-phase system as the volume per mole:

$$V_m \equiv V/n \qquad \textbf{(1.38)*}$$

V_m is a function of T and P; $V_m = k(T, P)$. For an ideal gas, $V_m = RT/P$. The m subscript in V_m is sometimes omitted when it is clear that a molar volume is meant. (A commonly used alternative symbol for V_m is $\bar{V}$.)

For any extensive property of a pure one-phase system, we can define a corresponding molar quantity. For example, the molar mass of a substance is m/n [Eq. (1.4)].

What about equations of state for real gases? We shall see in Chapter 14 that ignoring forces between the molecules leads to the ideal-gas equation of state $PV = nRT$. Actually, molecules initially attract each other as they approach and then repel each other when they collide. To allow for intermolecular forces, van der Waals in 1873 modified the ideal-gas equation to give the **van der Waals equation**

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \tag{1.39}$$

Each gas has its own a and b values. Determination of a and b from experimental data is discussed in Sec. 8.4, which lists some a and b values. Subtraction of nb from V corrects for intermolecular repulsion. Because of this repulsion, the volume available to the gas molecules is less than the volume V of the container. The constant b is approximately the volume of one mole of the gas molecules themselves. (In a liquid, the molecules are quite close together, so b is roughly the same as the molar volume of the liquid.) The term an^2/V^2 allows for intermolecular attraction. These attractions tend to make the pressure exerted by the gas [given by the van der Waals equation as $P = nRT/(V - nb) - an^2/V^2$] less than that predicted by the ideal-gas equation. The parameter a is a measure of the strength of the intermolecular attraction; b is a measure of molecular size.

For most liquids and solids at ordinary temperatures and pressures, an approximate equation of state is

$$V_{\text{m}} = c_1 + c_2T + c_3T^2 - c_4P - c_5PT \tag{1.40}$$

where $c_1, \ldots, c_5$ are positive constants that must be evaluated by fitting observed V_{m} versus T and P data. The term c_1 is much larger than each of the other terms, so V_{m} of the liquid or solid changes only slowly with T and P. In most work with solids or liquids, the pressure remains close to 1 atm. In this case, the terms involving P can be neglected to give $V_{\text{m}} = c_1 + c_2T + c_3T^2$. This equation is often written in the form $V_{\text{m}} = V_{\text{m},0}(1 + At + Bt^2)$, where $V_{\text{m},0}$ is the molar volume at 0°C and t is the Celsius temperature. Values of the constants A and B are tabulated in handbooks. The terms $c_2T + c_3T^2$ in (1.40) indicate that V_{m} usually increases as T increases. The terms $-c_4P - c_5PT$ indicate that V_{m} decreases as P increases.

For a single-phase, pure, closed system, the equation of state of the system can be written in the form $V_{\text{m}} = k(T, P)$. One can make a three-dimensional plot of the equation of state by plotting P, T, and V_{m} on the x, y, and z axes. Each possible state of the system gives a point in space, and the locus of all such points gives a surface whose equation is the equation of state. Figure 1.13 shows the equation-of-state surface for an ideal gas.

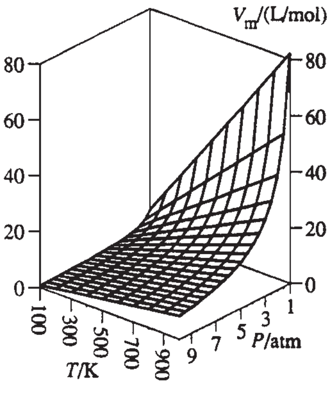


Figure 1.13

Equation-of-state surface for an ideal gas.

If we hold one of the three variables constant, we can make a two-dimensional plot. For example, holding T constant at the value T_1, we have $PV_{\text{m}} = RT_1$ as the equation of state of an ideal gas. An equation of the form $xy =$ constant gives a hyperbola when plotted. Choosing other values of T, we get a series of hyperbolas (Fig. 1.6*a*). The lines of constant temperature are called **isotherms,** and a constant-temperature process is called an **isothermal process.** We can also hold either P or V_{m} constant and plot **isobars** (P constant) or *isochores* (V_{m} constant).

Figure 1.14 shows some isotherms and isobars of liquid water.

We shall find that thermodynamics enables us to relate many thermodynamic properties of substances to partial derivatives of P, V_{m}, and T with respect to one another. This is useful because these partial derivatives can be readily measured. There are six such partial derivatives:

$$\left(\frac{\partial V_{\text{m}}}{\partial T}\right)_P, \quad \left(\frac{\partial V_{\text{m}}}{\partial P}\right)_T, \quad \left(\frac{\partial P}{\partial V_{\text{m}}}\right)_T, \quad \left(\frac{\partial P}{\partial T}\right)_{V_{\text{m}}}, \quad \left(\frac{\partial T}{\partial V_{\text{m}}}\right)_P, \quad \left(\frac{\partial T}{\partial P}\right)_{V_{\text{m}}}$$

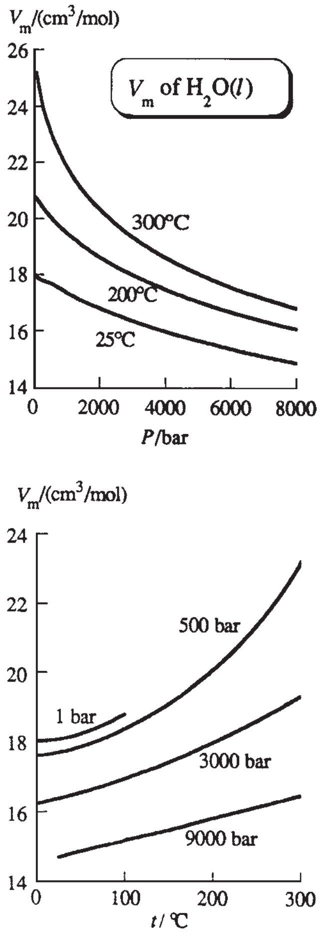


Figure 1.14

Molar volume of $H_2O(l)$ plotted versus P and versus T.

The relation $(\partial z/\partial x)_y = 1/(\partial x/\partial z)_y$ [Eq. (1.32)] shows that three of these six are the reciprocals of the other three:

$$\left(\frac{\partial T}{\partial P}\right)_{V_m} = \frac{1}{(\partial P/\partial T)_{V_m}}, \qquad \left(\frac{\partial T}{\partial V_m}\right)_P = \frac{1}{(\partial V_m/\partial T)_P}, \qquad \left(\frac{\partial P}{\partial V_m}\right)_T = \frac{1}{(\partial V_m/\partial P)_T} \tag{1.41}$$

Furthermore, the relation $(\partial x/\partial y)_z(\partial y/\partial z)_x(\partial z/\partial x)_y = -1$ [Eq. (1.34)] with x, y, and z replaced by P, V_m, and T, respectively, gives

$$\left(\frac{\partial P}{\partial V_m}\right)_T\left(\frac{\partial V_m}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_{V_m} = -1$$

$$\left(\frac{\partial P}{\partial T}\right)_{V_m} = -\left(\frac{\partial P}{\partial V_m}\right)_T\left(\frac{\partial V_m}{\partial T}\right)_P = -\frac{(\partial V_m/\partial T)_P}{(\partial V_m/\partial P)_T} \tag{1.42}$$

where $(\partial z/\partial x)_y = 1/(\partial x/\partial z)_y$ was used twice.

Hence there are only two independent partial derivatives: $(\partial V_m/\partial T)_P$ and $(\partial V_m/\partial P)_T$. The other four can be calculated from these two and need not be measured. We define the **thermal expansivity** (or **cubic expansion coefficient**) α (alpha) and the **isothermal compressibility** κ (kappa) of a substance by

$$\alpha(T, P) \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,n} \equiv \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_P \tag{1.43}^*$$

$$\kappa(T, P) \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n} \equiv -\frac{1}{V_m}\left(\frac{\partial V_m}{\partial P}\right)_T \tag{1.44}^*$$

α and κ tell how fast the volume of a substance increases with temperature and decreases with pressure. The purpose of the $1/V$ factor in their definitions is to make them intensive properties. Usually, α is positive; however, liquid water decreases in volume with increasing temperature between 0°C and 4°C at 1 atm. One can prove from the laws of thermodynamics that κ must always be positive (see *Zemansky and Dittman,* sec. 14-9, for the proof). Equation (1.42) can be written as

$$\left(\frac{\partial P}{\partial T}\right)_{V_m} = \frac{\alpha}{\kappa} \tag{1.45}$$

EXAMPLE 1.3 α and κ of an ideal gas

For an ideal gas, find expressions for α and κ and verify that Eq. (1.45) holds.

To find α and κ from the definitions (1.43) and (1.44), we need the partial derivatives of V_m. We therefore solve the ideal-gas equation of state $PV_m = RT$ for V_m and then differentiate the result. We have $V_m = RT/P$. Differentiation with respect to T gives $(\partial V_m/\partial T)_P = R/P$. Thus

$$\alpha = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_P = \frac{1}{V_m}\left(\frac{R}{P}\right) = \frac{P}{RT}\frac{R}{P} = \frac{1}{T} \tag{1.46}$$

$$\kappa = -\frac{1}{V_m}\left(\frac{\partial V_m}{\partial P}\right)_T = -\frac{1}{V_m}\left[\frac{\partial}{\partial P}\left(\frac{RT}{P}\right)\right]_T = -\frac{1}{V_m}\left(-\frac{RT}{P^2}\right) = \frac{1}{P} \tag{1.47}$$

$$\left(\frac{\partial P}{\partial T}\right)_{V_m} = \left[\frac{\partial}{\partial T}\left(\frac{RT}{V_m}\right)\right]_{V_m} = \frac{R}{V_m} \tag{1.48}$$

But from (1.45), we have $(\partial P/\partial T)_{V_m} = \alpha/\kappa = T^{-1}/P^{-1} = P/T = nRTV^{-1}/T = R/V_m$, which agrees with (1.48).

Exercise

For a gas obeying the equation of state $V_m = RT/P + B(T)$, where $B(T)$ is a certain function of T, (*a*) find α and κ; (*b*) find $(\partial P/\partial T)_{V_m}$ in two different ways. [*Answer:* $\alpha = (R/P + dB/dT)/V_m$; $\kappa = RT/V_m P^2$; $(\partial P/\partial T)_{V_m} = P/T + P^2(dB/dT)/RT$.]

For solids, α is typically 10^{-5} to 10^{-4} K^{-1}. For liquids, α is typically $10^{-3.5}$ to 10^{-3} K^{-1}. For gases, α can be estimated from the ideal-gas α, which is $1/T$; for temperatures of 100 to 1000 K, α for gases thus lies in the range 10^{-2} to 10^{-3} K^{-1}.

For solids, κ is typically 10^{-6} to 10^{-5} atm^{-1}. For liquids, κ is typically 10^{-4} atm^{-1}. Equation (1.47) for ideal gases gives κ as 1 and 0.1 atm^{-1} at P equal to 1 and 10 atm, respectively. Solids and liquids are far less compressible than gases because there isn't much space between molecules in liquids and solids.

The quantities α and κ can be used to find the volume change produced by a change in T or P.

EXAMPLE 1.4 Expansion due to a temperature increase

Estimate the percentage increase in volume produced by a 10°C temperature increase in a liquid with the typical α value 0.001 K^{-1}, approximately independent of temperature.

Equation (1.43) gives $dV_P = \alpha V\, dT_P$. Since we require only an approximate answer and since the changes in T and V are small (α is small), we can approximate the ratio dV_P/dT_P by the ratio $\Delta V_P/\Delta T_P$ of finite changes to get $\Delta V_P/V \approx \alpha\, \Delta T_P = (0.001\ \text{K}^{-1})\ (10\ \text{K}) = 0.01 = 1\%$.

Exercise

For water at 80°C and 1 atm, $\alpha = 6.412_7 \times 10^{-4}$ K^{-1} and $\rho = 0.971792$ g/cm^3. Using the approximation $dV_P/dT_P \approx \Delta V_P/\Delta T_P$ for ΔT_P small, find the density of water at 81°C and 1 atm and compare with the true value 0.971166 g/cm^3. (*Answer:* 0.971169 g/cm^3.)

1.8 INTEGRAL CALCULUS

Differential calculus was reviewed in Sec. 1.6. Before reviewing integral calculus, we recall some facts about sums.

Sums

The definition of the summation notation is

$$\sum_{i=1}^{n} a_i \equiv a_1 + a_2 + \cdots + a_n \qquad \textbf{(1.49)*}$$

For example, $\Sigma_{i=1}^{3}\, i^2 = 1^2 + 2^2 + 3^2 = 14$. When the limits of a sum are clear, they are often omitted. Some identities that follow from (1.49) are (Prob. 1.59)

$$\sum_{i=1}^{n} ca_i = c\sum_{i=1}^{n} a_i, \qquad \sum_{i=1}^{n} (a_i + b_i) = \sum_{i=1}^{n} a_i + \sum_{i=1}^{n} b_i \qquad \textbf{(1.50)*}$$

$$\sum_{i=1}^{n}\sum_{j=1}^{m} a_i b_j = \sum_{i=1}^{n} a_i \sum_{j=1}^{m} b_j \qquad (1.51)$$

Integral Calculus

Frequently one wants to find a function $y(x)$ whose derivative is known to be a certain function $f(x)$; $dy/dx = f(x)$. The most general function y that satisfies this equation is called the **indefinite integral** (or *antiderivative*) of $f(x)$ and is denoted by $\int f(x)\, dx$.

$$\text{If} \quad dy/dx = f(x) \qquad \text{then} \quad y = \int f(x)\, dx \tag{1.52)*}$$

The function $f(x)$ being integrated in (1.52) is called the **integrand.**

Since the derivative of a constant is zero, the indefinite integral of any function contains an arbitrary additive constant. For example, if $f(x) = x$, its indefinite integral $y(x)$ is $\frac{1}{2}x^2 + C$, where C is an arbitrary constant. This result is readily verified by showing that y satisfies (1.52), that is, by showing that $(d/dx)\,(\frac{1}{2}x^2 + C) = x$. To save space, tables of indefinite integrals usually omit the arbitrary constant C.

From the derivatives given in Sec. 1.6, it follows that

$$\int af(x)\, dx = a\int f(x)\, dx, \qquad \int [f(x) + g(x)]\, dx = \int f(x)\, dx + \int g(x)\, dx \tag{1.53)*}$$

$$\int dx = x + C, \qquad \int x^n\, dx = \frac{x^{n+1}}{n+1} + C \qquad \text{where } n \neq -1 \tag{1.54)*}$$

$$\int \frac{1}{x}\, dx = \ln x + C, \qquad \int e^{ax} dx = \frac{e^{ax}}{a} + C \tag{1.55)*}$$

$$\int \sin ax\, dx = -\frac{\cos ax}{a} + C, \qquad \int \cos ax\, dx = \frac{\sin ax}{a} + C \tag{1.56)*}$$

where a and n are nonzero constants and C is an arbitrary constant. For more complicated integrals than those in Eqs. (1.53) through (1.56), use a table of integrals or the website integrals.wolfram.com, which does indefinite integrals at no charge.

A second important concept in integral calculus is the definite integral. Let $f(x)$ be a continuous function, and let a and b be any two values of x. The **definite integral** of f between the limits a and b is denoted by the symbol

$$\int_a^b f(x)\, dx \tag{1.57}$$

The reason for the resemblance to the notation for an indefinite integral will become clear shortly. The definite integral (1.57) is a number whose value is found from the following definition. We divide the interval from a to b into n subintervals, each of width Δx, where $\Delta x = (b - a)/n$ (see Fig. 1.15). In each subinterval, we pick any point we please, denoting the chosen points by $x_1, x_2, \ldots, x_n$. We evaluate $f(x)$ at each of the n chosen points and form the sum

$$\sum_{i=1}^{n} f(x_i)\,\Delta x = f(x_1)\,\Delta x + f(x_2)\,\Delta x + \cdots + f(x_n)\,\Delta x \tag{1.58}$$

We now take the limit of the sum (1.58) as the number of subintervals n goes to infinity, and hence as the width Δx of each subinterval goes to zero. This limit is, by definition, the definite integral (1.57):

$$\int_a^b f(x)\, dx \equiv \lim_{\Delta x \to 0} \sum_{i=1}^{n} f(x_i)\,\Delta x \tag{1.59}$$

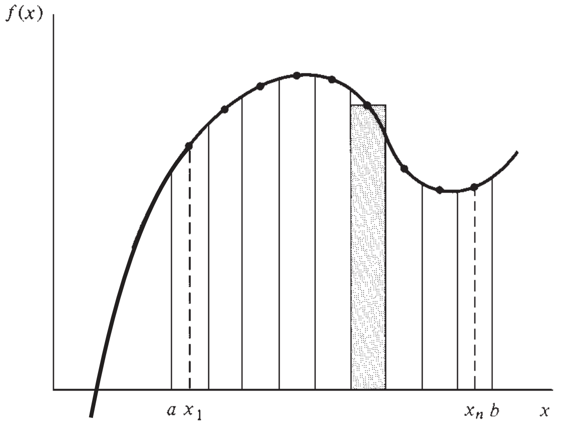


Figure 1.15

Definition of the definite integral.

The motivation for this definition is that the quantity on the right side of (1.59) occurs very frequently in physical problems.

Each term in the sum (1.58) is the area of a rectangle of width Δx and height $f(x_i)$. A typical rectangle is indicated by the shading in Fig. 1.15. As the limit $\Delta x \to 0$ is taken, the total area of these n rectangles becomes equal to the area under the curve $f(x)$ between a and b. Thus we can interpret the definite integral as an area. Areas lying below the x axis, where $f(x)$ is negative, make negative contributions to the definite integral.

Use of the definition (1.59) to evaluate a definite integral would be tedious. The fundamental theorem of integral calculus (proved in any calculus text) enables us to evaluate a definite integral of $f(x)$ in terms of an indefinite integral $y(x)$ of $f(x)$, as

$$\int_a^b f(x)\,dx = y(b) - y(a) \qquad \text{where } y(x) = \int f(x)\,dx \qquad \textbf{(1.60)*}$$

For example, if $f(x) = x$, $a = 2$, $b = 6$, we can take $y = \frac{1}{2}x^2$ (or $\frac{1}{2}x^2$ plus some constant) and (1.60) gives $\int_2^6 x\,dx = \frac{1}{2}x^2\,\big|_2^6 = \frac{1}{2}(6^2) - \frac{1}{2}(2^2) = 16$.

The integration variable x in the definite integral on the left side of (1.60) does not appear in the final result (the right side of this equation). It thus does not matter what symbol we use for this variable. If we evaluate $\int_2^6 z\,dz$, we still get 16. In general, $\int_a^b f(x)\,dx = \int_a^b f(z)\,dz$. For this reason the integration variable in a definite integral is called a **dummy variable.** (The integration variable in an indefinite integral is not a dummy variable.) Similarly it doesn't matter what symbol we use for the summation index in (1.49). Replacement of i by j gives exactly the same sum on the right side, and i in (1.49) is a dummy index.

Two identities that readily follow from (1.60) are $\int_a^b f(x)\,dx = -\int_b^a f(x)\,dx$ and $\int_a^b f(x)\,dx + \int_b^c f(x)\,dx = \int_a^c f(x)\,dx$.

An important method for evaluating integrals is a change in variables. For example, suppose we want $\int_2^3 x \exp(x^2)\,dx$. Let $z \equiv x^2$; then $dz = 2x\,dx$, and

$$\int_2^3 xe^{x^2}\,dx = \frac{1}{2}\int_4^9 e^z\,dz = \frac{1}{2}e^z\bigg|_4^9 = \frac{1}{2}(e^9 - e^4) = 4024.2$$

Note that the limits were changed in accord with the substitution $z = x^2$.

From (1.52), it follows that the derivative of an indefinite integral equals the integrand: $(d/dx)\int f(x)\,dx = f(x)$. Note, however, that a definite integral is simply a number and not a function; therefore $(d/dx)\int_a^b f(x)\,dx = 0$.

Integration with respect to x for a function of two variables is defined similarly to (1.52) and (1.59). If $y(x, z)$ is the most general function that satisfies

$$\left[\frac{\partial y(x, z)}{\partial x}\right]_z = f(x, z) \tag{1.61}$$

then the indefinite integral of $f(x, z)$ with respect to x is

$$\int f(x, z)\, dx = y(x, z) \tag{1.62}$$

For example, if $f(x, z) = xz^3$, then $y(x, z) = \frac{1}{2}x^2z^3 + g(z)$, where g is an arbitrary function of z. If y satisfies (1.61), one can show [in analogy with (1.60)] that a definite integral of $f(x, z)$ is given by

$$\int_a^b f(x, z)\, dx = y(b, z) - y(a, z) \tag{1.63}$$

For example, $\int_2^6 xz^3\, dx = \frac{1}{2}(6^2)z^3 + g(z) - \frac{1}{2}(2^2)z^3 - g(z) = 16z^3$.

The integrals (1.62) and (1.63) are similar to ordinary integrals of a function $f(x)$ of a single variable in that we regard the second independent variable z in these integrals as constant during the integration process; z acts as a parameter rather than as a variable. (A **parameter** is a quantity that is constant in a particular circumstance but whose value can change from one circumstance to another. For example, in Newton's second law $F = ma$, the mass m is a parameter. For any one particular body, m is constant, but its value can vary from one body to another.) In contrast to the integrals (1.62) and (1.63), in thermodynamics we shall often integrate a function of two or more variables in which all the variables are changing during the integration. Such integrals are called line integrals and will be discussed in Chapter 2.

An extremely common kind of physical chemistry problem is the use of the known derivative dz/dx to find the change Δz brought about by the change Δx. This kind of problem is solved by integration. Typically, the property z is a function of two variables x and y, and we want the change Δz due to Δx while property y is held constant. We use the partial derivative $(\partial z/\partial x)_y$, and it helps to write this partial derivative as

$$\left(\frac{\partial z}{\partial x}\right)_y = \frac{dz_y}{dx_y} \tag{1.64)*$$

where dz_y and dx_y are the infinitesimal changes in z and in x, while y is held constant.

EXAMPLE 1.5 Change in volume with applied pressure

For liquid water at 25°C, isothermal-compressibility data in the pressure range 1 to 401 bar are well fitted by the equation $\kappa = a + bP + cP^2$, where $a = 45.259 \times 10^{-6}\ \text{bar}^{-1}$, $b = -1.1706 \times 10^{-8}\ \text{bar}^{-2}$, and $c = 2.3214 \times 10^{-12}\ \text{bar}^{-3}$. The volume of one gram of water at 25°C and 1 bar is 1.002961 cm^3. Find the volume of one gram of water at 25°C and 401 bar. Compare the value with the experimental value 0.985846 cm^3.

We need to find a volume change ΔV due to a change in pressure ΔP at constant T. The compressibility is related to the rate of change of V with respect to P at constant T. The definition (1.44) of κ gives

$$\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\frac{dV_T}{dP_T} \tag{1.65}$$

where the subscripts on the differentials denote changes at constant T. We want to find ΔV. Therefore, we need to integrate this equation. The two variables are V and P, since T is constant. To integrate, we need to first *separate the variables,* putting everything that depends on V on one side and everything that depends on P on the other side. κ is an intensive quantity that depends on T and P, and T is constant, so κ belongs on the P side, as is obvious from the equation for κ given in the statement of the problem. To separate the variables, we multiply (1.65) by dP_T to get

$$\kappa\, dP_T = -\frac{1}{V}\, dV_T$$

Next, we integrate both sides from the initial state P_1, V_1 to the final state P_2, V_2, where P_1, V_1, and P_2 are known, and T is constant:

$$-\int_{V_1}^{V_2} \frac{1}{V}\, dV = \int_{P_1}^{P_2} \kappa\, dP = \int_{P_1}^{P_2} (a + bP + cP^2)\, dP$$

$$-\ln V\Big|_{V_1}^{V_2} = (aP + \tfrac{1}{2}bP^2 + \tfrac{1}{3}cP^3)\Big|_{P_1}^{P_2}$$

$$-(\ln V_2 - \ln V_1) = \ln(V_1/V_2) = a(P_2 - P_1) + \tfrac{1}{2}b(P_2^2 - P_1^2) + \tfrac{1}{3}c(P_2^3 - P_1^3)$$

$$\begin{aligned} \ln[(1.002961\ \text{cm}^3)/V_2] &= 45.259 \times 10^{-6}\ \text{bar}^{-1}\,(400\ \text{bar}) \\ &\quad - \tfrac{1}{2}(1.1706 \times 10^{-8}\ \text{bar}^{-2})(401^2 - 1^2)\text{bar}^2 \\ &\quad + \tfrac{1}{3}(2.3214 \times 10^{-12}\ \text{bar}^{-3})(401^3 - 1^3)\text{bar}^3 \\ \ln[(1.002961\ \text{cm}^3)/V_2] &= 0.0172123 \\ (1.002961\ \text{cm}^3)/V_2 &= 1.017361 \\ V_2 &= 0.985846\ \text{cm}^3 \end{aligned}$$

which agrees with the true value 0.985846 cm^3.

Exercise

A liquid with thermal expansivity α is initially at temperature and volume T_1 and V_1. If the liquid is heated from T_1 to T_2 at constant pressure, find an expression for V_2 using the approximation that α is independent of T. [*Answer:* $\ln V_2 \approx \ln V_1 + \alpha(T_2 - T_1)$.]

Exercise

For liquid water at 1 atm, thermal-expansivity data in the range 25°C to 50°C are well fitted by the equation $\alpha = e + f(t/°\text{C}) + g(t/°\text{C})^2$, where t is the Celsius temperature, $e = -1.00871 \times 10^{-5}\ \text{K}^{-1}$, $f = 1.20561 \times 10^{-5}\ \text{K}^{-1}$, and $g = -5.4150 \times 10^{-8}\ \text{K}^{-1}$. The volume of one gram of water at 30°C and 1 atm is 1.004372 cm^3. Find the volume of one gram of water at 50°C and 1 atm. Compare with the experimental value 1.012109 cm^3. (*Answer:* 1.012109 cm^3.)

Logarithms

Integration of $1/x$ gives the natural logarithm $\ln x$. Because logarithms are used so often in physical chemistry derivations and calculations, we now review their properties. If $x = a^s$, then the exponent s is said to be the **logarithm** (log) of x to the base a: if $a^s = x$, then $\log_a x = s$. The most important base is the irrational number $e = 2.71828\ldots$, defined as the limit of $(1 + b)^{1/b}$ as $b \to 0$. Logs to the base e are called **natural**

logarithms and are written as $\ln x$. For practical calculations, one often uses logs to the base 10, called **common logarithms** and written as $\log x$, $\log_{10} x$, or $\lg x$. We have

$$\ln x \equiv \log_e x, \qquad \log x \equiv \log_{10} x \qquad \textbf{(1.66)*}$$

$$\text{If } 10^t = x, \quad \text{then } \log x = t. \qquad \text{If } e^s = x, \quad \text{then } \ln x = s. \qquad (1.67)$$

From (1.67), we have

$$e^{\ln x} = x \qquad \text{and} \qquad 10^{\log x} = x \qquad (1.68)$$

From (1.67), it follows that $\ln e^s = s$. Since $e^{\ln x} = x = \ln e^x$, the exponential and natural logarithmic functions are inverses of each other. The function e^x is often written as $\exp x$. Thus, $\exp x \equiv e^x$. Since $e^1 = e$, $e^0 = 1$, and $e^{-\infty} = 0$, we have $\ln e = 1$, $\ln 1 = 0$, and $\ln 0 = -\infty$. One can take the logarithm or the exponential of a dimensionless quantity only.

