Chapter 19
The Second Law of Thermodynamics

Conceptual Problems

1 •

Determine the Concept Friction reduces the efficiency of the engine.

*2 •

Determine the Concept As described by the second law of thermodynamics, more heat must be transmitted to the outside world than is removed by a refrigerator or air conditioner. The heating coils on a refrigerator are inside the room–the refrigerator actually heats the room it is in. The heating coils on an air conditioner are outside, so the waste heat is vented to the outside.

3 •

Determine the Concept Increasing the temperature of the steam increases the Carnot efficiency, and generally increases the efficiency of any heat engine.

4 ••

Determine the Concept To condense, water must lose heat. Because its entropy change is given by $dS = dQ_{rev}/T$ and dQ_{rev} is negative, the entropy of the water decreases.
(c) is correct.

*5 •

Determine the Concept

(a) Because the temperature changes during an adiabatic process, the internal energy of the system changes continuously during the process.

(b) Both the pressure and volume change during an adiabatic process and hence work is done by the system.

(c) $\Delta Q = 0$ during an adiabatic process. Therefore $\Delta S = 0$. (c) is correct.

(d) Because the pressure and volume change during an adiabatic process, so does the temperature.

6 ••

(a) False. The complete conversion of mechanical energy into heat is not prohibited by either the 1st or 2nd laws of thermodynamics and is common place in energy transformations.

(b) True. This is the heat-engine statement of the 2nd law of thermodynamics.

(*c*) False. The efficiency of a heat engine is a function of the thermodynamic processes of its cycle.

(*d*) False. With the input of sufficient energy, a heat pump can transfer a given quantity of heat from a cold reservoir to a hot reservoir.

(*e*) False. The only restriction that the refrigerator statement of the 2nd law places on the COP is that it can not be infinite.

(*f*) True. The Carnot engine, as a consequence of its thermodynamic processes, is reversible.

(*g*) False. The entropy of one system can decrease at the expense of one or more other systems.

(*h*) True. This is one statement of the 2nd law of thermodynamics.

7   ••

Determine the Concept The two paths are shown on the *PV* diagram to the right. We can use the concept of a state function to choose from among the alternatives given as possible answers to the problem.
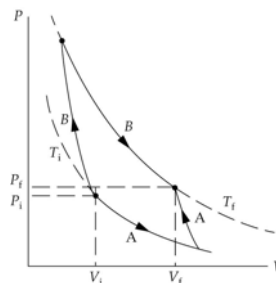

(*a*) Because E_{int} is a state function and the initial and final states are the same for the two paths and $\Delta E_{int, A} = \Delta E_{int, B}$.

(*b*) and (*c*) S, like E_{int}, is a state function and its change when the system moves from one state to another depends only on the system's initial and final states. It is not dependent on the process by which the change occurs and $\Delta S_A = \Delta S_B$.

(*d*) $\boxed{(d)\text{ is correct.}}$

*8 ••

Determine the Concept The processes
A→B and C→D are adiabatic; the
processes B→C and D→A are isothermal.
The cycle is therefore the Carnot cycle
shown in the adjacent *PV* diagram.
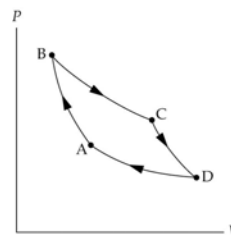
9 ••

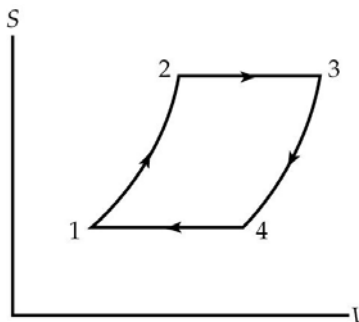**Determine the Concept** Note that A→B is an adiabatic expansion. B→C is a constant
volume process in which the entropy decreases; therefore heat is released. C→D is an
adiabatic compression. D→A is a constant volume process that returns the gas to its
original state. The cycle is that of the Otto engine (see Figure 19-3).

10 ••

Determine the Concept Refer to Figure
19-3. Here *a*→*b* is an adiabatic
compression, so *S* is constant and *T*
increases. Between *b* and *c*, heat is added
to the system and both *S* and *T* increase.
c→*d* is again isentropic, i.e., without
change in entropy. *d*→*a* releases heat and
both *S* and *T* decrease. The cycle on an *ST*
diagram is sketched in the adjacent figure.
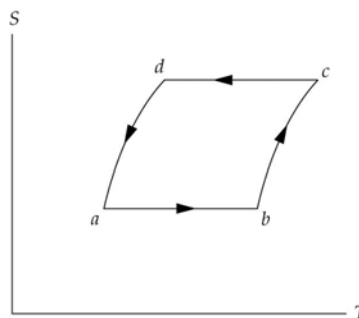
11 ••

Determine the Concept Referring to Figure
19-8, process 1→2 is an isothermal
expansion. In this process heat is added to
the system and the entropy and volume
increase. Process 2→3 is adiabatic, so *S* is
constant as *V* increases. Process 3→4 is an
isothermal compression in which *S*
decreases and *V* also decreases. Finally,
process 4→1 is adiabatic, i.e., isentropic,
and *S* is constant while *V* decreases. The
cycle is shown in the adjacent *SV* diagram.

12   ••

Picture the Problem The *SV* diagram of the Otto cycle is shown in Figure 19-13. (see Problem 9)

13   ••

Determine the Concept Process A→B is at constant entropy, i.e., an adiabatic process in which the pressure increases. Process B→C is one in which *P* is constant and *S* decreases; heat is exhausted from the system and the volume decreases. Process C→D is an adiabatic compression. Process D→A returns the system to its original state at constant pressure. The cycle is shown in the adjacent *PV* diagram.
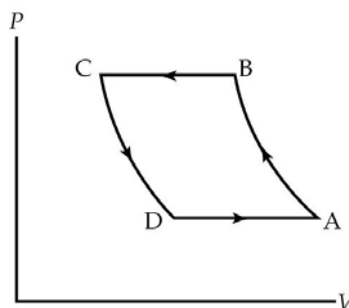
*14   •

Picture the Problem Let ΔT be the change in temperature and $\varepsilon = (T_h - T_c)/T_h$ be the initial efficiency. We can express the efficiencies of the Carnot engine resulting from the given changes in temperature and examine their ratio to decide which has the greater effect on increasing the efficiency.

If T_h is increased by ΔT, ε', the new efficiency is:

$$\varepsilon' = \frac{T_h + \Delta T - T_c}{T_h + \Delta T}$$

If T_c is reduced by ΔT, the efficiency is:

$$\varepsilon'' = \frac{T_h - T_c + \Delta T}{T_h}$$

Divide the second of these equations by the first to obtain:

$$\frac{\varepsilon''}{\varepsilon'} = \frac{\dfrac{T_h - T_c + \Delta T}{T_h}}{\dfrac{T_h + \Delta T - T_c}{T_h + \Delta T}} = \frac{T_h + \Delta T}{T_h} > 1$$

Therefore, a reduction in the temperature of the cold reservoir by ΔT increases the efficiency more than an equal increase in the temperature of the hot reservoir.

Estimation and Approximation

15 ••

Picture the Problem The maximum efficiency of an automobile engine is given by the efficiency of a Carnot engine operating between the same two temperatures. We can use the expression for the Carnot efficiency and the equation relating V and T for a quasi-static adiabatic expansion to express the Carnot efficiency of the engine in terms of its compression ratio.

Express the Carnot efficiency of an engine operating between the temperatures T_c and T_h:

$$\varepsilon_C = 1 - \frac{T_c}{T_h}$$

Relate the temperatures T_c and T_h to the volumes V_c and V_h for a quasi-static adiabatic compression from V_c to V_h:

$$T_c V_c^{\gamma-1} = T_h V_h^{\gamma-1}$$

Solve for the ratio of T_c to T_h:

$$\frac{T_c}{T_h} = \frac{V_h^{\gamma-1}}{V_c^{\gamma-1}} = \left(\frac{V_h}{V_c}\right)^{\gamma-1}$$

Substitute to obtain:

$$\varepsilon_C = 1 - \left(\frac{V_h}{V_c}\right)^{\gamma-1}$$

Express the compression ratio r:

$$r = \frac{V_c}{V_h}$$

Substitute once more to obtain:

$$\varepsilon_C = 1 - \frac{1}{r^{\gamma-1}}$$

Substitute numerical values for r and γ (1.4 for diatomic gases) and evaluate ε_C:

$$\varepsilon_C = 1 - \frac{1}{(8)^{1.4-1}} = 0.565 = \boxed{56.5\%}$$

*16 ••

Picture the Problem If we assume that the temperature on the inside of the refrigerator is 0°C (273 K) and the room temperature to be about 30°C (303 K), then the refrigerator must be able to maintain a temperature difference of about 30 K. We can use the definition of the COP of a refrigerator and the relationship between the temperatures of the hot and cold reservoir and $|Q_h|$ and Q_c to find an upper limit on the COP of a household refrigerator. In (*b*) we can solve the definition of COP for Q_c and differentiate the resulting equation with respect to time to estimate the rate at which heat is being drawn from the refrigerator compartment.

(*a*) Using its definition, express the COP of a household refrigerator:

$$\text{COP} = \frac{Q_c}{W} \qquad\qquad (1)$$

Apply the 1$^{\text{st}}$ law of thermodynamics to the refrigerator to obtain:	$W + Q_c = \left| Q_h \right|$

Substitute for W and simplify to obtain:

$$\text{COP} = \frac{Q_c}{\left| Q_h \right| - Q_c} = \frac{1}{\dfrac{\left| Q_h \right|}{Q_c} - 1}$$

Assume, for the sake of finding the upper limit on the COP, that the refrigerator is a Carnot refrigerator and relate the temperatures of the hot and cold reservoirs to $\left| Q_h \right|$ and Q_c:

$$\frac{\left| Q_h \right|}{Q_c} = \frac{T_h}{T_c}$$

Substitute to obtain:

$$\text{COP}_{\text{max}} = \frac{1}{\dfrac{T_h}{T_c} - 1}$$

Substitute numerical values and evaluate COP$_{\text{max}}$:

$$\text{COP}_{\text{max}} = \frac{1}{\dfrac{303\,\text{K}}{273\,\text{K}} - 1} = \boxed{9.10}$$

(b) Solve equation (1) for Q_c:

$$Q_c = W(\text{COP}) \qquad\qquad (2)$$

Differentiate equation (2) with respect to time to obtain:

$$\frac{dQ_c}{dt} = (\text{COP})\frac{dW}{dt}$$

Substitute numerical values and evaluate dQ_c/dt:

$$\frac{dQ_c}{dt} = (9.10)(600\,\text{J/s}) = \boxed{5.46\,\text{kW}}$$

17   ••

Picture the Problem We can use the definition of intensity to find the total power of sunlight hitting the earth and the definition of the change in entropy to find the changes in the entropy of the earth and the sun resulting from the radiation from the sun.

(*a*) Using its definition, express the intensity of the sun's radiation on the earth in terms of the power delivered to the earth P and the earth's cross sectional area A:

$$I = \frac{P}{A}$$

Solve for P and substitute for A to obtain:

$$P = IA = I\pi R^2$$
where R is the radius of the earth.

Substitute numerical values and evaluate P:

$$P = \pi\left(1.3\,\text{kW/m}^2\right)\left(6.37 \times 10^6\,\text{m}\right)^2$$
$$= \boxed{1.66 \times 10^{17}\,\text{W}}$$

(b) Express dS_{earth}/dt for the earth due to the flow of solar radiation:

$$\frac{dS_{\text{earth}}}{dt} = \frac{P}{T_{\text{earth}}}$$

Substitute numerical values and evaluate dS_{earth}/dt:

$$\Delta S_{\text{earth}} = \frac{1.66 \times 10^{17}\,\text{W}}{290\,\text{K}}$$
$$= \boxed{5.72 \times 10^{14}\,\text{J/K} \cdot \text{s}}$$

(c) Express dS_{sun}/dt for the sun due to the outflow of solar radiation *hitting the earth*:

$$\frac{dS_{\text{sun}}}{dt} = \frac{P}{T_{\text{sun}}}$$

Substitute numerical values and evaluate dS_{sun}/dt:

$$\frac{dS_{\text{sun}}}{dt} = \frac{1.66 \times 10^{17}\,\text{W}}{5400\,\text{K}}$$
$$= \boxed{3.07 \times 10^{13}\,\text{J/K} \cdot \text{s}}$$

18   ••

Picture the Problem We can use the definition of intensity to find the total power radiated by the sun and the definition of the change in entropy to find the change in the entropy of the universe resulting from the radiation of 10^{11} stars in 10^{11} galaxies.

