

1. (a) Since the gas is ideal, its pressure  $p$  is given in terms of the number of moles  $n$ , the volume  $V$ , and the temperature  $T$  by  $p = nRT/V$ . The work done by the gas during the isothermal expansion is

$$W = \int_{V_1}^{V_2} p \, dV = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \frac{V_2}{V_1} .$$

We substitute  $V_2 = 2.00V_1$  to obtain

$$W = nRT \ln 2.00 = (4.00 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(400 \text{ K}) \ln 2.00 = 9.22 \times 10^3 \text{ J}.$$

(b) Since the expansion is isothermal, the change in entropy is given by  $\Delta S = \int (1/T) \, dQ = Q/T$ , where  $Q$  is the heat absorbed. According to the first law of thermodynamics,  $\Delta E_{\text{int}} = Q - W$ . Now the internal energy of an ideal gas depends only on the temperature and not on the pressure and volume. Since the expansion is isothermal,  $\Delta E_{\text{int}} = 0$  and  $Q = W$ . Thus,

$$\Delta S = \frac{W}{T} = \frac{9.22 \times 10^3 \text{ J}}{400 \text{ K}} = 23.1 \text{ J/K}.$$

(c)  $\Delta S = 0$  for all reversible adiabatic processes.

2. From Eq. 20-2, we obtain

$$Q = T\Delta S = (405 \text{ K})(46.0 \text{ J/K}) = 1.86 \times 10^4 \text{ J}.$$

3. An isothermal process is one in which  $T_i = T_f$  which implies  $\ln(T_f/T_i) = 0$ . Therefore, with  $V_f/V_i = 2.00$ , Eq. 20-4 leads to

$$\Delta S = nR \ln \left( \frac{V_f}{V_i} \right) = (2.50 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K}) \ln(2.00) = 14.4 \text{ J/K}.$$

4. (a) This may be considered a reversible process (as well as isothermal), so we use  $\Delta S = Q/T$  where  $Q = Lm$  with  $L = 333 \text{ J/g}$  from Table 19-4. Consequently,

$$\Delta S = \frac{(333 \text{ J/g})(12.0 \text{ g})}{273 \text{ K}} = 14.6 \text{ J/K}.$$

(b) The situation is similar to that described in part (a), except with  $L = 2256 \text{ J/g}$ ,  $m = 5.00 \text{ g}$ , and  $T = 373 \text{ K}$ . We therefore find  $\Delta S = 30.2 \text{ J/K}$ .

5. We use the following relation derived in Sample Problem 20-2:

$$\Delta S = mc \ln \left( \frac{T_f}{T_i} \right).$$

(a) The energy absorbed as heat is given by Eq. 19-14. Using Table 19-3, we find

$$Q = cm\Delta T = \left( 386 \frac{\text{J}}{\text{kg} \cdot \text{K}} \right) (2.00 \text{ kg}) (75 \text{ K}) = 5.79 \times 10^4 \text{ J}$$

where we have used the fact that a change in Kelvin temperature is equivalent to a change in Celsius degrees.

(b) With  $T_f = 373.15 \text{ K}$  and  $T_i = 298.15 \text{ K}$ , we obtain

$$\Delta S = (2.00 \text{ kg}) \left( 386 \frac{\text{J}}{\text{kg} \cdot \text{K}} \right) \ln \left( \frac{373.15}{298.15} \right) = 173 \text{ J/K}.$$

6. An isothermal process is one in which  $T_i = T_f$  which implies  $\ln (T_f/T_i) = 0$ . Therefore, Eq. 20-4 leads to

$$\Delta S = nR \ln \left( \frac{V_f}{V_i} \right) \Rightarrow n = \frac{22.0}{(8.31) \ln(3.4/1.3)} = 2.75 \text{ mol.}$$

7. (a) The energy that leaves the aluminum as heat has magnitude  $Q = m_a c_a (T_{ai} - T_f)$ , where  $m_a$  is the mass of the aluminum,  $c_a$  is the specific heat of aluminum,  $T_{ai}$  is the initial temperature of the aluminum, and  $T_f$  is the final temperature of the aluminum-water system. The energy that enters the water as heat has magnitude  $Q = m_w c_w (T_f - T_{wi})$ , where  $m_w$  is the mass of the water,  $c_w$  is the specific heat of water, and  $T_{wi}$  is the initial temperature of the water. The two energies are the same in magnitude since no energy is lost. Thus,

$$m_a c_a (T_{ai} - T_f) = m_w c_w (T_f - T_{wi}) \Rightarrow T_f = \frac{m_a c_a T_{ai} + m_w c_w T_{wi}}{m_a c_a + m_w c_w}.$$

The specific heat of aluminum is 900 J/kg·K and the specific heat of water is 4190 J/kg·K. Thus,

$$\begin{aligned} T_f &= \frac{(0.200 \text{ kg})(900 \text{ J/kg} \cdot \text{K})(100^\circ\text{C}) + (0.0500 \text{ kg})(4190 \text{ J/kg} \cdot \text{K})(20^\circ\text{C})}{(0.200 \text{ kg})(900 \text{ J/kg} \cdot \text{K}) + (0.0500 \text{ kg})(4190 \text{ J/kg} \cdot \text{K})} \\ &= 57.0^\circ\text{C} \quad \text{or } 330 \text{ K}. \end{aligned}$$

(b) Now temperatures must be given in Kelvins:  $T_{ai} = 393 \text{ K}$ ,  $T_{wi} = 293 \text{ K}$ , and  $T_f = 330 \text{ K}$ . For the aluminum,  $dQ = m_a c_a dT$  and the change in entropy is

$$\begin{aligned} \Delta S_a &= \int \frac{dQ}{T} = m_a c_a \int_{T_{ai}}^{T_f} \frac{dT}{T} = m_a c_a \ln \frac{T_f}{T_{ai}} \\ &= (0.200 \text{ kg})(900 \text{ J/kg} \cdot \text{K}) \ln \left( \frac{330 \text{ K}}{373 \text{ K}} \right) = -22.1 \text{ J/K}. \end{aligned}$$

(c) The entropy change for the water is

$$\begin{aligned} \Delta S_w &= \int \frac{dQ}{T} = m_w c_w \int_{T_{wi}}^{T_f} \frac{dT}{T} = m_w c_w \ln \frac{T_f}{T_{wi}} \\ &= (0.0500 \text{ kg})(4190 \text{ J/kg} \cdot \text{K}) \ln \left( \frac{330 \text{ K}}{293 \text{ K}} \right) = +24.9 \text{ J/K}. \end{aligned}$$

(d) The change in the total entropy of the aluminum-water system is

$$\Delta S = \Delta S_a + \Delta S_w = -22.1 \text{ J/K} + 24.9 \text{ J/K} = +2.8 \text{ J/K}.$$

8. We concentrate on the first term of Eq. 20-4 (the second term is zero because the final and initial temperatures are the same, and because  $\ln(1) = 0$ ). Thus, the entropy change is

$$\Delta S = nR \ln(V_f/V_i) .$$

Noting that  $\Delta S = 0$  at  $V_f = 0.40 \text{ m}^3$ , we are able to deduce that  $V_i = 0.40 \text{ m}^3$ . We now examine the point in the graph where  $\Delta S = 32 \text{ J/K}$  and  $V_f = 1.2 \text{ m}^3$ ; the above expression can now be used to solve for the number of moles. We obtain  $n = 3.5 \text{ mol}$ .



9. This problem is similar to Sample Problem 20-2. The only difference is that we need to find the mass  $m$  of each of the blocks. Since the two blocks are identical the final temperature  $T_f$  is the average of the initial temperatures:

$$T_f = \frac{1}{2}(T_i + T_f) = \frac{1}{2}(305.5 \text{ K} + 294.5 \text{ K}) = 300.0 \text{ K}.$$

Thus from  $Q = mc\Delta T$  we find the mass  $m$ :

$$m = \frac{Q}{c\Delta T} = \frac{215 \text{ J}}{(386 \text{ J/kg} \cdot \text{K})(300.0 \text{ K} - 294.5 \text{ K})} = 0.101 \text{ kg}.$$

(a) The change in entropy for block  $L$  is

$$\Delta S_L = mc \ln \left( \frac{T_f}{T_{iL}} \right) = (0.101 \text{ kg})(386 \text{ J/kg} \cdot \text{K}) \ln \left( \frac{300.0 \text{ K}}{305.5 \text{ K}} \right) = -0.710 \text{ J/K}.$$

(b) Since the temperature of the reservoir is virtually the same as that of the block, which gives up the same amount of heat as the reservoir absorbs, the change in entropy  $\Delta S'_L$  of the reservoir connected to the left block is the opposite of that of the left block:  $\Delta S'_L = -\Delta S_L = +0.710 \text{ J/K}$ .

(c) The entropy change for block  $R$  is

$$\Delta S_R = mc \ln \left( \frac{T_f}{T_{iR}} \right) = (0.101 \text{ kg})(386 \text{ J/kg} \cdot \text{K}) \ln \left( \frac{300.0 \text{ K}}{294.5 \text{ K}} \right) = +0.723 \text{ J/K}.$$

(d) Similar to the case in part (b) above, the change in entropy  $\Delta S'_R$  of the reservoir connected to the right block is given by  $\Delta S'_R = -\Delta S_R = -0.723 \text{ J/K}$ .

(e) The change in entropy for the two-block system is

$$\Delta S_L + \Delta S_R = -0.710 \text{ J/K} + 0.723 \text{ J/K} = +0.013 \text{ J/K}.$$

(f) The entropy change for the entire system is given by

$$\Delta S = \Delta S_L + \Delta S'_L + \Delta S_R + \Delta S'_R = \Delta S_L - \Delta S_L + \Delta S_R - \Delta S_R = 0,$$

which is expected of a reversible process.

10. We follow the method shown in Sample Problem 20-2. Since

$$\Delta S = m c \int \frac{dT}{T} = mc \ln(T_f/T_i) ,$$

then with  $\Delta S = 50 \text{ J/K}$ ,  $T_f = 380 \text{ K}$ ,  $T_i = 280 \text{ K}$  and  $m = 0.364 \text{ kg}$ , we obtain  $c = 4.5 \times 10^2 \text{ J/kg K}$ .

11. The connection between molar heat capacity and the degrees of freedom of a diatomic gas is given by setting  $f = 5$  in Eq. 19-51. Thus,  $C_v = 5R/2$ ,  $C_p = 7R/2$ , and  $\gamma = 7/5$ . In addition to various equations from Chapter 19, we also make use of Eq. 20-4 of this chapter. We note that we are asked to use the ideal gas constant as  $R$  and not plug in its numerical value. We also recall that isothermal means constant-temperature, so  $T_2 = T_1$  for the  $1 \rightarrow 2$  process. The statement (at the end of the problem) regarding “per mole” may be taken to mean that  $n$  may be set identically equal to 1 wherever it appears.