Some identities that follow from the definition (1.67) are

$$\ln xy = \ln x + \ln y, \qquad \ln (x/y) = \ln x - \ln y \qquad \textbf{(1.69)*}$$

$$\ln x^k = k \ln x \qquad \textbf{(1.70)*}$$

$$\ln x = (\log_{10} x)/(\log_{10} e) = \log_{10} x \ln 10 = 2.3026 \log_{10} x \qquad (1.71)$$

To find the log of a number greater than 10^{100} or less than 10^{-100}, which cannot be entered on most calculators, we use $\log(ab) = \log a + \log b$ and $\log 10^b = b$. For example,

$$\log_{10} (2.75 \times 10^{-150}) = \log_{10} 2.75 + \log_{10} 10^{-150} = 0.439 - 150 = -149.561$$

To find the antilog of a number greater than 100 or less than -100, we proceed as follows. If we know that $\log_{10} x = -184.585$, then

$$x = 10^{-184.585} = 10^{-0.585}10^{-184} = 0.260 \times 10^{-184} = 2.60 \times 10^{-185}$$

1.9 STUDY SUGGESTIONS

A common reaction to a physical chemistry course is for a student to think, "This looks like a tough course, so I'd better memorize all the equations, or I won't do well." Such a reaction is understandable, especially since many of us have had teachers who emphasized rote memory, rather than understanding, as the method of instruction.

Actually, comparatively few equations need to be remembered (they have been marked with an asterisk), and most of these are simple enough to require little effort at conscious memorization. Being able to reproduce an equation is no guarantee of being able to apply that equation to solving problems. To use an equation properly, one must understand it. Understanding involves not only knowing what the symbols stand for but also knowing when the equation applies and when it does not apply. Everyone knows the ideal-gas equation $PV = nRT$, but it's amazing how often students will use this equation in problems involving liquids or solids. Another part of understanding an equation is knowing where the equation comes from. Is it simply a definition? Or is it a law that represents a generalization of experimental observations? Or is it a rough empirical rule with only approximate validity? Or is it a deduction from the laws of thermodynamics made without approximations? Or is it a deduction from the laws of thermodynamics made using approximations and therefore of limited validity?

As well as understanding the important equations, you should also know the meanings of the various defined terms (closed system, ideal gas, etc.). Boldface type (for example, **isotherm**) is used to mark very important terms when they are first defined. Terms of lesser importance are printed in italic type (for example, *isobar*). If you come across a term whose meaning you have forgotten, consult the index; the page number where a term is defined is printed in boldface type.

Working problems is essential to learning physical chemistry. Suggestions for solving problems are given in Sec. 2.12. It's a good idea to test your understanding of a section by working on some relevant problems as soon as you finish each section. Do not wait until you feel you have mastered a section before working some problems. The problems in this book are classified by section.

Keep up to date in assignments. Cramming does not work in physical chemistry because of the many concepts to learn and the large amount of practice in working problems that is needed to master these concepts. Most students find that physical chemistry requires a lot more study and problem-solving time than the typical college course, so be sure you allot enough time to this course.

Make studying an active process. Read with a pencil at hand and use it to verify equations, to underline key ideas, to make notes in the margin, and to write down questions you want to ask your instructor. Sort out the basic principles from what is simply illustrative detail and digression. In this book, small print is used for historical material, for more advanced material, and for minor points.

After reading a section, make a written summary of the important points. This is a far more effective way of learning than to keep rereading the material. You might think it a waste of time to make summaries, since chapter summaries are provided. However, preparing your own summary will make the material much more meaningful to you than if you simply read the one at the end of the chapter.

A psychologist carried out a project on improving student study habits that raised student grades dramatically. A key technique used was to have students close the textbook at the end of each section and spend a few minutes outlining the material; the outline was then checked against the section in the book. [L. Fox in R. Ulrich et al. (eds.), *Control of Human Behavior,* Scott, Foresman, 1966, pp. 85–90.]

Before reading a chapter in detail, browse through it first, reading only the section headings, the first paragraph of each section, the summary, and some of the problems at the end of the chapter. This gives an idea of the structure of the chapter and makes the reading of each section more meaningful. Reading the problems first lets you know what you are expected to learn from the chapter.

You might try studying occasionally with another person. Discussing problems with someone else can help clarify the material in your mind.

Set aside enough time to devote to this course. Physical chemistry is a demanding subject and requires a substantial investment of time to learn. A study of violin students found that those judged the best had accumulated at age 18 an average of 7400 hours of lifetime practice, as compared with 5300 hours for those violinists judged only as good, and 3400 hours of practice for violinists at a still-lower playing ability [K. A. Ericsson et al., *Psychologic. Rev.,* **100,** 363 (1993)]. Studies of experts in chess, sports, and medicine have found similar strong correlations between the level of expertise and the amount of practice. Ericsson stated that "The extensive evidence for modifiability by extended practice led my colleagues and me to question whether there is any firm evidence that innate talent is a necessary prerequisite for developing expert performance [see G. Schraw, *Educ. Psychol. Rev.,* **17,** 389 (2005)].

Additional support for the primary importance of effort are the following statements (C. S. Dweck, *Scientific American Mind,* Dec. 2007, p. 36): "research is converging on the conclusion that great accomplishment, and even what we call genius, is typically the result of years of passion and dedication and not something that flows naturally from a gift"; "hard work and discipline contribute much more to school achievement than IQ does"; "studies show that teaching people . . . to focus on effort rather than intelligence or talent, helps make them into high achievers in school and in life."

Ericsson emphasizes the importance of *deliberate* practice: "deliberate practice is a highly structured activity, the explicit goal of which is to improve performance. Specific tasks are invented to overcome weaknesses, and performance is carefully monitored to provide cues for ways to improve it further." [K. A. Ericsson et al., *Psychologic. Rev.,* **100,** 363 (1993)]. It's a good idea to analyze the kinds of mistakes you are making in physical chemistry and deliberately aim to improve in areas you are deficient in. If you are getting problems wrong because you are making mistakes in calculus or algebra, practice doing derivatives and integrals. If you get problems wrong because you are being inconsistent with units, get in the habit of always including the units of each quantity when you do problems, and take the time to make sure that units cancel so as to give the proper units for the answer; make sure you know what the SI units are for each physical quantity encountered. If you are getting problems wrong or are unable to do problems because you overlook or misinterpret or misapply the conditions given in the problems, make sure you are familiar with the precise definitions of such terms as isothermal and adiabatic, pay careful attention when you read a problem to what the conditions are, and when you learn starred equations, make sure you also learn the conditions of applicability for each equation.

As to studying, research has shown that students who study in a quiet place do better than those who study in a place with many distractions.

Get adequate sleep. The study of violinists mentioned previously found that the violinists considered adequate sleep to be an important factor in improving performance, and the two best groups of violinists averaged 5 hours more of sleep per week than the lowest level of violinists. College students are notoriously sleep deprived. Numerous studies have shown the negative effects of sleep deprivation on mental and physical performance. (For the amusing and insightful account of one college student, see A. R. Cohen, *Harvard Magazine,* Nov.–Dec. 2001, p. 83—www.harvardmagazine.com/on-line/110190.html.)

Some suggestions to help you prepare for exams are

1. Learn the meanings of all terms in boldface type.
2. Memorize all starred equations *and* their conditions of applicability. (Do not memorize unstarred equations.)
3. Make sure you *understand* all starred equations.
4. Review your class notes.
5. Rework homework problems you had difficulty with.
6. Work some unassigned problems for additional practice.
7. Make summaries if you have not already done so.
8. Check that you understand all the concepts mentioned in the end-of-chapter summaries.
9. Make sure you can do each type of calculation listed in the summaries.
10. Prepare a practice exam by choosing some relevant homework problems and work them in the time allotted for the exam.

My students often ask me whether the fact that they have to learn only the starred equations means that problems that require the use of unstarred equations will not appear on exams. My answer is that if an unstarred equation is needed, it will be included as given information on the exam.

Since, as with all of us, your capabilities for learning and understanding are finite and the time available to you is limited, it is best to accept the fact that there will probably be some material you may never fully understand. No one understands everything fully.

1.10 SUMMARY

The four branches of physical chemistry are thermodynamics, quantum chemistry, statistical mechanics, and kinetics.

Thermodynamics deals with the relationships between the macroscopic equilibrium properties of a system. Some important concepts in thermodynamics are *system* (*open* versus *closed; isolated* versus *nonisolated; homogeneous* versus *heterogeneous*);

surroundings; walls (*rigid* versus *nonrigid; permeable* versus *impermeable; adiabatic* versus *thermally conducting*); *equilibrium* (*mechanical, material, thermal*); *state functions* (*extensive* versus *intensive*); *phase;* and *equation of state.*

Temperature was defined as an intensive state function that has the same value for two systems in thermal equilibrium and a different value for two systems not in thermal equilibrium. The setting up of a temperature scale is arbitrary, but we chose to use the ideal-gas absolute scale defined by Eq. (1.15).

An ideal gas is one that obeys the equation of state $PV = nRT$. Real gases obey this equation only in the limit of zero density. At ordinary temperatures and pressures, the ideal-gas approximation will usually be adequate for our purposes. For an ideal gas mixture, $PV = n_{\text{tot}}RT$. The partial pressure of gas i in any mixture is $P_i \equiv x_i P$, where the mole fraction of i is $x_i \equiv n_i/n_{\text{tot}}$.

Differential and integral calculus were reviewed, and some useful partial-derivative relations were given [Eqs. (1.30), (1.32), (1.34), and (1.36)].

The thermodynamic properties α (thermal expansivity) and κ (isothermal compressibility) are defined by $\alpha \equiv (1/V)\,(\partial V/\partial T)_P$ and $\kappa \equiv -(1/V)\,(\partial V/\partial P)_T$ for a system of fixed composition.

Understanding, rather than mindless memorization, is the key to learning physical chemistry.

Important kinds of calculations dealt with in this chapter include

- Calculation of P (or V or T) of an ideal gas or ideal gas mixture using $PV = nRT$.
- Calculation of the molar mass of an ideal gas using $PV = nRT$ and $n = m/M$.
- Calculation of the density of an ideal gas.
- Calculations involving partial pressures.
- Use of α or κ to find volume changes produced by changes in T or P.
- Differentiation and partial differentiation of functions.
- Indefinite and definite integration of functions.

FURTHER READING AND DATA SOURCES

Temperature: *Quinn; Shoemaker, Garland, and Nibler,* chap. XVIII; *McGlashan,* chap. 3; *Zemansky and Dittman,* chap. 1. Pressure measurement: *Rossiter, Hamilton, and Baetzold,* vol. VI, chap. 2. Calculus: C. E. Swartz, *Used Math for the First Two Years of College Science,* Prentice-Hall, 1973.

ρ, α, and κ values: *Landolt-Börnstein,* 6th ed., vol. II, part 1, pp. 378–731.

PROBLEMS

Section 1.2

1.1 True or false? (*a*) A closed system cannot interact with its surroundings. (*b*) Density is an intensive property. (*c*) The Atlantic Ocean is an open system. (*d*) A homogeneous system must be a pure substance. (*e*) A system containing only one substance must be homogeneous.

1.2 State whether each of the following systems is closed or open and whether it is isolated or nonisolated: (*a*) a system enclosed in rigid, impermeable, thermally conducting walls; (*b*) a human being; (*c*) the planet earth.

1.3 How many phases are there in a system that consists of (*a*) $CaCO_3(s)$, $CaO(s)$, and $CO_2(g)$; (*b*) three pieces of solid AgBr, one piece of solid AgCl, and a saturated aqueous solution of these salts.

1.4 Explain why the definition of an adiabatic wall in Sec. 1.2 specifies that the wall be rigid and impermeable.

1.5 The density of Au is 19.3 g/cm^3 at room temperature and 1 atm. (*a*) Express this density in kg/m^3. (*b*) If gold is selling for \$800 per troy ounce, what would a cubic meter of it sell for? One troy ounce = 480 grains, 1 grain = $\frac{1}{7000}$ pound, 1 pound = 453.59 g.

Section 1.4

1.6 True or false? (*a*) One gram is Avogadro's number of times as heavy as 1 amu. (*b*) The Avogadro constant N_A has no units. (*c*) Mole fractions are intensive properties. (*d*) One mole of water contains Avogadro's number of water molecules.

1.7 For O_2, give (*a*) the molecular weight; (*b*) the molecular mass; (*c*) the relative molecular mass; (*d*) the molar mass.

1.8 A solution of HCl in water is 12.0% HCl by mass. Find the mole fractions of HCl and H_2O in this solution.

1.9 Calculate the mass in grams of (*a*) one atom of carbon; (*b*) one molecule of water.

1.10 The room-temperature density of Po is 9.20 g/cm^3 and its longest-lived isotope has mass number 209. The structure of solid Po can be described as follows. Imagine a layer of cubes like Fig. 23.8 but with many more cubes; the edge length of each cube is taken as equal to the diameter of a Po atom; then place another cube directly over each cube in the first layer and aligned with that cube, thereby forming a second layer; then add cubes directly over the second-layer cubes to form a third layer; and so on. If one Po atom is put into each cube with the atomic nucleus at the center of the cube, we have the Po structure. (*a*) Find the volume of one mole of Po. (*b*) Find the volume of the cube that surrounds one Po atom in the solid. (*c*) Find the diameter of a Po atom. (*d*) For a spherical nanoparticle of Po whose diameter is 2 nm, find the number of Po atoms present. (*e*) Repeat (*d*) for a Po spherical nanoparticle of diameter 100 nm. (*f*) For a cubic nanoparticle of Po whose edge length is 2 nm, calculate the percentage of Po atoms that are at the surface of the particle. (*g*) Repeat (*f*) for a Po cubic particle of edge length 100 nm. (The increasing percentage of atoms at the surface as the particle size decreases is one reason the properties of nanomaterials change with size.)

Section 1.5

1.11 True or false? (*a*) On the Celsius scale, the boiling point of water is slightly less than 100.00°C. (*b*) Doubling the absolute temperature of an ideal gas at fixed volume and amount of gas will double the pressure. (*c*) The ratio PV/mT is the same for all gases in the limit of zero pressure. (*d*) The ratio PV/nT is the same for all gases in the limit of zero pressure. (*e*) All ideal gases have the same density at 25°C and 1 bar. (*f*) All ideal gases have the same number of molecules per unit volume at 25°C and 10 bar.

1.12 Do these conversions: (*a*) 5.5 m^3 to cm^3; (*b*) 1.0 GPa to bar (where 1 GPa $\equiv 10^9$ Pa); (*c*) 1.000 hPa to torr (where 1 hPa $\equiv 10^2$ Pa); (*d*) 1.5 g/cm^3 to kg/m^3.

1.13 In Fig. 1.2, if the mercury levels in the left and right arms of the manometer are 30.43 and 20.21 cm, respectively, above the bottom of the manometer, and if the barometric pressure is 754.6 torr, find the pressure in the system. Neglect temperature corrections to the manometer and barometer readings.

1.14 (*a*) A seventeenth-century physicist built a water barometer that projected through a hole in the roof of his house so that his neighbors could predict the weather by the height of the water. Suppose that at 25°C a mercury barometer reads 30.0 in. What would be the corresponding height of the column in a water barometer? The densities of mercury and water at 25°C are 13.53 and 0.997 g/cm^3, respectively. (*b*) What pressure in atmospheres corresponds to a 30.0-in. mercury-barometer reading at 25°C at a location where $g = 978$ cm/s^2?

1.15 Derive Eq. (1.17) from Eq. (1.18).

1.16 (*a*) What is the pressure exerted by 24.0 g of carbon dioxide in a 5.00-L vessel at 0°C? (*b*) A rough rule of thumb is that 1 mole of gas occupies 1 ft^3 at room temperature and pressure (25°C and 1 atm). Calculate the percent error in this rule. One inch = 2.54 cm.

1.17 A sample of 65 mg of an ideal gas at 0.800 bar pressure has its volume doubled and its absolute temperature tripled. Find the final pressure.

1.18 For a certain hydrocarbon gas, 20.0 mg exerts a pressure of 24.7 torr in a 500-cm^3 vessel at 25°C. Find the molar mass and the molecular weight and identify the gas.

1.19 Find the density of N_2 at 20°C and 0.667 bar.

1.20 For 1.0000 mol of N_2 gas at 0.00°C, the following volumes are observed as a function of pressure:

P/atm	1.0000	3.0000	5.0000
V/cm^3	22405	7461.4	4473.1

Calculate and plot PV/nT versus P for these three points and extrapolate to $P = 0$ to evaluate R.

1.21 The measured density of a certain gaseous amine at 0°C as a function of pressure is

P/atm	0.2000	0.5000	0.8000
ρ/(g/L)	0.2796	0.7080	1.1476

Plot P/ρ versus P and extrapolate to $P = 0$ to find an accurate molecular weight. Identify the gas.

1.22 After 1.60 mol of NH_3 gas is placed in a 1600-cm^3 box at 25°C, the box is heated to 500 K. At this temperature, the ammonia is partially decomposed to N_2 and H_2, and a pressure measurement gives 4.85 MPa. Find the number of moles of each component present at 500 K.

1.23 A student attempts to combine Boyle's law and Charles' law as follows. "We have $PV = K_1$ and $V/T = K_2$. Equals multiplied by equals are equal; multiplication of one equation by the other gives $PV^2/T = K_1K_2$. The product K_1K_2 of two constants is a constant, so PV^2/T is a constant for a fixed amount of ideal gas." What is the fallacy in this reasoning?

1.24 Prove that the equations $PV/T = C_1$ for m constant and $V/m = C_2$ for T and P constant lead to $PV/mT =$ a constant.

1.25 A certain gas mixture is at 3450 kPa pressure and is composed of 20.0 g of O_2 and 30.0 g of CO_2. Find the CO_2 partial pressure.

1.26 A 1.00-L bulb of methane at a pressure of 10.0 kPa is connected to a 3.00-L bulb of hydrogen at 20.0 kPa; both bulbs are at the same temperature. (*a*) After the gases mix, what is the total pressure? (*b*) What is the mole fraction of each component in the mixture?

1.27 A student decomposes $KClO_3$ and collects 36.5 cm^3 of O_2 over water at 23°C. The laboratory barometer reads 751 torr. The vapor pressure of water at 23°C is 21.1 torr. Find the volume the dry oxygen would occupy at 0°C and 1.000 atm.

1.28 Two evacuated bulbs of equal volume are connected by a tube of negligible volume. One bulb is placed in a 200-K constant-temperature bath and the other in a 300-K bath, and then 1.00 mol of an ideal gas is injected into the system. Find the final number of moles of gas in each bulb.

1.29 An oil-diffusion pump aided by a mechanical forepump can readily produce a "vacuum" with pressure 10^{-6} torr. Various special vacuum pumps can reduce P to 10^{-11} torr. At 25°C, calculate the number of molecules per cm^3 in a gas at (*a*) 1 atm; (*b*) 10^{-6} torr; (*c*) 10^{-11} torr.

1.30 A certain mixture of He and Ne in a 356-cm^3 bulb weighs 0.1480 g and is at 20.0°C and 748 torr. Find the mass and mole fraction of He present.

1.31 The earth's radius is 6.37×10^6 m. Find the mass of the earth's atmosphere. (Neglect the dependence of g on altitude.)

1.32 (*a*) If $10^5 P/\text{bar} = 9.4$, what is P? (*b*) If $10^{-2} T/\text{K} = 4.60$, what is T? (*c*) If $P/(10^3 \text{ bar}) = 1.2$, what is P? (*d*) If $10^3(\text{K}/T) = 3.20$, what is T?

1.33 A certain mixture of N_2 and O_2 has a density of 1.185 g/L at 25°C and 101.3 kPa. Find the mole fraction of O_2 in the mixture. (*Hint:* The given data and the unknown are all intensive properties, so the problem can be solved by considering any convenient fixed amount of mixture.)

1.34 The mole fractions of the main components of dry air at sea level are $x_{\text{N}_2} = 0.78$, $x_{\text{O}_2} = 0.21$, $x_{\text{Ar}} = 0.0093$, $x_{\text{CO}_2} = 0.0004$. (*a*) Find the partial pressure of each of these gases in dry air at 1.00 atm and 20°C. (*b*) Find the mass of each of these gases in a 15 ft × 20 ft × 10 ft room at 20°C if the barometer reads 740 torr and the relative humidity is zero. Also, find the density of the air in the room. Which has a greater mass, you or the air in the room of this problem?

Section 1.6

1.35 On Fig. 1.15, mark all points where df/dx is zero and circle each portion of the curve where df/dx is negative.

1.36 Let $y = x^2 + x - 1$. Find the slope of the y-versus-x curve at $x = 1$ by drawing the tangent line to the graph at $x = 1$ and finding its slope. Compare your result with the exact slope found by calculus.

1.37 Find d/dx of (*a*) $2x^3 e^{-3x}$; (*b*) $4e^{-3x^2} + 12$; (*c*) $\ln 2x$; (*d*) $1/(1 - x)$; (*e*) $x/(x + 1)$; (*f*) $\ln (1 - e^{-2x})$; (*g*) $\sin^2 3x$.

1.38 (*a*) Find dy/dx if $xy = y - 2$. (*b*) Find $d^2(x^2 e^{3x})/dx^2$. (*c*) Find dy if $y = 5x^2 - 3x + 2/x - 1$.

1.39 Use a calculator to find: (*a*) $\lim_{x\to 0} x^x$ for $x > 0$; (*b*) $\lim_{x\to 0} (1 + x)^{1/x}$.

1.40 (*a*) Evaluate the first derivative of the function $y = e^{x^2}$ at $x = 2$ by using a calculator to evaluate $\Delta y/\Delta x$ for $\Delta x = 0.1$, 0.01, 0.001, etc. Note the loss of significant figures in Δy as Δx decreases. If you have a programmable calculator, you might try programming this problem. (*b*) Compare your result in (*a*) with the exact answer.

1.41 Find $\partial/\partial y$ of: (*a*) $5x^2 + y + \sin(axy) + 3$; (*b*) $\cos (by^2 z)$; (*c*) $xe^{x/y}$; (*d*) $\tan (3x + 1)$; (*e*) $1/(e^{-a/y} + 1)$; (*f*) $f(x)g(y)h(z)$.

1.42 Take $(\partial/\partial T)_{P,n}$ of (*a*) nRT/P; (*b*) P/nRT^2 (where R is a constant).

1.43 (*a*) If $y = 4x^3 + 6x$, find dy. (*b*) If $z = 3x^2y^3$, find dz. (*c*) If $P = nRT/V$, where R is a constant and all other quantities are variables, find dP.

1.44 If c is a constant and all other letters are variables, find (*a*) $d(PV)$; (*b*) $d(1/T)$; (*c*) $d(cT^2)$; (*d*) $d(U + PV)$.

1.45 Let $z = x^5/y^3$. Evaluate the four second partial derivatives of z; check that $\partial^2 z/(\partial x\, \partial y) = \partial^2 z/(\partial y\, \partial x)$.

1.46 (*a*) For an ideal gas, use an equation like (1.30) to show that $dP = P(n^{-1}\, dn + T^{-1}\, dT - V^{-1}\, dV)$ (which can be written as $d \ln P = d \ln n + d \ln T - d \ln V$). (*b*) Suppose 1.0000 mol of ideal gas at 300.00 K in a 30.000-L vessel has its temperature increased by 1.00 K and its volume increased by 0.050 L. Use the result of (*a*) to estimate the change in pressure, ΔP. (*c*) Calculate ΔP exactly for the change in (*b*) and compare with the estimate given by dP.

Section 1.7

1.47 Find the molar volume of an ideal gas at 20.0°C and 1.000 bar.

1.48 (*a*) Write the van der Waals equation (1.39) using the molar volume instead of V and n. (*b*) If one uses bars, cubic centimeters, moles, and kelvins as the units of P, V, n, and T, give the units of a and of b in the van der Waals equation.

1.49 For a liquid obeying the equation of state (1.40), find expressions for α and κ.

1.50 For H_2O at 50°C and 1 atm, $\rho = 0.98804$ g/cm^3 and $\kappa = 4.4 \times 10^{-10}$ Pa^{-1}. (*a*) Find the molar volume of water at 50°C and 1 atm. (*b*) Find the molar volume of water at 50°C and 100 atm. Neglect the pressure dependence of κ.

1.51 For an ideal gas: (*a*) sketch some isobars on a V_{m}-T diagram; (*b*) sketch some isochores on a P-T diagram.

1.52 A hypothetical gas obeys the equation of state $PV = nRT(1 + aP)$, where a is a constant. For this gas: (*a*) show that $\alpha = 1/T$ and $\kappa = 1/P(1 + aP)$; (*b*) verify that $(\partial P/\partial T)_V = \alpha/\kappa$.

1.53 Use the following densities of water as a function of T and P to estimate α, κ, and $(\partial P/\partial T)_{V_{\text{m}}}$ for water at 25°C and 1 atm: 0.997044 g/cm^3 at 25°C and 1 atm; 0.996783 g/cm^3 at 26°C and 1 atm; 0.997092 g/cm^3 at 25°C and 2 atm.

1.54 By drawing tangent lines and measuring their slopes, use Fig. 1.14 to estimate for water: (*a*) α at 100°C and 500 bar; (*b*) κ at 300°C and 2000 bar.

1.55 For H_2O at 17°C and 1 atm, $\alpha = 1.7 \times 10^{-4}$ K^{-1} and $\kappa = 4.7 \times 10^{-5}$ atm^{-1}. A closed, rigid container is completely filled with liquid water at 14°C and 1 atm. If the temperature is raised to 20°C, estimate the pressure in the container. Neglect the pressure and temperature dependences of α and κ.

1.56 Give a molecular explanation for each of the following facts. (*a*) For solids and liquids, κ usually decreases with increasing pressure. (*b*) For solids and liquids, $(\partial\kappa/\partial T)_P$ is usually positive.

1.57 Estimate the pressure increase needed to decrease isothermally by 1% the 1-atm volume of (*a*) a typical solid with $\kappa = 5 \times 10^{-6}$ atm^{-1}; (*b*) a typical liquid with $\kappa = 1 \times 10^{-4}$ atm^{-1}.

Section 1.8

1.58 (*a*) Evaluate $\Sigma_{J=0}^{4} (2J + 1)$. (*b*) Write the expression $x_1V_1 + x_2V_2 + \cdots + x_sV_s$ using summation notation. (*c*) Write out the individual terms of the double sum $\Sigma_{i=1}^{2} \Sigma_{j=4}^{6} b_{ij}$.

1.59 Prove the sum identities in (1.50) and (1.51). (*Hint:* Write out the individual terms of the sums.)

1.60 Evaluate: (*a*) $\int_3^{-2} (2V + 5V^2)\, dV$; (*b*) $\int_2^4 V^{-1}\, dV$; (*c*) $\int_1^\infty V^{-3}\, dV$; (*d*) $\int_0^{\pi/2} x^2 \cos x^3\, dx$.

