Thermodynamics: An Engineering Approach

Chapter 4

ENERGY ANALYSIS OF CLOSED SYSTEMS

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Introduction

- In this chapter, we apply the energy balance relation to systems that do not involve any mass flow across their boundaries; that is, closed systems.

- We start this chapter with a discussion of the moving boundary work or P dV work commonly encountered in reciprocating devices such as automotive engines and compressors.

- We continue by applying the general energy balance relation, which is simply expressed as $E_{in}-E_{out} = \Delta E_{system}$, to systems that involve pure substance.

- Then we define specific heats, obtain relations for the internal energy and enthalpy of ideal gases in terms of specific heats and temperature changes, and perform energy balances on various systems that involve ideal gases.

- We repeat this for systems that involve solids and liquids, which are approximated as incompressible substances.

Objectives

The objectives of Chapter 4 are to:

- Examine the moving boundary work or P dV work commonly encountered in reciprocating devices such as automotive engines and compressors.
- Identify the first law of thermodynamics as simply a statement of the conservation of energy principle for closed (fixed mass) systems.
- Develop the general energy balance applied to closed systems.
- Define the specific heat at constant volume and the specific heat at constant pressure.
- Relate the specific heats to the calculation of the changes in internal energy and enthalpy of ideal gases.
- Describe incompressible substances and determine the changes in their internal energy and enthalpy.
- Solve energy balance problems for closed (fixed mass) systems that involve heat and work interactions for general pure substances, ideal gases, and incompressible substances.

MOVING BOUNDARY WORK

- One form of mechanical work frequently encountered in practice is associated with the expansion or compression of a gas in a piston–cylinder device.

- During this process, part of the boundary (the inner face of the piston) moves back and forth. Therefore, the expansion and compression work is often called **moving boundary work,** or simply **boundary work** (Fig. 4–1).

- Some call it the *P dV* work for reasons explained later. Moving boundary work is the primary form of work involved in *automobile engines*. During their expansion, the combustion gases force the piston to move, which in turn forces the crankshaft to rotate.

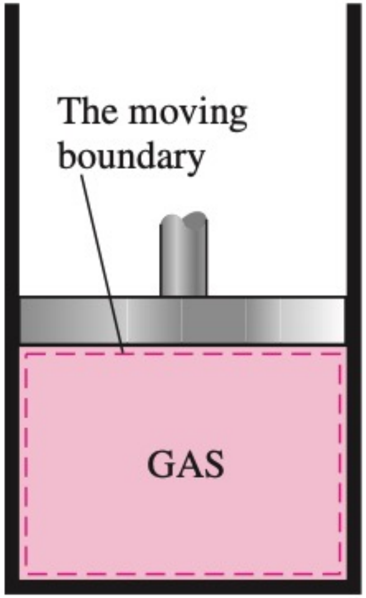


FIGURE 4–1

The work associated with a moving boundary is called *boundary work.*

- The moving boundary work associated with real engines or compressors cannot be determined exactly from a thermodynamic analysis alone because the piston usually moves at very high speeds, making it difficult for the gas inside to maintain equilibrium.

- Then the states through which the system passes during the process cannot be specified, and no process path can be drawn. Work, being a path function, cannot be determined analytically with- out a knowledge of the path. Therefore, the boundary work in real engines or compressors is determined by direct measurements.

- In this section, we analyze the moving boundary work for a *quasi- equilibrium process*, a process during which the system remains nearly in equilibrium at all times.

- A quasi-equilibrium process, also called a *quasi- static process*, is closely approximated by real engines, especially when the piston moves at low velocities.

- Under identical conditions, the work output of the engines is found to be a maximum, and the work input to the compressors to be a minimum when quasi-equilibrium processes are used in place of nonquasi-equilibrium processes. Below, the work associated with a moving boundary is evaluated for a quasi-equilibrium process.

Consider the gas enclosed in the piston cylinder device shown in Fig. 4–2. The initial pressure of the gas is P, the total volume is V, and the cross- sectional area of the piston is A. If the piston is allowed to move a distance *ds* in a quasi-equilibrium manner, the differential work done during this process is

$$\delta W_b = F\,ds = PA\,ds = P\,dV$$

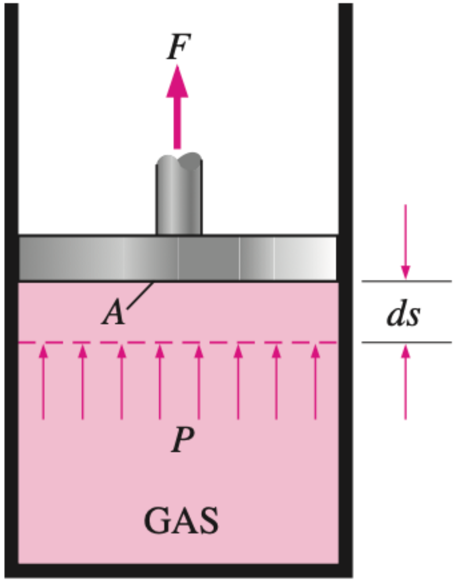


FIGURE 4–2

A gas does a differential amount of work δW_b as it forces the piston to move by a differential amount *ds*.

- That is, the boundary work in the differential form is equal to the product of the absolute pressure P and the differential change in the volume dV of the system.

- This expression also explains why the moving boundary work is sometimes called the $P\,dV$ work. Note in Eq. 4–1 that P is the absolute pressure, which is always positive.

- However, the volume change dV is positive during an expansion process (volume increasing) and negative during a compression process (volume decreasing).

- Thus, the boundary work is positive during an expansion process and negative during a compression process.

- Therefore, Eq. 4–1 can be viewed as an expression for boundary work output, $W_{b,\text{out}}$. A negative result indicates boundary work input (compression).

- The total boundary work done during the entire process as the piston moves is obtained by adding all the differential works from the initial state to the final state:

$$W_b = \int_1^2 P\,dV \qquad \text{(kJ)}$$

- This integral can be evaluated only if we know the functional relationship between *P* and V during the process. That is, *P* = *f*(V) should be available. Note that *P* = *f* (V) is simply the equation of the process path on a *P*-V diagram.

- The quasi-equilibrium expansion process described is shown on a P-V diagram in Fig. 4–3. On this diagram, the differential area dA is equal to $P\,dV$, which is the differential work. The total area A under the process curve 1–2 is obtained by adding these differential areas:

$$\text{Area} = A = \int_1^2 dA = \int_1^2 P\,dV$$

A comparison of this equation with Eq. 4–2 reveals that *the area under the process curve on a P-V diagram is equal, in magnitude, to the work done during a quasi-equilibrium expansion or compression process of a closed system*. (On the P-v diagram, it represents the boundary work done per unit mass.)

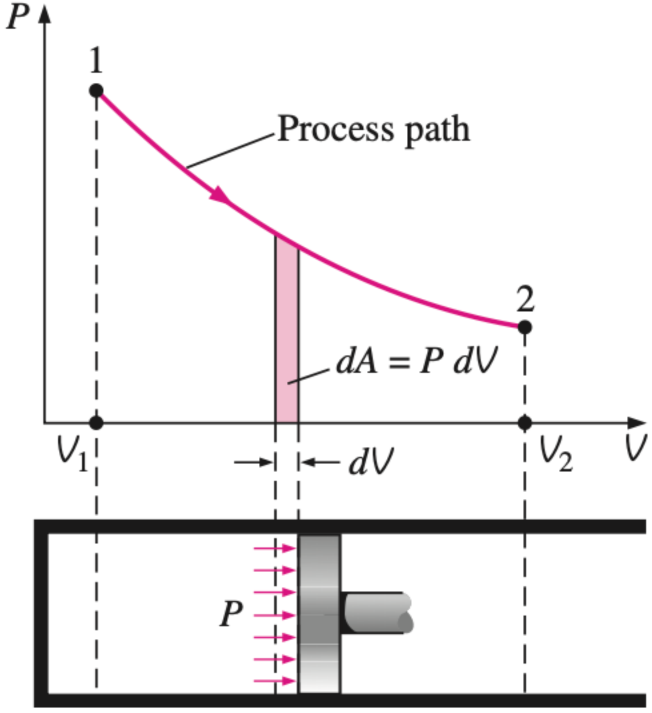


FIGURE 4–3

The area under the process curve on a P-V diagram represents the boundary work.

- A gas can follow several different paths as it expands from state 1 to state 2. In general, each path will have a different area underneath it, and since this area represents the magnitude of the work, the work done will be different for each process (Fig. 4–4).

- This is expected, since work is a path function (i.e., it depends on the path followed as well as the end states). If work were not a path function, no cyclic devices (car engines, power plants) could operate as work-producing devices.

- The work produced by these devices during one part of the cycle would have to be consumed during another part, and there would be no net work output.

- The cycle shown in Fig. 4–5 produces a net work output because the work done by the system during the expansion process (area under path *A*) is greater than the work done on the system during the compression part of the cycle (area under path *B*), and the difference between these two is the net work done during the cycle (the colored area).

- If the relationship between *P* and V during an expansion or a compression process is given in terms of experimental data instead of in a functional form, obviously we cannot perform the integration analytically.

- But we can always plot the *P*-V diagram of the process, using these data points, and cal- culate the area underneath graphically to determine the work done.

- Strictly speaking, the pressure *P* in Eq. 4–2 is the pressure at the inner surface of the piston. It becomes equal to the pressure of the gas in the cylinder only if the process is quasi-equilibrium and thus the entire gas in the cylinder is at the same pressure at any given time.

- Equation 4–2 can also be used for nonquasi-equilibrium processes provided that the pressure *at the inner face of the piston* is used for *P*. (Besides, we cannot speak of the pressure of a *system* during a nonquasi-equilibrium process since prop- erties are defined for equilibrium states only.)

- Therefore, we can generalize the boundary work relation by expressing it as

$$W_b = \int_1^2 P_i \, dV$$

where *Pi* is the pressure at the inner face of the piston.

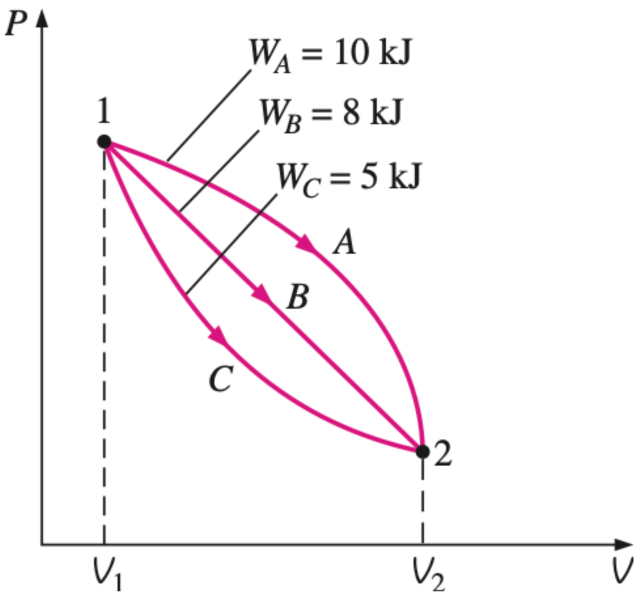


FIGURE 4–4

The boundary work done during a process depends on the path followed as well as the end states.

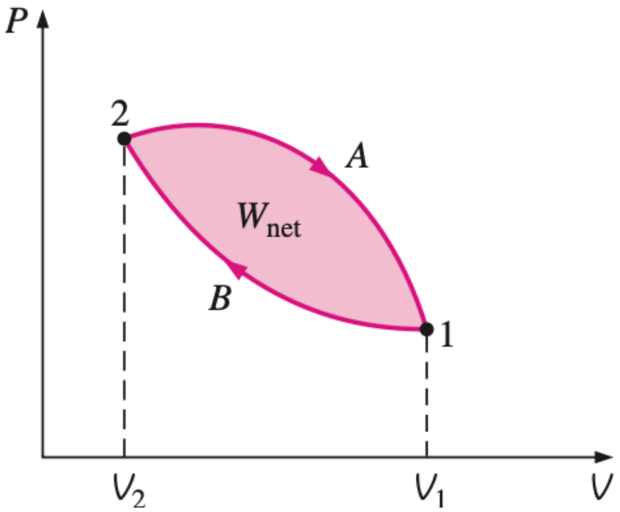


FIGURE 4–5

The net work done during a cycle is the difference between the work done by the system and the work done on the system.

- Note that work is a mechanism for energy interaction between a system and its surroundings, and *Wb* represents the amount of energy transferred from the system during an expansion process (or to the system during a compression process).

- Therefore, it has to appear somewhere else and we must be able to account for it since energy is conserved. In a car engine, for example, the boundary work done by the expanding hot gases is used to overcome friction between the piston and the cylinder, to push atmospheric air out of the way, and to rotate the crankshaft. Therefore

$$W_b = W_{\text{friction}} + W_{\text{atm}} + W_{\text{crank}} = \int_1^2 \left(F_{\text{friction}} + P_{\text{atm}}A + F_{\text{crank}}\right) dx$$

- Of course, the work used to overcome friction appears as frictional heat and the energy transmitted through the crankshaft is transmitted to other components (such as the wheels) to perform certain functions.

- But note that the energy transferred by the system as work must equal the energy received by the crankshaft, the atmosphere, and the energy used to overcome friction.

- The use of the boundary work relation is not limited to the quasi-equilibrium processes of gases only. It can also be used for solids and liquids.

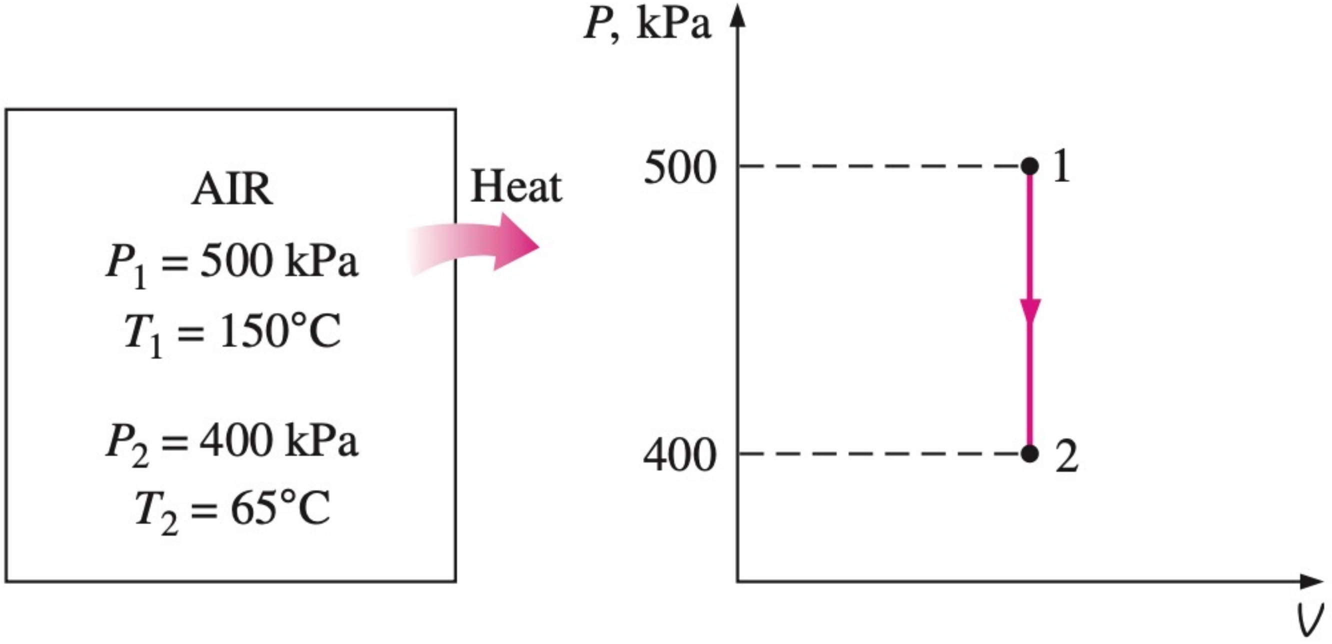
EXAMPLE 4–1 Boundary Work for a Constant-Volume Process

A rigid tank contains air at 500 kPa and 150°C. As a result of heat transfer to the surroundings, the temperature and pressure inside the tank drop to 65°C and 400 kPa, respectively. Determine the boundary work done during this process.

