System. Any arbitrarily specified mass of material or segment of apparatus to which we would like to devote our attention. A system must be defined by surrounding it with a system boundary. A system enclosed by a boundary that prohibits the transfer of mass across the boundary is termed a ***closed* system, or *nonflow* system,** in distinction to an ***open* system, or *flow* system,** in which the exchange of mass is permitted. All the mass or apparatus external to the defined system is termed the ***surroundings***. Reexamine some of the example problems in Chap. 2 for illustrations of the location of system boundaries. You should always draw similar boundaries in the solution of your problems, since this step will fix clearly the system and surroundings.

Property. A characteristic of material that can be measured, such as pressure, volume, or temperature—or calculated, if not directly measured, such as certain types of energy. The properties of a system are dependent on its condition at any given time and not on what has happened to the system in the past.

An ***extensive property*** (variable, parameter) is one whose value is the sum of the values of each of the subsystems comprising the whole system. For example, a gaseous system can be divided into two subsystems which have volumes or masses different from the original system. Consequently, mass or volume is an extensive property.

An ***intensive property*** (variable, parameter) is one whose value is not additive and does not vary with the quantity of material in the subsystem. For example, temperature, pressure, density (mass per volume), and so on, do not change if the system is sliced in half or if the halves are put together.

Two properties are *independent* of each other if at least one variation of state for the system can be found in which one property varies while the other remains fixed. The number of independent intensive properties necessary and sufficient to fix the state of the system can be ascertained from the phase rule of Sec. 3.7-1.

State. The given set of properties of material at a given time. The state of a system does not depend on the shape or configuration of the system but only on its intensive properties.

Now that we have reviewed the concepts of system, property, and state, we can discuss the various types of energy with which we will be involved in this chapter. What forms can energy take? We shall consider here six quantities: work, heat, kinetic energy, potential energy, internal energy, and enthalpy. You probably have encountered many of these terms before.

Work. Work (W) is a term that has wide usage in everyday life (such as "I am going to work"), but has a specialized meaning in connection with energy balances. Work is a form of energy that represents a **transfer** between the system and surroundings. Work cannot be stored. For a mechanical force

$$W = \int_{\text{state 1}}^{\text{state 2}} \mathbf{F} \cdot ds \tag{4.1}$$

where **F** is an external force in the direction of s acting on the system (or a system force acting on the surroundings).

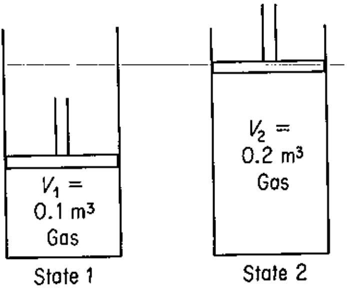
(a) The displacement may not be easy to define.
(b) Integration of $\mathbf{F} \cdot ds$ as shown in Eq. (4.1) does not always result in an equal amount of work being done by the system.
(c) Work can be exchanged without a mechanical force acting on the system boundaries (such as through magnetic or electric effects).

Note that unless the process (or path) under which work is carried out is specified from the initial to the final state of the system, you are not able to calculate the value of the work done. In other words, work done in going between the initial and final states can have *any* value, depending on the path taken. **Work is therefore called a *path function*,** and the value of W depends on the initial state, the path, and the final state of the system, as illustrated in the next example.

EXAMPLE 4.1 Calculation of Work by a Gas on a Piston

Suppose that an ideal gas at 300 K and 200 kPa is enclosed in a cylinder by a frictionless piston, and the gas slowly forces the piston up so that the volume of gas expands from 0.1 to 0.2 m^3. Examine Fig. E4.1a. Calculate the work done by the gas on the piston if two different paths are used to go from the initial state to the final state:

Path *A*: expansion occurs at constant pressure (p = 200 kPa)
Path *B*: expansion occurs at constant temperature (T = 300 K)



(a) **Figure E4.1a**

Solution

The work is

$$W = \int_{\text{state 1}}^{\text{state 2}} \frac{\mathbf{F}}{A} \cdot A\, ds = \int_{V_1}^{V_2} p\, dV$$

because p is exerted normally on the piston face.