1.61 Find (*a*) $\int \sin ax\, dx$; (*b*) $\int_0^\pi \sin ax\, dx$; (*c*) $(d/da) \int_0^\pi \sin ax\, dx$; (*d*) $\int (a/T^2)\, dT$.

1.62 For $H_2O(l)$ at 50°C and 1 atm, $\alpha = 4.576 \times 10^{-4}$ K^{-1}, $\kappa = 44.17 \times 10^{-6}$ bar^{-1}, and $V_m = 18.2334$ cm^3/mol. (*a*) Estimate V_{m,H_2O} at 52°C and 1 atm and compare the result with the experimental value 18.2504 cm^3/mol. Neglect the temperature dependence of α. (*b*) Estimate V_{m,H_2O} at 50°C and 200 bar and compare with the experimental value 18.078 cm^3/mol.

1.63 State whether each of the following is a number or is a function of x: (*a*) $\int e^{x^2}\, dx$; (*b*) $\int_1^2 e^{x^2}\, dx$; (*c*) $\Sigma_{x=1}^{203} e^{x^2}$.

1.64 In which of the following is t a dummy variable? (*a*) $\int e^{t^2}\, dt$; (*b*) $\int_0^3 e^{t^2}\, dt$; (*c*) $\Sigma_{t=1}^{100} t^5$.

1.65 (*a*) If $df(x)/dx = 2x^3 + 3e^{5x}$, find $f(x)$. (*b*) If $\int f(x)\, dx = 3x^8 + C$, where C is a constant, find $f(x)$.

1.66 (*a*) Use a programmable calculator or a computer to obtain approximations to the integral $\int_2^3 x^2\, dx$ by evaluating the sum (1.58) for $\Delta x = 0.1$, 0.01, and 0.001; take the x_i values at the left end of each subinterval. Compare your results with the exact value. (*b*) Use (1.58) with $\Delta x = 0.01$ to obtain an approximate value of $\int_0^1 e^{-x^2}\, dx$.

1.67 (*a*) Find $\log_{10} (4.2 \times 10^{1750})$. (*b*) Find $\ln (6.0 \times 10^{-200})$. (*c*) If $\log_{10} y = -138.265$, find y. (*d*) If $\ln z = 260.433$, find z.

1.68 Find (*a*) $\log_2 32$; (*b*) $\log_{43} 1$.

General

1.69 Classify each property as intensive or extensive; (*a*) temperature; (*b*) mass; (*c*) density; (*d*) electric field strength; (*e*) α; (*f*) mole fraction of a component.

1.70 For O_2 gas in thermal equilibrium with boiling sulfur, the following values of PV_m versus P are found:

P/torr	1000	500	250
PV_m/(L atm mol^{-1})	59.03	58.97	58.93

(Since P has units of pressure, P/torr is dimensionless.) From a plot of these data, find the boiling point of sulfur.

1.71 True or false? (*a*) Every isolated system is closed. (*b*) Every closed system is isolated. (*c*) For a fixed amount of an ideal gas, the product PV remains constant during any process. (*d*) The pressure of a nonideal gas mixture is equal to the sum of the partial pressures defined by $P_i \equiv x_iP$. (*e*) dy/dx is equal to $\Delta y/\Delta x$ for all functions y. (*f*) dy/dx is equal to $\Delta y/\Delta x$ only for functions that vary linearly with x according to $y = mx + b$. (*g*) $\ln (b/a) = -\ln (a/b)$. (*h*) If $\ln x$ is negative, then x lies between 0 and 1. (*i*) Ideal-gas isotherms farther away from the axes of a P-versus-V plot correspond to higher temperatures. (*j*) The partial derivative $(\partial P/\partial T)_V$ is an infinitesimally small quantity. (*k*) If G is a function of T and P, then $dG = (\partial G/\partial T)_P + (\partial G/\partial P)_T$.

CHAPTER

2

The First Law of Thermodynamics

CHAPTER OUTLINE

Chapter 1 introduced some of the vocabulary of thermodynamics and defined the important state function temperature. Another key state function in thermodynamics is the internal energy U, whose existence is postulated by the first law of thermodynamics; this law is the main topic of Chapter 2. The first law states that the total energy of system plus surroundings remains constant (is conserved). Closely related to the internal energy is the state function enthalpy H, defined in Sec. 2.5. Other important state functions introduced in this chapter are the heat capacities at constant volume and at constant pressure, C_V and C_P (Sec. 2.6), which give the rates of change of the internal energy and enthalpy with temperature [Eq. (2.53)]. As a preliminary to the main work of this chapter, Sec. 2.1 reviews classical mechanics.

The internal energy of a thermodynamic system is the sum of the molecular energies, as will be discussed in detail in Sec. 2.11. *Energy is a key concept in all areas of physical chemistry.* In quantum chemistry, a key step to calculating molecular properties is solving the Schrödinger equation, which is an equation that gives the allowed energy levels of a molecule. In statistical mechanics, the key to evaluating thermodynamic properties from molecular properties is to find something called the partition function, which is a certain sum over energy levels of the system. The rate of a chemical reaction depends strongly on the activation energy of the reaction. More generally, the kinetics of a reaction is determined by something called the potential-energy surface of the reaction.

The importance of energy in the economy is obvious. World consumption of energy increased from 3.0×10^{20} J in 1980 to 4.9×10^{20} J in 2005, with fossil fuels (oil, coal, natural gas) supplying 86% of the 2005 total.

Energy transformations play a key role in the functioning of biological organisms.

2.1 CLASSICAL MECHANICS

Two important concepts in thermodynamics are work and energy. Since these concepts originated in classical mechanics, we review this subject before continuing with thermodynamics.

Classical mechanics (first formulated by the alchemist, theologian, physicist, and mathematician Isaac Newton) deals with the laws of motion of macroscopic bodies whose speeds are small compared with the speed of light c. For objects with speeds not small compared with c, one must use Einstein's **relativistic mechanics.** Since the thermodynamic systems we consider will not be moving at high speeds, we need not worry about relativistic effects. For nonmacroscopic objects (for example, electrons), one must use **quantum mechanics.** Thermodynamic systems are of macroscopic size, so we shall not need quantum mechanics at this point.

Newton's Second Law

The fundamental equation of classical mechanics is **Newton's second law of motion:**

$$\mathbf{F} = m\mathbf{a} \qquad \mathbf{(2.1)^*}$$

where m is the mass of a body, $\mathbf{F}$ is the vector sum of all forces acting on it at some instant of time, and $\mathbf{a}$ is the acceleration the body undergoes at that instant. $\mathbf{F}$ and $\mathbf{a}$ are vectors, as indicated by the boldface type. **Vectors** have both magnitude and direction. **Scalars** (for example, m) have only a magnitude. To define acceleration, we set up a coordinate system with three mutually perpendicular axes x, y, and z. Let $\mathbf{r}$ be the vector from the coordinate origin to the particle (Fig. 2.1). The particle's **velocity v** is the instantaneous rate of change of its position vector $\mathbf{r}$ with respect to time:

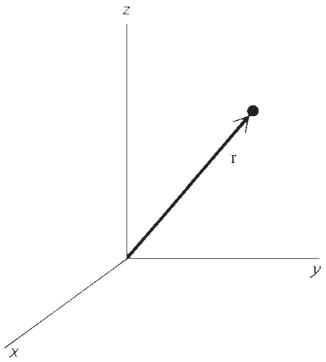


Figure 2.1

The displacement vector **r** from the origin to a particle.

$$\mathbf{v} \equiv d\mathbf{r}/dt \qquad \mathbf{(2.2)^*}$$

The magnitude (length) of the vector $\mathbf{v}$ is the particle's **speed** v. The particle's **acceleration a** is the instantaneous rate of change of its velocity:

$$\mathbf{a} \equiv d\mathbf{v}/dt = d^2\mathbf{r}/dt^2 \qquad \mathbf{(2.3)^*}$$

A vector in three-dimensional space has three components, one along each of the coordinate axes. Equality of vectors means equality of their corresponding components, so a vector equation is equivalent to three scalar equations. Thus Newton's second law $\mathbf{F} = m\mathbf{a}$ is equivalent to the three equations

$$F_x = ma_x, \qquad F_y = ma_y, \qquad F_z = ma_z \qquad (2.4)$$

where F_x and a_x are the x components of the force and the acceleration. The x component of the position vector $\mathbf{r}$ is simply x, the value of the particle's x coordinate. Therefore (2.3) gives $a_x = d^2x/dt^2$, and (2.4) becomes

$$F_x = m\frac{d^2x}{dt^2}, \qquad F_y = m\frac{d^2y}{dt^2}, \qquad F_z = m\frac{d^2z}{dt^2} \qquad (2.5)$$

The *weight* W of a body is the gravitational force exerted on it by the earth. If g is the acceleration due to gravity, Newton's second law gives

$$W = mg \qquad (2.6)$$

Units

In 1960 the General Conference on Weights and Measures recommended a single system of units for use in science. This system is called the **International System of Units** (*Système International d'Unités*), abbreviated **SI.** In mechanics, the SI uses meters (m) for length, kilograms (kg) for mass, and seconds (s) for time. A force that produces an acceleration of one meter per second^2 when applied to a one-kilogram mass is defined as one **newton** (N):

$$1\text{ N} \equiv 1\text{ kg m/s}^2 \qquad (2.7)$$

If one were to adhere to SI units, pressures would always be given in newtons/meter^2 (pascals). However, it seems clear that many scientists will continue to use such units as atmospheres and torrs for many years to come. The current scientific literature increasingly uses SI units, but since many non-SI units continue to be used, it is helpful to be familiar with both SI units and commonly used non-SI units. SI units for some quantities introduced previously are cubic meters (m^3) for volume, kg/m^3 for density, pascals for pressure, kelvins for temperature, moles for amount of substance, and kg/mol for molar mass.

Work

Suppose a force **F** acts on a body while the body undergoes an infinitesimal displacement dx in the x direction. The infinitesimal amount of **work** dw done on the body by the force **F** is defined as

$$dw \equiv F_x\,dx \qquad \textbf{(2.8)*}$$

where F_x is the component of the force in the direction of the displacement. If the infinitesimal displacement has components in all three directions, then

$$dw \equiv F_x\,dx + F_y\,dy + F_z\,dz \qquad (2.9)$$

Consider now a noninfinitesimal displacement. For simplicity, let the particle be moving in one dimension. The particle is acted on by a force $F(x)$ whose magnitude depends on the particle's position. Since we are using one dimension, F has only one component and need not be considered a vector. The work w done by F during displacement of the particle from x_1 to x_2 is the sum of the infinitesimal amounts of work (2.8) done during the displacement: $w = \sum F(x)\,dx$. But this sum of infinitesimal quantities is the definition of the definite integral [Eq. (1.59)], so

$$w = \int_{x_1}^{x_2} F(x)\,dx \qquad (2.10)$$

In the special case that F is constant during the displacement, (2.10) becomes

$$w = F(x_2 - x_1) \qquad \text{for } F \text{ constant} \qquad (2.11)$$

From (2.8), the units of work are those of force times length. The SI unit of work is the **joule** (J):

$$1\text{ J} \equiv 1\text{ N m} = 1\text{ kg m}^2/\text{s}^2 \qquad (2.12)$$

Power P is defined as the rate at which work is done. If an agent does work dw in time dt, then $P \equiv dw/dt$. The SI unit of power is the *watt* (W): 1 W $\equiv$ 1 J/s.

Mechanical Energy

We now prove the *work–energy theorem*. Let **F** be the total force acting on a particle, and let the particle move from point 1 to point 2. Integration of (2.9) gives as the total work done on the particle:

$$w = \int_1^2 F_x\,dx + \int_1^2 F_y\,dy + \int_1^2 F_z\,dz \qquad (2.13)$$

Newton's second law gives $F_x = ma_x = m(dv_x/dt)$. Also, $dv_x/dt = (dv_x/dx)\,(dx/dt) = (dv_x/dx)v_x$. Therefore $F_x = mv_x(dv_x/dx)$, with similar equations for F_y and F_z. We have $F_x\,dx = mv_x\,dv_x$, and (2.13) becomes

$$w = \int_1^2 mv_x\,dv_x + \int_1^2 mv_y\,dv_y + \int_1^2 mv_z\,dv_z$$

$$w = \tfrac{1}{2}m(v_{x2}^2 + v_{y2}^2 + v_{z2}^2) - \tfrac{1}{2}m(v_{x1}^2 + v_{y1}^2 + v_{z1}^2) \qquad (2.14)$$

We now define the **kinetic energy** K of the particle as

$$K \equiv \tfrac{1}{2}mv^2 = \tfrac{1}{2}m(v_x^2 + v_y^2 + v_z^2) \qquad \textbf{(2.15)*}$$

The right side of (2.14) is the final kinetic energy K_2 minus the initial kinetic energy K_1:

$$w = K_2 - K_1 = \Delta K \qquad \text{one-particle syst.} \qquad (2.16)$$

where ΔK is the change in kinetic energy. The *work–energy theorem* (2.16) states that the work done on the particle by the force acting on it equals the change in kinetic energy of the particle. It is valid because we defined kinetic energy in such a manner as to make it valid.

Besides kinetic energy, there is another kind of energy in classical mechanics. Suppose we throw a body up into the air. As it rises, its kinetic energy decreases, reaching zero at the high point. What happens to the kinetic energy the body loses as it rises? It proves convenient to introduce the notion of a *field* (in this case, a gravitational field) and to say that the decrease in kinetic energy of the body is accompanied by a corresponding increase in the *potential energy* of the field. Likewise, as the body falls back to earth, it gains kinetic energy and the gravitational field loses a corresponding amount of potential energy. Usually, we don't refer explicitly to the field but simply ascribe a certain amount of potential energy to the body itself, the amount depending on the location of the body in the field.

To put the concept of potential energy on a quantitative basis, we proceed as follows. Let the forces acting on the particle depend only on the particle's position and not on its velocity, or the time, or any other variable. Such a force **F** with $F_x = F_x(x, y, z)$, $F_y = F_y(x, y, z)$, $F_z = F_z(x, y, z)$ is called a *conservative force,* for a reason to be seen shortly. Examples of conservative forces are gravitational forces, electrical forces, and the Hooke's law force of a spring. Some nonconservative forces are air resistance, friction, and the force you exert when you kick a football. For a conservative force, we define the **potential energy** $V(x, y, z)$ as a function of x, y, and z whose partial derivatives satisfy

$$\frac{\partial V}{\partial x} \equiv -F_x, \qquad \frac{\partial V}{\partial y} \equiv -F_y, \qquad \frac{\partial V}{\partial z} \equiv -F_z \tag{2.17}$$

Since only the partial derivatives of V are defined, V itself has an arbitrary additive constant. We can set the zero level of potential energy anywhere we please.

From (2.13) and (2.17), it follows that

$$w = -\int_1^2 \frac{\partial V}{\partial x}\,dx - \int_1^2 \frac{\partial V}{\partial y}\,dy - \int_1^2 \frac{\partial V}{\partial z}\,dz \tag{2.18}$$

Since $dV = (\partial V/\partial x)\,dx + (\partial V/\partial y)\,dy + (\partial V/\partial z)\,dz$ [Eq. (1.30)], we have

$$w = -\int_1^2 dV = -(V_2 - V_1) = V_1 - V_2 \tag{2.19}$$

But Eq. (2.16) gives $w = K_2 - K_1$. Hence $K_2 - K_1 = V_1 - V_2$, or

$$K_1 + V_1 = K_2 + V_2 \tag{2.20}$$

When only conservative forces act, the sum of the particle's kinetic energy and potential energy remains constant during the motion. This is the law of conservation of mechanical energy. Using E_{mech} for the total **mechanical energy,** we have

$$E_{\text{mech}} = K + V \tag{2.21}$$

If only conservative forces act, E_{mech} remains constant.

What is the potential energy of an object in the earth's gravitational field? Let the x axis point outward from the earth with the origin at the earth's surface. We have $F_x = -mg$, $F_y = F_z = 0$. Equation (2.17) gives $\partial V/\partial x = mg$, $\partial V/\partial y = 0 = \partial V/\partial z$. Integration gives $V = mgx + C$, where C is a constant. (In doing the integration, we assumed the object's distance above the earth's surface was small enough for g to be considered constant.) Choosing the arbitrary constant as zero, we get

$$V = mgh \tag{2.22}$$

where h is the object's altitude above the earth's surface. As an object falls to earth, its potential energy mgh decreases and its kinetic energy $\frac{1}{2}mv^2$ increases. Provided the effect of air friction is negligible, the total mechanical energy $K + V$ remains constant as the object falls.

We have considered a one-particle system. Similar results hold for a many-particle system. (See H. Goldstein, *Classical Mechanics,* 2d ed., Addison-Wesley, 1980, sec. 1-2, for derivations.) The kinetic energy of an n-particle system is the sum of the kinetic energies of the individual particles:

$$K = K_1 + K_2 + \cdots + K_n = \frac{1}{2}\sum_{i=1}^{n} m_i v_i^2 \tag{2.23}$$

Let the particles exert conservative forces on one another. The potential energy V of the system is not the sum of the potential energies of the individual particles. Instead, V is a property of the system as a whole. V turns out to be the sum of contributions due to pairwise interactions between particles. Let V_{ij} be the contribution to V due to the forces acting between particles i and j. One finds

$$V = \sum_i \sum_{j>i} V_{ij} \tag{2.24}$$

The double sum indicates that we sum over all pairs of i and j values except those with i equal to or greater than j. Terms with $i = j$ are omitted because a particle does not exert a force on itself. Also, only one of the terms V_{12} and V_{21} is included, to avoid counting the interaction between particles 1 and 2 twice. For example, in a system of three particles, $V = V_{12} + V_{13} + V_{23}$. If external forces act on the particles of the system, their contributions to V must also be included. [V_{ij} is defined by equations similar to (2.17).]

One finds that $K + V = E_{\text{mech}}$ is constant for a many-particle system with only conservative forces acting.

The mechanical energy $K + V$ is a measure of the work the system can do. When a particle's kinetic energy decreases, the work–energy theorem $w = \Delta K$ [Eq. (2.16)] says that w, the work done on it, is negative; that is, the particle does work on the surroundings equal to its loss of kinetic energy. Since potential energy is convertible to kinetic energy, potential energy can also be converted ultimately to work done on the surroundings. Kinetic energy is due to motion. Potential energy is due to the positions of the particles.

EXAMPLE 2.1 Work

A woman slowly lifts a 30.0-kg object to a height of 2.00 m above its initial position. Find the work done on the object by the woman, and the work done by the earth.

The force exerted by the woman equals the weight of the object, which from Eq. (2.6) is $F = mg = (30.0 \text{ kg})(9.81 \text{ m/s}^2) = 294 \text{ N}$. From (2.10) and (2.11), the work she does on the object is

$$w = \int_{x_1}^{x_2} F(x)\,dx = F\,\Delta x = (294 \text{ N})(2.00 \text{ m}) = 588 \text{ J}$$

The earth exerts an equal and opposite force on the object compared with the lifter, so the earth does -588 J of work on the object. This work is negative because the force and the displacement are in opposite directions. The total work done on the object by all forces is zero. The work–energy theorem (2.16) gives $w = \Delta K = 0$, in agreement with the fact that the object started at rest and ended at rest. (We derived the work–energy theorem for a single particle, but it also applies to a perfectly rigid body.)

Exercise

A sphere of mass m is attached to a spring, which exerts a force $F = -kx$ on the sphere, where k (called the force constant) is a constant characteristic of the spring and x is the displacement of the sphere from its equilibrium position (the position where the spring exerts no force on the sphere). The sphere is initially at rest at its equilibrium position. Find the expression for the work w done by someone who slowly displaces the sphere to a final distance d from its equilibrium position. Calculate w if $k = 10$ N/m and $d = 6.0$ cm. (*Answer:* $\frac{1}{2}kd^2$, 0.018 J.)

2.2 *P-V* WORK

Work in thermodynamics is defined as in classical mechanics. When part of the surroundings exerts a macroscopically measurable force **F** on matter in the system while this matter moves a distance dx at the point of application of **F,** then the surroundings has done **work** $dw = F_x\,dx$ [Eq. (2.8)] on the system, where F_x is the component of **F** in the direction of the displacement. **F** may be a mechanical, electrical, or magnetic force and may act on and displace the entire system or only a part of the system. When F_x and the displacement dx are in the same direction, positive work is done on the system: $dw > 0$. When F_x and dx are in opposite directions, dw is negative.

Reversible *P-V* Work

The most common way work is done on a thermodynamic system is by a change in the system's volume. Consider the system of Fig. 2.2. The system consists of the matter contained within the piston and cylinder walls and has pressure P. Let the external pressure on the frictionless piston also be P. Equal opposing forces act on the piston, and it is in mechanical equilibrium. Let x denote the piston's location. If the external pressure on the piston is now increased by an infinitesimal amount, this increase will produce an infinitesimal imbalance in forces on the piston. The piston will move inward by an infinitesimal distance dx, thereby decreasing the system's volume and increasing its pressure until the system pressure again balances the external pressure. During this infinitesimal process, which occurs at an infinitesimal rate, the system will be infinitesimally close to equilibrium.

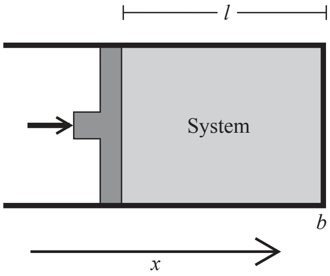


Figure 2.2

A system confined by a piston.

The piston, which is part of the surroundings, exerted a force, which we denote by F_x, on matter in the system at the system–piston boundary while this matter moved a distance dx. The surroundings therefore did work $dw = F_x\,dx$ on the system. Let F be the magnitude of the force exerted by the system on the piston. Newton's third law (action = reaction) gives $F = F_x$. The definition $P = F/A$ of the system's pressure P gives $F_x = F = PA$, where A is the piston's cross-sectional area. Therefore the work $dw = F_x\,dx$ done on the system in Fig. 2.2 is

$$dw = PA\,dx \tag{2.25}$$

The system has cross-sectional area A and length $l = b - x$ (Fig. 2.2), where x is the piston's position and b is the position of the fixed end of the system. The volume of this cylindrical system is $V = Al = Ab - Ax$. The change in system volume when the piston moves by dx is $dV = d(Ab - Ax) = -A\,dx$. Equation (2.25) becomes

$$dw_{\text{rev}} = -P\,dV \qquad \text{closed system, reversible process} \qquad \mathbf{(2.26)}^*$$

The subscript rev stands for reversible. The meaning of "reversible" will be discussed shortly. We implicitly assumed a closed system in deriving (2.26). When matter is transported between system and surroundings, the meaning of work becomes ambiguous; we shall not consider this case. We derived (2.26) for a particular shape of system, but it can be shown to be valid for every system shape (see *Kirkwood and Oppenheim,* sec. 3-1).

We derived (2.26) by considering a contraction of the system's volume ($dV < 0$). For an expansion ($dV > 0$), the piston moves outward (in the negative x direction), and the displacement dx of the matter at the system–piston boundary is negative ($dx < 0$). Since F_x is positive (the force exerted by the piston on the system is in the positive x direction), the work $dw = F_x\,dx$ done on the system by the surroundings is negative when the system expands. For an expansion, the system's volume change is still given by $dV = -A\,dx$ (where $dx < 0$ and $dV > 0$), and (2.26) still holds.

In a contraction, the work done on the system is positive ($dw > 0$). In an expansion, the work done on the system is negative ($dw < 0$). (In an expansion, the work done on the surroundings is positive.)

So far we have considered only an infinitesimal volume change. Suppose we carry out an infinite number of successive infinitesimal changes in the external pressure. At each such change, the system's volume changes by dV and work $-P\,dV$ is done on the system, where P is the current value of the system's pressure. The total work w done on the system is the sum of the infinitesimal amounts of work, and this sum of infinitesimal quantities is the following definite integral:

$$w_{\text{rev}} = -\int_1^2 P\,dV \qquad \text{closed syst., rev. proc.} \qquad (2.27)$$

where 1 and 2 are the initial and final states of the system, respectively.

The finite volume change to which (2.27) applies consists of an infinite number of infinitesimal steps and takes an infinite amount of time to carry out. In this process, the difference between the pressures on the two sides of the piston is always infinitesimally small, so finite unbalanced forces never act and the system remains infinitesimally close to equilibrium throughout the process. Moreover, the process can be reversed at any stage by an infinitesimal change in conditions, namely, by infinitesimally changing the external pressure. Reversal of the process will restore both system and surroundings to their initial conditions.

A **reversible process** is one where the system is always infinitesimally close to equilibrium, and an infinitesimal change in conditions can reverse the process to restore both system and surroundings to their initial states. A reversible process is obviously an idealization.

Equations (2.26) and (2.27) apply only to reversible expansions and contractions. More precisely, they apply to mechanically reversible volume changes. There could be a chemically irreversible process, such as a chemical reaction, occurring in the system during the expansion, but so long as the mechanical forces are only infinitesimally unbalanced, (2.26) and (2.27) apply.

The work (2.27) done in a volume change is called ***P-V* work.** Later on, we shall deal with electrical work and work of changing the system's surface area, but for now, only systems with P-V work will be considered.

We have defined the symbol w to stand for work done *on* the system by the surroundings. Some texts use w to mean work done *by* the system on its surroundings. Their w is the negative of ours.

Line Integrals

The integral $\int_1^2 P\,dV$ in (2.27) is not an ordinary integral. For a closed system of fixed composition, the system's pressure P is a function of its temperature and volume: $P = P(T, V)$. To calculate w_{rev}, we must evaluate the negative of

$$\int_1^2 P(T, V)\,dV \tag{2.28}$$

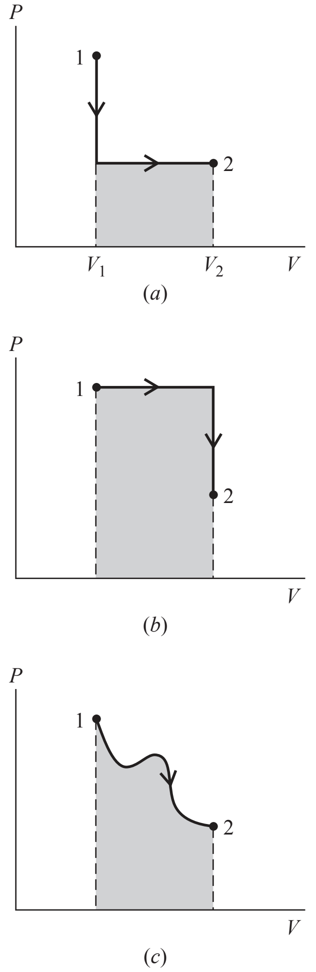
The integrand $P(T, V)$ is a function of *two* independent variables T and V. In an ordinary definite integral, the integrand is a function of *one* variable, and the value of the ordinary definite integral $\int_a^b f(x)\,dx$ is determined once the function f and the limits a and b are specified. For example, $\int_1^3 x^2\,dx = 3^3/3 - 1^3/3 = 26/3$. In contrast, in $\int_1^2 P(T, V)\,dV$, both of the independent variables T and V may change during the volume-change process, and the value of the integral depends on how T and V vary. For example, if the system is an ideal gas, then $P = nRT/V$ and $\int_1^2 P(T, V)\,dV = nR\int_1^2 (T/V)\,dV$. Before we can evaluate $\int_1^2 (T/V)\,dV$, we must know how both T and V change during the process.

