

Table 18-4 Some Heats of Transformation

Substance	Melting		Boiling	
	Melting Point (K)	Heat of Fusion L_F (kJ/kg)	Boiling Point (K)	Heat of Vaporization L_V (kJ/kg)
Hydrogen	14.0	58.0	20.3	455
Oxygen	54.8	13.9	90.2	213
Mercury	234	11.4	630	296
Water	273	333	373	2256
Lead	601	23.2	2017	858
Silver	1235	105	2323	2336
Copper	1356	207	2868	4730

Vaporizing. To *vaporize* a liquid means to change it from the liquid state to the vapor (gas) state. This process, like melting, requires energy because the molecules must be freed from their clusters. Boiling liquid water to transfer it to water vapor (or steam—a gas of individual water molecules) is a common example. *Condensing* a gas to form a liquid is the reverse of vaporizing; it requires that energy be removed from the gas, so that the molecules can cluster instead of flying away from one another.

The amount of energy per unit mass that must be transferred as heat when a sample completely undergoes a phase change is called the **heat of transformation** L . Thus, when a sample of mass m completely undergoes a phase change, the total energy transferred is

$$Q = Lm. \quad (18-16)$$

When the phase change is from liquid to gas (then the sample must absorb heat) or from gas to liquid (then the sample must release heat), the heat of transformation is called the **heat of vaporization** L_V . For water at its normal boiling or condensation temperature,

$$L_V = 539 \text{ cal/g} = 40.7 \text{ kJ/mol} = 2256 \text{ kJ/kg}. \quad (18-17)$$

When the phase change is from solid to liquid (then the sample must absorb heat) or from liquid to solid (then the sample must release heat), the heat of transformation is called the **heat of fusion** L_F . For water at its normal freezing or melting temperature,

$$L_F = 79.5 \text{ cal/g} = 6.01 \text{ kJ/mol} = 333 \text{ kJ/kg}. \quad (18-18)$$

Table 18-4 shows the heats of transformation for some substances.



Sample Problem 18.03 Hot slug in water, coming to equilibrium

A copper slug whose mass m_c is 75 g is heated in a laboratory oven to a temperature T of 312°C. The slug is then dropped into a glass beaker containing a mass $m_w = 220$ g of water. The heat capacity C_b of the beaker is 45 cal/K. The initial temperature T_i of the water and the beaker is 12°C. Assuming that the slug, beaker, and water are an isolated system and the water does not vaporize, find the final temperature T_f of the system at thermal equilibrium.

KEY IDEAS

(1) Because the system is isolated, the system's total energy cannot change and only internal transfers of thermal energy

can occur. (2) Because nothing in the system undergoes a phase change, the thermal energy transfers can only change the temperatures.

Calculations: To relate the transfers to the temperature changes, we can use Eqs. 18-13 and 18-14 to write

$$\text{for the water: } Q_w = c_w m_w (T_f - T_i); \quad (18-19)$$

$$\text{for the beaker: } Q_b = C_b (T_f - T_i); \quad (18-20)$$

$$\text{for the copper: } Q_c = c_c m_c (T_f - T). \quad (18-21)$$

Because the total energy of the system cannot change, the sum of these three energy transfers is zero:

$$Q_w + Q_b + Q_c = 0. \quad (18-22)$$

Substituting Eqs. 18-19 through 18-21 into Eq. 18-22 yields

$$c_w m_w (T_f - T_i) + C_b (T_f - T_i) + c_c m_c (T_f - T) = 0. \quad (18-23)$$

Temperatures are contained in Eq. 18-23 only as differences. Thus, because the differences on the Celsius and Kelvin scales are identical, we can use either of those scales in this equation. Solving it for T_f , we obtain

$$T_f = \frac{c_c m_c T + C_b T_i + c_w m_w T_i}{c_w m_w + C_b + c_c m_c}.$$

Using Celsius temperatures and taking values for c_c and c_w from Table 18-3, we find the numerator to be

