

## CHAPTER 20: Second Law of Thermodynamics

### Responses to Questions

13. 1 kg of liquid iron will have greater entropy, since it is less ordered than solid iron and its molecules have more thermal motion. In addition, heat must be added to solid iron to melt it; the addition of heat will increase the entropy of the iron.
15. The machine is clearly doing work to remove heat from some of the air in the room. The waste heat is dumped back into the room, and the heat generated in the process of doing work is also dumped into the room. The net result is the addition of heat into the room by the machine.
16. Some processes that would obey the first law of thermodynamics but not the second, if they actually occurred, include: a cup of tea warming itself by gaining thermal energy from the cooler air molecules around it, a ball sitting on a soccer field gathering energy from the grass and beginning to roll, and a bowl of popcorn placed in the refrigerator and unpopping as it cools.
17. No. While you have reduced the entropy of the papers, you have increased your own entropy by doing work, for which your muscles have consumed energy. The entropy of the universe has increased as a result of your actions.
19. No. Even if the powdered milk is added very slowly, it cannot be re-extracted from the water without very large investments of energy. This is not a reversible process.
20. Entropy is a state variable, so the change in entropy for the system will be the same for the two different irreversible processes that take the system from state a to state b. However, the change in entropy for the environment will not necessarily be the same. The total change in entropy (system plus environment) will be positive for irreversible processes, but the amount may be different for different irreversible processes.

## Solutions to Problems

In solving these problems, the authors did not always follow the rules of significant figures rigidly. We tended to take quoted temperatures as correct to the number of digits shown, especially where other values might indicate that.

32. Heat energy is taken away from the water, so the change in entropy will be negative. The heat transfer is the mass of the steam times the latent heat of vaporization.

$$\Delta S = \frac{Q}{T} = -\frac{mL_{\text{vap}}}{T} = -\frac{(0.25 \text{ kg})(22.6 \times 10^5 \text{ J/kg})}{(273 + 100) \text{ K}} = \boxed{-1500 \text{ J/K}}$$

33. Energy has been made “unavailable” in the frictional stopping of the sliding box. We take that “lost” kinetic energy as the heat term of the entropy calculation.

$$\Delta S = Q/T = \frac{1}{2}mv_i^2/T = \frac{1}{2}(7.5 \text{ kg})(4.0 \text{ m/s})^2/293 \text{ K} = \boxed{0.20 \text{ J/K}}$$

Since this is a decrease in “availability,” the entropy of the universe has increased.

35. Because the temperature change is small, we can approximate any entropy integrals by  $\Delta S = Q/T_{\text{avg}}$ . There are three terms of entropy to consider. First, there is a loss of entropy from the water for the freezing process,  $\Delta S_1$ . Second, there is a loss of entropy from that newly-formed ice as it cools to

$-10^\circ\text{C}$ ,  $\Delta S_2$ . That process has an “average” temperature of  $-5^\circ\text{C}$ . Finally, there is a gain of entropy by the “great deal of ice,”  $\Delta S_3$ , as the heat lost from the original mass of water in steps 1 and 2 goes into that great deal of ice. Since it is a large quantity of ice, we assume that its temperature does not change during the processes.

$$\Delta S_1 = \frac{Q_1}{T_1} = -\frac{mL_{\text{fusion}}}{T_1} = -\frac{(1.00 \times 10^3 \text{ kg})(3.33 \times 10^5 \text{ J/kg})}{273 \text{ K}} = -1.2198 \times 10^6 \text{ J/K}$$

$$\Delta S_2 = \frac{Q_2}{T_2} = -\frac{mc_{\text{ice}} \Delta T_2}{T_2} = -\frac{(1.00 \times 10^3 \text{ kg})(2100 \text{ J/kggC}^\circ)(10\text{C}^\circ)}{(-5 + 273) \text{ K}} = -7.8358 \times 10^4 \text{ J/K}$$

$$\Delta S_3 = \frac{Q_3}{T_3} = \frac{-Q_1 - Q_2}{T_3} = \frac{mL_{\text{fusion}} + mc_{\text{ice}} \Delta T_2}{T_3}$$