The integral (2.28) is called a **line integral.** Sometimes the letter L is put under the integral sign of a line integral. The value of the line integral (2.28) is defined as the sum of the infinitesimal quantities $P(T, V)\,dV$ for the particular process used to go from state 1 to state 2. This sum equals the area under the curve that plots P versus V. Figure 2.3 shows three of the many possible ways in which we might carry out a reversible volume change starting at the same initial state (state 1 with pressure P_1 and volume V_1) and ending at the same final state (state 2).

In process (*a*), we first hold the volume constant at V_1 and reduce the pressure from P_1 to P_2 by cooling the gas. We then hold the pressure constant at P_2 and heat the gas to expand it from V_1 to V_2. In process (*b*), we first hold P constant at P_1 and heat the gas until its volume reaches V_2. Then we hold V constant at V_2 and cool the gas until its pressure drops to P_2. In process (*c*), the independent variables V and T vary in an irregular way, as does the dependent variable P.

For each process, the integral $\int_1^2 P\,dV$ equals the shaded area under the P-versus-V curve. These areas clearly differ, and the integral $\int_1^2 P\,dV$ has different values for processes (*a*), (*b*), and (*c*). The reversible work $w_{\text{rev}} = -\int_1^2 P\,dV$ thus has different values for each of the processes (*a*), (*b*), and (*c*). We say that w_{rev} (which equals minus the shaded area under the P-versus-V curve) depends on the *path* used to go from state 1 to 2, meaning that it depends on the specific process used. There are an infinite number of ways of going from state 1 to state 2, and w_{rev} can have any positive or negative value for a given change of state.

The plots of Fig. 2.3 imply pressure equilibrium within the system during the process. In an irreversible expansion (see after Example 2.2), the system may have no single well-defined pressure, and we cannot plot such a process on a P-V diagram.



(*a*)

(*b*)

(*c*)

Figure 2.3

The work w done on the system in a reversible process (the heavy lines) equals minus the shaded area under the P-versus-V curve. The work depends on the process used to go from state 1 to state 2.

EXAMPLE 2.2 *P-V* work

Find the work w_{rev} for processes (*a*) and (*b*) of Fig. 2.3 if $P_1 = 3.00$ atm, $V_1 = 500\ \text{cm}^3$, $P_2 = 1.00$ atm, and $V_2 = 2000\ \text{cm}^3$. Also, find w_{rev} for the reverse of process (*a*).

We have $w_{\text{rev}} = -\int_1^2 P\,dV$. The line integral $\int_1^2 P\,dV$ equals the area under the P-versus-V curve. In Fig. 2.3*a*, this area is rectangular and equals

$$(V_2 - V_1)P_2 = (2000\ \text{cm}^3 - 500\ \text{cm}^3)(1.00\ \text{atm}) = 1500\ \text{cm}^3\ \text{atm}$$

Hence $w_{\text{rev}} = -1500\ \text{cm}^3$ atm. The units cm^3 atm are not customarily used for work, so we shall convert to joules by multiplying and dividing by the values of the gas constant $R = 8.314$ J/(mol K) and $R = 82.06$ cm^3 atm/(mol K) [Eqs. (1.19) and (1.20)]:

$$w_{\text{rev}} = -1500 \text{ cm}^3 \text{ atm } \frac{8.314 \text{ J mol}^{-1}\text{ K}^{-1}}{82.06 \text{ cm}^3 \text{ atm mol}^{-1}\text{ K}^{-1}} = -152 \text{ J}$$

An alternative procedure is to note that no work is done during the constant-volume part of process (*a*); all the work is done during the second step of the process, in which P is held constant at P_2. Therefore

$$w_{\text{rev}} = -\int_1^2 P\,dV = -\int_{V_1}^{V_2} P_2\,dV = -P_2\int_{V_1}^{V_2} dV = -P_2V\Big|_{V_1}^{V_2}$$

$$= -P_2(V_2 - V_1) = -(1.00 \text{ atm})(1500 \text{ cm}^3) = -152 \text{ J}$$

Similarly, we find for process (*b*) that $w = -4500$ cm^3 atm $= -456$ J (see the exercise in this example).

Processes (*a*) and (*b*) are expansions. Hence the system does positive work on its surroundings, and the work w done on the system is negative in these processes.

For the reverse of process (*a*), all the work is done during the first step, during which P is constant at 1.00 atm and V starts at 2000 cm^3 and ends at 500 cm^3. Hence $w = -\int_{2000 \text{ cm}^3}^{500 \text{ cm}^3} (1.00 \text{ atm})\,dV = -(1.00 \text{ atm})(500 \text{ cm}^3 - 2000 \text{ cm}^3) = 152$ J.

Exercise

Find w_{rev} for process (*b*) of Fig. 2.3 using the P_1, V_1, P_2, V_2 values given for process (*a*). (*Answer:* -4500 cm^3 atm $= -456$ J.)

Irreversible *P-V* Work

The work w in a mechanically irreversible volume change sometimes cannot be calculated with thermodynamics.

For example, suppose the external pressure on the piston in Fig. 2.2 is suddenly reduced by a finite amount and is held fixed thereafter. The inner pressure on the piston is then greater than the outer pressure by a finite amount, and the piston is accelerated outward. This initial acceleration of the piston away from the system will destroy the uniform pressure in the enclosed gas. The system's pressure will be lower near the piston than farther away from it. Moreover, the piston's acceleration produces turbulence in the gas. Thus we cannot give a thermodynamic description of the state of the system.

We have $dw = F_x\,dx$. For *P-V* work, F_x is the force at the system–surroundings boundary, which is where the displacement dx is occurring. This boundary is the inner face of the piston, so $dw_{\text{irrev}} = -P_{\text{surf}}\,dV$, where P_{surf} is the pressure the system exerts on the inner face of the piston. (By Newton's third law, P_{surf} is also the pressure the piston's inner face exerts on the system.) Because we cannot use thermodynamics to calculate P_{surf} during the turbulent, irreversible expansion, we cannot find dw_{irrev} from thermodynamics.

The law of conservation of energy can be used to show that, for a frictionless piston (Prob. 2.22),

$$dw_{\text{irrev}} = -P_{\text{ext}}\,dV - dK_{\text{pist}} \tag{2.29}$$

where P_{ext} is the external pressure on the outer face of the piston and dK_{pist} is the infinitesimal change in piston kinetic energy. The integrated form of (2.29) is $w_{\text{irrev}} = -\int_1^2 P_{\text{ext}}\,dV - \Delta K_{\text{pist}}$.

If we wait long enough, the piston's kinetic energy will be dissipated by the internal friction (viscosity—see Sec. 15.3) in the gas. The gas will be heated, and the piston will eventually come to rest (perhaps after undergoing oscillations). Once the piston has come to rest, we have $\Delta K_{\text{pist}} = 0 - 0 = 0$, since the piston started and ended at rest. We then have $w_{\text{irrev}} = -\int_1^2 P_{\text{ext}}\, dV$. Hence we can find w_{irrev} after the piston has come to rest. If, however, part of the piston's kinetic energy is transferred to some other body in the surroundings before the piston comes to rest, then thermodynamics cannot calculate the work exchanged between system and surroundings. For further discussion, see D. Kivelson and I. Oppenheim, *J. Chem. Educ.,* **43,** 233 (1966); G. L. Bertrand, ibid., **82,** 874 (2005); E. A. Gislason and N. C. Craig, ibid., **84,** 499 (2007).

Summary

For now, we shall deal only with work done due to a volume change. The work done *on* a closed system in an infinitesimal mechanically reversible process is $dw_{\text{rev}} = -P\, dV$. The work $w_{\text{rev}} = -\int_1^2 P\, dV$ depends on the path (the process) used to go from the initial state 1 to the final state 2.

2.3 HEAT

When two bodies at unequal temperatures are placed in contact, they eventually reach thermal equilibrium at a common intermediate temperature. We say that heat has flowed from the hotter body to the colder one. Let bodies 1 and 2 have masses m_1 and m_2 and initial temperatures T_1 and T_2, with $T_2 > T_1$; let T_f be the final equilibrium temperature. Provided the two bodies are isolated from the rest of the universe and no phase change or chemical reaction occurs, one experimentally observes the following equation to be satisfied for all values of T_1 and T_2:

$$m_2c_2(T_2 - T_f) = m_1c_1(T_f - T_1) \equiv q \tag{2.30}$$

where c_1 and c_2 are constants (evaluated experimentally) that depend on the composition of bodies 1 and 2. We call c_1 the **specific heat capacity** (or **specific heat**) of body 1. We define q, the amount of **heat** that flowed from body 2 to body 1, as equal to $m_2c_2(T_2 - T_f)$.

The unit of heat commonly used in the nineteenth and early twentieth centuries was the **calorie** (cal), defined as the quantity of heat needed to raise one gram of water from 14.5°C to 15.5°C at 1 atm pressure. (This definition is no longer used, as we shall see in Sec. 2.4.) By definition, $c_{H_2O} = 1.00$ cal/(g °C) at 15°C and 1 atm. Once the specific heat capacity of water has been defined, the specific heat capacity c_2 of any other substance can be found from (2.30) by using water as substance 1. When specific heats are known, the heat q transferred in a process can then be calculated from (2.30).

Actually, (2.30) does not hold exactly, because the specific heat capacities of substances are functions of temperature and pressure. When an infinitesimal amount of heat dq_P flows at constant pressure P into a body of mass m and specific heat capacity at constant pressure c_P, the body's temperature is raised by dT and

$$dq_P \equiv mc_P\, dT \tag{2.31}$$

where c_P is a function of T and P. Summing up the infinitesimal flows of heat, we get the total heat that flowed as a definite integral:

$$q_P = m\int_{T_1}^{T_2} c_P(T)\, dT \qquad \text{closed syst., } P \text{ const.} \tag{2.32}$$

The pressure dependence of c_P was omitted because P is held fixed for the process. The quantity mc_P is the *heat capacity at constant pressure* C_P of the body: $C_P \equiv mc_P$. From (2.31) we have

$$C_P = dq_P/dT \tag{2.33}$$

Equation (2.30) is more accurately written as

$$m_2 \int_{T_f}^{T_2} c_{P2}(T)\, dT = m_1 \int_{T_1}^{T_f} c_{P1}(T)\, dT = q_P \tag{2.34}$$

If the dependence of c_{P2} and c_{P1} on T is negligible, (2.34) reduces to (2.30).

We gave examples in Sec. 2.2 of reversible and irreversible ways of doing work on a system. Likewise, heat can be transferred reversibly or irreversibly. A reversible transfer of heat requires that the temperature difference between the two bodies be infinitesimal. When there is a finite temperature difference between the bodies, the heat flow is irreversible.

Two bodies need not be in direct physical contact for heat to flow from one to the other. Radiation transfers heat between two bodies at different temperatures (for example, the sun and the earth). The transfer occurs by emission of electromagnetic waves by one body and absorption of these waves by the second body. An adiabatic wall must be able to block radiation.

Equation (2.32) was written with the implicit assumption that the system is closed (m fixed). As is true for work, the meaning of heat is ambiguous for open systems. (See R. Haase, *Thermodynamics of Irreversible Processes,* Addison-Wesley, 1969, pp. 17–21, for a discussion of open systems.)

2.4 THE FIRST LAW OF THERMODYNAMICS

As a rock falls toward the earth, its potential energy is transformed into kinetic energy. When it hits the earth and comes to rest, what has happened to its energy of motion? Or consider a billiard ball rolling on a billiard table. Eventually it comes to rest. Again, what happened to its energy of motion? Or imagine that we stir some water in a beaker. Eventually the water comes to rest, and we again ask: What happened to its energy of motion? Careful measurement will show very slight increases in the temperatures of the rock, the billiard ball, and the water (and in their immediate surroundings). Knowing that matter is composed of molecules, we find it easy to believe that the macroscopic kinetic energies of motion of the rock, the ball, and the water were converted into energy at the molecular level. The average molecular translational, rotational, and vibrational energies in the bodies were increased slightly, and these increases were reflected in the temperature rises.

We therefore ascribe an **internal energy** U to a body, in addition to its macroscopic kinetic energy K and potential energy V, discussed in Sec. 2.1. This internal energy consists of: molecular translational, rotational, vibrational, and electronic energies; the relativistic rest-mass energy $m_{\text{rest}}c^2$ of the electrons and the nuclei; and potential energy of interaction between the molecules. These energies are discussed in Sec. 2.11.

The total energy E of a body is therefore

$$E = K + V + U \tag{2.35}$$

where K and V are the macroscopic (not molecular) kinetic and potential energies of the body (due to motion of the body through space and the presence of fields that act on the body) and U is the internal energy of the body (due to molecular motions and intermolecular interactions). Since thermodynamics is a macroscopic science, the development of thermodynamics requires no knowledge of the nature of U. All that is needed is some means of measuring the change in U for a process. This will be provided by the first law of thermodynamics.

In most applications of thermodynamics that we shall consider, the system will be at rest and external fields will not be present. Therefore, K and V will be zero, and the total energy E will be equal to the internal energy U. (The effect of the earth's gravitational field on thermodynamic systems is usually negligible, and gravity will usually be ignored; see, however, Sec. 14.8.) Chemical engineers often deal with systems of flowing fluids; here, $K \neq 0$.

With our present knowledge of the molecular structure of matter, we take it for granted that a flow of heat between two bodies involves a transfer of internal energy between them. However, in the eighteenth and nineteenth centuries the molecular theory of matter was controversial. The nature of heat was not well understood until about 1850. In the late 1700s, most scientists accepted the caloric theory of heat. (Some students still do, unhappily.) Caloric was a hypothetical fluid substance present in matter and supposed to flow from a hot body to a cold one. The amount of caloric lost by the hot body equaled the amount gained by the cold body. The total amount of caloric was believed to be conserved in all processes.

Strong evidence against the caloric theory was provided by Count Rumford in 1798. In charge of the army of Bavaria, he observed that, in boring a cannon, a virtually unlimited amount of heating was produced by friction, in contradiction to the caloric-theory notion of conservation of heat. Rumford found that a cannon borer driven by one horse for 2.5 hr heated 27 lb of ice-cold water to its boiling point. Addressing the Royal Society of London, Rumford argued that his experiments had proved the incorrectness of the caloric theory.

> Rumford began life as Benjamin Thompson of Woburn, Massachusetts. At 19 he married a wealthy widow of 30. He served the British during the American Revolution and settled in Europe after the war. He became Minister of War for Bavaria, where he earned extra money by spying for the British. In 1798 he traveled to London, where he founded the Royal Institution, which became one of Britain's leading scientific laboratories. In 1805 he married Lavoisier's widow, adding further to his wealth. His will left money to Harvard to establish the Rumford chair of physics, which still exists.

Despite Rumford's work, the caloric theory held sway until the 1840s. In 1842 Julius Mayer, a German physician, noted that the food that organisms consume goes partly to produce heat to maintain body temperature and partly to produce mechanical work performed by the organism. He then speculated that work and heat were both forms of energy and that the total amount of energy was conserved. Mayer's arguments were not found convincing, and it remained for James Joule to deal the death blow to the caloric theory.

Joule was the son of a wealthy English brewer. Working in a laboratory adjacent to the brewery, Joule did experiments in the 1840s showing that the same changes produced by heating a substance could also be produced by doing mechanical work on the substance, without transfer of heat. His most famous experiment used descending weights to turn paddle wheels in liquids. The potential energy of the weights was converted to kinetic energy of the liquid. The viscosity (internal friction) of the liquid then converted the liquid's kinetic energy to internal energy, increasing the temperature. Joule found that to increase the temperature of one pound of water by one degree Fahrenheit requires the expenditure of 772 foot-pounds of mechanical energy. Based on Joule's work, the first clear convincing statement of the law of conservation of energy was published by the German surgeon, physiologist, and physicist Helmholtz in 1847.

The internal energy of a system can be changed in several ways. Internal energy is an extensive property and thus depends on the amount of matter in the system. The internal energy of 20 g of H_2O at a given T and P is twice the internal energy of 10 g of H_2O at that T and P. For a pure substance, the **molar internal energy** U_m is defined as

$$U_m \equiv U/n \tag{2.36}$$

where n is the number of moles of the pure substance. U_m is an intensive property that depends on P and T.

We usually deal with closed systems. Here, the system's mass is held fixed.

Besides changing the mass of a system by adding or removing matter, we can change the energy of a system by doing work on it or by heating it. The **first law of thermodynamics** asserts that there exists an extensive state function E (called the **total energy** of the system) such that for any process in a closed system

$$\Delta E = q + w \qquad \text{closed syst.} \tag{2.37}$$

where ΔE is the energy change undergone by the system in the process, q is the heat flow into the system during the process, and w is the work done on the system during the process. The first law also asserts that a change in energy ΔE of the system is accompanied by a change in energy of the surroundings equal to $-\Delta E$, so *the total energy of system plus surroundings remains constant* (is conserved). For any process,

$$\Delta E_{\text{syst}} + \Delta E_{\text{surr}} = 0 \tag{2.38}$$

We shall restrict ourselves to systems at rest in the absence of external fields. Here $K = 0 = V$, and from (2.35) we have $E = U$. Equation (2.37) becomes

$$\Delta U = q + w \qquad \text{closed syst. at rest, no fields} \tag*{\textbf{(2.39)*}}$$

where ΔU is the change in internal energy of the system. U is an extensive state function.

Note that, when we write ΔU, we mean ΔU_{syst}. We always focus attention on the system, and *all thermodynamic state functions refer to the system* unless otherwise specified. The conventions for the signs of q and w are set from the system's viewpoint. When heat flows into the system from the surroundings during a process, q is positive ($q > 0$); an outflow of heat from the system to the surroundings means q is negative. When work is done on the system by the surroundings (for example, in a compression of the system), w is positive; when the system does work on its surroundings, w is negative. A positive q and a positive w each increase the internal energy of the system.

For an infinitesimal process, Eq. (2.39) becomes

$$dU = dq + dw \qquad \text{closed syst.} \tag{2.40}$$

where the other two conditions of (2.39) are implicitly understood. dU is the infinitesimal change in system energy in a process with infinitesimal heat dq flowing into the system and infinitesimal work dw done on the system.

The internal energy U is (just like P or V or T) a function of the state of the system. For any process, ΔU thus depends only on the final and initial states of the system and is independent of the path used to bring the system from the initial state to the final state. If the system goes from state 1 to state 2 by any process, then

$$\Delta U = U_2 - U_1 = U_{\text{final}} - U_{\text{initial}} \tag*{\textbf{(2.41)*}}$$

The symbol Δ *always means the final value minus the initial value.*

A process in which the final state of the system is the same as the initial state is called a **cyclic process;** here $U_2 = U_1$, and

$$\Delta U = 0 \qquad \text{cyclic proc.} \tag{2.42}$$

which must obviously be true for the change in any state function in a cyclic process.

In contrast to U, the quantities q and w are not state functions. Given only the initial and final states of the system, we cannot find q or w. The heat q and the work w depend on the path used to go from state 1 to state 2.

Suppose, for example, that we take 1.00 mole of liquid H_2O at 25.0°C and 1.00 atm and raise its temperature to 30.0°C, the final pressure being 1.00 atm. What is q? The answer is that we cannot calculate q because the process is not specified. We could, if we like, increase the temperature by heating at 1 atm. In this case, $q = mc_P\,\Delta T = 18.0\text{ g} \times 1.00\text{ cal/(g °C)} \times 5.0\text{°C} = 90\text{ cal}$. However, we could instead emulate James Joule and increase T solely by doing work on the water, stirring it with a paddle (made of an adiabatic substance) until the water reached 30.0°C. In this case, $q = 0$. Or we could heat the water to some temperature between 25°C and 30°C and then do enough stirring to bring it up to 30°C. In this case, q is between 0 and 90 cal. Each of these processes also has a different value of w. However, no matter how we bring the water from 25°C and 1.00 atm to 30.0°C and 1.00 atm, ΔU is always the same, since the final and initial states are the same in each process.

EXAMPLE 2.3 Calculation of ΔU

Calculate ΔU when 1.00 mol of H_2O goes from 25.0°C and 1.00 atm to 30.0°C and 1.00 atm.

Since U is a state function, we can use any process we like to calculate ΔU. A convenient choice is a reversible heating from 25°C to 30°C at a fixed pressure of 1 atm. For this process, $q = 90$ cal, as calculated above. During the heating, the water expands slightly, doing work on the surrounding atmosphere. At constant P, we have

$$w = w_{\text{rev}} = -\textstyle\int_1^2 P\,dV = -P\int_1^2 dV = -P(V_2 - V_1)$$

where (2.27) was used. Because P is constant, it can be taken outside the integral. The volume change is $\Delta V = V_2 - V_1 = m/\rho_2 - m/\rho_1$, where ρ_2 and ρ_1 are the final and initial densities of the water and $m = 18.0$ g. A handbook gives $\rho_2 = 0.9956\text{ g/cm}^3$ and $\rho_1 = 0.9970\text{ g/cm}^3$. We find $\Delta V = 0.025\text{ cm}^3$ and

$$\begin{aligned} w &= -0.025\text{ cm}^3\text{ atm} = -0.025\text{ cm}^3\text{ atm}\ \frac{1.987\text{ cal mol}^{-1}\text{ K}^{-1}}{82.06\text{ cm}^3\text{ atm mol}^{-1}\text{ K}^{-1}} \\ &= -0.0006\text{ cal} \end{aligned} \qquad (2.43)$$

where two values of R were used to convert w to calories. Thus, w is completely negligible compared with q, and $\Delta U = q + w = 90$ cal. Because volume changes of liquids and solids are small, usually P-V work is significant only for gases.

Exercise

Calculate q, w, and ΔU when 1.00 mol of water is heated from 0°C to 100°C at a fixed pressure of 1 atm. Densities of water are 0.9998 g/cm^3 at 0°C and 0.9854 g/cm^3 at 100°C. (*Answer:* 1800 cal, −0.006 cal, 1800 cal.)

Although the values of q and w for a change from state 1 to state 2 depend on the process used, the value of $q + w$, which equals ΔU, is the same for every process that goes from state 1 to state 2. This is the experimental content of the first law.

Since q and w are not state functions, it is meaningless to ask how much heat a system contains (or how much work it contains). Although one often says that "heat and work are forms of energy," this language, unless properly understood, can mislead one into the error of regarding heat and work as state functions. Heat and work are defined only in terms of processes. Before and after the process of energy transfer between system and surroundings, heat and work do not exist. *Heat is an energy transfer between system and surroundings due to a temperature difference. Work is an energy transfer between system and surroundings due to a macroscopic force acting through a distance.* Heat and work are forms of energy *transfer* rather than forms of energy. Work is energy transfer due to the action of macroscopically observable forces. Heat is energy transfer due to the action of forces at a molecular level. When bodies at different temperatures are placed in contact, collisions between molecules of the two bodies produce a net transfer of energy to the colder body from the hotter body, whose molecules have a greater average kinetic energy than those in the colder body. Heat is work done at the molecular level.

Much of the terminology of heat is misleading because it is a relic of the erroneous caloric theory of heat. Thus, one often refers to "heat flow" between system and surroundings. In reality, the so-called heat flow is really an energy flow due to a temperature difference. Likewise, the term "heat capacity" for C_P is misleading, since it implies that bodies store heat, whereas heat refers only to energy transferred in a process; bodies contain internal energy but do not contain heat.

Heat and work are measures of energy transfer, and both have the same units as energy. The unit of heat can therefore be defined in terms of the joule. Thus the definition of the calorie given in Sec. 2.3 is no longer used. The present definition is

$$1 \text{ cal} \equiv 4.184 \text{ J} \qquad \text{exactly} \qquad \textbf{(2.44)*}$$

where the value 4.184 was chosen to give good agreement with the old definition of the calorie. The calorie defined by (2.44) is called the *thermochemical calorie,* often designated cal_{th}. (Over the years, several slightly different calories have been used.)

It is not necessary to express heat in calories. The joule can be used as the unit of heat. This is what is done in the officially recommended SI units (Sec. 2.1), but since some of the available thermochemical tables use calories, we shall use both joules and calories as the units of heat, work, and internal energy.

Although we won't be considering systems with mechanical energy, it is worthwhile to consider a possible source of confusion that can arise when dealing with such systems. Consider a rock falling in vacuum toward the earth's surface. Its total energy is $E = K + V + U$. Since the gravitational potential energy V is included as part of the system's energy, the gravitational field (in which the potential energy resides) must be considered part of the system. In the first-law equation $\Delta E = q + w$, we do not include work that one part of the system does on another part of the system. Hence w in the first law does not include the work done by the gravitational field on the falling body. Thus for the falling rock, w is zero; also, q is zero. Therefore $\Delta E = q + w$ is zero, and E remains constant as the body falls (although both K and V vary). In general, w in $\Delta E = q + w$ does not include the work done by conservative forces (forces related to the potential energy V in $E = K + V + U$).

Sometimes people get the idea that Einstein's special relativity equation $E = mc^2$ invalidates the conservation of energy, the first law of thermodynamics. This is not so. All $E = mc^2$ says is that a mass m always has an energy mc^2 associated with it and an energy E always has a mass $m = E/c^2$ associated with it. The total energy of system plus surroundings is still conserved in special relativity; likewise, the total relativistic mass of system plus surroundings is conserved in special relativity. Energy cannot disappear; mass cannot disappear. The equation $\Delta E = q + w$ is still valid in special relativity. Consider, for example, nuclear fission. Although it is true that the sum of the *rest* masses of the nuclear fragments is less than the rest mass of the original nucleus, the fragments are moving at high speed. The relativistic mass of a body increases with increasing speed, and the total relativistic mass of the fragments exactly equals the relativistic mass of the original nucleus.

[Some physicists argue against the use of the concept of relativistic mass and the use of the formula $E = mc^2$ (where m is the relativistic mass). For opposing viewpoints, see G. Oas, arxiv.org/abs/physics/0504110; T. R. Sandin, *Am. J. Phys.,* **59,** 1032 (1991).]

2.5 ENTHALPY

The **enthalpy** H of a thermodynamic system whose internal energy, pressure, and volume are U, P, and V is defined as

$$H \equiv U + PV \qquad \textbf{(2.45)*}$$

Since U, P, and V are state functions, H is a state function. Note from $dw_{\text{rev}} = -P\,dV$ that the product of P and V has the dimensions of work and hence of energy. Therefore it is legitimate to add U and PV. Naturally, H has units of energy.

