TABLE 2.1 TYPES OF WORK

Types of Work	Variables	Equation for Work	Conventional Units
Volume expansion	Pressure (P), volume (V)	$w = -\int P_{external}\, dV$	Pa m^3 = J
Stretching	Force (F), length (l)	$w = -\int F\, dl$	N m = J
Surface expansion	Surface tension (γ), area (σ)	$w = -\int \gamma\, d\sigma$	(N m^{-1})(m^2) = J
Electrical	Electrical potential (ϕ), electrical charge (Q)	$w = \int \phi\, dQ$	V C = J

EXAMPLE PROBLEM 2.1

a. Calculate the work involved in expanding 20.0 L of an ideal gas to a final volume of 85.0 L against a constant external pressure of 2.50 bar.

b. A water bubble is expanded from a radius of 1.00 cm to a radius of 3.25 cm. The surface tension of water is 71.99 N m^{-1}. How much work is done in the process?

c. A current of 3.20 A is passed through a heating coil for 30.0 s. The electrical potential across the resistor is 14.5 V. Calculate the work done on the coil.

d. If the force to stretch a fiber a distance x is given by $F = -kx$ with $k = 100.\ \text{N cm}^{-1}$, how much work does it take to stretch the fiber 0.15 cm?

Solution

a. $$w = -\int P_{external}\, dV = -P_{external}(V_f - V_i)$$

$$= -2.50\ \text{bar} \times \frac{10^5\ \text{Pa}}{\text{bar}} \times (85.0\ \text{L} - 20.0\ \text{L}) \times \frac{10^{-3}\ \text{m}^3}{\text{L}} = -16.3\ \text{kJ}$$

b. A factor of 2 is included in the calculation below because a bubble has an inner and an outer surface:

$$w = -\int \gamma\, d\sigma = 2\gamma 4\pi(r_f^2 - r_i^2)$$

$$= -8\pi \times 71.99\ \text{N m}^{-1}(3.25^2\ \text{cm}^2 - 1.00^2\ \text{cm}^2) \times \frac{10^{-4}\ \text{m}^2}{\text{cm}^2}$$

$$= -1.73\ \text{J}$$

c. $$w = \int \phi\, dQ = \phi Q = I\phi t = 14.5\ \text{V} \times 3.20\ \text{A} \times 30.0\ \text{s} = 1.39\ \text{kJ}$$

d. Because the vectors **F** and **dl** point in opposite directions, $-\mathbf{F} \cdot d\mathbf{l} = Fdl$

$$w = -\int \mathbf{F} \cdot d\mathbf{l} = \int_{x_0}^{x_f} kx\, dx = \left[\frac{kx^2}{2}\right]_{x_0}^{x_f} = \left[\frac{100.\ \text{N m}^{-1} \times x^2}{2}\right]_0^{0.15} = 1.1\ \text{J}$$

2.3 HEAT

Heat[1] is defined in thermodynamics as the quantity of energy that flows across the boundary between the system and surroundings because of a temperature difference between the system and the surroundings. Heat always flows spontaneously from regions of high temperature to regions of low temperature. Just as for work, several important characteristics of heat are of importance:

- Heat is transitory, in that it only appears during a change in state of the system and surroundings. Only energy, and not heat, is associated with the initial and final states of the system and the surroundings.
- The net effect of heat is to change the internal energy of the system and surroundings in accordance with the first law. If the only change in the surroundings is a change in temperature of a reservoir, heat has flowed between system and surroundings. The quantity of heat that has flowed is directly proportional to the change in temperature of the reservoir.
- The sign convention for heat is as follows. If the temperature of the surroundings is lowered, q is positive; if it is raised, q is negative. It is common usage to say that if q is positive, heat is withdrawn from the surroundings and deposited in the system. If q is negative, heat is withdrawn from the system and deposited in the surroundings.

Defining the surroundings as the rest of the universe is impractical, because it is not realistic to search through the whole universe to see if a mass has been raised or lowered and if the temperature of a reservoir has changed. Experience shows that in general only those parts of the universe close to the system interact with the system. Experiments can be constructed to ensure that this is the case, as shown in Figure 2.3. Imagine that you are interested in an exothermic chemical reaction that is carried out in a rigid sealed container with diathermal walls. You define the system as consisting solely of the reactant and product mixture. The vessel containing the system is immersed in an inner water bath separated from an outer water bath by a container with rigid diathermal walls. During the reaction, heat flows out of the system ($q < 0$), and the temperature of the inner water bath increases to T_f. Using an electrical heater, the temperature of the outer water bath is increased so that at all times, $T_{outer} = T_{inner}$. Because of this condition, no heat flows across the boundary between the two water baths, and because the container enclosing the inner water bath is rigid, no work flows across this boundary. Therefore, $\Delta U = q + w = 0 + 0 = 0$ *for the composite system* made up of the inner water bath and everything within it. Therefore, this composite system is an isolated system that does not interact with the rest of the universe. To determine q and w for the reactant and product mixture, we need to examine only the composite system and can disregard the rest of the universe.

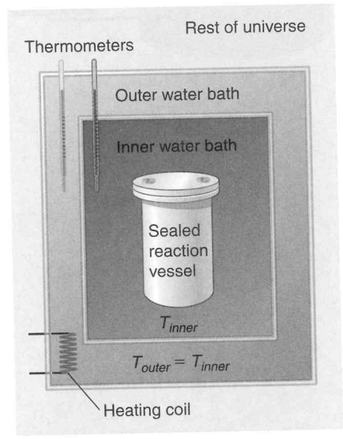

FIGURE 2.3
An isolated composite system is created in which the surroundings to the system of interest are limited in extent. The walls surrounding the inner water bath are rigid.

To emphasize the distinction between q and w, and the relationship between q, w, and ΔU, we discuss the two processes shown in Figure 2.4. They are carried out in an isolated system, divided into two subsystems, I and II. In both cases, system I consists solely of the liquid in the beaker, and everything else including the rigid adiabatic walls is in system II. We assume that the temperature of the liquid is well below its boiling point so that its vapor pressure is negligibly small. This ensures that no liquid is vaporized in the process, and both systems can be viewed as closed. We also assume that the change in temperature of system I is very small. System II can be viewed as the surroundings for system I and vice versa.

[1]Heat is perhaps the most misused term in thermodynamics as discussed by Robert Romer [*American Journal of Physics*, 69 (2001), 107–109]. In common usage, it is incorrectly referred to as a substance as in the phrase "Close the door; you're letting the heat out!" An equally inappropriate term is heat capacity (discussed in Section 2.4), because it implies that materials have the capacity to hold heat, rather than the capacity to store energy. We use the terms *heat flow* or *heat transfer* to emphasize the transitory nature of heat. However, you should not think of heat as a fluid or a substance.