

Chapter 2

The First Law and Other Basic Concepts

2.1 JOULE'S EXPERIMENTS

The present-day understanding of heat and its relation to work developed during the last half of the nineteenth century. Crucial to this understanding were the many experiments of James P. Joule¹ (1818–1889), carried out in the cellar of his home near Manchester, England, during the decade following 1840.

In their essential elements Joule's experiments were simple enough, but he took elaborate precautions to insure accuracy. In the most famous series of measurements, he placed known amounts of water, oil, and mercury in an insulated container and agitated the fluid with a rotating stirrer. The amounts of work done on the fluid by the stirrer were accurately measured, and the temperature changes of the fluid were carefully noted. He found for each fluid that a fixed amount of work was required per unit mass for every degree of temperature rise caused by the stirring, and that the original temperature of the fluid could be restored by the transfer of heat through simple contact with a cooler object. Thus Joule was able to show conclusively that a quantitative relationship exists between work and heat and, therefore, that heat is a form of energy.

2.2 INTERNAL ENERGY

In experiments such as those conducted by Joule, energy is added to a fluid as work, but is transferred from the fluid as heat. What happens to this energy between its addition to and transfer from the fluid? A rational concept is that it is contained in the fluid in another form, called *internal energy*.

The internal energy of a substance does not include energy that it may possess as a result of its macroscopic position or movement. Rather it refers to energy of the molecules internal to the substance. Because of their ceaseless motion, all molecules possess kinetic energy of translation; except for monatomic molecules, they also possess kinetic energy of rotation and

¹These experiments and their influence on the development of thermodynamics are described by H. J. Steffens, *James Prescott Joule and the Concept of Energy*, Neale Watson Academic Publications, Inc., New York, 1979.

of internal vibration. The addition of heat to a substance increases this molecular activity, and thus causes an increase in its internal energy. Work done on the substance can have the same effect, as was shown by Joule.

The internal energy of a substance also includes the potential energy resulting from intermolecular forces (Sec. 16.1). On a submolecular scale energy is associated with the electrons and nuclei of atoms, and with bond energy resulting from the forces holding atoms together as molecules. This form of energy is named *internal* to distinguish it from the kinetic and potential energy associated with a substance because of its macroscopic position or motion, which can be thought of as *external* forms of energy.

Internal energy, has no concise thermodynamic definition. It is a thermodynamic *primitive*. It cannot be directly measured; there are no internal-energy meters. As a result, absolute values are unknown. However, this is not a disadvantage in thermodynamic analysis, because only *changes* in internal energy are required.

2.3 THE FIRST LAW OF THERMODYNAMICS

The recognition of heat and internal energy as forms of energy makes possible a generalization of the law of conservation of mechanical energy (Sec. 1.8) to include heat and internal energy in addition to work and external potential and kinetic energy. Indeed, the generalization can be extended to still other forms, such as surface energy, electrical energy, and magnetic energy. This generalization was at first a postulate. However, the overwhelming evidence accumulated over time has elevated it to the stature of a law of nature, known as the first law of thermodynamics. One formal statement is:

Although energy assumes many forms, the total quantity of energy is constant, and when energy disappears in one form it appears simultaneously in other forms.

In application of the first law to a given process, the sphere of influence of the process is divided into two parts, the *system* and its *surroundings*. The region in which the process occurs is set apart as the system; everything with which the system interacts is the surroundings. The system may be of any size depending on the application, and its boundaries may be real or imaginary, rigid or flexible. Frequently a system consists of a single substance; in other cases it may be complex. In any event, the equations of thermodynamics are written with reference to some well-defined system. This focuses attention on the particular process of interest and on the equipment and material directly involved in the process. However, the first law applies to the system *and* surroundings, and not to the system alone. In its most basic form, the first law requires:

$$\Delta(\text{Energy of the system}) + \Delta(\text{Energy of surroundings}) = 0 \quad (2.1)$$

where the difference operator " Δ " signifies finite changes in the quantities enclosed in parentheses. The system may change in its internal energy, in its potential or kinetic energy, and in the potential or kinetic energy of its finite parts. Since attention is focused on the system, the nature of energy changes in the surroundings is not of interest.

In the thermodynamic sense, heat and work refer to energy *in transit across the boundary* which divides the system from its surroundings. These forms of energy are not stored, and are never *contained in* a body or system. Energy is stored in its potential, kinetic, and internal

forms; these reside with material objects and exist because of the position, configuration, and motion of matter.

2.4 ENERGY BALANCE FOR CLOSED SYSTEMS

If the boundary of a system does not permit the transfer of matter between the system and its surroundings, the system is said to be *closed*, and its mass is necessarily constant. The development of basic concepts in thermodynamics is facilitated by a careful examination of closed systems, and for this reason they are treated in detail in the following sections. Far more important for industrial practice are processes in which matter crosses the system boundary as streams that enter and leave process equipment. Such systems are said to be *open*, and they are treated later in this chapter, once the necessary foundation material has been presented.

Since no streams enter or leave a closed system, no internal energy is *transported* across the boundary of the system. All energy exchange between a closed system and its surroundings then appears as heat and work, and the total energy change of the surroundings equals the net energy transferred to or from it as heat and work. The second term of Eq. (2.1) may therefore be replaced by

$$\Delta(\text{Energy of surroundings}) = \pm Q \pm W$$

The choice of signs used with Q and W depends on which direction of transport is regarded as positive.

Heat Q and work W always refer to the system, and the modern sign convention makes the numerical values of both quantities positive for transfer *into* the system from the surroundings. The corresponding quantities taken with reference to the surroundings, Q_{surr} and W_{surr} , have the opposite sign, i.e., $Q_{\text{surr}} = -Q$ and $W_{\text{surr}} = -W$. With this understanding:

$$\Delta(\text{Energy of surroundings}) = Q_{\text{surr}} + W_{\text{surr}} = -Q - W$$

Equation (2.1) now becomes:²

$$\Delta(\text{Energy of the system}) = Q + W \quad (2.2)$$

This equation means that the total energy change of a closed system equals the net energy transferred into it as heat and work.

Closed systems often undergo processes that cause no change in the system other than in its *internal* energy. For such processes, Eq. (2.2) reduces to:

$$\boxed{\Delta U^t = Q + W} \quad (2.3)$$

where U^t is the total internal energy of the system. Equation (2.3) applies to processes involving *finite* changes in the internal energy of the system. For *differential* changes:

$$\boxed{dU^t = dQ + dW} \quad (2.4)$$

²The sign convention used here is recommended by the International Union of Pure and Applied Chemistry. However, the original choice of sign for work and the one used in the first four editions of this text was the opposite, and the right side of Eq. (2.2) was then written $Q - W$.

Both of these equations apply to closed systems which undergo changes in *internal* energy only. The system may be of any size, and the values of Q , W , and U^t are for the entire system, which must of course be clearly defined.

All terms in Eqs. (2.3) and (2.4) require expression in the same units. In the SI system the energy unit is the joule. Other energy units in use are the m kgf, the calorie, the (ft lb_f), and the (Btu).

Properties, such as volume V^t and internal energy U^t depend on the quantity of material in a system; such properties are said to be *extensive*. In contrast, temperature and pressure, the principal thermodynamic coordinates for homogeneous fluids, are independent of the quantity of material, and are known as *intensive* properties. An alternative means of expression for the extensive properties of a homogeneous system, such as V^t and U^t , is:

$$V^t = m V \quad \text{or} \quad V^t = n V \quad \text{and} \quad U^t = m U \quad \text{or} \quad U^t = n U$$

where the plain symbols V and U represent the volume and internal energy of a unit amount of material, either a unit mass or a mole. These are called *specific* or *molar* properties, and they are *intensive*, independent of the quantity of material actually present.

Although V^t and U^t for a homogeneous system of arbitrary size are extensive properties, specific and molar volume V (or density) and specific and molar internal energy U are intensive.

Note that the intensive coordinates T and P have no extensive counterparts.

For a closed system of n moles Eqs. (2.3) and (2.4) may now be written:

$$\Delta(nU) = n \Delta U = Q + W \quad (2.5)$$

$$d(nU) = n dU = dQ + dW \quad (2.6)$$

In this form, these equations show explicitly the amount of substance comprising the system.

The equations of thermodynamics are often written for a representative unit amount of material, either a unit mass or a mole. Thus for $n = 1$ Eqs. (2.5) and (2.6) become:

$$\Delta U = Q + W \quad \text{and} \quad dU = dQ + dW$$

The basis for Q and W is always implied by the quantity appearing on the left side of the energy equation.

Equation (2.6) is the ultimate source of all *property relations* that connect the internal energy to measurable quantities. It does not represent a *definition* of internal energy; there is none. Nor does it lead to *absolute* values for the internal energy. What it does provide is the means for calculating *changes* in this property. Without it, the first law of thermodynamics could not be formulated. Indeed, the first law requires prior affirmation of the existence of the internal energy, the essential nature of which is summarized in the following axiom:

There exists a form of energy, known as internal energy U , which is an intrinsic property of a system, functionally related to the measurable coordinates which characterize the system. For a closed system, not in motion, changes in this property are given by Eqs. (2.5) and (2.6).

Example 2.1

Water flows over a waterfall 100 m in height. Take 1 kg of the water as the system, and assume that it does not exchange energy with its surroundings.

- What is the potential energy of the water at the top of the falls with respect to the base of the falls?
- What is the kinetic energy of the water just before it strikes bottom?
- After the 1 kg of water enters the river below the falls, what change has occurred in its state?

Solution 2.1

The 1 kg of water exchanges no energy with the surroundings. Therefore Eq. (2.1) reduces to:

$$\Delta(\text{Energy of the system}) = 0$$

Since the system possesses energy in its internal, kinetic, and potential forms,

$$\Delta U + \Delta E_K + \Delta E_P = 0$$

This equation applies to each part of the process.

(a) From Eq. (1.7), with g equal to its standard value,

$$\begin{aligned} E_P &= mzg = 1 \text{ kg} \times 100 \text{ m} \times 9.8066 \text{ m s}^{-2} \\ &= 980.66 \frac{\text{kg m}^2}{\text{s}^2} = 980.66 \text{ N m} = 980.66 \text{ J} \end{aligned}$$

(b) During the free fall of the water no mechanism exists for conversion of potential or kinetic energy into internal energy. Thus ΔU must be zero:

$$\Delta E_K + \Delta E_P = E_{K_2} - E_{K_1} + E_{P_2} - E_{P_1} = 0$$

As an excellent approximation, let $E_{K_1} = E_{P_2} = 0$. Then,

$$E_{K_2} = E_{P_1} = 980.66 \text{ J}$$

(c) As the 1 kg of water strikes bottom and mixes with other falling water to form a river, the resulting turbulence has the effect of converting kinetic energy into internal energy. During this process, ΔE_P is essentially zero, and Eq. (2.1) becomes:

$$\Delta U + \Delta E_K = 0 \quad \text{or} \quad \Delta U = E_{K_2} - E_{K_1}$$

However, the river velocity is assumed small, making E_{K_1} negligible. Thus,

$$\Delta U = E_{K_2} = 980.66 \text{ J}$$

The overall result of the process is the conversion of potential energy of the water into internal energy of the water. This change in internal energy is manifested by a temperature rise of the water. Since energy in the amount of 4184 J kg^{-1} is required for a temperature rise of 1 K (1°C) in water, the temperature increase is $980.66/4184 = 0.234 \text{ K}$, if there is no heat transfer with the surroundings.