$$= \frac{(1.00 \times 10^3 \text{ kg})[(3.33 \times 10^5 \text{ J/kg}) + (2100 \text{ J/kggC}^\circ)(10\text{C}^\circ)]}{(-10 + 273) \text{ K}} = 1.3460 \times 10^6 \text{ J/K}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -1.2198 \times 10^6 \text{ J/K} - 7.8358 \times 10^4 \text{ J/K} + 1.3460 \times 10^6 \text{ J/K}$$

$$= 4.784 \times 10^4 \text{ J/K} \approx \boxed{5 \times 10^4 \text{ J/K}}$$

37. The same amount of heat that leaves the high temperature heat source enters the low temperature body of water. The temperatures of the heat source and body of water are constant, so the entropy is calculated without integration.

$$\Delta S = \Delta S_1 + \Delta S_2 = -\frac{Q}{T_{\text{high}}} + \frac{Q}{T_{\text{low}}} = Q \left( \frac{1}{T_{\text{low}}} - \frac{1}{T_{\text{high}}} \right) \rightarrow$$

$$\frac{\Delta S}{t} = \frac{Q}{t} \left( \frac{1}{T_{\text{low}}} - \frac{1}{T_{\text{high}}} \right) = (9.50 \text{ cal/s}) \left( \frac{4.186 \text{ J}}{1 \text{ cal}} \right) \left( \frac{1}{(22 + 273) \text{ K}} - \frac{1}{(225 + 273) \text{ K}} \right)$$

$$= \boxed{5.49 \times 10^{-2} \frac{\text{J/K}}{\text{s}}}$$

39. Because the process happens at a constant temperature, we have  $\Delta S = Q/T$ . The heat flow can be found from the first law of thermodynamics, the work for expansion at a constant temperature, and the ideal gas equation

$$\Delta E_{\text{int}} = Q - W = 0 \rightarrow Q = W = nRT \ln \frac{V_2}{V_1} = PV \ln \frac{P_1}{P_2} \rightarrow$$

$$\Delta S = \frac{Q}{T} = \frac{PV}{T} \ln \frac{P_1}{P_2} = \frac{(7.5)(1.013 \times 10^5 \text{ Pa})(2.50 \times 10^{-3} \text{ m}^3)}{410 \text{ K}} \ln \frac{7.5 \text{ atm}}{1.0 \text{ atm}} = \boxed{9.3 \text{ J/K}}$$

42. Since the process is at a constant volume,  $dQ = nC_V dT$ . For a diatomic gas in the temperature range of this problem,  $C_V = \frac{5}{2}R$ .

$$\Delta S = \int \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{nC_V dT}{T} = \frac{5}{2}nR \ln \frac{T_2}{T_1} = \frac{5}{2}(2.0 \text{ mol})(8.314 \text{ J/molgK}) \ln \frac{(273+55) \text{ K}}{(273+25) \text{ K}} = \boxed{4.0 \text{ J/K}}$$

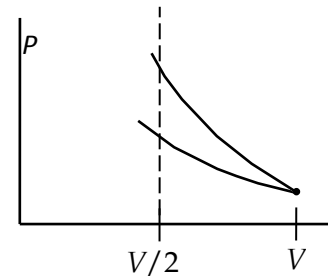
44. Entropy is a state variable, and so the entropy difference between two states is the same for any path. Since we are told that states a and b have the same temperature, we may find the entropy change by calculating the change in entropy for an isothermal process connecting the same two states. We also use the first law of thermodynamics.

$$\Delta E_{\text{int}} = nC_V \Delta T = 0 = Q - W \rightarrow Q = W = nRT \ln(V_b/V_a)$$

$$\Delta S = \int \frac{dQ}{T} = \frac{Q}{T} = \frac{nRT \ln(V_b/V_a)}{T} = \boxed{nR \ln(V_b/V_a)}$$

45. (a) The figure shows two processes that start at the same state. The

top process is adiabatic, and the bottom process is isothermic. We see from the figure that at a volume of  $V/2$ , the pressure is greater for the adiabatic process. We also prove it analytically.