Path A

$$W = p\int_{V_1}^{V_2} dV = p(V_2 - V_1)$$

$$= \begin{array}{c|c|c|c} 200 \times 10^3\ \text{Pa} & 1\dfrac{\text{N}}{\text{m}^2} & 0.1\ \text{m}^3 & 1\dfrac{\text{J}}{\text{m}} \\ \hline & 1\ \text{Pa} & & 1\ \text{N} \end{array}$$

$$= 20\ \text{kJ}$$

Path B

$$W = \int_{V_1}^{V_2} \frac{nRT}{V}\,dV = nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$n = \begin{array}{c|c|c|c} 200\ \text{kPa} & 0.1\ \text{m}^3 & & (\text{kg mol})(\text{K}) \\ \hline & & 300\ \text{K} & 8.314(\text{kPa})(\text{m}^3) \end{array}$$

$$= 0.00802\ \text{kg mol}$$

$$W = \begin{array}{c|c|c} 0.00802\ \text{kg mol} & 8.314\ \text{kJ} & 300\ \text{K} \\ \hline & (\text{kg mol})(\text{K}) & \end{array} \ln 2$$

$$= 20 \ln 2 = 13.86\ \text{kJ}$$

Figure E4.1b shows the two different quantities of work on a p–V plot.

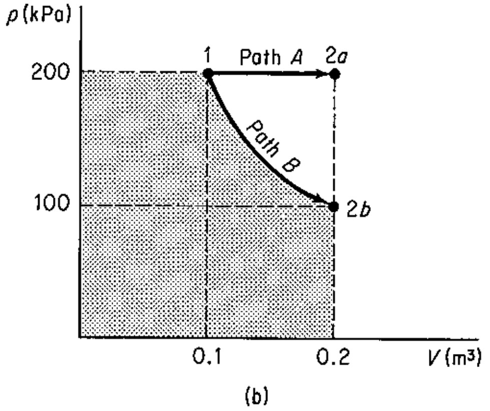


Figure E4.1b

Heat. In a discussion of *heat* we enter an area in which our everyday use of the term may cause confusion, since we are going to use heat in a very restricted sense when we apply the laws governing energy changes. Heat (Q) is commonly defined as that part of the total energy flow across a system boundary that is caused by a temperature difference between the system and the surroundings. Heat may be exchanged by conduction, convection, or radiation. Heat, as is work, is a path function. To evaluate heat transfer *quantitatively,* unless given a priori, you must apply the energy balance that is discussed in Sec. 4.5, evaluate all the terms except Q, and then solve for Q. Heat transfer can be *estimated* for engineering purposes by many empirical relations, which can be found in books treating heat transfer or transport processes. A typical relation to estimate the rate of heat transfer is that $\dot{Q}$ is proportional to the area for heat transfer and the temperature difference between the system at T_2 and its surroundings at T_1:

$$\dot{Q} = UA(T_2 - T_1)$$

where U is an empirical coefficient determined from experimental data.

Since heat and work are by definition mutually exclusive exchanges of energy between the system and the surroundings, we shall qualitatively classify work as energy that can be transferred to or from a mechanical state, or mode, of the system, while heat is the transfer of energy to atomic or molecular states, or modes, which are not macroscopically observable.

Kinetic energy. Kinetic energy (K) is the energy a system possesses because of its velocity relative to the surroundings at rest. Kinetic energy may be calculated from the relation

$$K = \tfrac{1}{2}mv^2 \tag{4.2a}$$

or

$$\hat{K} = \tfrac{1}{2}v^2 \tag{4.2b}$$

where the superscript caret (ˆ) refers to the energy per unit mass (or sometimes per mole) and not the total kinetic energy as in Eq. (4.2a).