2.5 THERMODYNAMIC STATE AND STATE FUNCTIONS

The notation of Eqs. (2.3) through (2.6) suggests that the terms on the left are different in kind from those on the right. The internal-energy terms on the left reflect *changes* in the internal state or the *thermodynamic state* of the system. It is this state that is reflected by its *thermodynamic properties*, among which are temperature, pressure, and density. We know from experience that for a homogeneous pure substance fixing two of these properties automatically fixes all the others, and thus determines its thermodynamic state. For example, nitrogen gas at a temperature of 300 K and a pressure of 10^5 kPa (1 bar) has a fixed specific volume or density and a fixed molar internal energy. Indeed, it has an established set of intensive thermodynamic properties. If this gas is heated or cooled, compressed or expanded, and then returned to its initial temperature and pressure, its intensive properties are restored to their initial values. Such properties do not depend on the past history of the substance nor on the means by which it reaches a given state. They depend only on present conditions, however reached. Such quantities are known as *state functions*. When two of them are held at fixed values for a homogeneous pure substance,³ the *thermodynamic state* of the substance is fully determined. This means that a state function, such as specific internal energy, is a property that always has a value; it may therefore be expressed mathematically as a function of other thermodynamic properties, such as temperature and pressure, or temperature and density, and its values may be identified with points on a graph.

On the other hand, the terms on the right sides of Eqs. (2.3) through (2.6), representing heat and work quantities, are not properties; they account for the energy changes that occur in the surroundings and appear only when changes occur in a system. They depend on the nature of the process causing the change, and are associated with areas rather than points on a graph, as suggested by Fig. 1.3. Although time is not a thermodynamic coordinate, the passage of time is inevitable whenever heat is transferred or work is accomplished.

The differential of a state function represents an infinitesimal *change* in its value. Integration of such a differential results in a finite difference between two of its values, e.g.:

$$\int_{P_1}^{P_2} dP = P_2 - P_1 = \Delta P \quad \text{and} \quad \int_{V_1}^{V_2} dV = V_2 - V_1 = \Delta V$$

The differentials of heat and work are not *changes*, but are infinitesimal *amounts*. When integrated, these differentials give not finite changes, but finite amounts. Thus,

$$\int dQ = Q \quad \text{and} \quad \int dW = W$$

³For systems more complex than a simple homogeneous pure substance, the number of properties or state functions that must be arbitrarily specified in order to define the state of the system may be different from two. The method of determining this number is the subject of Sec. 2.7.

For a closed system undergoing the same change in state by several processes, experiment shows that the amounts of heat and work required differ for different processes, but that *the sum $Q + W$ is the same for all processes*. This is the basis for identification of internal energy as a state function. The same value of $\Delta U'$ is given by Eq. (2.3) regardless of the process, provided only that the change in the system is between the same initial and final states.

Example 2.2

A gas is confined in a cylinder by a piston. The initial pressure of the gas is 7 bar, and the volume is 0.10 m^3 . The piston is held in place by latches in the cylinder wall. The whole apparatus is placed in a total vacuum. What is the energy change of the apparatus if the restraining latches are removed so that the gas suddenly expands to double its initial volume, the piston striking other latches at the end of the process?

Solution 2.2

Since the question concerns the entire apparatus, the system is taken as the gas, piston, and cylinder. No work is done during the process, because no force external to the system moves, and no heat is transferred through the vacuum surrounding the apparatus. Hence Q and W are zero, and the total energy of the system does not change. Without further information we can say nothing about the distribution of energy among the parts of the system. This may well be different than the initial distribution.

Example 2.3

If the process described in Ex. 2.2 is repeated, not in a vacuum but in air at atmospheric pressure of 101.3 kPa, what is the energy change of the apparatus? Assume the rate of heat exchange between the apparatus and the surrounding air is slow compared with the rate at which the process occurs.

Solution 2.3

The system is chosen exactly as before, but in this case work is done by the system in pushing back the atmosphere. This work is given by the product of the force exerted by atmospheric pressure on the back side of the piston and the displacement of the piston. If the area of the piston is A , the force is $F = P_{\text{atm}} A$. The displacement of the piston is equal to the volume change of the gas divided by the area of the piston, or $\Delta l = \Delta V' / A$. Work is done by the system on the surroundings. By Eq. (1.1),

$$\begin{aligned} \text{Work done by system} &= F \Delta l = P_{\text{atm}} \Delta V' \\ &= (101.3)(0.2 - 0.1) \text{ kPa m}^3 = 10.13 \frac{\text{kN}}{\text{m}^2} \text{ m}^3 \end{aligned}$$

Since W is work done *on* the system, it is the negative of this result:

$$W = -10.13 \text{ kN m} = -10.13 \text{ kJ}$$

Heat transfer between the system and surroundings is also possible in this case, but the problem is worked for the instant after the process has occurred and before appreciable heat transfer has had time to take place. Thus Q is assumed to be zero in Eq. (2.2), giving

$$\Delta(\text{Energy of the system}) = Q + W = 0 - 10.13 = -10.13 \text{ kJ}$$

The total energy of the system has *decreased* by an amount equal to the work done on the surroundings.

Example 2.4

When a system is taken from state a to state b in Fig. 2.1 along path acb , 100 J of heat flows into the system and the system does 40 J of work.

- How much heat flows into the system along path aeb if the work done by the system is 20 J?
- The system returns from b to a along path bda . If the work done on the system is 30 J, does the system absorb or liberate heat? How much?

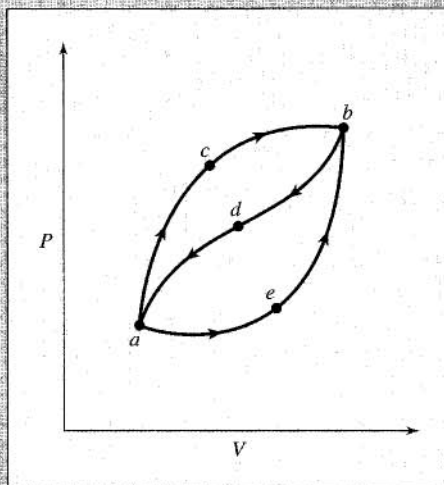


Figure 2.1 Diagram for Ex. 2.4

Solution 2.4

Assume that the system changes only in its internal energy and that Eq. (2.3) is applicable. For path acb ,

$$\Delta U_{ab}^i = Q_{acb} + W_{acb} = 100 - 40 = 60 \text{ J}$$

This internal energy change applies to the state change from a to b by *any* path.

- Thus for path aeb ,

$$\Delta U_{ab}^i = 60 = Q_{aeb} + W_{aeb} = Q_{aeb} - 20$$

Whence, $Q_{acb} = 80 \text{ J}$

(b) For path bda ,

$$\Delta U'_{ba} = -\Delta U'_{ab} = -60 = Q_{bda} + W_{bda} = Q_{bda} + 30$$

and $Q_{bda} = -60 - 30 = -90 \text{ J}$

Heat is therefore transferred from the system to the surroundings.

2.6 EQUILIBRIUM

Equilibrium is a word denoting a static condition, the absence of change. In thermodynamics it means not only the absence of change but the absence of any *tendency* toward change on a macroscopic scale. Thus a system at equilibrium exists under conditions such that no change in state can occur. Since any tendency toward change is caused by a driving force of one kind or another, the absence of such a tendency indicates also the absence of any driving force. Hence for a system at equilibrium all forces are in exact balance. Whether a change actually occurs in a system *not* at equilibrium depends on resistance as well as on driving force. Many systems undergo no measurable change even under the influence of large driving forces, because the resistance to change is very large.

Different kinds of driving forces tend to bring about different kinds of change. For example, imbalance of mechanical forces such as pressure on a piston tend to cause energy transfer as work; temperature differences tend to cause the flow of heat; gradients in chemical potential tend to cause substances to be transferred from one phase to another. At equilibrium all such forces are in balance.

In many applications of thermodynamics, chemical reactions are of no concern. For example, a mixture of hydrogen and oxygen at ordinary conditions is not in chemical equilibrium, because of the large driving force for the formation of water. However, if chemical reaction is not initiated, this system can exist in long-term thermal and mechanical equilibrium, and purely physical processes may be analyzed without regard to possible chemical reaction. This is an example of the fact that systems existing at partial equilibrium are often amenable to thermodynamic analysis.

2.7 THE PHASE RULE

As indicated earlier, the state of a pure homogeneous fluid is fixed whenever two intensive thermodynamic properties are set at definite values. In contrast, when *two* phases are in equilibrium, the state of the system is fixed when only a single property is specified. For example, a mixture of steam and liquid water in equilibrium at 101.325 kPa can exist only at 373.15 K (100°C). It is impossible to change the temperature without also changing the pressure if vapor and liquid are to continue to exist in equilibrium.

For *any* system at equilibrium, the number of independent variables that must be arbitrarily fixed to establish its *intensive* state is given by the celebrated phase rule of J. Willard

Gibbs,⁴ who deduced it by theoretical reasoning in 1875. It is presented here without proof in the form applicable to nonreacting systems:⁵

$$F = 2 - \pi + N \quad (2.7)$$

where n is the number of phases, N is the number of chemical species, and F is called the *degrees of freedom* of the system.

The intensive state of a system at equilibrium is established when its temperature, pressure, and the compositions of all phases are fixed. These are therefore phase-rule variables, but they are not all independent. The phase rule gives the number of variables from this set which must be arbitrarily specified to fix all remaining phase-rule variables.

A *phase* is a homogeneous region of matter. A gas or a mixture of gases, a liquid or a liquid solution, and a crystalline solid are examples of phases. A phase need not be continuous; examples of discontinuous phases are a gas dispersed as bubbles in a liquid, a liquid dispersed as droplets in another liquid with which it is immiscible, and solid crystals dispersed in either a gas or liquid. In each case a dispersed phase is distributed throughout a continuous phase. An abrupt change in properties always occurs at the boundary between phases. Various phases can coexist, but they *must be in equilibrium* for the phase rule to apply. An example of a three-phase system at equilibrium is a saturated aqueous salt solution at its boiling point with excess salt crystals present. The three phases ($\pi = 3$) are crystalline salt, the saturated aqueous solution, and vapor generated at the boiling point. The two chemical species ($N = 2$) are water and salt. For this system, $F = 1$.

The phase-rule variables are *intensive* properties, which are independent of the extent of the system and of the individual phases. Thus the phase rule gives the same information for a large system as for a small one and for different relative amounts of the phases present. Moreover, only the compositions of the individual phases are phase-rule variables. Overall or total compositions are not phase-rule variables when more than one phase is present.

The minimum number of degrees of freedom for any system is zero. When $F = 0$, the system is *invariant*; Eq. (2.7) becomes $\pi = 2 + N$. This value of π is the maximum number of phases which can coexist at equilibrium for a system containing N chemical species. When $N = 1$, this number is 3, characteristic of a triple point (Sec. 3.1). For example, the triple point of water, where liquid, vapor, and the common form of ice exist together in equilibrium, occurs at 273.16 K (0.01°C) and 0.0061 bar. Any change from these conditions causes at least one phase to disappear.

Example 2.5

How many degrees of freedom has each of the following systems?

- (a) Liquid water in equilibrium with its vapor.
- (b) Liquid water in equilibrium with a mixture of water vapor and nitrogen.
- (c) A liquid solution of alcohol in water in equilibrium with its vapor.

⁴Josiah Willard Gibbs (1839–1903), American mathematical physicist.

⁵The justification of the phase rule for nonreacting systems is given in Sec. 10.2, and the phase rule for reacting systems is considered in Sec. 13.8.

Solution 2.5

(a) The system contains a single chemical species existing as two phases (one liquid and one vapor). Thus,

$$F = 2 - \pi + N = 2 - 2 + 1 = 1$$

This result is in agreement with the fact that for a given pressure water has but one boiling point. Temperature or pressure, but not both, may be specified for a system comprised of water in equilibrium with its vapor.

(b) In this case two chemical species are present. Again there are two phases. Thus,

$$F = 2 - \pi + N = 2 - 2 + 2 = 2$$

The addition of an inert gas to a system of water in equilibrium with its vapor changes the characteristics of the system. Now temperature and pressure may be independently varied, but once they are fixed the system described can exist in equilibrium only at a particular composition of the vapor phase. (If nitrogen is considered negligibly soluble in water, the liquid phase is pure water.)