Solution Air in a rigid tank is cooled, and both the pressure and temperature drop. The boundary work done is to be determined.
Analysis A sketch of the system and the *P*-*V* diagram of the process are shown in Fig. 4–6. The boundary work can be determined from Eq. 4–2 to be

$$W_b = \int_1^2 P \, \cancelto{0}{dV} = \mathbf{0}$$

Discussion This is expected since a rigid tank has a constant volume and $dV = 0$ in this equation. Therefore, there is no boundary work done during this process. That is, the boundary work done during a constant-volume process is always zero. This is also evident from the *P*-*V* diagram of the process (the area under the process curve is zero).


AIR
$P_1 = 500$ kPa
$T_1 = 150°C$
$P_2 = 400$ kPa
$T_2 = 65°C$
Heat
P, kPa
500
400
1
2
V

EXAMPLE 4–2 Boundary Work for a Constant-Pressure Process

A frictionless piston–cylinder device contains 10 lbm of steam at 60 psia and 320°F. Heat is now transferred to the steam until the temperature reaches 400°F. If the piston is not attached to a shaft and its mass is constant, determine the work done by the steam during this process.

Solution Steam in a piston cylinder device is heated and the temperature rises at constant pressure. The boundary work done is to be determined.
Analysis A sketch of the system and the *P*-*v* diagram of the process are shown in Fig. 4–7.
Assumption The expansion process is quasi-equilibrium.
Analysis Even though it is not explicitly stated, the pressure of the steam within the cylinder remains constant during this process since both the atmospheric pressure and the weight of the piston remain constant. Therefore, this is a constant-pressure process, and, from Eq. 4–2

$$W_b = \int_1^2 P\,dV = P_0 \int_1^2 dV = P_0(V_2 - V_1) \tag{4–6}$$

or

$$W_b = mP_0(v_2 - v_1)$$

since $V = mv$. From the superheated vapor table (Table A–6E), the specific volumes are determined to be $v_1 = 7.4863$ ft³/lbm at state 1 (60 psia, 320°F) and $v_2 = 8.3548$ ft³/lbm at state 2 (60 psia, 400°F). Substituting these values yields

$$W_b = (10\text{ lbm})(60\text{ psia})[(8.3548 - 7.4863)\text{ ft}^3/\text{lbm}]\left(\frac{1\text{ Btu}}{5.404\text{ psia}\cdot\text{ft}^3}\right)$$

$$= \mathbf{96.4\ Btu}$$

Discussion The positive sign indicates that the work is done by the system. That is, the steam used 96.4 Btu of its energy to do this work. The magnitude of this work could also be determined by calculating the area under the process curve on the *P*-*V* diagram, which is simply $P_0\,\Delta V$ for this case.

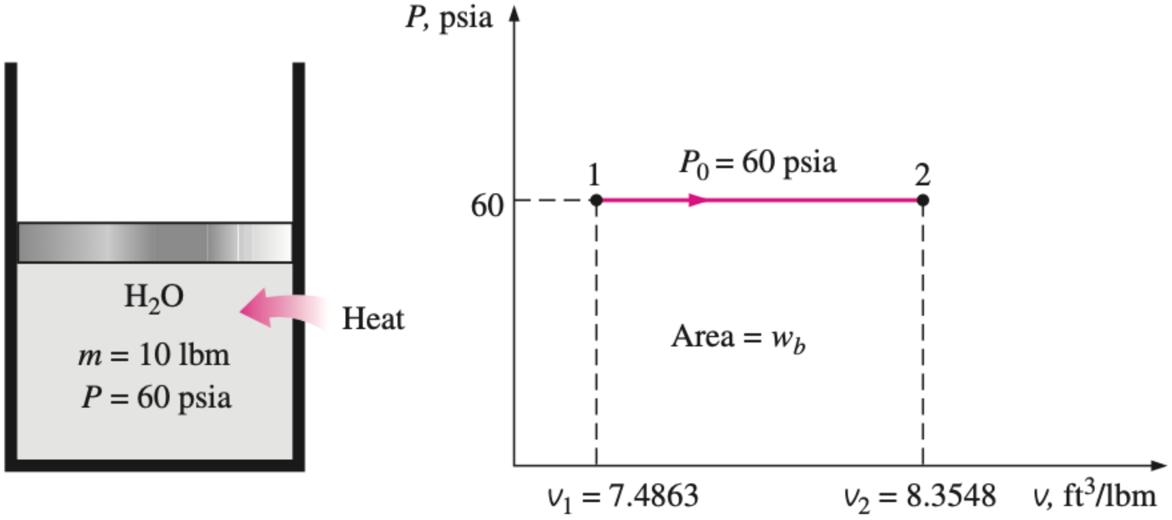


FIGURE 4–7

Schematic and P-v diagram for Example 4–2.

EXAMPLE 4–3 Isothermal Compression of an Ideal Gas

A piston–cylinder device initially contains 0.4 m^3 of air at 100 kPa and 80°C. The air is now compressed to 0.1 m^3 in such a way that the temperature inside the cylinder remains constant. Determine the work done during this process.

Solution Air in a piston–cylinder device is compressed isothermally. The boundary work done is to be determined.

Analysis A sketch of the system and the *P*-*V* diagram of the process are shown in Fig. 4–8.

Assumptions **1** The compression process is quasi-equilibrium. **2** At specified conditions, air can be considered to be an ideal gas since it is at a high temperature and low pressure relative to its critical-point values.

Analysis For an ideal gas at constant temperature T_0,

$$PV = mRT_0 = C \quad \text{or} \quad P = \frac{C}{V}$$

where *C* is a constant. Substituting this into Eq. 4–2, we have

$$W_b = \int_1^2 P\,dV = \int_1^2 \frac{C}{V}\,dV = C\int_1^2 \frac{dV}{V} = C\ \ln\frac{V_2}{V_1} = P_1V_1\ \ln\frac{V_2}{V_1} \qquad \textbf{(4–7)}$$

In Eq. 4–7, P_1V_1 can be replaced by P_2V_2 or mRT_0. Also, V_2/V_1 can be replaced by P_1/P_2 for this case since $P_1V_1 = P_2V_2$.

Substituting the numerical values into Eq. 4–7 yields

$$W_b = (100\text{ kPa})(0.4\text{ m}^3)\left(\ln\frac{0.1}{0.4}\right)\left(\frac{1\text{ kJ}}{1\text{ kPa}\cdot\text{m}^3}\right)$$

$$= \mathbf{-55.5\ kJ}$$

Discussion The negative sign indicates that this work is done on the system (a work input), which is always the case for compression processes.

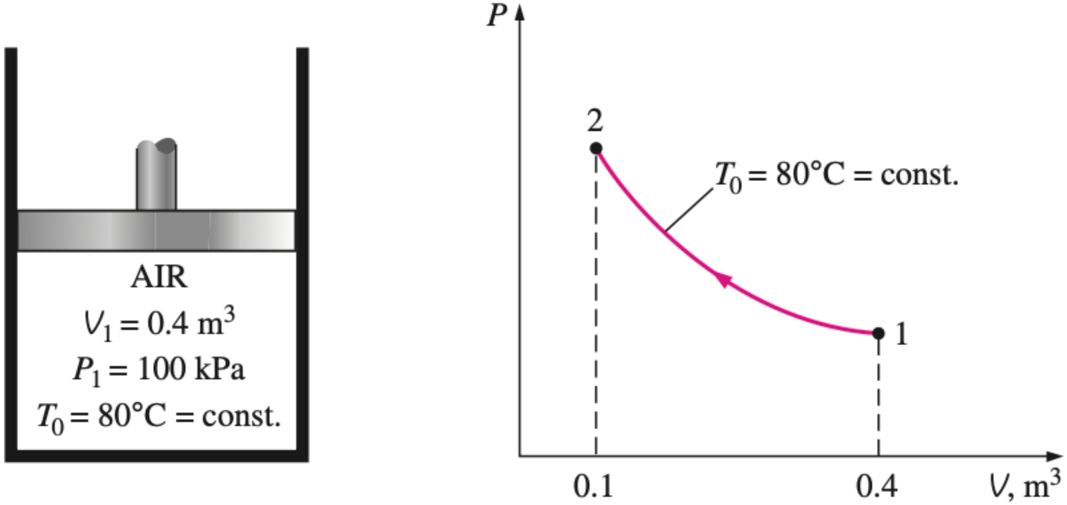


FIGURE 4–8

Schematic and *P*-*V* diagram for Example 4–3.

Polytropic Process

During actual expansion and compression processes of gases, pressure and volume are often related by $PV^n = C$, where n and C are constants. A process of this kind is called a **polytropic process** (Fig. 4–9). Below we develop a general expression for the work done during a polytropic process. The pressure for a polytropic process can be expressed as

$$P = CV^{-n} \tag{4–8}$$

Substituting this relation into Eq. 4–2, we obtain

$$W_b = \int_1^2 P\,dV = \int_1^2 CV^{-n}\,dV = C\frac{V_2^{-n+1} - V_1^{-n+1}}{-n+1} = \frac{P_2V_2 - P_1V_1}{1-n} \tag{4–9}$$

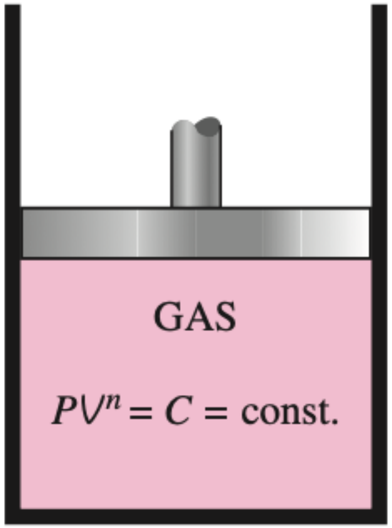
since $C = P_1V_1^n = P_2V_2^n$. For an ideal gas ($PV = mRT$), this equation can also be written as

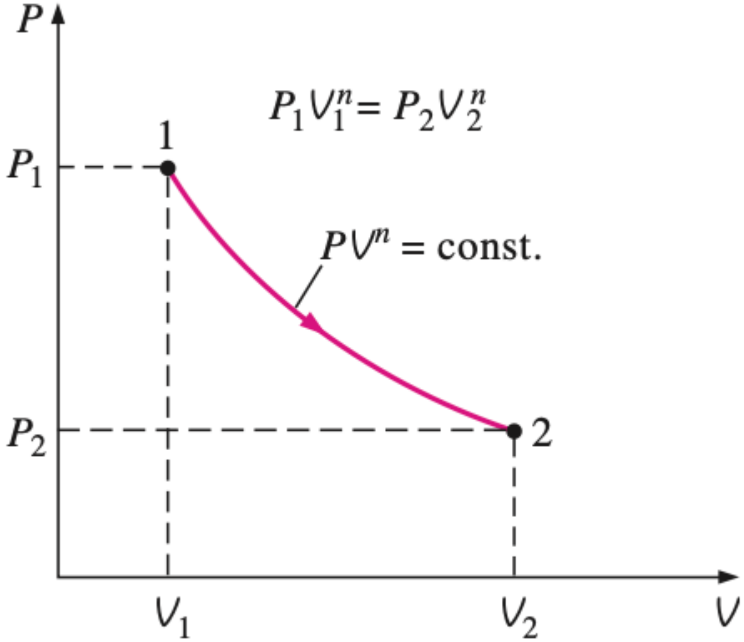
$$W_b = \frac{mR(T_2 - T_1)}{1-n} \qquad n \neq 1 \qquad \text{(kJ)} \tag{4–10}$$

For the special case of $n = 1$ the boundary work becomes

$$W_b = \int_1^2 P\,dV = \int_1^2 CV^{-1}\,dV = PV\ln\left(\frac{V_2}{V_1}\right)$$

For an ideal gas this result is equivalent to the isothermal process discussed in the previous example.


GAS
$PV^n = C = \text{const.}$


P
$P_1V_1^n = P_2V_2^n$
1
P_1
$PV^n = \text{const.}$
P_2
2
V_1
V_2
V

EXAMPLE 4–4 Expansion of a Gas against a Spring

A piston–cylinder device contains 0.05 m^3 of a gas initially at 200 kPa. At this state, a linear spring that has a spring constant of 150 kN/m is touching the piston but exerting no force on it. Now heat is transferred to the gas, causing the piston to rise and to compress the spring until the volume inside the cylinder doubles. If the cross-sectional area of the piston is 0.25 m^2, determine (*a*) the final pressure inside the cylinder, (*b*) the total work done by the gas, and (*c*) the fraction of this work done against the spring to compress it.

Solution A gas in a piston–cylinder device equipped with a linear spring expands as a result of heating. The final gas pressure, the total work done, and the fraction of the work done to compress the spring are to be determined.

Assumptions **1** The expansion process is quasi-equilibrium. **2** The spring is linear in the range of interest.

Analysis A sketch of the system and the *P-V* diagram of the process are shown in Fig. 4–10.

(*a*) The enclosed volume at the final state is

$$V_2 = 2V_1 = (2)(0.05 \text{ m}^3) = 0.1 \text{ m}^3$$

Then the displacement of the piston (and of the spring) becomes

$$x = \frac{\Delta V}{A} = \frac{(0.1 - 0.05) \text{ m}^3}{0.25 \text{ m}^2} = 0.2 \text{ m}$$

The force applied by the linear spring at the final state is

$$F = kx = (150 \text{ kN/m})(0.2 \text{ m}) = 30 \text{ kN}$$

The additional pressure applied by the spring on the gas at this state is

$$P = \frac{F}{A} = \frac{30 \text{ kN}}{0.25 \text{ m}^2} = 120 \text{ kPa}$$

Without the spring, the pressure of the gas would remain constant at 200 kPa while the piston is rising. But under the effect of the spring, the pressure rises linearly from 200 kPa to

$$200 + 120 = \mathbf{320 \text{ kPa}}$$

at the final state.

(*b*) An easy way of finding the work done is to plot the process on a *P-V* diagram and find the area under the process curve. From Fig. 4–10 the area under the process curve (a trapezoid) is determined to be

$$W = \text{area} = \frac{(200 + 320) \text{ kPa}}{2} [(0.1 - 0.05) \text{ m}^3]\left(\frac{1 \text{ kJ}}{1 \text{ kPa} \cdot \text{m}^3}\right) = \mathbf{13 \text{ kJ}}$$

Note that the work is done by the system.

