

# Chapter 21

1. An isothermal process is one in which  $T_i = T_f$  which implies  $\ln(T_f/T_i) = 0$ . Therefore, with  $V_f/V_i = 2$ , Eq. 21-4 leads to

$$\Delta S = nR \ln \left( \frac{V_f}{V_i} \right) = (2.50 \text{ mol}) \left( 8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \ln(2) = 14.4 \text{ J/K} .$$

2. From Eq. 21-2, we obtain

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

3. (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  $V_2 = 2V_1$  to obtain

$$W = nRT \ln 2 = (4.00 \text{ mol}) \left( 8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) (400 \text{ K}) \ln 2 = 9.22 \times 10^3 \text{ J} .$$

- (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.

4. An isothermal process is one in which  $T_i = T_f$  which implies  $\ln(T_f/T_i) = 0$ . Therefore, Eq. 21-4 leads to

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

5. We use the following relation derived in Sample Problem 21-2:

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

- (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  $T_f = 373.15$  K and  $T_i = 298.15$  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. (a) Isothermal means that the temperature remains constant during the process. ON a graph with temperature plotted along the vertical axis, this means that the points representing that process must lie on a horizontal line (all corresponding to a single value of  $T$ ). Therefore, process  $AE$  is isothermal. This conclusion does not depend on the nature of the material (that is,  $AE$  is isothermal irrespective of this substance being a monatomic ideal gas).
- (b) Isobaric means that the pressure stays constant during the process. Knowing that this is an ideal gas, and assuming (as usual) that  $n$  stays constant during the process, then the gas law in ratio form (see Sample Problem 20-1) leads to

$$\frac{T_f}{T_i} = \frac{V_f}{V_i} = 2 \quad (\text{see Figure 21-21}) .$$

Consequently, we see that process  $AC$  is isobaric for this ideal gas. That it should be linear is implied by the simple proportionality between  $T$  and  $V$  shown above.

- (c) For a monatomic gas,  $\gamma = 5/3$  (see the discussion in Chapter 20). Therefore,

$$T_f = T_i \left( \frac{V_i}{V_f} \right)^{\gamma-1} = T_0 \left( \frac{1}{2} \right)^{2/3} = 0.63 T_0$$

which implied process  $AF$  is adiabatic.

- (d) Since  $\ln(x)$  is positive for all  $x > 1$ , then Eq. 21-4 makes it clear that all processes (with the possible exception of  $AF$ ) have  $\Delta S > 0$ . We assume process  $AF$  to be reversibly adiabatic, in which case Eq. 21-1 gives  $\Delta S = 0$  (since  $Q = 0$  for the process, or any small portion of the process); in fact, if  $AF$  represented (in some sense) an irreversible process which generated entropy, then we would still end up with the overall conclusion that none of the processes shown are accompanied by an entropy decrease.
7. (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  $\Delta S = 30.2 \text{ J/K}$ .
8. (a) It is possible to motivate, starting from Eq. 21-3, 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. 21-3 (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  $(300 \text{ K})(15 \text{ J/K}) = 4500 \text{ J}$  for the energy absorbed as heat by the gas.

- (b) Using Table 20-3 and Eq. 20-45, we find

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

(c) By the first law of thermodynamics,

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

9. (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,

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

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

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

- (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

$$\begin{aligned} \Delta S_a &= \int \frac{dQ}{T} = m_a c_a \int_{T_{ai}}^{T_f} \frac{dT}{T} = m_a c_a \ln \frac{T_f}{T_{ai}} \\ &= (0.200 \text{ kg})(900 \text{ J/kg}\cdot\text{K}) \ln \left( \frac{330 \text{ K}}{393 \text{ K}} \right) = -22.1 \text{ J/K} . \end{aligned}$$

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

10. This problem is similar to Sample Problem 21-2. 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)

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

- (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.
11. From problem #10 we know that, if the process in Fig. 21-5 should happen in reverse, then the change in entropy for the left block, which now absorbs energy, is  $\Delta S_L = +0.710 \text{ J/K}$ ; while for the right block  $\Delta S_R = -0.723 \text{ J/K}$ . The net change in entropy of the two-block system would then be

$$\Delta S = \Delta S_L + \Delta S_R = +0.710 \text{ J/K} - 0.723 \text{ J/K} = -0.013 \text{ J/K} < 0 .$$

This is a clear violation of the second law.

12. The connection between molar heat capacity and the degrees of freedom of a diatomic gas is given by setting  $f = 5$  in Eq. 20-51. Thus,  $C_V = \frac{5}{2}R$ ,  $C_p = \frac{7}{2}R$ , and  $\gamma = \frac{7}{5}$ . In addition to various equations from Chapter 20, we also make use of Eq. 21-4 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 20-1) as well as the adiabatic relations Eq. 20-54 and Eq. 20-56 are used to obtain

$$\begin{aligned} p_2 &= p_1 \left( \frac{V_1}{V_2} \right) = \frac{p_1}{3} , \\ p_3 &= p_1 \left( \frac{V_1}{V_3} \right)^\gamma = \frac{p_1}{3^{1.4}} , \\ T_3 &= T_1 \left( \frac{V_1}{V_3} \right)^{\gamma-1} = \frac{T_1}{3^{0.4}} . \end{aligned}$$

- (b) The energy and entropy contributions from all the processes are

- process  $1 \rightarrow 2$

The internal energy change is  $\Delta E_{\text{int}} = 0$  since this is an ideal gas process without a temperature change (see Eq. 20-45).

The work is given by Eq. 20-14:  $W = nRT_1 \ln(V_2/V_1) = RT_1 \ln 3$  which is approximately  $1.10RT_1$ .

The energy absorbed as heat is given by the first law of thermodynamics:  $Q = \Delta E_{\text{int}} + W \approx 1.10RT_1$ .