EXAMPLE 4.2 Calculation of Kinetic Energy

Water is pumped from a storage tank into a tube of 3.00 cm inner diameter at the rate of 0.001 m³/s. See Fig. E4.2. What is the specific kinetic energy of the water?

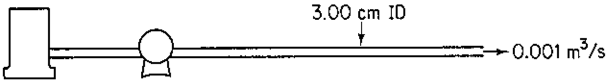


Figure E4.2

Solution

Assume that $\rho = \dfrac{1000\ \text{kg}}{\text{m}^3}$ $\qquad r = \tfrac{1}{2}(3.00) = 1.50\ \text{cm}$

$$v = \left.\frac{0.001\ \text{m}^3}{\text{s}}\right|\left.\frac{}{\pi(1.50)^2\ \text{cm}^2}\right|\left(\frac{100\ \text{cm}}{1\ \text{m}}\right)^2 = 1.415\ \text{m/s}$$

$$\hat{K} = \left.\frac{1}{2}\right|\left.\left(\frac{1.415\ \text{m}}{\text{s}}\right)^2\right|\left.\frac{1\ \text{N}}{1\ \dfrac{(\text{kg})(\text{m})}{\text{s}^2}}\right|\frac{1\ \text{J}}{1(\text{N})(\text{m})} = 1.00\ \text{J/kg}$$

Potential energy. Potential energy (P) is energy the system possesses because of the body force exerted on its mass by a gravitational or electromagnetic field with respect to a reference surface. Potential energy for a gravitational field can be calculated from

$$P = mgh \tag{4.3a}$$

or

$$\hat{P} = gh \tag{4.3b}$$

where h is the distance from the reference surface and where the symbol (ˆ) again means potential energy per unit mass (or sometimes per mole).

EXAMPLE 4.3 Calculation of Potential Energy

Water is pumped from one reservoir to another 300 ft away, as shown in Fig. E4.3. The water level in the second reservoir is 40 ft above the water level of the first reservoir. What is the increase in specific potential energy of the water in Btu/lb_m?

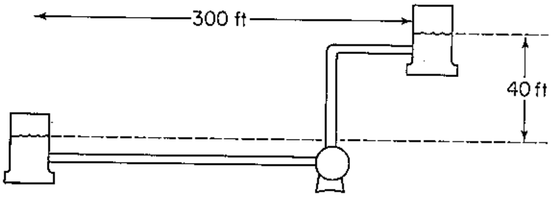


Figure E4.3

Solution

Let the water level in the first reservoir be the reference plane. Then $h = 40$ ft.

$$\hat{P} = \begin{array}{c|c|c|c} 32.2\text{ ft} & 40\text{ ft} & & 1\text{ Btu} \\ \hline \text{s}^2 & & \dfrac{32.2(\text{lb}_m)(\text{ft})}{(\text{lb}_f)(\text{s}^2)} & 778.2(\text{ft})(\text{lb}_f) \end{array} = 0.0514\text{ Btu/lb}_m$$

Internal energy. Internal energy (U) is a macroscopic measure of the molecular, atomic, and subatomic energies, all of which follow definite microscopic conservation rules for dynamic systems. Because no instruments exist with which to measure internal energy directly on a macroscopic scale, internal energy must be calculated from certain other variables that can be measured macroscopically, such as pressure, volume, temperature, and composition.

To calculate the internal energy per unit mass ($\hat{U}$) from the variables that can be measured, we make use of a special property of internal energy, namely, that it is an exact differential (because it is a *point* or *state* property, a matter to be described shortly) and, for a pure component, can be expressed in terms of just two intensive variables according to the phase rule for one phase:

$$F = C - \mathcal{P} + 2 = 1 - 1 + 2 = 2$$

Custom dictates the use of temperature and specific volume as the variables. If we say that $\hat{U}$ is a function of T and $\hat{V}$,

$$\hat{U} = \hat{U}(T, \hat{V})$$