# CHAPTER 20: Second Law of Thermodynamics

## Responses to Questions

1. Yes, mechanical energy can be transformed completely into heat or internal energy, as when an object moving over a surface is brought to rest by friction. All of the original mechanical energy is converted into heat. No, the reverse cannot happen (second law of thermodynamics) except in very special cases (reversible adiabatic expansion of an ideal gas). For example, in an explosion, a large amount of internal energy is converted into mechanical energy, but some internal energy is lost to heat or remains as internal energy of the explosion fragments.

2. Yes, you can warm a kitchen in winter by leaving the oven door open. The oven converts electrical energy to heat and leaving the door open will allow this heat to enter the kitchen. However, you cannot cool a kitchen in the summer by leaving the refrigerator door open. The refrigerator is a heat engine which (with an input of work) takes heat from the low-temperature reservoir (inside the refrigerator) and exhausts heat to the high-temperature reservoir (the room). As shown by the second law of thermodynamics, there is no "perfect refrigerator," so more heat will be exhausted into the room than removed from the inside of the refrigerator. Thus, leaving the refrigerator door open will actually warm the kitchen.

5. A 10ºC decrease in the low-temperature reservoir will give a greater improvement in the efficiency of a Carnot engine. By definition, $T_L$ is less than $T_H$, so a 10ºC change will be a larger percentage change in $T_L$ than in $T_H$, yielding a greater improvement in efficiency.

11. The isothermal process will result in a greater change in entropy. The entropy change for a reversible process is the integral of $dQ/T$. $Q = 0$ for an adiabatic process, so the change in entropy is also 0.

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

**1.** The efficiency of a heat engine is given by Eq. 20-1a. We also invoke energy conservation.

$$e = \frac{W}{Q_H} = \frac{W}{W + Q_L} = \frac{2600\ \text{J}}{2600\ \text{J} + 7800\ \text{J}} = 0.25 = \boxed{25\%}$$

6. (*a*) For the net work done by the engine to be positive, the path must be carried out $\boxed{\text{clockwise}}$. Then the work done by process bc is positive, the work done by process ca is negative, and the work done by process ab is 0. From the shape of the graph, we see that $|W_{bc}| > |W_{ca}|$.

    (*b*) The efficiency of the engine is given by Eq. 20-1a. So we need to find the work done and the heat input. At first glance we might assume that we need to find the pressure, volume, and temperature at the three points on the graph. But as shown here, only the temperatures and the first law of thermodynamics are needed, along with ratios that are obtained from the ideal gas law.

      ab:     $W_{ab} = P\Delta V = 0$ ; $Q_{ab} = \Delta E_{\text{int}\atop ab} = nC_V\left(T_b - T_a\right) = \tfrac{3}{2}nR\left(T_b - T_a\right) > 0$

      bc:     $\Delta E_{\text{int}\atop bc} = nC_V\left(T_c - T_b\right) = 0$ ; $Q_{bc} = W_{bc} = nRT_b \ln\dfrac{V_c}{V_b} = nRT_b \ln\dfrac{V_c}{V_a} = nRT_b \ln\dfrac{T_c}{T_a} > 0$

      ca:     $W_{ca} = P_a\left(V_a - V_c\right) = \dfrac{nRT_a}{V_a}\left(V_a - V_c\right) = nRT_a\left(1 - \dfrac{V_c}{V_a}\right) = nRT_a\left(1 - \dfrac{T_c}{T_a}\right) = nR\left(T_a - T_c\right)$

             $Q_{ca} = nC_P\left(T_a - T_c\right) = \tfrac{5}{2}nR\left(T_a - T_c\right) < 0$

$$e = \frac{W}{Q_{\text{input}}} = \frac{W_{bc} + W_{ca}}{Q_{ab} + Q_{bc}} = \frac{nRT_b \ln\dfrac{T_c}{T_a} + nR\left(T_a - T_c\right)}{\tfrac{3}{2}nR\left(T_b - T_a\right) + nRT_b \ln\dfrac{T_c}{T_a}} = \frac{T_b \ln\dfrac{T_c}{T_a} + \left(T_a - T_c\right)}{\tfrac{3}{2}\left(T_b - T_a\right) + T_b \ln\dfrac{T_c}{T_a}} = \frac{T_b \ln\dfrac{T_b}{T_a} + \left(T_a - T_b\right)}{\tfrac{3}{2}\left(T_b - T_a\right) + T_b \ln\dfrac{T_b}{T_a}}$$