The entropy change is  $\Delta S = Q/T_1 = 1.10R$ .

- process  $2 \rightarrow 3$

The work is zero since there is no volume change.

The internal energy change is

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

This  $(-0.889RT_1)$  is also the value for  $Q$  (by either the first law of thermodynamics or by the definition of  $C_V$ ).

For the entropy change, we obtain

$$\begin{aligned}\Delta S &= nR \ln\left(\frac{V_3}{V_1}\right) + nC_V \ln\left(\frac{T_3}{T_1}\right) \\ &= (1)R \ln(1) + (1)\left(\frac{5}{2}R\right) \ln\left(\frac{T_1/3^{0.4}}{T_1}\right) \\ &= 0 + \frac{5}{2}R \ln(3^{-0.4}) \approx -1.10R .\end{aligned}$$

- process  $3 \rightarrow 1$

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

13. (a) We refer to the copper block as block 1 and the lead block as block 2. The equilibrium temperature  $T_f$  satisfies  $m_1c_1(T_f - T_{i,1}) + m_2c_2(T_f - T_{i,2}) = 0$ , which we solve for  $T_f$ :

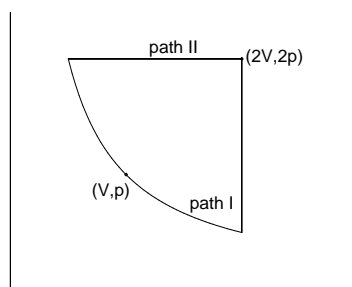
$$\begin{aligned}T_f &= \frac{m_1c_1T_{i,1} + m_2c_2T_{i,2}}{m_1c_1 + m_2c_2} \\ &= \frac{(50 \text{ g})(386 \text{ J/kg}\cdot\text{K})(400 \text{ K}) + (100 \text{ g})(128 \text{ J/kg}\cdot\text{K})(200 \text{ K})}{(50 \text{ g})(386 \text{ J/kg}\cdot\text{K}) + (100 \text{ g})(128 \text{ J/kg}\cdot\text{K})} \\ &= 320 \text{ K} .\end{aligned}$$

- (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

$$\begin{aligned}\Delta S &= \Delta S_1 + \Delta S_2 = m_1c_1 \ln\left(\frac{T_f}{T_{i,1}}\right) + m_2c_2 \ln\left(\frac{T_f}{T_{i,2}}\right) \\ &= (50 \text{ g})(386 \text{ J/kg}\cdot\text{K}) \ln\left(\frac{320 \text{ K}}{400 \text{ K}}\right) + (100 \text{ g})(128 \text{ J/kg}\cdot\text{K}) \ln\left(\frac{320 \text{ K}}{200 \text{ K}}\right) \\ &= +1.72 \text{ J/K} .\end{aligned}$$

14. (a) The  $pV$  diagram depicting the two “paths” is shown:



- (b) “Path I” consists of an isothermal (constant  $T$ ) process in which the volume doubles, followed by a constant-volume process. We consider the  $Q$  for each of these steps. 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. 20-51. Thus,  $C_V = \frac{3}{2}R$ ,  $C_p = \frac{5}{2}R$ , and  $\gamma = \frac{5}{3}$ .

- Isothermal: Since this is an ideal gas, Eq. 20-45 holds, which implies  $\Delta E_{\text{int}} = 0$  for this process. Eq. 20-14 also applies, so that by the first law of thermodynamics,  $Q = 0 + W = nRT \ln V_f/V_i = pV \ln 2$ . The ideal gas law is used in the last step.
- Constant-volume: The gas law in ratio form (see Sample Problem 20-1) implies that the pressure decreased by a factor of 2 during the isothermal portion, so that it needs to increase by a factor of 4 in this portion of “path I.” That same ratio form now applied to this constant-volume process, yielding  $4 = T_f/T_i$  which is used in the following:

$$\begin{aligned} Q &= nC_V \Delta T = n \left( \frac{3}{2} R \right) (T_f - T_i) \\ &= \frac{3}{2} nRT_i \left( \frac{T_f}{T_i} - 1 \right) \\ &= \frac{3}{2} pV (4 - 1) = \frac{9}{2} pV . \end{aligned}$$

“Path II” consists of an isothermal (constant  $T$ ) process in which the volume halves, followed by a isobaric (constant  $p$ ) process. We again consider the  $Q$  for each of these steps.

- Isothermal: Here the gas law applied to the isothermal portion leads to a volume half as big as the original. Since  $\ln \left( \frac{1}{2} \right) = -\ln 2$ , the reasoning used above leads to  $Q = -pV \ln 2$ .
- Isobaric: To obtain a final volume twice as big as the original, then this portion of the “path” needs to increase the volume by a factor of 4. Now, the gas law applied to this isobaric portion leads to a temperature ratio  $T_f/T_i = 4$ . Thus,

$$\begin{aligned} Q &= nC_p \Delta T = n \left( \frac{5}{2} R \right) (T_f - T_i) \\ &= \frac{5}{2} nRT_i \left( \frac{T_f}{T_i} - 1 \right) \\ &= \frac{5}{2} pV (4 - 1) = \frac{15}{2} pV . \end{aligned}$$

(c) Much of the reasoning has been given in part (b). Here and in the next part, we will be brief.