(*c*) The work represented by the rectangular area (region I) is done against the piston and the atmosphere, and the work represented by the triangular area (region II) is done against the spring. Thus,

$$W_{\text{spring}} = \tfrac{1}{2}[(320 - 200)\ \text{kPa}](0.05\ \text{m}^3)\left(\frac{1\ \text{kJ}}{1\ \text{kPa}\cdot\text{m}^3}\right) = \mathbf{3\ kJ}$$

Discussion This result could also be obtained from

$$W_{\text{spring}} = \tfrac{1}{2}k(x_2^2 - x_1^2) = \tfrac{1}{2}(150\ \text{kN/m})[(0.2\ \text{m})^2 - 0^2]\left(\frac{1\ \text{kJ}}{1\ \text{kN}\cdot\text{m}}\right) = 3\ \text{kJ}$$

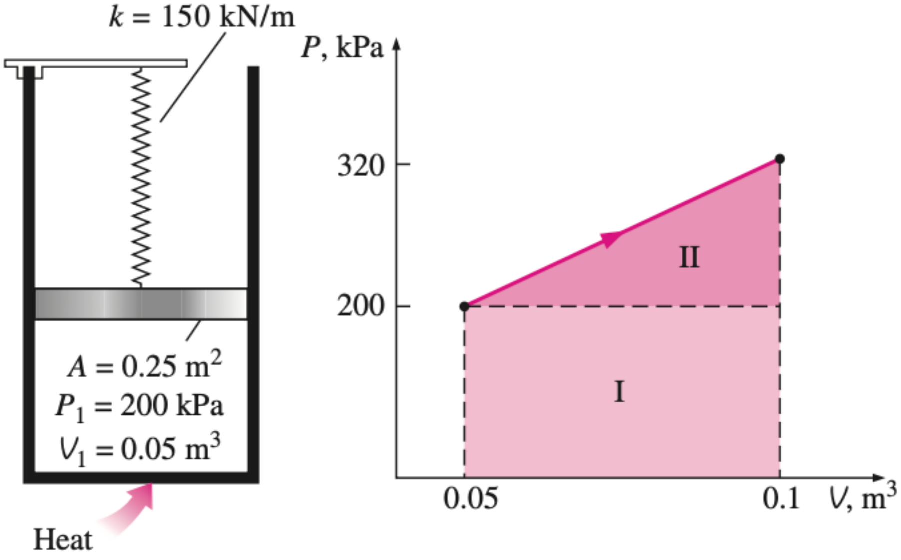


FIGURE 4–10

Schematic and P-V diagram for Example 4–4.

4–2 ▪ ENERGY BALANCE FOR CLOSED SYSTEMS

Energy balance for any system undergoing any kind of process was expressed as (see Chap. 2)

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\substack{\text{Net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{\text{system}}}_{\substack{\text{Change in internal, kinetic,} \\ \text{potential, etc., energies}}} \quad (\text{kJ}) \tag{4–11}$$

or, in the **rate form,** as

$$\underbrace{\dot{E}_{\text{in}} - \dot{E}_{\text{out}}}_{\substack{\text{Rate of net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{dE_{\text{system}}/dt}_{\substack{\text{Rate of change in internal,} \\ \text{kinetic, potential, etc., energies}}} \quad (\text{kW}) \tag{4–12}$$

For constant rates, the total quantities during a time interval Δt are related to the quantities per unit time as

$$Q = \dot{Q}\,\Delta t, \quad W = \dot{W}\,\Delta t, \quad \text{and} \quad \Delta E = (dE/dt)\Delta t \qquad (\text{kJ}) \tag{4–13}$$

The energy balance can be expressed on a **per unit mass** basis as

$$e_{\text{in}} - e_{\text{out}} = \Delta e_{\text{system}} \qquad (\text{kJ/kg}) \tag{4–14}$$

which is obtained by dividing all the quantities in Eq. 4–11 by the mass m of the system. Energy balance can also be expressed in the differential form as

$$\delta E_{\text{in}} - \delta E_{\text{out}} = dE_{\text{system}} \quad \text{or} \quad \delta e_{\text{in}} - \delta e_{\text{out}} = de_{\text{system}} \tag{4–15}$$

For a closed system undergoing a **cycle,** the initial and final states are identical, and thus $\Delta E_{\text{system}} = E_2 - E_1 = 0$. Then the energy balance for a cycle simplifies to $E_{\text{in}} - E_{\text{out}} = 0$ or $E_{\text{in}} = E_{\text{out}}$. Noting that a closed system does not involve any mass flow across its boundaries, the energy balance for a cycle can be expressed in terms of heat and work interactions as

$$W_{\text{net,out}} = Q_{\text{net,in}} \quad \text{or} \quad \dot{W}_{\text{net,out}} = \dot{Q}_{\text{net,in}} \qquad (\text{for a cycle}) \tag{4–16}$$

That is, the net work output during a cycle is equal to net heat input (Fig. 4–11).

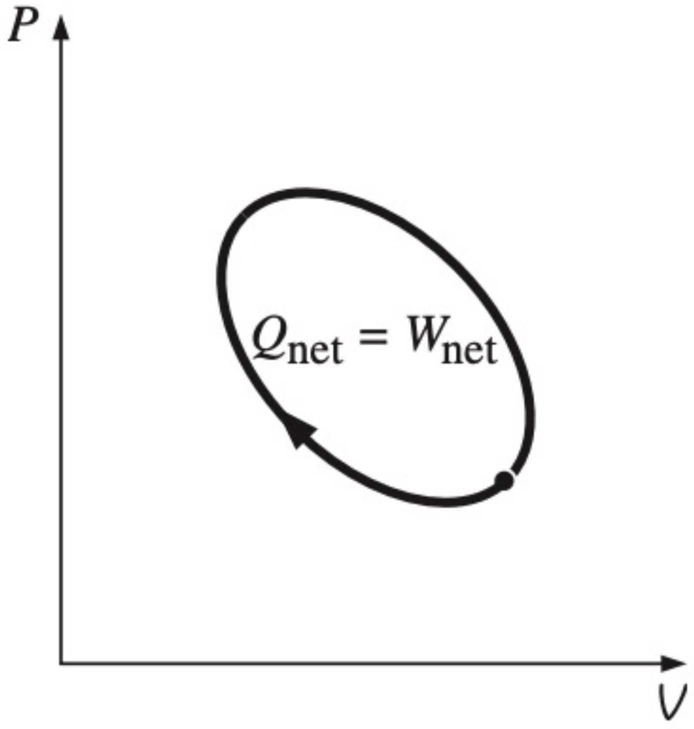


FIGURE 4–11

For a cycle $\Delta E = 0$, thus $Q = W$.

- The energy balance (or the first-law) relations already given are intuitive in nature and are easy to use when the magnitudes and directions of heat and work transfers are known.

- However, when performing a general analytical study or solving a problem that involves an unknown heat or work interaction, we need to assume a direction for the heat or work interactions.

- In such cases, it is common practice to use the classical thermodynamics sign convention and to assume heat to be transferred *into the system* (heat input) in the amount of Q and work to be done *by the system* (work output) in the amount of W, and then to solve the problem. The energy balance relation in that case for a closed system becomes

$$Q_{\text{net,in}} - W_{\text{net,out}} = \Delta E_{\text{system}} \quad \text{or} \quad Q - W = \Delta E \qquad \text{(4–17)}$$

Where

$Q = Q_{\text{net,in}} = Q_{\text{in}} - Q_{\text{out}}$ is the *net heat input*
and $W = W_{\text{net,out}} = W_{\text{out}} - W_{\text{in}}$ is the *net work output*.

- Obtaining a negative quantity for Q or W simply means that the assumed direction for that quantity is wrong and should be reversed. Various forms of this “traditional” first-law relation for closed systems are given in Fig. 4–12.

- The first law cannot be proven mathematically, but no process in nature is known to have violated the first law, and this should be taken as sufficient proof.

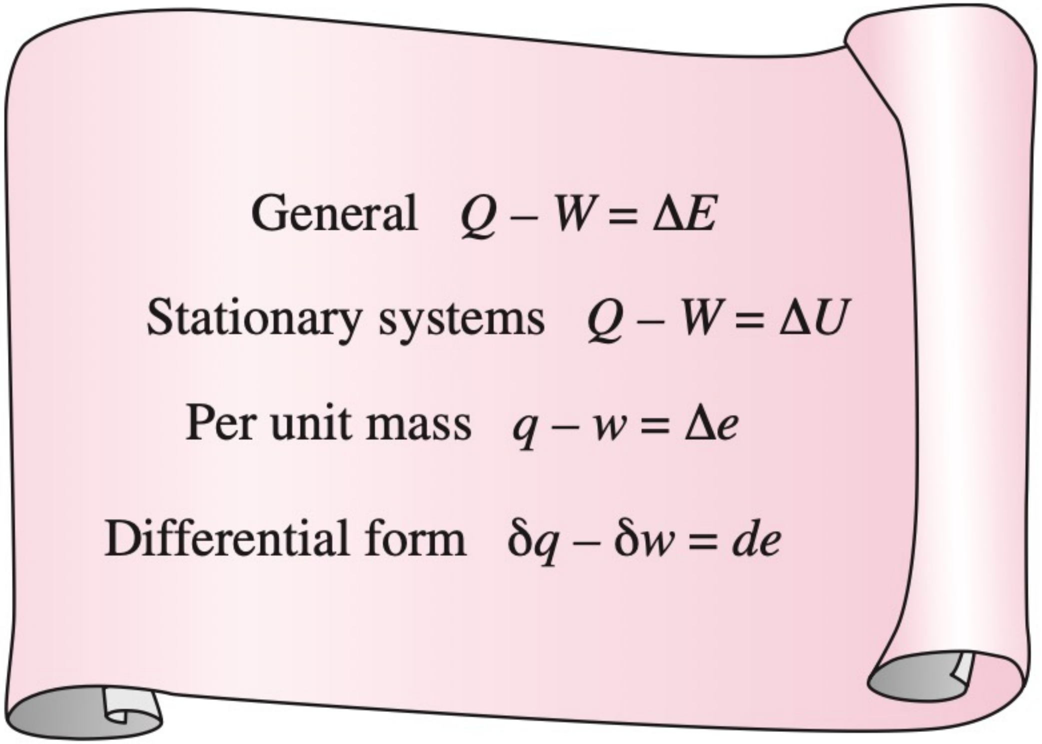
- Note that if it were possible to prove the first law on the basis of other physical principles, the first law then would be a consequence of those principles instead of being a fundamental physical law itself.

- As energy quantities, heat and work are not that different, and you probably wonder why we keep distinguishing them.

- After all, the change in the energy content of a system is equal to the amount of energy that crosses the system boundaries, and it makes no difference whether the energy crosses the boundary as heat or work.

- It seems as if the first-law relations would be much simpler if we had just one quantity that we could call *energy interaction* to represent both heat and work. Well, from the first-law point of view, heat and work are not different at all.

- From the second-law point of view, however, heat and work are very different, as is discussed in later chapters.



General $Q - W = \Delta E$

Stationary systems $Q - W = \Delta U$

Per unit mass $q - w = \Delta e$

Differential form $\delta q - \delta w = de$

FIGURE 4–12

Various forms of the first-law relation for closed systems.

EXAMPLE 4–5 Electric Heating of a Gas at Constant Pressure

A piston–cylinder device contains 25 g of saturated water vapor that is maintained at a constant pressure of 300 kPa. A resistance heater within the cylinder is turned on and passes a current of 0.2 A for 5 min from a 120-V source. At the same time, a heat loss of 3.7 kJ occurs. (*a*) Show that for a closed system the boundary work W_b and the change in internal energy ΔU in the first-law relation can be combined into one term, ΔH, for a constant-pressure process. (*b*) Determine the final temperature of the steam.

Solution Saturated water vapor in a piston–cylinder device expands at constant pressure as a result of heating. It is to be shown that $\Delta U + W_b = \Delta H$, and the final temperature is to be determined.

Assumptions **1** The tank is stationary and thus the kinetic and potential energy changes are zero, $\Delta \text{KE} = \Delta \text{PE} = 0$. Therefore, $\Delta E = \Delta U$ and internal energy is the only form of energy of the system that may change during this process. **2** Electrical wires constitute a very small part of the system, and thus the energy change of the wires can be neglected.

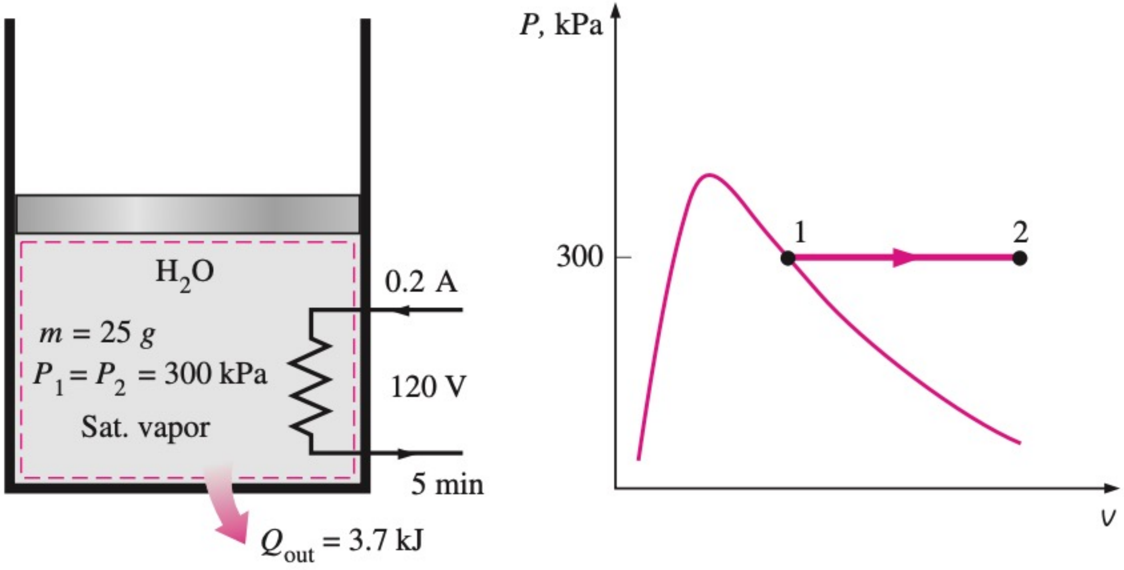


FIGURE 4–13

Schematic and P-v diagram for Example 4–5.

Analysis We take the contents of the cylinder, including the resistance wires, as the *system* (Fig. 4–13). This is a *closed system* since no mass crosses the system boundary during the process. We observe that a piston–cylinder device typically involves a moving boundary and thus boundary work W_b. The pressure remains constant during the process and thus $P_2 = P_1$. Also, heat is lost from the system and electrical work W_e is done on the system.

(*a*) This part of the solution involves a general analysis for a closed system undergoing a quasi-equilibrium constant-pressure process, and thus we consider a general closed system. We take the direction of heat transfer Q to be to the system and the work W to be done by the system. We also express the work as the sum of boundary and other forms of work (such as electrical and shaft). Then the energy balance can be expressed as

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\substack{\text{Net energy transfer}\\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{\text{system}}}_{\substack{\text{Change in internal, kinetic,}\\ \text{potential, etc., energies}}}$$

$$Q - W = \Delta U + \cancelto{0}{\Delta KE} + \cancelto{0}{\Delta PE}$$

$$Q - W_{\text{other}} - W_b = U_2 - U_1$$

For a constant-pressure process, the boundary work is given as $W_b = P_0(V_2 - V_1)$. Substituting this into the preceding relation gives

$$Q - W_{\text{other}} - P_0(V_2 - V_1) = U_2 - U_1$$

However,

$$P_0 = P_2 = P_1 \quad \rightarrow \quad Q - W_{\text{other}} = (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

Also $H = U + PV$, and thus

$$Q - W_{\text{other}} = H_2 - H_1 \qquad (\text{kJ}) \tag{4–18}$$

which is the desired relation (Fig. 4–14). This equation is very convenient to use in the analysis of closed systems undergoing a constant-pressure quasi-equilibrium process since the boundary work is automatically taken care of by the enthalpy terms, and one no longer needs to determine it separately.