$$= \frac{\left(423\,\text{K}\right)\ln\dfrac{423\,\text{K}}{273\,\text{K}} + \left(273\,\text{K} - 423\,\text{K}\right)}{\tfrac{3}{2}\left(423\,\text{K} - 273\,\text{K}\right) + \left(423\,\text{K}\right)\ln\dfrac{423\,\text{K}}{273\,\text{K}}} = 0.0859 = \boxed{8.59\%}$$

Of course, individual values could have been found for the work and heat on each process, and used in the efficiency equation instead of referring everything to the temperatures.

8.      The maximum efficiency is the Carnot efficiency, given in Eq. 20-3.

$$e = 1 - \frac{T_L}{T_H} = 1 - \frac{(365 + 273)\,\text{K}}{(550 + 273)\,\text{K}} = \boxed{0.225 \text{ or } 22.5\%}$$

We assume that both temperatures are measured to the same precision – the nearest degree.

12.  This is a perfect Carnot engine, and so its efficiency is given by Eq. 20-1a and Eq. 20-3.  Use these two expressions to solve for the rate of heat output.

$$e = 1 - \frac{T_L}{T_H} = 1 - \frac{(45 + 273)\,\text{K}}{(210 + 273)\,\text{K}} = 0.3416 \qquad e = \frac{W}{Q_H} = \frac{W}{W + Q_L} \quad \rightarrow \quad Q_L = W(1/e - 1)$$

$$Q_L / t = W/t(1/e - 1) = (950\ \text{W})(1/0.3416 - 1) = 1831\,\text{W} \approx \boxed{1800\,\text{W}}$$

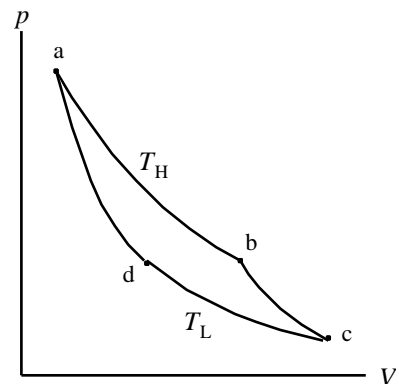18.  The heat input must come during the isothermal expansion. From section 20-3, page 534, we have

$$Q_H = nRT_H \ln \frac{V_b}{V_a} = nRT_H \ln 2. \text{  Since this is a Carnot cycle, we may}$$

use Eq. 20-3 combined with Eq. 20-1.



$$e = 1 - \frac{T_L}{T_H} = \frac{W}{Q_H} \quad \rightarrow$$

$$W = Q_H \left( \frac{T_H - T_L}{T_H} \right) = (nRT_H \ln 2)\left( \frac{T_H - T_L}{T_H} \right) = nR(T_H - T_L)\ln 2$$

The adiabatic relationship between points b and c and the ideal

gas law are used to express the temperature ratio in terms of the volume ratio.

$$P_b V_b^\gamma = P_c V_c^\gamma \quad \rightarrow \quad \frac{nRT_H}{V_b} V_b^\gamma = \frac{nRT_L}{V_c} V_c^\gamma \quad \rightarrow \quad T_H = T_L \left(\frac{V_c}{V_b}\right)^{\gamma-1} = T_L \left(5.7^{2/3}\right)$$

$$W = nR\left(T_H - T_L\right)\ln 2 = nRT_L\left(5.7^{2/3} - 1\right)\ln 2 \quad \rightarrow$$

$$T_L = \frac{W}{nR\ln 2\left[5.7^{2/3} - 1\right]} = \frac{920\,\text{J}}{(1.00\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})\ln 2\left[5.7^{2/3} - 1\right]} = 72.87\,\text{K} \approx \boxed{73\,\text{K}}$$

$$T_H = (72.87\,\text{K})\left(5.7^{2/3}\right) = 232.52\,\text{K} \approx \boxed{233\,\text{K}}$$