(a) The gas law in ratio form (see Sample Problem 19-1) is used to obtain

$$p_2 = p_1 \left( \frac{V_1}{V_2} \right) = \frac{p_1}{3} \Rightarrow \frac{p_2}{p_1} = \frac{1}{3} = 0.333.$$

(b) The adiabatic relations Eq. 19-54 and Eq. 19-56 lead to

$$p_3 = p_1 \left( \frac{V_1}{V_3} \right)^\gamma = \frac{p_1}{3^{1.4}} \Rightarrow \frac{p_3}{p_1} = \frac{1}{3^{1.4}} = 0.215.$$

(c) and

$$T_3 = T_1 \left( \frac{V_1}{V_3} \right)^{\gamma-1} = \frac{T_1}{3^{0.4}} \Rightarrow \frac{T_3}{T_1} = \frac{1}{3^{0.4}} = 0.644.$$

• process  $1 \rightarrow 2$

(d) The work is given by Eq. 19-14:  $W = nRT_1 \ln (V_2/V_1) = RT_1 \ln 3$  which is approximately  $1.10RT_1$ . Thus,  $W/nRT_1 = \ln 3 = 1.10$ .

(e) The internal energy change is  $\Delta E_{\text{int}} = 0$  since this is an ideal gas process without a temperature change (see Eq. 19-45). Thus, the energy absorbed as heat is given by the first law of thermodynamics:  $Q = \Delta E_{\text{int}} + W \approx 1.10RT_1$ , or  $Q/nRT_1 = \ln 3 = 1.10$ .

(f)  $\Delta E_{\text{int}} = 0$  or  $\Delta E_{\text{int}} / nRT_1 = 0$

(g) The entropy change is  $\Delta S = Q/T_1 = 1.10R$ , or  $\Delta S/R = 1.10$ .

• process  $2 \rightarrow 3$

(h) The work is zero since there is no volume change. Therefore,  $W/nRT_1 = 0$

(i) The internal energy change is

$$\Delta E_{\text{int}} = nC_V (T_3 - T_2) = (1) \left( \frac{5}{2} R \right) \left( \frac{T_1}{3^{0.4}} - T_1 \right) \approx -0.889 RT_1 \Rightarrow \frac{\Delta E_{\text{int}}}{nRT_1} \approx -0.889.$$

This ratio ( $-0.889$ ) is also the value for  $Q/nRT_1$  (by either the first law of thermodynamics or by the definition of  $C_V$ ).

(j)  $\Delta E_{\text{int}} / nRT_1 = -0.889.$

(k) For the entropy change, we obtain

$$\frac{\Delta S}{R} = n \ln \left( \frac{V_3}{V_1} \right) + n \frac{C_V}{R} \ln \left( \frac{T_3}{T_1} \right) = (1) \ln(1) + (1) \left( \frac{5}{2} \right) \ln \left( \frac{T_1/3^{0.4}}{T_1} \right) = 0 + \frac{5}{2} \ln(3^{-0.4}) \approx -1.10 .$$

• process 3  $\rightarrow$  1

(l) By definition,  $Q = 0$  in an adiabatic process, which also implies an absence of entropy change (taking this to be a reversible process). The internal change must be the negative of the value obtained for it in the previous process (since all the internal energy changes must add up to zero, for an entire cycle, and its change is zero for process 1  $\rightarrow$  2), so  $\Delta E_{\text{int}} = +0.889RT_1$ . By the first law of thermodynamics, then,

$$W = Q - \Delta E_{\text{int}} = -0.889RT_1,$$

or  $W / nRT_1 = -0.889.$

(m)  $Q = 0$  in an adiabatic process.

(n)  $\Delta E_{\text{int}} / nRT_1 = +0.889.$

(o)  $\Delta S / nR = 0$

12. We use Eq. 20-1:

$$\Delta S = \int \frac{nC_v dT}{T} = nA \int_{5.00}^{10.0} T^2 dT = \frac{nA}{3} \left[ (10.0)^3 - (5.00)^3 \right] = 0.0368 \text{ J/K}.$$

13. (a) We refer to the copper block as block 1 and the lead block as block 2. The equilibrium temperature  $T_f$  satisfies  $m_1 c_1 (T_f - T_{i,1}) + m_2 c_2 (T_f - T_{i,2}) = 0$ , which we solve for  $T_f$ :

$$T_f = \frac{m_1 c_1 T_{i,1} + m_2 c_2 T_{i,2}}{m_1 c_1 + m_2 c_2} = \frac{(50.0 \text{ g})(386 \text{ J/kg} \cdot \text{K})(400 \text{ K}) + (100 \text{ g})(128 \text{ J/kg} \cdot \text{K})(200 \text{ K})}{(50.0 \text{ g})(386 \text{ J/kg} \cdot \text{K}) + (100 \text{ g})(128 \text{ J/kg} \cdot \text{K})} \\ = 320 \text{ K}.$$

(b) Since the two-block system is thermally insulated from the environment, the change in internal energy of the system is zero.

(c) The change in entropy is

$$\Delta S = \Delta S_1 + \Delta S_2 = m_1 c_1 \ln \left( \frac{T_f}{T_{i,1}} \right) + m_2 c_2 \ln \left( \frac{T_f}{T_{i,2}} \right) \\ = (50.0 \text{ g})(386 \text{ J/kg} \cdot \text{K}) \ln \left( \frac{320 \text{ K}}{400 \text{ K}} \right) + (100 \text{ g})(128 \text{ J/kg} \cdot \text{K}) \ln \left( \frac{320 \text{ K}}{200 \text{ K}} \right) \\ = +1.72 \text{ J/K}.$$

14. (a) It is possible to motivate, starting from Eq. 20-3, the notion that heat may be found from the integral (or “area under the curve”) of a curve in a  $TS$  diagram, such as this one. Either from calculus, or from geometry (area of a trapezoid), it is straightforward to find the result for a “straight-line” path in the  $TS$  diagram:

$$Q_{\text{straight}} = \left( \frac{T_i + T_f}{2} \right) \Delta S$$

which could, in fact, be *directly* motivated from Eq. 20-3 (but it is important to bear in mind that this is rigorously true only for a process which forms a straight line in a graph that plots  $T$  versus  $S$ ). This leads to  $(300 \text{ K})(15 \text{ J/K}) = 4.5 \times 10^3 \text{ J}$  for the energy absorbed as heat by the gas.

(b) Using Table 19-3 and Eq. 19-45, we find

$$\Delta E_{\text{int}} = n \left( \frac{3}{2} R \right) \Delta T = (2.0 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(200 \text{ K} - 400 \text{ K}) = -5.0 \times 10^3 \text{ J}.$$

(c) By the first law of thermodynamics,

$$W = Q - \Delta E_{\text{int}} = 4.5 \text{ kJ} - (-5.0 \text{ kJ}) = 9.5 \text{ kJ}.$$

15. The ice warms to 0°C, then melts, and the resulting water warms to the temperature of the lake water, which is 15°C. As the ice warms, the energy it receives as heat when the temperature changes by  $dT$  is  $dQ = mc_I dT$ , where  $m$  is the mass of the ice and  $c_I$  is the specific heat of ice. If  $T_i$  ( $= 263$  K) is the initial temperature and  $T_f$  ( $= 273$  K) is the final temperature, then the change in its entropy is

$$\Delta S = \int \frac{dQ}{T} = mc_I \int_{T_i}^{T_f} \frac{dT}{T} = mc_I \ln \frac{T_f}{T_i} = (0.010 \text{ kg})(2220 \text{ J/kg} \cdot \text{K}) \ln \left( \frac{273 \text{ K}}{263 \text{ K}} \right) = 0.828 \text{ J/K}.$$

Melting is an isothermal process. The energy leaving the ice as heat is  $mL_F$ , where  $L_F$  is the heat of fusion for ice. Thus,

$$\Delta S = Q/T = mL_F/T = (0.010 \text{ kg})(333 \times 10^3 \text{ J/kg})/(273 \text{ K}) = 12.20 \text{ J/K}.$$

For the warming of the water from the melted ice, the change in entropy is

$$\Delta S = mc_w \ln \frac{T_f}{T_i},$$

where  $c_w$  is the specific heat of water ( $4190 \text{ J/kg} \cdot \text{K}$ ). Thus,

$$\Delta S = (0.010 \text{ kg})(4190 \text{ J/kg} \cdot \text{K}) \ln \left( \frac{288 \text{ K}}{273 \text{ K}} \right) = 2.24 \text{ J/K}.$$

The total change in entropy for the ice and the water it becomes is

$$\Delta S = 0.828 \text{ J/K} + 12.20 \text{ J/K} + 2.24 \text{ J/K} = 15.27 \text{ J/K}.$$

Since the temperature of the lake does not change significantly when the ice melts, the change in its entropy is  $\Delta S = Q/T$ , where  $Q$  is the energy it receives as heat (the negative of the energy it supplies the ice) and  $T$  is its temperature. When the ice warms to 0°C,

$$Q = -mc_I (T_f - T_i) = -(0.010 \text{ kg})(2220 \text{ J/kg} \cdot \text{K})(10 \text{ K}) = -222 \text{ J}.$$

When the ice melts,

$$Q = -mL_F = -(0.010 \text{ kg})(333 \times 10^3 \text{ J/kg}) = -3.33 \times 10^3 \text{ J}.$$

When the water from the ice warms,

$$Q = -mc_w (T_f - T_i) = -(0.010 \text{ kg})(4190 \text{ J/kg} \cdot \text{K})(15 \text{ K}) = -629 \text{ J}.$$



The total energy leaving the lake water is

$$Q = -222 \text{ J} - 3.33 \times 10^3 \text{ J} - 6.29 \times 10^2 \text{ J} = -4.18 \times 10^3 \text{ J}.$$

The change in entropy is

$$\Delta S = -\frac{4.18 \times 10^3 \text{ J}}{288 \text{ K}} = -14.51 \text{ J/K}.$$

The change in the entropy of the ice-lake system is  $\Delta S = (15.27 - 14.51) \text{ J/K} = 0.76 \text{ J/K}$ .

16. In coming to equilibrium, the heat lost by the  $100 \text{ cm}^3$  of liquid water (of mass  $m_w = 100 \text{ g}$  and specific heat capacity  $c_w = 4190 \text{ J/kg}\cdot\text{K}$ ) is absorbed by the ice (of mass  $m_i$  which melts and reaches  $T_f > 0^\circ\text{C}$ ). We begin by finding the equilibrium temperature:

$$\begin{aligned} \sum Q &= 0 \\ Q_{\text{warm water cools}} + Q_{\text{ice warms to } 0^\circ} + Q_{\text{ice melts}} + Q_{\text{melted ice warms}} &= 0 \\ c_w m_w (T_f - 20^\circ) + c_i m_i (0^\circ - (-10^\circ)) + L_F m_i + c_w m_i (T_f - 0^\circ) &= 0 \end{aligned}$$

which yields, after using  $L_F = 333000 \text{ J/kg}$  and values cited in the problem,  $T_f = 12.24^\circ$  which is equivalent to  $T_f = 285.39 \text{ K}$ . Sample Problem 19-2 shows that

$$\Delta S_{\text{temp change}} = mc \ln \left( \frac{T_2}{T_1} \right)$$

for processes where  $\Delta T = T_2 - T_1$ , and Eq. 20-2 gives

$$\Delta S_{\text{melt}} = \frac{L_F m}{T_o}$$

for the phase change experienced by the ice (with  $T_o = 273.15 \text{ K}$ ). The total entropy change is (with  $T$  in Kelvins)

$$\begin{aligned} \Delta S_{\text{system}} &= m_w c_w \ln \left( \frac{285.39}{293.15} \right) + m_i c_i \ln \left( \frac{273.15}{263.15} \right) + m_i c_w \ln \left( \frac{285.39}{273.15} \right) + \frac{L_F m_i}{273.15} \\ &= -11.24 + 0.66 + 1.47 + 9.75 = 0.64 \text{ J/K}. \end{aligned}$$

17. (a) The final mass of ice is  $(1773 \text{ g} + 227 \text{ g})/2 = 1000 \text{ g}$ . This means 773 g of water froze. Energy in the form of heat left the system in the amount  $mL_F$ , where  $m$  is the mass of the water that froze and  $L_F$  is the heat of fusion of water. The process is isothermal, so the change in entropy is

$$\Delta S = Q/T = -mL_F/T = -(0.773 \text{ kg})(333 \times 10^3 \text{ J/kg})/(273 \text{ K}) = -943 \text{ J/K}.$$

(b) Now, 773 g of ice is melted. The change in entropy is

$$\Delta S = \frac{Q}{T} = \frac{mL_F}{T} = +943 \text{ J/K}.$$

(c) Yes, they are consistent with the second law of thermodynamics. Over the entire cycle, the change in entropy of the water-ice system is zero even though part of the cycle is irreversible. However, the system is not closed. To consider a closed system, we must include whatever exchanges energy with the ice and water. Suppose it is a constant-temperature heat reservoir during the freezing portion of the cycle and a Bunsen burner during the melting portion. During freezing the entropy of the reservoir increases by 943 J/K. As far as the reservoir-water-ice system is concerned, the process is adiabatic and reversible, so its total entropy does not change. The melting process is irreversible, so the total entropy of the burner-water-ice system increases. The entropy of the burner either increases or else decreases by less than 943 J/K.