- Path I – Isothermal expansion: Eq. 20-14 gives  $W = nRT \ln V_f/V_i = pV \ln 2$ .
- Path I – constant-volume part:  $W = 0$ .
- Path II – Isothermal compression: Eq. 20-14 gives  $W = nRT \ln V_f/V_i = pV \ln 1/2 = -pV \ln 2$ .
- Path II – isobaric: The initial value of the volume, for this part of the process, is  $V_i = \frac{1}{2}V$ , and the final volume is  $V_f = 2V$ . The pressure maintained during this process is  $p' = 2p$ . The work is given by Eq. 20-16:

$$W = p' \Delta V = p' (V_f - V_i) = (2p) \left( 2V - \frac{1}{2}V \right) = 3pV .$$

(d) The change in internal energy between the very beginning and end of Path I is the same as that for Path II. We can calculate it directly from Eq. 20-45 (in which case the computation is very similar to one done in part (b)) or (indirectly) from the first law of thermodynamics. We illustrate the indirect approach, using information relevant to Path I:

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

(e) The change in entropy energy between the very beginning (when the temperature is  $T_i$ ) and the end of Path I (when the temperature is  $T_f = 4T_i$  – as noted in part (b)) is the same as the entropy change for Path II. We compute it using Eq. 21-4:

$$\Delta S = nR \ln \left( \frac{2V}{V} \right) + nC_V \ln \left( \frac{4T}{T} \right) = nR \ln 2 + n \left( \frac{3}{2} R \right) \ln 2^2 = nR \ln 2 + 3nR \ln 2 = 4nR \ln 2 .$$

15. The ice warms to  $0^\circ\text{C}$ , then melts, and the resulting water warms to the temperature of the lake water, which is  $15^\circ\text{C}$ . 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  $T_i$  ( $= 263\text{ K}$ ) is the initial temperature and  $T_f$  ( $= 273\text{ K}$ ) is the final temperature, then the change in its entropy is

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

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  $0^\circ\text{C}$ ,

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

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 20-2 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. 21-2 gives

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

for the phase change experienced by the ice (with  $T_o = 273.15$  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) In an adiabatic process  $Q = 0$ . This can be done by placing the gas in a thermally insulated container whose volume can be adjusted (say, by means of a movable piston). If the volume is *slowly* increased from  $V_i$  to  $V_x$ , then the process is reversible. To realize the reversible, constant-volume process from  $x$  to  $f$ , we would place the gas in a rigid container, which has a fixed volume  $V_f$  and is in thermal contact with a heat reservoir. If we *gradually* increase the temperature of the reservoir from  $T_x$  to  $T_f$ , the gas will undergo the desired reversible process from  $x$  to  $f$ .
- (b) For the two states  $i$  and  $x$  we have  $p_i V_i/T_i = p_x V_x/T_x$  and  $p_i V_i^\gamma = p_x V_x^\gamma$ . We eliminate  $p_i$  and  $p_x$  from these equations to obtain

$$\frac{T_x}{T_i} = \left(\frac{V_i}{V_x}\right)^{\gamma-1} .$$

For monatomic ideal gases  $\gamma = 5/3$  (see §20-8 and §20-11), so  $\gamma - 1 = 2/3$ . Also  $V_x = V_f$ . Substituting these into the equation above, we obtain  $T_x = T_i(V_i/V_f)^{2/3}$ .

- (c) For an ideal gas undergoing an isothermal process, Eq. 20-45 implies  $\Delta E_{\text{int}} = 0$ . And Eq. 20-14 gives  $W = nRT \ln(V_f/V_i)$  for such a process. Therefore, the first law of thermodynamics leads to

$$Q_{\text{path I}} = \Delta E_{\text{int I}} + W_I = nRT_i \ln\left(\frac{V_f}{V_i}\right) .$$

And for path II, we have

$$Q_{\text{path II}} = Q_{\text{adiabat}} + Q_{\text{const vol}} = 0 + nC_V \Delta T .$$



But  $C_V = \frac{3}{2}R$  (see Eq. 20-43), so we obtain

$$Q_{\text{path II}} = \frac{3}{2}nR(T_f - T_x) .$$

We see that  $Q_{\text{path I}} \neq Q_{\text{path II}}$ .

- (d) Since the first part of path II is reversibly adiabatic, then the entropy changes only during the second, constant-volume, part of the path:

$$\Delta S = \int_{T_x}^{T_f} \frac{nC_V dT}{T} = nC_V \ln\left(\frac{T_f}{T_x}\right) = \frac{3}{2}nR \ln\left(\frac{T_f}{T_x}\right) .$$

Entropy is a function of “where you are” on the  $pV$  diagram, not “how you got there.” Since the beginning and ending point of path I are the same as those of path II, then  $\Delta S$  is the same for both.

- (e) Using the result in part (b) with  $V_i/V_f = \frac{1}{2}$  and  $T_i = 500$  K, we find

$$T_x = (500 \text{ K}) \left(\frac{1}{2}\right)^{2/3} = 315 \text{ K} .$$

For path I, Eq. 21-2 gives  $Q_I = (\Delta S)T$  where  $T = T_i = T_f$  and  $\Delta S$  is the expression calculated in the part (d). Thus,

$$Q_I = \frac{3}{2}nRT_f \ln\left(\frac{T_f}{T_x}\right)$$

which can be alternatively derived from Eq. 20-14 and the first law of thermodynamics. With  $n = 1$  mol,  $T_f = T_i = 500$  K, we find

$$Q_I = \frac{3}{2}(1)(8.31)(500) \ln\left(\frac{500}{315}\right) = 2880 \text{ J} .$$

For path II,  $Q = Q_{\text{constant volume}} = nC_V\Delta T$  and we obtain

$$Q_{II} = (1) \left(\frac{3}{2}(8.31)\right) (500 - 315) = 2306 \text{ J} .$$

The issue of significant figures is problematic since the given “ $n = 1$ ” could be interpreted various ways (exact value, or just one figure?). From part (d),

$$\Delta S = \frac{3}{2}(1)(8.31) \ln\left(\frac{500}{315}\right) = 5.76 \text{ J/K} .$$

19. (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

$$W = \int_{V_0}^{4V_0} p_0 dV = p_0(4V_0 - V_0) = 3p_0V_0 .$$

- (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,  $C_V = \frac{3}{2}R$ . Use the ideal gas law to find that the initial temperature is  $T_b = p_bV_b/nR = 4p_0V_0/nR$  and that the final temperature is  $T_c = p_cV_c/nR = (2p_0)(4V_0)/nR = 8p_0V_0/nR$ . Thus,

$$Q = \frac{3}{2}nR \left( \frac{8p_0V_0}{nR} - \frac{4p_0V_0}{nR} \right) = 6p_0V_0 .$$

The change in the internal energy is  $\Delta E_{\text{int}} = 6p_0V_0$ . Since  $n = 1$  mol, this can also be written  $Q = 6RT_0$ . 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  $\Delta S = \frac{3}{2}R \ln 2$ .