20. (*a*)     We use the ideal gas law and the adiabatic process

   relationship to find the values of the pressure and volume at each of the four points.

$$P_a = \boxed{8.8\,\text{atm}} \; ; T_a = 623\,\text{K} \; ;$$

$$V_a = \frac{nRT_a}{P_a} = \frac{(1.00\,\text{mol})(0.0821\,\text{L}\cdot\text{atm/mol}\cdot\text{K})(623\,\text{K})}{8.8\,\text{atm}}$$

$$= 5.81\,\text{L} \approx \boxed{5.8\,\text{L}}$$

$$T_b = 623\,\text{K} \; ; V_b = 2V_a = 2(5.81\,\text{L}) = 11.62\,\text{L} \approx \boxed{11.6\,\text{L}}$$

$$P_b = P_a \frac{V_a}{V_b} = \tfrac{1}{2} P_a = \boxed{4.4\,\text{atm}}$$

$$T_c = 483\,\text{K} \; ; P_b V_b^\gamma = P_c V_c^\gamma \quad \rightarrow \quad \frac{nRT_b}{V_b} V_b^\gamma = \frac{nRT_c}{V_c} V_c^\gamma \quad \rightarrow$$

$$V_c = V_b \left(\frac{T_b}{T_c}\right)^{\frac{1}{\gamma-1}} = (11.62\,\text{L})\left(\frac{623\,\text{K}}{483\,\text{K}}\right)^{3/2} = 17.02\,\text{L} \approx \boxed{17.0\,\text{L}}$$

$$P_c = \frac{nRT_c}{V_c} = \frac{(1.00\,\text{mol})(0.0821\,\text{L}\cdot\text{atm/mol}\cdot\text{K})(483\,\text{K})}{17.02\,\text{L}} = 2.33\,\text{atm} \approx \boxed{2.3\,\text{atm}}$$

$$T_d = 483\,\text{K} \; ; V_d = V_a \left(\frac{T_a}{T_d}\right)^{\frac{1}{\gamma-1}} = (5.81\,\text{L})\left(\frac{623\,\text{K}}{483\,\text{K}}\right)^{3/2} = 8.51\,\text{L} \approx \boxed{8.5\,\text{L}}$$

$$P_d = \frac{nRT_d}{V_d} = \frac{(1.00\,\text{mol})(0.0821\,\text{L}\cdot\text{atm/mol}\cdot\text{K})(483\,\text{K})}{8.51\,\text{L}} = 4.66\,\text{atm} \approx \boxed{4.7\,\text{atm}}$$

To summarize:
$$P_a = \boxed{8.8\,\text{atm}} \; ; V_a = \boxed{5.8\,\text{L}} \; ; P_b = \boxed{4.4\,\text{atm}} \; ; V_b = \boxed{11.6\,\text{L}}$$
$$P_c = \boxed{2.3\,\text{atm}} \; ; V_c = \boxed{17.0\,\text{L}} \; ; P_d = \boxed{4.7\,\text{atm}} \; ; V_d = \boxed{8.5\,\text{L}}$$

(*b*) Isotherm ab:     $\Delta E_{\text{int}_{ab}} = \boxed{0}$ ;

$$Q_{ab} = W_{ab} = nRT_a \ln\frac{V_b}{V_a} = (1.00\,\text{mol})(8.314\,\text{J/molgK})(623\,\text{K})\ln 2 = 3590\,\text{J} \approx \boxed{3600\,\text{J}}$$

Adiabat bc:     $Q_{bc} = \boxed{0}$ ;

$$\Delta E_{\text{int}_{bc}} = nC_V\left(T_c - T_b\right) = \tfrac{3}{2}nR\left(T_c - T_b\right) = \tfrac{3}{2}(1.00\,\text{mol})(8.314\,\text{J/molgK})(-140\,\text{K})$$

$$= -1746\,\text{J} \approx \boxed{-1700\,\text{J}} \;\; ; \;\; W_{bc} = Q_{bc} - \Delta E_{\text{int}_{bc}} = 1746\,\text{J} \approx \boxed{1700\,\text{J}}$$