18. (a) Work is done only for the *ab* portion of the process. This portion is at constant pressure, so the work done by the gas is

$$W = \int_{V_0}^{4V_0} p_0 dV = p_0(4.00V_0 - 1.00V_0) = 3.00p_0V_0 \Rightarrow \frac{W}{p_0V_0} = 3.00$$

(b) We use the first law:  $\Delta E_{\text{int}} = Q - W$ . Since the process is at constant volume, the work done by the gas is zero and  $E_{\text{int}} = Q$ . The energy  $Q$  absorbed by the gas as heat is  $Q = nC_V \Delta T$ , where  $C_V$  is the molar specific heat at constant volume and  $\Delta T$  is the change in temperature. Since the gas is a monatomic ideal gas,  $C_V = 3R/2$ . Use the ideal gas law to find that the initial temperature is

$$T_b = \frac{p_b V_b}{nR} = \frac{4p_0 V_0}{nR}$$

and that the final temperature is

$$T_c = \frac{p_c V_c}{nR} = \frac{(2p_0)(4V_0)}{nR} = \frac{8p_0 V_0}{nR}.$$

Thus,

$$Q = \frac{3}{2} nR \left( \frac{8p_0 V_0}{nR} - \frac{4p_0 V_0}{nR} \right) = 6.00 p_0 V_0.$$

The change in the internal energy is  $\Delta E_{\text{int}} = 6p_0 V_0$  or  $\Delta E_{\text{int}}/p_0 V_0 = 6.00$ . Since  $n = 1$  mol, this can also be written  $Q = 6.00RT_0$ .

(c) For a complete cycle,  $\Delta E_{\text{int}} = 0$

(d) Since the process is at constant volume, use  $dQ = nC_V dT$  to obtain

$$\Delta S = \int \frac{dQ}{T} = nC_V \int_{T_b}^{T_c} \frac{dT}{T} = nC_V \ln \frac{T_c}{T_b}.$$

Substituting  $C_V = \frac{3}{2} R$  and using the ideal gas law, we write

$$\frac{T_c}{T_b} = \frac{p_c V_c}{p_b V_b} = \frac{(2p_0)(4V_0)}{p_0(4V_0)} = 2.$$

Thus,  $\Delta S = \frac{3}{2} nR \ln 2$ . Since  $n = 1$ , this is  $\Delta S = \frac{3}{2} R \ln 2 = 8.64 \text{ J/K}$ .

(e) For a complete cycle,  $\Delta E_{\text{int}} = 0$  and  $\Delta S = 0$ .

19. We note that the connection between molar heat capacity and the degrees of freedom of a monatomic gas is given by setting  $f = 3$  in Eq. 19-51. Thus,  $C_v = 3R/2$ ,  $C_p = 5R/2$ , and  $\gamma = 5/3$ .

(a) Since this is an ideal gas, Eq. 19-45 holds, which implies  $\Delta E_{\text{int}} = 0$  for this process. Eq. 19-14 also applies, so that by the first law of thermodynamics,

$$Q = 0 + W = nRT_1 \ln V_2/V_1 = p_1 V_1 \ln 2 \rightarrow Q/p_1 V_1 = \ln 2 = 0.693.$$

(b) The gas law in ratio form (see Sample Problem 19-1) implies that the pressure decreased by a factor of 2 during the isothermal expansion process to  $V_2 = 2.00V_1$ , so that it needs to increase by a factor of 4 in this step in order to reach a final pressure of  $p_2 = 2.00p_1$ . That same ratio form now applied to this constant-volume process, yielding  $4.00 = T_2/T_1$  which is used in the following:

$$Q = nC_v \Delta T = n \left( \frac{3}{2} R \right) (T_2 - T_1) = \frac{3}{2} nRT_1 \left( \frac{T_2}{T_1} - 1 \right) = \frac{3}{2} p_1 V_1 (4 - 1) = \frac{9}{2} p_1 V_1$$

or  $Q/p_1 V_1 = 9/2 = 4.50$ .

(c) The work done during the isothermal expansion process may be obtained by using Eq. 19-14:

$$W = nRT_1 \ln V_2/V_1 = p_1 V_1 \ln 2.00 \rightarrow W/p_1 V_1 = \ln 2 = 0.693.$$

(d) In step 2 where the volume is kept constant,  $W = 0$ .

(e) The change in internal energy can be calculated by combining the above results and applying the first law of thermodynamics:

$$\Delta E_{\text{int}} = Q_{\text{total}} - W_{\text{total}} = \left( p_1 V_1 \ln 2 + \frac{9}{2} p_1 V_1 \right) - (p_1 V_1 \ln 2 + 0) = \frac{9}{2} p_1 V_1$$

or  $\Delta E_{\text{int}}/p_1 V_1 = 9/2 = 4.50$ .

(f) The change in entropy may be computed by using Eq. 20-4:

$$\begin{aligned} \Delta S &= R \ln \left( \frac{2.00V_1}{V_1} \right) + C_v \ln \left( \frac{4.00T_1}{T_1} \right) = R \ln 2.00 + \left( \frac{3}{2} R \right) \ln (2.00)^2 \\ &= R \ln 2.00 + 3R \ln 2.00 = 4R \ln 2.00 = 23.0 \text{ J/K}. \end{aligned}$$

The second approach consists of an isothermal (constant  $T$ ) process in which the volume halves, followed by an isobaric (constant  $p$ ) process.

(g) Here the gas law applied to the first (isothermal) step leads to a volume half as big as the original. Since  $\ln(1/2.00) = -\ln 2.00$ , the reasoning used above leads to  $Q = -p_1 V_1 \ln 2.00$ , or  $Q/p_1 V_1 = -\ln 2.00 = -0.693$ .

(h) To obtain a final volume twice as big as the original, in this step we need to increase the volume by a factor of 4.00. Now, the gas law applied to this isobaric portion leads to a temperature ratio  $T_2/T_1 = 4.00$ . Thus,

$$Q = C_p \Delta T = \frac{5}{2} R (T_2 - T_1) = \frac{5}{2} R T_1 \left( \frac{T_2}{T_1} - 1 \right) = \frac{5}{2} p_1 V_1 (4 - 1) = \frac{15}{2} p_1 V_1$$

or  $Q/p_1 V_1 = 15/2 = 7.50$ .

(i) During the isothermal compression process, Eq. 19-14 gives

$$W = nRT_1 \ln V_2/V_1 = p_1 V_1 \ln (-1/2.00) = -p_1 V_1 \ln 2.00 \Rightarrow W/p_1 V_1 = -\ln 2 = -0.693.$$

(j) The initial value of the volume, for this part of the process, is  $V_i = V_1/2$ , and the final volume is  $V_f = 2V_1$ . The pressure maintained during this process is  $p' = 2.00p_1$ . The work is given by Eq. 19-16:

$$W = p' \Delta V = p' (V_f - V_i) = (2.00 p_1) \left( 2.00 V_1 - \frac{1}{2} V_1 \right) = 3.00 p_1 V_1 \Rightarrow W/p_1 V_1 = 3.00.$$

(k) Using the first law of thermodynamics, the change in internal energy is

$$\Delta E_{\text{int}} = Q_{\text{total}} - W_{\text{total}} = \left( \frac{15}{2} p_1 V_1 - p_1 V_1 \ln 2.00 \right) - (3 p_1 V_1 - p_1 V_1 \ln 2.00) = \frac{9}{2} p_1 V_1$$

or  $\Delta E_{\text{int}}/p_1 V_1 = 9/2 = 4.50$ . The result is the same as that obtained in part (e).

(l) Similarly,  $\Delta S = 4R \ln 2.00 = 23.0 \text{ J/K}$ . the same as that obtained in part (f).

20. (a) The final pressure is

$$p_f = (5.00 \text{ kPa}) e^{(V_i - V_f)/a} = (5.00 \text{ kPa}) e^{(1.00 \text{ m}^3 - 2.00 \text{ m}^3)/1.00 \text{ m}^3} = 1.84 \text{ kPa} .$$

(b) We use the ratio form of the gas law (see Sample Problem 19-1) to find the final temperature of the gas:

$$T_f = T_i \left( \frac{p_f V_f}{p_i V_i} \right) = (600 \text{ K}) \frac{(1.84 \text{ kPa})(2.00 \text{ m}^3)}{(5.00 \text{ kPa})(1.00 \text{ m}^3)} = 441 \text{ K} .$$

For later purposes, we note that this result can be written “exactly” as  $T_f = T_i (2e^{-1})$ . In our solution, we are avoiding using the “one mole” datum since it is not clear how precise it is.

(c) The work done by the gas is

$$\begin{aligned} W &= \int_i^f p dV = \int_{V_i}^{V_f} (5.00 \text{ kPa}) e^{(V_i - V)/a} dV = (5.00 \text{ kPa}) e^{V_i/a} \cdot \left[ -a e^{-V/a} \right]_{V_i}^{V_f} \\ &= (5.00 \text{ kPa}) e^{1.00} (1.00 \text{ m}^3) (e^{-1.00} - e^{-2.00}) \\ &= 3.16 \text{ kJ} . \end{aligned}$$

(d) Consideration of a two-stage process, as suggested in the hint, brings us simply to Eq. 20-4. Consequently, with  $C_V = \frac{3}{2} R$  (see Eq. 19-43), we find

$$\begin{aligned} \Delta S &= nR \ln \left( \frac{V_f}{V_i} \right) + n \left( \frac{3}{2} R \right) \ln \left( \frac{T_f}{T_i} \right) = nR \left( \ln 2 + \frac{3}{2} \ln (2e^{-1}) \right) = \frac{p_i V_i}{T_i} \left( \ln 2 + \frac{3}{2} \ln 2 + \frac{3}{2} \ln e^{-1} \right) \\ &= \frac{(5000 \text{ Pa})(1.00 \text{ m}^3)}{600 \text{ K}} \left( \frac{5}{2} \ln 2 - \frac{3}{2} \right) \\ &= 1.94 \text{ J/K} . \end{aligned}$$



21. (a) The efficiency is

$$\varepsilon = \frac{T_H - T_L}{T_H} = \frac{(235 - 115) \text{ K}}{(235 + 273) \text{ K}} = 0.236 = 23.6\% .$$

We note that a temperature difference has the same value on the Kelvin and Celsius scales. Since the temperatures in the equation must be in Kelvins, the temperature in the denominator is converted to the Kelvin scale.

