The First Law of Thermodynamics

5

Having completed our review of basic definitions and concepts, we are ready to discuss the first law of thermodynamics. This law is often called the *conservation of energy law* and, as we will see later, this is essentially true. Our procedure will be to state this law for a system (control mass) undergoing a cycle and then for a change of state of a system.

After the energy equation is formulated, we will use it to relate the change of state inside a control volume to the amount of energy that is transferred in a process as work or heat transfer. When a car engine has transferred some work to the car, the car's speed is increased, so we can relate the kinetic energy increase to the work; or, if a stove provides a certain amount of heat transfer to a pot with water, we can relate the water temperature increase to the heat transfer. More complicated processes can also occur, such as the expansion of very hot gases in a piston cylinder, as in a car engine, in which work is given out and at the same time heat is transferred to the colder walls. In other applications we can also see a change in state without any work or heat transfer, such as a falling object that changes kinetic energy at the same time it is changing elevation. The energy equation then relates the two forms of energy of the object.

5.1 THE FIRST LAW OF THERMODYNAMICS FOR A CONTROL MASS UNDERGOING A CYCLE

The first law of thermodynamics states that during any cycle a system (control mass) undergoes, the cyclic integral of the heat is proportional to the cyclic integral of the work.

To illustrate this law, consider as a control mass the gas in the container shown in Fig. 5.1. Let this system go through a cycle that is made up of two processes. In the first process, work is done on the system by the paddle that turns as the weight is lowered. Let the system then return to its initial state by transferring heat from the system until the cycle has been completed.

Historically, work was measured in mechanical units of force times distance, such as foot pounds force or joules, and heat was measured in thermal units, such as the British thermal unit or the calorie. Measurements of work and heat were made during a cycle for a wide variety of systems and for various amounts of work and heat. When the amounts of work and heat were compared, it was found that they were always proportional. Such
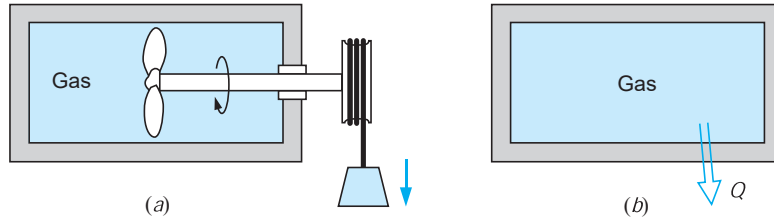
FIGURE 5.1 Example of a control mass undergoing a cycle.

observations led to the formulation of the first law of thermodynamics, which in equation form is written

$$J \oint \delta Q = \oint \delta W \tag{5.1}$$

The symbol $\oint \delta Q$, which is called the *cyclic integral of the heat transfer*, represents the net heat transfer during the cycle, and $\oint \delta W$, the *cyclic integral of the work*, represents the net work during the cycle. Here, J is a proportionality factor that depends on the units used for work and heat.

The basis of every law of nature is experimental evidence, and this is true also of the first law of thermodynamics. Many different experiments have been conducted on the first law, and every one thus far has verified it either directly or indirectly. The first law has never been disproved.

As was discussed in Chapter 4, the units for work and heat or for any other form of energy either are the same or are directly proportional. In SI units, the joule is used as the unit for both work and heat and for any other energy unit. In English units, the basic unit for work is the foot pound force, and the basic unit for heat is the British thermal unit (Btu). James P. Joule (1818–1889) did the first accurate work in the 1840s on measurement of the proportionality factor J, which relates these units. Today, the Btu is defined in terms of the basic SI metric units,

$$1 \text{ Btu} = 778.17 \text{ ft lbf}$$

This unit is termed the *International British thermal unit*. For much engineering work, the accuracy of other data does not warrant more accuracy than the relation 1 Btu = 778 ft lbf, which is the value used with English units in the problems in this book. Because these units are equivalent, it is not necessary to include the factor J explicitly in Eq. 5.1, but simply to recognize that for any system of units, each equation must have consistent units throughout. Therefore, we may write Eq. 5.1 as

$$\oint \delta Q = \oint \delta W \tag{5.2}$$

which can be considered the basic statement of the first law of thermodynamics.