(*b*) The only other form of work in this case is the electrical work, which can be determined from

$$W_e = \mathbf{V}I\ \Delta t = (120\ \text{V})(0.2\ \text{A})(300\ \text{s})\left(\frac{1\ \text{kJ/s}}{1000\ \text{VA}}\right) = 7.2\ \text{kJ}$$

$$\textit{State 1:}\quad \left.\begin{array}{l} P_1 = 300\ \text{kPa} \\ \text{sat. vapor} \end{array}\right\}\quad h_1 = h_{g\ @\ 300\ \text{kPa}} = 2724.9\ \text{kJ/kg} \qquad (\text{Table A–5})$$

The enthalpy at the final state can be determined directly from Eq. 4–18 by expressing heat transfer from the system and work done on the system as negative quantities (since their directions are opposite to the assumed directions). Alternately, we can use the general energy balance relation with the simplification that the boundary work is considered automatically by replacing ΔU by ΔH for a constant-pressure expansion or compression process:

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\substack{\text{Net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{\text{system}}}_{\substack{\text{Change in internal, kinetic,} \\ \text{potential, etc., energies}}}$$

$$W_{e,\text{in}} - Q_{\text{out}} - W_b = \Delta U$$

$$W_{e,\text{in}} - Q_{\text{out}} = \Delta H = m(h_2 - h_1) \qquad (\text{since } P = \text{constant})$$

$$7.2\ \text{kJ} - 3.7\ \text{kJ} = (0.025\ \text{kg})(h_2 - 2724.9)\ \text{kJ/kg}$$

$$h_2 = 2864.9\ \text{kJ/kg}$$

Now the final state is completely specified since we know both the pressure and the enthalpy. The temperature at this state is

$$\textit{State 2:}\quad \left.\begin{array}{l} P_2 = 300\ \text{kPa} \\ h_2 = 2864.9\ \text{kJ/kg} \end{array}\right\}\quad T_2 = \mathbf{200°C} \qquad (\text{Table A–6})$$

Therefore, the steam will be at 200°C at the end of this process.

Discussion Strictly speaking, the potential energy change of the steam is not zero for this process since the center of gravity of the steam rose somewhat. Assuming an elevation change of 1 m (which is rather unlikely), the change in the potential energy of the steam would be 0.0002 kJ, which is very small compared to the other terms in the first-law relation. Therefore, in problems of this kind, the potential energy term is always neglected.

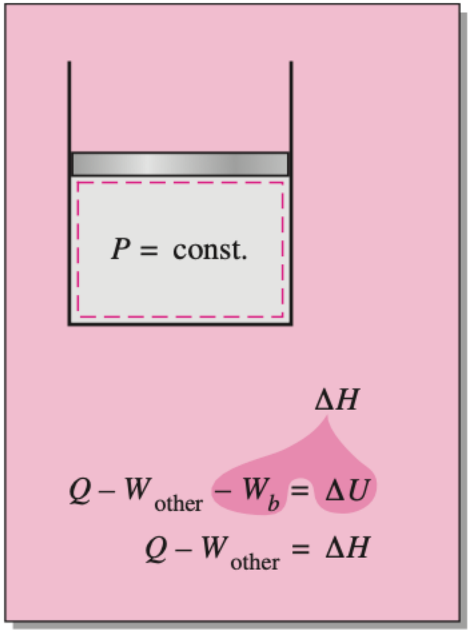


FIGURE 4–14

For a closed system undergoing a quasi-equilibrium, P = constant process, $\Delta U + W_b = \Delta H$.

EXAMPLE 4–6 Unrestrained Expansion of Water

A rigid tank is divided into two equal parts by a partition. Initially, one side of the tank contains 5 kg of water at 200 kPa and 25°C, and the other side is evacuated. The partition is then removed, and the water expands into the entire tank. The water is allowed to exchange heat with its surroundings until the temperature in the tank returns to the initial value of 25°C. Determine (*a*) the volume of the tank, (*b*) the final pressure, and (*c*) the heat transfer for this process.

Solution One half of a rigid tank is filled with liquid water while the other side is evacuated. The partition between the two parts is removed and water is allowed to expand and fill the entire tank while the temperature is maintained constant. The volume of tank, the final pressure, and the heat transfer are to be to determined.

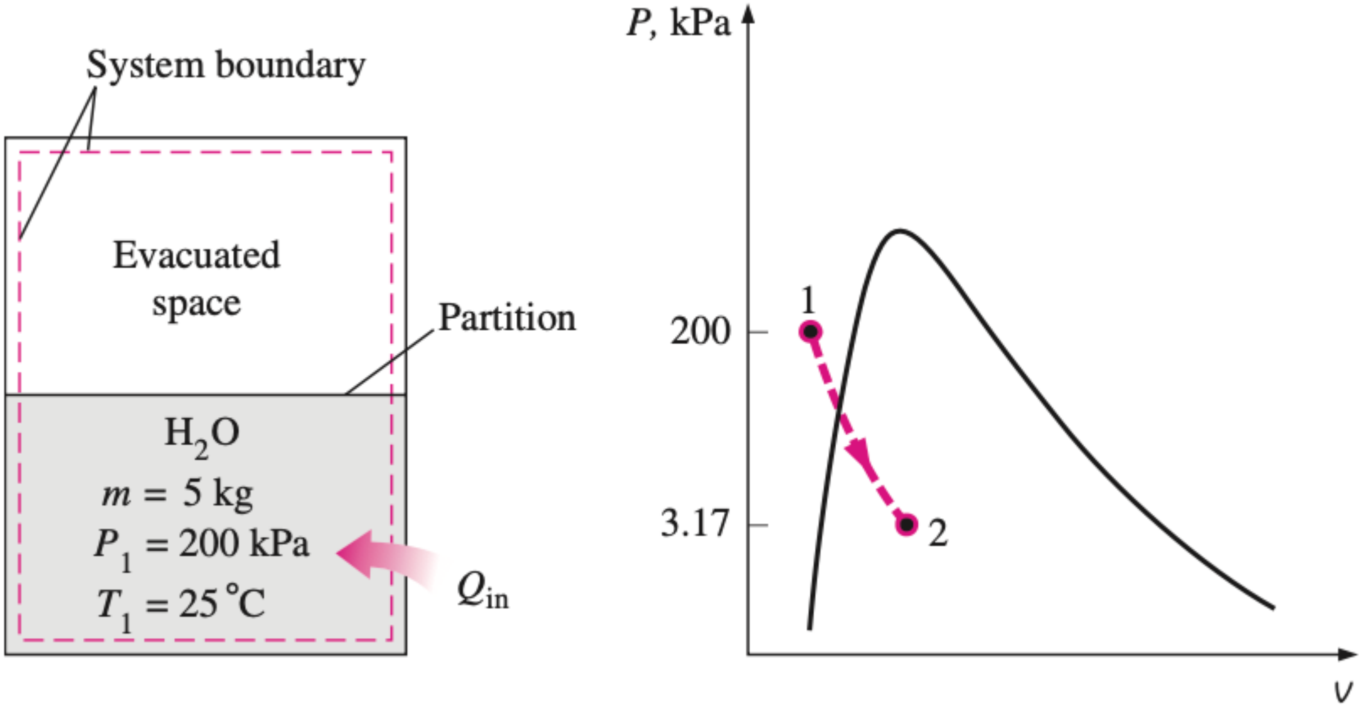


FIGURE 4–15

Schematic and P-v diagram for Example 4–6.

Assumptions 1 The system is stationary and thus the kinetic and potential energy changes are zero, $\Delta KE = \Delta PE = 0$ and $\Delta E = \Delta U$. **2** The direction of heat transfer is to the system (heat gain, Q_{in}). A negative result for Q_{in} indicates the assumed direction is wrong and thus it is a heat loss. **3** The volume of the rigid tank is constant, and thus there is no energy transfer as boundary work. **4** The water temperature remains constant during the process. **5** There is no electrical, shaft, or any other kind of work involved.

Analysis We take the contents of the tank, including the evacuated space, as the *system* (Fig. 4–15). This is a *closed system* since no mass crosses the system boundary during the process. We observe that the water fills the entire tank when the partition is removed (possibly as a liquid–vapor mixture).

(*a*) Initially the water in the tank exists as a compressed liquid since its pressure (200 kPa) is greater than the saturation pressure at 25°C (3.1698 kPa). Approximating the compressed liquid as a saturated liquid at the given temperature, we find

$$v_1 \cong v_{f\,@\,25^\circ\mathrm{C}} = 0.001003\ \mathrm{m^3/kg} \cong 0.001\ \mathrm{m^3/kg} \qquad \text{(Table A–4)}$$

Then the initial volume of the water is

$$V_1 = mv_1 = (5\ \mathrm{kg})(0.001\ \mathrm{m^3/kg}) = 0.005\ \mathrm{m^3}$$

The total volume of the tank is twice this amount:

$$V_{\text{tank}} = (2)(0.005\ \mathrm{m^3}) = \mathbf{0.01\ m^3}$$

(*b*) At the final state, the specific volume of the water is

$$v_2 = \frac{V_2}{m} = \frac{0.01\ \mathrm{m^3}}{5\ \mathrm{kg}} = 0.002\ \mathrm{m^3/kg}$$

which is twice the initial value of the specific volume. This result is expected since the volume doubles while the amount of mass remains constant.

$$\text{At } 25^\circ\text{C:} \quad v_f = 0.001003\ \mathrm{m^3/kg} \quad \text{and} \quad v_g = 43.340\ \mathrm{m^3/kg} \qquad \text{(Table A–4)}$$

Since $v_f < v_2 < v_g$, the water is a saturated liquid–vapor mixture at the final state, and thus the pressure is the saturation pressure at 25°C:

$$P_2 = P_{\text{sat}\,@\,25^\circ\mathrm{C}} = \mathbf{3.1698\ kPa} \qquad \text{(Table A–4)}$$

(*c*) Under stated assumptions and observations, the energy balance on the system can be expressed as

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\substack{\text{Net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{\text{system}}}_{\substack{\text{Change in internal, kinetic,} \\ \text{potential, etc., energies}}}$$

$$Q_{\text{in}} = \Delta U = m(u_2 - u_1)$$

Notice that even though the water is expanding during this process, the system chosen involves fixed boundaries only (the dashed lines) and therefore the moving boundary work is zero (Fig. 4–16). Then $W = 0$ since the system does not involve any other forms of work. (Can you reach the same conclusion by choosing the water as our system?) Initially,

$$u_1 \cong u_{f @ 25^\circ\text{C}} = 104.83 \text{ kJ/kg}$$

The quality at the final state is determined from the specific volume information:

$$x_2 = \frac{v_2 - v_f}{v_{fg}} = \frac{0.002 - 0.001}{43.34 - 0.001} = 2.3 \times 10^{-5}$$

Then

$$\begin{aligned} u_2 &= u_f + x_2 u_{fg} \\ &= 104.83 \text{ kJ/kg} + (2.3 \times 10^{-5})(2304.3 \text{ kJ/kg}) \\ &= 104.88 \text{ kJ/kg} \end{aligned}$$

Substituting yields

$$Q_{\text{in}} = (5 \text{ kg})[(104.88 - 104.83) \text{ kJkg}] = \mathbf{0.25 \text{ kJ}}$$

Discussion The positive sign indicates that the assumed direction is correct, and heat is transferred to the water.

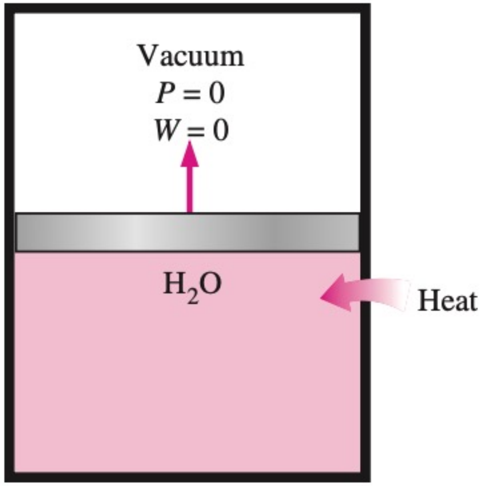


FIGURE 4–16

Expansion against a vacuum involves no work and thus no energy transfer.

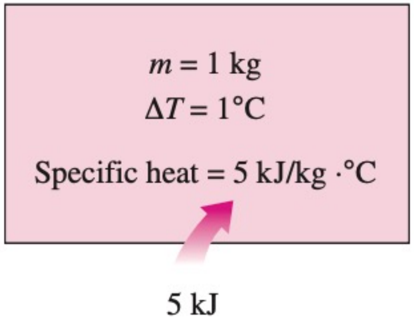


FIGURE 4–18

Specific heat is the energy required to raise the temperature of a unit mass of a substance by one degree in a specified way.

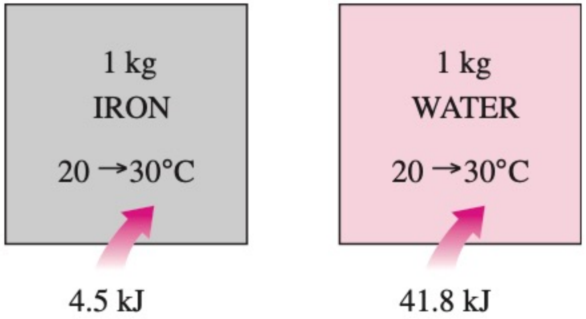


FIGURE 4–17

It takes different amounts of energy to raise the temperature of different substances by the same amount.

4–3 SPECIFIC HEATS

- We know from experience that it takes different amounts of energy to raise the temperature of identical masses of different substances by one degree.

- For example, we need about 4.5 kJ of energy to raise the temperature of 1 kg of iron from 20 to 30°C, whereas it takes about 9 times this energy (41.8 kJ to be exact) to raise the temperature of 1 kg of liquid water by the same amount (Fig. 4–17).

- Therefore, it is desirable to have a property that will enable us to compare the energy storage capabilities of various substances. This property is the specific heat.

- The **specific heat** is defined as *the energy required to raise the temperature of a unit mass of a substance by one degree* (Fig. 4–18). In general, this energy depends on how the process is executed.

- In thermodynamics, we are interested in two kinds of specific heats: **specific heat at constant volume** *c*v and **specific heat at constant pressure** *cp*.

- Physically, the specific heat at constant volume *cv* can be viewed as *the energy required to raise the temperature of the unit mass of a substance by one degree as the volume is maintained constant*.

- The energy required to do the same as the pressure is maintained constant is the specific heat at constant pressure *cp*. This is illustrated in Fig. 4–19.

- The specific heat at constant pressure *cp* is always greater than *cv* because at constant pressure the system is allowed to expand and the energy for this expansion work must also be supplied to the system.

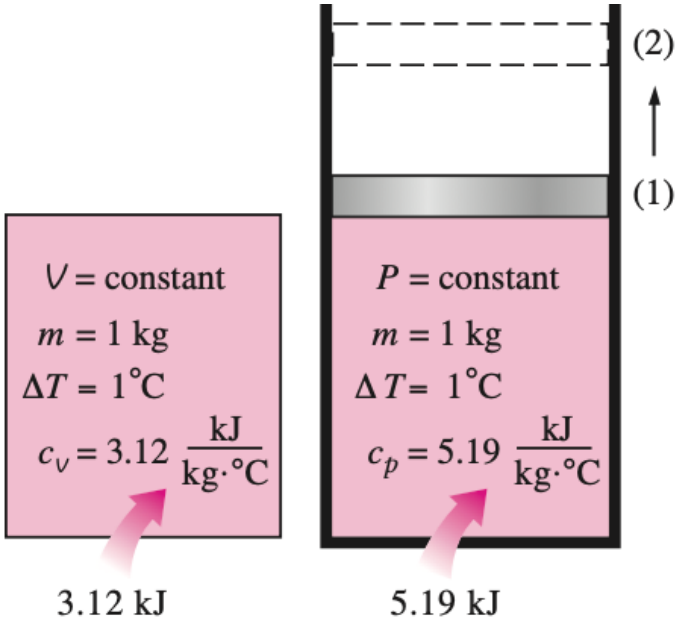


FIGURE 4–19

Constant-volume and constant-pressure specific heats c_v and c_p (values given are for helium gas).

Now we attempt to express the specific heats in terms of other thermodynamic properties. First, consider a fixed mass in a stationary closed system undergoing a constant-volume process (and thus no expansion or compression work is involved). The conservation of energy principle $e_{\text{in}} - e_{\text{out}} = \Delta e_{\text{system}}$ for this process can be expressed in the differential form as

$$\delta e_{\text{in}} - \delta e_{\text{out}} = du$$

The left-hand side of this equation represents the net amount of energy transferred to the system. From the definition of c_v, this energy must be equal to $c_v\, dT$, where dT is the differential change in temperature. Thus,

$$c_v\, dT = du \qquad \text{at constant volume}$$

or

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v \tag{4–19}$$

Similarly, an expression for the specific heat at constant pressure c_p can be obtained by considering a constant-pressure expansion or compression process. It yields

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p \tag{4–20}$$

- Note that c_v and c_p are expressed in terms of other properties; thus, they must be properties themselves. Like any other property, the specific heats of a substance depend on the state that, in general, is specified by two independent, intensive properties.