(b) Since the efficiency is given by  $\varepsilon = |W|/|Q_H|$ , the work done is given by

$$|W| = \varepsilon |Q_H| = 0.236(6.30 \times 10^4 \text{ J}) = 1.49 \times 10^4 \text{ J} .$$

22. The answers to this exercise do not depend on the engine being of the Carnot design. Any heat engine that intakes energy as heat (from, say, consuming fuel) equal to  $|Q_H| = 52 \text{ kJ}$  and exhausts (or discards) energy as heat equal to  $|Q_L| = 36 \text{ kJ}$  will have these values of efficiency  $\varepsilon$  and net work  $W$ .

(a) Eq. 20-10 gives

$$\varepsilon = 1 - \left| \frac{Q_L}{Q_H} \right| = 0.31 = 31\% .$$

(b) Eq. 20-6 gives

$$W = |Q_H| - |Q_L| = 16 \text{ kJ} .$$

23. With  $T_L = 290$  K, we find

$$\varepsilon = 1 - \frac{T_L}{T_H} \Rightarrow T_H = \frac{T_L}{1 - \varepsilon} = \frac{290 \text{ K}}{1 - 0.40}$$

which yields the (initial) temperature of the high-temperature reservoir:  $T_H = 483$  K. If we replace  $\varepsilon = 0.40$  in the above calculation with  $\varepsilon = 0.50$ , we obtain a (final) high temperature equal to  $T'_H = 580$  K. The difference is

$$T'_H - T_H = 580 \text{ K} - 483 \text{ K} = 97 \text{ K}.$$

24. Eq. 20-11 leads to

$$\varepsilon = 1 - \frac{T_L}{T_H} = 1 - \frac{373 \text{ K}}{7 \times 10^8 \text{ K}} = 0.9999995$$

quoting more figures than are significant. As a percentage, this is  $\varepsilon = 99.99995\%$ .

25. We solve (b) first

(b) For a Carnot engine, the efficiency is related to the reservoir temperatures by Eq. 20-11. Therefore,

$$T_H = \frac{T_H - T_L}{\epsilon} = \frac{75 \text{ K}}{0.22} = 341 \text{ K}$$

which is equivalent to  $68^\circ\text{C}$ .

(a) The temperature of the cold reservoir is  $T_L = T_H - 75 = 341 \text{ K} - 75 \text{ K} = 266 \text{ K}$ .

26. (a) Eq. 20-11 leads to

$$\mathcal{E} = 1 - \frac{T_L}{T_H} = 1 - \frac{333 \text{ K}}{373 \text{ K}} = 0.107.$$

We recall that a Watt is Joule-per-second. Thus, the (net) work done by the cycle per unit time is the given value 500 J/s. Therefore, by Eq. 20-9, we obtain the heat input per unit time:

$$\mathcal{E} = \frac{W}{|Q_H|} \Rightarrow \frac{0.500 \text{ kJ/s}}{0.107} = 4.67 \text{ kJ/s}.$$

(b) Considering Eq. 20-6 on a per unit time basis, we find  $(4.67 - 0.500) \text{ kJ/s} = 4.17 \text{ kJ/s}$  for the rate of heat exhaust.

27. (a) Energy is added as heat during the portion of the process from  $a$  to  $b$ . This portion occurs at constant volume ( $V_b$ ), so  $Q_{\text{in}} = nC_V \Delta T$ . The gas is a monatomic ideal gas, so  $C_V = 3R/2$  and the ideal gas law gives

$$\Delta T = (1/nR)(p_b V_b - p_a V_a) = (1/nR)(p_b - p_a) V_b.$$

Thus,  $Q_{\text{in}} = \frac{3}{2}(p_b - p_a)V_b$ .  $V_b$  and  $p_b$  are given. We need to find  $p_a$ . Now  $p_a$  is the same as  $p_c$  and points  $c$  and  $b$  are connected by an adiabatic process. Thus,  $p_c V_c^\gamma = p_b V_b^\gamma$  and

$$p_a = p_c = \left(\frac{V_b}{V_c}\right)^\gamma p_b = \left(\frac{1}{8.00}\right)^{5/3} (1.013 \times 10^6 \text{ Pa}) = 3.167 \times 10^4 \text{ Pa}.$$

The energy added as heat is

$$Q_{\text{in}} = \frac{3}{2}(1.013 \times 10^6 \text{ Pa} - 3.167 \times 10^4 \text{ Pa})(1.00 \times 10^{-3} \text{ m}^3) = 1.47 \times 10^3 \text{ J}.$$

(b) Energy leaves the gas as heat during the portion of the process from  $c$  to  $a$ . This is a constant pressure process, so

$$\begin{aligned} Q_{\text{out}} &= nC_p \Delta T = \frac{5}{2}(p_a V_a - p_c V_c) = \frac{5}{2} p_a (V_a - V_c) \\ &= \frac{5}{2}(3.167 \times 10^4 \text{ Pa})(-7.00)(1.00 \times 10^{-3} \text{ m}^3) = -5.54 \times 10^2 \text{ J}, \end{aligned}$$

or  $|Q_{\text{out}}| = 5.54 \times 10^2 \text{ J}$ . The substitutions  $V_a - V_c = V_a - 8.00 V_a = -7.00 V_a$  and  $C_p = \frac{5}{2} R$  were made.

(c) For a complete cycle, the change in the internal energy is zero and

$$W = Q = 1.47 \times 10^3 \text{ J} - 5.54 \times 10^2 \text{ J} = 9.18 \times 10^2 \text{ J}.$$

(d) The efficiency is  $\mathcal{E} = W/Q_{\text{in}} = (9.18 \times 10^2 \text{ J})/(1.47 \times 10^3 \text{ J}) = 0.624 = 62.4\%$ .

28. From Fig. 20-28, we see  $Q_H = 4000 \text{ J}$  at  $T_H = 325 \text{ K}$ . Combining Eq. 20-9 with Eq. 20-11, we have

$$\frac{W}{Q_H} = 1 - \frac{T_C}{T_H} \Rightarrow W = 923 \text{ J}.$$

Now, for  $T'_H = 550 \text{ K}$ , we have

$$\frac{W}{Q'_H} = 1 - \frac{T_C}{T'_H} \Rightarrow Q'_H = 1692 \text{ J} \approx 1.7 \text{ kJ}$$



29. (a) The net work done is the rectangular “area” enclosed in the  $pV$  diagram:

$$W = (V - V_0) (p - p_0) = (2V_0 - V_0) (2p_0 - p_0) = V_0 p_0.$$

Inserting the values stated in the problem, we obtain  $W = 2.27$  kJ.

(b) We compute the energy added as heat during the “heat-intake” portions of the cycle using Eq. 19-39, Eq. 19-43, and Eq. 19-46:

$$\begin{aligned} Q_{abc} &= nC_V (T_b - T_a) + nC_p (T_c - T_b) = n \left( \frac{3}{2} R \right) T_a \left( \frac{T_b}{T_a} - 1 \right) + n \left( \frac{5}{2} R \right) T_a \left( \frac{T_c}{T_a} - \frac{T_b}{T_a} \right) \\ &= nRT_a \left( \frac{3}{2} \left( \frac{T_b}{T_a} - 1 \right) + \frac{5}{2} \left( \frac{T_c}{T_a} - \frac{T_b}{T_a} \right) \right) = p_0 V_0 \left( \frac{3}{2} (2 - 1) + \frac{5}{2} (4 - 2) \right) \\ &= \frac{13}{2} p_0 V_0 \end{aligned}$$

where, to obtain the last line, the gas law in ratio form has been used (see Sample Problem 19-1). Therefore, since  $W = p_0 V_0$ , we have  $Q_{abc} = 13W/2 = 14.8$  kJ.

(c) The efficiency is given by Eq. 20-9:

$$\mathcal{E} = \frac{W}{|Q_H|} = \frac{2}{13} = 0.154 = 15.4\%.$$

(d) A Carnot engine operating between  $T_c$  and  $T_a$  has efficiency equal to

$$\mathcal{E} = 1 - \frac{T_a}{T_c} = 1 - \frac{1}{4} = 0.750 = 75.0\%$$

where the gas law in ratio form has been used.

(e) This is greater than our result in part (c), as expected from the second law of thermodynamics.

30. All terms are assumed to be positive. The total work done by the two-stage system is  $W_1 + W_2$ . The heat-intake (from, say, consuming fuel) of the system is  $Q_1$  so we have (by Eq. 20-9 and Eq. 20-6)

$$\varepsilon = \frac{W_1 + W_2}{Q_1} = \frac{(Q_1 - Q_2) + (Q_2 - Q_3)}{Q_1} = 1 - \frac{Q_3}{Q_1}.$$

Now, Eq. 20-8 leads to

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3}$$

where we assume  $Q_2$  is absorbed by the second stage at temperature  $T_2$ . This implies the efficiency can be written

$$\varepsilon = 1 - \frac{T_3}{T_1} = \frac{T_1 - T_3}{T_1}.$$

31. (a) We use  $\varepsilon = |W/Q_H|$ . The heat absorbed is  $|Q_H| = \frac{|W|}{\varepsilon} = \frac{8.2 \text{ kJ}}{0.25} = 33 \text{ kJ}$ .

(b) The heat exhausted is then  $|Q_L| = |Q_H| - |W| = 33 \text{ kJ} - 8.2 \text{ kJ} = 25 \text{ kJ}$ .

(c) Now we have  $|Q_H| = \frac{|W|}{\varepsilon} = \frac{8.2 \text{ kJ}}{0.31} = 26 \text{ kJ}$ .

(d) and  $|Q_C| = |Q_H| - |W| = 26 \text{ kJ} - 8.2 \text{ kJ} = 18 \text{ kJ}$ .

32. (a) Using Eq. 19-54 for process  $D \rightarrow A$  gives

$$p_D V_D^\gamma = p_A V_A^\gamma \quad \Rightarrow \quad \frac{p_0}{32} (8V_0)^\gamma = p_0 V_0^\gamma$$

which leads to  $8^\gamma = 32 \Rightarrow \gamma = 5/3$ . The result (see §19-9 and §19-11) implies the gas is monatomic.

