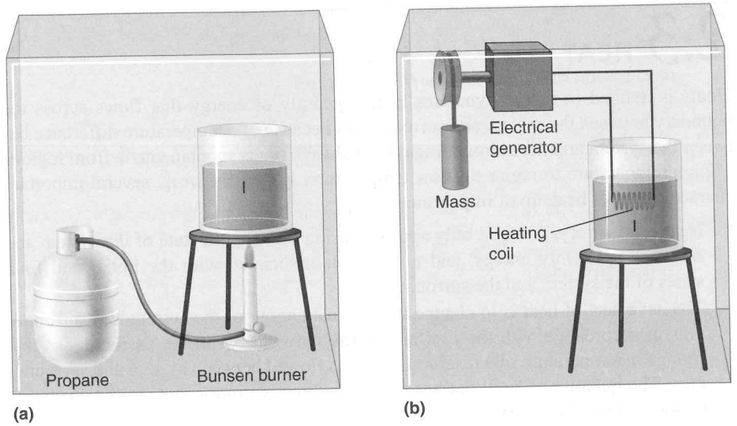


FIGURE 2.4
Two systems, I and II, are enclosed in a rigid adiabatic enclosure. System I consists solely of the liquid in the beaker for each case. System II consists of everything else in the enclosure. **(a)** Process in which the liquid is heated using a flame. **(b)** Heating using a resistive coil through which an electrical current flows.

In Figure 2.4a, a Bunsen burner fueled by a propane canister is used to heat the liquid (system I). The boundary between systems I and II is the surface that encloses the liquid, and heat can flow between systems I and II all across this wall. It is observed that $\Delta T_{\mathrm{I}} > 0$. From general chemistry, we know that the internal energy of a monatomic gas increases linearly with T. This result can be generalized to state that U is a monotonically increasing function of T for a uniform single-phase system of constant composition. Therefore, because $\Delta T_{\mathrm{I}} > 0$, $\Delta U_{\mathrm{I}} > 0$.

We next consider the changes in system II. From the first law, $\Delta U_{\mathrm{II}} = -\Delta U_{\mathrm{I}} < 0$. No weights in system II have been lowered as a result of the process, and the volume of both systems has remained constant. We conclude that $w_{\mathrm{I}} = w_{\mathrm{II}} = 0$. Therefore, if $\Delta U_{\mathrm{I}} > 0$, $q_{\mathrm{I}} > 0$ and $q_{\mathrm{II}} = -q_{\mathrm{I}} < 0$. Is $\Delta U_{\mathrm{II}} < 0$ consistent with $\Delta T_{\mathrm{I}} = \Delta T_{\mathrm{II}} > 0$?

We now consider Figure 2.4b. In this case, the boundary between systems I and II lies just inside the inner wall of the beaker, passes across the open top of the beaker, and just outside of the surface of the heating coil. Note that the heating coil is entirely in system II. Heat can flow between systems I and II across the boundary surface. Upon letting the mass in system II fall, electricity flows through the heating coil. It is our experience that the temperature of the liquid (system I) will increase. We again conclude that $\Delta U_{\mathrm{I}} > 0$. What values do q_{I} and w_{I} have for the process?

To answer this question, consider the changes in system II of this composite system. From the first law, $\Delta U_{\mathrm{II}} = -\Delta U_{\mathrm{I}} < 0$. We see that a mass has been lowered in system II, so $w_{\mathrm{II}} < 0$. Can we conclude that $w_{\mathrm{I}} > 0$? The lowering of the mass in system II shows that $w_{\mathrm{II}} < 0$, *but it is being done only on the heating coil, which is also in system* II *because the current flow never crosses the boundary between systems I and II.* No weight changes its height in system I and the volume is constant. Therefore, $w_{\mathrm{I}} = 0$. However, $\Delta U_{\mathrm{I}} > 0$, so we conclude that $q_{\mathrm{I}} > 0$. The increase in U_{I} is due to heat flow from system II to system I caused by the difference between the temperature of the heating filament and the liquid and not by the electrical work done on the filament. Note that because $\Delta U_{\mathrm{I}} + \Delta U_{\mathrm{II}} = 0$, the heat flow from system II to system I can be calculated from the electrical work done entirely within system II, $q_{\mathrm{I}} = -w_{\mathrm{II}} = I\phi t$. Is $\Delta U_{\mathrm{II}} < 0$ consistent with $\Delta T_{\mathrm{I}} = \Delta T_{\mathrm{II}} > 0$?