Of course, we could take any dimensionally correct combination of state functions to define a new state function. Thus, we might define $(3U - 5PV)/T^3$ as the state function "enwhoopee." The motivation for giving a special name to the state function $U + PV$ is that this combination of U, P, and V occurs often in thermodynamics. For example, let q_P be the heat absorbed in a constant-pressure process in a closed system. The first law $\Delta U = q + w$ [Eq. (2.39)] gives

$$U_2 - U_1 = q + w = q - \int_{V_1}^{V_2} P\,dV = q_P - P\int_{V_1}^{V_2} dV = q_P - P(V_2 - V_1)$$

$$q_P = U_2 + PV_2 - U_1 - PV_1 = (U_2 + P_2V_2) - (U_1 + P_1V_1) = H_2 - H_1$$

$$\Delta H = q_P \qquad \text{const. } P\text{, closed syst., } P\text{-}V \text{ work only} \qquad \textbf{(2.46)*}$$

since $P_1 = P_2 = P$. In the derivation of (2.46), we used (2.27) ($w_{\text{rev}} = -\int_1^2 P\,dV$) for the work w. Equation (2.27) gives the work associated with a volume change of the system. Besides a volume change, there are other ways that system and surroundings can exchange work, but we won't consider these possibilities until Chapter 7. Thus (2.46) is valid only when no kind of work other than volume-change work is done. Note also that (2.27) is for a mechanically reversible process. A constant-pressure process is mechanically reversible since, if there were unbalanced mechanical forces acting, the system's pressure P would not remain constant. Equation (2.46) says that for a closed system that can do only P-V work, the heat q_P absorbed in a constant-pressure process equals the system's enthalpy change.

For any change of state, the enthalpy change is

$$\Delta H = H_2 - H_1 = U_2 + P_2V_2 - (U_1 + P_1V_1) = \Delta U + \Delta(PV) \qquad (2.47)$$

where $\Delta(PV) \equiv (PV)_2 - (PV)_1 = P_2V_2 - P_1V_1$. For a constant-pressure process, $P_2 = P_1 = P$ and $\Delta(PV) = PV_2 - PV_1 = P\,\Delta V$. Therefore

$$\Delta H = \Delta U + P\,\Delta V \qquad \text{const. } P \qquad (2.48)$$

An error students sometimes make is to equate $\Delta(PV)$ with $P\,\Delta V + V\,\Delta P$. We have

$$\begin{aligned}\Delta(PV) &= P_2V_2 - P_1V_1 = (P_1 + \Delta P)(V_1 + \Delta V) - P_1V_1 \\ &= P_1\,\Delta V + V_1\,\Delta P + \Delta P\,\Delta V\end{aligned}$$

Because of the $\Delta P\,\Delta V$ term, $\Delta(PV) \neq P\,\Delta V + V\,\Delta P$. For infinitesimal changes, we have $d(PV) = P\,dV + V\,dP$, since $d(uv) = u\,dv + v\,du$ [Eq. (1.28)], but the corresponding equation is not true for finite changes. [For an infinitesimal change, the equation after (2.48) becomes $d(PV) = P\,dV + V\,dP + dP\,dV = P\,dV + V\,dP$, since the product of two infinitesimals can be neglected.]

Since U and V are extensive, H is extensive. The molar enthalpy of a pure substance is $H_m = H/n = (U + PV)/n = U_m + PV_m$.

Consider now a constant-volume process. If the closed system can do only P-V work, then w must be zero, since no P-V work is done in a constant-volume process. The first law $\Delta U = q + w$ then becomes for a constant-volume process

$$\Delta U = q_V \qquad \text{closed syst., } P\text{-}V \text{ work only, } V \text{ const.} \tag{2.49}$$

where q_V is the heat absorbed at constant volume. Comparison of (2.49) and (2.46) shows that in a constant-pressure process H plays a role analogous to that played by U in a constant-volume process.

From Eq. (2.47), we have $\Delta H = \Delta U + \Delta(PV)$. Because solids and liquids have comparatively small volumes and undergo only small changes in volume, in nearly all processes that involve only solids or liquids (*condensed* phases) at low or moderate pressures, the $\Delta(PV)$ term is negligible compared with the ΔU term. (For example, recall the example in Sec. 2.4 of heating liquid water, where we found $\Delta U = q_P$.) For condensed phases not at high pressures, the enthalpy change in a process is essentially the same as the internal-energy change: $\Delta H \approx \Delta U$.

2.6 HEAT CAPACITIES

The **heat capacity** C_{pr} of a closed system for an infinitesimal process pr is defined as

$$C_{pr} \equiv dq_{pr}/dT \tag{2.50*}$$

where dq_{pr} and dT are the heat flowing into the system and the temperature change of the system in the process. The subscript on C indicates that the heat capacity depends on the nature of the process. For example, for a constant-pressure process we get C_P, the **heat capacity at constant pressure** (or *isobaric heat capacity*):

$$C_P \equiv \frac{dq_P}{dT} \tag{2.51*}$$

Similarly, the **heat capacity at constant volume** (or *isochoric heat capacity*) C_V of a closed system is

$$C_V \equiv \frac{dq_V}{dT} \tag{2.52*}$$

where dq_V and dT are the heat added to the system and the system's temperature change in an infinitesimal constant-volume process. Strictly speaking, Eqs. (2.50) to (2.52) apply only to reversible processes. In an irreversible heating, the system may develop temperature gradients, and there will then be no single temperature assignable to the system. If T is undefined, the infinitesimal change in temperature dT is undefined.

Equations (2.46) and (2.49) written for an infinitesimal process give $dq_P = dH$ at constant pressure and $dq_V = dU$ at constant volume. Therefore (2.51) and (2.52) can be written as

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P, \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad \text{closed syst. in equilib., } P\text{-}V \text{ work only} \tag{2.53*}$$

C_P and C_V give the rates of change of H and U with temperature.

To measure C_P of a solid or liquid, one holds it at constant pressure in an adiabatically enclosed container and heats it with an electrical heating coil. For a current I flowing for a time t through a wire with a voltage drop V across the wire, the heat generated by the coil is VIt. If the measured temperature increase ΔT in the substance is small, Eq. (2.51) gives $C_P = VIt/\Delta T$, where C_P is the value at the average temperature of the experiment and at the pressure of the experiment. C_P of a gas is found from the temperature increase produced by electrically heating the gas flowing at a known rate.

The thermodynamic state of an equilibrium system at rest in the absence of applied fields is specified by its composition (the number of moles of each component present in each phase) and by any two of the three variables P, V, and T. Commonly, P and T are used. For a closed system of fixed composition, the state is specified by P and T. Any state function has a definite value once the system's state is specified. Therefore any state function of a closed equilibrium system of fixed composition is a function of T and P. For example, for such a system, $H = H(T, P)$. The partial derivative $(\partial H(T, P)/\partial T)_P$ is also a function of T and P. Hence C_P is a function of T and P and is therefore a state function. Similarly, U can be taken as a function of T and V, and C_V is a state function.

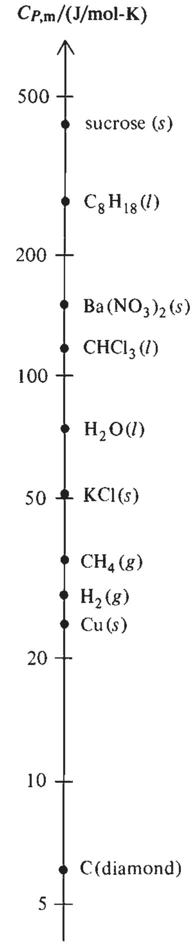


Figure 2.4

Molar heat capacities $C_{P,\mathrm{m}}$ at 25°C and 1 bar. The scale is logarithmic.

For a pure substance, the **molar heat capacities** at constant P and at constant V are $C_{P,\mathrm{m}} = C_P/n$ and $C_{V,\mathrm{m}} = C_V/n$. Some $C_{P,\mathrm{m}}$ values at 25°C and 1 atm are plotted in Fig. 2.4. The Appendix gives further values. Clearly, $C_{P,\mathrm{m}}$ increases with increasing size of the molecules. See Sec. 2.11 for discussion of $C_{P,\mathrm{m}}$ values.

For a one-phase system of mass m, the **specific heat capacity** c_P is $c_P \equiv C_P/m$. The adjective **specific** means "divided by mass." Thus, the **specific volume** v and **specific enthalpy** h of a phase of mass m are $v \equiv V/m = 1/\rho$ and $h \equiv H/m$.

Do not confuse the heat capacity C_P (which is an extensive property) with the molar heat capacity $C_{P,\mathrm{m}}$ or the specific heat capacity c_P (which are intensive properties). We have

$$C_{P,\mathrm{m}} \equiv C_P/n \qquad \text{pure substance} \qquad \textbf{(2.54)*}$$

$$c_P \equiv C_P/m \qquad \text{one-phase system} \qquad \textbf{(2.55)*}$$

$C_{P,\mathrm{m}}$ and c_P are functions of T and P. Figure 2.5 plots some data for $H_2O(g)$. These curves are discussed in Sec. 8.6.

One can prove from the laws of thermodynamics that for a closed system, C_P and C_V must both be positive. (See *Münster,* sec. 40.)

$$C_P > 0, \qquad C_V > 0 \tag{2.56}$$

Exceptions to (2.56) are systems where gravitational effects are important. Such systems (for example, black holes, stars, and star clusters) can have negative heat capacities [D. Lynden-Bell, *Physica A,* **263,** 293 (1999)].

What is the relation between C_P and C_V? We have

$$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial (U + PV)}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \tag{2.57}$$

We expect $(\partial U/\partial T)_P$ and $(\partial U/\partial T)_V$ in (2.57) to be related to each other. In $(\partial U/\partial T)_V$, the internal energy is taken as a function of T and V; $U = U(T, V)$. The total differential of $U(T, V)$ is [Eq. (1.30)]

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{2.58}$$

Equation (2.58) is valid for any infinitesimal process, but since we want to relate $(\partial U/\partial T)_V$ to $(\partial U/\partial T)_P$, we impose the restriction of constant P on (2.58) to give

$$dU_P = \left(\frac{\partial U}{\partial T}\right)_V dT_P + \left(\frac{\partial U}{\partial V}\right)_T dV_P \tag{2.59}$$

where the P subscripts indicate that the infinitesimal changes dU, dT, and dV occur at constant P. Division by dT_P gives

$$\frac{dU_P}{dT_P} = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \frac{dV_P}{dT_P}$$

The ratio of infinitesimals dU_P/dT_P is the partial derivative $(\partial U/\partial T)_P$, so

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \tag{2.60}$$

Substitution of (2.60) into (2.57) gives the desired relation:

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P \tag{2.61}$$

The state function $(\partial U/\partial V)_T$ in (2.61) has dimensions of pressure and is sometimes called the *internal pressure.* Clearly, $(\partial U/\partial V)_T$ is related to that part of the internal energy U that is due to intermolecular potential energy. A change in the system's volume V will change the average intermolecular distance and hence the average intermolecular potential energy. For gases not at high pressure, the smallness of intermolecular forces makes $(\partial U/\partial V)_T$ in (2.61) small. For liquids and solids, where molecules are close to one another, the large intermolecular forces make $(\partial U/\partial V)_T$ large. Measurement of $(\partial U/\partial V)_T$ in gases is discussed in Sec. 2.7.

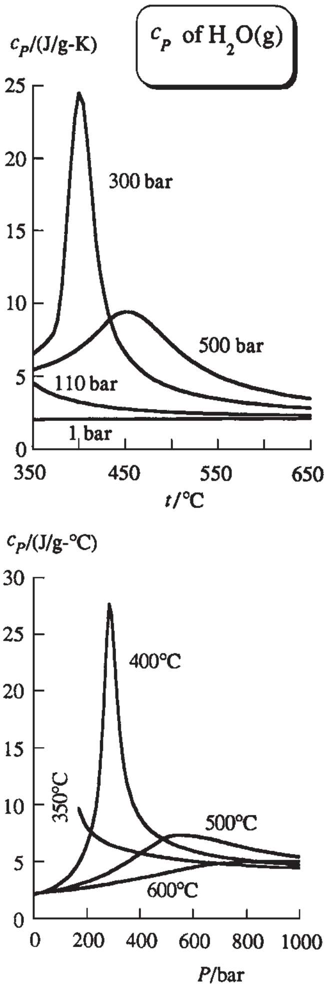


Figure 2.5

Specific heat of $H_2O(g)$ plotted versus T and versus P.

2.7 THE JOULE AND JOULE–THOMSON EXPERIMENTS

In 1843 Joule tried to determine $(\partial U/\partial V)_T$ for a gas by measuring the temperature change after free expansion of the gas into a vacuum. This experiment was repeated by Keyes and Sears in 1924 with an improved setup (Fig. 2.6).

Initially, chamber A is filled with a gas, and chamber B is evacuated. The valve between the chambers is then opened. After equilibrium is reached, the temperature change in the system is measured by the thermometer. Because the system is surrounded by adiabatic walls, q is 0; no heat flows into or out of the system. The expansion into a vacuum is highly irreversible. Finite unbalanced forces act within the system, and as the gas rushes into B, there is turbulence and lack of pressure equilibrium. Therefore $dw = -P\,dV$ does not apply. However, we can readily calculate the work $-w$ done by the system. The only motion that occurs is within the system itself. Therefore the gas does no work on its surroundings, and vice versa. Hence $w = 0$ for expansion into a vacuum. Since $\Delta U = q + w$ for a closed system, we have $\Delta U = 0 + 0 = 0$. This is a constant-energy process. The experiment measures the temperature change with change in volume at constant internal energy, $(\partial T/\partial V)_U$. More precisely, the experiment measures $\Delta T/\Delta V$ at constant U. The method used to get $(\partial T/\partial V)_U$ from $\Delta T/\Delta V$ measurements is similar to that described later in this section for $(\partial T/\partial P)_H$.

We define the *Joule coefficient* μ_J (mu jay) as

$$\mu_J \equiv (\partial T/\partial V)_U \tag{2.62}$$

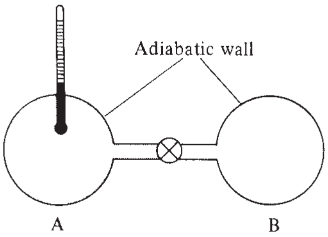


Figure 2.6

The Keyes–Sears modification of the Joule experiment.

How is the measured quantity $(\partial T/\partial V)_U = \mu_J$ related to $(\partial U/\partial V)_T$? The variables in these two partial derivatives are the same (namely, T, U, and V). Hence we can use

$(\partial x/\partial y)_z(\partial y/\partial z)_x(\partial z/\partial x)_y = -1$ [Eq. (1.34)] to relate these partial derivatives. Replacement of x, y, and z with T, U, and V gives

$$\left(\frac{\partial T}{\partial U}\right)_V\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_U = -1$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -\left[\left(\frac{\partial T}{\partial U}\right)_V\right]^{-1}\left[\left(\frac{\partial V}{\partial T}\right)_U\right]^{-1} = -\left(\frac{\partial U}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_U$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -C_V\mu_J \tag{2.63}$$

where $(\partial z/\partial x)_y = 1/(\partial x/\partial z)_y$, $(\partial U/\partial T)_V = C_V$, and $\mu_J = (\partial T/\partial V)_U$ [Eqs. (1.32), (2.53), and (2.62)] were used.

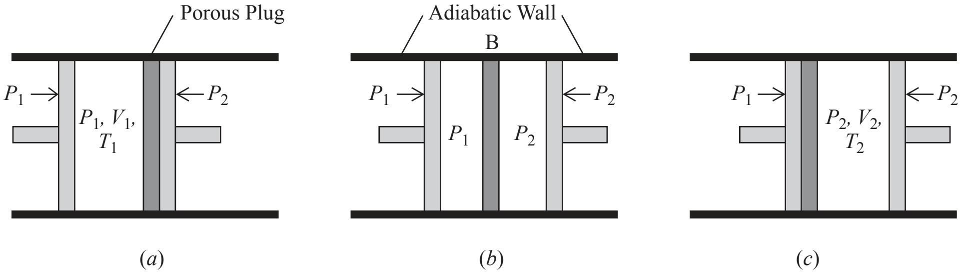
Joule's 1843 experiment gave zero for μ_J and hence zero for $(\partial U/\partial V)_T$. However, his setup was so poor that his result was meaningless. The 1924 Keyes–Sears experiment showed that $(\partial U/\partial V)_T$ is small but definitely nonzero for gases. Because of experimental difficulties, only a few rough measurements were made.

In 1853 Joule and William Thomson (in later life Lord Kelvin) did an experiment similar to the Joule experiment but allowing far more accurate results to be obtained. The **Joule–Thomson experiment** involves the slow throttling of a gas through a rigid, porous plug. An idealized sketch of the experiment is shown in Fig. 2.7. The system is enclosed in adiabatic walls. The left piston is held at a fixed pressure P_1. The right piston is held at a fixed pressure $P_2 < P_1$. The partition B is porous but not greatly so. This allows the gas to be slowly forced from one chamber to the other. Because the throttling process is slow, pressure equilibrium is maintained in each chamber. Essentially all the pressure drop from P_1 to P_2 occurs in the porous plug.

We want to calculate w, the work done on the gas in throttling it through the plug. The overall process is irreversible since P_1 exceeds P_2 by a finite amount, and an infinitesimal change in pressures cannot reverse the process. However, the pressure drop occurs almost completely in the plug. The plug is rigid, and the gas does no work on the plug, or vice versa. The exchange of work between system and surroundings occurs solely at the two pistons. Since pressure equilibrium is maintained at each piston, we can use $dw_{\text{rev}} = -P\,dV$ to calculate the work at each piston. The left piston does work w_L on the gas. We have $dw_L = -P_L\,dV = -P_1\,dV$, where we use subscripts L and R for left and right. Let all the gas be throttled through. The initial and final volumes of the left chamber are V_1 and 0, so

$$w_L = -\int_{V_1}^{0} P_1\,dV = -P_1\int_{V_1}^{0} dV = -P_1(0 - V_1) = P_1V_1$$

The right piston does work dw_R on the gas. (w_R is negative, since the gas in the right chamber does positive work on the piston.) We have $w_R = -\int_0^{V_2} P_2\,dV = -P_2V_2$. The work done on the gas is $w = w_L + w_R = P_1V_1 - P_2V_2$.



(*a*) (*b*) (*c*)

Figure 2.7

The Joule–Thomson experiment.

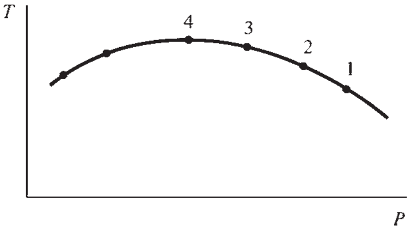


Figure 2.8

An isenthalpic curve obtained from a series of Joule–Thomson experiments.

The first law for this adiabatic process ($q = 0$) gives $U_2 - U_1 = q + w = w$, so $U_2 - U_1 = P_1V_1 - P_2V_2$ or $U_2 + P_2V_2 = U_1 + P_1V_1$. Since $H \equiv U + PV$, we have

$$H_2 = H_1 \qquad \text{or} \qquad \Delta H = 0$$

The initial and final enthalpies are equal in a Joule–Thomson expansion.

Measurement of the temperature change $\Delta T = T_2 - T_1$ in the Joule–Thomson experiment gives $\Delta T/\Delta P$ at constant H. This may be compared with the Joule experiment, which measures $\Delta T/\Delta V$ at constant U.

We define the **Joule–Thomson coefficient** μ_{JT} by

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_H \qquad \textbf{(2.64)*}$$

μ_{JT} is the ratio of infinitesimal changes in two intensive properties and therefore is an intensive property. Like any intensive property, it is a function of T and P (and the nature of the gas).

A single Joule–Thomson experiment yields only $(\Delta T/\Delta P)_H$. To find $(\partial T/\partial P)_H$ values, we proceed as follows. Starting with some initial P_1 and T_1, we pick a value of P_2 less than P_1 and do the throttling experiment, measuring T_2. We then plot the two points (T_1, P_1) and (T_2, P_2) on a T-P diagram; these are points 1 and 2 in Fig. 2.8. Since $\Delta H = 0$ for a Joule–Thomson expansion, states 1 and 2 have equal enthalpies. A repetition of the experiment with the same initial P_1 and T_1 but with the pressure on the right piston set at a new value P_3 gives point 3 on the diagram. Several repetitions, each with a different final pressure, yield several points that correspond to states of equal enthalpy. We join these points with a smooth curve (called an *isenthalpic curve*). The slope of this curve at any point gives $(\partial T/\partial P)_H$ for the temperature and pressure at that point. Values of T and P for which μ_{JT} is negative (points to the right of point 4) correspond to warming on Joule–Thomson expansion. At point 4, μ_{JT} is zero. To the left of point 4, μ_{JT} is positive, and the gas is cooled by throttling. To generate further isenthalpic curves and get more values of $\mu_{JT}(T, P)$, we use different initial temperatures T_1.

Values of μ_{JT} for gases range from +3 to −0.1°C/atm, depending on the gas and on its temperature and pressure. Figure 2.9 plots some μ_{JT} data for N_2 gas.

Joule–Thomson throttling is used to liquefy gases. For a gas to be cooled by a Joule–Thomson expansion ($\Delta P < 0$), its μ_{JT} must be positive over the range of T and P involved. In Joule–Thomson liquefaction of gases, the porous plug is replaced by a narrow opening (a needle valve). Another method of gas liquefaction is an approximately reversible adiabatic expansion against a piston.

A procedure similar to that used to derive (2.63) yields (Prob. 2.35*a*)

$$\left(\frac{\partial H}{\partial P}\right)_T = -C_P\mu_{JT} \qquad (2.65)$$

We can use thermodynamic identities to relate the Joule and Joule–Thomson coefficients; see Prob. 2.35*b*.

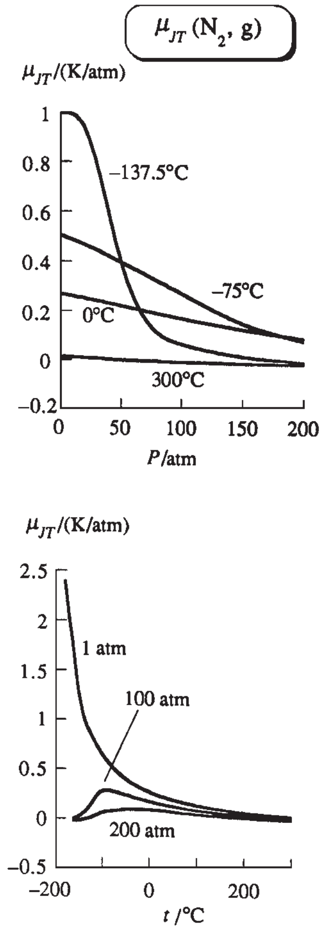


Figure 2.9

The Joule–Thomson coefficient of $N_2(g)$ plotted versus P and versus T.

2.8 PERFECT GASES AND THE FIRST LAW

Perfect Gases

An ideal gas was defined in Chapter 1 as a gas that obeys the equation of state $PV = nRT$. The molecular picture of an ideal gas is one with no intermolecular forces. If we change the volume of an ideal gas while holding T constant, we change the average distance between the molecules, but since intermolecular forces are zero, this distance change will not affect the internal energy U. Also, the average translational kinetic energy of the gas molecules is a function of T only (as is also true of the molecular rotational and vibrational energies—see Sec. 2.11) and will not change with volume. We therefore expect that, for an ideal gas, U will not change with V at constant T and $(\partial U/\partial V)_T$ will be zero. However, we are not yet in a position to prove this thermodynamically. To maintain the logical development of thermodynamics, we therefore now define a **perfect gas** as one that obeys both the following equations:

$$PV = nRT \quad \text{and} \quad (\partial U/\partial V)_T = 0 \qquad \text{perfect gas} \qquad \textbf{(2.66)*}$$

An ideal gas is required to obey only $PV = nRT$. Once we have postulated the second law of thermodynamics, we shall prove that $(\partial U/\partial V)_T = 0$ follows from $PV = nRT$, so there is in fact no distinction between an ideal gas and a perfect gas. Until then, we shall maintain the distinction between the two.

For a closed system in equilibrium, the internal energy (and any other state function) can be expressed as a function of temperature and volume: $U = U(T, V)$. However, (2.66) states that for a perfect gas U is independent of volume. Therefore U of a perfect gas depends only on temperature:

$$U = U(T) \qquad \text{perf. gas} \qquad \textbf{(2.67)*}$$

Since U is independent of V for a perfect gas, the partial derivative $(\partial U/\partial T)_V$ in Eq. (2.53) for C_V becomes an ordinary derivative: $C_V = dU/dT$ and

$$dU = C_V\, dT \qquad \text{perf. gas} \qquad \textbf{(2.68)*}$$

It follows from (2.67) and $C_V = dU/dT$ that C_V of a perfect gas depends only on T:

$$C_V = C_V(T) \qquad \text{perf. gas} \qquad \textbf{(2.69)*}$$

For a perfect gas, $H \equiv U + PV = U + nRT$. Hence (2.67) shows that H depends only on T for a perfect gas. Using $C_P = (\partial H/\partial T)_P$ [Eq. (2.53)], we then have

$$H = H(T), \qquad C_P = dH/dT, \qquad C_P = C_P(T) \qquad \text{perf. gas} \qquad \textbf{(2.70)*}$$

Use of $(\partial U/\partial V)_T = 0$ [Eq. (2.66)] in $C_P - C_V = [(\partial U/\partial V)_T + P](\partial V/\partial T)_P$ [Eq. (2.61)] gives

$$C_P - C_V = P(\partial V/\partial T)_P \qquad \text{perf. gas} \qquad (2.71)$$

From $PV = nRT$, we get $(\partial V/\partial T)_P = nR/P$. Hence for a perfect gas $C_P - C_V = nR$ or

$$C_{P,\text{m}} - C_{V,\text{m}} = R \qquad \text{perf. gas} \qquad \textbf{(2.72)*}$$

We have $\mu_J C_V = -(\partial U/\partial V)_T$ [Eq. (2.63)]. Since $(\partial U/\partial V)_T = 0$ for a perfect gas, it follows that $\mu_J = 0$ for a perfect gas. Also, $\mu_{JT} C_P = -(\partial H/\partial P)_T$ [Eq. (2.65)]. Since H depends only on T for a perfect gas, we have $(\partial H/\partial P)_T = 0$ for such a gas, and $\mu_{JT} = 0$ for a perfect gas. Surprisingly, as Fig. 2.9 shows, μ_{JT} for a real gas does not go to zero as P goes to zero. (See Prob. 8.37 for analysis of this fact.)

We now apply the first law to a perfect gas. For a reversible volume change, $dw = -P\, dV$ [Eq. (2.26)]. Also, (2.68) gives $dU = C_V\, dT$ for a perfect gas. For a fixed amount of a perfect gas, the first law $dU = dq + dw$ (closed system) becomes

$$dU = C_V\, dT = dq - P\, dV \qquad \text{perf. gas, rev. proc., } P\text{-}V \text{ work only} \qquad (2.73)$$

EXAMPLE 2.4 Calculation of q, w, and ΔU

Suppose 0.100 mol of a perfect gas having $C_{V,\mathrm{m}} = 1.50R$ independent of temperature undergoes the reversible cyclic process $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$ shown in Fig. 2.10, where either P or V is held constant in each step. Calculate q, w, and ΔU for each step and for the complete cycle.

Since we know how P varies in each step and since the steps are reversible, we can readily find w for each step by integrating $dw_{\mathrm{rev}} = -P\,dV$. Since either V or P is constant in each step, we can integrate $dq_V = C_V\,dT$ and $dq_P = C_P\,dT$ [Eqs. (2.51) and (2.52)] to find the heat in each step. The first law $\Delta U = q + w$ then allows calculation of ΔU.