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

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 20-1) 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

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

(d) Consideration of a two-stage process as suggested in the hint, brings us simply to Eq. 21-4. Consequently, with  $C_V = \frac{3}{2}R$  (see Eq. 20-43), 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. The answers to this exercise do not depend on the engine being of the Carnot design. Any heat engine that in-takes 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. 21-10 gives

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

(b) Eq. 21-6 gives

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

22. With  $T_L = 290 \text{ K}$ , we find

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

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

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

23. (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

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

24. Eq. 21-11 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. For an Carnot engine, the efficiency is related to the reservoir temperatures by Eq. 21-11. Therefore,

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

which is equivalent to  $68^\circ\text{C}$ . The temperature of the cold reservoir is  $T_L = T_H - 75 = 341 \text{ K} - 75 \text{ K} = 266 \text{ K}$ .

26. (a) Eq. 21-11 leads to

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

We recall that a Watt is Joule-per-second. Thus, the (net) work done by the cycle per unit time is the given value  $500 \text{ J/s}$ . Therefore, by Eq. 21-9, we obtain the heat input per unit time:

$$\varepsilon = \frac{W}{|Q_H|} \implies \frac{0.500 \text{ kJ/s}}{0.107} = 4.66 \text{ kJ/s} .$$

(b) Considering Eq. 21-6 on a per unit time basis, we find  $4.66 - 0.500 = 4.16 \text{ kJ/s}$  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  $C_V = \frac{3}{2}R$  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

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

The substitutions  $V_a - V_c = V_a - 8.00V_a = -7.00V_a$  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  $\varepsilon = W/Q_{\text{in}} = (9.18 \times 10^2 \text{ J})/(1.47 \times 10^3 \text{ J}) = 0.624$ .
28. During the adiabatic processes (the vertical lines in Fig. 21-9) there is no heat transfer, so we only consider the isothermal processes (the horizontal lines). We can interpret Eq. 21-2,  $Q = T\Delta S$ , as represent the “area” (with appropriate  $\pm$  sign) under the horizontal lines. Since  $a \rightarrow b$  is in the positive direction while  $c \rightarrow d$  is in the negative direction, then there is a partial cancellation in the “areas” under the two lines, and the net contribution is the rectangular area between them. This can be seen explicitly as follows:

$$Q_{\text{net}} = T_H(S_b - S_a) + T_L(S_d - S_c) = (T_H - T_L)(S_{\text{max}} - S_{\text{min}})$$

where we have used the fact that  $S_b = S_c = S_{\text{max}}$  and  $S_a = S_d = S_{\text{min}}$ .

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  $W = 2.27 \text{ kJ}$ .

- (b) We compute the energy added as heat during the “heat-intake” portions of the cycle using Eq. 20-39, Eq. 20-43, and Eq. 20-46:

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

where, to obtain the last line, the gas law in ratio form has been used (see Sample Problem 20-1). Therefore, since  $W = p_0 V_0$ , we have  $Q_{abc} = 13W/2 = 14.8 \text{ kJ}$ .

(c) The efficiency is given by Eq. 21-9:

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

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

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

where the gas law in ratio form has been used. 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. 21-9 and Eq. 21-6)

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

Now, Eq. 21-8 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) 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

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

(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,

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

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  $800^\circ\text{C}$ .

32. (a) Using Eq. 20-54 for process  $D \rightarrow A$  gives

$$\begin{aligned} p_D V_D^\gamma &= p_A V_A^\gamma \\ \frac{p_0}{32} (8V_0)^\gamma &= p_0 V_0^\gamma \end{aligned}$$

which leads to

$$8^\gamma = 32 \implies \gamma = \frac{5}{3}$$

which (see §20-9 and §20-11) 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 20-1). Therefore, Eq. 21-10 leads to

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

33. (a) The pressure at 2 is  $p_2 = 3p_1$ , as given in the problem statement. The volume is  $V_2 = V_1 = nRT_1/p_1$ . The temperature is

$$T_2 = \frac{p_2 V_2}{nR} = \frac{3p_1 V_1}{nR} = 3T_1 .$$

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

$$p_4 = \left( \frac{V_1}{V_4} \right)^\gamma p_1 = \frac{p_1}{4^\gamma} ,$$

since  $V_4 = 4V_1$ . The temperature at 4 is

$$T_4 = \frac{p_4 V_4}{nR} = \left( \frac{p_1}{4^\gamma} \right) \left( \frac{4nRT_1}{p_1} \right) \left( \frac{1}{nR} \right) = \frac{T_1}{4^{\gamma-1}} .$$

The process  $2 \rightarrow 3$  is adiabatic, so  $p_2 V_2^\gamma = p_3 V_3^\gamma$  and  $p_3 = (V_2/V_3)^\gamma p_2$ . Substitute  $V_3 = 4V_1$ ,  $V_2 = V_1$ , and  $p_2 = 3p_1$  to obtain

$$p_3 = \frac{3p_1}{4^\gamma} .$$

The temperature is

$$T_3 = \frac{p_3 V_3}{nR} = \left( \frac{1}{nR} \right) \left( \frac{3p_1}{4^\gamma} \right) \left( \frac{4nRT_1}{p_1} \right) = \frac{3T_1}{4^{\gamma-1}} ,$$

where  $V_3 = V_4 = 4V_1 = 4nRT/p_1$  is used.