5.2 THE FIRST LAW OF THERMODYNAMICS FOR A CHANGE IN STATE OF A CONTROL MASS

Equation 5.2 states the first law of thermodynamics for a control mass during a cycle. Many times, however, we are concerned with a process rather than a cycle. We now consider the first law of thermodynamics for a control mass that undergoes a change of state. We begin by introducing a new property, energy, which is given the symbol E. Consider a system

that undergoes a cycle in which it changes from state 1 to state 2 by process A and returns from state 2 to state 1 by process B. This cycle is shown in Fig. 5.2 on a pressure (or other intensive property)–volume (or other extensive property) diagram. From the first law of thermodynamics, Eq. 5.2, we have

$$\oint \delta Q = \oint \delta W$$

Considering the two separate processes, we have

$$\int_1^2 \delta Q_A + \int_2^1 \delta Q_B = \int_1^2 \delta W_A + \int_2^1 \delta W_B$$

Now consider another cycle in which the control mass changes from state 1 to state 2 by process C and returns to state 1 by process B, as before. For this cycle we can write

$$\int_1^2 \delta Q_C + \int_2^1 \delta Q_B = \int_1^2 \delta W_C + \int_2^1 \delta W_B$$

Subtracting the second of these equations from the first, we obtain

$$\int_1^2 \delta Q_A - \int_1^2 \delta Q_C = \int_1^2 \delta W_A - \int_1^2 \delta W_C$$

or, by rearranging,

$$\int_1^2 (\delta Q - \delta W)_A = \int_1^2 (\delta Q - \delta W)_C \tag{5.3}$$

Since A and C represent arbitrary processes between states 1 and 2, the quantity $\delta Q - \delta W$ is the same for all processes between states 1 and 2. Therefore, $\delta Q - \delta W$ depends only on the initial and final states and not on the path followed between the two states. We conclude that this is a point function, and therefore it is the differential of a property of the mass. This property is the energy of the mass and is given the symbol E. Thus we can write

$$dE = \delta Q - \delta W \tag{5.4}$$

Because E is a property, its derivative is written dE. When Eq. 5.4 is integrated from an initial state 1 to a final state 2, we have

$$E_2 - E_1 = {}_1Q_2 - {}_1W_2 \tag{5.5}$$

where E_1 and E_2 are the initial and final values of the energy E of the control mass, ${}_1Q_2$ is the heat transferred to the control mass during the process from state 1 to state 2, and ${}_1W_2$ is the work done by the control mass during the process.
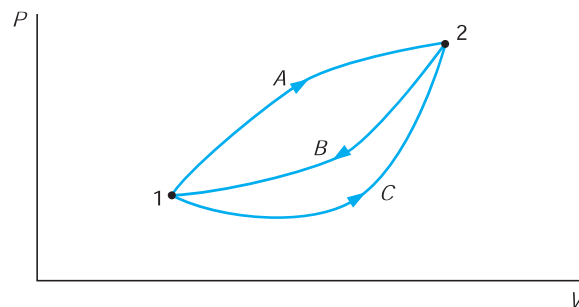

FIGURE 5.2
Demonstration of the existence of thermodynamic property E.

Note that a control mass may be made up of several different subsystems, as shown in Fig. 5.3. In this case, each part must be analyzed and included separately in applying the first law, Eq. 5.5. We further note that Eq. 5.5 is an expression of the general form

$$\Delta \text{ Energy} = + \text{ in} - \text{out}$$

in terms of the standard sign conventions for heat and work.