(a) Using its definition, express the intensity of the sun's radiation on the location of earth in terms of the total power it delivers to space P and the area of a sphere A whose radius is the distance from the sun to the earth:

$$I = \frac{P}{A}$$

Solve for P and substitute for A to obtain:

$$P = IA = 4\pi IR^2$$
where R is the distance from the sun to the earth.

Substitute numerical values and evaluate P:

$$P = 4\pi\left(1.3\,\text{kW/m}^2\right)\left(1.5 \times 10^{11}\,\text{m}\right)^2$$
$$= \boxed{3.68 \times 10^{26}\,\text{W}}$$

(b) Express $\Delta S_{\text{universe}}$:

$$\Delta S_{\text{universe}} = \frac{P}{T_{\text{universe}}}$$

Substitute numerical values and evaluate $\Delta S_{universe}$:

$$\Delta S_{universe} = \frac{10^{22}\left(3.68\times10^{26}\,\text{W}\right)}{2.73\,\text{K}}$$

$$= \boxed{1.35\times10^{48}\,\text{J/K}\cdot\text{s}}$$

19   ••

Picture the Problem We can use the definition of entropy change to estimate the increase in entropy of the universe as a result of the heat produced by a typical human body. The entropy change is equivalent to the entropy change if the heat from the body were added to the universe reversibly.

Express the increase in entropy of the universe as a result of the heat produced by a human body:

$$\Delta S_u = \frac{\Delta Q_{day}}{T_{day}} + \frac{\Delta Q_{night}}{T_{night}}$$

Using the definition of power, express the total heat produced by a human body:

$$\Delta Q = P\Delta t$$

Assume that half of the heat is produced during the day and half at night:

$$\Delta Q_{day} = \Delta Q_{night} = \tfrac{1}{2}P\Delta t$$

Substitute to obtain:

$$\Delta S_u = \frac{\tfrac{1}{2}P\Delta t}{T_{day}} + \frac{\tfrac{1}{2}P\Delta t}{T_{night}}$$

$$= \tfrac{1}{2}P\Delta t\left(\frac{1}{T_{day}} + \frac{1}{T_{night}}\right)$$

Use $T = \tfrac{5}{9}\left(t_F - 32\right) + 273$ to obtain: $T_{day} = 294\text{ K}$ and $T_{night} = 286\text{ K}$

Substitute numerical values and evaluate ΔS_u:

$$\Delta S_u = \tfrac{1}{2}\left(100\,\text{J/s}\right)\left(24\,\text{h/d}\right)\left(3600\,\text{s/h}\right)\left(\frac{1}{294\,\text{K}} + \frac{1}{286\,\text{K}}\right) = \boxed{29.8\,\text{kJ/K}}$$

*20   •••

Picture the Problem If you had one molecule in a box, it would have a 50% chance of being on one side or the other. We don't care which side the molecules are on as long as they all are on one side, so with one molecule you have a 100% chance of it being on one side or the other. With two molecules, there are four possible combinations (both on one side, both on the other, one on one side and one on the other, and the reverse), so there is a 25% (1 in 4) chance of them both being on a particular side, or a 50% chance of them both being on either side. Extending this logic, the probability of N molecules all being on one side of the box is $P = 2/2^N$, which means that, if the molecules shuffle 100 times a second, the time it would take them to cover all the combinations and all get on one side or the other is $t = \dfrac{2^N}{2(100)}$. In (*e*) we can apply the ideal gas law to find the number of

molecules in 1 L of air at a pressure of 10^{-12} torr and an assumed temperature of 300 K.

(*a*) Evaluate *t* for *N* = 10 molecules:

$$t = \frac{2^{10}}{2(100)} = \boxed{5.12\,\text{s}}$$

(*b*) Evaluate *t* for *N* = 100 molecules:

$$t = \frac{2^{100}}{2(100)} = 6.34 \times 10^{27}\,\text{s}$$

$$= \boxed{2.01 \times 10^{20}\,\text{y}}$$

(*c*) Evaluate *t* for *N* = 1000 molecules:

$$t = \frac{2^{1000}}{2(100)}$$

To evaluate 2^{1000} let $10^x = 2^{1000}$ and take the logarithm of both sides of the equation to obtain:

$$(1000)\ln 2 = x \ln 10$$

Solve for *x* to obtain:

$$x = 301$$

Substitute to obtain:

$$t = \frac{10^{301}}{2(100)} = 0.5 \times 10^{299}\,\text{s}$$

$$= \boxed{1.58 \times 10^{290}\,\text{y}}$$

(*d*) Evaluate *t* for $N = 6.02 \times 10^{23}$ molecules:

$$t = \frac{2^{6.02 \times 10^{23}}}{2(100)}$$

To evaluate $2^{6.02 \times 10^{23}}$ let $10^x = 2^{6.02 \times 10^{23}}$ and take the logarithm of both sides of the equation to obtain:

$$(6.02 \times 10^{23})\ln 2 = x \ln 10$$

Solve for *x* to obtain:

$$x \approx 10^{23}$$

Substitute to obtain:

$$t \approx \frac{10^{10^{23}}}{2(100)} \approx \boxed{10^{10^{23}}\,\text{y}}$$

(*e*) Solve the ideal gas law for the number of molecules *N* in the gas:

$$N = \frac{PV}{kT}$$

Assuming the gas to be at room temperature (300 K), substitute numerical values and evaluate *N*:

$$N = \frac{(10^{-12}\,\text{torr})(133.32\,\text{Pa/torr})(10^{-3}\,\text{m}^3)}{(1.381 \times 10^{-23}\,\text{J/K})(300\,\text{K})}$$

$$= 3.22 \times 10^7\,\text{molecules}$$

Evaluate T for $N = 3.22 \times 10^7$ molecules:	$t = \dfrac{2^{3.22 \times 10^7}}{2(100)}$

To evaluate $2^{3.22 \times 10^7}$ let $10^x = 2^{3.22 \times 10^7}$ and take the logarithm of both sides of the equation to obtain:	$(3.22 \times 10^7) \ln 2 = x \ln 10$

Solve for x to obtain:	$x \approx 10^7$

Substitute to obtain:	$T = \dfrac{10^{10^7}}{2(100)} \approx \boxed{10^{10^7} \text{ y}}$

Express the ratio of this waiting time to the lifetime of the universe T_{universe}:	$\dfrac{T}{T_{\text{universe}}} = \dfrac{10^{10^7} \text{ y}}{10^{10} \text{ y}} \approx 10^{10^7}$ or $T \approx \boxed{10^{10^7} T_{\text{universe}}}$

Heat Engines and Refrigerators

21 •

Picture the Problem We can use the definition of the efficiency of a heat engine to relate the work done W, the heat absorbed Q_{in}, and the heat rejected each cycle Q_{out}.

(a) Express Q_{in} in terms of W and ε:	$Q_{\text{in}} = \dfrac{W}{\varepsilon} = \dfrac{100\,\text{J}}{0.2} = \boxed{500\,\text{J}}$

(b) Solve the definition of efficiency for and evaluate $|Q_{\text{out}}|$:	$|Q_{\text{out}}| = Q_{\text{in}}(1 - \varepsilon) = (500\,\text{J})(1 - 0.2)$ $= \boxed{400\,\text{J}}$

22 •

Picture the Problem We can use its definition to find the efficiency of a heat engine from the work done, the heat absorbed, and the heat rejected each cycle.

(a) Use the definition of the efficiency of a heat engine:	$\varepsilon \equiv \dfrac{W}{Q_{\text{in}}} = \dfrac{120\,\text{J}}{400\,\text{J}} = \boxed{30\%}$

(b) Solve the definition of efficiency for and evaluate $|Q_{\text{out}}|$:	$|Q_{\text{out}}| = Q_{\text{in}}(1 - \varepsilon) = (400\,\text{J})(1 - 0.3)$ $= \boxed{280\,\text{J}}$

23 •

Picture the Problem We can use its definition to find the efficiency of the engine and the definition of power to find its power output.

(*a*) Apply the definition of the efficiency of a heat engine:

$$\varepsilon = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{60\,J}{100\,J} = \boxed{40.0\%}$$

(*b*) Use the definition of power to find the power output of this engine:

$$P = \frac{\Delta W}{\Delta t} = \frac{\varepsilon Q_{in}}{\Delta t} = \frac{0.4(100\,J)}{0.5\,s} = \boxed{80.0\,W}$$

*24 •

Picture the Problem We can apply their definitions to find the COP of the refrigerator and the efficiency of the heat engine.

(*a*) Using the definition of the COP, relate the heat absorbed from the cold reservoir to the work done each cycle:

$$COP = \frac{Q_c}{W}$$

Relate the work done per cycle to Q_h and Q_c:

$$W = |Q_h| - Q_c$$

Substitute to obtain:

$$COP = \frac{Q_c}{|Q_h| - Q_c}$$

Substitute numerical values and evaluate COP:

$$COP = \frac{5\,kJ}{|8\,kJ| - 5\,kJ} = \boxed{1.67}$$

(*b*) Use the definition of efficiency to relate the work done per cycle to the heat absorbed from the high-temperature reservoir:

$$\varepsilon = \frac{W}{Q_h}$$

Substitute numerical values and evaluate ε:

$$\varepsilon = \frac{3\,kJ}{8\,kJ} = \boxed{37.5\%}$$

25   ••

Picture the Problem To find the heat added during each step we need to find the temperatures in states 1, 2, 3, and 4. We can then find the work done on or by the gas along each pass from the area under each straight-line segment and the heat that enters or leaves the system from $Q = C_V \Delta T$ and $Q = C_P \Delta T$. We can find the efficiency of the cycle from the work done each cycle and the heat that *enters* the system each cycle.

(*a*) The cycle is shown to the right:
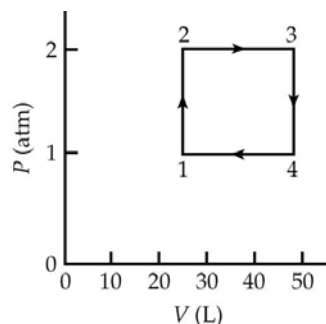
Apply the ideal-gas law to state 1 to find T_1:

$$T_1 = \frac{P_1 V_1}{nR}$$

$$= \frac{(1\,\text{atm})(24.6\,\text{L})}{(1\,\text{mol})(8.206 \times 10^{-2}\,\text{L} \cdot \text{atm/mol} \cdot \text{K})}$$

$$= 300\,\text{K}$$

The pressure doubles while the volume remains constant between states 1 and 2. Hence:

$$T_2 = 2T_1 = 600\,K$$

The volume doubles while the pressure remains constant between states 2 and 3. Hence:

$$T_3 = 2T_2 = 1200\,K$$

The pressure is halved while the volume remains constant between states 3 and 4. Hence:

$$T_4 = \tfrac{1}{2}T_3 = 600\,K$$

For path 1→2:

$$W_{1 \to 2} = P\Delta V_{1 \to 2} = \boxed{0}$$

and

$$Q_{1 \to 2} = \Delta E_{\text{int},1 \to 2} = C_V \Delta T_{1 \to 2} = \tfrac{3}{2} R \Delta T_{1 \to 2} = \tfrac{3}{2}(8.314\,\text{J/mol} \cdot \text{K})(600\,\text{K} - 300\,\text{K})$$

$$= \boxed{3.74\,\text{kJ}}$$

For path 2→3:

$$W_{2 \to 3} = P \Delta V_{2 \to 2} = (2\,\text{atm})(49.2\,\text{L} - 24.6\,\text{L}) = 49.20\,\text{L} \cdot \text{atm} \times \frac{101.325\,\text{J}}{\text{L} \cdot \text{atm}}$$

$$= \boxed{4.99\,\text{kJ}}$$

and

$$Q_{2 \to 3} = C_P \Delta T_{2 \to 3} = \tfrac{5}{2} R \Delta T_{2 \to 3} = \tfrac{5}{2}(8.314\,\text{J/mol} \cdot \text{K})(1200\,\text{K} - 600\,\text{K})$$

$$= \boxed{12.5\,\text{kJ}}$$

For path 3→4:

$$W_{3 \to 4} = P \Delta V_{3 \to 4} = \boxed{0}$$

and

$$Q_{3 \to 4} = \Delta E_{\text{int},3 \to 4} = C_V \Delta T_{3 \to 4} = \tfrac{3}{2} R \Delta T_{3 \to 4} = \tfrac{3}{2}(8.314\,\text{J/mol} \cdot \text{K})(600\,\text{K} - 1200\,\text{K})$$

$$= \boxed{-7.48\,\text{kJ}}$$

For path 4→1:

$$W_{4 \to 1} = P \Delta V_{4 \to 1} = (1\,\text{atm})(24.6\,\text{L} - 49.2\,\text{L}) = -24.6\,\text{L} \cdot \text{atm} \times \frac{101.3\,\text{J}}{\text{L} \cdot \text{atm}}$$

$$= \boxed{2.49\,\text{kJ}}$$

and

$$Q_{4 \to 1} = C_P \Delta T_{4 \to 1} = \tfrac{5}{2} R \Delta T_{4 \to 1} = \tfrac{5}{2}(8.314\,\text{J/mol} \cdot \text{K})(300\,\text{K} - 600\,\text{K})$$

$$= \boxed{-6.24\,\text{kJ}}$$

(*b*) Use its definition to find the efficiency of this cycle:

$$\varepsilon = \frac{W}{Q_{\text{in}}} = \frac{W_{2 \to 3} + W_{4 \to 1}}{Q_{1 \to 2} + Q_{2 \to 3}}$$

$$= \frac{4.99\,\text{kJ} - 2.49\,\text{kJ}}{3.74\,\text{kJ} + 12.5\,\text{kJ}} = \boxed{15.4\%}$$

Remarks: Note that the work done per cycle is the area bounded by the rectangular path.