- (b) The efficiency of the cycle is  $\varepsilon = W/Q_{12}$ , 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  $V_2 = V_1$ ,  $V_3 = 4V_1$ , and  $p_3 = 3p_1$  to obtain

$$W_{23} = \left( \frac{3p_1 V_1}{1 - \gamma} \right) \left( 1 - \frac{1}{4^{\gamma-1}} \right) = \left( \frac{3nRT_1}{\gamma - 1} \right) \left( 1 - \frac{1}{4^{\gamma-1}} \right).$$

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

$$W_{41} = \left( \frac{p_1 V_1^\gamma}{\gamma - 1} \right) (V_4^{1-\gamma} - V_1^{1-\gamma}) = - \left( \frac{p_1 V_1}{\gamma - 1} \right) \left( 1 - \frac{1}{4^{\gamma-1}} \right) = - \left( \frac{nRT_1}{\gamma - 1} \right) \left( 1 - \frac{1}{4^{\gamma-1}} \right).$$

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

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

34. (a) We use Eq. 21-12,

$$K = \frac{|Q_L|}{|W|} = \frac{600}{200} = 3.$$

(b) Energy conservation for a refrigeration cycle requires  $|Q_L| + |W| = |Q_H|$ , so that the result is 800 J.

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. 21-8 still holds (particularly due to its use of absolute values), and energy conservation implies  $|W| + Q_L = Q_H$ . Therefore, with  $T_L = 268.15 \text{ K}$  and  $T_H = 290.15 \text{ K}$ , 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  $|W| = 1.0 \text{ J}$ ) leads to

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

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. 21-12 and Eq. 21-14, 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. 21-12 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 Btu/h = 0.0003929 hp, so our result may be expressed as  $|W|/t = 0.25 \text{ hp}$ .

40. The work done by the motor in  $t = 10.0 \text{ min}$  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

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

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  $Q_3/Q_1$ :

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

42. We need nine labels:

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



The multiplicity  $W$  is computed using Eq. 21-18. 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. 21-19)

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

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

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

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

For instance, in the solution of problem #42, above, there are a total of  $2^8 = 256$  states, as one can readily verify. It is possible to check this with the textbook example, too, but it is important to realize that there are three additional configurations beyond what are shown in Table 21-1: one with  $n_1 = 0$  and  $n_2 = 6$ , another with  $n_1 = 1$  and  $n_2 = 5$ , and so on. When all these are included, there are a total of  $2^6 = 64$  microstates.

44. (a) We denote the configuration with  $n$  heads out of  $N$  trials as  $(n; N)$ . We use Eq. 21-18:

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

- (b) We use the result of problem #43:  $\mathcal{N}_{\text{total}} = 2^{50} = 1.13 \times 10^{15}$ .

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

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

- (d) We use  $W(N/2, N) = N! / [(N/2)!]^2$ ,  $\mathcal{N}_{\text{total}} = 2^N$  and  $p(N/2; N) = W(N/2, N) / \mathcal{N}_{\text{total}}$ . The results are as follows: For  $N = 100$ ,  $W(N/2, N) = 1.01 \times 10^{29}$ ,  $\mathcal{N}_{\text{total}} = 1.27 \times 10^{30}$ , and  $p(N/2; N) = 8.0\%$ .

- (e) Similarly, for  $N = 250$ , we obtain  $W(N/2, N) = 9.25 \times 10^{58}$ ,  $\mathcal{N}_{\text{total}} = 1.61 \times 10^{60}$ , and  $p(N/2; N) = 5.7\%$ .

- (f) 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.

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  $N = 100$ ,

$$\frac{W_A}{W_B} = \frac{50! 50!}{33! 33! 34!} = 4.16 \times 10^{16} .$$

46. The first law requires that  $Q_H = W + Q_L$ , while the second law requires that

$$\varepsilon = \frac{W}{Q_H} \leq 1 - \frac{T_L}{T_H} .$$

Thus, we see that the first law is violated in engine A; both laws are violated in B; the second law is violated in C; and, neither of the laws is violated in D.

47. (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

$$\begin{aligned} |Q_H| &= \frac{|W|}{\varepsilon} = \frac{8.2 \text{ kJ}}{0.31} = 26 \text{ kJ} \\ \text{and } |Q_C| &= |Q_H| - |W| = 26 \text{ kJ} - 8.2 \text{ kJ} = 18 \text{ kJ} . \end{aligned}$$

48. We find the “percent error” in the use of Stirling’s approximation by computing

$$\frac{(N(\ln N) - N) - \ln(N!)}{\ln(N!)} = \frac{(N(\ln N) - N)}{\ln(N!)} - 1$$

which would be multiplied by 100% to be expressed as a percentage.

- (a) For  $N = 50$ , the percent error is

$$\frac{50 \ln(50) - 50}{\ln(50!)} - 1 = \frac{145.6}{\ln(3.04 \times 10^{64})} - 1 = \frac{145.6}{148.5} - 1$$

which yields  $-1.9\%$ , meaning Stirling’s approximation produces a value that is 1.9% lower than the correct one.

- (b) For  $N = 100$ , this procedure gives the result  $-0.89\%$ .  
 (c) And for  $N = 250$ , we obtain  $-0.32\%$ .  
 (d) The trend is such that Stirling's approximation becomes a better estimate of  $\ln(N!)$  for larger values of  $N$ .