The physical significance of the property E is that it represents all the energy of the system in the given state. This energy might be present in a variety of forms, such as the kinetic or potential energy of the system as a whole with respect to the chosen coordinate frame, energy associated with the motion and position of the molecules, energy associated with the structure of the atom, chemical energy present in a storage battery, energy present in a charged capacitor, or any of a number of other forms.

In the study of thermodynamics, it is convenient to consider the bulk kinetic and potential energy separately and then to consider all the other energy of the control mass in a single property that we call the internal energy and to which we give the symbol U. Thus, we would write

$$E = \text{Internal energy} + \text{kinetic energy} + \text{potential energy}$$

or

$$E = U + \text{KE} + \text{PE}$$

The kinetic and potential energy of the control mass are associated with the coordinate frame that we select and can be specified by the macroscopic parameters of mass, velocity, and elevation. The internal energy U includes all other forms of energy of the control mass and is associated with the thermodynamic state of the system.

Since the terms comprising E are point functions, we can write

$$dE = dU + d(\text{KE}) + d(\text{PE}) \tag{5.6}$$

The first law of thermodynamics for a change of state may therefore be written

$$dE = dU + d(\text{KE}) + d(\text{PE}) = \delta Q - \delta W \tag{5.7}$$

In words, this equation states that as a control mass undergoes a change of state, energy may cross the boundary as either heat or work, and each may be positive or negative. The net change in the energy of the system will be exactly equal to the net energy that
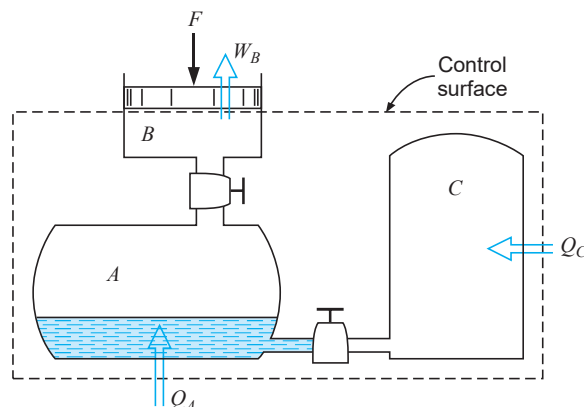

FIGURE 5.3 A control mass with several different subsystems.

crosses the boundary of the system. The energy of the system may change in any of three ways—by a change in internal energy, in kinetic energy, or in potential energy.

This section concludes by deriving an expression for the kinetic and potential energy of a control mass. Consider a mass that is initially at rest relative to the earth, which is taken as the coordinate frame. Let this system be acted on by an external horizontal force F that moves the mass a distance dx in the direction of the force. Thus, there is no change in potential energy. Let there be no heat transfer and no change in internal energy. Then from the first law, Eq. 5.7, we have

$$\delta W = -F\,dx = -d\mathrm{KE}$$

But

$$F = ma = m\frac{d\mathbf{V}}{dt} = m\frac{dx}{dt}\frac{d\mathbf{V}}{dx} = m\mathbf{V}\frac{d\mathbf{V}}{dx}$$

Then

$$d\mathrm{KE} = F\,dx = m\mathbf{V}\,d\mathbf{V}$$

Integrating, we obtain

$$\int_{\mathrm{KE}=0}^{\mathrm{KE}} d\mathrm{KE} = \int_{\mathbf{V}=0}^{\mathbf{V}} m\mathbf{V}\,d\mathbf{V}$$

$$\mathrm{KE} = \frac{1}{2}m\mathbf{V}^2 \tag{5.8}$$

A similar expression for potential energy can be found. Consider a control mass that is initially at rest and at the elevation of some reference level. Let this mass be acted on by a vertical force F of such magnitude that it raises (in elevation) the mass with constant velocity an amount dZ. Let the acceleration due to gravity at this point be g. From the first law, Eq. 5.7, we have

$$\delta W = -F\,dZ = -d\,\mathrm{PE}$$
$$F = ma = mg$$

Then

$$d\,\mathrm{PE} = F\,dZ = mg\,dZ$$

Integrating gives

$$\int_{\mathrm{PE}_1}^{\mathrm{PE}_2} d\,\mathrm{PE} = m\int_{Z_1}^{Z_2} g\,dZ$$