Isotherm cd:     $\Delta E_{\text{int}_{cd}} = \boxed{0}$ ;

$$Q_{cd} = W_{cd} = nRT_c \ln\frac{V_d}{V_c} = (1.00\,\text{mol})(8.314\,\text{J/molgK})(483\,\text{K})\ln\tfrac{1}{2} = -2783\,\text{J} \approx \boxed{-2800\,\text{J}}$$

Adiabat da:     $Q_{da} = \boxed{0}$ ;

$$\Delta E_{\text{int}_{bc}} = nC_V\left(T_c - T_b\right) = \tfrac{3}{2}nR\left(T_c - T_b\right) = \tfrac{3}{2}(1.00\,\text{mol})(8.314\,\text{J/molgK})(140\,\text{K})$$

$$= 1746\,\text{J} \approx \boxed{1700\,\text{J}} \;\; ; \;\; W_{bc} = Q_{bc} - \Delta E_{\text{int}_{bc}} = 1746\,\text{J} \approx \boxed{-1700\,\text{J}}$$

To summarize:   ab : $\Delta E_{\text{int}} = 0$ ;        $Q = 3600\,\text{J}$ ;   $W = 3600\,\text{J}$

bc:  $\Delta E_{\text{int}} = -1700\,\text{J}$ ; $Q = 0$ ;        $W = 1700\,\text{J}$

cd:  $\Delta E_{\text{int}} = 0$ ;        $Q = -2800\,\text{J}$ ; $W = -2800\,\text{J}$

da:  $\Delta E_{\text{int}} = 1700\,\text{J}$ ; $Q = 0$ ;        $W = -1700\,\text{J}$

(*c*) Using Eq. 20-1:   $e = \dfrac{W}{Q_{\text{input}}} = \dfrac{3590\,\text{J} + 1746\,\text{J} - 2783\,\text{J} - 1746\,\text{J}}{3590\,\text{J}} = \dfrac{807\,\text{J}}{3590\,\text{J}} = 0.2248 \approx \boxed{0.22}$

Using Eq. 20-3:   $e = 1 - \dfrac{T_L}{T_H} = 1 - \dfrac{(273 + 210)\,\text{K}}{(273 + 350)\,\text{K}} = 0.2247 \approx \boxed{0.22}$

The slight disagreement is due to rounding of various calculations.

26. The coefficient of performance for an ideal refrigerator is given by Eq. 20-4c, with temperatures in Kelvins. Use that expression to find the temperature inside the refrigerator.

$$\text{COP} = \frac{T_L}{T_H - T_L} \quad \rightarrow \quad T_L = T_H \frac{\text{COP}}{1 + \text{COP}} = \left[(32 + 273)\,\text{K}\right]\frac{5.0}{6.0} = 254\,\text{K} = \boxed{-19°\text{C}}$$

27. The efficiency of a perfect Carnot engine is given by Eq. 20-1a and Eq. 20-3. Equate these two expressions to solve for the work required.

$$e = 1 - \frac{T_L}{T_H} = \; ; \; e = \frac{W}{Q_H} \quad \rightarrow \quad 1 - \frac{T_L}{T_H} = \frac{W}{Q_H} \quad \rightarrow \quad W = Q_H \left(1 - \frac{T_L}{T_H}\right)$$

(a) $W = Q_H \left(1 - \dfrac{T_L}{T_H}\right) = (3100\,\text{J})\left(1 - \dfrac{0 + 273}{22 + 273}\right) = 231.2\,\text{J} \approx \boxed{230\,\text{J}}$

(b) $W = Q_H \left(1 - \dfrac{T_L}{T_H}\right) = (3100\,\text{J})\left(1 - \dfrac{-15 + 273}{22 + 273}\right) = 388.8\,\text{J} \approx \boxed{390\,\text{J}}$

31. The coefficient of performance is the heat removed from the low-temperature area divided by the work done to remove the heat. In this case, the heat removed is the latent heat released by the freezing ice, and the work done is 1.2 kW times the elapsed time. The mass of water frozen is its density times its volume.

$$\text{COP} = \frac{Q_L}{W} = \frac{mL_f}{W} = \frac{\rho V L_f}{Pt} \quad \rightarrow$$

$$V = \frac{(\text{COP})Pt}{\rho L_f} = \frac{(7.0)(1200\,\text{W})(3600\,\text{s})}{(1.0 \times 10^3\,\text{kg/m}^3)(3.33 \times 10^5\,\text{J/kg})} = 0.0908\,\text{m}^3 \approx \boxed{91\,\text{L}}$$

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.