49. (a) From problem #43, we have  $\mathcal{N}_{\text{total}} = 2^{100} = 1.27 \times 10^{30}$  microstates.

(b) Using Eq. 21-18, we find

$$\begin{aligned} \frac{W}{\mathcal{N}_{\text{total}}} &= \frac{\left(\frac{100!}{(50!)(50!)}\right)}{1.27 \times 10^{30}} = \frac{12611418068195524166851562157}{158456325028528675187087900672} \\ &= 0.079589 \approx 8.0\% . \end{aligned}$$

(c) Similarly, for  $n_1 = 48$  and  $n_2 = 52$  we obtain

$$\begin{aligned} \frac{W}{\mathcal{N}_{\text{total}}} &= \frac{\left(\frac{100!}{(48!)(52!)}\right)}{1.27 \times 10^{30}} = \frac{23301639718762469237395420275}{316912650057057350374175801344} \\ &= 0.073527 \approx 7.4\% . \end{aligned}$$

(d) With  $n_1 = 52$  and  $n_2 = 48$ , we obtain the same result as in part (c).

(e) For  $n_1 = 40$  and  $n_2 = 60$  we obtain

$$\begin{aligned} \frac{W}{\mathcal{N}_{\text{total}}} &= \frac{\left(\frac{100!}{(40!)(60!)}\right)}{1.27 \times 10^{30}} = \frac{1718279268225351437658421215}{158456325028528675187087900672} \\ &= 0.010844 \approx 1.1\% . \end{aligned}$$

(f) Finally, for  $n_1 = 30$  and  $n_2 = 70$  we find

$$\begin{aligned} \frac{W}{\mathcal{N}_{\text{total}}} &= \frac{\left(\frac{100!}{(30!)(70!)}\right)}{1.27 \times 10^{30}} = \frac{1835771238850684051497735}{79228162514264337593543950336} \\ &= 0.00002317 \approx 0.0023\% . \end{aligned}$$

50. (a) We use Eq. 21-14. 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,

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

(d) We use these formulas for  $N = 100$ :  $W_A = 1.01 \times 10^{29}$ ,  $W_B = 1.37 \times 10^{28}$ , and  $f \approx 0.14$ .

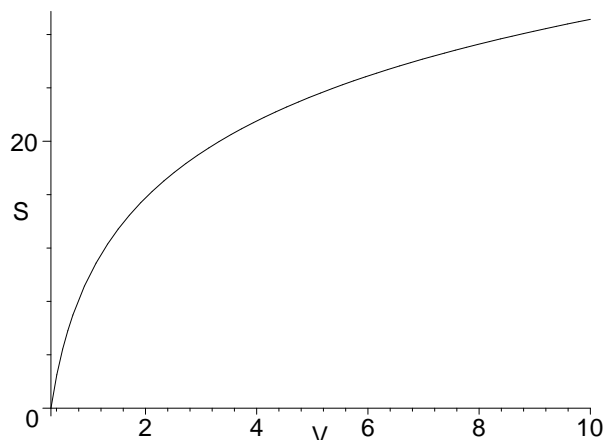
(e) For  $N = 200$  we have  $W_A = 9.05 \times 10^{58}$ ,  $W_B = 1.64 \times 10^{57}$ , and  $f = 0.018$ .

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

51. Since isothermal means constant temperature, then this would be a flat horizontal line on a  $T$  versus  $S$  graph (with  $T$  being the vertical axis). Since this concerns an ideal gas (also see Figure 21-3) then  $\Delta E_{\text{int}} = 0$  (by Eq. 20-45), so this isothermal process would be a vertical line on an  $S$  versus  $E_{\text{int}}$  graph (with  $E_{\text{int}}$  being the horizontal axis). When  $T = T_i$  Eq. 21-4 reduces to

$$S - S_i = nR \ln \left( \frac{V}{V_i} \right)$$

which is shown in the graph below for  $n = 1$  mol,  $V_i = 1 \text{ m}^3$ , and  $S_i = 10 \text{ J/K}$  (arbitrarily picked).



52. The change in entropy for the ideal gas is found from Eq. 21-2, Eq. 20-14, and the first law of thermodynamics (using the fact that  $\Delta E_{\text{int}} = 0$  for an ideal gas isothermal process).

$$\Delta S = \frac{Q}{T} = \frac{W}{T} = \frac{nRT}{T} \ln \left( \frac{V_f}{V_i} \right) = nR \ln 2 ,$$

which is independent of the temperature  $T$  of the reservoir. Thus the change in entropy of the reservoir,  $\Delta S' = -\Delta S = -nR \ln 2$ , is also independent of  $T$ . Here we noticed that the net change in entropy for the entire system (the ideal gas plus the reservoir) is  $\Delta S_{\text{total}} = \Delta S + \Delta S' = 0$  for a reversible process so  $\Delta S' = -\Delta S$ .

53. (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.

From Eq. 21-1, we have

$$\Delta S_{\text{copper}} = \int_{353}^{314} \frac{c m dT}{T} = (386)(0.6) \ln \left( \frac{314}{353} \right) = -27.2 \text{ J/K} .$$

- (b) Also,

$$\Delta S_{\text{water}} = \int_{283}^{314} \frac{c m dT}{T} = (4190)(0.07) \ln \left( \frac{314}{283} \right) = 30.4 \text{ J/K} .$$

- (c) The net result for the system is  $30.3 - 27.2 = 3.2 \text{ J/K}$ . (Note: these calculations are fairly sensitive to round-off errors. To arrive at this final answers, the value 273.15 was used to convert to Kelvins, and all intermediate steps were retained to full calculator accuracy.)

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

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

which is equivalent to 229 K.