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Picture the Problem The three steps in the process are shown on the *PV* diagram. We can find the efficiency of the cycle by finding the work done by the gas and the heat that enters the system per cycle.
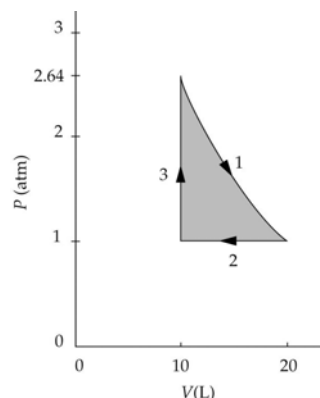
Express the efficiency of the cycle:

$$\varepsilon = \frac{W}{Q_{in}}$$

Find the heat entering or leaving the system during the adiabatic expansion:

$$Q_1 = 0$$

Find the heat entering or leaving the system during the isobaric compression:

$$Q_2 = C_V \Delta T_2 = \tfrac{7}{2} R \Delta T_2 = \tfrac{7}{2} P \Delta V_2$$
$$= \tfrac{7}{2}(1\,\text{atm})(10\,\text{L} - 20\,\text{L}) = -35\,\text{atm} \cdot \text{L}$$

Find the heat entering or leaving the system during the constant-volume process:

$$Q_3 = C_V \Delta T_3 = \tfrac{5}{2} R \Delta T_3 = \tfrac{5}{2} \Delta P V_3$$
$$= \tfrac{5}{2}(2.64\,\text{atm} - 1\,\text{atm})(10\,\text{L})$$
$$= 41\,\text{atm} \cdot \text{L}$$

Apply the 1st law of thermodynamics to the cycle ($\Delta E_{int, cycle} = 0$) to

obtain:

$$W_{on} = \Delta E_{int} - Q_{in} = -Q_{in}$$
$$= Q_1 + Q_2 + Q_3$$
$$= 0 - 35\,\text{atm} \cdot \text{L} + 41\,\text{atm} \cdot \text{L}$$
$$= 6\,\text{atm} \cdot \text{L}$$

Substitute and evaluate ε:

$$\varepsilon = \frac{6\,\text{atm} \cdot \text{L}}{41\,\text{atm} \cdot \text{L}} = \boxed{14.6\%}$$

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Picture the Problem We can find the efficiency of the cycle by finding the work done by the gas and the heat that enters the system per cycle.
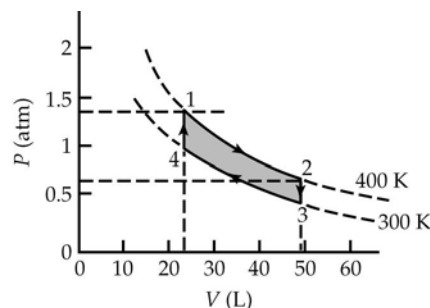
Apply the ideal-gas law to states 1, 2, 3, and 4 to find the pressures at these points:

$$P_1 = \frac{nRT_1}{V_1} = \frac{(1\,\text{mol})(8.206 \times 10^{-2}\,\text{L} \cdot \text{atm/mol} \cdot \text{K})(400\,\text{K})}{24.6\,\text{K}} = 1.33\,\text{atm}$$

Proceed as above to obtain the values shown in the table:

Point	P	V	T
	(atm)	(L)	(K)
1	1.330	24.6	400
2	0.667	49.2	400
3	0.500	49.2	300
4	1.000	24.6	300

The *PV* diagram is shown to the right:

Express the efficiency of the cycle:

$$\varepsilon = \frac{W}{Q_{\text{in}}} \qquad (1)$$

Find the work done by the gas and the heat that enters the system during the isothermal expansion from 1 to 2:

$$W_{1\to2} = Q_{1\to2} = nRT_1 \ln\!\left(\frac{V_2}{V_1}\right) = (1\,\text{mol})(8.314\,\text{J/mol} \cdot \text{K})(400\,\text{K})\ln\!\left(\frac{49.2\,\text{L}}{24.6\,\text{L}}\right)$$

$$= 2.305\,\text{kJ}$$

Find the work done by the gas and the heat that enters the system during the constant-volume compression from 2 to 3:

$$W_{2\to3} = 0$$

and

$$Q_{2\to3} = C_V \Delta T_{2\to3} = (21\,\text{J/K})(300\,\text{K} - 400\,\text{K}) = -2.10\,\text{kJ}$$

Find the work done by the gas and the heat that enters the system during the isothermal expansion from 3 to 4:

$$W_{3 \to 4} = Q_{3 \to 4} = nRT_3 \ln\left(\frac{V_4}{V_3}\right) = (1\,\text{mol})(8.314\,\text{J/mol} \cdot \text{K})(300\,\text{K}) \ln\left(\frac{24.6\,\text{L}}{49.2\,\text{L}}\right)$$
$$= -1.729\,\text{kJ}$$

Find the work done by the gas and the heat that enters the system during the constant-volume process from 4 to 1:

$$W_{4 \to 1} = 0$$

and

$$Q_{4 \to 1} = C_V \Delta T_{4 \to 1} = (21\,\text{J/K})(400\,\text{K} - 300\,\text{K}) = 2.10\,\text{kJ}$$

Evaluate the work done each cycle:

$$W = W_{1 \to 2} + W_{2 \to 3} + W_{3 \to 4} + W_{4 \to 1}$$
$$= 2.305\,\text{kJ} + 0 - 1.729\,\text{kJ} + 0$$
$$= 0.5760\,\text{kJ}$$

Find the heat that enters the system each cycle:

$$Q_{\text{in}} = Q_{1 \to 2} + Q_{4 \to 1}$$
$$= 2.305\,\text{kJ} + 2.100\,\text{kJ}$$
$$= 4.405\,\text{kJ}$$

Substitute numerical values in equation (1) and evaluate ε:

$$\varepsilon = \frac{0.5760\,\text{kJ}}{4.405\,\text{kJ}} = \boxed{13.1\%}$$

*28 ••

Picture the Problem We can use the ideal-gas law to find the temperatures of each state of the gas and the heat capacities at constant volume and constant pressure to find the heat flow for the constant-volume and isobaric processes. Because the change in internal energy is zero for the isothermal process, we can use the expression for the work done on or by a gas during an isothermal process to find the heat flow during such a process. Finally, we can find the efficiency of the cycle from its definition.

(a) Use the ideal-gas law to find the temperature at point 1:

$$T_1 = \frac{P_1 V_1}{nR} = \frac{(100\,\text{kPa})(25\,\text{L})}{(1\,\text{mol})(8.314\,\text{J/mol} \cdot \text{K})}$$
$$= \boxed{301\,\text{K}}$$

Use the ideal-gas law to find the temperatures at points 2 and 3:

$$T_2 = T_3 = \frac{P_2 V_2}{nR} = \frac{(200\,\text{kPa})(25\,\text{L})}{(1\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})}$$

$$= \boxed{601\,\text{K}}$$

(b) Find the heat entering or leaving the system for the constant-volume process from 1 to 2:

$$Q_{1\to2} = C_V \Delta T_{1\to2} = \tfrac{3}{2}R\Delta T_{1\to2} = \tfrac{3}{2}(8.314\,\text{J/mol}\cdot\text{K})(601\,\text{K} - 301\,\text{K})$$

$$= \boxed{3.74\,\text{kJ}}$$

Find the heat entering or leaving the system for the isothermal process from 2 to 3:

$$Q_{2\to3} = nRT_2 \ln\left(\frac{V_3}{V_2}\right) = (1\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})(601\,\text{K})\ln\left(\frac{50\,\text{L}}{25\,\text{L}}\right) = \boxed{3.46\,\text{kJ}}$$

Find the heat entering or leaving the system during the isobaric compression from 3 to 1:

$$Q_{3\to1} = C_P \Delta T_{3\to1} = \tfrac{5}{2}R\Delta T_{3\to1} = \tfrac{5}{2}(8.314\,\text{J/mol}\cdot\text{K})(301\,\text{K} - 601\,\text{K})$$

$$= \boxed{-6.24\,\text{kJ}}$$

(c) Express the efficiency of the cycle:

$$\varepsilon = \frac{W}{Q_{\text{in}}} = \frac{W}{Q_{1\to2} + Q_{2\to3}} \qquad (1)$$

Apply the 1$^{\text{st}}$ law of thermodynamics to the cycle:

$$W = \sum Q = Q_{1\to2} + Q_{2\to3} + Q_{3\to1}$$
$$= 3.74\,\text{kJ} + 3.46\,\text{kJ} - 6.24\,\text{kJ}$$
$$= 0.960\,\text{kJ}$$

because, for the cycle, $\Delta U = 0$.

Substitute numerical values in equation (1) and evaluate ε:

$$\varepsilon = \frac{0.960\,\text{kJ}}{3.74\,\text{kJ} + 3.46\,\text{kJ}} = \boxed{13.3\%}$$

29   ••

Picture the Problem We can use the ideal-gas law to find the temperatures of each state of the gas. We can find the efficiency of the cycle from its definition; using the area enclosed by the cycle to find the work done per cycle and the heat entering the system between states 1 and 2 and 2 and 3 to determine Q_{in}.

(*a*) Use the ideal-gas law for a fixed amount of gas to find the temperature in state 2 to the temperature in state 1:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Solve for and evaluate T_2:

$$T_2 = T_1 \frac{P_2 V_2}{P_1 V_1} = T_1 \frac{P_2}{P_1} = (200\,\text{K})\frac{(3\,\text{atm})}{(1\,\text{atm})}$$
$$= \boxed{600\,\text{K}}$$

Apply the ideal-gas law for a fixed amount of gas to states 2 and 3 to obtain:

$$T_3 = T_2 \frac{P_3 V_3}{P_2 V_2} = T_2 \frac{V_3}{V_2} = (600\,\text{K})\frac{(300\,\text{L})}{(100\,\text{L})}$$
$$= \boxed{1800\,\text{K}}$$

Apply the ideal-gas law for a fixed amount of gas to states 3 and 4 to obtain:

$$T_4 = T_3 \frac{P_4 V_4}{P_3 V_3} = T_3 \frac{P_4}{P_3} = (1800\,\text{K})\frac{(1\,\text{atm})}{(3\,\text{atm})}$$
$$= \boxed{600\,\text{K}}$$

(*b*) Express the efficiency of the cycle:

$$\varepsilon = \frac{W}{Q_{\text{in}}} \qquad (1)$$

Use the area of the rectangle to find the work done each cycle:

$$W = \Delta P \Delta V$$
$$= (300\,\text{L} - 100\,\text{L})(3\,\text{atm} - 1\,\text{atm})$$
$$= 400\,\text{atm} \cdot \text{L}$$

Apply the ideal-gas law to state 1 to find the product of n and R:

$$nR = \frac{P_1 V_1}{T_1} = \frac{(1\,\text{atm})(100\,\text{L})}{200\,\text{K}}$$
$$= 0.5\,\text{L} \cdot \text{atm/K}$$

Noting that heat enters the system between states 1 and 2 and states 2 and 3, express Q_{in}:

$$Q_{\text{in}} = Q_{1\to 2} + Q_{2\to 3}$$
$$= C_V \Delta T_{1\to 2} + C_P \Delta T_{2\to 3}$$
$$= \tfrac{5}{2} nR \Delta T_{1\to 2} + \tfrac{7}{2} nR \Delta T_{2\to 3}$$
$$= \left(\tfrac{5}{2} \Delta T_{1\to 2} + \tfrac{7}{2} \Delta T_{2\to 3} \right) nR$$

Substitute numerical values and evaluate Q_{in}:

$$Q_{\text{in}} = \left[\tfrac{5}{2}(600\,\text{K} - 200\,\text{K}) + \tfrac{7}{2}(1800\,\text{K} - 600\,\text{K}) \right](0.5\,\text{L} \cdot \text{atm/K}) = 2600\,\text{atm} \cdot \text{L}$$

Substitute numerical values in equation (1) and evaluate ε:

$$\varepsilon = \frac{400\,\text{atm}\cdot\text{L}}{2600\,\text{atm}\cdot\text{L}} = \boxed{15.4\%}$$

30   •••

Picture the Problem To find the efficiency of the diesel cycle we can find the heat that enters the system and the heat that leaves the system and use the expression that gives the efficiency in terms of these quantities. Note that no heat enters or leaves the system during the adiabatic processes $a{\to}b$ and $c{\to}d$.