(c) Here $N = 2$, and $\pi = 2$. Thus,

$$F = 2 - \pi + N = 2 - 2 + 2 = 2$$

The phase-rule variables are temperature, pressure, and the phase compositions. The composition variables are either the mass or mole fractions of the species in a phase, and they must sum to unity for each phase. Thus fixing the mole fraction of the water in the liquid phase automatically fixes the mole fraction of the alcohol. These two compositions cannot both be arbitrarily specified.

2.8 THE REVERSIBLE PROCESS

The development of thermodynamics is facilitated by introduction of a special kind of closed-system process characterized as *reversible*:

A process is reversible when its direction can be reversed at any point by an infinitesimal change in external conditions.

Reversible Expansion of a Gas

The nature of reversible processes is illustrated by the example of a simple expansion of gas in a piston/cylinder arrangement. The apparatus shown in Fig. 2.2 is imagined to exist in an evacuated space. The gas trapped inside the cylinder is chosen as the system; all else is the surroundings. Expansion processes result when mass is removed from the piston. For simplicity, assume that the piston slides within the cylinder without friction and that the piston and cylinder neither absorb nor transmit heat. Moreover, because the density of the gas in the cylinder is low and because the mass of gas is small, we ignore the effects of gravity on the contents of the

cylinder. This means that gravity-induced pressure gradients in the gas are very small relative to its pressure and that changes in potential energy of the gas are negligible in comparison with the potential-energy changes of the piston assembly.

The piston in Fig. 2.2 confines the gas at a pressure just sufficient to balance the weight of the piston and all that it supports. This is a condition of equilibrium, for the system has no tendency to change. Mass must be removed from the piston if it is to rise. Imagine first that a mass m is suddenly slid from the piston to a shelf (at the same level). The piston assembly accelerates upward, reaching its maximum velocity at the point where the upward force on the piston just balances its weight. Its momentum then carries it to a higher level, where it reverses direction. If the piston were held in this position of maximum elevation, its potential-energy increase would very nearly equal the work done by the gas during the initial stroke. However, when unconstrained, the piston assembly oscillates, with decreasing amplitude, ultimately coming to rest at a new equilibrium position at a level above its initial position.

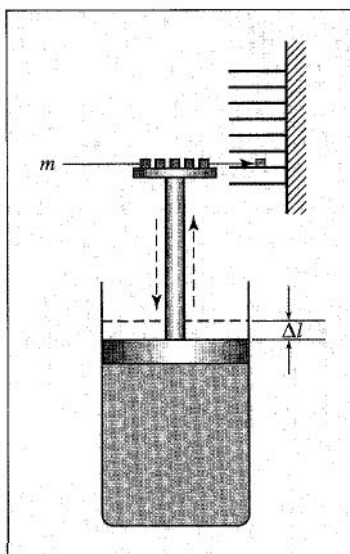


Figure 2.2 Expansion of a gas

The oscillations of the piston assembly are damped out because the viscous nature of the gas gradually converts gross directed motion of the molecules into chaotic molecular motion. This *dissipative* process transforms some of the work initially done by the gas in accelerating the piston back into internal energy of the gas. Once the process is initiated, no *infinitesimal* change in external conditions can reverse its direction; the process is *irreversible*.

All processes carried out in finite time with real substances are accompanied in some degree by dissipative effects of one kind or another, and all are therefore irreversible. However, one can *imagine* processes that are free of dissipative effects. For the expansion process of Fig. 2.2, such effects have their origin in the sudden removal of a finite mass from the piston. The resulting imbalance of forces acting on the piston causes its acceleration, and leads to its subsequent oscillation. The sudden removal of smaller mass increments reduces but does not eliminate this dissipative effect. Even the removal of an infinitesimal mass leads to piston

oscillations of infinitesimal amplitude and a consequent dissipative effect. However, one may *imagine* a process wherein small mass increments are removed one after another at a rate such that the piston's rise is continuous, with minute oscillation only at the end of the process.

The limiting case of removal of a succession of infinitesimal masses from the piston is approximated when the masses m in Fig. 2.2 are replaced by a pile of powder, blown in a very fine stream from the piston. During this process, the piston rises at a uniform but very slow rate, and the powder collects in storage at ever higher levels. The system is never more than differentially displaced from internal equilibrium or from equilibrium with its surroundings. If the removal of powder from the piston is stopped and the direction of transfer of powder is reversed, the process reverses direction and proceeds backwards along its original path. Both the system and its surroundings are ultimately restored to their initial conditions. The original process is *reversible*.

Without the assumption of a frictionless piston, we cannot imagine a reversible process. If the piston sticks because of friction, a finite mass must be removed before the piston breaks free. Thus the equilibrium condition necessary to reversibility is not maintained. Moreover, friction between two sliding parts is a mechanism for the dissipation of mechanical energy into internal energy.

This discussion has centered on a single closed-system process, the expansion of a gas in a cylinder. The opposite process, compression of a gas in a cylinder, is described in exactly the same way. There are, however, many processes which are driven by the imbalance of forces other than mechanical forces. For example, heat flow occurs when a temperature difference exists, electricity flows under the influence of an electromotive force, and chemical reactions occur because a chemical potential exists. In general, a process is reversible when the net force driving it is only differential in size. Thus heat is transferred reversibly when it flows from a finite object at temperature T to another such object at temperature $T - dT$.

Reversible Chemical Reaction

The concept of a reversible chemical reaction is illustrated by the decomposition of calcium carbonate, which when heated forms calcium oxide and carbon dioxide gas. At equilibrium, this system exerts a definite decomposition pressure of CO_2 for a given temperature. When the pressure falls below this value, CaCO_3 decomposes. Assume that a cylinder is fitted with a frictionless piston and contains CaCO_3 , CaO , and CO_2 in equilibrium. It is immersed in a constant-temperature bath, as shown in Fig. 2.3, with the temperature adjusted to a value such that the decomposition pressure is just sufficient to balance the weight on the piston. The system is in mechanical equilibrium, the temperature of the system is equal to that of the bath, and the chemical reaction is held in balance by the pressure of the CO_2 . Any change of conditions, however slight, upsets the equilibrium and causes the reaction to proceed in one direction or the other.

If the weight is differentially increased, the CO_2 pressure rises differentially, and CO_2 combines with CaO to form CaCO_3 , allowing the weight to fall slowly. The heat given off by this reaction raises the temperature in the cylinder, and heat flows to the bath. Decreasing the weight differentially sets off the opposite chain of events. The same results are obtained if the temperature of the bath is raised or lowered. If the temperature of the bath is raised differentially, heat flows into the cylinder and calcium carbonate decomposes. The CO_2 generated causes the pressure to rise differentially, which in turn raises the piston and weight. This continues until the

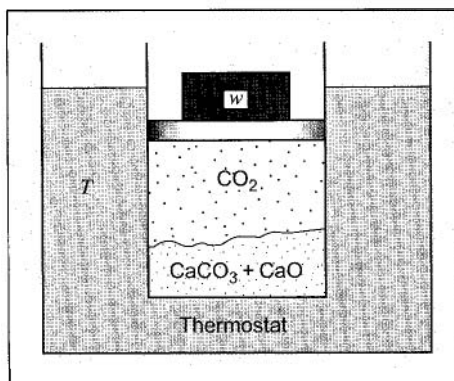
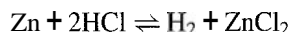


Figure 2.3 Reversibility of a chemical reaction

CaCO_3 is completely decomposed. The process is reversible, for the system is never more than differentially displaced from equilibrium, and only a differential lowering of the temperature of the bath causes the system to return to its initial state.

Chemical reactions can sometimes be carried out in an electrolytic cell, and in this case they may be held in balance by an applied potential difference. If such a cell consists of two electrodes, one of zinc and the other of platinum, immersed in an aqueous solution of hydrochloric acid, the reaction that occurs is:



The cell is held under fixed conditions of temperature and pressure, and the electrodes are connected externally to a potentiometer. If the electromotive force produced by the cell is exactly balanced by the potential difference of the potentiometer, the reaction is held in equilibrium. The reaction may be made to proceed in the forward direction by a slight decrease in the opposing potential difference, and it may be reversed by a corresponding increase in the potential difference above the emf of the cell.

Summary Remarks on Reversible Processes

A reversible process:

- Is frictionless
- Is never more than differentially removed from equilibrium
- Traverses a succession of equilibrium states
- Is driven by forces whose imbalance is differential in magnitude
- Can be reversed at any point by a differential change in external conditions
- When reversed, retraces its forward path, and restores the initial state of system and surroundings

The work of compression or expansion of a gas caused by the differential displacement of a piston in a cylinder is derived in Sec. 1.7:

$$dW = -P dV' \quad (1.2)$$

The work done on the system is given by this equation only when certain characteristics of the reversible process are realized. The first requirement is that the system be no more than infinitesimally displaced from a state of *internal* equilibrium characterized by uniformity of temperature and pressure. The system then always has an identifiable set of properties, including pressure P . The second requirement is that the system be no more than infinitesimally displaced from mechanical equilibrium with its surroundings. In this event, the internal pressure P is never more than minutely out of balance with the external force, and we may make the substitution $F = PA$ that transforms Eq. (1.1) into Eq. (1.2). Processes for which these requirements are met are said to be *mechanically reversible*, and Eq. (1.2) may be integrated:

$$W = - \int_{V_1'}^{V_2'} P dV' \quad (1.3)$$

The reversible process is ideal in that it can never be fully realized; it represents a limit to the performance of actual processes. In thermodynamics, the calculation of work is usually made for reversible processes, because of their tractability to mathematical analysis. The choice is between these calculations and no calculations at all. Results for reversible processes in combination with appropriate *efficiencies* yield reasonable approximations of the work for actual processes.

Example 2.6

A horizontal piston/cylinder arrangement is placed in a constant-temperature bath. The piston slides in the cylinder with negligible friction, and an external force holds it in place against an initial gas pressure of 14 bar. The initial gas volume is 0.03 m^3 . The external force on the piston is reduced gradually, and the gas expands isothermally as its volume doubles. If the volume of the gas is related to its pressure so that the product PV' is constant, what is the work done by the gas in moving the external force?

How much work would be done if the external force were suddenly reduced to half its initial value instead of being gradually reduced?

Solution 2.6

The process, carried out as first described, is mechanically reversible, and Eq. (1.3) is applicable. If $PV' = k$, then $P = k/V'$, and

$$W = - \int_{V_1'}^{V_2'} P dV' = -k \int_{V_1'}^{V_2'} \frac{dV'}{V'} = -k \ln \frac{V_2'}{V_1'}$$

With $V_1' = 0.03 \text{ m}^3$ $V_2' = 0.06 \text{ m}^3$

and $k = PV' = P_1 V_1' = (14 \times 10^5)(0.03) = 42\,000 \text{ J}$

$$W = -42\,000 \ln 2 = -29\,112 \text{ J}$$

The final pressure is

$$P_2 = \frac{k}{V_2'} = \frac{42\,000}{0.06} = 700\,000 \text{ Pa} \quad \text{or} \quad 7 \text{ bar}$$

In the second case, after half the initial force has been removed, the gas undergoes a sudden expansion against a constant force equivalent to a pressure of 7 bar. Eventually, heat transfer returns the system to an equilibrium condition identical with the final state attained in the reversible process. Thus $\Delta V'$ is the same as before, and the net work accomplished equals the equivalent external pressure times the volume change:

$$W = -(7 \times 10^5)(0.06 - 0.03) = -21\,000 \text{ J}$$

This process is clearly irreversible, and compared with the reversible process is said to have an efficiency of:

$$\frac{21\,000}{29\,112} = 0.721 \quad \text{or} \quad 72.1\%$$

Example 2.7

The piston/cylinder arrangement shown in Fig. 2.4 contains nitrogen gas trapped below the piston at a pressure of 7 bar. The piston is held in place by latches. The space above the piston is evacuated. A pan is attached to the piston rod and a mass m of 45 kg is fastened to the pan. The piston, piston rod, and pan together have a mass of 23 kg. The latches holding the piston are released, allowing the piston to rise rapidly until it strikes the top of the cylinder. The distance moved by the piston is 0.5 m. The local acceleration of gravity is 9.8 m s^{-2} . Discuss the energy changes that occur because of this process.