To evaluate integrals like $\int_1^2 C_V\,dT$, we will need to know the temperatures of states 1, 2, 3, and 4. We therefore begin by using $PV = nRT$ to find these temperatures. For example, $T_1 = P_1V_1/nR = 122$ K. Similarly, $T_2 = 366$ K, $T_3 = 732$ K, $T_4 = 244$ K.

Step $1 \rightarrow 2$ is at constant volume, no work is done, and $w_{1\rightarrow 2} = 0$. Step $2 \rightarrow 3$ is at constant pressure and

$$w_{2\rightarrow 3} = -\int_2^3 P\,dV = -P(V_3 - V_2) = -(3.00\text{ atm})(2000\text{ cm}^3 - 1000\text{ cm}^3)$$

$$= -3000\text{ cm}^3\text{ atm }(8.314\text{ J})/(82.06\text{ cm}^3\text{ atm}) = -304\text{ J}$$

where two values of R were used to convert to joules. Similarly, $w_{3\rightarrow 4} = 0$ and $w_{4\rightarrow 1} = 101$ J. The work w for the complete cycle is the sum of the works for the four steps, so $w = -304\text{ J} + 0 + 101\text{ J} + 0 = -203$ J.

Step $1 \rightarrow 2$ is at constant volume, and

$$q_{1\rightarrow 2} = \int_1^2 C_V\,dT = nC_{V,\mathrm{m}}\int_1^2 dT = n(1.50R)(T_2 - T_1)$$

$$= (0.100\text{ mol})1.50[8.314\text{ J/(mol K)}](366\text{ K} - 122\text{ K}) = 304\text{ J}$$

Step $2 \rightarrow 3$ is at constant pressure, and $q_{2\rightarrow 3} = \int_2^3 C_P\,dT$. Equation (2.72) gives $C_{P,\mathrm{m}} = C_{V,\mathrm{m}} + R = 2.50R$, and we find $q_{2\rightarrow 3} = 761$ J. Similarly, $q_{3\rightarrow 4} = -608\frac{1}{2}$ J and $q_{4\rightarrow 1} = -253\frac{1}{2}$ J. The total heat for the cycle is $q = 304\text{ J} + 761\text{ J} - 608\frac{1}{2}\text{ J} - 253\frac{1}{2}\text{ J} = 203$ J.

We have $\Delta U_{1\rightarrow 2} = q_{1\rightarrow 2} + w_{1\rightarrow 2} = 304\text{ J} + 0 = 304$ J. Similarly, we find $\Delta U_{2\rightarrow 3} = 457$ J, $\Delta U_{3\rightarrow 4} = -608\frac{1}{2}$ J, $\Delta U_{4\rightarrow 1} = -152\frac{1}{2}$ J. For the complete cycle, $\Delta U = 304\text{ J} + 457\text{ J} - 608\frac{1}{2}\text{ J} - 152\frac{1}{2}\text{ J} = 0$, which can also be found from $q + w$ as $203\text{ J} - 203\text{ J} = 0$. An alternative procedure is to use the perfect-gas equation $dU = C_V\,dT$ to find ΔU for each step.

For this cyclic process, we found $\Delta U = 0$, $q \neq 0$, and $w \neq 0$. These results are consistent with the fact that U is a state function but q and w are not.

Exercise

Use the perfect-gas equation $dU = C_V\,dT$ to find ΔU for each step in the cycle of Fig. 2.10. (*Answer:* 304 J, 456 J, −609 J, −152 J.)

Exercise

Verify that w for the reversible cyclic process in this example equals minus the area enclosed by the lines in Fig. 2.10.

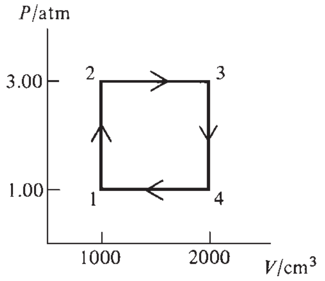


Figure 2.10

A reversible cyclic process.

Reversible Isothermal Process in a Perfect Gas

Consider the special case of a reversible isothermal (constant-T) process in a perfect gas. (Throughout this section, the system is assumed closed.) For a fixed amount of a perfect gas, U depends only on T [Eq. (2.67)]. Therefore $\Delta U = 0$ for an isothermal change of state in a perfect gas. This also follows from $dU = C_V\, dT$ for a perfect gas. The first law $\Delta U = q + w$ becomes $0 = q + w$ and $q = -w$. Integration of $dw_{\text{rev}} = -P\, dV$ and use of $PV = nRT$ give

$$w = -\int_1^2 P\, dV = -\int_1^2 \frac{nRT}{V}\, dV = -nRT\int_1^2 \frac{1}{V}\, dV = -nRT(\ln V_2 - \ln V_1)$$

$$w = -q = nRT \ln \frac{V_1}{V_2} = nRT \ln \frac{P_2}{P_1} \qquad \text{rev. isothermal proc., perf. gas} \qquad (2.74)$$

where Boyle's law was used. If the process is an expansion ($V_2 > V_1$), then w (the work done *on* the gas) is negative and q (the heat added to the gas) is positive. All the added heat appears as work done by the gas, maintaining U as constant for the perfect gas. It is best *not* to memorize an equation like (2.74), since it can be quickly derived from $dw = -P\, dV$.

To carry out a reversible isothermal volume change in a gas, we imagine the gas to be in a cylinder fitted with a frictionless piston. We place the cylinder in a very large constant-temperature bath (Fig. 2.11) and change the external pressure on the piston at an infinitesimal rate. If we increase the pressure, the gas is slowly compressed. The work done on it will transfer energy to the gas and will tend to increase its temperature at an infinitesimal rate. This infinitesimal temperature increase will cause heat to flow out of the gas to the surrounding bath, thereby maintaining the gas at an essentially constant temperature. If we decrease the pressure, the gas slowly expands, thereby doing work on its surroundings, and the resulting infinitesimal drop in gas temperature will cause heat to flow into the gas from the bath, maintaining constant temperature in the gas.

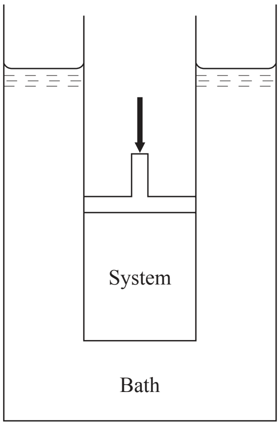


Figure 2.11

Setup for an isothermal volume change.

EXAMPLE 2.5 Calculation of q, w, and ΔU

A cylinder fitted with a frictionless piston contains 3.00 mol of He gas at $P = 1.00$ atm and is in a large constant-temperature bath at 400 K. The pressure is reversibly increased to 5.00 atm. Find w, q, and ΔU for this process.

It is an excellent approximation to consider the helium as a perfect gas. Since T is constant, ΔU is zero [Eq. (2.68)]. Equation (2.74) gives

$$w = (3.00 \text{ mol})(8.314 \text{ J mol}^{-1}\text{ K}^{-1})(400 \text{ K}) \ln (5.00/1.00) = (9980 \text{ J}) \ln 5.00$$

$$w = (9980 \text{ J})(1.609) = 1.61 \times 10^4 \text{ J}$$

Also, $q = -w = -1.61 \times 10^4$ J. Of course, w (the work done on the gas) is positive for the compression. The heat q is negative because heat must flow from the gas to the surrounding constant-temperature bath to maintain the gas at 400 K as it is compressed.

Exercise

0.100 mol of a perfect gas with $C_{V,\text{m}} = 1.50R$ expands reversibly and isothermally at 300 K from 1.00 to 3.00 L. Find q, w, and ΔU for this process. (*Answer:* 274 J, -274 J, 0.)

Reversible Constant-*P* (or Constant-*V*) Process in a Perfect Gas

The calculations of q, w, and ΔU for these processes were shown in Example 2.4.

Reversible Adiabatic Process in a Perfect Gas

For an adiabatic process, $dq = 0$. For a reversible process in a system with only P-V work, $dw = -P\,dV$. For a perfect gas, $dU = C_V\,dT$ [Eq. (2.68)]. Therefore, for a reversible adiabatic process in a perfect gas, the first law $dU = dq + dw$ becomes

$$C_V\,dT = -P\,dV = -(nRT/V)\,dV$$
$$C_{V,\text{m}}\,dT = -(RT/V)\,dV$$

where $PV = nRT$ and $C_{V,\text{m}} = C_V/n$ were used. To integrate this equation, we separate the variables, putting all functions of T on one side and all functions of V on the other side. We get $(C_{V,\text{m}}/T)\,dT = -(R/V)\,dV$. Integration gives

$$\int_1^2 \frac{C_{V,\text{m}}}{T}\,dT = -\int_1^2 \frac{R}{V}\,dV = -R(\ln V_2 - \ln V_1) = R\ln\frac{V_1}{V_2} \qquad (2.75)$$

For a perfect gas, $C_{V,\text{m}}$ is a function of T [Eq. (2.69)]. If the temperature change in the process is small, $C_{V,\text{m}}$ will not change greatly and can be taken as approximately constant. Another case where $C_{V,\text{m}}$ is nearly constant is for monatomic gases, where $C_{V,\text{m}}$ is essentially independent of T over a very wide temperature range (Sec. 2.11 and Fig. 2.15). The approximation that $C_{V,\text{m}}$ is constant gives $\int_1^2 (C_{V,\text{m}}/T)\,dT = C_{V,\text{m}}\int_1^2 T^{-1}\,dT = C_{V,\text{m}}\ln(T_2/T_1)$, and Eq. (2.75) becomes $C_{V,\text{m}}\ln(T_2/T_1) = R\ln(V_1/V_2)$ or

$$\ln(T_2/T_1) = \ln(V_1/V_2)^{R/C_{V,\text{m}}}$$

where $k\ln x = \ln x^k$ [Eq. (1.70)] was used. If $\ln a = \ln b$, then $a = b$. Therefore

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_{V,\text{m}}} \qquad \text{perf. gas, rev. adiabatic proc., } C_V \text{ const.} \qquad (2.76)$$

Since C_V is always positive [Eq. (2.56)], Eq. (2.76) says that, when $V_2 > V_1$, we will have $T_2 < T_1$. A perfect gas is cooled by a reversible adiabatic expansion. In expanding adiabatically, the gas does work on its surroundings, and since q is zero, U must decrease; therefore T decreases. A near-reversible, near-adiabatic expansion is one method used in refrigeration.

An alternative equation is obtained by using $P_1V_1/T_1 = P_2V_2/T_2$. Equation (2.76) becomes

$$P_2V_2/P_1V_1 = (V_1/V_2)^{R/C_{V,\text{m}}} \quad \text{and} \quad P_1V_1^{1+R/C_{V,\text{m}}} = P_2V_2^{1+R/C_{V,\text{m}}}$$

The exponent is $1 + R/C_{V,\text{m}} = (C_{V,\text{m}} + R)/C_{V,\text{m}} = C_{P,\text{m}}/C_{V,\text{m}}$, since $C_{P,\text{m}} - C_{V,\text{m}} = R$ for a perfect gas [Eq. (2.72)]. Defining the *heat-capacity ratio* γ (gamma) as

$$\gamma \equiv C_P/C_V$$

we have

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} \qquad \text{perf. gas, rev. ad. proc., } C_V \text{ const.} \qquad (2.77)$$

For an adiabatic process, $\Delta U = q + w = w$. For a perfect gas, $dU = C_V\,dT$. With the approximation of constant C_V, we have

$$\Delta U = C_V(T_2 - T_1) = w \qquad \text{perf. gas, ad. proc., } C_V \text{ const.} \qquad (2.78)$$

To carry out a reversible adiabatic process in a gas, the surrounding constant-temperature bath in Fig. 2.11 is replaced by adiabatic walls, and the external pressure is slowly changed.

We might compare a reversible isothermal expansion of a perfect gas with a reversible adiabatic expansion of the gas. Let the gas start from the same initial P_1 and V_1 and go to the same V_2. For the isothermal process, $T_2 = T_1$. For the adiabatic expansion, we showed that $T_2 < T_1$. Hence the final pressure P_2 for the adiabatic expansion must be less than P_2 for the isothermal expansion (Fig. 2.12).

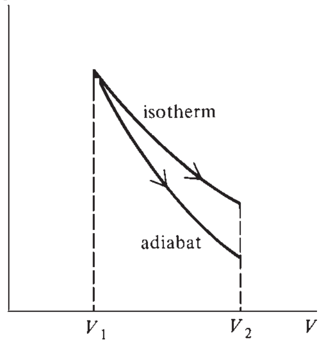


Figure 2.12

Ideal-gas reversible isothermal and adiabatic expansions that start from the same state.

Summary

A perfect gas obeys $PV = nRT$, has $(\partial U/\partial V)_T = 0 = (\partial H/\partial P)_T$, has U, H, C_V, and C_P depending on T only, has $C_P - C_V = nR$, and has $dU = C_V\,dT$ and $dH = C_P\,dT$. These equations are valid only for a perfect gas. A common error students make is to use one of these equations where it does not apply.

2.9 CALCULATION OF FIRST-LAW QUANTITIES

This section reviews thermodynamic processes and then summarizes the available methods for the calculation of q, w, ΔU, and ΔH in a process.

Thermodynamic Processes

When a thermodynamic system undergoes a change of state, we say it has undergone a **process.** The **path** of a process consists of the series of thermodynamic states through which the system passes on its way from the initial state to the final state. Two processes that start at the same initial state and end at the same final state but go through different paths (for example, *a* and *b* in Fig. 2.3) are different processes. (The term "change of state" should not be confused with the term "phase change." In thermodynamics, a system undergoes a **change of state** whenever one or more of the thermodynamic properties defining the system's state change their values.)

In a **cyclic** process, the system's final state is the same as the initial state. In a cyclic process, the change in each state function is zero: $0 = \Delta T = \Delta P = \Delta V = \Delta U = \Delta H$, etc. However, q and w need not be zero for a cyclic process (recall Example 2.4 in Sec. 2.8).

In a **reversible** process, the system is always infinitesimally close to equilibrium, and an infinitesimal change in conditions can restore both system and surroundings to their initial states. To perform a process reversibly, one must have only infinitesimal differences in pressures and temperatures, so that work and heat will flow slowly. Any changes in chemical composition must occur slowly and reversibly; moreover, there must be no friction. We found that the work in a mechanically reversible process is given by $dw_{\text{rev}} = -P\,dV$. In Chapter 3, we shall relate the heat dq_{rev} in a reversible process to state functions [see Eq. (3.20)].

In an **isothermal** process, T is constant throughout the process. To achieve this, one encloses the system in thermally conducting walls and places it in a large constant-temperature bath. For a perfect gas, U is a function of T only, so U is constant in an isothermal process; this is not necessarily true for systems other than perfect gases.

In an **adiabatic** process, $dq = 0$ and $q = 0$. This can be achieved by surrounding the system with adiabatic walls.

In a **constant-volume** (isochoric) process, V is held constant throughout the process. Here, the system is enclosed in rigid walls. Provided the system is capable of only P-V work, the work w is zero in an isochoric process.

In a **constant-pressure** (isobaric) process, P is held constant throughout the process. Experiments with solids and liquids are often performed with the system open to the atmosphere; here P is constant at the atmospheric pressure. To perform a constant-P process in a gas, one encloses the gas in a cylinder with a movable piston, holds the external pressure on the piston fixed at the initial pressure of the gas, and slowly warms or cools the gas, thereby changing its volume and temperature at constant P. For a constant-pressure process, we found that $\Delta H = q_P$.

Students are often confused in thermodynamics because they do not understand whether a quantity refers to a *property* of a system in some particular thermodynamic state or whether it refers to a *process* a system undergoes. For example, H is a property of a system and has a definite value once the system's state is defined; in contrast, $\Delta H \equiv H_2 - H_1$ is the *change* in enthalpy for a process in which the system goes from state 1 to state 2. Each state of a thermodynamic system has a definite value of H. Each change of state has a definite value of ΔH.

There are two kinds of quantities for a process. The value of a quantity such as ΔH, which is the change in a state function, is independent of the path of the process and depends only on the final and the initial states: $\Delta H = H_2 - H_1$. The value of a quantity such as q or w, which are not changes in state functions, depends on the path of the process and cannot be found from the final and initial states alone.

We now review calculation of q, w, ΔU, and ΔH for various processes. In this review, we assume that the system is closed and that only P-V work is done.

1. **Reversible phase change at constant *T* and *P*.** A **phase change** or **phase transition** is a process in which at least one new phase appears in a system without the occurrence of a chemical reaction. Examples include the melting of ice to liquid water, the transformation from orthorhombic solid sulfur to monoclinic solid sulfur (Sec. 7.4), and the freezing out of ice from an aqueous solution (Sec. 12.3). For now, we shall be concerned only with phase transitions involving pure substances.

   The heat q is found from the measured latent heat (Sec. 7.2) of the phase change. The work w is found from $w = -\int_1^2 P\,dV = -P\,\Delta V$, where ΔV is calculated from the densities of the two phases. If one phase is a gas, we can use $PV = nRT$ to find its volume (unless the gas is at high density). ΔH for this constant-pressure process is found from $\Delta H = q_P = q$. Finally, ΔU is found from $\Delta U = q + w$. As an example, the measured (latent) heat of fusion (melting) of H_2O at 0°C and 1 atm is 333 J/g. For the fusion of 1 mol (18.0 g) of ice at this T and P, $q = \Delta H = 6.01$ kJ. Thermodynamics cannot furnish us with the values of the latent heats of phase changes or with heat capacities. These quantities must be measured. (One can use statistical mechanics to calculate theoretically the heat capacities of certain systems, as we shall later see.)
2. **Constant-pressure heating with no phase change.** A constant-pressure process is mechanically reversible, so

$$w = w_{\text{rev}} = -\int_1^2 P\,dV = -P\,\Delta V \qquad \text{const. } P$$

   where ΔV is found from the densities at the initial and final temperatures or from $PV = nRT$ if the substance is a perfect gas. If the heating (or cooling) is reversible, then T of the system is well defined and $C_P = dq_P/dT$ applies. Integration of this equation and use of $\Delta H = q_P$ give

$$\Delta H = q_P = \int_{T_1}^{T_2} C_P(T)\,dT \qquad \text{const. } P \qquad (2.79)$$

   Since P is constant, we didn't bother to indicate that C_P depends on P as well as on T. The dependence of C_P and C_V on pressure is rather weak. Unless one deals with high pressures, a value of C_P measured at 1 atm can be used at other pressures. ΔU is found from $\Delta U = q + w = q_P + w$.

   If the constant-pressure heating is irreversible (for example, if during the heating there is a finite temperature difference between system and surroundings or if temperature gradients exist in the system), the relation $\Delta H = \int_1^2 C_P\,dT$ still applies, so long as the initial and final states are equilibrium states. This is so because H is a state function and the value of ΔH is independent of the path (process) used to connect states 1 and 2. If ΔH equals $\int_1^2 C_P\,dT$ for a reversible path between states 1 and 2, then ΔH must equal $\int_1^2 C_P\,dT$ for any irreversible path between states 1 and 2. Also, in deriving $\Delta H = q_P$ [Eq. (2.46)], we did not assume the heating was reversible, only that P was constant. Thus, Eq. (2.79) holds for any constant-pressure temperature change in a closed system with P-V work only.

Since H is a state function, we can use the integral in (2.79) to find ΔH for any process whose initial and final states have the same pressure, whether or not the entire process occurs at constant pressure.

3. **Constant-volume heating with no phase change.** Since V is constant, $w = 0$. Integration of $C_V = dq_V/dT$ and use of $\Delta U = q + w = q_V$ give

$$\Delta U = \int_1^2 C_V\, dT = q_V \qquad V \text{ const.} \tag{2.80}$$

   As with (2.79), Eq. (2.80) holds whether or not the heating is reversible. ΔH is found from $\Delta H = \Delta U + \Delta(PV) = \Delta U + V\,\Delta P$.

4. **Perfect-gas change of state.** Since U and H of a perfect gas depend on T only, we integrate $dU = C_V\, dT$ and $dH = C_P\, dT$ [(2.68) and (2.70)] to give

$$\Delta U = \int_{T_1}^{T_2} C_V(T)\, dT, \qquad \Delta H = \int_{T_1}^{T_2} C_P(T)\, dT \qquad \text{perf. gas} \tag{2.81}$$

   If $C_V(T)$ or $C_P(T)$ is known, we can use $C_P - C_V = nR$ and integrate to find ΔU and ΔH. The equations of (2.81) apply to any perfect-gas change of state including irreversible changes and changes in which P and V change. The values of q and w depend on the path. If the process is reversible, then $w = -\int_1^2 P\, dV = -nR \int_1^2 (T/V)\, dV$, and we can find w if we know how T varies as a function of V. Having found w, we use $\Delta U = q + w$ to find q.

5. **Reversible isothermal process in a perfect gas.** Since U and H of the perfect gas are functions of T only, we have $\Delta U = 0$ and $\Delta H = 0$. Also, $w = -\int_1^2 P\, dV = -nRT \ln (V_2/V_1)$ [Eq. (2.74)] and $q = -w$, since $q + w = \Delta U = 0$.
6. **Reversible adiabatic process in a perfect gas.** The process is adiabatic, so $q = 0$. We find ΔU and ΔH from Eq. (2.81). The first law gives $w = \Delta U$. If C_V is essentially constant, the final state of the gas can be found from $P_1V_1^\gamma = P_2V_2^\gamma$ [Eq. (2.77)], where $\gamma \equiv C_P/C_V$.
7. **Adiabatic expansion of a perfect gas into vacuum.** Here (Sec. 2.7) $q = 0$, $w = 0$, $\Delta U = q + w = 0$, and $\Delta H = \Delta U + \Delta(PV) = \Delta U + nR\,\Delta T = 0$.

Equations (2.79) and (2.80) tell us how a temperature change at constant P or at constant V affects H and U. At this point, we are not yet able to find the effects of a change in P or V on H and U. This will be dealt with in Chapter 4.

A word about units. Heat-capacity and latent-heat data are sometimes tabulated in calories, so q is sometimes calculated in calories. Pressures are often given in atmospheres, so P-V work is often calculated in cm^3 atm. The SI unit for q, w, ΔU, and ΔH is the joule. Hence we frequently want to convert between joules, calories, and cm^3 atm. We do this by using the values of R in (1.19) to (1.21). See Example 2.2 in Sec. 2.2.

A useful strategy to find a quantity such as ΔU or q for a process is to write the expression for the corresponding infinitesimal quantity and then integrate this expression from the initial state to the final state. For example, to find ΔU in an ideal-gas change of state, we write $dU = C_V\, dT$ and $\Delta U = \int_1^2 C_V(T)\, dT$; to find q in a constant-pressure process, we write $dq_P = C_P\, dT$ and $q_P = \int_1^2 C_P\, dT$. The infinitesimal change in a state function under the condition of constant P or T or V can often be found from the appropriate partial derivative. For example, if we want dU in a constant-volume process, we use $(\partial U/\partial T)_V = C_V$ to write $dU = C_V\, dT$ for V constant, and $\Delta U = \int_1^2 C_V\, dT$, where the integration is at constant V.

When evaluating an integral from state 1 to 2, you can take quantities that are constant outside the integral, but anything that varies during the process must remain inside the integral. Thus, for a constant-pressure process, $\int_1^2 P\, dV = P \int_1^2 dV = P(V_2 - V_1)$, and for an isothermal process, $\int_1^2 (nRT/V)\, dV = nRT \int_1^2 (1/V)\, dV = nRT \ln (V_2/V_1)$.

However, in evaluating $\int_1^2 C_P(T)\,dT$, we cannot take C_P outside the integral, unless we know that it is constant in the temperature range from T_1 to T_2.

EXAMPLE 2.6 Calculation of ΔH

$C_{P,\text{m}}$ of a certain substance in the temperature range 250 to 500 K at 1 bar pressure is given by $C_{P,\text{m}} = b + kT$, where b and k are certain known constants. If n moles of this substance is heated from T_1 to T_2 at 1 bar (where T_1 and T_2 are in the range 250 to 500 K), find the expression for ΔH.

Since P is constant for the heating, we use (2.79) to get

$$\Delta H = q_P = \int_1^2 nC_{P,\text{m}}\,dT = n\int_{T_1}^{T_2} (b + kT)\,dT = n(bT + \tfrac{1}{2}kT^2)\Big|_{T_1}^{T_2}$$

$$\Delta H = n[b(T_2 - T_1) + \tfrac{1}{2}k(T_2^2 - T_1^2)]$$

Exercise

Find the ΔH expression when n moles of a substance with $C_{P,\text{m}} = r + sT^{1/2}$, where r and s are constants, is heated at constant pressure from T_1 to T_2. [*Answer:* $nr(T_2 - T_1) + \frac{2}{3}ns(T_2^{3/2} - T_1^{3/2})$.]

2.10 STATE FUNCTIONS AND LINE INTEGRALS

We now discuss ways to test whether some quantity is a state function. Let the system go from state 1 to state 2 by some process. We subdivide the process into infinitesimal steps. Let db be some infinitesimal quantity associated with each infinitesimal step. For example, db might be the infinitesimal amount of heat that flows into the system in an infinitesimal step ($db = dq$), or it might be the infinitesimal change in system pressure ($db = dP$), or it might be the infinitesimal heat flow divided by the system's temperature ($db = dq/T$), etc. To determine whether db is the differential of a state function, we consider the line integral $_L\int_1^2 db$, where the L indicates that the integral's value depends in general on the process (path) used to go from state 1 to state 2.

The line integral $_L\int_1^2 db$ equals the sum of the infinitesimal quantities db for the infinitesimal steps into which we have divided the process. If b is a state function, then the sum of the infinitesimal changes in b is equal to the overall change $\Delta b \equiv b_2 - b_1$ in b from the initial state to the final state. For example, if b is the temperature, then $_L\int_1^2 dT = \Delta T = T_2 - T_1$; similarly, $_L\int_1^2 dU = U_2 - U_1$. We have

$$\int_{1\atop L}^{2} db = b_2 - b_1 \qquad \text{if } b \text{ is a state function} \tag{2.82}$$

Since $b_2 - b_1$ is independent of the path used to go from state 1 to state 2 and depends only on the initial and final states 1 and 2, the value of the line integral $_L\int_1^2 db$ is independent of the path when b is a state function.

Suppose b is not a state function. For example, let $db = dq$, the infinitesimal heat flowing into a system. The sum of the infinitesimal amounts of heat is equal to the total heat q flowing into the system in the process of going from state 1 to state 2; we have $_L\int_1^2 dq = q$; similarly, $_L\int_1^2 dw = w$, where w is the work in the process. We have seen that q and w are not state functions but depend on the path from state 1 to state 2. The values of the integrals ${}_L\int_1^2 dq$ and ${}_L\int_1^2 dw$ depend on the path from 1 to 2. In general, if b is not a state function, then ${}_L\int_1^2 db$ depends on the path. Differentials of a state function, for example, dU, are called *exact differentials* in mathematics; the differentials dq and dw are *inexact.* Some texts use a special symbol to denote inexact differentials and write $đq$ and $đw$ (or Dq and Dw) instead of dq and dw.