Assuming that g does not vary with Z (which is a very reasonable assumption for moderate changes in elevation), we obtain

$$\mathrm{PE}_2 - \mathrm{PE}_1 = mg(Z_2 - Z_1) \tag{5.9}$$

EXAMPLE 5.1 A car of mass 1100 kg drives with a velocity such that it has a kinetic energy of 400 kJ (see Fig. 5.4). Find the velocity. If the car is raised with a crane, how high should it be lifted in the standard gravitational field to have a potential energy that equals the kinetic energy?
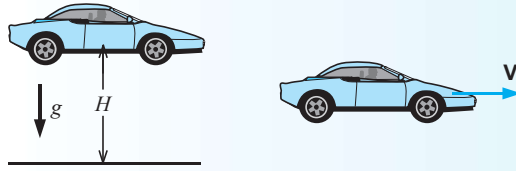
FIGURE 5.4 Sketch for Example 5.1.

Solution

The standard kinetic energy of the mass is

$$\mathrm{KE} = \frac{1}{2}m\mathbf{V}^2 = 400\ \mathrm{kJ}$$

From this we can solve for the velocity:

$$\mathbf{V} = \sqrt{\frac{2\ \mathrm{KE}}{m}} = \sqrt{\frac{2 \times 400\ \mathrm{kJ}}{1100\ \mathrm{kg}}}$$

$$= \sqrt{\frac{800 \times 1000\ \mathrm{N\,m}}{1100\ \mathrm{kg}}} = \sqrt{\frac{8000\ \mathrm{kg\,m\,s^{-2}\,m}}{11\ \mathrm{kg}}} = 27\ \mathrm{m/s}$$

Standard potential energy is

$$\mathrm{PE} = mgH$$

so when this is equal to the kinetic energy we get

$$H = \frac{\mathrm{KE}}{mg} = \frac{400\,000\ \mathrm{N\,m}}{1100\ \mathrm{kg} \times 9.807\ \mathrm{m\,s^{-2}}} = 37.1\ \mathrm{m}$$

Notice the necessity of converting the kJ to J in both calculations.

EXAMPLE 5.1E A car of mass 2400 lbm drives with a velocity such that it has a kinetic energy of 400 Btu. Find the velocity. If the car is raised with a crane, how high should it be lifted in the standard gravitational field to have a potential energy that equals the kinetic energy?

Solution

The standard kinetic energy of the mass is

$$\mathrm{KE} = \frac{1}{2}m\mathbf{V}^2 = 400\ \mathrm{Btu}$$

From this we can solve for the velocity:

$$\mathbf{V} = \sqrt{\frac{2\mathrm{KE}}{m}} = \sqrt{\frac{2 \times 400\ \mathrm{Btu} \times 778.17\dfrac{\mathrm{ft\,lbf}}{\mathrm{Btu}} \times 32.174\dfrac{\mathrm{lbm\,ft}}{\mathrm{lbf\,s^2}}}{2400\ \mathrm{lbm}}}$$

$$= 91.4\ \mathrm{ft/s}$$

Standard potential energy is

$$\text{PE} = mgH$$

so when this is equal to the kinetic energy KE we get

$$H = \frac{\text{KE}}{mg} = \frac{400\,\text{Btu} \times 778.17\frac{\text{ft lbf}}{\text{Btu}} \times 32.174\frac{\text{lbm ft}}{\text{lbf s}^2}}{2400\,\text{lbm} \times 32.174\frac{\text{ft}}{\text{s}^2}}$$

$$= 129.7\,\text{ft}$$

Note the necessity of using the conversion constant $32.174\frac{\text{lbm ft}}{\text{lbf s}^2}$ in both calculations.