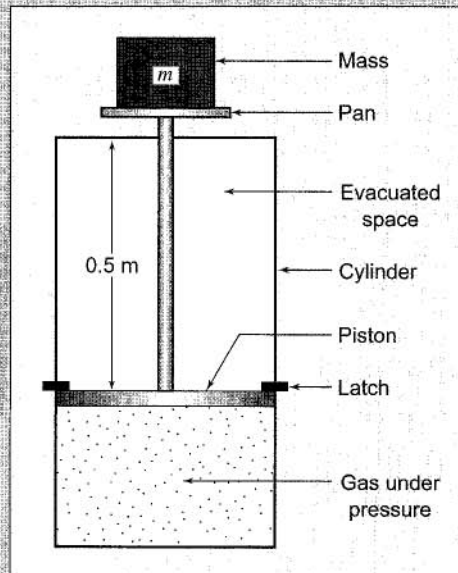


Figure 2.4 Diagram for Ex. 2.7

Solution 2.7

This example serves to illustrate some of the difficulties encountered when irreversible nonflow processes are analyzed. Take the gas alone as the system. According to the basic definition, the work done by the gas on the surroundings is equal to $\int P' dV'$, where P' is the pressure exerted on the face of the piston by the gas. Because the expansion is very rapid, pressure gradients exist in the gas, and neither P' nor the integral can be evaluated. However, a return to Eq. (2.1) avoids the calculation of work. The total energy change of the system (the gas) is its internal-energy change, ΔU_{sys}^t . For $Q = 0$, the energy changes in the surroundings consist of potential-energy changes of the piston, rod, pan, and mass m and of internal-energy changes of the piston, rod, and cylinder. Therefore, Eq. (2.1) may be written:

$$\Delta U_{\text{sys}}^t + (\Delta U_{\text{surr}}^t + \Delta E_{P \text{ surr}}) = 0$$

The potential-energy term is:

$$\Delta E_{P \text{ surr}} = (45 + 23)(9.8)(0.5) = 333.2 \text{ N m}$$

Therefore
$$\Delta U_{\text{sys}}^t + \Delta U_{\text{surr}}^t = -333.2 \text{ N m} = -333.2 \text{ J}$$

and one cannot determine the split of internal-energy change between system and surroundings.

2.9 CONSTANT-V AND CONSTANT-P PROCESSES

The energy balance for a homogeneous closed system of n moles is:

$$d(nU) = dQ + dW \quad (2.6)$$

where Q and W always represent total heat and work, whatever the value of n .

The work of a mechanically reversible, closed-system process is given by Eq. (1.2), here written:

$$dW = -P d(nV)$$

These two equations combine:

$$d(nU) = dQ - P d(nV) \quad (2.8)$$

This is the general first-law equation for a mechanically reversible, closed-system process.

Constant-Volume Process

If the process occurs at constant total volume, the work is zero. Moreover, for closed systems the last term of Eq. (2.8) is also zero, because n and V are both constant. Thus,

$$dQ = d(nU) \quad (\text{const } V) \quad (2.9)$$

Integration yields:

$$Q = n \Delta U \quad (\text{const } V) \quad (2.10)$$

Thus for a mechanically reversible, constant-volume, closed-system process, the heat transferred is equal to the internal-energy change of the system.

Constant-Pressure Process

Solved for dQ , Eq. (2.8) becomes:

$$dQ = d(nU) + P d(nV)$$

For a constant-pressure change of state:

$$dQ = d(nU) + d(nPV) = d[n(U + PV)]$$

The appearance of the group $U + PV$, both here and in other applications, suggests the definition for convenience of a new thermodynamic property. Thus, the mathematical (and only) definition of enthalpy (en-thal'-py)⁶ is:

$$\boxed{H \equiv U + PV} \quad (2.11)$$

where H , U , and V are molar or unit-mass values. The preceding equation may now be written:

$$dQ = d(nH) \quad (\text{const } P) \quad (2.12)$$

Integration yields:

$$Q = n \Delta H \quad (\text{const } P) \quad (2.13)$$

Thus for a mechanically reversible, constant-pressure, closed-system process, the heat transferred equals the enthalpy change of the system. Comparison of the last two equations with Eqs. (2.9) and (2.10) shows that the enthalpy plays a role in constant-pressure processes analogous to the internal energy in constant-volume processes.

2.10 ENTHALPY

The usefulness of the enthalpy is suggested by Eqs. (2.12) and (2.13). It also appears in energy balances for flow processes as applied to heat exchangers, evaporators, distillation columns, pumps, compressors, turbines, engines, etc., for calculation of heat and work.

The tabulation of values of Q and W for the infinite array of possible processes is impossible. The intensive state functions, however, such as specific volume, specific internal energy, and specific enthalpy, are intrinsic properties of matter. Once determined, their values can be tabulated as functions of temperature and pressure for each phase of a particular substance for future use in the calculation of Q and W for any process involving that substance. The determination of numerical values for these state functions and their correlation and use are treated in later chapters.

All terms of Eq. (2.11) must be expressed in the same units. The product PV has units of energy per mole or per unit mass, as does U ; therefore H also has units of energy per mole or

⁶A word proposed by H. Kamerlingh Onnes, Dutch physicist who first liquefied helium in 1908, discovered superconductivity in 1911, and won the Nobel prize for physics in 1913. (See: *Communications from the Physical Laboratory of the University of Leiden*, no. 109, p. 3, footnote 2, 1909.)

per unit mass. In the SI system the basic unit of pressure is the pascal or N m^{-2} and, for molar volume, $\text{m}^3 \text{mol}^{-1}$. The PV product then has the units N m mol^{-1} or J mol^{-1} . In the metric engineering system a common unit for the PV product is the m kgf kg^{-1} , which arises when pressure is in kg m^{-2} with volume in $\text{m}^3 \text{kg}^{-1}$. This result is usually converted to kcal kg^{-1} through division by 426.935 for use in Eq. (2.11), because the common metric engineering unit for U and H is the kcal kg^{-1} .

Since U , P , and V are all state functions, H as defined by Eq. (2.11) is also a state function. Like U and V , H is an intensive property of the system. The differential form of Eq. (2.11) is:

$$dH = dU + d(PV) \quad (2.14)$$

This equation applies whenever a differential change occurs in the system. Upon integration, it becomes an equation for a finite change in the system:

$$\Delta H = \Delta U + \Delta(PV) \quad (2.15)$$

Equations (2.11), (2.14), and (2.15) apply to a unit mass of substance or to a mole.

Example 2.8

Calculate ΔU and ΔH for 1 kg of water when it is vaporized at the constant temperature of 373.15 K (100°C) and the constant pressure of 101.325 kPa. The specific volumes of liquid and vapor water at these conditions are 0.00104 and $1.673 \text{ m}^3 \text{kg}^{-1}$. For this change, heat in the amount of 2256.9 kJ is added to the water.

Solution 2.8

The kilogram of water is taken as the system, because it alone is of interest. Imagine the fluid contained in a cylinder by a frictionless piston which exerts a constant pressure of 101.33 kPa. As heat is added, the water expands from its initial to its final volume. Equation (2.13) as written for the 1-kg system is:

$$\Delta H = Q = 2256.9 \text{ kJ}$$

By Eq. (2.15),

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - P \Delta V$$

Evaluate the final term:

$$\begin{aligned} P \Delta V &= 101.33 \text{ kPa} \times (1.673 - 0.001) \text{ m}^3 \\ &= 169.4 \text{ kPa m}^3 = 169.4 \text{ kN m}^{-2} \text{ m}^3 \\ &= 169.4 \text{ kJ} \end{aligned}$$

Then

$$\Delta U = 2256.9 - 169.4 = 2087.5 \text{ kJ.}$$

2.11 HEAT CAPACITY

We remarked earlier that heat is often viewed in relation to its effect on the object to which or from which it is transferred. This is the origin of the idea that a body has a capacity for heat. The smaller the temperature change in a body caused by the transfer of a given quantity of heat, the greater its capacity. Indeed, a *heat capacity* might be defined:

$$C \equiv \frac{dQ}{dT}$$

The difficulty with this is that it makes C , like Q , a process-dependent quantity rather than a state function. However, it does suggest the possibility that more than one useful heat capacity might be defined. In fact two heat capacities are in common use for homogeneous fluids; although their names belie the fact, both are state functions, defined unambiguously in relation to other state functions.

Heat Capacity at Constant Volume

The constant-volume heat capacity is *defined* as:

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V \quad (2.16)$$

This definition accommodates both the molar heat capacity and the specific heat capacity (usually called specific heat), depending on whether U is the molar or specific internal energy. Although this definition makes no reference to any process, it relates in an especially simple way to a constant-volume process in a closed system, for which Eq. (2.16) may be written:

$$dU = C_V dT \quad (\text{const } V) \quad (2.17)$$

Integration yields:

$$\Delta U = \int_{T_1}^{T_2} C_V dT \quad (\text{const } V) \quad (2.18)$$

The combination of this result with Eq. (2.10) for a mechanically reversible, constant-volume process⁷ gives:

$$Q = n \Delta U = n \int_{T_1}^{T_2} C_V dT \quad (\text{const } V) \quad (2.19)$$

If the volume varies during the process but returns at the end of the process to its initial value, the process cannot rightly be called one of constant volume, even though $V_2 = V_1$ and $\Delta V = 0$. However, changes in state functions or properties are independent of path, and are the same for all processes which result in the same change of state. Property changes are therefore

⁷These restrictions serve to rule out work of stirring, which is inherently irreversible

calculated from the equations for a truly constant-volume process leading from the same initial to the same final conditions. For such processes Eq. (2.18) gives $\Delta U = \int C_V dT$, because U , C_V , and T are all state functions or properties. On the other hand, Q does depend on path, and Eq. (2.19) is a valid expression for Q only for a *constant-volume* process. For the same reason, W is in general zero only for a truly constant-volume process. This discussion illustrates the reason for the careful distinction between state functions and heat and work. The principle that state functions are independent of the process is an important and useful concept.

For the calculation of property changes, an actual process may be replaced by any other process which accomplishes the same change in state.

Such an alternative process may be selected, for example, because of its simplicity.

Heat Capacity at Constant Pressure

The constant-pressure heat capacity is *defined* as:

$$C_P \equiv \left(\frac{\partial H}{\partial T} \right)_P \quad (2.20)$$

Again, the definition accommodates both molar and specific heat capacities, depending on whether H is the molar or specific enthalpy. This heat capacity relates in an especially simple way to a constant-pressure, closed-system process, for which Eq. (2.20) is equally well written:

$$dH = C_P dT \quad (\text{const } P) \quad (2.21)$$

whence

$$\Delta H = \int_{T_1}^{T_2} C_P dT \quad (\text{const } P) \quad (2.22)$$

For a mechanically reversible, constant-pressure process, this result may be combined with Eq. (2.13) to give

$$Q = n \Delta H = n \int_{T_1}^{T_2} C_P dT \quad (\text{const } P) \quad (2.23)$$

Since H , C_P , and T are all state functions, Eq. (2.22) applies to any process for which $P_2 = P_1$ whether or not it is actually carried out at constant pressure. However, only for the mechanically reversible, constant-pressure process can heat and work be calculated by the equations $Q = n \Delta H$, $Q = n \int C_P dT$, and $W = -Pn \Delta V$.

Example 2.9

Air at 1 bar and 298.15 K (25°C) is compressed to 5 bar and 298.15 K (25°C) by two different mechanically reversible processes:

- (a) Cooling at constant pressure followed by heating at constant volume.
- (b) Heating at constant volume followed by cooling at constant pressure.