From (2.82), it follows that, if the value of the line integral ${}_L\int_1^2 db$ depends on the path from state 1 to state 2, then b cannot be a state function.

Conversely, if ${}_L\int_1^2 db$ has the same value for every possible path from state 1 to state 2, b is a state function whose value for any state of the system can be defined as follows. We pick a reference state r and assign it some value of b, which we denote by b_r. The b value of an arbitrary state 2 is then defined by

$$b_2 - b_r = \int_r^2 db \tag{2.83}$$

Since, by hypothesis, the integral in (2.83) is independent of the path, the value of b_2 depends only on state 2; $b_2 = b_2(T_2, P_2)$, and b is thus a state function.

If A is any state function, ΔA must be zero for any cyclic process. To indicate a cyclic process, one adds a circle to the line-integral symbol. If b is a state function, then (2.82) gives $\oint db = 0$ for any cyclic process. For example, $\oint dU = 0$. But note that $\oint dq = q$ and $\oint dw = w$, where the heat q and work w are not necessarily zero for a cyclic process.

We now show that, if

$$\oint db = 0$$

for every cyclic process, then the value of ${}_L\int_1^2 db$ is independent of the path and hence b is a state function. Figure 2.13 shows three processes connecting states 1 and 2. Processes I and II constitute a cycle. Hence the equation $\oint db = 0$ gives

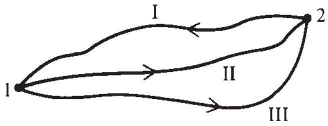


Figure 2.13

Three processes connecting states 1 and 2.

$$\int_{2 \atop \mathrm{I}}^{1} db + \int_{1 \atop \mathrm{II}}^{2} db = 0 \tag{2.84}$$

Likewise, processes I and III constitute a cycle, and

$$\int_{2 \atop \mathrm{I}}^{1} db + \int_{1 \atop \mathrm{III}}^{2} db = 0 \tag{2.85}$$

Subtraction of (2.85) from (2.84) gives

$$\int_{1 \atop \mathrm{II}}^{2} db = \int_{1 \atop \mathrm{III}}^{2} db \tag{2.86}$$

Since processes II and III are arbitrary processes connecting states 1 and 2, Eq. (2.86) shows that the line integral ${}_L\int_1^2 db$ has the same value for every process between states 1 and 2. Therefore b must be a state function.

Summary

If b is a state function, then ${}_L\int_1^2 db$ equals $b_2 - b_1$ and is independent of the path from state 1 to state 2. If b is a state function, then $\oint db = 0$.

If the value of ${}_L\int_1^2 db$ is independent of the path from 1 to 2, then b is a state function. If $\oint db = 0$ for every cyclic process, then b is a state function.

2.11 THE MOLECULAR NATURE OF INTERNAL ENERGY

Internal energy is energy at the molecular level. The molecular description of internal energy is outside the scope of thermodynamics, but a qualitative understanding of molecular energies is helpful.

Consider first a gas. The molecules are moving through space. A molecule has a translational kinetic energy $\frac{1}{2}mv^2$, where m and v are the mass and speed of the molecule. A **translation** is a motion in which every point of the body moves the same distance in the same direction. We shall later use statistical mechanics to show that the total molecular translational kinetic energy $U_{\text{tr,m}}$ of one mole of a gas is directly proportional to the absolute temperature and is given by [Eq. (14.14)] $U_{\text{tr,m}} = \frac{3}{2}RT$, where R is the gas constant.

If each gas molecule has more than one atom, then the molecules undergo rotational and vibrational motions in addition to translation. A **rotation** is a motion in which the spatial orientation of the body changes, but the distances between all points in the body remain fixed and the center of mass of the body does not move (so that there is no translational motion). In Chapter 21, we shall use statistical mechanics to show that except at very low temperatures the energy of molecular rotation $U_{\text{rot,m}}$ in one mole of gas is RT for linear molecules and $\frac{3}{2}RT$ for nonlinear molecules [Eq. (21.112)]: $U_{\text{rot,lin,m}} = RT$; $U_{\text{rot,nonlin,m}} = \frac{3}{2}RT$.

Besides translational and rotational energies, the atoms in a molecule have vibrational energy. In a molecular **vibration,** the atoms oscillate about their equilibrium positions in the molecule. A molecule has various characteristic ways of vibrating, each way being called a vibrational normal mode (see, for example, Figs. 20.26 and 20.27). Quantum mechanics shows that the lowest possible vibrational energy is not zero but is equal to a certain quantity called the molecular zero-point vibrational energy (so-called because it is present even at absolute zero temperature). The vibrational energy contribution U_{vib} to the internal energy of a gas is a complicated function of temperature [Eq. (21.113)]. For most light diatomic (two-atom) molecules (for example, H_2, N_2, HF, CO) at low and moderate temperatures (up to several hundred kelvins), the average molecular vibrational energy remains nearly fixed at the zero-point energy as the temperature increases. For polyatomic molecules (especially those with five or more atoms) and for heavy diatomic molecules (for example, I_2) at room temperature, the molecules usually have significant amounts of vibrational energy above the zero-point energy.

Figure 2.14 shows translational, rotational, and vibrational motions in CO_2.

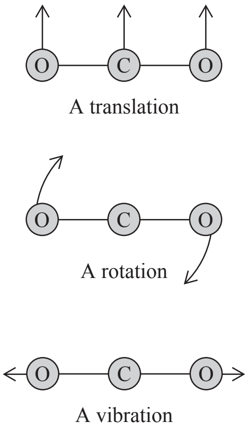


Figure 2.14

Kinds of motions in the CO_2 molecule.

In classical mechanics, energy has a continuous range of possible values. Quantum mechanics (Chapter 17) shows that the possible energies of a molecule are restricted to certain values called the **energy levels.** For example, the possible rotational-energy values of a diatomic molecule are $J(J + 1)b$ [Eq. (17.81)], where b is a constant for a given molecule and J can have the values 0, 1, 2, etc. One finds (Sec. 21.5) that there is a **distribution** of molecules over the possible energy levels. For example, for CO gas at 298 K, 0.93% of the molecules are in the $J = 0$ level, 2.7% are in the $J = 1$ level, 4.4% are in the $J = 2$ level, . . . , 3.1% are in the $J = 15$ level, ... As the temperature increases, more molecules are found in higher energy levels, the average molecular energy increases, and the thermodynamic internal energy and enthalpy increase (Fig. 5.11).

Besides translational, rotational, and vibrational energies, a molecule possesses **electronic energy** ε_{el} (epsilon el). We define this energy as $\varepsilon_{\text{el}} \equiv \varepsilon_{\text{eq}} - \varepsilon_{\infty}$, where ε_{eq} is the energy of the molecule with the nuclei at rest (no translation, rotation, or vibration) at positions corresponding to the equilibrium molecular geometry, and ε_{∞} is the energy when all the nuclei and electrons are at rest at positions infinitely far apart from one another, so as to make the electrical interactions between all the charged particles vanish. (The quantity ε_{∞} is given by the special theory of relativity as the sum of the rest-mass energies $m_{\text{rest}}c^2$ for the electrons and nuclei.) For a stable molecule, ε_{eq} is less than ε_{∞}.

The electronic energy ε_{el} can be changed by exciting a molecule to a higher electronic energy level. Nearly all common molecules have a very large gap between the lowest electronic energy level and higher electronic levels, so at temperatures below, say, 5000 K, virtually all the molecules are in the lowest electronic level and the contribution of electronic energy to the internal energy remains constant as the temperature increases (provided no chemical reactions occur).

In a chemical reaction, the electronic energies of the product molecules differ from those of the reactant molecules, and a chemical reaction changes the thermodynamic internal energy U primarily by changing the electronic energy. Although the other kinds of molecular energy generally also change in a reaction, the electronic energy undergoes the greatest change.

Besides translational, rotational, vibrational, and electronic energies, the gas molecules possess energy due to attractions and repulsions between them **(intermolecular forces);** intermolecular attractions cause gases to liquefy. The nature of intermolecular forces will be discussed in Sec. 21.10. Here, we shall just quote some key results for forces between neutral molecules.

The force between two molecules depends on the orientation of one molecule relative to the other. For simplicity, one often ignores this orientation effect and uses a force averaged over different orientations so that it is a function solely of the distance r between the centers of the interacting molecules. Figure 21.21*a* shows the typical behavior of the potential energy v of interaction between two molecules as a function of r; the quantity σ (sigma) is the average diameter of the two molecules. Note that, when the intermolecular distance r is greater than $2\frac{1}{2}$ or 3 times the molecular diameter σ, the intermolecular potential energy v is negligible. *Intermolecular forces are generally short-range.* When r decreases below 3σ, the potential energy decreases at first, indicating an attraction between the molecules, and then rapidly increases when r becomes close to σ, indicating a strong repulsion. Molecules initially attract each other as they approach and then repel each other when they collide. The magnitude of intermolecular attractions increases as the size of the molecules increases, and it increases as the molecular dipole moments increase.

The average distance between centers of molecules in a gas at 1 atm and 25°C is about 35 Å (Prob. 2.55), where the **angstrom** (Å) is

$$1\ \text{Å} \equiv 10^{-8}\ \text{cm} \equiv 10^{-10}\ \text{m} \equiv 0.1\ \text{nm} \qquad \textbf{(2.87)*}$$

Typical diameters of reasonably small molecules are 3 to 6 Å [see (15.26)]. The average distance between gas molecules at 1 atm and 25°C is 6 to 12 times the molecular diameter. Since intermolecular forces are negligible for separations beyond 3 times the molecular diameter, the intermolecular forces in a gas at 1 atm and 25°C are quite small and make very little contribution to the internal energy U. Of course, the spatial distribution of gas molecules is not actually uniform, and even at 1 atm significant numbers of molecules are quite close together, so intermolecular forces contribute slightly to U. At 40 atm and 25°C, the average distance between gas molecules is only 10 Å, and intermolecular forces contribute substantially to U.

Let $U_{\text{intermol,m}}$ be the contribution of intermolecular interactions to U_{m}. $U_{\text{intermol,m}}$ differs for different gases, depending on the strength of the intermolecular forces. Problem 4.22 shows that, for a gas, $U_{\text{intermol,m}}$ is typically -1 to -10 cal/mol at 1 atm and 25°C, and -40 to -400 cal/mol at 40 atm and 25°C. (U_{intermol} is negative because intermolecular attractions lower the internal energy.) These numbers may be compared with the 25°C value $U_{\text{tr,m}} = \frac{3}{2}RT = 900$ cal/mol.

The fact that it is very hard to compress liquids and solids tells us that in condensed phases the molecules are quite close to one another, with the average distance between molecular centers being only slightly greater than the molecular diameter. Here, intermolecular forces contribute very substantially to U. In a liquid, the molecular translational, rotational, and vibrational energies are, to a good approximation (Sec. 21.11), the same as in a gas at the same temperature. We can therefore find U_{intermol} in a liquid by measuring ΔU when the liquid vaporizes to a low-pressure gas. For common liquids, ΔU_{m} for vaporization typically lies in the range 3 to 15 kcal/mol, indicating $U_{\text{intermol,m}}$ values of -3000 to -15000 cal/mol, far greater in magnitude than $U_{\text{intermol,m}}$ in gases and $U_{\text{tr,m}}$ in room-temperature liquids and gases.

Discussion of U in solids is complicated by the fact that there are several kinds of solids (see Sec. 23.3). Here, we consider only molecular solids, those in which the structural units are individual molecules, these molecules being held together by intermolecular forces. In solids, the molecules generally don't undergo translation or rotation, and the translational and rotational energies found in gases and liquids are absent. Vibrations within the individual molecules contribute to the internal energy. In addition, there is the contribution U_{intermol} of intermolecular interactions to the internal energy. Intermolecular interactions produce a potential-energy well (similar to that in Fig. 21.21*a*) within which each entire molecule as a unit undergoes a vibrationlike motion that involves both kinetic and potential energies. Estimates of $U_{\text{intermol,m}}$ from heats of sublimation of solids to vapors indicate that for molecular crystals, $U_{\text{intermol,m}}$ is in the same range as for liquids.

For a gas or liquid, the molar internal energy is

$$U_{\text{m}} = U_{\text{tr,m}} + U_{\text{rot,m}} + U_{\text{vib,m}} + U_{\text{el,m}} + U_{\text{intermol,m}} + U_{\text{rest,m}}$$

where $U_{\text{rest,m}}$ is the molar rest-mass energy of the electrons and nuclei, and is a constant. Provided no chemical reactions occur and the temperature is not extremely high, $U_{\text{el,m}}$ is a constant. $U_{\text{intermol,m}}$ is a function of T and P. $U_{\text{tr,m}}$, $U_{\text{rot,m}}$, and $U_{\text{vib,m}}$ are functions of T.

For a perfect gas, $U_{\text{intermol,m}} = 0$. The use of $U_{\text{tr,m}} = \frac{3}{2}RT$, $U_{\text{rot,nonlin,m}} = \frac{3}{2}RT$, and $U_{\text{rot,lin,m}} = RT$ gives

$$U_{\text{m}} = \tfrac{3}{2}RT + \tfrac{3}{2}RT\,(\text{or } RT) + U_{\text{vib,m}}(T) + \text{const.} \qquad \text{perf. gas} \tag{2.88}$$

For monatomic gases (for example, He, Ne, Ar), $U_{\text{rot,m}} = 0 = U_{\text{vib,m}}$, so

$$U_{\text{m}} = \tfrac{3}{2}RT + \text{const.} \qquad \text{perf. monatomic gas} \tag{2.89}$$

The use of $C_{V,\text{m}} = (\partial U_{\text{m}}/\partial T)_V$ and $C_{P,\text{m}} - C_{V,\text{m}} = R$ gives

$$C_{V,\text{m}} = \tfrac{3}{2}R, \qquad C_{P,\text{m}} = \tfrac{5}{2}R \qquad \text{perf. monatomic gas} \tag{2.90}$$

provided T is not extremely high.

For polyatomic gases, the translational contribution to $C_{V,\text{m}}$ is $C_{V,\text{tr,m}} = \frac{3}{2}R$; the rotational contribution is $C_{V,\text{rot,lin,m}} = R$, $C_{V,\text{rot,nonlin,m}} = \frac{3}{2}R$ (provided T is not extremely low); $C_{V,\text{vib,m}}$ is a complicated function of T—for light diatomic molecules, $C_{V,\text{vib,m}}$ is negligible at room temperature.

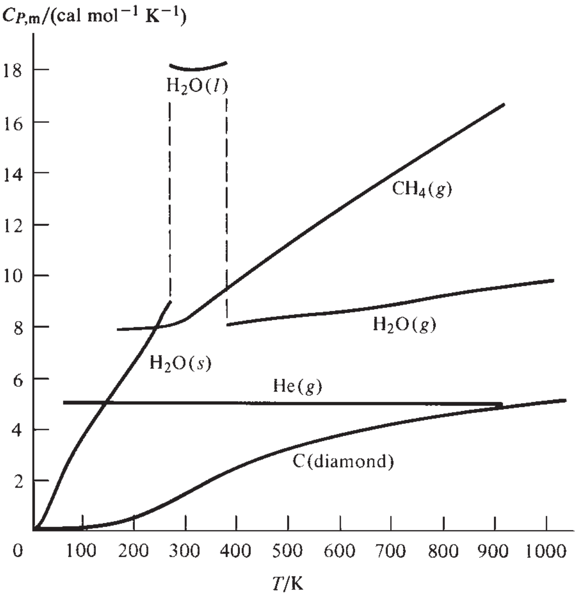
Figure 2.15 plots $C_{P,\text{m}}$ at 1 atm versus T for several substances. Note that $C_{P,\text{m}} = \frac{5}{2}R = 5$ cal/(mol K) for He gas between 50 and 1000 K. For H_2O gas, $C_{P,\text{m}}$ starts at $4R = 8$ cal/(mol K) at 373 K and increases as T increases. $C_{P,\text{m}} = 4R$ means $C_{V,\text{m}} = 3R$. The value $3R$ for this nonlinear molecule comes from $C_{V,\text{tr,m}} + C_{V,\text{rot,m}} = \frac{3}{2}R + \frac{3}{2}R$. The increase above $3R$ as T increases is due to the contribution from $C_{V,\text{vib,m}}$ as excited vibrational levels become populated.

The high value of $C_{P,\text{m}}$ of liquid water compared with that for water vapor results from the contribution of intermolecular interactions to U. Usually C_P for a liquid is substantially greater than that for the corresponding vapor.

The theory of heat capacities of solids will be discussed in Sec. 23.12. For all solids, $C_{P,\text{m}}$ goes to zero as T goes to zero.

Figure 2.15

$C_{P,\mathrm{m}}$ at 1 atm versus T for several substances; *s*, *l*, and *g* stand for solid, liquid, and gas.



The heat capacities $C_{P,\mathrm{m}} = (\partial H_\mathrm{m}/\partial T)_P$ and $C_{V,\mathrm{m}} = (\partial U_\mathrm{m}/\partial T)_V$ are measures of how much energy must be added to a substance to produce a given temperature increase. The more ways (translation, rotation, vibration, intermolecular interactions) a substance has of absorbing added energy, the greater will be its $C_{P,\mathrm{m}}$ and $C_{V,\mathrm{m}}$ values.

2.12 PROBLEM SOLVING

Trying to learn physical chemistry solely by reading a textbook without working problems is about as effective as trying to improve your physique by reading a book on body conditioning without doing the recommended physical exercises.

If you don't see how to work a problem, it often helps to carry out these steps:

1. List all the relevant information that is given.
2. List the quantities to be calculated.
3. Ask yourself what equations, laws, or theorems connect what is known to what is unknown.
4. Apply the relevant equations to calculate what is unknown from what is given.

Although these steps are just common sense, they can be quite useful. The point is that problem solving is an active process. Listing the given information and the unknown quantities and actively searching for relationships that connect them gets your mind working on the problem, whereas simply reading the problem over and over may not get you anywhere. In listing the given information, it is helpful to *translate the words in the problem into equations.* For example, the phrase "adiabatic process" is translated into $dq = 0$ and $q = 0$; "isothermal process" is translated into $dT = 0$ and $T =$ constant.

In steps 1 and 2, sketches of the system and the process may be helpful. In working a problem in thermodynamics, one must have clearly in mind which portion of the universe is the system and which is the surroundings. The nature of the system should be noted—whether it is a perfect gas (for which many special relations hold), a nonideal gas, a liquid, a solid, a heterogeneous system, etc. Likewise, be aware of the kind of process involved—whether it is adiabatic, isothermal (T constant), isobaric (P constant), isochoric (V constant), reversible, etc.

Of course, the main hurdle is step 3. Because of the many equations in physical chemistry, it might seem a complex task to find the right equation to use in a problem. However, there are relatively few equations that are best committed to memory. These are usually the most fundamental equations, and usually they have fairly simple forms. For example, we have several equations for mechanically reversible *P-V* work in a closed system: $dw_{\text{rev}} = -P\,dV$ gives the work in an infinitesimal reversible process; $w_{\text{rev}} = -\int_1^2 P\,dV$ gives the work in a finite reversible process; the work in a constant-pressure process is $-P\,\Delta V$; the work in an isothermal reversible process in a perfect gas is $w = nRT \ln (V_1/V_2)$. The only one of these equations worth memorizing is $dw_{\text{rev}} = -P\,dV$, since the others can be quickly derived from it. Moreover, rederiving an equation from a fundamental equation reminds you of the conditions under which the equation is valid. *Do not memorize unstarred equations.* Readers who have invested their time mainly in achieving an understanding of the ideas and equations of physical chemistry will do better than those who have spent their time memorizing formulas.

Many of the errors students make in thermodynamics arise from using an equation where it does not apply. To help prevent this, many of the equations have the conditions of validity stated next to them. *Be sure the equations you are using are applicable to the system and process involved.* For example, students asked to calculate q in a reversible isothermal expansion of a perfect gas sometimes write "$dq = C_P\,dT$ and since $dT = 0$, we have $dq = 0$ and $q = 0$." This conclusion is erroneous. Why? (See Prob. 2.63.)

If you are baffled by a problem, the following suggestions may help you. (*a*) Ask yourself what given information you have not yet used, and see how this information might help solve the problem. (*b*) Instead of working forward from the known quantities to the unknown, try working backward from the unknown to the known. To do this, ask yourself what quantities you must know to find the unknown; then ask yourself what you must know to find these quantities; etc. (*c*) Write down the definition of the desired quantity. For example, if a density is wanted, write $\rho \equiv m/V$ and ask yourself how to find m and V. If an enthalpy change is wanted, write $H \equiv U + PV$ and $\Delta H = \Delta U + \Delta(PV)$ and see if you can find ΔU and $\Delta(PV)$. (*d*) In analyzing a thermodynamic process, ask yourself which state functions stay constant and which change. Then ask what conclusions can be drawn from the fact that certain state functions stay constant. For example, if V is constant in a process, then the *P-V* work must be zero. (*e*) Stop working on the problem and go on to something else. The solution method might occur to you when you are not consciously thinking about the problem. A lot of mental activity occurs outside of our conscious awareness.

When dealing with abstract quantities, it often helps to take specific numerical values. For example, suppose we want the relation between the rates of change dn_A/dt and dn_B/dt for the chemical reaction $A + 2B \rightarrow$ products, where n_A and n_B are the moles of A and B and t is time. Typically, students will say either that $dn_A/dt = 2\,dn_B/dt$ or that $dn_A/dt = \frac{1}{2}dn_B/dt$. (Before reading further, which do you think is right?) To help decide, suppose that in a tiny time interval $dt = 10^{-3}$ s, 0.001 mol of A reacts, so that $dn_A = -0.001$ mol. For the reaction $A + 2B \rightarrow$ products, find the corresponding value of dn_B and then find dn_A/dt and dn_B/dt and compare them.

In writing equations, a useful check is provided by the fact that *each term in an equation must have the same dimensions.* Thus, an equation that contains the expression $U + TV$ cannot be correct, because U has dimensions of energy = mass × length^2/time^2, whereas TV has dimensions of temperature × volume = temperature × length^3. From the definitions (1.25) and (1.29) of a derivative and a partial derivative, it follows that $(\partial z/\partial x)_y$ has the same dimensions as z/x. The definitions (1.52) and (1.59) of indefinite and definite integrals show that $\int f\,dx$ and $\int_a^b f\,dx$ have the same dimensions as fx.

When writing equations, do not mix finite and infinitesimal changes in the same equation. Thus, an equation that contains the expression $P\,dV + V\,\Delta P$ must be wrong because dV is an infinitesimal change and ΔP is a finite change. If one term in an equation contains a single change in a state function, then another term that contains only state functions must contain a change. Thus, an equation cannot contain the expression $PV + V\,\Delta P$ or the expression $PV + V\,dP$.

As to step 4, performing the calculations, errors can be minimized by carrying units of all quantities as part of the calculation. *Make sure you are using a self-consistent set of units.* Do not mix joules and kilojoules or joules and calories or joules and cm^3 atm in the same equation. If you are confused about what units to use, a strategy that avoids errors is to express all quantities in SI units. *Inconsistent use of units is one of the most common student errors in physical chemistry.*

Express your answer with the proper units. *A numerical answer with no units is meaningless*.

> In September 1999, the $125 million U.S. Mars Climate Orbiter spacecraft was lost. It turned out that the engineers at Lockheed Martin sent data on the thrust of the spacecraft's thrusters to scientists at the Jet Propulsion Laboratory in units of pounds-force, but the JPL scientists assumed the thrust was in units of newtons, and so their programming of rocket firings to correct the trajectory produced an erroneous path that did not achieve orbit (*New York Times,* Oct. 1, 1999, p. A1). You don't have to be a rocket scientist to mess up on units.
>
> On July 23, 1983, Air Canada Flight 143 ran out of fuel at 28,000 feet altitude and only halfway to its destination. When the plane had been refueled in Ottawa, the plane's on-board fuel gauge was not working. Captain Robert Pearson knew that the plane needed 22,000 kg of fuel for the trip. The fuel-truck gauge read in liters, so Pearson asked the mechanic for the density of the fuel. He was told "1.77." Pearson assumed this was 1.77 kg/L, and used this figure to calculate the volume of the fuel needed. The plane was a new Boeing 767, and in line with Canada's conversion to metric units, its fuel load was measured in kilograms, in contrast to older planes, which used pounds. The mechanic was used to dealing with fuel loads in pounds (lb), so the figure of 1.77 he gave was actually 1.77 lb/L, which is 0.80 kg/L. Because of this miscommunication due to omission of units, Pearson requested a bit less than half the fuel volume he needed and took off with 22,000 pounds of fuel instead of 22,000 kg.
>
> Although the plane was out of fuel, an emergency electric generator (the ram air turbine) that uses the air stream resulting from the plane's speed to supply power to the plane's hydraulic system gave Pearson some control of the plane. Also, emergency battery power kept a few of the plane's instrument-panel gauges working. Pearson was an experienced glider pilot and flew the plane for 17 minutes after it ran out of fuel. He headed for an abandoned Canadian Air Force base at Gimli. Approaching Gimli, he realized the plane was coming in too high and too fast for a safe landing, so he executed a maneuver used with gliders to lose speed and altitude; this maneuver had never been tried with a commercial jet, but it worked. When the plane reached the runway, the crew saw people on the runway—the abandoned runway was being used for car races. The crew used a backup system to drop the landing gear; the nose wheel got stuck partway down and collapsed on landing; the scraping of the nose along the ground, together with Pearson's application of the brakes, brought the plane to a stop before it reached the people on the runway. There were no fatalities and only a few minor injuries when the passengers evacuated the plane.

Express the answer to the proper number of significant figures. Use a calculator with keys for exponentials and logarithms for calculations. After the calculation is completed, it is a good idea to check the entire solution. If you are like most of us, you are probably too lazy to do a complete check, but it takes only a few seconds to check that the sign and the magnitude of the answer are physically reasonable. Sign errors are especially common in thermodynamics, since most quantities can be either positive or negative.

A solutions manual for problems in this textbook is available.

2.13 SUMMARY

The work done on a closed system when it undergoes a mechanically reversible infinitesimal volume change is $dw_{\text{rev}} = -P\,dV$.

The line integral $\int_1^2 P(T, V)\,dV$ (which equals $-w_{\text{rev}}$) is defined to be the sum of the infinitesimal quantities $P(T, V)\,dV$ for the process from state 1 to state 2. In general, the value of a line integral depends on the path from state 1 to state 2.

The heat transferred to a body of constant composition when it undergoes a temperature change dT at constant pressure is $dq_P = C_P\,dT$, where C_P is the body's heat capacity at constant pressure.

The first law of thermodynamics expresses the conservation of the total energy of system plus surroundings. For a closed system at rest in the absence of fields, the total energy equals the internal energy U, and the change in U in a process is $\Delta U = q + w$, where q and w are the heat flowing into and the work done on the system in the process. U is a state function, but q and w are not state functions. The internal energy U is energy that exists at the molecular level and includes molecular kinetic and potential energies.

The state function enthalpy H is defined by $H \equiv U + PV$. For a constant-pressure process, $\Delta H = q_P$ in a closed system with P-V work only.

The heat capacities at constant pressure and constant volume are $C_P = dq_P/dT = (\partial H/\partial T)_P$ and $C_V = dq_V/dT = (\partial U/\partial T)_V$.