Express the efficiency of the cycle in terms of Q_c and Q_h:

$$\varepsilon = 1 - \frac{|Q_c|}{Q_h}$$

Express Q for the isobaric warming process $b{\to}c$:

$$Q_{b\to c} = |Q_h| = C_P(T_c - T_b)$$

Express Q for the constant-volume cooling process $d{\to}a$:

$$Q_{d\to a} = |Q_c| = C_V(T_d - T_a)$$

Substitute to obtain:

$$\varepsilon = 1 - \frac{C_V(T_d - T_a)}{C_P(T_c - T_b)}$$
$$= 1 - \frac{(T_d - T_a)}{\gamma(T_c - T_b)}$$

Using the equation of state for an adiabatic process, relate the temperatures T_a and T_b:

$$T_a V_a^{\gamma-1} = T_b V_b^{\gamma-1} \qquad (1)$$

Proceeding similarly, relate the temperatures T_c and T_d:

$$T_c V_c^{\gamma-1} = T_d V_d^{\gamma-1} \qquad (2)$$

Use equations (1) and (2) to eliminate T_a and T_d:

$$\varepsilon = 1 - \frac{\left(T_c \dfrac{V_c^{\gamma-1}}{V_d^{\gamma-1}} - T_b \dfrac{V_b^{\gamma-1}}{V_a^{\gamma-1}}\right)}{\gamma(T_c - T_b)}$$

$$= 1 - \frac{\left(\left(\dfrac{V_c}{V_a}\right)^{\gamma-1} - \dfrac{T_b}{T_c}\left(\dfrac{V_b}{V_a}\right)^{\gamma-1}\right)}{\gamma\left(1 - \dfrac{T_b}{T_c}\right)}$$

because $V_a = V_d$.

Apply the ideal-gas law for a fixed amount of gas to relate T_b and T_c:

$$\frac{T_b}{T_c} = \frac{V_b}{V_c}$$

because $P_b = P_c$.

Substitute and simplify to obtain:

$$\varepsilon = 1 - \frac{\left(\left(\frac{V_c}{V_a} \right)^{\gamma-1} - \frac{V_b}{V_c} \left(\frac{V_b}{V_a} \right)^{\gamma-1} \right)}{\gamma \left(1 - \frac{V_b}{V_c} \right)} \cdot \frac{\frac{V_c}{V_a}}{\frac{V_c}{V_a}} = 1 - \frac{\left(\left(\frac{V_c}{V_a} \right)^{\gamma} - \frac{V_b}{V_a} \left(\frac{V_b}{V_a} \right)^{\gamma-1} \right)}{\gamma \left(\frac{V_c}{V_a} - \frac{V_b}{V_a} \right)}$$

$$= \boxed{1 - \frac{\left(\left(\frac{V_c}{V_a} \right)^{\gamma} - \left(\frac{V_b}{V_a} \right)^{\gamma} \right)}{\gamma \left(\frac{V_c}{V_a} - \frac{V_b}{V_a} \right)}}$$

*31 ••

Picture the Problem We can use the efficiency of a Carnot engine operating between reservoirs at body temperature and typical outdoor temperatures to find an upper limit on the efficiency of an engine operating between these temperatures.

(a) Express the maximum efficiency of an engine operating between body temperature and 70°F:

$$\varepsilon_C = 1 - \frac{T_c}{T_h}$$

Use $T = \frac{5}{9}(t_F - 32) + 273$ to obtain:

$T_{body} = 310 \text{ K}$ and $T_{room} = 294 \text{ K}$

Substitute numerical values and evaluate ε_C:

$$\varepsilon_C = 1 - \frac{294 \text{ K}}{310 \text{ K}} = \boxed{5.16\%}$$

> The fact that this efficiency is considerably less than the actual efficiency of a human body does not contradict the second law of thermodynamics. The application of the second law to chemical reactions such as the ones that supply the body with energy have not been discussed in the text but we can note that don't get our energy from heat swapping between our body and the environment. Rather, we eat food to get the energy that we need.

(b) | Most warm – blooded animals survive under roughly the same conditions as humans. To make a heat engine work with appreciable efficiency, internal body temperatures would have to be maintained at an unreasonably high level.

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Picture the Problem The Carnot cycle's four segments (shown to the right) are: (A) an isothermal expansion at $T = T_h$ from V_1 to V_2, (B) an adiabatic expansion from V_2 to V_3, (C) an isothermal compression from V_3 to V_4 at $T = T_c$, and (D) an adiabatic compression from V_4 to V_1. We can find the Carnot efficiency for a gas described by the Clausius equation by expressing the ratio of the work done per cycle to the heat entering the system per cycle.
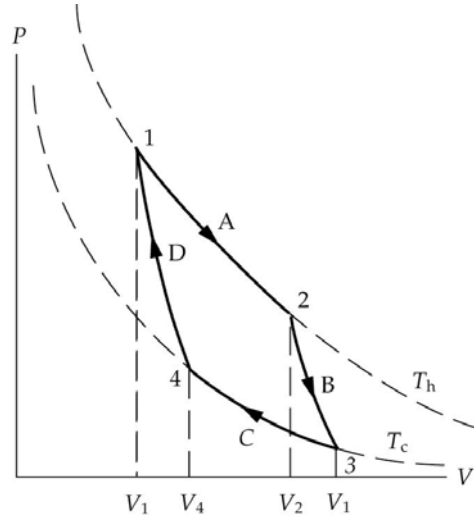
Express the efficiency of the Carnot cycle in terms of the work done and the heat that enters the system per cycle:

$$\varepsilon = \frac{W}{Q_h}$$

Apply the first law of thermodynamics to segment A:

$$Q_A = W_A + \Delta E_{int, A} = W_A = \int_{V_1}^{V_2} PdV$$

$$= nRT_h \int_{V_1}^{V_2} \frac{dV}{V - bn} = nRT_h \ln\left(\frac{V_2 - bn}{V_1 - bn}\right)$$

$$= Q_h$$

Follow the same procedure for segment C to obtain:

$$Q_C = W_C + \Delta E_{int, C} = W_C = \int_{V_3}^{V_4} PdV$$

$$= nRT_c \int_{V_3}^{V_4} \frac{dV}{V - bn} = nRT_c \ln\left(\frac{V_4 - bn}{V_3 - bn}\right)$$

and

$$|Q_c| = nRT_c \ln\left(\frac{V_3 - bn}{V_4 - bn}\right)$$

Apply the first law of thermodynamics to the complete cycle ($\Delta E_{\text{int, cycle}} = 0$) to express W:

$$W = Q_h - |Q_c|$$

$$= nRT_h \ln\left(\frac{V_2 - bn}{V_1 - bn}\right) - nRT_c \ln\left(\frac{V_3 - bn}{V_4 - bn}\right)$$

Substitute and simplify to obtain:

$$\varepsilon = \frac{nRT_h \ln\left(\frac{V_2 - bn}{V_1 - bn}\right) - nRT_c \ln\left(\frac{V_3 - bn}{V_4 - bn}\right)}{nRT_h \ln\left(\frac{V_2 - bn}{V_1 - bn}\right)}$$

$$= 1 - \frac{T_c \ln\left(\frac{V_3 - bn}{V_4 - bn}\right)}{T_h \ln\left(\frac{V_2 - bn}{V_1 - bn}\right)}$$

Apply the first law of thermodynamics to the adiabatic processes B and D:

$$dQ_B = 0 = dW_B + dE_{\text{int, B}} = PdV + C_V dT$$

$$= \frac{nRT}{V - bn} dV + C_V dT$$

Separate variables and integrate to obtain:

$$\int \frac{dT}{T} = -\frac{nT}{C_V} \int \frac{dV}{V - bn}$$

$$= -(\gamma - 1) \int \frac{dV}{V - bn}$$

or

$$\ln T = -(\gamma - 1)\ln(V - bn) + \text{constant}$$

$$= \ln(V - bn)^{\gamma - 1} + \text{constant}$$

Simplify to obtain:

$$\ln T + \ln(V - bn)^{\gamma - 1} = \text{constant}$$

or

$$\ln T(V - bn)^{\gamma - 1} = \text{constant}$$

and

$$T(V - bn)^{\gamma - 1} = \text{constant}$$

Using this result, relate V_2 and V_3 to T_h and T_c:

$$T_h(V_2 - bn)^{\gamma - 1} = T_c(V_3 - bn)^{\gamma - 1} \quad (1)$$

Relate V_1 and V_4 to T_h and T_c:

$$T_h(V_1 - bn)^{\gamma - 1} = T_c(V_4 - bn)^{\gamma - 1} \quad (2)$$

Divide equation (1) by equation (2) and simplify to obtain:

$$\frac{T_h(V_2 - bn)^{\gamma - 1}}{T_h(V_1 - bn)^{\gamma - 1}} = \frac{T_c(V_3 - bn)^{\gamma - 1}}{T_h(V_4 - bn)^{\gamma - 1}}$$

or

$$\frac{V_2 - bn}{V_1 - bn} = \frac{V_3 - bn}{V_4 - bn}$$

Substitute in our expression for ε and simplify:

$$\varepsilon = 1 - \frac{T_c \ln\left(\dfrac{V_2 - bn}{V_1 - bn}\right)}{T_h \ln\left(\dfrac{V_2 - bn}{V_1 - bn}\right)} = \boxed{1 - \frac{T_c}{T_h}}$$

the same as for an ideal gas.

Second Law of Thermodynamics

33   ••

Determine the Concept The relationship of the perfect engine and the refrigerator to each other and to the hot and cold reservoirs is shown below. To remove 500 J from the cold reservoir and reject 800 J to the hot reservoir, 300 J of work must be done on the system. Assuming that the heat-engine statement is false, one could use the 800 J rejected to the hot reservoir to do 300 J of work. Thus, running the refrigerator connected to the "perfect" heat engine would have the effect of transferring 500 J of heat from the cold to the hot reservoir without any work being done, in violation of the refrigerator statement of the second law.
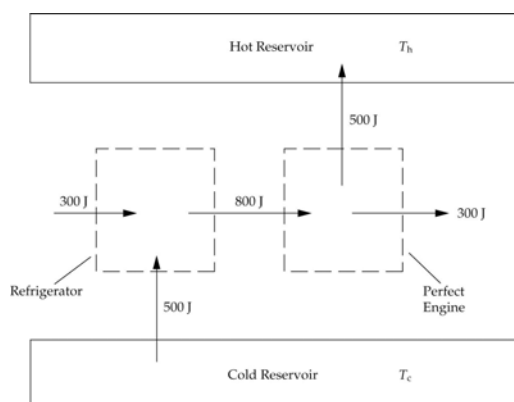
*34   ••

Determine the Concept The work done by the system is the area enclosed by the cycle, where we assume that we start with the isothermal expansion. It is only in this expansion that heat is extracted from a reservoir. There is no heat transfer in the adiabatic expansion or compression. Thus, we would completely convert heat to mechanical energy, without exhausting any heat to a cold reservoir, in violation of the second law.