- (b) From Eq. 21-1, we have

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

- (c) Also,

$$\Delta S_{\text{silver}} = \int_{153}^{229} \frac{c m dT}{T} = (236)(0.025) \ln\left(\frac{229}{153}\right) = 2.37 \text{ J/K} .$$

- (d) The net result for the system is  $2.37 - 1.69 = 0.68 \text{ J/K}$ . (Note: these calculations are fairly sensitive to round-off errors. To arrive at this final answers, the value 273.15 was used to convert to Kelvins, and all intermediate steps were retained to full calculator accuracy.)

55. The Carnot efficiency (Eq. 21-11) depends linearly on  $T_L$  so that we can take a derivative

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

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

56. (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 20,  $C_V = \frac{3}{2}R$ ,  $C_p = \frac{5}{2}R$ , and  $\gamma = \frac{5}{3}$ . 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  $T = 300 \text{ K}$  and  $T' = 800 \text{ K}$ ) the result  $Q_H = 25.5 \times 10^3 \text{ J}$ .

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

- (c) Using Eq. 21-9, we find that the efficiency is

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

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

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

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

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

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

58. 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:  $dQ = dE_{\text{int}} = \frac{3}{2}nR dT$ . Thus

$$\begin{aligned}\Delta S &= \int \frac{dQ}{T} = \int_{T_i}^{T_f} \frac{(3nR/2)dT}{T} = \frac{3}{2}nR \ln \left( \frac{T_f}{T_i} \right) \\ &= \frac{3}{2}(1.0 \text{ mol}) \left( 8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \ln \left( \frac{400 \text{ K}}{300 \text{ K}} \right) = 3.59 \text{ J/K} .\end{aligned}$$

59. Now

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

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

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

60. (a) The ideal gas is diatomic, so  $f = 5$  (see Table 20-3). Since this is an isobaric (constant pressure) process, with no change in the number of moles, then the ideal gas in ratio form (see Sample Problem 20-1) leads to

$$\frac{V_f}{V_i} = \frac{T_f}{T_i} = \frac{8}{3} .$$

With  $C_V = \frac{f}{2}R$ , Eq. 21-4 gives

$$\Delta S_{\text{gas}} = nR \ln \left( \frac{8}{3} \right) + n \left( \frac{5}{2}R \right) \ln \left( \frac{8}{3} \right)$$

where  $n$  is the number of moles (25 mol), not to be confused with the number of reservoirs (also denoted “ $n$ ” in the later parts of this problem). Consequently, we obtain

$$\Delta S_{\text{gas}} = \frac{7}{2}(25 \text{ mol}) \left( 8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \ln \left( \frac{8}{3} \right) = 713 \text{ J/K} .$$

Since  $Q = nC_p \Delta T$  for this process, the entropy change of the reservoir (which transfers energy  $Q$  to the gas, so it (the heat) is negative-valued in this context) is (using Eq. 21-2)

$$\Delta S_{\text{res}} = \frac{-Q}{T} = - \frac{n \left( \frac{7}{2}R \right) (800 \text{ K} - 300 \text{ K})}{800 \text{ K}} = -454 \text{ J/K} .$$

Therefore,  $\Delta S_{\text{system}} = \Delta S_{\text{gas}} + \Delta S_{\text{res}} = 259 \text{ J/K}$ .

- (b) The change in entropy of the gas is the same regardless of the number of intermediate reservoirs, so long as the beginning state and final state of the gas is unchanged. The difference (relative to part (a)) is that the sum of these *two* reservoirs' entropy changes is not equivalent to that of the one reservoir in the previous part:

$$\begin{aligned}\Delta S_{\text{res1}} + \Delta S_{\text{res2}} &= \frac{-Q_1}{T_1} + \frac{-Q_2}{T_2} \\ &= - \frac{(25 \text{ mol}) \left( \frac{7}{2}R \right) (550 \text{ K} - 300 \text{ K})}{550 \text{ K}} - \frac{(25 \text{ mol}) \left( \frac{7}{2}R \right) (800 \text{ K} - 550 \text{ K})}{800 \text{ K}} \\ &= -(25 \text{ mol}) \left( \frac{7}{2}R \right) (250 \text{ K}) \left( \frac{1}{550 \text{ K}} + \frac{1}{800 \text{ K}} \right)\end{aligned}$$

which yields  $-558 \text{ J/K}$  for the total loss of entropy from the reservoirs. The entire system change in entropy is therefore  $713 - 558 = 155 \text{ J/K}$ .

- (c) Towards the end of the calculation in part (b), a pattern emerges in the computation of the total entropy loss from the original high-temperature reservoir plus the  $n$  intermediate reservoirs:

$$\Delta S_{\text{res total}} = -(25 \text{ mol}) \left( \frac{7}{2} R \right) \left( \frac{500 \text{ K}}{n+1} \right) \left( \sum_{\text{reservoirs}}^{n+1} \frac{1}{T} \right)$$

where the temperature of a particular reservoir (the  $j^{\text{th}}$  reservoir, where  $1 \leq j \leq n+1$ ) is  $T = 300 + \left( \frac{500}{n+1} \right)$  (in Kelvins). For  $n = 10$ , this leads to  $\Delta S_{\text{res total}} = -680 \text{ J/K}$  and therefore  $713 - 680 = 33 \text{ J/K}$  for the entire system (including the gas) entropy change.

- (d) For  $n = 50$ , this leads to  $\Delta S_{\text{res total}} = -705.82 \text{ J/K}$  and therefore  $713.19 - 705.82 = 7.37 \text{ J/K}$  for the entire system (including the gas) entropy change.
- (e) For  $n = 100$ , this leads to  $\Delta S_{\text{res total}} = -709.45 \text{ J/K}$  and therefore  $713.19 - 709.45 = 3.74 \text{ J/K}$  for the entire system (including the gas) entropy change.
61. (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. 21-1 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. 21-1)  $dQ = p dV$ . Therefore,

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

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

- (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,  $\Delta S_2 = 23.0 \text{ J/K}$ .
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. 21-9, the efficiency is

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

63. We adapt the discussion of §21-7 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. 21-18, 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,

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

- (e) We use Eq. 21-19 with our result in part (c) to obtain

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

- (f) Similarly for the 5 particle case (using the result from part (d)), we find  $S = k \ln 10 = 3.2 \times 10^{-23} \text{ J/K}$ .