- That is, the energy required to raise the temperature of a substance by one degree is different at different temperatures and pressures (Fig. 4–21). But this difference is usually not very large

- A few observations can be made from Eqs. 4–19 and 4–20. First, these equations are *property relations* and as such *are independent of the type of processes*.

- They are valid for *any* substance undergoing *any* process. The only relevance c_v has to a constant-volume process is that c_v happens to be the energy transferred to a system during a constant-volume process per unit mass per unit degree rise in temperature.

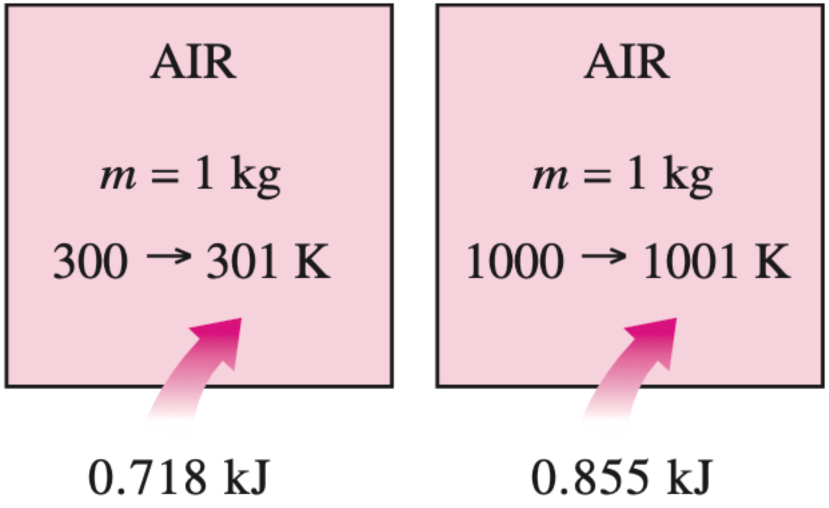


FIGURE 4–21

The specific heat of a substance changes with temperature.

- This is how the values of *c*v are determined. This is also how the name *specific heat at constant volume* originated. Likewise, the energy transferred to a system per unit mass per unit temperature rise during a constant-pressure process happens to be equal to *cp*.

- This is how the values of *cp* can be determined and also explains the origin of the name *specific heat at constant pressure*.

- Another observation that can be made from Eqs. 4–19 and 4–20 is that *c*v is related to the changes in *internal energy* and *cp* to the changes in *enthalpy*.

- In fact, it would be more proper to define *c*v as *the change in the internal energy of a substance per unit change in temperature at constant volume*. Likewise, *cp* can be defined as *the change in the enthalpy of a substance per unit change in temperature at constant pressure*.

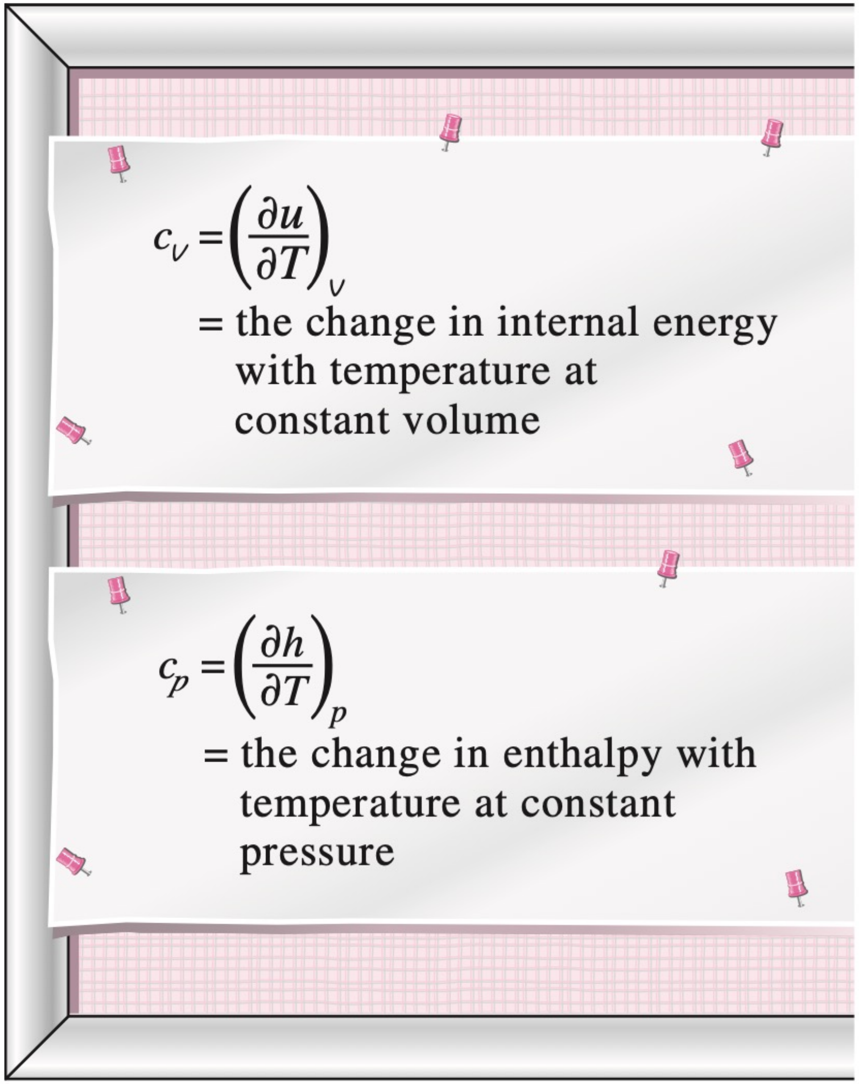
- In other words, *c*v is a measure of the variation of internal energy of a substance with temperature, and *cp* is a measure of the variation of enthalpy of a substance with temperature.

- Both the internal energy and enthalpy of a substance can be changed by the transfer of *energy* in any form, with heat being only one of them.

- Therefore, the term *specific energy* is probably more appropriate than the term *specific heat*, which implies that energy is transferred (and stored) in the form of heat.

- A common unit for specific heats is kJ/kg · °C or kJ/kg · K. Notice that these two units are *identical* since ΔT(°C) = ΔT(K), and 1°C change in temperature is equivalent to a change of 1 K.

- The specific heats are some- times given on a *molar basis*. They are then denoted by *c*–v and *c–p* and have the unit kJ/kmol · °C or kJ/kmol · K.



$$c_v = \left(\frac{\partial u}{\partial T}\right)_v$$

= the change in internal energy with temperature at constant volume

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p$$

= the change in enthalpy with temperature at constant pressure

FIGURE 4–20

Formal definitions of c_v and c_p.

4-4 INTERNAL ENERGY, ENTHALPY, AND SPECIFIC HEATS OF IDEAL GASES

- We defined an ideal gas as a gas whose temperature, pressure, and specific volume are related by

$$Pv = RT$$

It has been demonstrated mathematically (Chap. 12) and experimentally (Joule, 1843) that for an ideal gas the internal energy is a function of the temperature only. That is,

$$u = u(T) \tag{4–21}$$

- In his classical experiment, Joule submerged two tanks connected with a pipe and a valve in a water bath, as shown in Fig. 4–22.

- Initially, one tank contained air at a high pressure and the other tank was evacuated. When thermal equilibrium was attained, he opened the valve to let air pass from one tank to the other until the pressures equalized. Joule observed no change in the temperature of the water bath and assumed that no heat was transferred to or from the air.

- Since there was also no work done, he concluded that the internal energy of the air did not change even though the volume and the pressure changed.

- Therefore, he reasoned, the internal energy is a function of temperature only and not a function of pressure or specific volume. (Joule later showed that for gases that deviate significantly from ideal-gas behavior, the internal energy is not a function of temperature alone.)

- Using the definition of enthalpy and the equation of state of an ideal gas, we have

$$\left.\begin{aligned} h &= u + P\mathrm{v} \\ P\mathrm{v} &= RT \end{aligned}\right\} \quad h = u + RT$$

Since R is constant and $u = u(T)$, it follows that the enthalpy of an ideal gas is also a function of temperature only:

$$h = h(T) \tag{4–22}$$

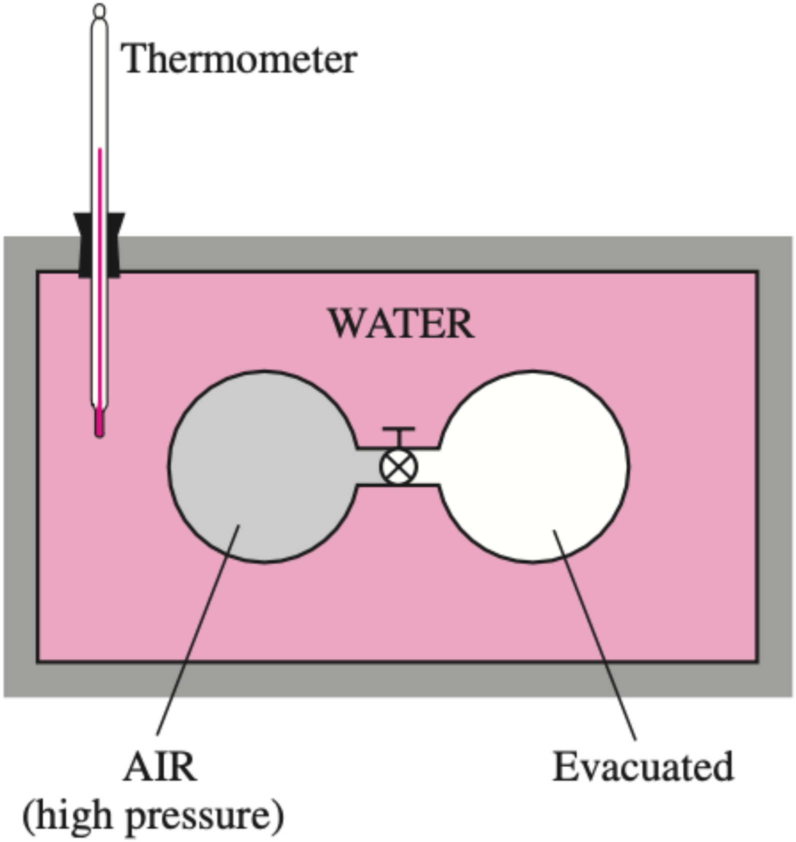


FIGURE 4–22

Schematic of the experimental apparatus used by Joule.

Since u and h depend only on temperature for an ideal gas, the specific heats c_v and c_p also depend, at most, on temperature only. Therefore, at a given temperature, u, h, c_v, and c_p of an ideal gas have fixed values regardless of the specific volume or pressure (Fig. 4–23). Thus, for ideal gases, the partial derivatives in Eqs. 4–19 and 4–20 can be replaced by ordinary derivatives. Then the differential changes in the internal energy and enthalpy of an ideal gas can be expressed as

$$du = c_v(T)\,dT \tag{4–23}$$

and

$$dh = c_p(T)\,dT \tag{4–24}$$

The change in internal energy or enthalpy for an ideal gas during a process from state 1 to state 2 is determined by integrating these equations:

$$\Delta u = u_2 - u_1 = \int_1^2 c_v(T)\,dT \qquad (\text{kJ/kg}) \tag{4–25}$$

and

$$\Delta h = h_2 - h_1 = \int_1^2 c_p(T)\,dT \qquad (\text{kJ/kg}) \tag{4–26}$$

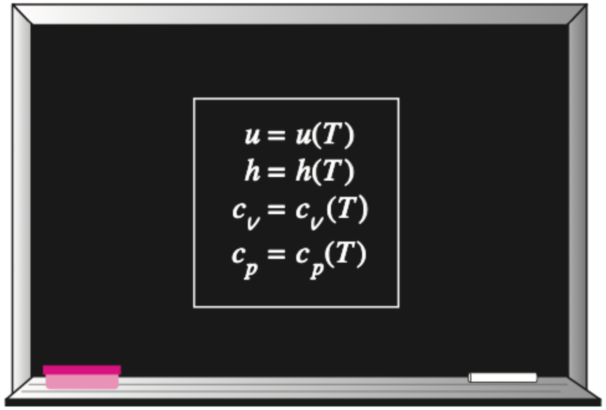


FIGURE 4–23

For ideal gases, u, h, c_v, and c_p vary with temperature only.

- To carry out these integrations, we need to have relations for *c*v and *cp* as functions of temperature.

- At low pressures, all real gases approach ideal-gas behavior, and therefore their specific heats depend on temperature only.

- The specific heats of real gases at low pressures are called *ideal-gas specific heats*, or *zero-pressure specific heats*, and are often denoted c_{p0} and c_{v0}.

- Accurate analytical expressions for ideal-gas specific heats, based on direct measurements or calculations from statistical behavior of molecules, are available and are given as third-degree polynomials in the appendix (Table A–2*c*) for several gases. A plot of $\bar{c}_{p0}(T)$ data for some common gases is given in Fig. 4–24.

- The use of ideal-gas specific heat data is limited to low pressures, but these data can also be used at moderately high pressures with reasonable accuracy as long as the gas does not deviate from ideal-gas behavior significantly.

- The integrations in Eqs. 4 –25 and 4 –26 are straightforward but rather time-consuming and thus impractical. To avoid these laborious calculations, u and h data for a number of gases have been tabulated over small temperature intervals.

- These tables are obtained by choosing an arbitrary reference point and performing the integrations in Eqs. 4–25 and 4–26 by treating state 1 as the reference state.

- In the ideal-gas tables given in the appendix, zero kelvin is chosen as the reference state, and both the enthalpy and the internal energy are assigned zero values at that state (Fig. 4–25).

- The choice of the reference state has no effect on $\square u$ or $\square h$ calculations. The u and h data are given in kJ/kg for air (Table A–17) and usually in kJ/kmol for other gases.

- The unit kJ/kmol is very convenient in the thermodynamic analysis of chemical reactions.

- Some observations can be made from Fig. 4–24. First, the specific heats of gases with complex molecules (molecules with two or more atoms) are higher and increase with temperature.

- Also, the variation of specific heat with temperature is smooth and may be approximated as linear over small temperature intervals (a few hundred degrees or less).