$$\text{Isothermal: } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \rightarrow P_2 = P_1 \frac{V_1 T_2}{V_2 T_1} = P_1 \left( \frac{V}{\frac{1}{2}V} \right) (1) = 2P_1$$

$$\text{Adiabatic: } P_1 V_1^\gamma = P_2 V_2^\gamma \rightarrow P_2 = P_1 \left( \frac{V_1}{V_2} \right)^\gamma = P_1 \left( \frac{V}{\frac{1}{2}V} \right)^\gamma = 2^\gamma P_1$$

Since  $\gamma > 1$ , we see that  $(P_2)_{\text{adiabatic}} > (P_2)_{\text{isothermic}}$ . The ratio is  $\frac{(P_2)_{\text{adiabatic}}}{(P_2)_{\text{isothermic}}} = \frac{2^\gamma P_1}{2P_1} = 2^{\gamma-1}$ .

- (b) For the adiabatic process: No heat is transferred to or from the gas, so  $\Delta S_{\text{adiabatic}} = \int \frac{dQ}{T} = \boxed{0}$ .

$$\text{For the isothermal process: } \Delta E_{\text{int isothermal}} = 0 \rightarrow Q_{\text{isothermal}} = W_{\text{isothermal}} = nRT \ln \left( \frac{V_2}{V_1} \right)$$

$$\begin{aligned}\Delta S_{\text{isothermal}} &= \int \frac{dQ_{\text{isothermal}}}{T} = \frac{1}{T} \int dQ_{\text{isothermal}} = \frac{\Delta Q_{\text{isothermal}}}{T} = \frac{nRT \ln(V_2/V_1)}{T} \\ &= nR \ln(V_2/V_1) = nR \ln\left(\frac{1}{2}\right) = \boxed{-nR \ln 2}\end{aligned}$$

(c) Since each process is reversible, the energy change of the universe is 0, and so

$$\begin{aligned}\Delta S_{\text{surroundings}} &= -\Delta S_{\text{system}}. \text{ For the adiabatic process, } \Delta S_{\text{surroundings}} = \boxed{0}. \text{ For the isothermal process,} \\ \Delta S_{\text{surroundings}} &= \boxed{nR \ln 2}.\end{aligned}$$

46. (a) The equilibrium temperature is found using calorimetry, from Chapter 19. The heat lost by the water is equal to the heat gained by the aluminum.

$$\begin{aligned}m_{\text{H}_2\text{O}}c_{\text{H}_2\text{O}}(T_{\text{H}_2\text{O}} - T_f) &= m_{\text{Al}}c_{\text{Al}}(T_f - T_{\text{Al}}) \rightarrow \\ T_f &= \frac{m_{\text{Al}}c_{\text{Al}}T_{\text{Al}} + m_{\text{H}_2\text{O}}c_{\text{H}_2\text{O}}T_{\text{H}_2\text{O}}}{m_{\text{Al}}c_{\text{Al}} + m_{\text{H}_2\text{O}}c_{\text{H}_2\text{O}}} \\ &= \frac{(0.150 \text{ kg})(900 \text{ J/kg}\cdot\text{C}^\circ)(15^\circ\text{C}) + (0.215 \text{ kg})(4186 \text{ J/kg}\cdot\text{C}^\circ)(100^\circ\text{C})}{(0.150 \text{ kg})(900 \text{ J/kg}\cdot\text{C}^\circ) + (0.215 \text{ kg})(4186 \text{ J/kg}\cdot\text{C}^\circ)} \\ &= 88.91^\circ\text{C} = \boxed{89^\circ\text{C}}\end{aligned}$$

$$\begin{aligned}(b) \Delta S &= \Delta S_{\text{Al}} + \Delta S_{\text{H}_2\text{O}} = \int_{T_{\text{Al}}}^{T_{\text{final}}} \frac{dQ_{\text{Al}}}{T} + \int_{T_{\text{H}_2\text{O}}}^{T_{\text{final}}} \frac{dQ_{\text{H}_2\text{O}}}{T} = m_{\text{Al}}c_{\text{Al}} \int_{T_{\text{Al}}}^{T_{\text{final}}} \frac{dT}{T} + m_{\text{H}_2\text{O}}c_{\text{H}_2\text{O}} \int_{T_{\text{H}_2\text{O}}}^{T_{\text{final}}} \frac{dT}{T} \\ &= m_{\text{Al}}c_{\text{Al}} \ln \frac{T_{\text{final}}}{T_{\text{Al}}} + m_{\text{H}_2\text{O}}c_{\text{H}_2\text{O}} \ln \frac{T_{\text{final}}}{T_{\text{H}_2\text{O}}} \\ &= (0.150 \text{ kg})(900 \text{ J/kg}\cdot\text{K}) \ln \frac{(273.15 + 88.91) \text{ K}}{(273.15 + 15) \text{ K}} \\ &\quad + (0.215 \text{ kg})(4186 \text{ J/kg}\cdot\text{K}) \ln \frac{(273.15 + 88.91) \text{ K}}{(273.15 + 100) \text{ K}} = \boxed{3.7 \text{ J/K}}\end{aligned}$$