Calculate the heat and work requirements and ΔU and ΔH of the air for each path. The following heat capacities for air may be assumed independent of temperature:

$$C_V = 20.78 \quad \text{and} \quad C_P = 29.10 \text{ J mol}^{-1} \text{ K}^{-1}$$

Assume also for air that PV/T is a constant, regardless of the changes it undergoes. At 298.15 K (25°C) and 1 bar the molar volume of air is $0.024\,79 \text{ m}^3 \text{ mol}^{-1}$.

Solution 2.9

In each case take the system as 1 mol of air contained in an imaginary piston/cylinder arrangement. Since the processes considered are mechanically reversible, the piston is imagined to move in the cylinder without friction. The final volume is:

$$V_2 = V_1 \frac{P_1}{P_2} = 0.024\,79 \left(\frac{1}{5} \right) = 0.004\,958 \text{ m}^3$$

(a) During the first step the air is cooled at the constant pressure of 1 bar until the final volume of 0.004958 m^3 is reached. The temperature of the air at the end of this cooling step is:

$$T' = T_1 \frac{V_2}{V_1} = 298.15 \left(\frac{0.004\,958}{0.024\,79} \right) = 59.63 \text{ K}$$

By Eq. (2.23),

$$Q = \Delta H = C_P \Delta T = (29.10)(59.63 - 298.15) = -6941 \text{ J}$$

Also,

$$\begin{aligned} \Delta U &= \Delta H - \Delta(PV) = \Delta H - P \Delta V \\ &= -6941 - (1 \times 10^5)(0.004\,958 - 0.024\,79) = -4958 \text{ J} \end{aligned}$$

During the second step the volume is held constant at V_2 while the air is heated to its final state. By Eq. (2.19),

$$\Delta U = Q = C_V \Delta T = (20.78)(298.15 - 59.63) = 4958 \text{ J}$$

The complete process represents the sum of its steps. Hence,

$$Q = -6941 + 4958 = -1983 \text{ J}$$

and

$$\Delta U = -4958 + 4958 = 0$$

Since the first law applies to the entire process, $\Delta U = Q + W$, and therefore,

$$0 = -1983 + W$$

Whence

$$W = 1983 \text{ J}$$

Equation (2.15), $\Delta H = \Delta U + \Delta(PV)$, also applies to the entire process. But $T_1 = T_2$, and therefore, $P_1 V_1 = P_2 V_2$. Hence $\Delta(PV) = 0$, and

$$\Delta H = \Delta U = 0$$

(b) Two different steps are used in this case to reach the same final state of the air. In the first step the air is heated at a constant volume equal to its initial value until the final pressure of 5 bar is reached. The air temperature at the end of this step is:

$$T' = T_1 \frac{P_2}{P_1} = 298.15 \left(\frac{5}{1} \right) = 1490.75 \text{ K}$$

For this step the volume is constant, and

$$Q = \Delta U = C_V \Delta T = (20.78)(1490.75 - 298.15) = 24\,788 \text{ J}$$

During the second step the air is cooled at the constant pressure of 5 bar to its final state:

$$Q = \Delta H = C_P \Delta T = (29.10)(298.15 - 1490.75) = -34\,703 \text{ J}$$

Also,

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - P \Delta V$$

$$\Delta U = -34\,703 - (5 \times 10^5)(0.004\,958 - 0.024\,79) = -24\,788 \text{ J}$$

For the two steps combined,

$$Q = 24\,788 - 34\,703 = -9915 \text{ J}$$

$$\Delta U = 24\,788 - 24\,788 = 0$$

$$W = \Delta U - Q = 0 - (-9915) = 9915 \text{ J}$$

and as before

$$\Delta H = \Delta U = 0$$

The property changes ΔU and ΔH calculated for the given change in state are the same for both paths. On the other hand the answers to parts (a) and (b) show that Q and W depend on the path.

Example 2.10

Calculate the internal-energy and enthalpy changes that occur when air is changed from an initial state of 277 K and 10 bar, where its molar volume is $2.28 \text{ m}^3 \text{ kmol}^{-1}$ to a final state of 333 K and 1 atm. Assume for air that PV/T is constant and that $C_V = 21$ and $C_P = 29.3 \text{ kJ kmol}^{-1} \text{ K}^{-1}$.

Solution 2.10

Since property changes are independent of the process that brings them about, we can base calculations on a simple two-step, mechanically reversible process in which 1 kmol of air is (a) cooled at constant volume to the final pressure, and

(b) heated at constant pressure to the final temperature. The absolute temperatures here are on the Kelvin scale:

$$T_1 = 277 \text{ K}$$

$$T_2 = 333 \text{ K}$$

Since $PV = kT$, the ratio T/P is constant for step (a). The intermediate temperature between the two steps is therefore

$$T' = (277)(1/10) = 27.7 \text{ K}$$

and the temperature changes for the two steps are

$$\Delta T_a = 27.7 - 277 = -249.3 \text{ K}$$

$$\Delta T_b = 333 - 27.7 = 305.3 \text{ K}$$

For step (a), by Eqs. (2.18) and (2.15)

$$\Delta U_a = C_v \Delta T_a$$

$$\Delta U_a = (21)(-249.3) = -5235.3 \text{ kJ kmol}^{-1}$$

$$\Delta H_a = \Delta U_a + V \Delta P_a$$

$$\Delta H_a = -5235.3 + (2.28)(1 - 10)(10^5)/(10^3) = -7287.3 \text{ kJ kmol}^{-1}$$

The final volume of the air is given by

$$V_2 = V_1 \frac{P_1 T_2}{P_2 T_1} = \frac{(2.28)(10)(333)}{(1)(277)}$$

from which we find that $V_2 = 27.41 \text{ m}^3 \text{ kmol}^{-1}$.

For step (b), by Eqs. (2.21) and (2.15)

$$\Delta H_b = C_p \Delta T_b$$

$$\Delta H_b = (29.3)(305.3) = 8945.3 \text{ kJ kmol}^{-1}$$

$$\Delta U_b = \Delta H_b - P \Delta V_b$$

$$\Delta U_b = 8945.3 - (1)(27.41 - 2.28)(10^5)/(10^3) = 6432.3 \text{ kJ kmol}^{-1}$$

For the two steps together,

$$\Delta U = -5235.3 + 6432.3 = 1197 \text{ kJ kmol}^{-1}$$

$$\Delta H = -7287.3 + 8945.3 = 1658 \text{ kJ kmol}^{-1}$$

2.12 MASS AND ENERGY BALANCES FOR OPEN SYSTEMS

Although the focus of the preceding sections has been on closed systems, the concepts presented find far more extensive application. The laws of mass and energy conservation apply to *all* processes, to open as well as to closed systems. Indeed, the open system includes the closed system as a special case. The remainder of this chapter is therefore devoted to the treatment of open systems and thus to the development of equations of wide applicability.

Measures of Flow

Open systems are characterized by flowing streams, for which there are four common measures of flow:

- Mass flowrate, m
- Molar flowrate, n
- Volumetric flowrate, q
- Velocity, u

The measures of flow are interrelated:

$$\dot{m} = M\dot{n} \quad \text{and} \quad q = uA$$

where M is molar mass. Importantly, mass and molar flowrates relate to velocity:

$$\dot{m} = uA\rho \quad (2.24a)$$

$$\dot{n} = uA\rho \quad (2.24b)$$

The area for flow A is the cross-sectional area of a conduit, and ρ is specific or molar density. Although velocity is a *vector quantity*, its scalar magnitude u is used here as the average speed of a stream in the direction normal to A . Flowrates m , n , and q represent measures of quantity per unit of time. Velocity u is quite different in nature, as it does not suggest the magnitude of flow. Nevertheless, it is an important design parameter.

Mass Balance for Open Systems

The region of space identified for analysis of open systems is called a *control volume*; it is separated from its surroundings by a *control surface*. The fluid within the control volume is the thermodynamic system for which mass and energy balances are written. The control volume shown schematically in Fig. 2.5 is separated from its surroundings by an extensible control surface. Two streams with flow rates \dot{m}_1 and \dot{m}_2 are shown directed into the control volume, and one stream with flow rate \dot{m}_3 is directed out. Since mass is conserved, the rate of change of mass within the control volume, dm_{cv}/dt , equals the net rate of flow of mass into the control volume. The convention is that flow is positive when directed into the control volume and negative when directed out. The mass balance is expressed mathematically by:

$$\frac{dm_{cv}}{dt} + \Delta(\dot{m})_{fs} = 0 \quad (2.25)$$

where the second term for the control volume shown in Fig. 2.5 is:

$$\Delta(\dot{m})_{fs} = \dot{m}_3 - \dot{m}_1 - \dot{m}_2$$

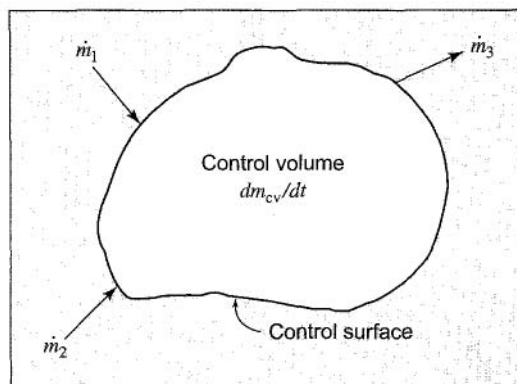


Figure 2.5 Schematic representation of a control volume

The difference operator "A" here signifies the difference between exit and entrance flows and the subscript "fs" indicates that the term applies to all flowing streams.

When the mass flowrate m is given by Eq. (2.24a), Eq. (2.25) becomes:

$$\frac{dm_{cv}}{dt} + \Delta(\rho u A)_{fs} = 0 \quad (2.26)$$

In this form the mass-balance equation is often called the *continuity equation*.

The flow process characterized as *steady state* is an important special case for which conditions within the control volume do not change with time. The control volume then contains a constant mass of fluid, and the first or *accumulation* term of Eq. (2.25) is zero, reducing Eq. (2.26) to:

$$\Delta(\rho u A)_{fs} = 0$$

The term "steady state" does not necessarily imply that flowrates are constant, merely that the inflow of mass is exactly matched by the outflow of mass.

When there is but a single entrance and a single exit stream, the mass flowrate \dot{m} is the same for both streams; then,

$$\rho_2 u_2 A_2 - \rho_1 u_1 A_1 = 0$$

or

$$m = \text{const} = \rho_2 u_2 A_2 = \rho_1 u_1 A_1$$

Since specific volume is the reciprocal of density,

$$\dot{m} = \frac{u_1 A_1}{V_1} = \frac{u_2 A_2}{V_2} = \frac{u A}{V} \quad (2.27)$$

This form of the continuity equation finds frequent use.

The General Energy Balance

Since energy, like mass, is conserved, the rate of change of energy within the control volume equals the net rate of energy transfer into the control volume. Streams flowing into and out

of the control volume have associated with them energy in its internal, potential, and kinetic forms, and all contribute to the energy change of the system. Each unit mass of a stream carries with it a total energy $U + \frac{1}{2}u^2 + zg$, where u is the average velocity of the stream, z is its elevation above a datum level, and g is the local acceleration of gravity. Thus, each stream transports energy at the rate $(U + \frac{1}{2}u^2 + zg)\dot{m}$. The net energy transported into the system by the flowing streams is therefore $-\Delta[(U + \frac{1}{2}u^2 + zg)\dot{m}]_{fs}$, where the effect of the minus sign with "A" is to make the term read in – out. The rate of energy accumulation within the control volume includes this quantity in addition to the heat transfer rate Q and work rate:

$$\frac{d(mU)_{cv}}{dt} = -\Delta[(U + \frac{1}{2}u^2 + zg)\dot{m}]_{fs} + Q + \text{work rate}$$

The work rate may include work of several forms. First, work is associated with moving the flowing streams through entrances and exits. The fluid at any entrance or exit has a set of average properties, P , V , U , H , etc. Imagine that a unit mass of fluid with these properties exists at an entrance or exit, as shown in Fig. 2.6 (at the entrance). This unit mass of fluid is acted upon by additional fluid, here replaced by a piston which exerts the constant pressure P . The work done by this piston in moving the unit mass through the entrance is PV , and the work rate is $(PV)\dot{m}$. Since "A" denotes the difference between exit and entrance quantities, the net work done on the system when all entrance and exit sections are taken into account is $-\Delta[(PV)\dot{m}]_{fs}$.