64. (a) The most obvious input-heat step is the constant-volume process. Since the gas is monatomic, we know from Chapter 20 that  $C_V = \frac{3}{2}R$ . Therefore,

$$\begin{aligned} Q_V &= nC_V\Delta T \\ &= (1 \text{ mol}) \left( \frac{3}{2} \right) \left( 8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) (600 \text{ K} - 300 \text{ K}) \\ &= 3740 \text{ J .} \end{aligned}$$

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. 20-45). 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. 20-14 and Eq. 20-16, 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 20-1) the volume ratio is

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

Thus, the net work is

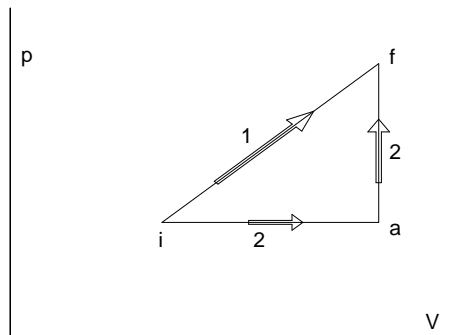
$$\begin{aligned} W &= nRT_H \ln 2 + p_{\text{min}} V_{\text{min}} \left( 1 - \frac{V_{\text{max}}}{V_{\text{min}}} \right) \\ &= nRT_H \ln 2 + nRT_L (1 - 2) \\ &= nR (T_H \ln 2 - T_L) \\ &= (1 \text{ mol}) \left( 8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) ((600 \text{ K}) \ln 2 - (300 \text{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

- (c) Eq. 21-9 gives

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



65. First we show that  $\int dQ$  is path-dependent. To do this all we need is to show that  $\int dQ$  is different for at least two separate paths, say path 1 and 2, as depicted in the figure below. We write  $\int dQ = \int p dV + \int nC_V dT$ . The second term on the right,  $\int nC_V dT$ , yields  $nC_V \Delta T$  upon integration and is obviously path-independent. The first term,  $\int p dV$ , however, is different for the two paths. In fact  $\int_i^f p dV$  along path 1 is greater than that along path 2, by the area of the shaded triangle enclosed by the two paths. Therefore,  $\int dQ$  is indeed path-dependent.



Now we consider  $\int T dQ = \int pT dV + \int nC_V T dT$ . Once again the second term on the right,  $\int nC_V T dT$ , yields  $\frac{1}{2}nC_V \Delta T^2$  upon integration and is path-independent. The first term,  $\int pT dV$ , however, yields a higher value along path 1 than path 2. To see that, note that

$$\int_2 pT dV = \int_{i \rightarrow a} pT dV + \int_{a \rightarrow f} pT dV = \int_{i \rightarrow a} pT dV .$$

Now, if we compare the two integrals,  $\int_1 pT dV$  and  $\int_{i \rightarrow a} pT dV$ , we realize that the average values of both  $T$  and  $p$  along path 1 are greater than their respective corresponding values along the  $i \rightarrow a$  segment of path 2. Hence, the integrand  $f(p, T) = pT$  is always greater along path 1. Thus, the two integrals over  $V$ , which have the same upper and lower limits, are not equal to each other:

$$\int_1 pT dV > \int_{i \rightarrow a} pT dV = \int_2 pT dV .$$

We see then that  $\int T dQ$  is greater along path 1 than path 2 and is therefore path-dependent. Similarly, one can show that for  $\int dQ/T^2 = \int p dV/T^2 + \int nC_V dT/T^2$ , the second term on the right is path-independent, while for the first term

$$\int p dV/T^2 = nR \int \frac{dV}{TV} ,$$

we have

$$nR \int_2 \frac{dV}{TV} = nR \int_{i \rightarrow a} \frac{dV}{TV} > nR \int_1 \frac{dV}{TV} ,$$

since the average value of  $1/T$  is greater along the  $i \rightarrow a$  segment of path 2 than on path 1. Consequently,  $\int dQ/T^2$  is less along path 1 than path 2 and is therefore path-dependent.

66. We consider a three-step reversible process as follows: the supercooled water drop (of mass  $m$ ) starts at state 1 ( $T_1 = 268$  K), moves on to state 2 (still in liquid form but at  $T_2 = 273$  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:  $\Delta S_{12} = mc_w \ln(T_2/T_1)$ ,  $\Delta S_{23} = -mL_F/T_2$ , and  $\Delta S_{34} = mc_I \ln(T_4/T_3) = mc_I \ln(T_1/T_2) = -mc_I \ln(T_2/T_1)$ . Thus the net entropy change for the water

drop is

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

67. Eq. 21-8 gives

$$\left| \frac{Q_H}{Q_L} \right| = \frac{T_H}{T_L} = \frac{300 \text{ K}}{4.0 \text{ K}} = 75 .$$

68. (a) Eq. 21-13 provides

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

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

(b) From §21-5 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. 21-14.

69. (a) Combining Eq. 21-9 with Eq. 21-11, we obtain

$$|W| = |Q_H| \left( 1 - \frac{T_L}{T_H} \right) = (500 \text{ J}) \left( 1 - \frac{260 \text{ K}}{320 \text{ K}} \right) = 94 \text{ J} .$$

(b) Combining Eq. 21-12 with Eq. 21-14, we find

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