$$(0.0923 \text{ cal/g} \cdot \text{K})(75 \text{ g})(312^\circ\text{C}) + (45 \text{ cal/K})(12^\circ\text{C}) \\ + (1.00 \text{ cal/g} \cdot \text{K})(220 \text{ g})(12^\circ\text{C}) = 5339.8 \text{ cal},$$

and the denominator to be

$$(1.00 \text{ cal/g} \cdot \text{K})(220 \text{ g}) + 45 \text{ cal/K} \\ + (0.0923 \text{ cal/g} \cdot \text{K})(75 \text{ g}) = 271.9 \text{ cal/}^\circ\text{C}.$$

We then have

$$T_f = \frac{5339.8 \text{ cal}}{271.9 \text{ cal/}^\circ\text{C}} = 19.6^\circ\text{C} \approx 20^\circ\text{C}. \quad (\text{Answer})$$

From the given data you can show that

$$Q_w \approx 1670 \text{ cal}, \quad Q_b \approx 342 \text{ cal}, \quad Q_c \approx -2020 \text{ cal}.$$

Apart from rounding errors, the algebraic sum of these three heat transfers is indeed zero, as required by the conservation of energy (Eq. 18-22).

Sample Problem 18.04 Heat to change temperature and state

(a) How much heat must be absorbed by ice of mass $m = 720 \text{ g}$ at -10°C to take it to the liquid state at 15°C ?



KEY IDEAS

The heating process is accomplished in three steps: (1) The ice cannot melt at a temperature below the freezing point—so initially, any energy transferred to the ice as heat can only increase the temperature of the ice, until 0°C is reached. (2) The temperature then cannot increase until all the ice melts—so any energy transferred to the ice as heat now can only change ice to liquid water, until all the ice melts. (3) Now the energy transferred to the liquid water as heat can only increase the temperature of the liquid water.

Warming the ice: The heat Q_1 needed to take the ice from the initial $T_i = -10^\circ\text{C}$ to the final $T_f = 0^\circ\text{C}$ (so that the ice can then melt) is given by Eq. 18-14 ($Q = cm \Delta T$). Using the specific heat of ice c_{ice} in Table 18-3 gives us

$$Q_1 = c_{\text{ice}} m (T_f - T_i) \\ = (2220 \text{ J/kg} \cdot \text{K})(0.720 \text{ kg})[0^\circ\text{C} - (-10^\circ\text{C})] \\ = 15\,984 \text{ J} \approx 15.98 \text{ kJ}.$$

Melting the ice: The heat Q_2 needed to melt all the ice is given by Eq. 18-16 ($Q = Lm$). Here L is the heat of fusion L_F , with the value given in Eq. 18-18 and Table 18-4. We find

$$Q_2 = L_F m = (333 \text{ kJ/kg})(0.720 \text{ kg}) \approx 239.8 \text{ kJ}.$$

Warming the liquid: The heat Q_3 needed to increase the temperature of the water from the initial value $T_i = 0^\circ\text{C}$ to the final value $T_f = 15^\circ\text{C}$ is given by Eq. 18-14 (with the specific heat of liquid water c_{liq}):

$$Q_3 = c_{\text{liq}} m (T_f - T_i) \\ = (4186.8 \text{ J/kg} \cdot \text{K})(0.720 \text{ kg})(15^\circ\text{C} - 0^\circ\text{C}) \\ = 45\,217 \text{ J} \approx 45.22 \text{ kJ}.$$

Total: The total required heat Q_{tot} is the sum of the amounts required in the three steps:

$$Q_{\text{tot}} = Q_1 + Q_2 + Q_3 \\ = 15.98 \text{ kJ} + 239.8 \text{ kJ} + 45.22 \text{ kJ} \\ \approx 300 \text{ kJ}. \quad (\text{Answer})$$

Note that most of the energy goes into melting the ice rather than raising the temperature.

(b) If we supply the ice with a total energy of only 210 kJ (as heat), what are the final state and temperature of the water?