Carnot Engines

35 •

Picture the Problem We can find the efficiency of the Carnot engine using $\varepsilon = 1 - T_c/T_h$ and the work done per cycle from $\varepsilon = W/Q_h$. We can apply conservation of energy to find the heat rejected each cycle from the heat absorbed and the work done each cycle. We can find the COP of the engine working as a refrigerator from its definition.

(*a*) Express the efficiency of the Carnot engine in terms of the temperatures of the hot and cold reservoirs:

$$\varepsilon_C = 1 - \frac{T_c}{T_h} = 1 - \frac{200\,\text{K}}{300\,\text{K}} = \boxed{33.3\%}$$

(*b*) Using the definition of efficiency, relate the work done each cycle to the heat absorbed from the hot reservoir:

$$W = \varepsilon_C Q_h = (0.333)(100\,\text{J}) = \boxed{33.3\,\text{J}}$$

(*c*) Apply conservation of energy to relate the heat given off each cycle to the heat absorbed and the work done:

$$|Q_c| = Q_h - W = 100\,\text{J} - 33.3\,\text{J} = \boxed{66.7\,\text{J}}$$

(*d*) Using its definition, express and evaluate the refrigerator's coefficient of performance:

$$\text{COP} = \frac{|Q_c|}{W} = \frac{66.7\,\text{J}}{33.3\,\text{J}} = \boxed{2.00}$$

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Picture the Problem We can find the efficiency of the engine from its definition and the additional work done if the engine were reversible from $W = \varepsilon_C Q_h$, where ε_C is the Carnot efficiency.

(*a*) Express the efficiency of the engine in terms of the heat absorbed from the high-temperature reservoir and the heat exhausted to the low-temperature reservoir:

$$\varepsilon = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$
$$= 1 - \frac{200\,\text{J}}{250\,\text{J}} = \boxed{20.0\%}$$

(*b*) Express the additional work done if the engine is reversible:

$$\Delta W = W_{\text{Carnot}} - W_{\text{part }a}$$

Relate the work done by a reversible engine to its Carnot efficiency:

$$W = \varepsilon_C Q_h = \left(1 - \frac{T_c}{T_h}\right) Q_h$$

$$= \left(1 - \frac{200\,K}{300\,K}\right)(250\,J) = 83.3\,J$$

Substitute and evaluate ΔW:

$$\Delta W = 83.3\,J - 50\,J = \boxed{33.3\,J}$$

37   ••

Determine the Concept Let the first engine be run as a refrigerator. Then it will remove 140 J from the cold reservoir, deliver 200 J to the hot reservoir, and require 60 J of energy to operate. Now take the second engine and run it between the same reservoirs, and let it eject 140 J into the cold reservoir, thus replacing the heat removed by the refrigerator. If ε_2, the efficiency of this engine, is greater than 30%, then Q_{h2}, the heat removed from the hot reservoir by this engine, is $140\,J/(1 - \varepsilon_2) > 200$ J, and the work done by this engine is $W = \varepsilon_2 Q_{h2} > 60$ J. The end result of all this is that the second engine can run the refrigerator, replacing the heat taken from the cold reservoir, and do additional mechanical work. The two systems working together then convert heat into mechanical energy without rejecting any heat to a cold reservoir, in violation of the second law.

38   ••

Determine the Concept If the reversible engine is run as a refrigerator, it will require 100 J of mechanical energy to take 400 J of heat from the cold reservoir and deliver 500 J to the hot reservoir. Now let the second engine, with $\varepsilon_2 > 0.2$, operate between the same two heat reservoirs and use it to drive the refrigerator. Because $\varepsilon_2 > 0.2$, this engine will remove less than 500 J from the hot reservoir in the process of doing 100 J of work. The net result is then that no net work is done by the two systems working together, but a finite amount of heat is transferred from the cold to the hot reservoir, in violation of the refrigerator statement of the second law.

*39   ••

Picture the Problem We can use the definition of efficiency to find the efficiency of the Carnot engine operating between the two reservoirs.

(*a*) Use its definition to find the efficiency of the Carnot engine:

$$\varepsilon_C = \frac{W}{Q_h} = \frac{50\,J}{150\,J} = \boxed{33.3\%}$$

(*b*) If COP > 2, then 50 J of work will remove more than 100 J of heat from the cold reservoir and put more than 150 J of heat into the hot reservoir. So running engine (*a*) to operate the refrigerator with a COP > 2 will result in the transfer of heat from the cold to the hot reservoir without doing any net mechanical work in violation of the second law.

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Picture the Problem We can use the definitions of the efficiency of a Carnot engine and the coefficient of performance of a refrigerator to find these quantities. The work done each cycle by the Carnot engine is given by $W = \varepsilon_C Q_h$ and we can use the conservation of energy to find the heat rejected to the low-temperature reservoir.

(*a*) Use the definition of the efficiency of a Carnot engine to obtain:

$$\varepsilon_C = 1 - \frac{T_c}{T_h} = 1 - \frac{77\,\text{K}}{300\,\text{K}} = \boxed{74.3\%}$$

(*b*) Express the work done each cycle in terms of the efficiency of the engine and the heat absorbed from the high-temperature reservoir:

$$W = \varepsilon_C Q_h = (0.743)(100\,\text{J}) = \boxed{74.3\,\text{J}}$$

(*c*) Apply conservation of energy to obtain:

$$|Q_c| = Q_h - W = 100\,\text{J} - 74.3\,\text{J} = \boxed{25.7\,\text{J}}$$

(*d*) Using its definition, express and evaluate the refrigerator's coefficient of performance:

$$\text{COP} = \frac{|Q_c|}{W} = \frac{25.7\,\text{J}}{74.3\,\text{J}} = \boxed{0.346}$$

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Picture the Problem We can use the ideal-gas law for a fixed amount of gas and the equations of state for an adiabatic process to find the temperatures, volumes, and pressures at the end points of each process in the given cycle. We can use $Q = C_V \Delta T$ and $Q = C_P \Delta T$ to find the heat entering and leaving during the constant-volume and isobaric processes and the first law of thermodynamics to find the work done each cycle. Once we've calculated these quantities, we can use its definition to find the efficiency of the cycle and the definition of the Carnot efficiency to find the efficiency of a Carnot engine operating between the extreme temperatures.

(*a*) Apply the ideal-gas law for a fixed amount of gas to relate the temperature at point 3 to the temperature at point 1:

$$\frac{P_1 V_1}{T_1} = \frac{P_3 V_3}{T_3}$$

or, because $P_1 = P_3$,

$$T_3 = T_1 \frac{V_3}{V_1} \qquad (1)$$

Apply the ideal-gas law for a fixed amount of gas to relate the pressure at point 2 to the temperatures at points 1 and 2 and the pressure at 1:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

or, because $V_1 = V_2$,

$$P_2 = P_1 \frac{T_2}{T_1} = (1\,\text{atm}) \frac{423\,\text{K}}{273\,\text{K}} = 1.55\,\text{atm}$$

Apply the state equation for an adiabatic process to relate the pressures and volumes at points 2 and 3:

$$P_1 V_1^\gamma = P_3 V_3^\gamma$$

Noting that $V_1 = 22.4$ L, solve for and evaluate V_3:

$$V_3 = V_1 \left(\frac{P_1}{P_3} \right)^{\frac{1}{\gamma}} = (22.4\,\text{L}) \left(\frac{1.55\,\text{atm}}{1\,\text{atm}} \right)^{\frac{1}{1.4}}$$

$$= 30.6\,\text{L}$$

Substitute in equation (1) and evaluate T_3:

$$T_3 = (273\,\text{K}) \frac{30.6\,\text{L}}{22.4\,\text{L}} = 373\,\text{K}$$

and

$$t_3 = T_3 - 273 = \boxed{100°\text{C}}$$

(b) Process 1→2 takes place at constant volume (note that $\gamma = 1.4$ corresponds to a diatomic gas and that $C_P - C_V = R$):

$$Q_{1\rightarrow 2} = C_V \Delta T_{1\rightarrow 2} = \tfrac{5}{2} R \Delta T_{1\rightarrow 2}$$
$$= \tfrac{5}{2}(8.314\,\text{J/mol} \cdot \text{K})(423\,\text{K} - 273\,\text{K})$$
$$= \boxed{3.12\,\text{kJ}}$$

Process 2→3 takes place adiabatically:

$$Q_{2\rightarrow 3} = \boxed{0}$$

Process 3→1 is isobaric (note that $C_P = C_V + R$):

$$Q_{3\rightarrow 1} = C_P \Delta T_{3\rightarrow 1} = \tfrac{7}{2} R \Delta T_{1\rightarrow 2}$$
$$= \tfrac{7}{2}(8.314\,\text{J/mol} \cdot \text{K})(273\,\text{K} - 373\,\text{K})$$
$$= \boxed{-2.91\,\text{kJ}}$$

(c) Use its definition to express the efficiency of this cycle:

$$\varepsilon = \frac{W}{Q_{\text{in}}}$$

Apply the first law of thermodynamics to the cycle:

$$\Delta K_{\text{int}} = Q_{\text{in}} + W_{\text{on}}$$

or, because $\Delta E_{\text{int, cycle}} = 0$ (the system begins and ends in the same state) and

$W_{\text{on}} = - W_{\text{by the gas}} = W$, $W = Q_{\text{in}}$.

Evaluate W:

$$W = \sum Q = Q_{1\to2} + Q_{2\to3} + Q_{3\to1}$$
$$= 3.12\,\text{kJ} + 0 - 2.91\,\text{kJ}$$
$$= 0.210\,\text{kJ}$$

Substitute and evaluate ε:

$$\varepsilon = \frac{0.210\,\text{kJ}}{3.12\,\text{kJ}} = \boxed{6.73\%}$$

(*d*) Express and evaluate the efficiency of a Carnot cycle operating between 423 K and 273 K:

$$\varepsilon_\text{C} = 1 - \frac{T_\text{c}}{T_\text{h}} = 1 - \frac{273\,\text{K}}{423\,\text{K}} = \boxed{35.5\%}$$

42   ••

Picture the Problem We can find the maximum efficiency of the steam engine by calculating the Carnot efficiency of an engine operating between the given temperatures. We can apply the definition of efficiency to find the heat discharged to the engine's surroundings in 1 h.

(*a*) Find the efficiency of a Carnot engine operating between these temperatures:

$$\varepsilon_\text{max} = 1 - \frac{T_\text{c}}{T_\text{h}} = 1 - \frac{323\,\text{K}}{543\,\text{K}} = 40.5\%$$

Find the efficiency of the steam engine as a percentage of the maximum possible efficiency:

$$\varepsilon_\text{steam engine} = \frac{0.30}{0.405}\varepsilon_\text{max} = \boxed{0.741\varepsilon_\text{max}}$$

(*b*) Relate the heat discharged to the engine's surroundings to Q_h and the efficiency of the engine:

$$|Q_\text{c}| = (1-\varepsilon)Q_\text{h}$$

Using its definition, relate the efficiency of the engine to the heat intake of the engine and the work it does each cycle:

$$Q_\text{h} = \frac{W}{\varepsilon} = \frac{P\Delta t}{\varepsilon}$$

Substitute and evaluate $|Q_\text{c}|$ in 1 h:

$$|Q_\text{c}| = (1-\varepsilon)\frac{P\Delta t}{\varepsilon}$$
$$= (1-0.3)\frac{(200\,\text{kJ/s})(3600\,\text{s})}{0.3}$$
$$= \boxed{1.68\,\text{GJ}}$$

Heat Pumps

*43 •

Picture the Problem We can use the definition of the COP_{HP} and the Carnot efficiency of an engine to express the maximum efficiency of the refrigerator in terms of the reservoir temperatures. We can apply equation 19-10 and the definition of power to find the minimum power needed to run the heat pump.