(b) The input heat is that absorbed during process  $A \rightarrow B$ :

$$Q_H = nC_p \Delta T = n \left( \frac{5}{2} R \right) T_A \left( \frac{T_B}{T_A} - 1 \right) = nRT_A \left( \frac{5}{2} \right) (2 - 1) = p_0 V_0 \left( \frac{5}{2} \right)$$

and the exhaust heat is that liberated during process  $C \rightarrow D$ :

$$Q_L = nC_p \Delta T = n \left( \frac{5}{2} R \right) T_D \left( 1 - \frac{T_L}{T_D} \right) = nRT_D \left( \frac{5}{2} \right) (1 - 2) = -\frac{1}{4} p_0 V_0 \left( \frac{5}{2} \right)$$

where in the last step we have used the fact that  $T_D = \frac{1}{4} T_A$  (from the gas law in ratio form — see Sample Problem 19-1). Therefore, Eq. 20-10 leads to

$$\mathcal{E} = 1 - \left| \frac{Q_L}{Q_H} \right| = 1 - \frac{1}{4} = 0.75 = 75\%.$$

33. (a) The pressure at 2 is  $p_2 = 3.00p_1$ , as given in the problem statement. The volume is  $V_2 = V_1 = nRT_1/p_1$ . The temperature is

$$T_2 = \frac{p_2 V_2}{nR} = \frac{3.00 p_1 V_1}{nR} = 3.00 T_1 \Rightarrow \frac{T_2}{T_1} = 3.00.$$

(b) The process  $2 \rightarrow 3$  is adiabatic, so  $T_2 V_2^{\gamma-1} = T_3 V_3^{\gamma-1}$ . Using the result from part (a),  $V_3 = 4.00V_1$ ,  $V_2 = V_1$  and  $\gamma=1.30$ , we obtain

$$\frac{T_3}{T_1} = \frac{T_3}{T_2 / 3.00} = 3.00 \left( \frac{V_2}{V_3} \right)^{\gamma-1} = 3.00 \left( \frac{1}{4.00} \right)^{0.30} = 1.98.$$

(c) The process  $4 \rightarrow 1$  is adiabatic, so  $T_4 V_4^{\gamma-1} = T_1 V_1^{\gamma-1}$ . Since  $V_4 = 4.00V_1$ , we have

$$\frac{T_4}{T_1} = \left( \frac{V_1}{V_4} \right)^{\gamma-1} = \left( \frac{1}{4.00} \right)^{0.30} = 0.660.$$

(d) The process  $2 \rightarrow 3$  is adiabatic, so  $p_2 V_2^\gamma = p_3 V_3^\gamma$  or  $p_3 = (V_2/V_3)^\gamma p_2$ . Substituting  $V_3 = 4.00V_1$ ,  $V_2 = V_1$ ,  $p_2 = 3.00p_1$  and  $\gamma=1.30$ , we obtain

$$\frac{p_3}{p_1} = \frac{3.00}{(4.00)^{1.30}} = 0.495.$$

(e) The process  $4 \rightarrow 1$  is adiabatic, so  $p_4 V_4^\gamma = p_1 V_1^\gamma$  and

$$\frac{p_4}{p_1} = \left( \frac{V_1}{V_4} \right)^\gamma = \frac{1}{(4.00)^{1.30}} = 0.165,$$

where we have used  $V_4 = 4.00V_1$ .

(f) The efficiency of the cycle is  $\mathcal{E} = W/Q_{12}$ , where  $W$  is the total work done by the gas during the cycle and  $Q_{12}$  is the energy added as heat during the  $1 \rightarrow 2$  portion of the cycle, the only portion in which energy is added as heat. The work done during the portion of the cycle from 2 to 3 is  $W_{23} = \int p dV$ . Substitute  $p = p_2 V_2^\gamma / V^\gamma$  to obtain

$$W_{23} = p_2 V_2^\gamma \int_{V_2}^{V_3} V^{-\gamma} dV = \left( \frac{p_2 V_2^\gamma}{\gamma-1} \right) (V_2^{1-\gamma} - V_3^{1-\gamma}).$$

Substitute  $V_2 = V_1$ ,  $V_3 = 4.00V_1$ , and  $p_3 = 3.00p_1$  to obtain

$$W_{23} = \left( \frac{3p_1V_1}{1-\gamma} \right) \left( 1 - \frac{1}{4^{\gamma-1}} \right) = \left( \frac{3nRT_1}{\gamma-1} \right) \left( 1 - \frac{1}{4^{\gamma-1}} \right).$$

Similarly, the work done during the portion of the cycle from 4 to 1 is

$$W_{41} = \left( \frac{p_1V_1^\gamma}{\gamma-1} \right) (V_4^{1-\gamma} - V_1^{1-\gamma}) = - \left( \frac{p_1V_1}{\gamma-1} \right) \left( 1 - \frac{1}{4^{\gamma-1}} \right) = - \left( \frac{nRT_1}{\gamma-1} \right) \left( 1 - \frac{1}{4^{\gamma-1}} \right).$$

No work is done during the  $1 \rightarrow 2$  and  $3 \rightarrow 4$  portions, so the total work done by the gas during the cycle is

$$W = W_{23} + W_{41} = \left( \frac{2nRT_1}{\gamma-1} \right) \left( 1 - \frac{1}{4^{\gamma-1}} \right).$$

The energy added as heat is

$$Q_{12} = nC_V(T_2 - T_1) = nC_V(3T_1 - T_1) = 2nC_VT_1,$$

where  $C_V$  is the molar specific heat at constant volume. Now

$$\gamma = C_p/C_V = (C_V + R)/C_V = 1 + (R/C_V),$$

so  $C_V = R/(\gamma - 1)$ . Here  $C_p$  is the molar specific heat at constant pressure, which for an ideal gas is  $C_p = C_V + R$ . Thus,  $Q_{12} = 2nRT_1/(\gamma - 1)$ . The efficiency is

$$\varepsilon = \frac{2nRT_1}{\gamma-1} \left( 1 - \frac{1}{4^{\gamma-1}} \right) \frac{\gamma-1}{2nRT_1} = 1 - \frac{1}{4^{\gamma-1}}.$$

With  $\gamma = 1.30$ , the efficiency is  $\varepsilon = 0.340$  or 34.0%.

34. (a) Eq. 20-13 provides

$$K_C = \frac{|Q_L|}{|Q_H| - |Q_L|} \Rightarrow |Q_H| = |Q_L| \left( \frac{1 + K_C}{K_C} \right)$$

which yields  $|Q_H| = 49 \text{ kJ}$  when  $K_C = 5.7$  and  $|Q_L| = 42 \text{ kJ}$ .

(b) From §20-5 we obtain

$$|W| = |Q_H| - |Q_L| = 49.4 \text{ kJ} - 42.0 \text{ kJ} = 7.4 \text{ kJ}$$

if we take the initial 42 kJ datum to be accurate to three figures. The given temperatures are not used in the calculation; in fact, it is possible that the given room temperature value is not meant to be the high temperature for the (reversed) Carnot cycle — since it does not lead to the given  $K_C$  using Eq. 20-14.

35. A Carnot refrigerator working between a hot reservoir at temperature  $T_H$  and a cold reservoir at temperature  $T_L$  has a coefficient of performance  $K$  that is given by  $K = T_L / (T_H - T_L)$ . For the refrigerator of this problem,  $T_H = 96^\circ \text{ F} = 309 \text{ K}$  and  $T_L = 70^\circ \text{ F} = 294 \text{ K}$ , so  $K = (294 \text{ K}) / (309 \text{ K} - 294 \text{ K}) = 19.6$ . The coefficient of performance is the energy  $Q_L$  drawn from the cold reservoir as heat divided by the work done:  $K = |Q_L| / |W|$ . Thus,  $|Q_L| = K|W| = (19.6)(1.0 \text{ J}) = 20 \text{ J}$ .



36. Eq. 20-8 still holds (particularly due to its use of absolute values), and energy conservation implies  $|W| + Q_L = Q_H$ . Therefore, with  $T_L = 268.15$  K and  $T_H = 290.15$  K, we find

$$|Q_H| = |Q_L| \left( \frac{T_H}{T_L} \right) = (|Q_H| - |W|) \left( \frac{290.15}{268.15} \right)$$

which (with  $|W| = 1.0$  J) leads to

$$|Q_H| = |W| \left( \frac{1}{1 - 268.15/290.15} \right) = 13 \text{ J.}$$

37. The coefficient of performance for a refrigerator is given by  $K = |Q_L|/|W|$ , where  $Q_L$  is the energy absorbed from the cold reservoir as heat and  $W$  is the work done during the refrigeration cycle, a negative value. The first law of thermodynamics yields  $Q_H + Q_L - W = 0$  for an integer number of cycles. Here  $Q_H$  is the energy ejected to the hot reservoir as heat. Thus,  $Q_L = W - Q_H$ .  $Q_H$  is negative and greater in magnitude than  $W$ , so  $|Q_L| = |Q_H| - |W|$ . Thus,

$$K = \frac{|Q_H| - |W|}{|W|}.$$

The solution for  $|W|$  is  $|W| = |Q_H|/(K + 1)$ . In one hour,

$$|W| = \frac{7.54 \text{ MJ}}{3.8 + 1} = 1.57 \text{ MJ}.$$

The rate at which work is done is  $(1.57 \times 10^6 \text{ J})/(3600 \text{ s}) = 440 \text{ W}$ .

38. (a) Using Eq. 20-12 and Eq. 20-14, we obtain

$$|W| = \frac{|Q_L|}{K_C} = (1.0 \text{ J}) \left( \frac{300 \text{ K} - 280 \text{ K}}{280 \text{ K}} \right) = 0.071 \text{ J}.$$

(b) A similar calculation (being sure to use absolute temperature) leads to 0.50 J in this case.

(c) with  $T_L = 100 \text{ K}$ , we obtain  $|W| = 2.0 \text{ J}$ .

(d) Finally, with the low temperature reservoir at 50 K, an amount of work equal to  $|W| = 5.0 \text{ J}$  is required.

39. We are told  $K = 0.27K_C$  where

$$K_C = \frac{T_L}{T_H - T_L} = \frac{294 \text{ K}}{307 \text{ K} - 294 \text{ K}} = 23$$

where the Fahrenheit temperatures have been converted to Kelvins. Expressed on a per unit time basis, Eq. 20-12 leads to

$$\frac{|W|}{t} = \frac{\left(\frac{|Q_L|}{t}\right)}{K} = \frac{4000 \text{ Btu/h}}{(0.27)(23)} = 643 \text{ Btu/h.}$$

Appendix D indicates  $1 \text{ Btu/h} = 0.0003929 \text{ hp}$ , so our result may be expressed as  $|W|/t = 0.25 \text{ hp}$ .

40. (a) Eq. 20-11 gives the Carnot efficiency as  $1 - T_L/T_H$ . This gives 0.222 in this case. Using this value with Eq. 20-9 leads to  $W = (0.222)(750 \text{ J}) = 167 \text{ J}$ .

(b) Now, Eq. 20-14 gives  $K_C = 3.5$ . Then, Eq. 20-12 yields  $|W| = 1200/3.5 = 343 \text{ J}$ .

41. The efficiency of the engine is defined by  $\varepsilon = W/Q_1$  and is shown in the text to be  $\varepsilon = (T_1 - T_2)/T_1$ , so  $W/Q_1 = (T_1 - T_2)/T_1$ . The coefficient of performance of the refrigerator is defined by  $K = Q_4/W$  and is shown in the text to be  $K = T_4/(T_3 - T_4)$ , so  $Q_4/W = T_4/(T_3 - T_4)$ . Now  $Q_4 = Q_3 - W$ , so  $(Q_3 - W)/W = T_4/(T_3 - T_4)$ . The work done by the engine is used to drive the refrigerator, so  $W$  is the same for the two. Solve the engine equation for  $W$  and substitute the resulting expression into the refrigerator equation. The engine equation yields  $W = (T_1 - T_2)Q_1/T_1$  and the substitution yields

$$\frac{T_4}{T_3 - T_4} = \frac{Q_3}{W} - 1 = \frac{Q_3 T_1}{Q_1 (T_1 - T_2)} - 1.$$

Solve for  $Q_3/Q_1$ :

$$\frac{Q_3}{Q_1} = \left( \frac{T_4}{T_3 - T_4} + 1 \right) \left( \frac{T_1 - T_2}{T_1} \right) = \left( \frac{T_3}{T_3 - T_4} \right) \left( \frac{T_1 - T_2}{T_1} \right) = \frac{1 - (T_2/T_1)}{1 - (T_4/T_3)}.$$

With  $T_1 = 400$  K,  $T_2 = 150$  K,  $T_3 = 325$  K, and  $T_4 = 225$  K, the ratio becomes  $Q_3/Q_1 = 2.03$ .