Now, substituting the expressions for kinetic and potential energy into Eq. 5.6, we have

$$dE = dU + m\mathbf{V}\,d\mathbf{V} + mg\,dZ$$

Integrating for a change of state from state 1 to state 2 with constant g, we get

$$E_2 - E_1 = U_2 - U_1 + \frac{m\mathbf{V}_2^2}{2} - \frac{m\mathbf{V}_1^2}{2} + mgZ_2 - mgZ_1$$

Similarly, substituting these expressions for kinetic and potential energy into Eq. 5.7, we have

$$dE = dU + \frac{d(m\mathbf{V}^2)}{2} + d(mgZ) = \delta Q - \delta W \tag{5.10}$$

Assuming g is a constant, in the integrated form of this equation,

$$U_2 - U_1 + \frac{m(\mathbf{V}_2^2 - \mathbf{V}_1^2)}{2} + mg(Z_2 - Z_1) = {}_1Q_2 - {}_1W_2 \tag{5.11}$$

Three observations should be made regarding this equation. The first observation is that the property E, the energy of the control mass, was found to exist, and we were able to write the first law for a change of state using Eq. 5.5. However, rather than deal with this property E, we find it more convenient to consider the internal energy and the kinetic and potential energies of the mass. In general, this procedure will be followed in the rest of this book.

The second observation is that Eqs. 5.10 and 5.11 are in effect a statement of the conservation of energy. The net change of the energy of the control mass is always equal to the net transfer of energy across the boundary as heat and work. This is somewhat analogous to a joint checking account shared by a husband and wife. There are two ways in which deposits and withdrawals can be made—either by the husband or by the wife—and the balance will always reflect the net amount of the transaction. Similarly, there are two ways in which energy can cross the boundary of a control mass—either as heat or as work—and the energy of the mass will change by the exact amount of the net energy crossing the boundary. The concept of energy and the law of the conservation of energy are basic to thermodynamics.

The third observation is that Eqs. 5.10 and 5.11 can give only changes in internal energy, kinetic energy, and potential energy. We can learn nothing about absolute values of these quantities from these equations. If we wish to assign values to internal energy, kinetic energy, and potential energy, we must assume reference states and assign a value to the quantity in this reference state. The kinetic energy of a body with zero velocity relative to the earth is assumed to be zero. Similarly, the value of the potential energy is assumed to be zero when the body is at some reference elevation. With internal energy, therefore, we must also have a reference state if we wish to assign values of this property. This matter is considered in the following section.

EXAMPLE 5.2   A tank containing a fluid is stirred by a paddle wheel. The work input to the paddle wheel is 5090 kJ. The heat transfer from the tank is 1500 kJ. Consider the tank and the fluid inside a control surface and determine the change in internal energy of this control mass.

The first law of thermodynamics is (Eq. 5.11)

$$U_2 - U_1 + \frac{1}{2}m(\mathbf{V}_2^2 - \mathbf{V}_1^2) + mg(Z_2 - Z_1) = {}_1Q_2 - {}_1W_2$$

Since there is no change in kinetic and potential energy, this reduces to

$$U_2 - U_1 = {}_1Q_2 - {}_1W_2$$
$$U_2 - U_1 = -1500 - (-5090) = 3590 \text{ kJ}$$

EXAMPLE 5.3   Consider a stone having a mass of 10 kg and a bucket containing 100 kg of liquid water. Initially the stone is 10.2 m above the water, and the stone and the water are at the same temperature, state 1. The stone then falls into the water.

Determine ΔU, ΔKE, ΔPE, Q, and W for the following changes of state, assuming standard gravitational acceleration of 9.806 65 m/s^2.

a. The stone is about to enter the water, state 2.
b. The stone has just come to rest in the bucket, state 3.
c. Heat has been transferred to the surroundings in such an amount that the stone and water are at the same temperature, T_1, state 4.