Another form of work is the shaft work indicated in Fig. 2.6 by rate \dot{W}_s . In addition work may be associated with expansion or contraction of the control volume and there may be stirring work. These forms of work are all included in a rate term represented by \dot{W} . The preceding equation may now be written:

$$\frac{d(mU)_{cv}}{dt} = -\Delta[(U + \frac{1}{2}u^2 + zg)\dot{m}]_{fs} + \dot{Q} - \Delta[(PV)\dot{m}]_{fs} + \dot{W}$$

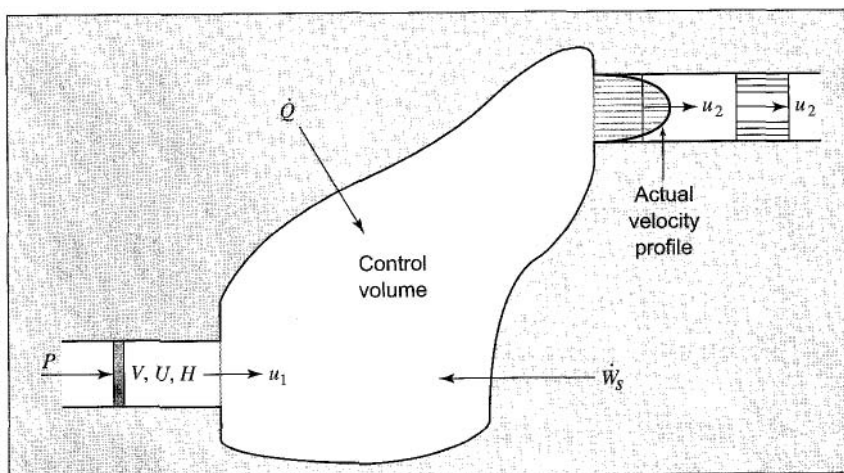


Figure 2.6 Control volume with one entrance and one exit

Combination of terms in accord with the definition of enthalpy, $H = U + PV$, leads to:

$$\frac{d(mU)_{cv}}{dt} = -\Delta \left[\left(H + \frac{1}{2}u^2 + zg \right) \dot{m} \right]_{fs} + \dot{Q} + \dot{W}$$

which is usually written:

$$\boxed{\frac{d(mU)_{cv}}{dt} + \Delta \left[\left(H + \frac{1}{2}u^2 + zg \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}} \quad (2.28)$$

The velocity u in the kinetic-energy terms of energy balances is the bulk-mean velocity as defined by the equation, $u = \dot{m}/\rho A$. Fluids flowing in pipes exhibit a velocity profile, as shown in Fig. 2.6, which rises from zero at the wall (the no-slip condition) to a maximum at the center of the pipe. The kinetic energy of a fluid in a pipe depends on its velocity profile. For the case of laminar flow, the profile is parabolic, and integration across the pipe shows that the kinetic-energy term should properly be u^2 . In fully developed turbulent flow, the more common case in practice, the velocity across the major portion of the pipe is not far from uniform, and the expression $u^2/2$, as used in the energy equations, is more nearly correct.

Although Eq. (2.28) is an energy balance of reasonable generality, it has limitations. In particular, it reflects the tacit assumption that the center of mass of the control volume is stationary. Thus no terms for kinetic- and potential-energy changes of the fluid in the control volume are included. For virtually all applications of interest to chemical engineers, Eq. (2.28) is adequate. For many (but not all) applications, kinetic- and potential-energy changes in the flowing streams are also negligible, and Eq. (2.28) then simplifies to:

$$\frac{d(mU)_{cv}}{dt} + \Delta(H\dot{m})_{fs} = \dot{Q} + \dot{W} \quad (2.29)$$

Example 2.11

Show that Eq. (2.29) reduces to Eq. (2.3) for the case of a closed system.

Solution 2.11

The second term of Eq. (2.29) is omitted in the absence of flowing streams, and the equation is then multiplied by dt :

$$d(mU)_{cv} = Q dt + W dt$$

Integration over time gives:

$$\Delta(mU)_{cv} = \int_{t_1}^{t_2} \dot{Q} dt + \int_{t_1}^{t_2} \dot{W} dt$$

or

$$\Delta U' = Q - W$$

The Q and W terms are defined by the integrals of the preceding equation.

Equation (2.29) may be applied to a variety of processes of a transient nature, as illustrated in the following examples.

Example 2.12

An evacuated tank is filled with gas from a constant-pressure line. What is the relation between the enthalpy of the gas in the entrance line and the internal energy of the gas in the tank? Neglect heat transfer between the gas and the tank.

Solution 2.12

The tank with its single entrance serves as the control volume. Since there is no expansion work, stirring work, or shaft work, $W = 0$. If kinetic- and potential-energy changes are negligible, Eq. (2.29) becomes:

$$\frac{d(mU)_{\text{tank}}}{dt} - H' \dot{m}' = 0$$

where the prime (') identifies the entrance stream and the minus sign is required because it is an entrance stream. The mass balance is:

$$\dot{m}' = \frac{dm_{\text{tank}}}{dt}$$

Combining these two balance equations yields:

$$\frac{d(mU)_{\text{tank}}}{dt} - H' \frac{dm_{\text{tank}}}{dt} = 0$$

Multiplying by dt and integrating over time (noting that H' is constant) gives:

$$\Delta(mU)_{\text{tank}} - H' \Delta m_{\text{tank}} = 0$$

Whence $m_2 U_2 - m_1 U_1 = H'(m_2 - m_1)$

where subscripts 1 and 2 denote initial and final conditions in the tank.

Since the mass in the tank initially is zero, $m_1 = 0$; then,

$$U_2 = H'$$

a result showing that in the absence of heat transfer the energy of the gas contained within the tank at the end of the process is equal to the enthalpy of the gas added.

Example 2.13

An insulated, electrically heated tank for hot water contains 190 kg of liquid water at 333.15 K (60°C) when a power outage occurs. If water is withdrawn from the tank at a steady rate of $\dot{m} = 0.2 \text{ kg s}^{-1}$, how long will it take for the temperature of the water in the tank to drop from 333.15 to 308.15 K (60 to 35°C)? Assume that cold water enters the tank at 283.15 K (10°C), and that heat losses from the tank are negligible. For liquid water let $C_v = C_p = C$, independent of T and P .

Solution 2.13

Here, $Q = W = 0$. Additionally, assume perfect mixing of the contents of the tank; this implies that the properties of the water leaving the tank are those of the

water in the tank. With the mass flowrate into the tank equal to the mass flowrate out, m_{cv} is constant; moreover, the differences between inlet and outlet kinetic and potential energies can be neglected. Equation (2.29) is therefore written:

$$m \frac{dU}{dt} + m(H - H_1) = 0$$

where unsubscripted quantities refer to the contents of the tank and H_1 is the specific enthalpy of the water entering the tank. Since $C_V = C_P = C$,

$$\frac{dU}{dt} = C \frac{dT}{dt} \quad \text{and} \quad H - H_1 = C(T - T_1)$$

The energy balance then becomes, on rearrangement,

$$dt = -\frac{m}{\dot{m}} \frac{dT}{T - T_1}$$

Integration from $t = 0$ (where $T = T_0$) to arbitrary time t yields:

$$t = -\frac{m}{\dot{m}} \ln \left(\frac{T - T_1}{T_0 - T_1} \right)$$

Substitution of numerical values into this equation gives, for the conditions of this problem,

$$t = -\frac{190}{0.2} \ln \left(\frac{308.15 - 283.15}{333.15 - 283.15} \right) = 658.5 \text{ s} \approx 11 \text{ min}$$

Thus, it takes about 11 minutes for the water temperature in the tank to drop from 333.15 to 308.15 K (60 to 35°C).

Energy Balances for Steady-State Flow Processes

Flow processes for which the accumulation term of Eq. (2.28), $d(mU)_{cv}/dt$, is zero are said to occur at *steady state*. As discussed with respect to the mass balance, this means that the mass of the system within the control volume is constant; it also means that no changes occur with time in the properties of the fluid within the control volume nor at its entrances and exits. No expansion of the control volume is possible under these circumstances. The only work of the process is shaft work, and the general energy balance, Eq. (2.28), becomes:

$$\Delta \left[\left(H + \frac{1}{2}u^2 + zg \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}_s \quad (2.30)$$

Although "steady state" does not necessarily imply "steady flow," the usual application of this equation is to steady-state, steady-flow processes, because such processes represent the industrial norm.⁸

⁸An example of a steady-state process that is not steady flow is a water heater in which variations in flow rate are exactly compensated by changes in the rate of heat transfer so that temperatures throughout remain constant.

A further specialization results when the control volume has but one entrance and one exit. The same mass flowrate \dot{m} then applies to both streams, and Eq. (2.30) then reduces to:

$$\Delta \left(H + \frac{1}{2}u^2 + zg \right) \dot{m} = \dot{Q} + \dot{W}_s \quad (2.31)$$

where subscript "fs" has been omitted in this simple case and "A" denotes the change from entrance to exit. Division by \dot{m} gives:

$$\Delta \left(H + \frac{1}{2}u^2 + zg \right) = \frac{\dot{Q}}{\dot{m}} + \frac{\dot{W}_s}{\dot{m}} = Q + W_s$$

or

$$\boxed{\Delta H + \frac{\Delta u^2}{2} + g \Delta z = Q + W_s} \quad (2.32a)$$

This equation is the mathematical expression of the first law for a steady-state, steady-flow process between one entrance and one exit. All terms represent energy per unit mass of fluid.

In all of the energy-balance equations so far written, the energy unit is presumed to be the joule, in accord with the SI system of units. For the metric engineering system of units, the kinetic- and potential-energy terms, wherever they appear, require division by the dimensional constant g_c (Secs. 1.4 and 1.8). In this event Eq. (2.32a), for example, is written:

$$\boxed{\Delta H + \frac{\Delta u^2}{2g_c} + \frac{g}{g_c} \Delta z = Q + W_s} \quad (2.32b)$$

Here, the usual unit for ΔH and Q is the kcal; kinetic energy, potential energy, and work are usually expressed as (ft lb_f). Therefore the factor 426.935 m kgf kcal⁻¹ must be used with the appropriate terms to put them all in consistent units of either m kgf or kcal.

In many applications, kinetic- and potential-energy terms are omitted, because they are negligible compared with other terms.⁹ For such cases, Eqs. (2.32a) and (2.32b) reduce to:

$$\Delta H = Q + W_s \quad (2.33)$$

This expression of the first law for a steady-state, steady-flow process is analogous to Eq. (2.3) for a nonflow process. However, enthalpy rather than internal energy is the thermodynamic property of importance.

A Flow Calorimeter for Enthalpy Measurements

The application of Eqs. (2.32) and (2.33) to the solution of practical problems requires enthalpy values. Since H is a state function and a property of matter, its values depend only on point conditions; once determined, they may be tabulated for subsequent use whenever the same sets of conditions are encountered. To this end, Eq. (2.33) may be applied to laboratory processes designed specifically to measure enthalpy data.

A simple flow calorimeter is illustrated schematically in Fig. 2.7. Its essential feature is an electric resistance heater immersed in a flowing fluid. The design provides for minimal

⁹Exceptions are applications to nozzles, metering devices, wind tunnels, and hydroelectric power stations.