48. (a) The gases do not interact since they are ideal, and so each gas expands to twice its volume with no change in temperature. Even though the actual process is not reversible, the entropy change can be calculated for a reversible process that has the same initial and final states. This is discussed in Example 20-7.

$$\Delta S_{N_2} = \Delta S_{Ar} = nR \ln \frac{V_2}{V_1} = nR \ln 2$$

$$\Delta S_{\text{total}} = \Delta S_{N_2} + \Delta S_{Ar} = 2nR \ln 2 = 2(1.00 \text{ mol})(8.314 \text{ J/molgK}) \ln 2 = \boxed{11.5 \text{ J/K}}$$

(b) Because the containers are insulated, no heat is transferred to or from the environment. Thus

$$\Delta S_{\text{surroundings}} = \int \frac{dQ}{T} = \boxed{0}.$$

(c) Let us assume that the argon container is twice the size of the nitrogen container. Then the final nitrogen volume is 3 times the original volume, and the final argon volume is 1.5 times the original volume.

$$\Delta S_{N_2} = nR \ln \left( \frac{V_2}{V_1} \right)_{N_2} = nR \ln 3 ; \quad \Delta S_{Ar} = nR \ln \left( \frac{V_2}{V_1} \right)_{Ar} = nR \ln 1.5$$

$$\begin{aligned} \Delta S_{\text{total}} &= \Delta S_{N_2} + \Delta S_{Ar} = nR \ln 3 + nR \ln 1.5 = nR \ln 4.5 = (1.00 \text{ mol})(8.314 \text{ J/molgK}) \ln 4.5 \\ &= \boxed{12.5 \text{ J/K}} \end{aligned}$$

50. We assume that the process is reversible, so that the entropy change is given by Eq. 20-8. The heat transfer is given by  $dQ = nC_v dT$ .

$$\begin{aligned} S &= \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{nC_v dT}{T} = \int_{T_1}^{T_2} \frac{n(aT + bT^3) dT}{T} = \int_{T_1}^{T_2} n \left( a + bT^2 \right) dT = n \left( aT + \frac{1}{3} bT^3 \right) \Big|_{T_1}^{T_2} \\ &= (0.15 \text{ mol}) \left[ \left( 2.08 \text{ J/molgK}^2 \right) (1.0 \text{ K} - 3.0 \text{ K}) + \frac{1}{3} \left( 2.57 \text{ J/molgK}^4 \right) \left[ (1.0 \text{ K})^3 - (3.0 \text{ K})^3 \right] \right] \\ &= \boxed{-4.0 \text{ mJ/K}} \end{aligned}$$

69. All of the processes are either constant pressure or constant volume, and so the heat input and output can be calculated with specific heats at constant pressure or constant volume. This tells us that heat is input when the temperature increases, and heat is exhausted when the temperature decreases. The lowest temperature will be the temperature at point b. We use the ideal gas law to find the temperatures.

$$PV = nRT \rightarrow T = \frac{PV}{nR} \rightarrow$$

$$T_b = \frac{P_0 V_0}{nR}, T_a = \frac{P_0 (2V_0)}{nR} = 2T_b, T_c = \frac{(3P_0)V_0}{nR} = 3T_b, T_d = \frac{(3P_0)(2V_0)}{nR} = 6T_b$$