(*a*) Express the COP_{HP} in terms of T_h and T_c:

$$COP_{HP} = \frac{|Q_h|}{W} = \frac{|Q_h|}{|Q_h| - Q_c}$$

$$= \frac{1}{1 - \dfrac{Q_c}{|Q_h|}} = \frac{1}{1 - \dfrac{T_c}{T_h}}$$

$$= \frac{T_h}{T_h - T_c}$$

Substitute numerical values and evaluate the COP_{HP}:

$$COP_{HP} = \frac{313\,K}{313\,K - 263\,K} = \boxed{6.26}$$

(*b*) Using its definition, express the power output of the engine:

$$P = \frac{W}{\Delta t}$$

Use equation 19-10 to express the work done by the heat pump:

$$W = \frac{|Q_h|}{1 + COP_{HP}}$$

Substitute and evaluate P:

$$P = \frac{|Q_h|/\Delta t}{1 + COP_{HP}} = \frac{20\,kW}{1 + 6.26} = \boxed{2.75\,kW}$$

(*c*) Find the minimum power if the COP is 60% of the efficiency of an ideal pump:

$$P_{min} = \frac{|Q_c|/\Delta t}{1 + 0.6(COP_{HP,max})} = \frac{20\,kW}{1 + 0.6(6.26)}$$

$$= \boxed{4.21\,kW}$$

44 •

Picture the Problem We can use the definition of the COP to relate the heat removed from the refrigerator to its power rating and operating time. By expressing the COP in terms of T_c and T_h we can write the amount of heat removed from the refrigerator as a function of T_c, T_h, P, and Δt.

(a) Express the amount of heat the refrigerator can remove in a given period of time as a function of its COP:

$$Q_c = (COP)W$$
$$= (COP)P\Delta t$$

Express the COP in terms of T_h and T_c:

$$COP = \frac{|Q_c|}{W} = \frac{|Q_c|}{\varepsilon Q_h} = \frac{Q_h - W}{\varepsilon Q_h}$$
$$= \frac{1 - \varepsilon}{\varepsilon} = \frac{1}{\varepsilon} - 1 = \frac{1}{1 - \dfrac{T_c}{T_h}} - 1$$
$$= \frac{T_c}{T_h - T_c}$$

Substitute to obtain:

$$Q_c = \left(\frac{T_c}{T_h - T_c}\right)P\Delta t$$

Substitute numerical values and evaluate Q_c:

$$Q_c = \left(\frac{273\,K}{293\,K - 273\,K}\right)(370\,W)(60\,s)$$
$$= \boxed{303\,kJ}$$

(b) Find the heat removed if the COP is 70% of the efficiency of an ideal pump:

$$Q_c' = (0.7)\left(\frac{273\,K}{293\,K - 273\,K}\right)(370\,W)(60\,s)$$
$$= \boxed{212\,kJ}$$

45 •

Picture the Problem We can use the definition of the COP to relate the heat removed from the refrigerator to its power rating and operating time. By expressing the COP in terms of T_c and T_h we can write the amount of heat removed from the refrigerator as a function of T_c, T_h, P, and Δt.

(a) Express the amount of heat the refrigerator can remove in a given period of time as a function of its COP:

$$Q_c = (COP)W$$
$$= (COP)P\Delta t$$

Express the COP in terms of T_h and
T_c:

$$COP = \frac{|Q_c|}{W} = \frac{|Q_c|}{\varepsilon Q_h} = \frac{Q_h - W}{\varepsilon Q_h}$$

$$= \frac{1 - \varepsilon}{\varepsilon} = \frac{1}{\varepsilon} - 1$$

$$= \frac{1}{1 - \dfrac{T_c}{T_h}} - 1 = \frac{T_c}{T_h - T_c}$$

Substitute to obtain:

$$Q_c = \left(\frac{T_c}{T_h - T_c}\right) P \Delta t$$

Substitute numerical values and
evaluate Q_c:

$$Q_c = \left(\frac{273\,K}{308\,K - 273\,K}\right)(370\,W)(60\,s)$$

$$= \boxed{173\,kJ}$$

(b) Find the heat removed if the
COP is 70% of the efficiency of an
ideal pump:

$$Q_c' = (0.7)\left(\frac{273\,K}{308\,K - 273\,K}\right)(370\,W)(60\,s)$$

$$= \boxed{121\,kJ}$$

Entropy Changes

46 •

Picture the Problem We can use the definition of entropy change to find the change in
entropy of the water as it freezes.

Apply the definition of entropy
change to obtain:

$$\Delta S = \frac{\Delta Q}{T} = \frac{-mL_f}{T}$$

Substitute numerical values and
evaluate ΔS:

$$\Delta S = \frac{-(18\,g)(333.5\,J/g)}{273\,K} = \boxed{-22.0\,J/K}$$

*47 ••

Picture the Problem The change in the entropy of the world resulting from the freezing
of this water and the cooling of the ice formed is the sum of the entropy changes of the
water-ice and the freezer. Note that, while the entropy of the water decreases, the entropy
of the freezer increases.

Express the change in entropy of the
universe resulting from this freezing and
cooling process:

$$\Delta S_u = \Delta S_{water} + \Delta S_{freezer} \qquad (1)$$

Express ΔS_{water}:

$$\Delta S_{water} = \Delta S_{freezing} + \Delta S_{cooling} \qquad (2)$$

Express $\Delta S_{freezing}$:

$$\Delta S_{freezing} = \frac{-Q_{freezing}}{T_{freezing}} \qquad (3)$$

where the minus sign is a consequence of the fact that heat is leaving the water as it freezes.

Relate $Q_{freezing}$ to the latent heat of fusion and the mass of the water:

$$Q_{freezing} = mL_f$$

Substitute in equation (3) to obtain:

$$\Delta S_{freezing} = \frac{-mL_f}{T_{freezing}}$$

Express $\Delta S_{cooling}$:

$$\Delta S_{cooling} = mC_p \ln\left(\frac{T_f}{T_i}\right)$$

Substitute in equation (2) to obtain:

$$\Delta S_{water} = \frac{-mL_f}{T_{freezing}} + mC_p \ln\left(\frac{T_f}{T_i}\right)$$

Noting that the freezer gains heat (at 263 K) from the freezing water and cooling ice, express $\Delta S_{freezer}$:

$$\Delta S_{freezer} = \frac{\Delta Q_{ice}}{T_{freezer}} + \frac{\Delta Q_{cooling\,ice}}{T_{freezer}}$$

$$= \frac{mL_f}{T_{freezer}} + \frac{mC_p \Delta T}{T_{freezer}}$$

Substitute for ΔS_{water} and $\Delta S_{freezer}$ in equation (1):

$$\Delta S_u = \frac{-mL_f}{T_{freezing}} + mC_p \ln\left(\frac{T_f}{T_i}\right) + \frac{mL_f}{T_{freezer}} + \frac{mC_p \Delta T}{T_{freezer}}$$

$$= m\left[\frac{-L_f}{T_{freezing}} + C_p \ln\left(\frac{T_f}{T_i}\right) + \frac{L_f}{T_{freezer}} + \frac{C_p \Delta T}{T_{freezer}}\right]$$

Substitute numerical values and evaluate ΔS_u:

$$\Delta S_u = (0.05\,\text{kg}) \left[-\frac{333.5 \times 10^3\,\text{J/kg}}{273\,\text{K}} + (2100\,\text{J/kg} \cdot \text{K}) \ln\left(\frac{263\,\text{K}}{273\,\text{K}}\right) + \frac{333.5 \times 10^3\,\text{J/kg}}{263\,\text{K}} \right.$$

$$\left. + \frac{(2100\,\text{J/kg} \cdot \text{K})(273\,\text{K} - 263\,\text{K})}{263\,\text{K}} \right]$$

$$= \boxed{2.40\,\text{J/K}}$$

and, because $\Delta S_u > 0$, the entropy of the universe increases.

48   •

Picture the Problem We can use the definition of entropy change and the first law of thermodynamics to express ΔS for the ideal gas as a function of its initial and final volumes.

(*a*) Use its definition to express the entropy change of the gas:

$$\Delta S = \frac{\Delta Q}{T}$$

Apply the first law of thermodynamics to the isothermal process:

$$\Delta Q = \Delta E_{\text{int}} - W_{\text{on}} = -\left[-nRT \ln\left(\frac{V_f}{V_i}\right) \right]$$

because $\Delta E_{\text{int}} = 0$ for an isothermal process.

Substitute to obtain:

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$$

$$= (2\,\text{mol})(8.314\,\text{J/mol} \cdot \text{K}) \ln\left(\frac{80\,\text{L}}{40\,\text{L}}\right)$$

$$= \boxed{11.5\,\text{J/K}}$$

(*b*) Because the process is reversible:

$$\Delta S_u = \boxed{0}$$

Remarks: The entropy change of the environment of the gas is −11.5 J/K.

49   •

Picture the Problem We can use the definition of entropy change and the 1$^{\text{st}}$ law of thermodynamics to express ΔS for the ideal gas as a function of its initial and final volumes.

(*a*) Use its definition to express the entropy change of the gas:

$$\Delta S = \frac{\Delta Q}{T}$$

Apply the first law of thermodynamics to the isothermal process:

$$\Delta Q = \Delta E_{int} - W_{on} = -\left[-nRT \ln\left(\frac{V_f}{V_i}\right) \right]$$

because $\Delta E_{int} = 0$ for an isothermal process.

Substitute to obtain:

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$$

$$= (2\,\text{mol})(8.314\,\text{J/mol} \cdot \text{K}) \ln\left(\frac{80\,\text{L}}{40\,\text{L}}\right)$$

$$= \boxed{11.5\,\text{J/K}}$$

(*b*) Because the process is not quasi-static, it is non-reversible:

$$\Delta S_u > \boxed{0}$$

50   •

Picture the Problem We can use the definition of entropy change to find the change in entropy of the water as it changes to steam.

Apply the definition of entropy change to obtain:

$$\Delta S = \frac{\Delta Q}{T} = \frac{mL_v}{T}$$

Substitute numerical values and evaluate ΔS:

$$\Delta S = \frac{(1\,\text{kg})(2.26\,\text{MJ/kg})}{373\,\text{K}} = \boxed{6.06\,\text{kJ/K}}$$

51   •

Picture the Problem We can use the definition of entropy change to find the change in entropy of the ice as it melts.

Apply the definition of entropy change to obtain:

$$\Delta S = \frac{\Delta Q}{T} = \frac{mL_f}{T}$$

Substitute numerical values and evaluate ΔS:

$$\Delta S = \frac{(1\,\text{kg})(333.5\,\text{kJ/kg})}{273\,\text{K}} = \boxed{1.22\,\text{kJ/K}}$$

52   ••

Picture the Problem We can use the first law of thermodynamics to find the change in the internal energy of the system and the change in the entropy of the system from the

change in entropy of the hot- and cold-reservoirs.

(a) Apply the 1st law of thermodynamics to find the change in the internal energy of the system:

$$\Delta E_{int} = Q_{in} + W_{on}$$
$$= (200\,J - 100\,J) - 50\,J$$
$$= \boxed{50\,J}$$

(b) Express the change in entropy of the system as the sum of the entropy changes of the high- and low-temperature reservoirs:

$$\Delta S = \Delta S_h - \Delta S_c = \frac{Q_h}{T_h} - \frac{Q_c}{T_c}$$
$$= \frac{200\,J}{300\,K} - \frac{100\,J}{200\,K} = \boxed{0.167\,J/K}$$

(c) Because the process is reversible:

$$\Delta S_u = \boxed{0}$$

(d) Because S_{system} is a state function:

$$\Delta E_{int} = \boxed{50\,J}, \ \Delta S = \boxed{0.167\,J/K},$$
and
$$\boxed{\Delta S_u > 0}$$

*53   ••

Picture the Problem We can use the fact that the system returns to its original state to find the entropy change for the complete cycle. Because the entropy change for the complete cycle is the sum of the entropy changes for each process, we can find the temperature T from the entropy changes during the 1st two processes and the heat rejected during the third.

(a) Because S is a state function of the system:

$$\Delta S_{complete\,cycle} = \boxed{0}$$

(b) Relate the entropy change for the complete cycle to the entropy change for each process:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T} = 0$$

Substitute numerical values to obtain:

$$\frac{300\,J}{300\,K} + \frac{200\,J}{400\,K} + \frac{-400\,J}{T} = 0$$

Solve for T:

$$T = \boxed{267\,K}$$

54   ••

Picture the Problem We can use the definition of entropy change and the 1st law of

thermodynamics to express ΔS for the ideal gas as a function of its initial and final volumes.

(a) Use its definition to express the entropy change of the gas:

$$\Delta S = \frac{\Delta Q}{T}$$

Apply the first law of thermodynamics to the isothermal process:

$$\Delta Q_{in} = \Delta E_{int} - W_{on} = -\left[-nRT \ln\left(\frac{V_f}{V_i}\right) \right]$$

because $\Delta E_{int} = 0$ for free expansion.