42. The work done by the motor in  $t = 10.0$  min is  $|W| = Pt = (200 \text{ W})(10.0 \text{ min})(60 \text{ s/min}) = 1.20 \times 10^5 \text{ J}$ . The heat extracted is then

$$|Q_L| = K|W| = \frac{T_L |W|}{T_H - T_L} = \frac{(270 \text{ K})(1.20 \times 10^5 \text{ J})}{300 \text{ K} - 270 \text{ K}} = 1.08 \times 10^6 \text{ J}.$$

43. We need nine labels:

Label	Number of molecules on side 1	Number of molecules on side 2
I	8	0
II	7	1
III	6	2
IV	5	3
V	4	4
VI	3	5
VII	2	6
VIII	1	7
IX	0	8

The multiplicity  $W$  is computed using Eq. 20-18. For example, the multiplicity for label IV is

$$W = \frac{8!}{(5!)(3!)} = \frac{40320}{(120)(6)} = 56$$

and the corresponding entropy is (using Eq. 20-19)

$$S = k \ln W = (1.38 \times 10^{-23} \text{ J/K}) \ln(56) = 5.6 \times 10^{-23} \text{ J/K}.$$

In this way, we generate the following table:

Label	$W$	$S$
I	1	0
II	8	$2.9 \times 10^{-23} \text{ J/K}$
III	28	$4.6 \times 10^{-23} \text{ J/K}$
IV	56	$5.6 \times 10^{-23} \text{ J/K}$
V	70	$5.9 \times 10^{-23} \text{ J/K}$
VI	56	$5.6 \times 10^{-23} \text{ J/K}$
VII	28	$4.6 \times 10^{-23} \text{ J/K}$
VIII	8	$2.9 \times 10^{-23} \text{ J/K}$
IX	1	0



44. (a) We denote the configuration with  $n$  heads out of  $N$  trials as  $(n; N)$ . We use Eq. 20-18:

$$W(25; 50) = \frac{50!}{(25!)(50-25)!} = 1.26 \times 10^{14}.$$

(b) There are 2 possible choices for each molecule: it can either be in side 1 or in side 2 of the box. If there are a total of  $N$  independent molecules, the total number of available states of the  $N$ -particle system is

$$N_{\text{total}} = 2 \times 2 \times 2 \times \cdots \times 2 = 2^N.$$

With  $N = 50$ , we obtain  $N_{\text{total}} = 2^{50} = 1.13 \times 10^{15}$ .

(c) The percentage of time in question is equal to the probability for the system to be in the central configuration:

$$p(25; 50) = \frac{W(25; 50)}{2^{50}} = \frac{1.26 \times 10^{14}}{1.13 \times 10^{15}} = 11.1\%.$$

With  $N = 100$ , we obtain

$$(d) W(N/2, N) = N! / [(N/2)!]^2 = 1.01 \times 10^{29},$$

$$(e) N_{\text{total}} = 2^N = 1.27 \times 10^{30},$$

$$(f) \text{ and } p(N/2; N) = W(N/2, N) / N_{\text{total}} = 8.0\%.$$

Similarly, for  $N = 200$ , we obtain

$$(g) W(N/2, N) = 9.25 \times 10^{58},$$

$$(h) N_{\text{total}} = 1.61 \times 10^{60},$$

$$(i) \text{ and } p(N/2; N) = 5.7\%.$$

(j) As  $N$  increases the number of available microscopic states increase as  $2^N$ , so there are more states to be occupied, leaving the probability less for the system to remain in its central configuration. Thus, the time spent in there decreases with an increase in  $N$ .

45. (a) Suppose there are  $n_L$  molecules in the left third of the box,  $n_C$  molecules in the center third, and  $n_R$  molecules in the right third. There are  $N!$  arrangements of the  $N$  molecules, but  $n_L!$  are simply rearrangements of the  $n_L$  molecules in the left third,  $n_C!$  are rearrangements of the  $n_C$  molecules in the center third, and  $n_R!$  are rearrangements of the  $n_R$  molecules in the right third. These rearrangements do not produce a new configuration. Thus, the multiplicity is

$$W = \frac{N!}{n_L!n_C!n_R!}.$$

(b) If half the molecules are in the right half of the box and the other half are in the left half of the box, then the multiplicity is

$$W_B = \frac{N!}{(N/2)!(N/2)!}.$$

If one-third of the molecules are in each third of the box, then the multiplicity is

$$W_A = \frac{N!}{(N/3)!(N/3)!(N/3)!}.$$

The ratio is

$$\frac{W_A}{W_B} = \frac{(N/2)!(N/2)!}{(N/3)!(N/3)!(N/3)!}.$$

(c) For  $N = 100$ ,

$$\frac{W_A}{W_B} = \frac{50!50!}{33!33!34!} = 4.2 \times 10^{16}.$$

46. We consider a three-step reversible process as follows: the supercooled water drop (of mass  $m$ ) starts at state 1 ( $T_1 = 268 \text{ K}$ ), moves on to state 2 (still in liquid form but at  $T_2 = 273 \text{ K}$ ), freezes to state 3 ( $T_3 = T_2$ ), and then cools down to state 4 (in solid form, with  $T_4 = T_1$ ). The change in entropy for each of the stages is given as follows:

$$\Delta S_{12} = mc_w \ln (T_2/T_1),$$

$$\Delta S_{23} = -mL_F/T_2,$$

$$\Delta S_{34} = mc_I \ln (T_4/T_3) = mc_I \ln (T_1/T_2) = -mc_I \ln (T_2/T_1).$$

Thus the net entropy change for the water drop is

$$\begin{aligned} \Delta S &= \Delta S_{12} + \Delta S_{23} + \Delta S_{34} = m(c_w - c_I) \ln \left( \frac{T_2}{T_1} \right) - \frac{mL_F}{T_2} \\ &= (1.00 \text{ g})(4.19 \text{ J/g} \cdot \text{K} - 2.22 \text{ J/g} \cdot \text{K}) \ln \left( \frac{273 \text{ K}}{268 \text{ K}} \right) - \frac{(1.00 \text{ g})(333 \text{ J/g})}{273 \text{ K}} \\ &= -1.18 \text{ J/K}. \end{aligned}$$

47. (a) A good way to (mathematically) think of this is: consider the terms when you expand  $(1 + x)^4 = 1 + 4x + 6x^2 + 4x^3 + x^4$ . The coefficients correspond to the multiplicities. Thus, the smallest coefficient is 1.

(b) The largest coefficient is 6.

(c) Since the logarithm of 1 is zero, then Eq. 20-19 gives  $S = 0$  for the least case.

(d)  $S = k \ln(6) = 2.47 \times 10^{-23} \text{ J/K}$ .

48. The net work is figured from the (positive) isothermal expansion (Eq. 19-14) and the (negative) constant-pressure compression (Eq. 19-48). Thus,

$$W_{\text{net}} = nRT_H \ln(V_{\text{max}}/V_{\text{min}}) + nR(T_L - T_H)$$

where  $n = 3.4$ ,  $T_H = 500$  K,  $T_L = 200$  K and  $V_{\text{max}}/V_{\text{min}} = 5/2$  (same as the ratio  $T_H/T_L$ ). Therefore,  $W_{\text{net}} = 4468$  J. Now, we identify the “input heat” as that transferred in steps 1 and 2:

$$Q_{\text{in}} = Q_1 + Q_2 = nC_V(T_H - T_L) + nRT_H \ln(V_{\text{max}}/V_{\text{min}})$$

where  $C_V = 5R/2$  (see Table 19-3). Consequently,  $Q_{\text{in}} = 34135$  J. Dividing these results gives the efficiency:  $W_{\text{net}}/Q_{\text{in}} = 0.131$  (or about 13.1%).

49. Using Eq. 19-34 and Eq. 19-35, we arrive at

$$\Delta v = (\sqrt{3} - \sqrt{2})\sqrt{RT/M}$$

(a) We find, with  $M = 28 \text{ g/mol} = 0.028 \text{ kg/mol}$  (see Table 19-1),  $\Delta v_i = 87 \text{ m/s}$  at 250 K,

(b) and  $\Delta v_f = 122 \approx 1.2 \times 10^2 \text{ m/s}$  at 500 K.

(c) The expression above for  $\Delta v$  implies

$$T = \frac{M}{R(\sqrt{3} - \sqrt{2})^2} (\Delta v)^2$$

which we can plug into Eq. 20-4 to yield

$$\Delta S = nR \ln(V_f/V_i) + nC_V \ln(T_f/T_i) = 0 + nC_V \ln[(\Delta v_f)^2/(\Delta v_i)^2] = 2nC_V \ln(\Delta v_f/\Delta v_i).$$

Using Table 19-3 to get  $C_V = 5R/2$  (see also Table 19-2) we then find, for  $n = 1.5 \text{ mol}$ ,  $\Delta S = 22 \text{ J/K}$ .

50. (a) Eq. 20-2 gives the entropy change for each reservoir (each of which, by definition, is able to maintain constant temperature conditions within itself). The net entropy change is therefore

$$\Delta S = \frac{+|Q|}{273 + 24} + \frac{-|Q|}{273 + 130} = 4.45 \text{ J/K}$$

where we set  $|Q| = 5030 \text{ J}$ .

(b) We have assumed that the conductive heat flow in the rod is “steady-state”; that is, the situation described by the problem has existed and will exist for “long times.” Thus there are no entropy change terms included in the calculation for elements of the rod itself.