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

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.

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

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 $\Delta S = Q/T_{avg}$. 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°C, $\Delta S_2$. That process has an "average" temperature of –5°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.

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

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

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

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

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

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

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.

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

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

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

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

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

$$\Delta S = \frac{Q}{T} = \frac{PV}{T}\ln\frac{P_1}{P_2} = \frac{(7.5)\left(1.013\times10^5\,\text{Pa}\right)\left(2.50\times10^{-3}\,\text{m}^3\right)}{410\,\text{K}}\ln\frac{7.5\,\text{atm}}{1.0\,\text{atm}} = \boxed{9.3\,\text{J/K}}$$

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.

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

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

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.

Isothermal: $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2} \rightarrow P_2 = P_1\dfrac{V_1 T_2}{V_2 T_1} = P_1\left(\dfrac{V}{\frac{1}{2}V}\right)(1) = 2P_1$

Adiabatic: $P_1V_1^{\gamma} = P_2V_2^{\gamma} \rightarrow P_2 = P_1\left(\dfrac{V_1}{V_2}\right)^{\gamma} = P_1\left(\dfrac{V}{\frac{1}{2}V}\right)^{\gamma} = 2^{\gamma}P_1$
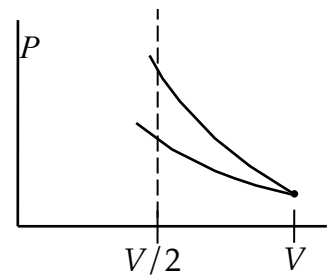
Since $\gamma > 1$, we see that $\left(P_2\right)_{\text{adiabatic}} > \left(P_2\right)_{\text{isothermic}}$. The ratio is $\dfrac{\left(P_2\right)_{\text{adiabatic}}}{\left(P_2\right)_{\text{isothermic}}} = \dfrac{2^\gamma P_1}{2P_1} = 2^{\gamma-1}$.

(b) For the adiabatic process: No heat is transferred to or from the gas, so

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

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

$$\Delta S_{\text{isothermal}} = \int \frac{dQ_{\text{isothermal}}}{T} = \frac{1}{T}\int dQ_{\text{isothermal}} = \frac{\Delta Q_{\text{isothermal}}}{T} = \frac{nRT\ln\left(V_2/V_1\right)}{T}$$

$$= nR\ln\left(V_2/V_1\right) = nR\ln\left(\tfrac{1}{2}\right) = \boxed{-nR\ln 2}$$

(c) Since each process is reversible, the energy change of the universe is 0, and so $\Delta S_{\text{surroundings}} = -\Delta S_{\text{system}}$. For the adiabatic process, $\Delta S_{\text{surroundings}} = \boxed{0}$. For the isothermal process, $\Delta S_{\text{surroundings}} = \boxed{nR\ln 2}$.

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.

$$m_{\text{H}_2\text{O}}c_{\text{H}_2\text{O}}\left(T_{\text{H}_2\text{O}} - T_f\right) = m_{\text{Al}}c_{\text{Al}}\left(T_f - T_{\text{Al}}\right) \;\rightarrow$$

$$T_f = \frac{m_{\text{Al}}c_{\text{Al}}T_{\text{Al}} + m_{\text{H}_2\text{O}}c_{\text{H}_2\text{O}}T_{\text{H}_2\text{O}}}{m_{\text{Al}}c_{\text{Al}} + m_{\text{H}_2\text{O}}c_{\text{H}_2\text{O}}}$$

$$= \frac{(0.150\,\text{kg})(900\,\text{J/kg}\,\text{C}°)(15°\text{C}) + (0.215\,\text{kg})(4186\,\text{J/kg}\,\text{C}°)(100°\text{C})}{(0.150\,\text{kg})(900\,\text{J/kg}\,\text{C}°) + (0.215\,\text{kg})(4186\,\text{J/kg}\,\text{C}°)}$$