(a) process ab:  $W_{ab} = P\Delta V = P_0(-V_0) = -P_0V_0$ ;  $Q_{ab} < 0$

process bc:

$$W_{bc} = P\Delta V = 0; Q_{bc} = nC_V\Delta T = \frac{3}{2}nR(T_c - T_b) = \frac{3}{2}nR(2T_b) = \frac{3}{2}nR\left(2\frac{P_0V_0}{nR}\right) = 3P_0V_0$$

process cd:  $W_{bc} = P\Delta V = 3P_0V_0$ ;

$$Q_{cd} = nC_P\Delta T = \frac{5}{2}nR(T_d - T_c) = \frac{5}{2}nR(3T_b) = \frac{5}{2}nR\left(3\frac{P_0V_0}{nR}\right) = \frac{15}{2}P_0V_0$$

process da:  $W_{da} = P\Delta V = 0$ ;  $Q_{da} < 0$

$$e_{\text{rectangle}} = \frac{W}{Q_H} = \frac{3P_0V_0 - P_0V_0}{3P_0V_0 + \frac{15}{2}P_0V_0} = \frac{2}{\frac{21}{2}} = 0.1905 \approx \boxed{0.19}$$

(b)  $e_{\text{Carnot}} = \frac{T_H - T_L}{T_H} = \frac{6T_b - T_b}{6T_b} = 0.8333$ ;  $\frac{e_{\text{rectangle}}}{e_{\text{Carnot}}} = \frac{0.1905}{0.8333} = \boxed{0.23}$

72. We have a monatomic gas, so  $\gamma = \frac{5}{3}$ . Also the pressure, volume, and temperature for state a are known. We use the ideal gas law, the adiabatic relationship, and the first law of thermodynamics.

(a) Use the ideal gas equation to relate states a and b. Use the adiabatic relationship to relate states a and c.

$$\frac{P_b V_b}{T_b} = \frac{P_a V_a}{T_a} \rightarrow$$

$$P_b = P_a \frac{V_a T_b}{V_b T_a} = (1.00 \text{ atm}) \left( \frac{22.4 \text{ L}}{56.0 \text{ L}} \right) \left( \frac{273 \text{ K}}{273 \text{ K}} \right) = \boxed{0.400 \text{ atm}}$$

$$P_a V_a^\gamma = P_c V_c^\gamma \rightarrow$$

$$P_c = P_a \left( \frac{V_a}{V_c} \right)^\gamma = (1.00 \text{ atm}) \left( \frac{22.4 \text{ L}}{56.0 \text{ L}} \right)^{5/3} = 0.2172 \text{ atm} \approx \boxed{0.217 \text{ atm}}$$

(b) Use the ideal gas equation to calculate the temperature at c.

$$\frac{P_b V_b}{T_b} = \frac{P_c V_c}{T_c} \rightarrow T_c = T_b \frac{P_c V_c}{P_b V_b} = (273 \text{ K}) \left( \frac{0.2172 \text{ atm}}{0.400 \text{ atm}} \right) (1) = \boxed{148 \text{ K}}$$

(c) Process ab:  $\Delta E_{\text{int}} = nC_v \Delta T = \boxed{0}$  ;

$$Q_{\text{ab}} = W_{\text{ab}} = nRT \ln \frac{V_b}{V_a} = (1.00 \text{ mol})(8.314 \text{ J/molgK})(273 \text{ K}) \ln 2.5$$

$$= 2079.7 \text{ J} \approx \boxed{2080 \text{ J}}$$

$$\Delta S_{\text{ab}} = \frac{Q_{\text{ab}}}{T_{\text{ab}}} = \frac{2079.7 \text{ J}}{273 \text{ K}} = \boxed{7.62 \text{ J/K}}$$

Process bc:  $W_{\text{bc}} = \boxed{0}$  ;

$$\Delta E_{\text{int}} = Q_{\text{bc}} = nC_v \Delta T = (1.00 \text{ mol}) \frac{3}{2} (8.314 \text{ J/molgK})(148 \text{ K} - 273 \text{ K})$$

$$= -1559 \text{ J} \approx \boxed{-1560 \text{ J}}$$

$$\Delta S_{\text{bc}} = \int_b^c \frac{dQ}{T} = \int_{T_b}^{T_c} \frac{nC_v dT}{T} = nC_v \ln \frac{T_c}{T_b} = (1.00 \text{ mol}) \frac{3}{2} (8.314 \text{ J/molgK}) \ln \frac{148 \text{ K}}{273 \text{ K}}$$

$$= \boxed{-7.64 \text{ J/K}}$$

Process ca:  $Q_{\text{ca}} = \boxed{0}$  ;  $\Delta S_{\text{bc}} = \boxed{0}$  (adiabatic) ;

$$\Delta E_{\text{int}} = -W = -\Delta E_{\text{int}} - \Delta E_{\text{int}} = -0 - (-1560 \text{ J}) \rightarrow$$

$$\Delta E_{\text{int}} = \boxed{1560 \text{ J}} ; W_{\text{ca}} = \boxed{-1560 \text{ J}}$$