Analysis and Solution

The first law for any of the steps is

$$Q = \Delta U + \Delta\text{KE} + \Delta\text{PE} + W$$

and each term can be identified for each of the changes of state.

a. The stone has fallen from Z_1 to Z_2, and we assume no heat transfer as it falls. The water has not changed state; thus

$$\Delta U = 0, \qquad {}_1Q_2 = 0, \qquad {}_1W_2 = 0$$

and the first law reduces to

$$\Delta KE + \Delta PE = 0$$
$$\Delta KE = -\Delta PE = -mg(Z_2 - Z_1)$$
$$= -10 \text{ kg} \times 9.806\,65 \text{ m/s}^2 \times (-10.2 \text{ m})$$
$$= 1000 \text{ J} = 1 \text{ kJ}$$

That is, for the process from state 1 to state 2,

$$\Delta KE = 1 \text{ kJ} \quad \text{and} \quad \Delta PE = -1 \text{ kJ}$$

b. For the process from state 2 to state 3 with zero kinetic energy, we have

$$\Delta PE = 0, \quad {}_2Q_3 = 0, \quad {}_2W_3 = 0$$

Then

$$\Delta U + \Delta KE = 0$$
$$\Delta U = -\Delta KE = 1 \text{ kJ}$$

c. In the final state, there is no kinetic or potential energy, and the internal energy is the same as in state 1.

$$\Delta U = -1 \text{ kJ}, \qquad \Delta KE = 0, \qquad \Delta PE = 0, \qquad {}_3W_4 = 0$$
$${}_3Q_4 = \Delta U = -1 \text{ kJ}$$

In-Text Concept Questions

a. In a complete cycle, what is the net change in energy and in volume?

b. Explain in words what happens with the energy terms for the stone in Example 5.3. What would happen if the object was a bouncing ball falling to a hard surface?

c. Make a list of at least five systems that store energy, explaining which form of energy is involved.

d. A constant mass goes through a process in which 100 J of heat transfer comes in and 100 J of work leaves. Does the mass change state?

5.3 INTERNAL ENERGY—A THERMODYNAMIC PROPERTY

Internal energy is an extensive property because it depends on the mass of the system. Kinetic and potential energies are also extensive properties.

The symbol U designates the internal energy of a given mass of a substance. Following the convention used with other extensive properties, the symbol u designates the internal energy per unit mass. We could speak of u as the specific internal energy, as we do with specific volume. However, because the context will usually make it clear whether u or U is referred to, we will use the term *internal energy* to refer to both internal energy per unit mass and the total internal energy.

In Chapter 3 we noted that in the absence of motion, gravity, surface effects, electricity, or other effects, the state of a pure substance is specified by two independent properties.

It is very significant that, with these restrictions, the internal energy may be one of the independent properties of a pure substance. This means, for example, that if we specify the pressure and internal energy (with reference to an arbitrary base) of superheated steam, the temperature is also specified.

Thus, in tables of thermodynamic properties such as the steam tables, the value of internal energy can be tabulated along with other thermodynamic properties. Tables 1 and 2 of the steam tables (Tables B.1.1 and B.1.2) list the internal energy for saturated states. Included are the internal energy of saturated liquid u_f, the internal energy of saturated vapor u_g, and the difference between the internal energy of saturated liquid and saturated vapor u_{fg}. The values are given in relation to an arbitrarily assumed reference state, which, for water in the steam tables, is taken as zero for saturated liquid at the triple-point temperature, 0.01°C. All values of internal energy in the steam tables are then calculated relative to this reference (note that the reference state cancels out when finding a difference in u between any two states). Values for internal energy are found in the steam tables in the same manner as for specific volume. In the liquid–vapor saturation region,

$$U = U_{liq} + U_{vap}$$

or

$$mu = m_{liq}u_f + m_{vap}u_g$$

Dividing by m and introducing the quality x gives

$$u = (1 - x)u_f + xu_g$$
$$u = u_f + xu_{fg}$$

As an example, the specific internal energy of saturated steam having a pressure of 0.6 MPa and a quality of 95% can be calculated as

$$u = u_f + xu_{fg} = 669.9 + 0.95(1897.5) = 2472.5 \text{ kJ/kg}$$

Values for u in the superheated vapor region are tabulated in Table B.1.3, for compressed liquid in Table B.1.4, and for solid–vapor in Table B.1.5.