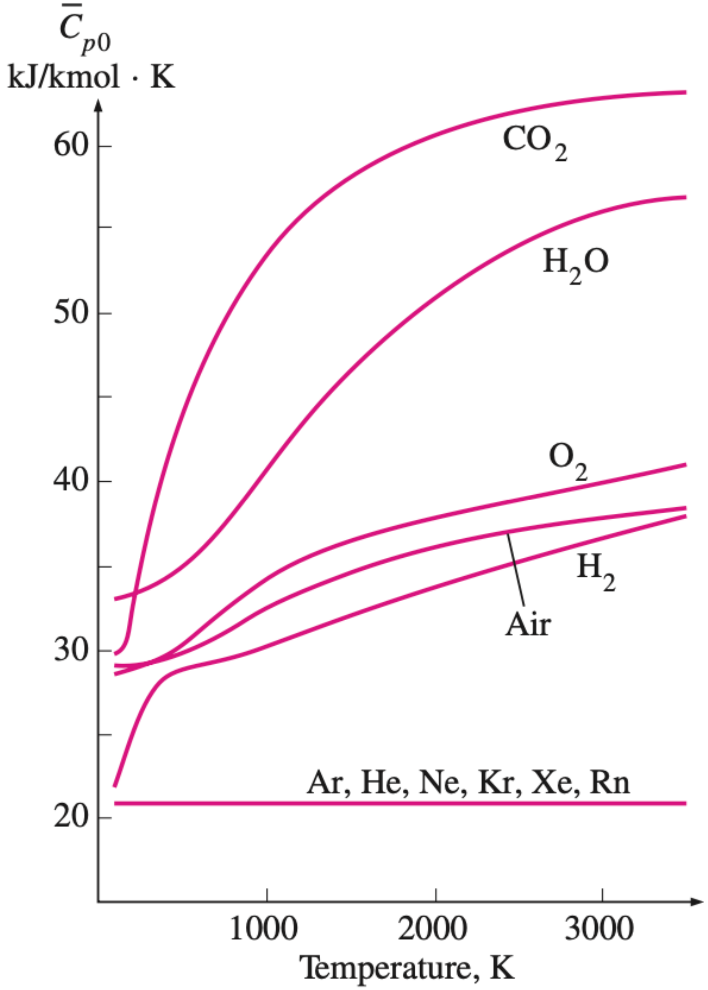


FIGURE 4–24

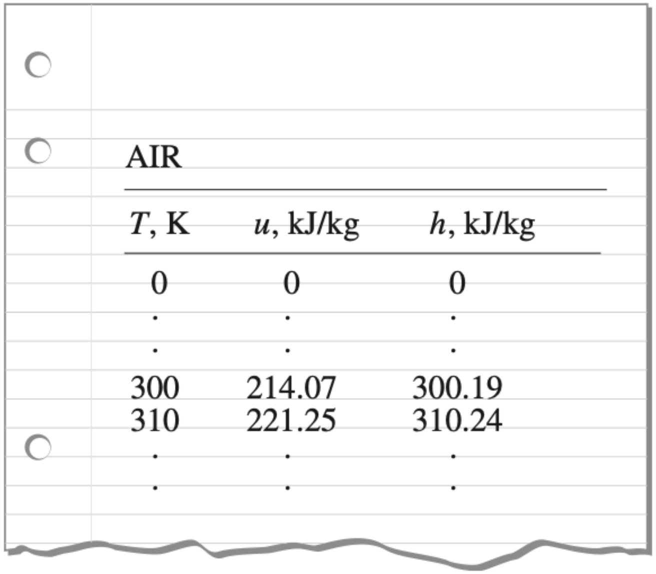
Ideal-gas constant-pressure specific heats for some gases (see Table A–2*c* for c_p equations).

- Therefore, the specific heat functions in Eqs. 4–25 and 4–26 can be replaced by the constant average specific heat values. Then the integrations in these equations can be per- formed, yielding

$$u_2 - u_1 = c_{v,\text{avg}}(T_2 - T_1) \qquad \text{(kJ/kg)} \tag{4–27}$$

and

$$h_2 - h_1 = c_{p,\text{avg}}(T_2 - T_1) \qquad \text{(kJ/kg)} \tag{4–28}$$



AIR

T, K	u, kJ/kg	h, kJ/kg
0	0	0
.	.	.
.	.	.
300	214.07	300.19
310	221.25	310.24
.	.	.
.	.	.

FIGURE 4–25

In the preparation of ideal-gas tables, 0 K is chosen as the reference temperature.

- The specific heat values for some common gases are listed as a function of temperature in Table A–2*b*. The average specific heats $c_{p,\text{avg}}$ and $c_{\text{v,avg}}$ are evaluated from this table at the average temperature ($T1 + T2$)/2, as shown in Fig. 4–26.

- If the final temperature $T2$ is not known, the specific heats may be evaluated at $T1$ or at the anticipated average temperature. Then $T2$ can be determined by using these specific heat values. The value of $T2$ can be refined, if necessary, by evaluating the specific heats at the new average temperature.

- Another way of determining the average specific heats is to evaluate them at $T1$ and $T2$ and then take their average. Usually both methods give reasonably good results, and one is not necessarily better than the other.

- Another observation that can be made from Fig. 4–24 is that the ideal-gas specific heats of *monatomic gases* such as argon, neon, and helium remain constant over the entire temperature range. Thus, Δu and Δh of monatomic gases can easily be evaluated from Eqs. 4–27 and 4–28.

- Note that the Δu and Δh relations given previously are not restricted to any kind of process. They are valid for all processes. The presence of the constant-volume specific heat c_v in an equation should not lead one to believe that this equation is valid for a constant-volume process only.

- On the contrary, the relation $\Delta u = c_{v,avg} \Delta T$ is valid for *any* ideal gas undergoing *any* process (Fig. 4–27). A similar argument can be given for *cp* and Δh.

- To summarize, there are three ways to determine the internal energy and enthalpy changes of ideal gases (Fig. 4–28):

1. By using the tabulated *u* and *h* data. This is the easiest and most accu- rate way when tables are readily available.

2. By using the *cv* or *cp* relations as a function of temperature and per- forming the integrations. This is very inconvenient for hand calculations but quite desirable for computerized calculations. The results obtained are very accurate.

3. By using average specific heats. This is very simple and certainly very convenient when property tables are not available. The results obtained are reasonably accurate if the temperature interval is not very large.

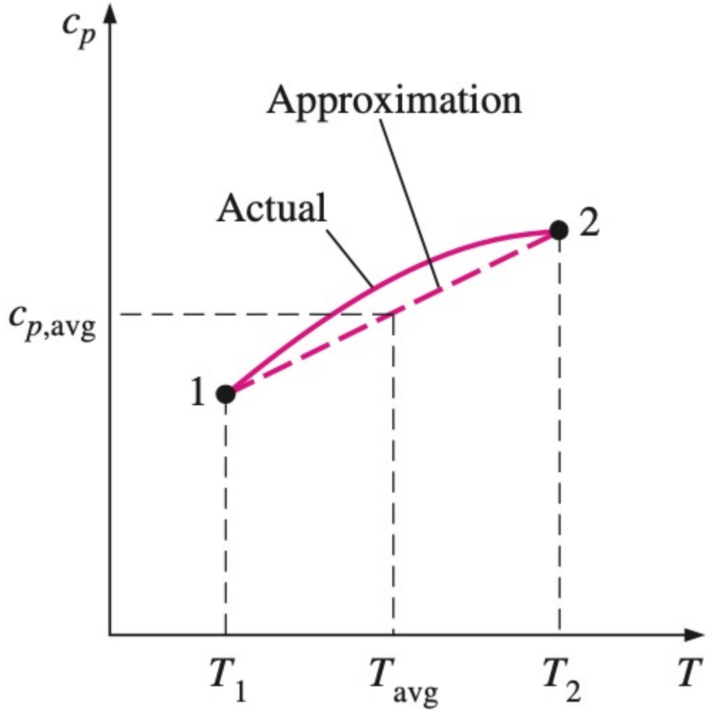


FIGURE 4–26

For small temperature intervals, the specific heats may be assumed to vary linearly with temperature.

Specific Heat Relations of Ideal Gases

A special relationship between cp and cv for ideal gases can be obtained by differentiating the relation $h = u + RT$, which yields

$$dh = du + R\,dT$$

Replacing dh by $c_p\,dT$ and du by $c_v\,dT$ and dividing the resulting expression by dT, we obtain

$$c_p = c_v + R \qquad (\text{kJ/kg}\cdot\text{K}) \tag{4–29}$$

This is an important relationship for ideal gases since it enables us to determine c_v from a knowledge of c_p and the gas constant R.

When the specific heats are given on a molar basis, R in the above equation should be replaced by the universal gas constant R_u (Fig. 4–29).

$$\bar{c}_p = \bar{c}_v + R_u \qquad (\text{kJ/kmol}\cdot\text{K}) \tag{4–30}$$

At this point, we introduce another ideal-gas property called the **specific heat ratio** k, defined as

$$k = \frac{c_p}{c_v} \tag{4–31}$$

The specific ratio also varies with temperature, but this variation is very mild. For monatomic gases, its value is essentially constant at 1.667. Many diatomic gases, including air, have a specific heat ratio of about 1.4 at room temperature.

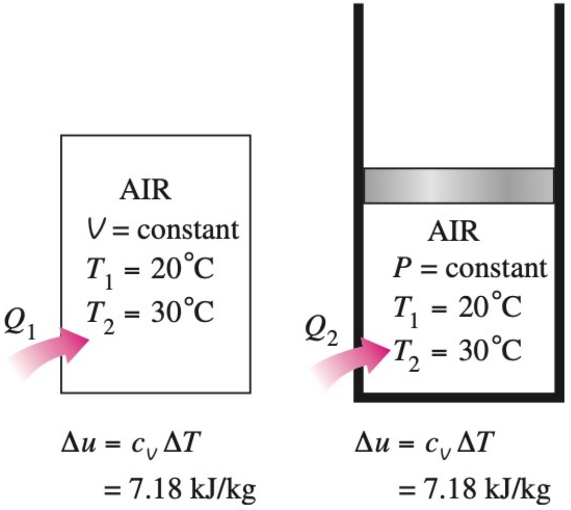
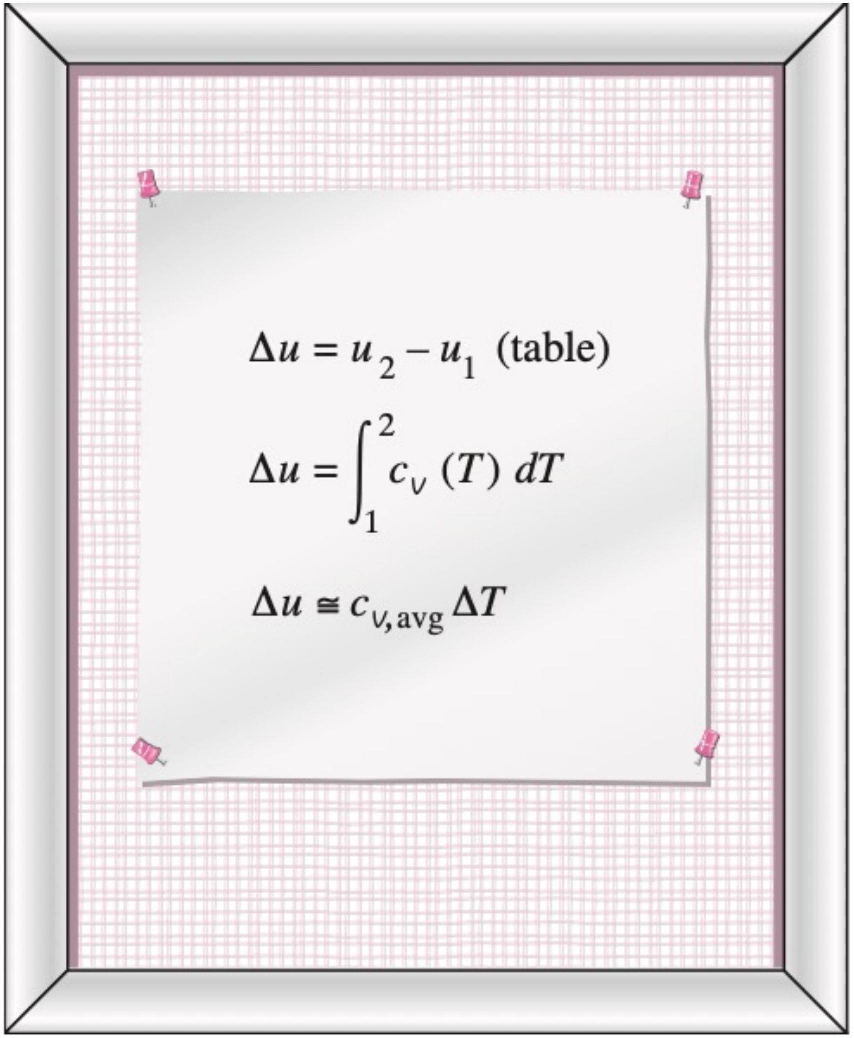


FIGURE 4–27

The relation $\Delta u = c_v\,\Delta T$ is valid for *any* kind of process, constant-volume or not.



$$\Delta u = u_2 - u_1 \text{ (table)}$$

$$\Delta u = \int_1^2 c_v(T)\, dT$$

$$\Delta u \cong c_{v,\mathrm{avg}}\, \Delta T$$

FIGURE 4–28

Three ways of calculating Δu.

EXAMPLE 4–7 Evaluation of the Δu of an Ideal Gas

Air at 300 K and 200 kPa is heated at constant pressure to 600 K. Determine the change in internal energy of air per unit mass, using (*a*) data from the air table (Table A–17), (*b*) the functional form of the specific heat (Table A–2*c*), and (*c*) the average specific heat value (Table A–2*b*).

Solution The internal energy change of air is to be determined in three different ways.

Assumptions At specified conditions, air can be considered to be an ideal gas since it is at a high temperature and low pressure relative to its critical-point values.

Analysis The internal energy change Δu of ideal gases depends on the initial and final temperatures only, and not on the type of process. Thus, the following solution is valid for any kind of process.

(*a*) One way of determining the change in internal energy of air is to read the u values at T_1 and T_2 from Table A–17 and take the difference:

$$u_1 = u_{@\,300\text{ K}} = 214.07\text{ kJ/kg}$$

$$u_2 = u_{@\,600\text{ K}} = 434.78\text{ kJ/kg}$$

Thus,

$$\Delta u = u_2 - u_1 = (434.78 - 214.07)\text{ kJ/kg} = \mathbf{220.71\ kJ/kg}$$

(*b*) The $\bar{c}_p(T)$ of air is given in Table A–2*c* in the form of a third-degree polynomial expressed as

$$\bar{c}_p(T) = a + bT + cT^2 + dT^3$$

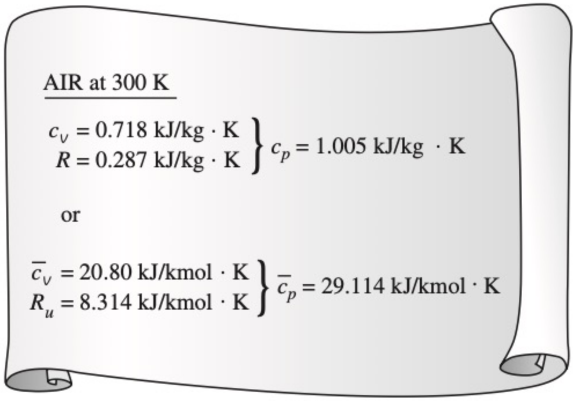


FIGURE 4–29

The c_p of an ideal gas can be determined from a knowledge of c_v and R.

where $a = 28.11$, $b = 0.1967 \times 10^{-2}$, $c = 0.4802 \times 10^{-5}$, and $d = -1.966 \times 10^{-9}$. From Eq. 4–30,

$$\bar{c}_v(T) = \bar{c}_p - R_u = (a - R_u) + bT + cT^2 + dT^3$$

From Eq. 4–25,

$$\Delta\bar{u} = \int_1^2 \bar{c}_v(T)\ dT = \int_{T_1}^{T_2} [(a - R_u) + bT + cT^2 + dT^3]\ dT$$

Performing the integration and substituting the values, we obtain

$$\Delta\bar{u} = 6447 \text{ kJ/kmol}$$

The change in the internal energy on a unit-mass basis is determined by dividing this value by the molar mass of air (Table A–1):

$$\Delta u = \frac{\Delta\bar{u}}{M} = \frac{6447 \text{ kJ/kmol}}{28.97 \text{ kg/kmol}} = \mathbf{222.5 \text{ kJ/kg}}$$

which differs from the tabulated value by 0.8 percent.

(*c*) The average value of the constant-volume specific heat $c_{v,\text{avg}}$ is determined from Table A–2*b* at the average temperature of $(T_1 + T_2)/2 = 450$ K to be

$$c_{v,\text{avg}} = c_{v\ @\ 450\text{ K}} = 0.733 \text{ kJ/kg} \cdot \text{K}$$

Thus,

$$\begin{aligned}\Delta u &= c_{v,\text{avg}}(T_2 - T_1) = (0.733 \text{ kJ/kg} \cdot \text{K})[(600 - 300)\text{K}] \\ &= 220 \text{ kJ/kg}\end{aligned}$$

Discussion This answer differs from the tabulated value (220.71 kJ/kg) by only 0.4 percent. This close agreement is not surprising since the assumption that c_v varies linearly with temperature is a reasonable one at temperature intervals of only a few hundred degrees. If we had used the c_v value at $T_1 = 300$ K instead of at T_{avg}, the result would be 215.4 kJ/kg, which is in error by about 2 percent. Errors of this magnitude are acceptable for most engineering purposes.