The Joule and Joule–Thomson experiments measure $(\partial T/\partial V)_U$ and $(\partial T/\partial P)_H$; these derivatives are closely related to $(\partial U/\partial V)_T$ and $(\partial H/\partial P)_T$.

A perfect gas obeys $PV = nRT$ and $(\partial U/\partial V)_T = 0$. The changes in thermodynamic properties for a perfect gas are readily calculated for reversible isothermal and reversible adiabatic processes.

The methods used to calculate q, w, ΔU, and ΔH for various kinds of thermodynamic processes were summarized in Sec. 2.9.

The line integral ${}_L\int_1^2 db$ is independent of the path from state 1 to state 2 if and only if b is a state function. The line integral $\oint db$ is zero for every cyclic process if and only if b is a state function.

The molecular interpretation of internal energy in terms of intramolecular and intermolecular energies was discussed in Sec. 2.11.

Important kinds of calculations dealt with in this chapter include calculations of q, w, ΔU, and ΔH for

- Phase changes (for example, melting).
- Heating a substance at constant pressure.
- Heating at constant volume.
- An isothermal reversible process in a perfect gas.
- An adiabatic reversible process in a perfect gas with C_V constant.
- An adiabatic expansion of a perfect gas into vacuum.
- A constant-pressure reversible process in a perfect gas.
- A constant-volume reversible process in a perfect gas.

FURTHER READING

Zemansky and Dittman, chaps. 3, 4, 5; *Andrews* (1971), chaps. 5, 6, 7; *de Heer,* chaps. 3, 9; *Kestin,* chap. 5; *Reynolds and Perkins,* chaps. 1, 2; *Van Wylen and Sonntag,* chaps. 4, 5.

PROBLEMS

Section 2.1

2.1 True or false? (*a*) The kinetic energy of a system of several particles equals the sum of the kinetic energies of the individual particles. (*b*) The potential energy of a system of interacting particles equals the sum of the potential energies of the individual particles.

2.2 Give the SI units of (*a*) energy; (*b*) work; (*c*) volume; (*d*) force; (*e*) speed; (*f*) mass.

2.3 Express each of these units as a combination of meters, kilograms, and seconds: (*a*) joule; (*b*) pascal; (*c*) liter; (*d*) newton; (*e*) watt.

2.4 An apple of mass 155 g falls from a tree and is caught by a small boy. If the apple fell a distance of 10.0 m, find (*a*) the work done on the apple by the earth's gravitational field; (*b*) the kinetic energy of the apple just before it was caught; (*c*) the apple's speed just before it was caught.

2.5 An apple of mass 102 g is ground up into applesauce (with no added sugar) and spread evenly over an area of 1.00 m^2 on the earth's surface. What is the pressure exerted by the applesauce?

2.6 In the obsolete cgs system of mechanical units, length is expressed in centimeters, mass in grams, and time in seconds. The cgs unit of force is the dyne and the cgs unit of energy is the erg. Find the relation between dynes and newtons. Find the relation between ergs and joules.

Section 2.2

2.7 True or false? (*a*) The P-V work in a mechanically reversible process in a closed system always equals $-P\,\Delta V$. (*b*) The symbol w in this book means work done on the system by the surroundings. (*c*) The infinitesimal P-V work in a mechanically reversible process in a closed system always equals $-P\,dV$. (*d*) The value of the work w in a reversible process in a closed system can be found if we know the initial state and the final state of the system. (*e*) The value of the integral $\int_1^2 P\,dV$ is fixed once the initial and final states 1 and 2 and the equation of state $P = P(T, V)$ are known. (*f*) The equation $w_{\text{rev}} = -\int_1^2 P\,dV$ applies only to constant-pressure processes. (*g*) $\int_1^2 P\,dV = \int_1^2 nR\,dT$ for every reversible process in an ideal gas.

2.8 If $P_1 = 175$ torr, $V_1 = 2.00$ L, $P_2 = 122$ torr, $V_2 = 5.00$ L, find w_{rev} for process (*b*) of Fig. 2.3 by (*a*) finding the area under the curve; (*b*) using $w_{\text{rev}} = -\int_1^2 P\,dV$.

2.9 A nonideal gas is heated slowly and expands reversibly at a constant pressure of 275 torr from a volume of 385 cm^3 to 875 cm^3. Find w in joules.

2.10 Using the P_1, V_1, P_2, and V_2 values of Example 2.2, find w for a reversible process that goes from state 1 to state 2 in Fig. 2.3 via a straight line (*a*) by calculating the area under the curve; (*b*) by using $w_{\text{rev}} = -\int_1^2 P\,dV$. [*Hint:* The equation of the straight line that goes through points x_1, y_1 and x_2, y_2 is $(y - y_1)/(x - x_1) = (y_2 - y_1)/(x_2 - x_1)$.]

2.11 It was stated in Sec. 2.2 that for a given change of state, w_{rev} can have any positive or negative value. Consider a change of state for which $P_2 = P_1$ and $V_2 > V_1$. For this change of state, use a P-V diagram to (*a*) sketch a process with $w_{\text{rev}} < 0$; (*b*) sketch a process with $w_{\text{rev}} > 0$. Remember that neither P nor V can be negative.

Section 2.3

2.12 Specific heats can be measured in a *drop calorimeter;* here, a heated sample is dropped into the calorimeter and the final temperature is measured. When 45.0 g of a certain metal at 70.0°C is added to 24.0 g of water (with $c_P = 1.00$ cal/g-°C) at 10.0°C in an insulated container, the final temperature is 20.0°C. (*a*) Find the specific heat capacity of the metal. (*b*) How much heat flowed from the metal to the water? *Note:* In (*a*), we are finding the average c_P over the temperature range of the experiment. To determine c_P as a function of T, one repeats the experiment many times, using different initial temperatures for the metal.

Section 2.4

2.13 True or false? (*a*) For every process, $\Delta E_{\text{syst}} = -\Delta E_{\text{surr}}$. (*b*) For every cyclic process, the final state of the system is the same as the initial state. (*c*) For every cyclic process, the final state of the surroundings is the same as the initial state of the surroundings. (*d*) For a closed system at rest with no fields present, the sum $q + w$ has the same value for every process that goes from a given state 1 to a given state 2. (*e*) If systems A and B each consist of pure liquid water at 1 bar pressure and if $T_A > T_B$, then the internal energy of system A must be greater than that of B.

2.14 For which of these systems is the system's energy conserved in every process: (*a*) a closed system; (*b*) an open system; (*c*) an isolated system; (*d*) a system enclosed in adiabatic walls?

2.15 One food calorie = 10^3 cal = 1 kcal. A typical adult ingests 2200 kcal/day. (*a*) Show that an adult uses energy at about the same rate as a 100-W lightbulb. (*b*) Calculate the total annual metabolic-energy expenditure of the 7×10^9 people on earth and compare it with the 5×10^{20} J per year energy used by the world economy. (Neglect the fact that children use less metabolic energy than adults.)

2.16 A mole of water vapor initially at 200°C and 1 bar undergoes a cyclic process for which $w = 338$ J. Find q for this process.

2.17 William Thomson tells of running into Joule in 1847 at Mont Blanc; Joule had with him his bride and a long thermometer with which he was going to "try for elevation of temperature in waterfalls." The Horseshoe Falls at Niagara Falls is 167 ft high and has a summer daytime flow rate of 2.55×10^6 L/s. (*a*) Calculate the maximum possible temperature difference between the water at the top and at the bottom of the falls. (The maximum possible increase occurs if no energy is transferred to such parts of the surroundings as the rocks at the base of the falls.) (*b*) Calculate the maximum possible internal-energy increase of the 2.55×10^6 L that falls each second. (Before it reaches the falls, more than half the water of the Niagara River is diverted to a canal or underground tunnels for use in hydroelectric power plants beyond the falls. These plants generate 4.4×10^9 W. A power surge at one of these plants led to the great blackout of November 9, 1965, which left 30 million people in the northeast United States and Ontario, Canada, without power for many hours.)

2.18 Imagine an isolated system divided into two parts, 1 and 2, by a rigid, impermeable, thermally conducting wall. Let heat q_1 flow into part 1. Use the first law to show that the heat flow for part 2 must be $q_2 = -q_1$.

2.19 Sometimes one sees the notation Δq and Δw for the heat flow into a system and the work done during a process. Explain why this notation is misleading.

2.20 Explain how liquid water can go from 25°C and 1 atm to 30°C and 1 atm in a process for which $q < 0$.

2.21 The potential energy stored in a spring is $\frac{1}{2}kx^2$, where k is the force constant of the spring and x is the distance the spring is stretched from equilibrium. Suppose a spring with force constant 125 N/m is stretched by 10.0 cm, placed in 112 g of water in an adiabatic container, and released. The mass of the spring is 20 g, and its specific heat capacity is 0.30 cal/(g °C). The initial temperature of the water and the spring is 18.000°C. The water's specific heat capacity is 1.00 cal/(g °C). Find the final temperature of the water.

2.22 Consider a system enclosed in a vertical cylinder fitted with a frictionless piston. The piston is a plate of negligible mass, on which is glued a mass m whose cross-sectional area is the same as that of the plate. Above the piston is a vacuum. (*a*) Use conservation of energy in the form $dE_{\text{syst}} + dE_{\text{surr}} = 0$ to show that for an adiabatic volume change $dE_{\text{syst}} = -mg\,dh - dK_{\text{pist}}$, where dh is the infinitesimal change in piston height, g is the gravitational acceleration, and dK_{pist} is the infinitesimal change in kinetic energy of the mass m. (*b*) Show that the equation in part (*a*) gives $dw_{\text{irrev}} = -P_{\text{ext}}\,dV - dK_{\text{pist}}$ for the irreversible work done on the system, where P_{ext} is the pressure exerted by the mass m on the piston plate.

2.23 Suppose the system of Prob. 2.22 is initially in equilibrium with $P = 1.000$ bar and $V = 2.00$ dm^3. The external mass m is instantaneously reduced by 50% and held fixed thereafter, so that P_{ext} remains at 0.500 bar during the expansion. After undergoing oscillations, the piston eventually comes to rest. The final system volume is 6.00 dm^3. Calculate w_{irrev}.

Section 2.5

2.24 True or false? (*a*) The quantities H, U, PV, ΔH, and $P\,\Delta V$ all have the same dimensions. (*b*) ΔH is defined only for a constant-pressure process. (*c*) For a constant-volume process in a closed system, $\Delta H = \Delta U$.

2.25 Which of the following have the dimensions of energy: force, work, mass, heat, pressure, pressure times volume, enthalpy, change in enthalpy, internal energy, force times length?

2.26 The state function H used to be called "the heat content." (*a*) Explain the origin of this name. (*b*) Why is this name misleading?

2.27 We showed $\Delta H = q$ for a constant-pressure process. Consider a process in which P is not constant throughout the entire process, but for which the final and initial pressures are equal. Need ΔH be equal to q here? (*Hint:* One way to answer this is to consider a cyclic process.)

2.28 A certain system is surrounded by adiabatic walls. The system consists of two parts, 1 and 2. Each part is closed, is held at constant P, and is capable of P-V work only. Apply $\Delta H = q_P$ to the entire system and to each part to show that $q_1 + q_2 = 0$ for heat flow between the parts.

Section 2.6

2.29 True or false? (*a*) C_P is a state function. (*b*) C_P is an extensive property.

2.30 (*a*) For CH$_4$(*g*) at 2000 K and 1 bar, $C_{P,\text{m}} = 94.4$ J mol^{-1} K^{-1}. Find C_P of 586 g of CH$_4$(*g*) at 2000 K and 1 bar. (*b*) For C(diamond), $C_{P,\text{m}} = 6.115$ J mol^{-1} K^{-1} at 25°C and 1 bar. For a 10.0-carat diamond, find c_P and C_P. One carat = 200 mg.

2.31 For H$_2$O(*l*) at 100°C and 1 atm, $\rho = 0.958$ g/cm^3. Find the specific volume of H$_2$O(*l*) at 100°C and 1 atm.

Section 2.7

2.32 (*a*) What state function must remain constant in the Joule experiment? (*b*) What state function must remain constant in the Joule–Thomson experiment?

2.33 For air at temperatures near 25°C and pressures in the range 0 to 50 bar, the μ_{JT} values are all reasonably close to 0.2°C/bar. Estimate the final temperature of the gas if 58 g of air at 25°C and 50 bar undergoes a Joule–Thomson throttling to a final pressure of 1 bar.

2.34 Rossini and Frandsen found that, for air at 28°C and pressures in the range 1 to 40 atm, $(\partial U_{\text{m}}/\partial P)_T = -6.08$ J mol^{-1} atm^{-1}. Calculate $(\partial U_{\text{m}}/\partial V_{\text{m}})_T$ for air at (*a*) 28°C and 1.00 atm; (*b*) 28°C and 2.00 atm. [*Hint:* Use (1.35).]

2.35 (*a*) Derive Eq. (2.65). (*b*) Show that

$$\mu_{JT} = -(V/C_P)(\kappa C_V \mu_J - \kappa P + 1)$$

where κ is defined by (1.44). [*Hint:* Start by taking $(\partial/\partial P)_T$ of $H = U + PV$.]

2.36 Is μ_J an intensive property? Is μ_J an extensive property?

Section 2.8

2.37 For a fixed amount of a perfect gas, which of these statements must be true? (*a*) U and H each depend only on T. (*b*) C_P is a constant. (*c*) $P\,dV = nR\,dT$ for every infinitesimal process. (*d*) $C_{P,\text{m}} - C_{V,\text{m}} = R$. (*e*) $dU = C_V\,dT$ for a reversible process.

2.38 (*a*) Calculate q, w, ΔU, and ΔH for the reversible isothermal expansion at 300 K of 2.00 mol of a perfect gas from

500 cm^3 to 1500 cm^3. (*b*) What would ΔU and w be if the expansion connects the same initial and final states as in (*a*) but is done by having the perfect gas expand into vacuum?

2.39 One mole of He gas with $C_{V,\text{m}} = 3R/2$ essentially independent of temperature expands reversibly from 24.6 L and 300 K to 49.2 L. Calculate the final pressure and temperature if the expansion is (*a*) isothermal; (*b*) adiabatic. (*c*) Sketch these two processes on a P-V diagram.

2.40 For $N_2(g)$, $C_{P,\text{m}}$ is nearly constant at $3.5R = 29.1$ J/(mol K) for temperatures in the range 100 to 400 K and low or moderate pressures. (*a*) Calculate q, w, ΔU, and ΔH for the reversible adiabatic compression of 1.12 g of $N_2(g)$ from 400 torr and 1000 cm^3 to a final volume of 250 cm^3. Assume perfect-gas behavior. (*b*) Suppose we want to cool a sample of $N_2(g)$ at room T and P (25°C and 101 kPa) to 100 K using a reversible adiabatic expansion. What should the final pressure be?

2.41 Find q, w, ΔU, and ΔH if 2.00 g of He(g) with $C_{V,\text{m}} = \frac{3}{2}R$ essentially independent of temperature undergoes (*a*) a reversible constant-pressure expansion from 20.0 dm^3 to 40.0 dm^3 at 0.800 bar; (*b*) a reversible heating with P going from 0.600 bar to 0.900 bar while V remains fixed at 15.0 dm^3.

Section 2.9

2.42 True or false? (*a*) A thermodynamic process is defined by the final state and the initial state. (*b*) $\Delta T = 0$ for every isothermal process. (*c*) Every process that has $\Delta T = 0$ is an isothermal process. (*d*) $\Delta U = 0$ for a reversible phase change at constant T and P. (*e*) q must be zero for an isothermal process. (*f*) ΔT must be zero for an adiabatic process.

2.43 State whether each of the following is a property of a thermodynamic system or refers to a noninfinitesimal process: (*a*) q; (*b*) U; (*c*) ΔH; (*d*) w; (*e*) C_V; (*f*) μ_{JT}; (*g*) H.

2.44 Give the value of C_{pr} [Eq. (2.50)] for (*a*) the melting of ice at 0°C and 1 atm; (*b*) the freezing of water at 0°C and 1 atm; (*c*) the reversible isothermal expansion of a perfect gas; (*d*) the reversible adiabatic expansion of a perfect gas.

2.45 (*This problem is especially instructive.*) For each of the following processes deduce whether each of the quantities q, w, ΔU, and ΔH is positive, zero, or negative. (*a*) Reversible melting of solid benzene at 1 atm and the normal melting point. (*b*) Reversible melting of ice at 1 atm and 0°C. (*c*) Reversible adiabatic expansion of a perfect gas. (*d*) Reversible isothermal expansion of a perfect gas. (*e*) Adiabatic expansion of a perfect gas into a vacuum (Joule experiment). (*f*) Joule–Thomson adiabatic throttling of a perfect gas. (*g*) Reversible heating of a perfect gas at constant P. (*h*) Reversible cooling of a perfect gas at constant V.

2.46 For each process state whether each of q, w, and ΔU is positive, zero, or negative. (*a*) Combustion of benzene in a sealed container with rigid, adiabatic walls. (*b*) Combustion of benzene in a sealed container that is immersed in a water bath at 25°C and has rigid, thermally conducting walls. (*c*) Adiabatic expansion of a nonideal gas into vacuum.

2.47 One mole of liquid water at 30°C is adiabatically compressed, P increasing from 1.00 to 10.00 atm. Since liquids and solids are rather incompressible, it is a fairly good approximation to take V as unchanged for this process. With this approximation, calculate q, ΔU, and ΔH for this process.

2.48 The molar heat capacity of oxygen at constant pressure for temperatures in the range 300 to 400 K and for low or moderate pressures can be approximated as $C_{P,\text{m}} = a + bT$, where $a = 6.15$ cal mol^{-1} K^{-1} and $b = 0.00310$ cal mol^{-1} K^{-2}. (*a*) Calculate q, w, ΔU, and ΔH when 2.00 mol of O_2 is reversibly heated from 27°C to 127°C with P held fixed at 1.00 atm. Assume perfect-gas behavior. (*b*) Calculate q, w, ΔU, and ΔH when 2.00 mol of O_2 initially at 1.00 atm is reversibly heated from 27°C to 127°C with V held fixed.

2.49 For this problem use 333.6 J/g and 2256.7 J/g as the latent heats of fusion and vaporization of water at the normal melting and boiling points, $c_P = 4.19$ J g^{-1} K^{-1} for liquid water, $\rho = 0.917$ g/cm^3 for ice at 0°C and 1 atm, $\rho = 1.000$ g/cm^3 and 0.958 g/cm^3 for water at 1 atm and 0°C and 100°C, respectively. (For liquid water, c_P varies slightly with T. The value given is an average over the range 0°C to 100°C; see Fig. 2.15.) Calculate q, w, ΔU, and ΔH for (*a*) the melting of 1 mol of ice at 0°C and 1 atm; (*b*) the reversible constant-pressure heating of 1 mol of liquid water from 0°C to 100°C at 1 atm; (*c*) the vaporization of 1 mol of water at 100°C and 1 atm.

2.50 Calculate ΔU and ΔH for each of the following changes in state of 2.50 mol of a perfect monatomic gas with $C_{V,\text{m}} = 1.5R$ for all temperatures: (*a*) (1.50 atm, 400 K) → (3.00 atm, 600 K); (*b*) (2.50 atm, 20.0 L) → (2.00 atm, 30.0 L); (*c*) (28.5 L, 400 K) → (42.0 L, 400 K).

2.51 Can q and w be calculated for the processes of Prob. 2.50? If the answer is yes, calculate them for each process.

2.52 For a certain perfect gas, $C_{V,\text{m}} = 2.5R$ at all temperatures. Calculate q, w, ΔU, and ΔH when 2.00 mol of this gas undergoes each of the following processes: (*a*) a reversible isobaric expansion from (1.00 atm, 20.0 dm^3) to (1.00 atm, 40.0 dm^3); (*b*) a reversible isochoric change of state from (1.00 atm, 40.0 dm^3) to (0.500 atm, 40.0 dm^3); (*c*) a reversible isothermal compression from (0.500 atm, 40.0 dm^3) to (1.00 atm, 20.0 dm^3). Sketch each process on the same P-V diagram and calculate q, w, ΔU, and ΔH for a cycle that consists of steps (*a*), (*b*), and (*c*).

Section 2.11

2.53 Classify each of the following as kinetic energy, potential energy, or both: (*a*) translational energy; (*b*) rotational energy; (*c*) vibrational energy; (*d*) electronic energy.

2.54 Explain why $C_{P,\text{m}}$ of He gas at 10 K and 1 atm is larger than $\frac{5}{2}R$.

2.55 (*a*) Calculate the volume of 1 mole of ideal gas at 25°C and 1 atm. Let the gas be in a cubic container. If the gas molecules are distributed uniformly in space with equal spacing between adjacent molecules (of course, this really isn't so), the gas volume can be divided into Avogadro's number of imaginary equal-sized cubes, each cube containing a molecule at its center. Calculate the edge length of each such cube. (*b*) What is the distance between the centers of the uniformly distributed gas molecules at 25°C and 1 atm? (*c*) Answer (*b*) for a gas at 25°C and 40 atm.

2.56 Estimate $C_{V,\mathrm{m}}$ and $C_{P,\mathrm{m}}$ at 300 K and 1 atm for (*a*) Ne(*g*); (*b*) CO(*g*).

2.57 Use Fig. 2.15 to decide whether U_{intermol} of liquid water increases or decreases as T increases.

General

2.58 (*a*) Use Rumford's data given in Sec. 2.4 to estimate the relation between the "old" calorie (as defined in Sec. 2.3) and the joule. Use 1 horsepower $= 746$ W. (*b*) The same as (*a*) using Joule's data given in Sec. 2.4.

2.59 Students often make significant-figure errors in taking reciprocals, in taking logs and antilogs, and in taking the difference of nearly equal numbers. (*a*) For a temperature of 1.8°C, calculate T^{-1} (where T is the absolute temperature) to the proper number of significant figures. (*b*) Find the common logs of the following numbers: 4.83 and 4.84; 4.83×10^{20} and 4.84×10^{20}. From the results, formulate a rule as to the proper number of significant figures in the log of a number known to n significant figures. (*c*) Calculate $(210.6\ \mathrm{K})^{-1} - (211.5\ \mathrm{K})^{-1}$ to the proper number of significant figures.

2.60 (*a*) A gas obeying the van der Waals equation of state (1.39) undergoes a reversible isothermal volume change from V_1 to V_2. Obtain the expression for the work w. Check that your result reduces to (2.74) for $a = 0 = b$. (*b*) Use the result of (*a*) to find w for 0.500 mol of N_2 expanding reversibly from 0.400 L to 0.800 L at 300 K. See Sec. 8.4 for the a and b values of N_2. Compare the result with that found if N_2 is assumed to be a perfect gas.

2.61 (*a*) If the temperature of a system decreases by 8.0°C, what is ΔT in kelvins? (*b*) A certain system has $C_P = 5.00$ J/°C. What is its C_P in joules per kelvin?

2.62 Explain why Boyle's law $PV =$ constant for an ideal gas does not contradict the equation $PV^{\gamma} =$ constant for a reversible adiabatic process in a perfect gas with C_V constant.

2.63 Point out the error in the Sec. 2.12 reasoning that gave $q = 0$ for a reversible isothermal process in a perfect gas.

2.64 A perfect gas with $C_{V,\mathrm{m}} = 3R$ independent of T expands adiabatically into a vacuum, thereby doubling its volume. Two students present the following conflicting analyses. Genevieve uses Eq. (2.76) to write $T_2/T_1 = (V_1/2V_1)^{R/3R}$ and $T_2 = T_1/2^{1/3}$. Wendy writes $\Delta U = q + w = 0 + 0 = 0$ and $\Delta U = C_V\,\Delta T$, so $\Delta T = 0$ and $T_2 = T_1$. Which student is correct? What error did the other student make?

2.65 A perfect gas undergoes an expansion process at constant pressure. Does its internal energy increase or decrease? Justify your answer.

2.66 Classify each of the following properties as intensive or extensive and give the SI units of each: (*a*) density; (*b*) U; (*c*) H_{m}; (*d*) C_P; (*e*) c_P; (*f*) $C_{P,\mathrm{m}}$; (*g*) P; (*h*) molar mass; (*i*) T.

2.67 A student attempting to remember a certain formula comes up with $C_P - C_V = TV\alpha^m/\kappa^n$, where m and n are certain integers whose values the student has forgotten and where the remaining symbols have their usual meanings. Use dimensional considerations to find m and n.

2.68 Because the heat capacities per unit volume of gases are small, accurate measurement of C_P or C_V for gases is not easy. Accurate measurement of the heat-capacity ratio γ of a gas (for example, by measurement of the speed of sound in the gas) is easy. For gaseous CCl_4 at 0.1 bar and 20°C, experiment gives $\gamma = 1.13$. Find $C_{P,\mathrm{m}}$ and $C_{V,\mathrm{m}}$ for $CCl_4(g)$ at 20°C and 1 bar.

2.69 Give the SI units of each of the following properties and state whether each is extensive or intensive. (*a*) $(\partial V/\partial T)_P$; (*b*) $V^{-1}(\partial V/\partial T)_P$; (*c*) $(\partial V_{\mathrm{m}}/\partial P)_T$; (*d*) $(\partial U/\partial V)_T$; (*e*) $(\partial^2 V/\partial T^2)_P$.

2.70 State whether or not each of the following quantities is infinitesimally small. (*a*) ΔV; (*b*) dw_{rev}; (*c*) $(\partial H/\partial T)_P$; (*d*) $V\,dP$.

2.71 True or false? (*a*) ΔH is a state function. (*b*) C_V is independent of T for every perfect gas. (*c*) $\Delta U = q + w$ for every thermodynamic system at rest in the absence of external fields. (*d*) A process in which the final temperature equals the initial temperature must be an isothermal process. (*e*) For a closed system at rest in the absence of external fields, $U = q + w$. (*f*) U remains constant in every isothermal process in a closed system. (*g*) $q = 0$ for every cyclic process. (*h*) $\Delta U = 0$ for every cyclic process. (*i*) $\Delta T = 0$ for every adiabatic process in a closed system. (*j*) A thermodynamic process is specified by specifying the initial state and the final state of the system. (*k*) If a closed system at rest in the absence of external fields undergoes an adiabatic process that has $w = 0$, then the system's temperature must remain constant. (*l*) P-V work is usually negligible for solids and liquids. (*m*) If neither heat nor matter can enter or leave a system, that system must be isolated. (*n*) For a closed system with P-V work only, a constant-pressure process that has $q > 0$ must have $\Delta T > 0$. (*o*) $\int_1^2 (1/V)\,dV = \ln(V_2 - V_1)$. (*p*) The value of ΔU is independent of the path (process) used to go from state 1 to state 2. (*q*) For any process, $\Delta T = \Delta t$, where T and t are the Kelvin and Celsius temperatures. (*r*) If $q = 0$ for a process, then the process must be isothermal. (*s*) For a reversible process, P must be constant. (*t*) $\int_{T_1}^{T_2}(1/T)\,dT = (\ln T_2)/(\ln T_1)$. (*u*) If the final temperature equals the initial temperature, the process must be an isothermal process. (*v*) $\int_{T_1}^{T_2} T\,dT = \frac{1}{2}(T_2 - T_1)^2$.