These examples show that the distinction between heat and work must be made carefully with a clear knowledge of the position and nature of the boundary between the system and the surroundings.

EXAMPLE PROBLEM 2.2

A heating coil is immersed in a 100.-g sample of H_2O liquid at 100.°C in an open insulated beaker on a laboratory bench at 1 bar pressure. In this process, 10.0% of the liquid is converted to the gaseous form at a pressure of 1 bar. A current of 2.00 A flows through the heater from a 12.0-V battery for 1.00×10^3 s to effect the transformation. The densities of liquid and gaseous water under these conditions are 997 and 0.590 kg m^{-3}, respectively.

a. It is often useful to replace a real process by a model that exhibits the important features of the process. Design a model system and surroundings, like those shown in Figures 2.1 and 2.2, that would allow you to measure the heat and work associated with this transformation. For the model system, define the system and surroundings as well as the boundary between them.

b. Calculate q and w for the process.

c. How can you define the system for the open insulated beaker on the laboratory bench such that the work is properly described?

Solution

a. The model system is shown in the figure to the right. The cylinder walls and the piston form adiabatic walls. The external pressure is held constant by a suitable weight.

b. In the system shown, the heat input to the liquid water can be equated with the work done on the heating coil. Therefore,

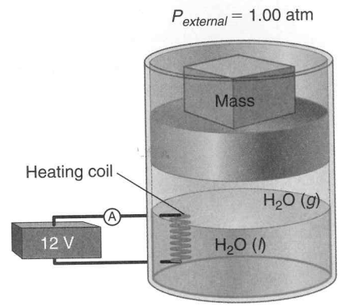
$$q = I\phi t = 2.00\ \mathrm{A} \times 12.0\ \mathrm{V} \times 1.00 \times 10^3\ \mathrm{s} = 24.0\ \mathrm{kJ}$$

As the liquid is vaporized, the volume of the system increases at a constant external pressure. Therefore, the work done by the system on the surroundings is

$$w = -P_{external}(V_f - V_i) = -10^5\ \mathrm{Pa} \times \left(\frac{10.0 \times 10^{-3}\ \mathrm{kg}}{0.590\ \mathrm{kg\,m^{-3}}} + \frac{90.0 \times 10^{-3}\ \mathrm{kg}}{997\ \mathrm{kg\,m^{-3}}} - \frac{100.0 \times 10^{-3}\ \mathrm{kg}}{997\ \mathrm{kg\,m^{-3}}} \right) = -1.70\ \mathrm{kJ}$$

Note that the electrical work done on the heating coil is much larger than the P–V work done in the expansion.

c. Define the system as the liquid in the beaker and the volume containing only molecules of H_2O in the gas phase. This volume will consist of disconnected volume elements dispersed in the air above the laboratory bench.



2.4 HEAT CAPACITY

The process shown in Figure 2.4 provides a way to quantify heat flow in terms of the easily measured electrical work done on the heating coil, $w = I\phi t$. The response of a single-phase system of constant composition to heat input is an increase in T. This is not the case if the system undergoes a phase change, such as the vaporization of a liquid. The temperature of an equilibrium mixture of liquid and gas at the boiling point remains constant as heat flows into the system. However, the mass of the gas phase increases at the expense of the liquid phase.

The response of the system to heat flow is described by a very important thermodynamic property called the **heat capacity**, which is a measure of the amount of heat needed to change the temperature of a substance by a given amount. Heat capacity is a material-dependent property; as will be discussed in Section 3.2. Mathematically, heat capacity is defined by the relation

$$C = \lim_{\Delta T \to 0} \frac{q}{T_f - T_i} = \frac{dq}{dT} \tag{2.9}$$