$$= 88.91°\text{C} = \boxed{89°\text{C}}$$

(b) $\Delta S = \Delta S_{\text{Al}} + \Delta S_{\text{H}_2\text{O}} = \displaystyle\int_{T_{\text{Al}}}^{T_{\text{final}}} \frac{dQ_{\text{Al}}}{T} + \int_{T_{\text{H}_2\text{O}}}^{T_{\text{final}}} \frac{dQ_{\text{H}_2\text{O}}}{T} = m_{\text{Al}}c_{\text{Al}}\int_{T_{\text{Al}}}^{T_{\text{final}}} \frac{dT}{T} + m_{\text{H}_2\text{O}}c_{\text{H}_2\text{O}}\int_{T_{\text{H}_2\text{O}}}^{T_{\text{final}}} \frac{dT}{T}$

$$= m_{\text{Al}}c_{\text{Al}}\ln\frac{T_{\text{final}}}{T_{\text{Al}}} + m_{\text{H}_2\text{O}}c_{\text{H}_2\text{O}}\ln\frac{T_{\text{final}}}{T_{\text{H}_2\text{O}}}$$

$$= (0.150\,\text{kg})(900\,\text{J/kg}\,\text{K})\ln\frac{(273.15 + 88.91)\,\text{K}}{(273.15 + 15)\,\text{K}}$$

$$+ (0.215\,\text{kg})(4186\,\text{J/kg}\,\text{K})\ln\frac{(273.15 + 88.91)\,\text{K}}{(273.15 + 100)\,\text{K}} = \boxed{3.7\,\text{J/K}}$$

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.
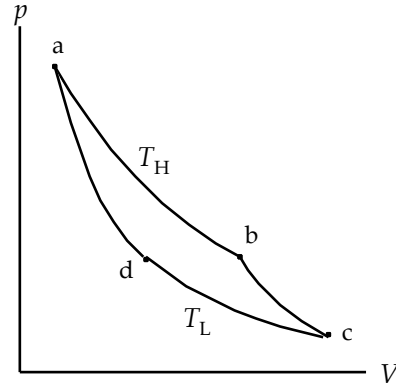


$$\Delta S_{N_2} = \Delta S_{Ar} = nR\ln\frac{V_2}{V_1} = nR\ln 2$$

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

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

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

(*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.

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

$$\Delta S_{total} = \Delta S_{N_2} + \Delta S_{Ar} = nR\ln 3 + nR\ln 1.5 = nR\ln 4.5 = (1.00\,\text{mol})(8.314\,\text{J/molgK})\ln 4.5$$

$$= \boxed{12.5\,\text{J/K}}$$

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 $dQ = nC_V dT$.

$$S = \int_{T_1}^{T_2}\frac{dQ}{T} = \int_{T_1}^{T_2}\frac{nC_V dT}{T} = \int_{T_1}^{T_2}\frac{n(aT + bT^3)dT}{T} = \int_{T_1}^{T_2}n(a + bT^2)dT = n(aT + \tfrac{1}{3}bT^3)\Big|_{T_1}^{T_2}$$

$$= (0.15\,\text{mol})\Big[(2.08\,\text{mJ/molgK}^2)(1.0\,\text{K} - 3.0\,\text{K}) + \tfrac{1}{3}(2.57\,\text{mJ/molgK}^4)\big[(1.0\,\text{K})^3 - (3.0\,\text{K})^3\big]\Big]$$

$$= \boxed{-4.0\,\text{mJ/K}}$$

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.

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

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

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

process bc:

$$W_{bc} = P\Delta V = 0 \; ; \; Q_{bc} = nC_V \Delta T = \tfrac{3}{2}nR(T_c - T_b) = \tfrac{3}{2}nR(2T_b) = \tfrac{3}{2}nR\left(2\frac{P_0 V_0}{nR}\right) = 3P_0 V_0$$

process cd:  $W_{bc} = P\Delta V = 3P_0 V_0$ ;

$$Q_{cd} = nC_P \Delta T = \tfrac{5}{2}nR(T_d - T_c) = \tfrac{5}{2}nR(3T_b) = \tfrac{5}{2}nR\left(3\frac{P_0 V_0}{nR}\right) = \tfrac{15}{2}P_0 V_0$$