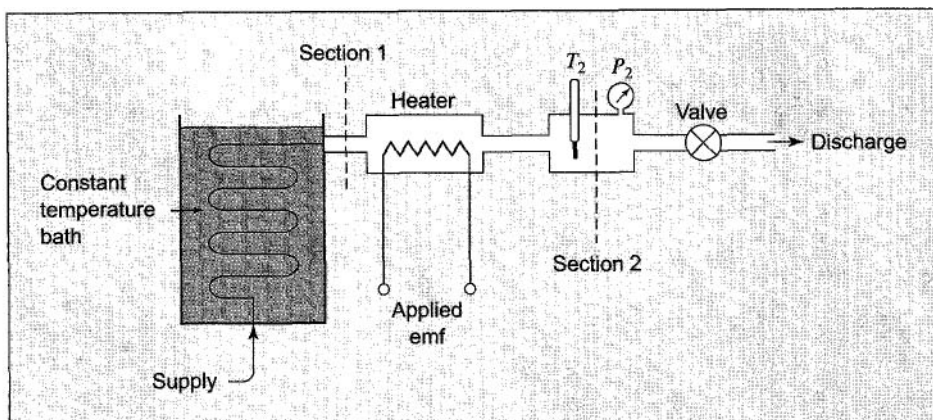


Figure 2.7 Flow calorimeter

velocity and elevation changes from section 1 to section 2, making kinetic- and potential-energy changes of the fluid negligible. Furthermore, no shaft work is accomplished between sections 1 and 2. Hence Eq. (2.33) reduces to:

$$\Delta H = H_2 - H_1 = Q$$

The rate of heat transfer to the fluid is determined from the resistance of the heater and the current passing through it. In practice a number of details need attention, but in principle the operation of the flow calorimeter is simple. Measurements of the heat rate and the rate of flow of the fluid allow calculation of values of ΔH between sections 1 and 2.

As an example, consider the measurement of enthalpies of H_2O , both as liquid and as vapor. Liquid water is supplied to the apparatus. The constant-temperature bath is filled with a mixture of crushed ice and water to maintain a temperature of 273.15 K (0°C). The coil which carries water through the constant-temperature bath is long enough so that the fluid emerges essentially at the bath temperature of 273.15 K (0°C). Thus the fluid at section 1 is always liquid water at 273.15 K (0°C). The temperature and pressure at section 2 are measured by suitable instruments. Values of the enthalpy of H_2O for various conditions at section 2 are given by:

$$H_2 = H_1 + Q$$

where Q is the heat added per unit mass of water flowing.

Clearly, H_2 depends not only on Q but also on H_1 . The conditions at section 1 are always the same, i.e., liquid water at 273.15 K (0°C), except that the pressure varies from run to run. However, pressure in the range encountered here has a negligible effect on the properties of liquids, and for practical purposes H_1 is a constant. Absolute values of enthalpy, like absolute values of internal energy, are unknown. An arbitrary value may therefore be assigned to H_1 as the *basis* for all other enthalpy values. Setting $H_1 = 0$ for liquid water at 273.15 K (0°C) makes:

$$H_2 = H_1 + Q = 0 + Q = Q$$

Enthalpy values may be tabulated for the temperatures and pressures existing at section 2 for a large number of runs. In addition, specific-volume measurements made for these same conditions may be added to the table, along with corresponding values of the internal energy

calculated by Eq. (2.11), $U = H - PV$. In this way tables of thermodynamic properties are compiled over the entire useful range of conditions. The most widely used such tabulation is for H_2O and is known as the *steam tables*.¹⁰

The enthalpy may be taken as zero for some other state than liquid at 273.15 K (0°C). The choice is arbitrary. The equations of thermodynamics, such as Eqs. (2.32) and (2.33), apply to *changes* of state, for which the enthalpy *differences* are independent of the location of the zero point. However, once an arbitrary zero point is selected for the enthalpy, an arbitrary choice cannot be made for the internal energy, for values of internal energy are then calculable from the enthalpy by Eq. (2.11).

Example 2.14

For the flow calorimeter just discussed, the following data are taken with water as the test fluid:

Flow rate = 4.15 g s^{-1} $T_1/t_1 = 273.15 \text{ K}/0^\circ\text{C}$ $T_2/t_2 = 573.15 \text{ K}/300^\circ\text{C}$ $P_2 = 3 \text{ bar}$

Rate of heat addition from resistance heater = 12 740 W

It is observed that the water is completely vaporized in the process. Calculate the enthalpy of steam at 300°C and 3 bar based on $H = 0$ for liquid water at 273.15 K (0°C).

Solution 2.14

If Δz and Δu^2 are negligible and if W_s and H_1 are zero, then $H_2 = Q$, and

$$H_2 = \frac{12\,740 \text{ J s}^{-1}}{4.15 \text{ g s}^{-1}} = 3070 \text{ J g}^{-1}$$

Example 2.15

Air at 1 bar and 298.15 K (25°C) enters a compressor at low velocity, discharges at 3 bar, and enters a nozzle in which it expands to a final velocity of 600 m s^{-1} at the initial conditions of pressure and temperature. If the work of compression is 240 kJ per kilogram of air, how much heat must be removed during compression?

Solution 2.15

Since the air returns to its initial conditions of T and P , the overall process produces no change in enthalpy of the air. Moreover, the potential-energy change of the air is presumed negligible. Neglecting also the initial kinetic energy of the air, we write Eq. (2.32a) as:

$$Q = \frac{u_2^2}{2} - W_s$$

¹⁰Steam tables are given in App. F. Tables for various other substances are found in the literature. A discussion of compilations of thermodynamic properties appears in Chap. 6.

The kinetic-energy term is evaluated as follows:

$$\begin{aligned}\frac{1}{2}u_2^2 &= \frac{1}{2} \left(600 \frac{\text{m}}{\text{s}} \right)^2 = 180\,000 \frac{\text{m}^2}{\text{s}^2} \\ &= 180\,000 \frac{\text{m}^2}{\text{s}^2} \cdot \frac{\text{kg}}{\text{kg}} = 180\,000 \text{ N m kg}^{-1} = 180 \text{ kJ kg}^{-1}\end{aligned}$$

Then $Q = 180 - 240 = -60 \text{ kJ kg}^{-1}$

Thus, heat must be removed in the amount of 60 kJ for each kilogram of air compressed.

Example 2.16

Water at 366.65 K (93.5 °C) is pumped from a storage tank at the rate of $3.15 \times 10^{-3} \text{ m}^3 \text{ s}^{-1}$. The motor for the pump supplies work at the rate of 1.5 kW. The water goes through a heat exchanger, giving up heat at the rate of 700 kW, and is delivered to a second storage tank at an elevation 15 m above the first tank. What is the temperature of the water delivered to the second tank?

Solution 2.16

This is a steady-state steady-flow process for which Eq. (2.9b) applies. The initial and final velocities of water in the storage tanks are negligible, and the term $\Delta u^2/2g_c$ may be omitted. The remaining terms are expressed in units of kJ kg^{-1} through use of appropriate conversion factors. At 366.65 K the density of water is 958 kg m^{-3} thus the mass flow rate is

$$(3.15)(10^{-3})(958) = 3.018 \text{ kg s}^{-1}$$

from which we obtain

$$Q = -700/3.018 = -231.9 \text{ kJ kg}^{-1}$$

Since 1 kW is equivalent to 1 kJ s^{-1} , the shaft work is

$$W_s = (1.5)(1)/(3.018) = 0.497 \text{ kJ kg}^{-1}$$

If the local acceleration of gravity is taken as the standard value of 9.807 m s^{-2} , the potential-energy term becomes

$$\frac{g}{g_c} \Delta z = \left(\frac{9.807}{9.807} \right) \frac{(15)(9.807)}{(1000)} = 0.147 \text{ kJ kg}^{-1}$$

Equation (2.32b) now yields ΔH :

$$\Delta H = Q + W_s - \frac{g}{g_c} \Delta z = -231.9 + 0.497 - 0.147 = -231.55 \text{ kJ kg}^{-1}$$

The enthalpy of water at 366.65 K (93.5 °C) is given in the steam tables as 391.6 kJ kg^{-1} . Thus

$$\Delta H = H_2 - H_1 = H_2 - 391.6 = -231.55$$

and

$$H_2 = 391.6 - 231.55 = 160.05 \text{ kJ kg}^{-1}$$

The temperature of water having this enthalpy is found from the steam tables to be

$$t = 38.2^\circ\text{C} \quad \text{or} \quad T = 311.35 \text{ K}$$

In this example W , and $(g/g_c)\Delta z$ are small compared with Q , and for practical purposes they could be neglected.

PROBLEMS

- 2.1.** A nonconducting container filled with 25 kg of water at 293.15 K (20°C) is fitted with a stirrer, which is made to turn by gravity acting on a weight of mass 35 kg. The weight falls slowly through a distance of 5 m in driving the stirrer. Assuming that all work done on the weight is transferred to the water and that the local acceleration of gravity is 9.8 m s^{-2} , determine:
- The amount of work done on the water.
 - The internal-energy change of the water.
 - The final temperature of the water, for which $C_P = 4.18 \text{ kJ kg}^{-1} ^\circ\text{C}^{-1}$.
 - The amount of heat that must be removed from the water to return it to its initial temperature.
 - The total energy change of the universe because of (1) the process of lowering the weight, (2) the process of cooling the water back to its initial temperature, and (3) both processes together.
- 2.2.** Rework Prob. 2.1 for an insulated container that changes in temperature along with the water and has a heat capacity equivalent to 5 kg of water. Work the problem with:
- The water and container as the system; (b) The water alone as the system.
- 2.3.** An egg, initially at rest, is dropped onto a concrete surface and breaks. With the egg treated as the system,
- What is the sign of W ?
 - What is the sign of ΔE_P ?
 - What is ΔE_K ?
 - What is ΔU^t ?
 - What is the sign of Q ?
- In modeling this process, assume the passage of sufficient time for the broken egg to return to its initial temperature. What is the origin of the heat transfer of part (e)?
- 2.4.** An electric motor under steady load draws 9.7 amperes at 110 volts, delivering 0.93 kW of mechanical energy. What is the rate of heat transfer from the motor, in kW?

- 2.5.** One mole of gas in a closed system undergoes a four-step thermodynamic cycle. Use the data given in the following table to determine numerical values for the missing quantities, i.e., "fill in the blanks."

Step	$\Delta U^\circ/\text{J}$	Q/J	W/J
12	-200	?	-6000
23	?	-3800	?
34	?	-800	300
41	4700	?	?
12341	?	?	-1400

- 2.6.** Comment on the feasibility of cooling your kitchen in the summer by opening the door to the electrically powered refrigerator.
- 2.7.** A renowned laboratory reports quadruple-point coordinates of 10.2 Mbar and 297.25 K (24.1°C) for four-phase equilibrium of allotropic solid forms of the exotic chemical β -miasmone. Evaluate the claim.
- 2.8.** A closed, nonreactive system contains species 1 and 2 in vapor/liquid equilibrium. Species 2 is a very light gas, essentially insoluble in the liquid phase. The vapor phase contains both species 1 and 2. Some additional moles of species 2 are added to the system, which is then restored to its initial T and P. As a result of the process, does the total number of moles of liquid increase, decrease, or remain unchanged?
- 2.9.** A system comprised of chloroform, 1,4-dioxane, and ethanol exists as a two-phase vapor/liquid system at 323.15 K (50°C) and 55 kPa. It is found, after the addition of some pure ethanol, that the system can be returned to two-phase equilibrium at the initial T and P. In what respect has the system changed, and in what respect has it not changed?
- 2.10.** For the system described in Pb. 2.9:
- How many phase-rule variables in addition to T and P must be chosen so as to fix the compositions of both phases?
 - If the temperature and pressure are to remain the same, can the overall composition of the system be changed (by adding or removing material) without affecting the compositions of the liquid and vapor phases?
- 2.11.** A tank containing 20 kg of water at 293.15 K (20°C) is fitted with a stirrer that delivers work to the water at the rate of 0.25 kW. How long does it take for the temperature of the water to rise to 303.15 K (30°C) if no heat is lost from the water? For water, $C_p = 4.18 \text{ kJ kg}^{-1} \text{ } ^\circ\text{C}^{-1}$.
- 2.12.** Heat in the amount of 7.5 kJ is added to a closed system while its internal energy decreases by 12 kJ. How much energy is transferred as work? For a process causing the same change of state but for which the work is zero, how much heat is transferred?
- 2.13.** A steel casting weighing 2 kg has an initial temperature of 773.15 K (500°C); 40 kg of water initially at 298.15 K (25°C) is contained in a perfectly insulated steel tank

weighing 5 kg. The casting is immersed in the water and the system is allowed to come to equilibrium. What is its final temperature? Ignore any effect of expansion or contraction, and assume constant specific heats of $4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ for water and $0.50 \text{ kJ kg}^{-1} \text{ K}^{-1}$ for steel.