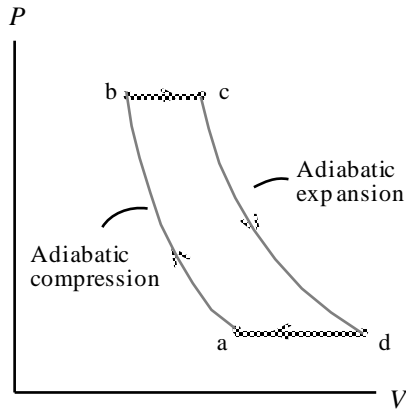
(d)  $e = \frac{W}{Q_{\text{input}}} = \frac{2080 \text{ J} - 1560 \text{ J}}{2080 \text{ J}} = \boxed{0.25}$

**73.** Take the energy transfer to use as the initial kinetic energy of the cars, because this energy becomes “unusable” after the collision – it is transferred to the environment.

$$\Delta S = \frac{Q}{T} = \frac{2\left(\frac{1}{2}mv_i^2\right)}{T} = \frac{(1100 \text{ kg}) \left[ (75 \text{ km/h}) \left( \frac{1 \text{ m/s}}{3.6 \text{ km/h}} \right) \right]^2}{(15 + 273) \text{ K}} = \boxed{1700 \text{ J/K}}$$



78. Since two of the processes are adiabatic, no heat transfer occurs in those processes. Thus the heat transfer must occur along the isobaric processes.



$$Q_H = Q_{bc} = nC_p(T_c - T_b) ; Q_L = Q_{da} = nC_p(T_d - T_a)$$

$$e = 1 - \frac{Q_L}{Q_H} = 1 - \frac{nC_p(T_d - T_a)}{nC_p(T_c - T_b)} = 1 - \frac{(T_d - T_a)}{(T_c - T_b)}$$

Use the ideal gas relationship, which says that  $PV = nRT$ .

$$e = 1 - \frac{(T_d - T_a)}{(T_c - T_b)} = 1 - \frac{\left(\frac{PV_d}{nR} - \frac{PV_a}{nR}\right)}{\left(\frac{PV_c}{nR} - \frac{PV_b}{nR}\right)} = 1 - \frac{(PV_d - PV_a)}{(PV_c - PV_b)}$$

$$= 1 - \frac{P_a(V_d - V_a)}{P_b(V_c - V_b)}$$

Because process ab is adiabatic, we have  $P_a V_a^\gamma = P_b V_b^\gamma \rightarrow V_a = V_b \left(\frac{P_b}{P_a}\right)^{1/\gamma}$ . Because process cd is

adiabatic, we have  $P_b V_c^\gamma = P_a V_d^\gamma \rightarrow V_d = V_c \left(\frac{P_b}{P_a}\right)^{1/\gamma}$ . Substitute these into the efficiency expression.

$$\begin{aligned}
e &= 1 - \frac{P_a(V_d - V_a)}{P_b(V_c - V_b)} = 1 - \frac{P_a \left( V_c \left( \frac{P_b}{P_a} \right)^{1/\gamma} - V_b \left( \frac{P_b}{P_a} \right)^{1/\gamma} \right)}{P_b(V_c - V_b)} = 1 - \frac{P_a \left( \frac{P_b}{P_a} \right)^{1/\gamma} (V_c - V_b)}{P_b(V_c - V_b)} \\
&= 1 - \left( \frac{P_b}{P_a} \right)^{\frac{1}{\gamma} - 1} = \boxed{1 - \left( \frac{P_b}{P_a} \right)^{\frac{1-\gamma}{\gamma}}}
\end{aligned}$$