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

$$e_{\text{rectangle}} = \frac{W}{Q_H} = \frac{3P_0 V_0 - P_0 V_0}{3P_0 V_0 + \tfrac{15}{2}P_0 V_0} = \frac{2}{\tfrac{21}{2}} = 0.1905 \approx \boxed{0.19}$$

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

72. We have a monatomic gas, so $\gamma = \tfrac{5}{3}$. 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.



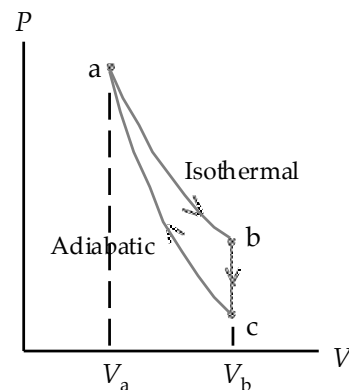$$\frac{P_b V_b}{T_b} = \frac{P_a V_a}{T_a} \quad \rightarrow$$

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

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

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

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

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

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

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

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

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

$$\Delta E_{\text{int}_{bc}} = Q_{bc} = nC_V\Delta T = (1.00\,\text{mol})\tfrac{3}{2}(8.314\,\text{J/molg K})(148\,\text{K} - 273\,\text{K})$$

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

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

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

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

$$\Delta E_{\text{int}_{ca}} = -W = -\Delta E_{\text{int}_{ab}} - \Delta E_{\text{int}_{bc}} = -0 - (-1560\,\text{J}) \quad \rightarrow$$

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

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

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.

$$\Delta S = \frac{Q}{T} = \frac{2\left(\frac{1}{2}mv_i^2\right)}{T} = \frac{(1100\,\text{kg})\left[(75\,\text{km/h})\left(\dfrac{1\,\text{m/s}}{3.6\,\text{km/h}}\right)\right]^2}{(15+273)\,\text{K}} = \boxed{1700\,\text{J/K}}$$
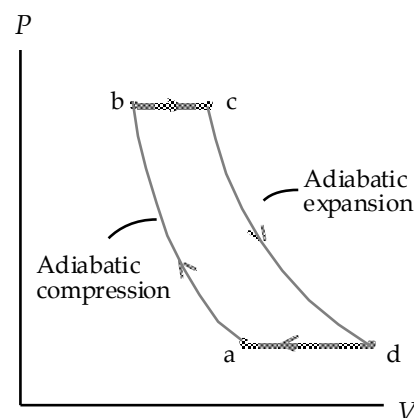
78. Since two of the processes are adiabatic, no heat transfer occurs in those processes. Thus the heat transfer must occur along the isobaric processes.

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

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

Use the ideal gas relationship, which says that

$PV = nRT$.

$$e = 1 - \frac{\left(T_d - T_a\right)}{\left(T_c - T_b\right)} = 1 - \frac{\left(\dfrac{P_d V_d}{nR} - \dfrac{P_a V_a}{nR}\right)}{\left(\dfrac{P_c V_c}{nR} - \dfrac{P_b V_b}{nR}\right)} = 1 - \frac{\left(P_d V_d - P_a V_a\right)}{\left(P_c V_c - P_b V_b\right)}$$

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

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

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

efficiency expression.

$$e = 1 - \frac{P_a\left(V_d - V_a\right)}{P_b\left(V_c - V_b\right)} = 1 - \frac{P_a\left(V_c\left(\dfrac{P_b}{P_a}\right)^{1/\gamma} - V_b\left(\dfrac{P_b}{P_a}\right)^{1/\gamma}\right)}{P_b\left(V_c - V_b\right)} = 1 - \frac{P_a\left(\dfrac{P_b}{P_a}\right)^{1/\gamma}\left(V_c - V_b\right)}{P_b\left(V_c - V_b\right)}$$

$$= 1 - \left(\dfrac{P_b}{P_a}\right)^{\frac{1}{\gamma}-1} = \boxed{1 - \left(\dfrac{P_b}{P_a}\right)^{\frac{1-\gamma}{\gamma}}}$$