- 2.14.** An incompressible fluid ($p = \text{constant}$) is contained in an insulated cylinder fitted with a frictionless piston. Can energy as work be transferred to the fluid? What is the change in internal energy of the fluid when the pressure is increased from P_1 to P_2 ?

- 2.15.** One kg of liquid water at 298.15 K (25°C):

- (a) Experiences a temperature increase of 1 K. What is ΔU^t , in kJ?
- (b) Experiences a change in elevation Δz . The change in potential energy ΔE_p is the same as ΔU^t for part (a). What is Δz , in meters?
- (c) Is accelerated from rest to final velocity u . The change in kinetic energy ΔE_K is the same as ΔU^t for part (a). What is u , in m s^{-1} ?

Compare and discuss the results of the three preceding parts.

- 2.16.** An electric motor runs "hot" under load, owing to internal irreversibilities. It has been suggested that the associated energy loss be minimized by thermally insulating the motor casing. Comment critically on this suggestion.

- 2.17.** A hydroturbine operates with a head of 50 m of water. Inlet and outlet conduits are 2 m in diameter. Estimate the mechanical power developed by the turbine for an outlet velocity of 5 m s^{-1} .

- 2.18.** Liquid water at 453.15 K (180°C) and 1002.7 kPa has an internal energy (on an arbitrary scale) of 762.0 kJ kg^{-1} and a specific volume of $1.128 \text{ cm}^3 \text{ g}^{-1}$.

- (a) What is its enthalpy?
- (b) The water is brought to the vapor state at 573.15 K (300°C) and 1500 kPa, where its internal energy is $2784.4 \text{ kJ kg}^{-1}$ and its specific volume is $169.7 \text{ cm}^3 \text{ g}^{-1}$. Calculate ΔU and ΔH for the process.

- 2.19.** A solid body at initial temperature T_0 is immersed in a bath of water at initial temperature T_{w0} . Heat is transferred from the solid to the water at a rate $Q = K \cdot (T_w - T)$, where K is a constant and T_w and T are instantaneous values of the temperatures of the water and solid. Develop an expression for T as a function of time t . Check your result for the limiting cases, $t = 0$ and $t = \infty$. Ignore effects of expansion or contraction, and assume constant specific heats for both water and solid.

- 2.20.** A list of common unit operations follows:

- (a) Single-pipe heat exchanger; (b) Double-pipe heat exchanger; (c) Pump;
- (d) Gas compressor; (e) Gas turbine; (f) Throttle valve; (g) Nozzle.

Develop a simplified form of the general steady-state energy balance appropriate for each operation. State carefully, and justify, any assumptions you make.

- 2.21.** The Reynolds number Re is a dimensionless group which characterizes the intensity of a flow. For large Re , a flow is turbulent; for small Re , it is laminar. For pipe flow, $Re \equiv \rho u D / \mu$, where D is pipe diameter and μ is dynamic viscosity.

- (a) If D and μ are fixed, what is the effect of increasing mass flowrate \dot{m} on Re ?
 (b) If m and μ are fixed, what is the effect of increasing D on Re ?

2.22. An incompressible ($\rho = \text{constant}$) liquid flows steadily through a conduit of circular cross-section and increasing diameter. At location 1, the diameter is 2.5 cm and the velocity is 2 m s^{-1} ; at location 2, the diameter is 5 cm.

- (a) What is the velocity at location 2?
 (b) What is the kinetic-energy change (J kg^{-1}) of the fluid between locations 1 and 2?

2.23. A stream of warm water is produced in a steady-flow mixing process by combining 1.0 kg s^{-1} of cool water at 298.15 K (25°C) with 0.8 kg s^{-1} of hot water at 348.15 K (75°C). During mixing, heat is lost to the surroundings at the rate of 30 kW . What is the temperature of the warm-water stream? Assume the specific heat of water constant at $4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$.

2.24. Gas is bled from a tank. Neglecting heat transfer between the gas and the tank, show that mass and energy balances produce the differential equation:

$$\frac{dU}{H' - U} = \frac{dm}{m}$$

Here, U and m refer to the gas remaining in the tank; H' is the specific enthalpy of the gas leaving the tank. Under what conditions can one assume $H' = H$?

2.25. Water at 301.15 K (28°C) flows in a straight horizontal pipe in which there is no exchange of either heat or work with the surroundings. Its velocity is 14 m s^{-1} in a pipe with an internal diameter of 2.5 cm until it flows into a section where the pipe diameter abruptly increases. What is the temperature change of the water if the downstream diameter is 3.8 cm? If it is 7.5 cm? What is the maximum temperature change for an enlargement in the pipe?

2.26. Fifty (50) kmol per hour of air is compressed from $P_1 = 1.2 \text{ bar}$ to $P_2 = 6.0 \text{ bar}$ in a steady-flow compressor. Delivered mechanical power is 98.8 kW . Temperatures and velocities are:

$$\begin{array}{ll} T_1 = 300 \text{ K} & T_2 = 520 \text{ K} \\ u_1 = 10 \text{ m s}^{-1} & u_2 = 3.5 \text{ m s}^{-1} \end{array}$$

Estimate the rate of heat transfer from the compressor. Assume for air that $C_p = \frac{7}{2}R$ and that enthalpy is independent of pressure.

2.27. Nitrogen flows at steady state through a horizontal, insulated pipe with inside diameter of 38.1 mm. A pressure drop results from flow through a partially opened valve. Just upstream from the valve the pressure is 690 kPa , the temperature is 322.15 K (49°C), and the average velocity is 6.09 m s^{-1} . If the pressure just downstream from the valve is 138 kPa , what is the temperature? Assume for nitrogen that PV/T is constant, $C_v = (5/2)R$, and $C_p = (7/2)R$. (Values for R are given in App. A.)

2.28. Water flows through a horizontal coil heated from the outside by high-temperature flue gases. As it passes through the coil the water changes state from liquid at 200 kPa and

353.15 K (80°C) to vapor at 100 kPa and 398.15 K (125°C). Its entering velocity is 3 m s^{-1} and its exit velocity is 200 m s^{-1} . Determine the heat transferred through the coil per unit mass of water. Enthalpies of the inlet and outlet streams are:

Inlet: 334.9 kJ kg^{-1} ; Outlet: $2726.5 \text{ kJ kg}^{-1}$

- 2.29.** Steam flows at steady state through a converging, insulated nozzle, 25 cm long and with an inlet diameter of 5 cm. At the nozzle entrance (state 1), the temperature and pressure are 598.15 K (325°C) and 700 kPa, and the velocity is 30 m s^{-1} . At the nozzle exit (state 2), the steam temperature and pressure are 513.15 K (240°C) and 350 kPa. Property values are:

$$H_1 = 3112.5 \text{ kJ kg}^{-1} \quad V_1 = 388.61 \text{ cm}^3 \text{ g}^{-1}$$

$$H_2 = 2945.7 \text{ kJ kg}^{-1} \quad V_2 = 667.75 \text{ cm}^3 \text{ g}^{-1}$$

What is the velocity of the steam at the nozzle exit, and what is the exit diameter?

- 2.30.** In the following take $C_V = 20.8$ and $C_P = 29.1 \text{ J mol}^{-1} \text{ }^\circ\text{C}^{-1}$ for nitrogen gas:
- (a) Three moles of nitrogen at 303.15 K (30°C), contained in a rigid vessel, is heated to 523.15 K (250°C). How much heat is required if the vessel has a negligible heat capacity? If the vessel weighs 100 kg and has a heat capacity of $0.5 \text{ kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$, how much heat is required?
 - (b) Four moles of nitrogen at 473.15 K (200°C) is contained in a piston/cylinder arrangement. How much heat must be extracted from this system, which is kept at constant pressure, to cool it to 313.15 K (40°C) if the heat capacity of the piston and cylinder is neglected?
- 2.31.** In the following take $C_V = 21$ and $C_P = 29.3 \text{ kJ kmol}^{-1} \text{ K}^{-1}$ for nitrogen gas:
- (a) 1.5 kmol of nitrogen at 294.15 K (21°C) contained in a rigid vessel, is heated to 450.15 K (177°C). How much heat is required if the vessel has a negligible heat capacity? If it weighs 90.7 kg and has a heat capacity of $0.5 \text{ kJ kg}^{-1} \text{ K}^{-1}$, how much heat is required?
 - (b) 2 kmol of nitrogen at 447.15 K (174°C) is contained in a piston/cylinder arrangement. How much heat must be extracted from this system, which is kept at constant pressure, to cool it to 338.15 K (65°C) if the heat capacity of the piston and cylinder is neglected?
- 2.32.** Find the equation for the work of a reversible, isothermal compression of 1 mol of gas in a piston/cylinder assembly if the molar volume of the gas is given by

$$V = \frac{RT}{P} + b$$

where b and R are positive constants.

- 2.33.** Steam at 14 bar and 588.15 K (315°C) [state 1] enters a turbine through a 75 mm-diameter pipe with a velocity of 3 m s^{-1} . The exhaust from the turbine is carried through a 250 mm-diameter pipe and is at 0.35 bar and 366.15 K (93°C) [state 2]. What is the power output of the turbine?

$$H_1 = 3074.5 \text{ kJ kg}^{-1} \quad V_1 = 0.1909 \text{ m}^3 \text{ kg}^{-1}$$

$$H_2 = 2871.6 \text{ kJ kg}^{-1} \quad V_2 = 4.878 \text{ m}^3 \text{ kg}^{-1}$$

- 2.34.** Carbon dioxide gas enters a water-cooled compressor at the initial conditions $P_1 = 1.04$ bar and $T_1 = 284.15$ K (10°C) and is discharged at the final conditions $P_2 = 35.8$ bar and $T_2 = 366.15$ K (93°C). The entering CO₂ flows through a 100 mm-diameter pipe with a velocity of 6 s m⁻¹, and is discharged through a 25 mm-diameter pipe. The shaft work supplied to the compressor is 12 500 kJ kmol⁻¹. What is the heat-transfer rate from the compressor in kW?

$$H_1 = 714 \text{ kJ kg}^{-1} \quad V_1 = 0.5774 \text{ m}^3 \text{ kg}^{-1}$$

$$H_2 = 768 \text{ kJ kg}^{-1} \quad V_2 = 0.0175 \text{ m}^3 \text{ kg}^{-1}.$$

- 2.35.** Show that W and Q for an arbitrary mechanically reversible nonflow process are given by:

$$W = \int V dP - \Delta(PV) \qquad Q = \Delta H - \int V dP$$

- 2.36.** One kilogram of air is heated reversibly at constant pressure from an initial state of 300 K and 1 bar until its volume triples. Calculate W , Q , ΔU , and ΔH for the process. Assume for air that $P V/T = 83.14$ bar cm³ mol⁻¹ K⁻¹ and $C_P = 29$ J mol⁻¹ K⁻¹.
- 2.37.** The conditions of a gas change in a steady-flow process from 293.15 K (20°C) and 1000 kPa to 333.15 K (60°C) and 100 kPa. Devise a reversible nonflow process (any number of steps) for accomplishing this change of state, and calculate ΔU and ΔH for the process on the basis of 1 mol of gas. Assume for the gas that $P V/T$ is constant, $C_V = (5/2)R$, and $C_P = (7/2)R$.