EXAMPLE 4–8 Heating of a Gas in a Tank by Stirring

An insulated rigid tank initially contains 1.5 lbm of helium at 80°F and 50 psia. A paddle wheel with a power rating of 0.02 hp is operated within the tank for 30 min. Determine (*a*) the final temperature and (*b*) the final pressure of the helium gas.

Solution Helium gas in an insulated rigid tank is stirred by a paddle wheel. The final temperature and pressure of helium are to be determined.
Assumptions **1** Helium is an ideal gas since it is at a very high temperature relative to its critical-point value of −451°F. **2** Constant specific heats can be used for helium. **3** The system is stationary and thus the kinetic and potential energy changes are zero, $\Delta KE = \Delta PE = 0$ and $\Delta E = \Delta U$. **4** The volume of the tank is constant, and thus there is no boundary work. **5** The system is adiabatic and thus there is no heat transfer.

Analysis We take the contents of the tank as the *system* (Fig. 4–30). This is a *closed system* since no mass crosses the system boundary during the process. We observe that there is shaft work done on the system.

(*a*) The amount of paddle-wheel work done on the system is

$$W_{\text{sh}} = \dot{W}_{\text{sh}}\,\Delta t = (0.02\text{ hp})(0.5\text{ h})\left(\frac{2545\text{ Btu/h}}{1\text{ hp}}\right) = 25.45\text{ Btu}$$

Under the stated assumptions and observations, the energy balance on the system can be expressed as

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\substack{\text{Net energy transfer}\\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{\text{system}}}_{\substack{\text{Change in internal, kinetic,}\\ \text{potential, etc., energies}}}$$

$$W_{\text{sh,in}} = \Delta U = m(u_2 - u_1) = mc_{v,\text{avg}}(T_2 - T_1)$$

As we pointed out earlier, the ideal-gas specific heats of monatomic gases (helium being one of them) are constant. The c_v value of helium is determined from Table A–2E*a* to be $c_v = 0.753$ Btu/lbm · °F. Substituting this and other known quantities into the above equation, we obtain

$$25.45\text{ Btu} = (1.5\text{ lbm})(0.753\text{ Btu/lbm}\cdot{}^\circ\text{F})(T_2 - 80^\circ\text{F})$$

$$T_2 = \mathbf{102.5^\circ F}$$

(*b*) The final pressure is determined from the ideal-gas relation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

where V_1 and V_2 are identical and cancel out. Then the final pressure becomes

$$\frac{50\text{ psia}}{(80 + 460)\text{ R}} = \frac{P_2}{(102.5 + 460)\text{R}}$$

$$P_2 = \mathbf{52.1\ psia}$$

Discussion Note that the pressure in the ideal-gas relation is always the absolute pressure.

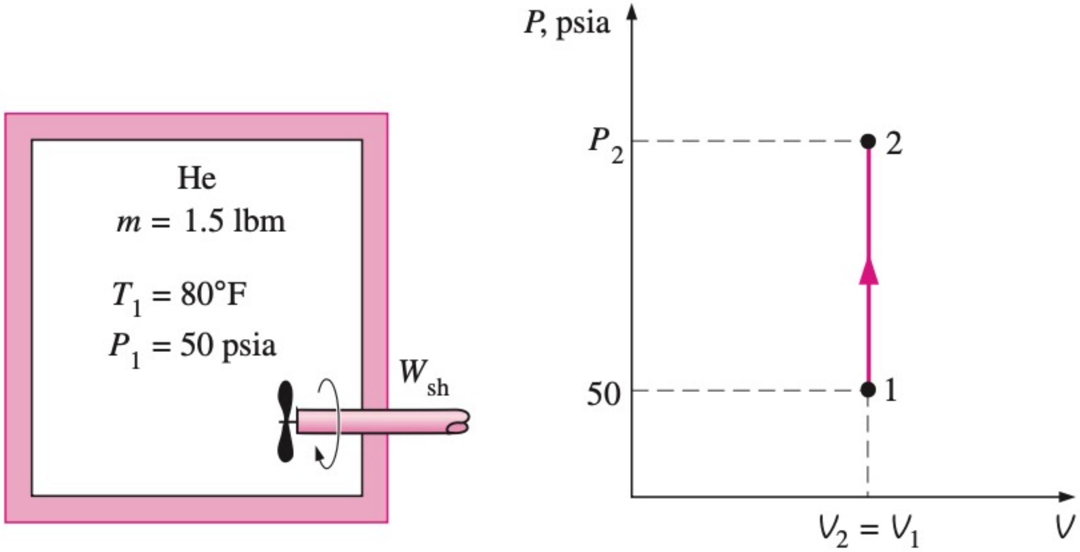


FIGURE 4–30

Schematic and P-V diagram for Example 4–8.

EXAMPLE 4–9 Heating of a Gas by a Resistance Heater

A piston–cylinder device initially contains 0.5 m^3 of nitrogen gas at 400 kPa and 27°C. An electric heater within the device is turned on and is allowed to pass a current of 2 A for 5 min from a 120-V source. Nitrogen expands at constant pressure, and a heat loss of 2800 J occurs during the process. Determine the final temperature of nitrogen.

Solution Nitrogen gas in a piston–cylinder device is heated by an electric resistance heater. Nitrogen expands at constant pressure while some heat is lost. The final temperature of nitrogen is to be determined.

Assumptions **1** Nitrogen is an ideal gas since it is at a high temperature and low pressure relative to its critical-point values of −147°C, and 3.39 MPa. **2** The system is stationary and thus the kinetic and potential energy changes are zero, $\Delta KE = \Delta PE = 0$ and $\Delta E = \Delta U$. **3** The pressure remains constant during the process and thus $P_2 = P_1$. **4** Nitrogen has constant specific heats at room temperature.

Analysis We take the contents of the cylinder as the *system* (Fig. 4–31). This is a *closed system* since no mass crosses the system boundary during the process. We observe that a piston–cylinder device typically involves a moving boundary and thus boundary work, W_b. Also, heat is lost from the system and electrical work W_e is done on the system.

First, let us determine the electrical work done on the nitrogen:

$$W_e = \mathbf{V}I\,\Delta t = (120\ \text{V})(2\ \text{A})(5 \times 60\ \text{s})\left(\frac{1\ \text{kJ/s}}{1000\ \text{VA}}\right) = 72\ \text{kJ}$$

The mass of nitrogen is determined from the ideal-gas relation:

$$m = \frac{P_1V_1}{RT_1} = \frac{(400\ \text{kPa})(0.5\ \text{m}^3)}{(0.297\ \text{kPa}\cdot\text{m}^3/\text{kg}\cdot\text{K})(300\ \text{K})} = 2.245\ \text{kg}$$

Under the stated assumptions and observations, the energy balance on the system can be expressed as

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\substack{\text{Net energy transfer}\\ \text{by heat, work, and mass}}} \quad = \quad \underbrace{\Delta E_{\text{system}}}_{\substack{\text{Change in internal, kinetic,}\\ \text{potential, etc., energies}}}$$

$$W_{e,\text{in}} - Q_{\text{out}} - W_{b,\text{out}} = \Delta U$$

$$W_{e,\text{in}} - Q_{\text{out}} = \Delta H = m(h_2 - h_1) = mc_p(T_2 - T_1)$$

since $\Delta U + W_b \equiv \Delta H$ for a closed system undergoing a quasi-equilibrium expansion or compression process at constant pressure. From Table A–2a, $c_p = 1.039$ kJ/kg · K for nitrogen at room temperature. The only unknown quantity in the previous equation is T_2, and it is found to be

$$72 \text{ kJ} - 2.8 \text{ kJ} = (2.245 \text{ kg})(1.039 \text{ kJ/kg} \cdot \text{K})(T_2 - 27°\text{C})$$

$$T_2 = \mathbf{56.7°C}$$

Discussion Note that we could also solve this problem by determining the boundary work and the internal energy change rather than the enthalpy change.

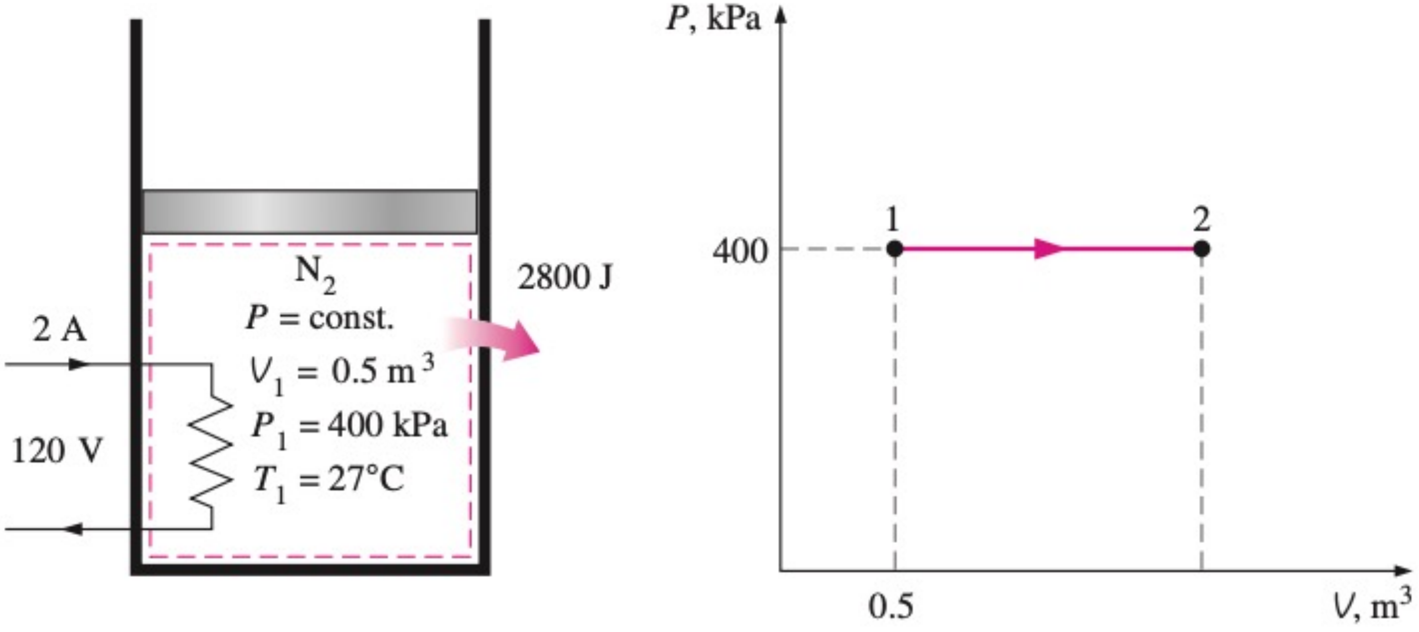


FIGURE 4–31

Schematic and P-V diagram for Example 4–9.

EXAMPLE 4–10 **Heating of a Gas at Constant Pressure**

A piston–cylinder device initially contains air at 150 kPa and 27°C. At this state, the piston is resting on a pair of stops, as shown in Fig. 4–32, and the enclosed volume is 400 L. The mass of the piston is such that a 350-kPa pressure is required to move it. The air is now heated until its volume has doubled. Determine (*a*) the final temperature, (*b*) the work done by the air, and (*c*) the total heat transferred to the air.

Solution Air in a piston–cylinder device with a set of stops is heated until its volume is doubled. The final temperature, work done, and the total heat transfer are to be determined.

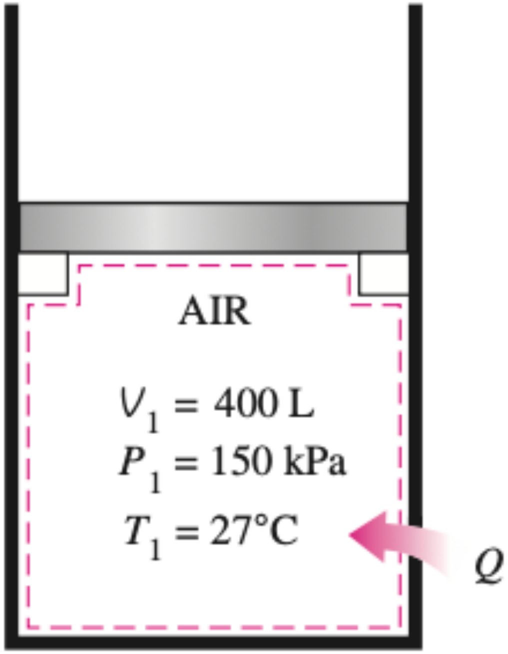
Assumptions **1** Air is an ideal gas since it is at a high temperature and low pressure relative to its critical-point values. **2** The system is stationary and thus the kinetic and potential energy changes are zero, $\Delta KE = \Delta PE = 0$ and $\Delta E = \Delta U$. **3** The volume remains constant until the piston starts moving, and the pressure remains constant afterwards. **4** There are no electrical, shaft, or other forms of work involved.

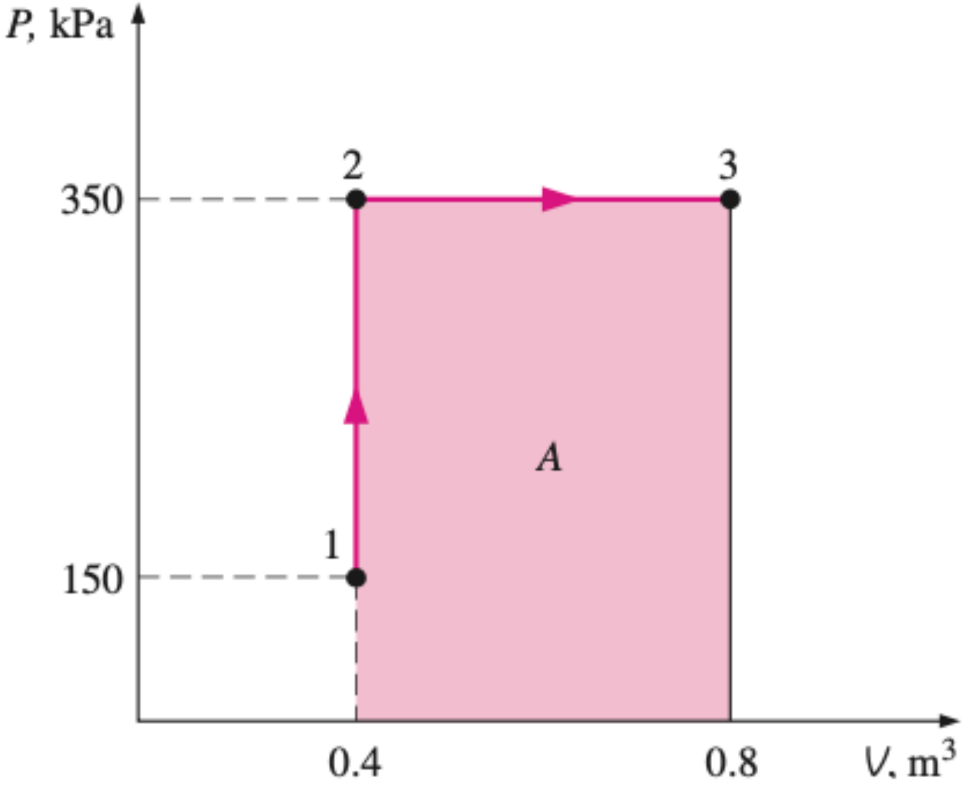
Analysis We take the contents of the cylinder as the *system* (Fig. 4–32). This is a *closed system* since no mass crosses the system boundary during the process. We observe that a piston-cylinder device typically involves a moving boundary and thus boundary work, W_b. Also, the boundary work is done by the system, and heat is transferred to the system.