Substitute to obtain:

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$$

$$= (2\,\text{mol})(8.314\,\text{J/mol} \cdot \text{K}) \ln\left(\frac{80\,\text{L}}{40\,\text{L}}\right)$$

$$= \boxed{11.5\,\text{J/K}}$$

(b) Because the process is irreversible, $S_u > 0$ and, because no heat is exchanged:

$$\Delta S_u = \boxed{11.5\,\text{J/K}}$$

55 ••

Picture the Problem Because the ice gains heat as it melts, its entropy change is positive and can be calculated from its definition. Because the temperature of the lake is just slightly greater than 0°C and the mass of water is so much greater than that of the block of ice, the absolute value of the entropy change of the lake will be approximately equal to the entropy change of the ice as it melts.

(a) Use the definition of entropy change to find the entropy change of the ice:

$$\Delta S_{ice} = \frac{mL_f}{T} = \frac{(200\,\text{kg})(333.5\,\text{kJ/kg})}{273\,\text{K}}$$

$$= \boxed{244\,\text{kJ/K}}$$

(b) Relate the entropy change of the lake to the entropy change of the ice:

$$\Delta S_{lake} \approx -\Delta S_{ice} = \boxed{-244\,\text{kJ/K}}$$

(c) Because the temperature of the lake is slightly greater than that of the ice, the magnitude of the entropy change of the lake is less than 244 kJ/K and the entropy change of the universe is greater than zero. The melting of the ice is an irreversible process and $\boxed{\Delta S_u > 0}$.

56 ••

Picture the Problem We can use conservation of energy to find the equilibrium temperature of the water and apply the equations for the entropy change during a melting process and for constant-pressure processes to find the entropy change of the universe, i.e., the piece of ice and the water in the insulated container.

(*a*) Apply conservation of energy to obtain:

$$Q_{lost} = Q_{gained}$$

or

$$Q_{cooling\,water} = Q_{melting\,ice} + Q_{warming\,water}$$

Substitute to relate the masses of the ice and water to their temperatures, specific heats, and the final temperature of the water:

$$(100\,\text{g})(1\,\text{cal/g} \cdot \text{C}°)(100°\text{C} - t) = (100\,\text{g})(79.7\,\text{cal/g}) + (100\,\text{g})(1\,\text{cal/g} \cdot \text{C}°)(t)$$

Solve for *t* to obtain:

$$t = \boxed{10.2°\text{C}}$$

(*b*) Express the entropy change of the universe:

$$\Delta S_u = \Delta S_{ice} + \Delta S_{water}$$

Using the expression for the entropy change for a constant-pressure process, express the entropy change of the melting ice and warming ice-water:

$$\Delta S_{ice} = \Delta S_{melting\,ice} + \Delta S_{warming\,water}$$

$$= \frac{mL_f}{T_f} + mc_P \ln\!\left(\frac{T_f}{T_i}\right)$$

Substitute numerical values to obtain:

$$\Delta S_{ice} = \frac{(0.1\,\text{kg})(333.5\,\text{kJ/kg})}{273\,\text{K}} + (0.1\,\text{kg})(4.184\,\text{kJ/kg} \cdot \text{K})\ln\!\left(\frac{283.2\,\text{K}}{273\,\text{K}}\right) = 138\,\text{J/K}$$

Find the entropy change of the cooling water:

$$\Delta S_{water} = (0.1\,\text{kg})(4.18\,\text{kJ/kg} \cdot \text{K})\ln\!\left(\frac{283.2\,\text{K}}{373\,\text{K}}\right) = -115\,\text{J/K}$$

Substitute for ΔS_{ice} and ΔS_{water} and evaluate the entropy change of the universe:

$$\Delta S_u = 138\,\text{J/K} - 115\,\text{J/K}$$

$$= \boxed{23.0\,\text{J/K}}$$

Remarks: The result that $\Delta S_u > 0$ tells us that this process is irreversible.

*57 ••

Picture the Problem We can use conservation of energy to find the equilibrium temperature of the water and apply the equations for the entropy change during a constant pressure process to find the entropy changes of the copper block, the water, and the universe.

(*a*) Using the equation for the entropy change during a constant-pressure process, express the entropy change of the copper block:

$$\Delta S_{Cu} = m_{Cu}c_{Cu} \ln\left(\frac{T_f}{T_i}\right) \qquad (1)$$

Apply conservation of energy to obtain:

$$Q_{lost} = Q_{gained}$$

or

$$Q_{copper\ block} = Q_{warming\ water}$$

Substitute to relate the masses of the block and water to their temperatures, specific heats, and the final temperature T_f of the water:

$$(1\,\text{kg})(0.386\,\text{kJ/kg}\cdot\text{K})(373.15\,\text{K} - T_f) = (4\,\text{L})(1\,\text{kg/L})(4.184\ \text{kJ/kg}\cdot\text{K})(T_f - 273.15\,\text{K})$$

Solve for T_f:

$$T_f = 275.40\,\text{K}$$

Substitute numerical values in equation (1) and evaluate ΔS_{Cu}:

$$\Delta S_{Cu} = (1\,\text{kg})(0.386\,\text{kJ/kg}\cdot\text{K})\ln\left(\frac{275.40\,\text{K}}{373.15\,\text{K}}\right) = \boxed{-117\,\text{J/K}}$$

(*b*) Express the entropy change of the water:

$$\Delta S_{water} = m_{water}c_{water} \ln\left(\frac{T_f}{T_i}\right)$$

Substitute numerical values and evaluate ΔS_{water}:

$$\Delta S_{water} = (4\,\text{kg})(4.184\,\text{kJ/kg}\cdot\text{K})\ln\left(\frac{275.40\,\text{K}}{273.15\,\text{K}}\right) = \boxed{137\,\text{J/K}}$$

(*c*) Substitute for ΔS_{Cu} and ΔS_{water} and evaluate the entropy change of the universe:

$$\Delta S_u = \Delta S_{Cu} + \Delta S_{water}$$
$$= -117\,J/K + 137\,J/K$$
$$= \boxed{20.3\,J/K}$$

Remarks: The result that $\Delta S_u > 0$ tells us that this process is irreversible.

58 ••

Picture the Problem Because the mass of the water in the lake is so much greater than the mass of the piece of lead, the temperature of the lake will increase only slightly and we can reasonably assume that its final temperature is 10°C. We can apply the equation for the entropy change during a constant pressure process to find the entropy changes of the piece of lead, the water in the lake, and the universe.

Express the entropy change of the universe in terms of the entropy changes of the lead and the water in the lake:

$$\Delta S_u = \Delta S_{Pb} + \Delta S_w$$

Using the equation for the entropy change during a constant-pressure process, express and evaluate the entropy change of the lead:

$$\Delta S_{Pb} = m_{Pb}c_{Pb}\,\ln\!\left(\frac{T_f}{T_i}\right) = (2\,kg)(0.128\,kJ/kg\cdot K)\ln\!\left(\frac{283.15\,K}{373.15\,K}\right) = -70.66\,J/K$$

Find the entropy change of the water in the lake:

$$\Delta S_w = \frac{Q_w}{T_w} = \frac{Q_{Pb}}{T_w} = \frac{m_{Pb}c_{Pb}\Delta T_{Pb}}{T_w}$$
$$= \frac{(2\,kg)(0.128\,kJ/kg\cdot K)(90\,K)}{283.15\,K}$$
$$= 81.37\,J/K$$

Substitute and evaluate ΔS_u:

$$\Delta S_u = -70.66\,J/K + 81.37\,J/K$$
$$= \boxed{10.7\,J/K}$$

59 ••

Picture the Problem Because the air temperature will not change appreciably as a result of this crash; we can assume that the kinetic energy of the car is transformed into heat at a temperature of 20°C. We can use the definition of entropy change to find the entropy change of the universe.

Express the entropy change of the universe as a consequence of the kinetic energy of the car being transformed into heat:

$$\Delta S_{\mathrm{u}} = \frac{Q}{T} = \frac{\frac{1}{2}mv^2}{T}$$

Substitute numerical values and evaluate ΔS_{u}:

$$\Delta S_{\mathrm{u}} = \frac{\frac{1}{2}(1500\,\mathrm{kg})\left(100\dfrac{\mathrm{km}}{\mathrm{h}} \times \dfrac{1\mathrm{h}}{3600\,\mathrm{s}}\right)^2}{293.15\,\mathrm{K}}$$

$$= \boxed{1.97\,\mathrm{kJ/K}}$$

*60 ••
Picture the Problem The total change in entropy resulting from the mixing of these gases is the sum of the changes in their entropies.

(*a*) Express the total change in entropy resulting from the mixing of the gases:

$$\Delta S = \Delta S_{\mathrm{A}} + \Delta S_{\mathrm{B}}$$

Express the change in entropy of each of the gases:

$$\Delta S_{\mathrm{A}} = nR\ln\!\left(\frac{V_{\mathrm{fA}}}{V_{\mathrm{iA}}}\right)$$

and

$$\Delta S_{\mathrm{B}} = nR\ln\!\left(\frac{V_{\mathrm{fB}}}{V_{\mathrm{iB}}}\right)$$

Because the initial and final volumes of the gases are the same and both volumes double:

$$\Delta S = 2nR\ln\!\left(\frac{V_{\mathrm{f}}}{V_{\mathrm{i}}}\right) = 2nR\ln(2)$$

Substitute numerical values and evaluate ΔS:

$$\Delta S = 2(1\,\mathrm{mol})(8.314\,\mathrm{J/mol}\cdot\mathrm{K})\ln(2)$$

$$= \boxed{11.5\,\mathrm{J/K}}$$

> Because the gas molecules are indistinguishable, the entropy doesn't change.
> (*b*) A complete description of this phonomenon has been derived using quantum mechanics.

Entropy and Work Lost

*61 ••
Picture the Problem We can find the entropy change of the universe from the entropy changes of the high- and low-temperature reservoirs. The maximum amount of the 500 J of heat that could be converted into work can be found from the maximum efficiency of an engine operating between the two reservoirs.

(*a*) Express the entropy change of the universe:

$$\Delta S_u = \Delta S_h + \Delta S_c = -\frac{Q}{T_h} + \frac{Q}{T_c}$$

$$= -Q\left(\frac{1}{T_h} - \frac{1}{T_c}\right)$$

Substitute numerical values and evaluate ΔS_u:

$$\Delta S_u = \left(-500\,\text{J}\right)\left(\frac{1}{400\,\text{K}} - \frac{1}{300\,\text{K}}\right)$$

$$= \boxed{0.417\,\text{J/K}}$$

(*b*) Express the heat that could have been converted into work in terms of the maximum efficiency of an engine operating between the two reservoirs:

$$W = \varepsilon_{max} Q_h$$

Express the maximum efficiency of an engine operating between the two reservoir temperatures:

$$\varepsilon_{max} = \varepsilon_C = 1 - \frac{T_c}{T_h}$$

Substitute and evaluate W:

$$W = \left(1 - \frac{T_c}{T_h}\right)Q_h = \left(1 - \frac{300\,\text{K}}{400\,\text{K}}\right)\left(500\,\text{J}\right)$$

$$= \boxed{125\,\text{J}}$$

62   ••

Picture the Problem Although in the adiabatic free expansion no heat is lost by the gas, the process is irreversible and the entropy of the gas increases. In the isothermal reversible process that returns the gas to its original state, the gas releases heat to the surroundings. However, because the process is reversible, the entropy change of the universe is zero. Consequently, the net entropy change is the negative of that of the gas in the isothermal compression.

(*a*) Relate the entropy change of the universe to the entropy change of the gas during the isothermal compression:

$$\Delta S_u = -\Delta S_{gas} = -nR\ln\left(\frac{V_f}{V_i}\right)$$

Substitute numerical values and evaluate ΔS_u:

$$\Delta S_u = -(1\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})\ln\left(\frac{12.3\,\text{L}}{24.6\,\text{L}}\right) = \boxed{5.76\,\text{J/K}}$$

(b) | To the extent that the initial expansion was isothermal and reversible, no work was done and none was wasted in the cycle.

(c) Express the wasted work in terms of T and the entropy change of the universe:

$$W_{\text{lost}} = T\Delta S_u = (300\,\text{K})(5.76\,\text{J/K})$$
$$= \boxed{1.73\,\text{kJ}}$$

General Problems

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Picture the Problem We can use the definition of power to find the work done each cycle and the definition of efficiency to find the heat that is absorbed each cycle. Application of the first law of thermodynamics will yield the heat given off each cycle.