EXAMPLE 5.4   Determine the missing property (P, T, or x) and v for water at each of the following states:

a. $T = 300$°C, $u = 2780$ kJ/kg
b. $P = 2000$ kPa, $u = 2000$ kJ/kg

For each case, the two properties given are independent properties and therefore fix the state. For each, we must first determine the phase by comparison of the given information with phase boundary values.

a. At 300°C, from Table B.1.1, $u_g = 2563.0$ kJ/kg. The given $u > u_g$, so the state is in the superheated vapor region at some P less than P_g, which is 8581 kPa. Searching through Table B.1.3 at 300°C, we find that the value $u = 2780$ is between given values of u at 1600 kPa (2781.0) and 1800 kPa (2776.8). Interpolating linearly, we obtain

$$P = 1648 \text{ kPa}$$

Note that quality is undefined in the superheated vapor region. At this pressure, by linear interpolation, we have $v = 0.1542$ m^3/kg.

b. At $P = 2000$ kPa, from Table B.1.2, the given u of 2000 kJ/kg is greater than u_f (906.4) but less than u_g (2600.3). Therefore, this state is in the two-phase region with $T = T_g = 212.4°$C, and

$$u = 2000 = 906.4 + x1693.8, \qquad x = 0.6456$$

Then,

$$v = 0.001\ 177 + 0.6456 \times 0.098\ 45 = 0.064\ 74 \text{ m}^3/\text{kg}.$$

In-Text Concept Questions

e. Water is heated from 100 kPa, 20°C to 1000 kPa, 200°C. In one case, pressure is raised at $T = C$, then T is raised at $P = C$. In a second case, the opposite order is used. Does that make a difference for $_1Q_2$ and $_1W_2$?

f. A rigid insulated tank A contains water at 400 kPa, 800°C. A pipe and valve connect this to another rigid insulated tank B of equal volume having saturated water vapor at 100 kPa. The valve is opened and stays open while the water in the two tanks comes to a uniform final state. Which two properties determine the final state?

5.4 PROBLEM ANALYSIS AND SOLUTION TECHNIQUE

At this point in our study of thermodynamics, we have progressed sufficiently far (that is, we have accumulated sufficient tools with which to work) that it is worthwhile to develop a somewhat formal technique or procedure for analyzing and solving thermodynamic problems. For the time being, it may not seem entirely necessary to use such a rigorous procedure for many of our problems, but we should keep in mind that as we acquire more analytical tools, the problems that we are capable of dealing with will become much more complicated. Thus, it is appropriate that we begin to practice this technique now in anticipation of these future problems.

Our problem analysis and solution technique is contained within the framework of the following questions that must be answered in the process of an orderly solution of a thermodynamic problem.

1. What is the control mass or control volume? Is it useful, or necessary, to choose more than one? It may be helpful to draw a sketch of the system at this point, illustrating all heat and work flows, and indicating forces such as external pressures and gravitation.
2. What do we know about the initial state (that is, which properties are known)?
3. What do we know about the final state?
4. What do we know about the process that takes place? Is anything constant or zero? Is there some known functional relation between two properties?
5. Is it helpful to draw a diagram of the information in steps 2 to 4 (for example, a T–v or P–v diagram)?
6. What is our thermodynamic model for the behavior of the substance (for example, steam tables, ideal gas, and so on)?