(*a*) The final temperature can be determined easily by using the ideal-gas relation between states 1 and 3 in the following form:

$$\frac{P_1V_1}{T_1} = \frac{P_3V_3}{T_3} \longrightarrow \frac{(150\text{ kPa})(V_1)}{300\text{ K}} = \frac{(350\text{ kPa})(2V_1)}{T_3}$$

$$T_3 = \mathbf{1400\ K}$$


AIR
V_1 = 400 L
P_1 = 150 kPa
T_1 = 27°C
Q


P, kPa
350
150
2
3
1
A
0.4
0.8
V, m^3

(*b*) The work done could be determined by integration, but for this case it is much easier to find it from the area under the process curve on a *P*-*V* diagram, shown in Fig. 4–32:

$$A = (V_2 - V_1)P_2 = (0.4\ \text{m}^3)(350\ \text{kPa}) = 140\ \text{m}^3 \cdot \text{kPa}$$

Therefore,

$$W_{13} = \mathbf{140\ kJ}$$

The work is done by the system (to raise the piston and to push the atmospheric air out of the way), and thus it is work output.

(*c*) Under the stated assumptions and observations, the energy balance on the system between the initial and final states (process 1–3) can be expressed as

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\substack{\text{Net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{\text{system}}}_{\substack{\text{Change in internal, kinetic,} \\ \text{potential, etc., energies}}}$$

$$Q_{\text{in}} - W_{b,\text{out}} = \Delta U = m(u_3 - u_1)$$

The mass of the system can be determined from the ideal-gas relation:

$$m = \frac{P_1V_1}{RT_1} = \frac{(150\ \text{kPa})(0.4\ \text{m}^3)}{(0.287\ \text{kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(300\ \text{K})} = 0.697\ \text{kg}$$

The internal energies are determined from the air table (Table A–17) to be

$$u_1 = u_{@\ 300\ \text{K}} = 214.07\ \text{kJ/kg}$$

$$u_3 = u_{@\ 1400\ \text{K}} = 1113.52\ \text{kJ/kg}$$

Thus,

$$Q_{\text{in}} - 140\ \text{kJ} = (0.697\ \text{kg})[(1113.52 - 214.07)\ \text{kJ/kg}]$$

$$Q_{\text{in}} = \mathbf{767\ kJ}$$

Discussion The positive sign verifies that heat is transferred to the system.

4–5 NTERNAL ENERGY, ENTHALPY, AND SPECIFIC HEATS OF SOLIDS AND LIQUIDS

- A substance whose specific volume (or density) is constant is called an **incompressible substance.**

- The specific volumes of solids and liquids essentially remain constant during a process (Fig. 4–33). Therefore, liquids and solids can be approximated as incompressible substances without sacrificing much in accuracy. The constant-volume assumption should be taken to imply that the energy associated with the volume change is negligible compared with other forms of energy.

- Otherwise, this assumption would be ridiculous for studying the thermal stresses in solids (caused by volume change with temperature) or analyzing liquid-in-glass thermometers.

- It can be mathematically shown that (see Chap. 12) the constant-volume and constant-pressure specific heats are identical for incompressible substances (Fig. 4–34).

- Therefore, for solids and liquids, the subscripts on cp and cv can be dropped, and both specific heats can be represented by a single symbol c. That is,

$$cp = cv = c \quad (4–32)$$

- This result could also be deduced from the physical definitions of constant-volume and constant-pressure specific heats. Specific heat values for several common liquids and solids are given in Table A–3.

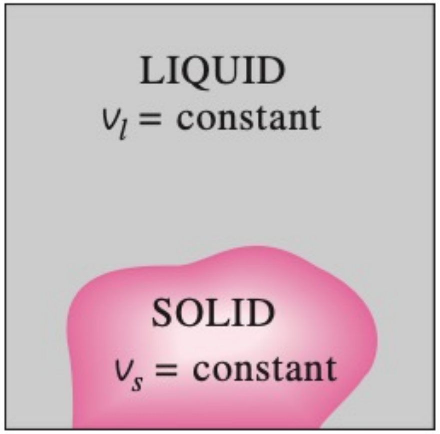


FIGURE 4–33

The specific volumes of incompressible substances remain constant during a process.

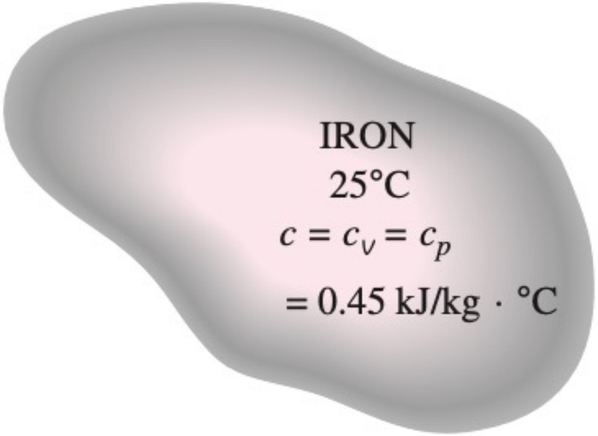


FIGURE 4–34

The c_v and c_p values of incompressible substances are identical and are denoted by c.

Internal Energy Changes

Like those of ideal gases, the specific heats of incompressible substances depend on temperature only. Thus, the partial differentials in the defining equation of c_v can be replaced by ordinary differentials, which yield

$$du = c_v\, dT = c(T)\, dT \tag{4–33}$$

The change in internal energy between states 1 and 2 is then obtained by integration:

$$\Delta u = u_2 - u_1 = \int_1^2 c(T)\, dT \qquad \text{(kJ/kg)} \tag{4–34}$$

The variation of specific heat c with temperature should be known before this integration can be carried out. For small temperature intervals, a c value at the average temperature can be used and treated as a constant, yielding

$$\Delta u \cong c_{\text{avg}}(T_2 - T_1) \qquad \text{(kJ/kg)} \tag{4–35}$$

Enthalpy Changes

Using the definition of enthalpy $h = u + P\mathrm{v}$ and noting that $\mathrm{v} =$ constant, the differential form of the enthalpy change of incompressible substances can be determined by differentiation to be

$$dh = du + \mathrm{v}\,dP + P\,\overset{0}{\nearrow}\!\!d\mathrm{v} = du + \mathrm{v}\,dP \qquad \textbf{(4–36)}$$

Integrating,

$$\Delta h = \Delta u + \mathrm{v}\,\Delta P \cong c_{\mathrm{avg}}\,\Delta T + \mathrm{v}\,\Delta P \qquad (\mathrm{kJ/kg}) \qquad \textbf{(4–37)}$$

For *solids*, the term $\mathrm{v}\,\Delta P$ is insignificant and thus $\Delta h = \Delta u \cong c_{\mathrm{avg}}\Delta T$. For *liquids*, two special cases are commonly encountered:

1. *Constant-pressure processes,* as in heaters ($\Delta P = 0$): $\Delta h = \Delta u \cong c_{\mathrm{avg}}\Delta T$
2. *Constant-temperature processes,* as in pumps ($\Delta T = 0$): $\Delta h = \mathrm{v}\,\Delta P$

For a process between states 1 and 2, the last relation can be expressed as $h_2 - h_1 = v(P_2 - P_1)$. By taking state 2 to be the compressed liquid state at a given T and P and state 1 to be the saturated liquid state at the same temperature, the enthalpy of the compressed liquid can be expressed as

$$h_{@P,T} \cong h_{f\,@\,T} + v_{f\,@\,T}(P - P_{\text{sat}\,@\,T}) \tag{4–38}$$

as discussed in Chap. 3. This is an improvement over the assumption that the enthalpy of the compressed liquid could be taken as h_f at the given temperature (that is, $h_{@\,P,T} \cong h_{f\,@\,T}$). However, the contribution of the last term is often very small, and is neglected. (Note that at high temperature and pressures, Eq. 4–38 may overcorrect the enthalpy and result in a larger error than the approximation $h \cong h_{f\,@\,T}$.)

EXAMPLE 4–11 Enthalpy of Compressed Liquid

Determine the enthalpy of liquid water at 100°C and 15 MPa (*a*) by using compressed liquid tables, (*b*) by approximating it as a saturated liquid, and (*c*) by using the correction given by Eq. 4–38.

Solution The enthalpy of liquid water is to be determined exactly and approximately.

Analysis At 100°C, the saturation pressure of water is 101.42 kPa, and since $P > P_{\text{sat}}$, the water exists as a compressed liquid at the specified state.

(*a*) From compressed liquid tables, we read

$$\left.\begin{aligned} P &= 15\ \text{MPa} \\ T &= 100^\circ\text{C} \end{aligned}\right\} \quad h = \mathbf{430.39\ kJ/kg} \qquad \text{(Table A–7)}$$

This is the exact value.

(*b*) Approximating the compressed liquid as a saturated liquid at 100°C, as is commonly done, we obtain

$$h \cong h_{f\,@\,100^\circ\text{C}} = \mathbf{419.17\ kJ/kg}$$

This value is in error by about 2.6 percent.

(*c*) From Eq. 4–38,

$$\begin{aligned} h_{@P,T} &\cong h_{f\,@\,T} + v_{f\,@\,T}(P - P_{\text{sat}\,@\,T}) \\ &= (419.17\ \text{kJ/kg}) + (0.001\ \text{m}^3\ \text{kg})[(15{,}000 - 101.42)\ \text{kPa}]\left(\frac{1\ \text{kJ}}{1\ \text{kPa}\cdot\text{m}^3}\right) \\ &= \mathbf{434.07\ kJ/kg} \end{aligned}$$

Discussion Note that the correction term reduced the error from 2.6 to about 1 percent in this case. However, this improvement in accuracy is often not worth the extra effort involved.

EXAMPLE 4–12 Cooling of an Iron Block by Water

A 50-kg iron block at 80°C is dropped into an insulated tank that contains 0.5 m^3 of liquid water at 25°C. Determine the temperature when thermal equilibrium is reached.

Solution An iron block is dropped into water in an insulated tank. The final temperature when thermal equilibrium is reached is to be determined.

Assumptions **1** Both water and the iron block are incompressible substances. **2** Constant specific heats at room temperature can be used for water and the iron. **3** The system is stationary and thus the kinetic and potential energy changes are zero, $\Delta KE = \Delta PE = 0$ and $\Delta E = \Delta U$. **4** There are no electrical, shaft, or other forms of work involved. **5** The system is well-insulated and thus there is no heat transfer.

Analysis We take the entire contents of the tank as the *system* (Fig. 4–35). This is a *closed system* since no mass crosses the system boundary during the process. We observe that the volume of a rigid tank is constant, and thus there is no boundary work. The energy balance on the system can be expressed as

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\substack{\text{Net energy transfer}\\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{\text{system}}}_{\substack{\text{Change in internal, kinetic,}\\ \text{potential, etc., energies}}}$$

$$0 = \Delta U$$

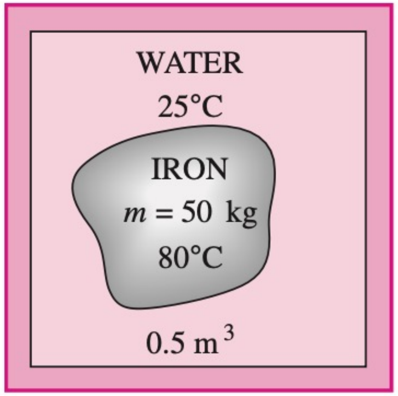


FIGURE 4–35

Schematic for Example 4–12.

The total internal energy *U* is an extensive property, and therefore it can be expressed as the sum of the internal energies of the parts of the system. Then the total internal energy change of the system becomes

$$\Delta U_{\text{sys}} = \Delta U_{\text{iron}} + \Delta U_{\text{water}} = 0$$

$$[mc(T_2 - T_1)]_{\text{iron}} + [mc(T_2 - T_1)]_{\text{water}} = 0$$

The specific volume of liquid water at or about room temperature can be taken to be 0.001 m^3/kg. Then the mass of the water is

$$m_{\text{water}} = \frac{V}{v} = \frac{0.5\ \text{m}^3}{0.001\ \text{m}_3/\text{kg}} = 500\ \text{kg}$$

The specific heats of iron and liquid water are determined from Table A–3 to be $c_{\text{iron}} = 0.45$ kJ/kg · °C and $c_{\text{water}} = 4.18$ kJ/kg · °C. Substituting these values into the energy equation, we obtain

$$(50\ \text{kg})(0.45\ \text{kJ/kg}\cdot{}^\circ\text{C})(T_2 - 80^\circ\text{C}) + (500\ \text{kg})(4.18\ \text{kJ/kg}\cdot{}^\circ\text{C})(T_2 - 25^\circ\text{C}) = 0$$

$$T_2 = \mathbf{25.6^\circ C}$$

Therefore, when thermal equilibrium is established, both the water and iron will be at 25.6°C.

Discussion The small rise in water temperature is due to its large mass and large specific heat.

EXAMPLE 4–13 **Temperature Rise due to Slapping**

If you ever slapped someone or got slapped yourself, you probably remember the burning sensation. Imagine you had the unfortunate occasion of being slapped by an angry person, which caused the temperature of the affected area of your face to rise by 1.8°C (ouch!). Assuming the slapping hand has a mass of 1.2 kg and about 0.150 kg of the tissue on the face and the hand is affected by the incident, estimate the velocity of the hand just before impact. Take the specific heat of the tissue to be 3.8 kJ/kg · °C.

Solution The face of a person is slapped. For the specified temperature rise of the affected part, the impact velocity of the hand is to be determined.
Assumptions **1** The hand is brought to a complete stop after the impact. **2** The face takes the blow without significant movement. **3** No heat is transferred from the affected area to the surroundings, and thus the process is adiabatic. **4** No work is done on or by the system. **5** The potential energy change is zero, $\Delta\text{PE} = 0$ and $\Delta E = \Delta U + \Delta\text{KE}$.

Analysis We analyze this incident in a professional manner without involving any emotions. First, we identify the system, draw a sketch of it, and state our observations about the specifics of the problem. We take the hand and the affected portion of the face as the *system* (Fig. 4–36). This is a *closed system* since it involves a fixed amount of mass (no mass transfer). We observe that the kinetic energy of the hand decreases during the process, as evidenced by a decrease in velocity from initial value to zero, while the internal energy of the affected area increases, as evidenced by an increase in the temperature. There seems to be no significant energy transfer between the system and its surroundings during this process.

Under the stated assumptions and observations, the energy balance on the system can be expressed as

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\substack{\text{Net energy transfer}\\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{\text{system}}}_{\substack{\text{Change in internal, kinetic,}\\ \text{potential, etc., energies}}}$$

$$0 = \Delta U_{\text{affected tissue}} + \Delta \text{KE}_{\text{hand}}$$

$$0 = (mc\Delta T)_{\text{affected tissue}} + [m(0 - V^2)/2]_{\text{hand}}$$

That is, the decrease in the kinetic energy of the hand must be equal to the increase in the internal energy of the affected area. Solving for the velocity and substituting the given quantities, the impact velocity of the hand is determined to be

$$V_{\text{hand}} = \sqrt{\frac{2(mc\Delta T)_{\text{affected tissue}}}{m_{\text{hand}}}}$$

$$= \sqrt{\frac{2(0.15\text{ kg})(3.8\text{ kJ/kg}\cdot{}^\circ\text{C})(1.8^\circ\text{C})}{1.2\text{ kg}}\left(\frac{1000\text{ m}^2/\text{s}^2}{1\text{ kJ/kg}}\right)}$$

$$= \mathbf{41.4\ m/s}\ (\text{or } 149\text{ km/h})$$

Discussion Reconstruction of events such as this by making appropriate assumptions are commonly used in forensic engineering.