KEY IDEA

From step 1, we know that 15.98 kJ is needed to raise the temperature of the ice to the melting point. The remaining heat Q_{rem} is then $210 \text{ kJ} - 15.98 \text{ kJ}$, or about 194 kJ. From step 2, we can see that this amount of heat is insufficient to melt all the ice. Because the melting of the ice is incomplete, we must end up with a mixture of ice and liquid; the temperature of the mixture must be the freezing point, 0°C .

Calculations: We can find the mass m of ice that is melted by the available energy Q_{rem} by using Eq. 18-16 with L_F :

$$m = \frac{Q_{\text{rem}}}{L_F} = \frac{194 \text{ kJ}}{333 \text{ kJ/kg}} = 0.583 \text{ kg} \approx 580 \text{ g}.$$

Thus, the mass of the ice that remains is $720 \text{ g} - 580 \text{ g}$, or 140 g, and we have

$$580 \text{ g water} \quad \text{and} \quad 140 \text{ g ice}, \quad \text{at } 0^\circ\text{C}. \quad (\text{Answer})$$



18-5 THE FIRST LAW OF THERMODYNAMICS

Learning Objectives

After reading this module, you should be able to . . .

- 18.20** If an enclosed gas expands or contracts, calculate the work W done by the gas by integrating the gas pressure with respect to the volume of the enclosure.
- 18.21** Identify the algebraic sign of work W associated with expansion and contraction of a gas.
- 18.22** Given a p - V graph of pressure versus volume for a process, identify the starting point (the initial state) and the final point (the final state) and calculate the work by using graphical integration.
- 18.23** On a p - V graph of pressure versus volume for a gas, identify the algebraic sign of the work associated with a right-going process and a left-going process.
- 18.24** Apply the first law of thermodynamics to relate the change in the internal energy ΔE_{int} of a gas, the energy Q transferred as heat to or from the gas, and the work W done on or by the gas.
- 18.25** Identify the algebraic sign of a heat transfer Q that is associated with a transfer to a gas and a transfer from the gas.
- 18.26** Identify that the internal energy ΔE_{int} of a gas tends to increase if the heat transfer is to the gas, and it tends to decrease if the gas does work on its environment.
- 18.27** Identify that in an adiabatic process with a gas, there is no heat transfer Q with the environment.
- 18.28** Identify that in a constant-volume process with a gas, there is no work W done by the gas.
- 18.29** Identify that in a cyclical process with a gas, there is no net change in the internal energy ΔE_{int} .
- 18.30** Identify that in a free expansion with a gas, the heat transfer Q , work done W , and change in internal energy ΔE_{int} are each zero.

✓✓ Key Ideas

- A gas may exchange energy with its surroundings through work. The amount of work W done by a gas as it expands or contracts from an initial volume V_i to a final volume V_f is given by

$$W = \int dW = \int_{V_i}^{V_f} p \, dV.$$

The integration is necessary because the pressure p may vary during the volume change.

- The principle of conservation of energy for a thermodynamic process is expressed in the first law of thermodynamics, which may assume either of the forms

$$\Delta E_{\text{int}} = E_{\text{int},f} - E_{\text{int},i} = Q - W \quad (\text{first law})$$

or
$$dE_{\text{int}} = dQ - dW \quad (\text{first law}).$$

E_{int} represents the internal energy of the material, which depends only on the material's state (temperature,

pressure, and volume). Q represents the energy exchanged as heat between the system and its surroundings; Q is positive if the system absorbs heat and negative if the system loses heat. W is the work done by the system; W is positive if the system expands against an external force from the surroundings and negative if the system contracts because of an external force.