51. (a) If  $T_H$  is the temperature of the high-temperature reservoir and  $T_L$  is the temperature of the low-temperature reservoir, then the maximum efficiency of the engine is

$$\varepsilon = \frac{T_H - T_L}{T_H} = \frac{(800 + 40) \text{ K}}{(800 + 273) \text{ K}} = 0.78 \text{ or } 78\%.$$

(b) The efficiency is defined by  $\varepsilon = |W|/|Q_H|$ , where  $W$  is the work done by the engine and  $Q_H$  is the heat input.  $W$  is positive. Over a complete cycle,  $Q_H = W + |Q_L|$ , where  $Q_L$  is the heat output, so  $\varepsilon = W/(W + |Q_L|)$  and  $|Q_L| = W[(1/\varepsilon) - 1]$ . Now  $\varepsilon = (T_H - T_L)/T_H$ , where  $T_H$  is the temperature of the high-temperature heat reservoir and  $T_L$  is the temperature of the low-temperature reservoir. Thus,

$$\frac{1}{\varepsilon} - 1 = \frac{T_L}{T_H - T_L} \text{ and } |Q_L| = \frac{WT_L}{T_H - T_L}.$$

The heat output is used to melt ice at temperature  $T_i = -40^\circ\text{C}$ . The ice must be brought to  $0^\circ\text{C}$ , then melted, so  $|Q_L| = mc(T_f - T_i) + mL_F$ , where  $m$  is the mass of ice melted,  $T_f$  is the melting temperature ( $0^\circ\text{C}$ ),  $c$  is the specific heat of ice, and  $L_F$  is the heat of fusion of ice. Thus,

$$WT_L/(T_H - T_L) = mc(T_f - T_i) + mL_F.$$

We differentiate with respect to time and replace  $dW/dt$  with  $P$ , the power output of the engine, and obtain  $PT_L/(T_H - T_L) = (dm/dt)[c(T_f - T_i) + L_F]$ . Thus,

$$\frac{dm}{dt} = \left( \frac{PT_L}{T_H - T_L} \right) \left( \frac{1}{c(T_f - T_i) + L_F} \right).$$

Now,  $P = 100 \times 10^6 \text{ W}$ ,  $T_L = 0 + 273 = 273 \text{ K}$ ,  $T_H = 800 + 273 = 1073 \text{ K}$ ,  $T_i = -40 + 273 = 233 \text{ K}$ ,  $T_f = 0 + 273 = 273 \text{ K}$ ,  $c = 2220 \text{ J/kg}\cdot\text{K}$ , and  $L_F = 333 \times 10^3 \text{ J/kg}$ , so

$$\begin{aligned} \frac{dm}{dt} &= \left[ \frac{(100 \times 10^6 \text{ J/s})(273 \text{ K})}{1073 \text{ K} - 273 \text{ K}} \right] \left[ \frac{1}{(2220 \text{ J/kg}\cdot\text{K})(273 \text{ K} - 233 \text{ K}) + 333 \times 10^3 \text{ J/kg}} \right] \\ &= 82 \text{ kg/s}. \end{aligned}$$

We note that the engine is now operated between  $0^\circ\text{C}$  and  $800^\circ\text{C}$ .



52. (a) Combining Eq. 20-9 with Eq. 20-11, we obtain

$$|W| = |Q_H| \left( 1 - \frac{T_L}{T_H} \right) = (500 \text{ J}) \left( 1 - \frac{260 \text{ K}}{320 \text{ K}} \right) = 93.8 \text{ J}.$$

(b) Combining Eq. 20-12 with Eq. 20-14, we find

$$|W| = \frac{|Q_L|}{\left( \frac{T_L}{T_H - T_L} \right)} = \frac{1000 \text{ J}}{\left( \frac{260 \text{ K}}{320 \text{ K} - 260 \text{ K}} \right)} = 231 \text{ J}.$$

53. (a) We denote the mass of the ice (which turns to water and warms to  $T_f$ ) as  $m$  and the mass of original-water (which cools from  $80^\circ$  down to  $T_f$ ) as  $m'$ . From  $\Sigma Q = 0$  we have

$$L_F m + cm (T_f - 0^\circ) + cm' (T_f - 80^\circ) = 0 \quad .$$

Since  $L_F = 333 \times 10^3$  J/kg,  $c = 4190$  J/(kg·C°),  $m' = 0.13$  kg and  $m = 0.012$  kg, we find  $T_f = 66.5^\circ$ , which is equivalent to  $339.67$  K.

(b) The process of ice at  $0^\circ$  C turning to water at  $0^\circ$  C involves an entropy change of

$$\frac{Q}{T} = \frac{L_F m}{273.15 \text{ K}} = 14.6 \text{ J/K}$$

using Eq. 20-2.

(c) The process of  $m = 0.012$  kg of water warming from  $0^\circ$  C to  $66.5^\circ$  C involves an entropy change of

$$\int_{273.15}^{339.67} \frac{cm dT}{T} = cm \ln \left( \frac{339.67}{273.15} \right) = 11.0 \text{ J/K}$$

using Eq.20-1.

(d) Similarly, the cooling of the original-water involves an entropy change of

$$\int_{353.15}^{339.67} \frac{cm' dT}{T} = cm' \ln \left( \frac{339.67}{353.15} \right) = -21.2 \text{ J/K}$$

(e) The net entropy change in this calorimetry experiment is found by summing the previous results; we find (by using more precise values than those shown above)  $\Delta S_{\text{net}} = 4.39$  J/K.

54. (a) Starting from  $\sum Q = 0$  (for calorimetry problems) we can derive (when no phase changes are involved)

$$T_f = \frac{c_1 m_1 T_1 + c_2 m_2 T_2}{c_1 m_1 + c_2 m_2} = 40.9^\circ\text{C},$$

which is equivalent to 314 K.

(b) From Eq. 20-1, we have

$$\Delta S_{\text{copper}} = \int_{353}^{314} \frac{cm dT}{T} = (386)(0.600) \ln\left(\frac{314}{353}\right) = -27.1 \text{ J/K}.$$

(c) For water, the change in entropy is

$$\Delta S_{\text{water}} = \int_{283}^{314} \frac{cm dT}{T} = (4190)(0.0700) \ln\left(\frac{314}{283}\right) = 30.5 \text{ J/K}.$$

(d) The net result for the system is  $(30.5 - 27.1) \text{ J/K} = 3.4 \text{ J/K}$ . (Note: these calculations are fairly sensitive to round-off errors. To arrive at this final answer, the value 273.15 was used to convert to Kelvins, and all intermediate steps were retained to full calculator accuracy.)

55. For an isothermal ideal gas process, we have  $Q = W = nRT \ln(V_f/V_i)$ . Thus,

$$\Delta S = Q/T = W/T = nR \ln(V_f/V_i)$$

(a)  $V_f/V_i = (0.800)/(0.200) = 4.00$ ,  $\Delta S = (0.55)(8.31)\ln(4.00) = 6.34 \text{ J/K}$ .

(b)  $V_f/V_i = (0.800)/(0.200) = 4.00$ ,  $\Delta S = (0.55)(8.31)\ln(4.00) = 6.34 \text{ J/K}$ .

(c)  $V_f/V_i = (1.20)/(0.300) = 4.00$ ,  $\Delta S = (0.55)(8.31)\ln(4.00) = 6.34 \text{ J/K}$ .

(d)  $V_f/V_i = (1.20)/(0.300) = 4.00$ ,  $\Delta S = (0.55)(8.31)\ln(4.00) = 6.34 \text{ J/K}$ .

56. Eq. 20-4 yields

$$\Delta S = nR \ln(V_f/V_i) + nC_V \ln(T_f/T_i) = 0 + nC_V \ln(425/380)$$

where  $n = 3.20$  and  $C_V = \frac{3}{2}R$  (Eq. 19-43). This gives 4.46 J/K.

57. Except for the phase change (which just uses Eq. 20-2), this has some similarities with Sample Problem 20-2. Using constants available in the Chapter 19 tables, we compute

$$\Delta S = m[c_{\text{ice}} \ln(273/253) + \frac{L_f}{273} + c_{\text{water}} \ln(313/273)] = 1.18 \times 10^3 \text{ J/K}.$$

58. (a) It is a reversible set of processes returning the system to its initial state; clearly,  $\Delta S_{\text{net}} = 0$ .

(b) Process 1 is adiabatic and reversible (as opposed to, say, a free expansion) so that Eq. 20-1 applies with  $dQ = 0$  and yields  $\Delta S_1 = 0$ .

(c) Since the working substance is an ideal gas, then an isothermal process implies  $Q = W$ , which further implies (regarding Eq. 20-1)  $dQ = p dV$ . Therefore,

$$\int \frac{dQ}{T} = \int \frac{p dV}{\left(\frac{pV}{nR}\right)} = nR \int \frac{dV}{V}$$

which leads to  $\Delta S_3 = nR \ln(1/2) = -23.0 \text{ J/K}$ .

(d) By part (a),  $\Delta S_1 + \Delta S_2 + \Delta S_3 = 0$ . Then, part (b) implies  $\Delta S_2 = -\Delta S_3$ . Therefore,  $\Delta S_2 = 23.0 \text{ J/K}$ .

59. Eq. 20-8 gives

$$\left| \frac{Q_{\text{to}}}{Q_{\text{from}}} \right| = \frac{T_{\text{to}}}{T_{\text{from}}} = \frac{300 \text{ K}}{4.0 \text{ K}} = 75.$$



60. (a) The most obvious input-heat step is the constant-volume process. Since the gas is monatomic, we know from Chapter 19 that  $C_V = \frac{3}{2}R$ . Therefore,

$$Q_V = nC_V\Delta T = (1.0 \text{ mol})\left(\frac{3}{2}\right)\left(8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)(600 \text{ K} - 300 \text{ K}) = 3740 \text{ J}.$$

Since the heat transfer during the isothermal step is positive, we may consider it also to be an input-heat step. The isothermal  $Q$  is equal to the isothermal work (calculated in the next part) because  $\Delta E_{\text{int}} = 0$  for an ideal gas isothermal process (see Eq. 19-45). Borrowing from the part (b) computation, we have

$$Q_{\text{isotherm}} = nRT_H \ln 2 = (1 \text{ mol})\left(8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)(600 \text{ K}) \ln 2 = 3456 \text{ J}.$$

Therefore,  $Q_H = Q_V + Q_{\text{isotherm}} = 7.2 \times 10^3 \text{ J}$ .

(b) We consider the sum of works done during the processes (noting that no work is done during the constant-volume step). Using Eq. 19-14 and Eq. 19-16, we have

$$W = nRT_H \ln\left(\frac{V_{\text{max}}}{V_{\text{min}}}\right) + p_{\text{min}}(V_{\text{min}} - V_{\text{max}})$$

where (by the gas law in ratio form, as illustrated in Sample Problem 19-1) the volume ratio is

$$\frac{V_{\text{max}}}{V_{\text{min}}} = \frac{T_H}{T_L} = \frac{600 \text{ K}}{300 \text{ K}} = 2.$$

Thus, the net work is

$$\begin{aligned} W &= nRT_H \ln 2 + p_{\text{min}} V_{\text{min}} \left(1 - \frac{V_{\text{max}}}{V_{\text{min}}}\right) = nRT_H \ln 2 + nRT_L (1 - 2) = nR(T_H \ln 2 - T_L) \\ &= (1 \text{ mol})\left(8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)((600 \text{ K}) \ln 2 - (300 \text{ K})) \\ &= 9.6 \times 10^2 \text{ J}. \end{aligned}$$

(c) Eq. 20-9 gives

$$\varepsilon = \frac{W}{Q_{\text{H}}} = 0.134 \approx 13\%.$$

61. We adapt the discussion of §20-7 to 3 and 5 particles (as opposed to the 6 particle situation treated in that section).

(a) The least multiplicity configuration is when all the particles are in the same half of the box. In this case, using Eq. 20-18, we have

$$W = \frac{3!}{3!0!} = 1.$$

(b) Similarly for box  $B$ ,  $W = 5!/(5!0!) = 1$  in the “least” case.

(c) The most likely configuration in the 3 particle case is to have 2 on one side and 1 on the other. Thus,

$$W = \frac{3!}{2!1!} = 3.$$

(d) The most likely configuration in the 5 particle case is to have 3 on one side and 2 on the other. Thus,

$$W = \frac{5!}{3!2!} = 10.$$

(e) We use Eq. 20-19 with our result in part (c) to obtain

$$S = k \ln W = (1.38 \times 10^{-23}) \ln 3 = 1.5 \times 10^{-23} \text{ J/K}.$$

(f) Similarly for the 5 particle case (using the result from part (d)), we find

$$S = k \ln 10 = 3.2 \times 10^{-23} \text{ J/K}.$$

62. A metric ton is 1000 kg, so that the heat generated by burning 380 metric tons during one hour is  $(380000 \text{ kg})(28 \text{ MJ/kg}) = 10.6 \times 10^6 \text{ MJ}$ . The work done in one hour is

$$W = (750 \text{ MJ/s})(3600 \text{ s}) = 2.7 \times 10^6 \text{ MJ}$$

where we use the fact that a Watt is a Joule-per-second. By Eq. 20-9, the efficiency is

$$\mathcal{E} = \frac{2.7 \times 10^6 \text{ MJ}}{10.6 \times 10^6 \text{ MJ}} = 0.253 = 25\%.$$

63. Since the volume of the monatomic ideal gas is kept constant it does not do any work in the heating process. Therefore the heat  $Q$  it absorbs is equal to the change in its internal

energy:  $dQ = dE_{\text{int}} = \frac{3}{2}nRdT$ . Thus

$$\begin{aligned}\Delta S &= \int \frac{dQ}{T} = \int_{T_i}^{T_f} \frac{(3nR/2)dT}{T} = \frac{3}{2}nR \ln\left(\frac{T_f}{T_i}\right) = \frac{3}{2}(1.00 \text{ mol})\left(8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right) \ln\left(\frac{400 \text{ K}}{300 \text{ K}}\right) \\ &= 3.59 \text{ J/K}.\end{aligned}$$

64. With the pressure kept constant,

$$dQ = nC_p dT = n(C_v + R) dT = \left(\frac{3}{2}nR + nR\right) dT = \frac{5}{2}nR dT,$$

so we need to replace the factor  $3/2$  in the last problem by  $5/2$ . The rest is the same. Thus the answer now is

$$\Delta S = \frac{5}{2}nR \ln\left(\frac{T_f}{T_i}\right) = \frac{5}{2}(1.00 \text{ mol})\left(8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right) \ln\left(\frac{400 \text{ K}}{300 \text{ K}}\right) = 5.98 \text{ J/K}.$$

65. The change in entropy in transferring a certain amount of heat  $Q$  from a heat reservoir at  $T_1$  to another one at  $T_2$  is  $\Delta S = \Delta S_1 + \Delta S_2 = Q(1/T_2 - 1/T_1)$ .

(a)  $\Delta S = (260 \text{ J})(1/100 \text{ K} - 1/400 \text{ K}) = 1.95 \text{ J/K}$ .

(b)  $\Delta S = (260 \text{ J})(1/200 \text{ K} - 1/400 \text{ K}) = 0.650 \text{ J/K}$ .

(c)  $\Delta S = (260 \text{ J})(1/300 \text{ K} - 1/400 \text{ K}) = 0.217 \text{ J/K}$ .

(d)  $\Delta S = (260 \text{ J})(1/360 \text{ K} - 1/400 \text{ K}) = 0.072 \text{ J/K}$ .

(e) We see that as the temperature difference between the two reservoirs decreases, so does the change in entropy.

66. (a) Processes 1 and 2 both require the input of heat, which is denoted  $Q_H$ . Noting that rotational degrees of freedom are not involved, then, from the discussion in Chapter 19,  $C_V = 3R/2$ ,  $C_p = 5R/2$ , and  $\gamma = 5/3$ . We further note that since the working substance is an ideal gas, process 2 (being isothermal) implies  $Q_2 = W_2$ . Finally, we note that the volume ratio in process 2 is simply 8/3. Therefore,

$$Q_H = Q_1 + Q_2 = nC_V (T' - T) + nRT' \ln \frac{8}{3}$$

which yields (for  $T = 300$  K and  $T' = 800$  K) the result  $Q_H = 25.5 \times 10^3$  J.

(b) The net work is the net heat ( $Q_1 + Q_2 + Q_3$ ). We find  $Q_3$  from  $nC_p (T - T') = -20.8 \times 10^3$  J. Thus,  $W = 4.73 \times 10^3$  J.

(c) Using Eq. 20-9, we find that the efficiency is

$$\varepsilon = \frac{|W|}{|Q_H|} = \frac{4.73 \times 10^3}{25.5 \times 10^3} = 0.185 \text{ or } 18.5\%.$$



67. The Carnot efficiency (Eq. 20-11) depends linearly on  $T_L$  so that we can take a derivative

$$\varepsilon = 1 - \frac{T_L}{T_H} \Rightarrow \frac{d\varepsilon}{dT_L} = -\frac{1}{T_H}$$

and quickly get to the result. With  $d\varepsilon \rightarrow \Delta\varepsilon = 0.100$  and  $T_H = 400$  K, we find  $dT_L \rightarrow \Delta T_L = -40$  K.

68. (a) Starting from  $\sum Q = 0$  (for calorimetry problems) we can derive (when no phase changes are involved)

$$T_f = \frac{c_1 m_1 T_1 + c_2 m_2 T_2}{c_1 m_1 + c_2 m_2} = -44.2^\circ\text{C},$$

which is equivalent to 229 K.

(b) From Eq. 20-1, we have

$$\Delta S_{\text{tungsten}} = \int_{303}^{229} \frac{cm dT}{T} = (134)(0.045) \ln\left(\frac{229}{303}\right) = -1.69 \text{ J/K}.$$

(c) Also,

$$\Delta S_{\text{silver}} = \int_{153}^{229} \frac{cm dT}{T} = (236)(0.0250) \ln\left(\frac{229}{153}\right) = 2.38 \text{ J/K}.$$

(d) The net result for the system is  $(2.38 - 1.69) \text{ J/K} = 0.69 \text{ J/K}$ . (Note: these calculations are fairly sensitive to round-off errors. To arrive at this final answer, the value 273.15 was used to convert to Kelvins, and all intermediate steps were retained to full calculator accuracy.)

69. (a) We use Eq. 20-14. For configuration A

$$W_A = \frac{N!}{(N/2)!(N/2)!} = \frac{50!}{(25!)(25!)} = 1.26 \times 10^{14}.$$

(b) For configuration B

$$W_B = \frac{N!}{(0.6N)!(0.4N)!} = \frac{50!}{[0.6(50)]![0.4(50)]!} = 4.71 \times 10^{13}.$$

(c) Since all microstates are equally probable,

$$f = \frac{W_B}{W_A} = \frac{1265}{3393} \approx 0.37.$$

We use these formulas for  $N = 100$ . The results are

$$(d) W_A = \frac{N!}{(N/2)!(N/2)!} = \frac{100!}{(50!)(50!)} = 1.01 \times 10^{29}.$$

$$(e) W_B = \frac{N!}{(0.6N)!(0.4N)!} = \frac{100!}{[0.6(100)]![0.4(100)]!} = 1.37 \times 10^{28}.$$

(f) and  $f = W_B/W_A \approx 0.14$ .

Similarly, using the same formulas for  $N = 200$ , we obtain

$$(g) W_A = 9.05 \times 10^{58},$$

$$(h) W_B = 1.64 \times 10^{57},$$

(i) and  $f = 0.018$ .

(j) We see from the calculation above that  $f$  decreases as  $N$  increases, as expected.

70. From the formula for heat conduction, Eq. 19-32, using Table 19-6, we have

$$H = kA \frac{T_H - T_C}{L} = (401) (\pi(0.02)^2) 270/1.50$$

which yields  $H = 90.7$  J/s. Using Eq. 20-2, this is associated with an entropy rate-of-decrease of the high temperature reservoir (at 573 K) equal to  $\Delta S/t = -90.7/573 = -0.158$  (J/K)/s. And it is associated with an entropy rate-of-increase of the low temperature reservoir (at 303 K) equal to  $\Delta S/t = +90.7/303 = 0.299$  (J/K)/s. The net result is  $0.299 - 0.158 = 0.141$  (J/K)/s.

71. (a) Eq. 20-12 gives  $K = 560/150 = 3.73$ .

(b) Energy conservation requires the exhaust heat to be  $560 + 150 = 710$  J.

72. (a) From Eq. 20-1, we infer  $Q = \int T dS$ , which corresponds to the “area under the curve” in a  $T$ - $S$  diagram. Thus, since the area of a rectangle is (height) $\times$ (width), we have  $Q_{1\rightarrow 2} = (350)(2.00) = 700\text{J}$ .

(b) With no “area under the curve” for process  $2 \rightarrow 3$ , we conclude  $Q_{2\rightarrow 3} = 0$ .

(c) For the cycle, the (net) heat should be the “area inside the figure,” so using the fact that the area of a triangle is  $\frac{1}{2}(\text{base}) \times (\text{height})$ , we find

$$Q_{\text{net}} = \frac{1}{2}(2.00)(50) = 50 \text{ J} .$$

(d) Since we are dealing with an ideal gas (so that  $\Delta E_{\text{int}} = 0$  in an isothermal process), then

$$W_{1\rightarrow 2} = Q_{1\rightarrow 2} = 700 \text{ J} .$$

(e) Using Eq. 19-14 for the isothermal work, we have

$$W_{1\rightarrow 2} = nRT \ln \frac{V_2}{V_1} .$$

where  $T = 350 \text{ K}$ . Thus, if  $V_1 = 0.200 \text{ m}^3$ , then we obtain

$$V_2 = V_1 \exp(W/nRT) = (0.200) e^{0.12} = 0.226 \text{ m}^3 .$$

(f) Process  $2 \rightarrow 3$  is adiabatic; Eq. 19-56 applies with  $\gamma = 5/3$  (since only translational degrees of freedom are relevant, here).

$$T_2 V_2^{\gamma-1} = T_3 V_3^{\gamma-1}$$

This yields  $V_3 = 0.284 \text{ m}^3$ .

(g) As remarked in part (d),  $\Delta E_{\text{int}} = 0$  for process  $1 \rightarrow 2$ .

(h) We find the change in internal energy from Eq. 19-45 (with  $C_V = \frac{3}{2}R$ ):

$$\Delta E_{\text{int}} = nC_V(T_3 - T_2) = -1.25 \times 10^3 \text{ J} .$$

(i) Clearly, the net change of internal energy for the entire cycle is zero. This feature of a closed cycle is as true for a  $T$ - $S$  diagram as for a  $p$ - $V$  diagram.

(j) For the adiabatic ( $2 \rightarrow 3$ ) process, we have  $W = -\Delta E_{\text{int}}$ . Therefore,  $W = 1.25 \times 10^3 \text{ J}$ . Its positive value indicates an expansion.

73. (a) Eq. 20-13 can be written as  $|Q_H| = |Q_L|(1 + 1/K_C) = (35)(1 + \frac{1}{4.6}) = 42.6 \text{ kJ}$ .

(b) Similarly, Eq. 20-12 leads to  $|W| = |Q_L|/K = 35/4.6 = 7.61 \text{ kJ}$ .

74. Since the inventor's claim implies that less heat (typically from burning fuel) is needed to operate his engine than, say, a Carnot engine (for the same magnitude of net work), then  $Q_H' < Q_H$  (See Fig. 20-34(a)) which implies that the Carnot (ideal refrigerator) unit is delivering more heat to the high temperature reservoir than engine X draws from it. This (using also energy conservation) immediately implies Fig. 20-34(b) which violates the second law.