- Q and W are path dependent; ΔE_{int} is path independent.
- The first law of thermodynamics finds application in several special cases:

adiabatic processes: $Q = 0, \quad \Delta E_{\text{int}} = -W$

constant-volume processes: $W = 0, \quad \Delta E_{\text{int}} = Q$

cyclical processes: $\Delta E_{\text{int}} = 0, \quad Q = W$

free expansions: $Q = W = \Delta E_{\text{int}} = 0$

A Closer Look at Heat and Work

Here we look in some detail at how energy can be transferred as heat and work between a system and its environment. Let us take as our system a gas confined to a cylinder with a movable piston, as in Fig. 18-13. The upward force on the piston due to the pressure of the confined gas is equal to the weight of lead shot loaded onto the top of the piston. The walls of the cylinder are made of insulating material that does not allow any transfer of energy as heat. The bottom of the cylinder rests on a reservoir for thermal energy, a *thermal reservoir* (perhaps a hot plate) whose temperature T you can control by turning a knob.

The system (the gas) starts from an *initial state* i , described by a pressure p_i , a volume V_i , and a temperature T_i . You want to change the system to a *final state* f , described by a pressure p_f , a volume V_f , and a temperature T_f . The procedure by which you change the system from its initial state to its final state is called a *thermodynamic process*. During such a process, energy may be trans-

ferred into the system from the thermal reservoir (positive heat) or vice versa (negative heat). Also, work can be done by the system to raise the loaded piston (positive work) or lower it (negative work). We assume that all such changes occur slowly, with the result that the system is always in (approximate) thermal equilibrium (every part is always in thermal equilibrium).

Suppose that you remove a few lead shot from the piston of Fig. 18-13, allowing the gas to push the piston and remaining shot upward through a differential displacement $d\vec{s}$ with an upward force \vec{F} . Since the displacement is tiny, we can assume that \vec{F} is constant during the displacement. Then \vec{F} has a magnitude that is equal to pA , where p is the pressure of the gas and A is the face area of the piston.

✓ The differential work dW done by the gas during the displacement is

$$dW = \vec{F} \cdot d\vec{s} = (pA)(ds) = p(A ds) = p dV, \tag{18-24}$$

in which dV is the differential change in the volume of the gas due to the movement of the piston. When you have removed enough shot to allow the gas to change its volume from V_i to V_f , the total work done by the gas is

✓

$$W = \int dW = \int_{V_i}^{V_f} p dV. \tag{18-25}$$

During the volume change, the pressure and temperature may also change. To evaluate Eq. 18-25 directly, we would need to know how pressure varies with volume for the actual process by which the system changes from state i to state f .

One Path. There are actually many ways to take the gas from state i to state f .

One way is shown in Fig. 18-14a, which is a plot of the pressure of the gas versus its volume and which is called a p - V diagram. In Fig. 18-14a, the curve indicates that the

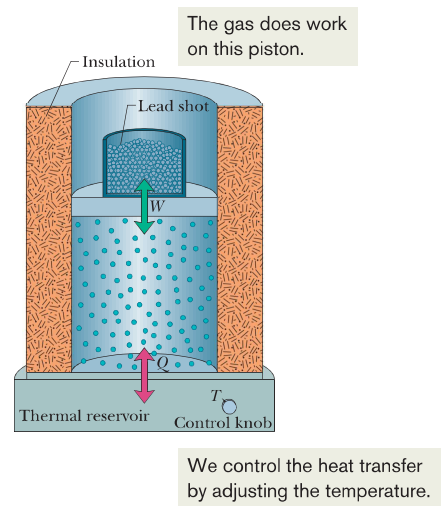


Figure 18-13 A gas is confined to a cylinder with a movable piston. Heat Q can be added to or withdrawn from the gas by regulating the temperature T of the adjustable thermal reservoir. Work W can be done by the gas by raising or lowering the piston.

✓ **Figure 18-14** (a) The shaded area represents the work W done by a system as it goes from an initial state i to a final state f . Work W is positive because the system's volume increases. (b) W is still positive, but now greater. (c) W is still positive, but now smaller. (d) W can be even smaller (path $icdf$) or larger (path $ighf$). (e) Here the system goes from state f to state i as the gas is compressed to less volume by an external force. The work W done by the system is now negative. (f) The net work W_{net} done by the system during a complete cycle is represented by the shaded area.