(a) Use the definition of power to relate the work done in each cycle to the period of each cycle:

$$W_{\text{cycle}} = P\Delta t = (200\,\text{W})(0.1\,\text{s})$$
$$= \boxed{20.0\,\text{J}}$$

(b) Express the heat absorbed in each cycle in terms of the work done and the efficiency of the engine:

$$Q_{\text{h,cycle}} = \frac{W_{\text{cycle}}}{\varepsilon} = \frac{20\,\text{J}}{0.3} = \boxed{66.7\,\text{J}}$$

Apply the 1$^{\text{st}}$ law of thermodynamics to find the heat given off in each cycle:

$$\left|Q_{\text{c,cycle}}\right| = Q_{\text{h,cycle}} - W = 66.7\,\text{J} - 20\,\text{J}$$
$$= \boxed{46.7\,\text{J}}$$

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Picture the Problem We can use their definitions to find the efficiency of the engine and that of a Carnot engine operating between the same reservoirs.

(a) Apply the definition of efficiency:

$$\varepsilon = \frac{W}{Q_h} = 1 - \frac{\left|Q_c\right|}{Q_h} = 1 - \frac{125\,\text{J}}{150\,\text{J}} = \boxed{16.7\%}$$

(b) Find the efficiency of a Carnot engine operating between the same reservoirs:

$$\varepsilon_C = 1 - \frac{T_c}{T_h} = 1 - \frac{293.15}{373.15} = 21.4\%$$

Express the ratio of the two efficiencies:

$$\frac{\varepsilon}{\varepsilon_C} = \frac{16.7\%}{21.4\%} = \boxed{0.780}$$

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Picture the Problem We can use the definition of efficiency to find the work done by the engine during each cycle and the first law of thermodynamics to find the heat exhausted in each cycle.

(a) Express the efficiency of the engine in terms of the efficiency of a Carnot engine working between the same reservoirs:

$$\varepsilon = 0.85\varepsilon_C = 0.85\left(1 - \frac{T_c}{T_h}\right)$$

$$= 0.85\left(1 - \frac{200\,\text{K}}{500\,\text{K}}\right) = \boxed{51.0\%}$$

(b) Use the definition of efficiency to find the work done in each cycle:

$$W = \varepsilon Q_h = 0.51(200\,\text{kJ}) = \boxed{102\,\text{kJ}}$$

(c) Apply the first law of thermodynamics to the cycle to obtain:

$$\left|Q_{c,cycle}\right| = Q_{h,cycle} - W = 200\,\text{kJ} - 102\,\text{kJ}$$

$$= \boxed{98.0\,\text{kJ}}$$

*66   ••

Picture the Problem We can use the expression for the Carnot efficiency of the plant to find the highest efficiency this plant can have. We can then use this efficiency to find the power that must be supplied to the plant to generate 1 GW of power and, from this value, the power that is wasted. The rate at which heat is being delivered to the river is related to the requisite flow rate of the river by $dQ/dt = c\Delta T\rho\, dV/dt$.

(a) Express the Carnot efficiency of a plant operating between temperatures T_c and T_h:

$$\varepsilon_{max} = \varepsilon_C = 1 - \frac{T_c}{T_h}$$

Substitute numerical values and evaluate ε_C:

$$\varepsilon_{max} = 1 - \frac{298\,\text{K}}{500\,\text{K}} = \boxed{0.404}$$

(c) Find the power that must be supplied, at 40.4% efficiency, to produce an output of 1 GW:

$$P_{supplied} = \frac{P_{output}}{\varepsilon_{max}} = \frac{1\,\text{GW}}{0.404} = \boxed{2.48\,\text{GW}}$$

(*b*) Relate the wasted power to the power generated and the power supplied:

$$P_{wasted} = P_{supplied} - P_{generated}$$

Substitute numerical values and evaluate P_{wasted}:

$$P_{wasted} = 2.48\,GW - 1\,GW = \boxed{1.48\,GW}$$

(*d*) Express the rate at which heat is being dumped into the river:

$$\frac{dQ}{dt} = c\Delta T \frac{dm}{dt} = c\Delta T \frac{d}{dt}(\rho V)$$

$$= c\Delta T \rho \frac{dV}{dt}$$

Solve for the flow rate dV/dt of the river:

$$\frac{dV}{dt} = \frac{dQ/dt}{c\Delta T \rho}$$

Substitute numerical values (see Table 19-1 for the specific heat of water) and evaluate dV/dt:

$$\frac{dV}{dt} = \frac{1.48\times10^9\,J/s}{(4180\,J/kg)(0.5\,K)(10^3\,kg/m^3)}$$

$$= 708\,m^3/s = \boxed{7.08\times10^5\,L/s}$$

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Picture the Problem We can find the rate at which the house contributes to the increase in the entropy of the universe from the ratio of ΔS to Δt.

Using the definition of entropy change, express the rate of increase in the entropy of the universe:

$$\frac{\Delta S}{\Delta t} = \frac{\Delta Q/T}{\Delta t} = \frac{\Delta Q/\Delta t}{T}$$

Substitute numerical values and evaluate $\Delta S/\Delta t$:

$$\frac{\Delta S}{\Delta t} = \frac{30\,kW}{266\,K} = \boxed{113\,W/K}$$

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Picture the Problem Because the cycle represented in Figure 19-12 is a Carnot cycle, its efficiency is that of a Carnot engine operating between the temperatures of its isotherms.

Express the Carnot efficiency of the cycle:

$$\varepsilon_C = 1 - \frac{T_c}{T_h}$$

Substitute numerical values and evaluate ε_C:

$$\varepsilon_C = 1 - \frac{300\,K}{750\,K} = \boxed{60.0\%}$$

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Picture the Problem All 500 J of mechanical energy are lost, i.e., transformed into heat in process (1). For process (2), we can find the heat that would be converted to work by a Carnot engine operating between the given temperatures and subtract amount of work from 1 kJ to find the energy that is lost. In part (*b*) we can use its definition to find the change in entropy for each process.

(*a*) For process (2):

$$W_{2,\max} = W_{\text{recovered}} = \varepsilon_C Q_{\text{in}}$$

Find the efficiency of a Carnot engine operating between 400 K and 300 K:

$$\varepsilon_C = 1 - \frac{T_c}{T_h} = 1 - \frac{300\,K}{400\,K} = 0.25$$

Substitute to obtain:

$$W_{\text{recovered}} = 0.25(1\,\text{kJ}) = 250\,\text{J}$$

or

750 J are lost.

> Process (1) is more wasteful of *mechanical* energy. Process (2) is more wasteful of *total* energy.

(*b*) Find the change in entropy of the universe for process (1):

$$\Delta S_1 = \frac{\Delta Q}{T} = \frac{500\,\text{J}}{300\,\text{K}} = \boxed{1.67\,\text{J/K}}$$

Express the change in entropy of the universe for process (2):

$$\Delta S_2 = \Delta S_h + \Delta S_c = -\frac{\Delta Q}{T_h} + \frac{\Delta Q}{T_c}$$

$$= \Delta Q \left(\frac{1}{T_c} - \frac{1}{T_h} \right)$$

Substitute numerical values and evaluate ΔS_2:

$$\Delta S_2 = (1\,\text{kJ}) \left(\frac{1}{300\,\text{K}} - \frac{1}{400\,\text{K}} \right)$$

$$= \boxed{0.833\,\text{J/K}}$$

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Picture the Problem Denote the three states of the gas as 1, 2, and 3 with 1 being the initial state. We can use the ideal-gas law and the equation of state for an adiabatic process to find the temperatures, volumes, and pressures at points 1, 2, and 3. To find the work done during each cycle, we can use the equations for the work done during isothermal, isobaric, and adiabatic processes. Finally, we find the efficiency of the cycle from the work done each cycle and the heat that enters the system during the isothermal expansion.

(a) Apply the ideal-gas law to the isothermal expansion $1 \rightarrow 2$ to find P_2:

$$P_2 = P_1 \frac{V_1}{V_2} = (16\,\text{atm})\frac{1\,\text{L}}{4\,\text{L}} = 4\,\text{atm}$$
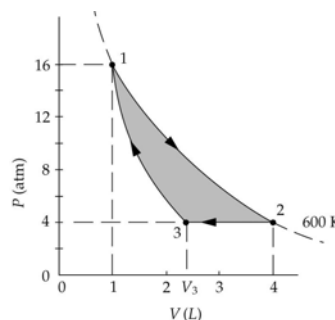
Apply the equation of state for an adiabatic process to relate the pressures and volumes at 1 and 3:

$$P_1 V_1^{\gamma} = P_3 V_3^{\gamma}$$

and

$$V_3 = V_1 \left(\frac{P_1}{P_3}\right)^{1/\gamma} = (1\,\text{L})\left(\frac{16\,\text{atm}}{4\,\text{atm}}\right)^{1/1.67}$$

$$= 2.29\,\text{L}$$

The *PV* diagram is shown to the right:

(b) From (a) we have:

$$V_3 = \boxed{2.29\,\text{L}}$$

Apply the equation of state for an adiabatic process ($\gamma = 1.67$) to relate the temperatures and volumes at 1 and 3:

$$T_3 V_3^{\gamma-1} = T_1 V_1^{\gamma-1}$$

and

$$T_3 = T_1 \left(\frac{V_1}{V_3}\right)^{\gamma-1} = (600\,\text{K})\left(\frac{1\,\text{L}}{2.29\,\text{L}}\right)^{1.67-1}$$

$$= \boxed{344\,\text{K}}$$

(c) Express the work done each cycle:

$$W = W_{1 \rightarrow 2} + W_{2 \rightarrow 3} + W_{3 \rightarrow 1} \qquad (1)$$

For the process $1 \rightarrow 2$:

$$W_{1 \rightarrow 2} = nRT_1 \ln\left(\frac{V_2}{V_1}\right) = P_1 V_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$= (16\,\text{atm})(1\,\text{L})\ln\left(\frac{4\,\text{L}}{1\,\text{L}}\right)$$

$$= 22.2\,\text{atm}\cdot\text{L}$$

For the process $2 \rightarrow 3$:

$$W_{2 \rightarrow 3} = P_2 \Delta V_{2 \rightarrow 3}$$

$$= (4\,\text{atm})(2.29\,\text{L} - 4\,\text{L})$$

$$= -6.84\,\text{atm}\cdot\text{L}$$

For the process 3→1:

$$W_{3\to1} = -C_V\Delta T_{3\to1} = -\tfrac{3}{2}nR(T_1 - T_3)$$
$$= -\tfrac{3}{2}(P_1V_1 - P_3V_3)$$
$$= -\tfrac{3}{2}[(16\,\text{atm})(1\,\text{L}) - (4\,\text{atm})(2.29\,\text{L})]$$
$$= -10.3\,\text{atm}\cdot\text{L}$$

Substitute numerical values in equation (1) and evaluate W:

$$W = 22.2\,\text{atm}\cdot\text{L} - 6.84\,\text{atm}\cdot\text{L}$$
$$-10.3\,\text{atm}\cdot\text{L}$$
$$= \boxed{5.06\,\text{atm}\cdot\text{L}}$$

(d) Using its definition, express and evaluate the efficiency of the cycle:

$$\varepsilon = \frac{W}{Q_{\text{in}}} = \frac{W}{Q_{1\to2}} = \frac{W}{W_{1\to2}}$$
$$= \frac{5.06\,\text{atm}\cdot\text{L}}{22.2\,\text{atm}\cdot\text{L}} = \boxed{22.8\%}$$

*71   ••

Picture the Problem We can express the temperature of the cold reservoir as a function of the Carnot efficiency of an ideal engine and, given that the efficiency of the heat engine is half that of a Carnot engine, relate T_c to the work done by and the heat input to the real heat engine.

Using its definition, relate the efficiency of a Carnot engine working between the same reservoirs to the temperature of the cold reservoir:

$$\varepsilon_C = 1 - \frac{T_c}{T_h}$$

Solve for T_c:

$$T_c = T_h(1 - \varepsilon_C)$$

Relate the efficiency of the heat engine to that of a Carnot engine working between the same temperatures:

$$\varepsilon = \frac{W}{Q_{\text{in}}} = \tfrac{1}{2}\varepsilon_C \text{ or } \varepsilon_C = \frac{2W}{Q_{\text{in}}}$$

Substitute to obtain:

$$T_c = T_h\left(1 - \frac{2W}{Q_{\text{in}}}\right)$$

The work done by the gas in expanding the balloon is:

$$W = P\Delta V = (1\,\text{atm})(4\,\text{L}) = 4\,\text{atm}\cdot\text{L}$$

Substitute numerical values and evaluate T_c:

$$T_c = (393.15\,\text{K}) \left(1 - \frac{2\left(4\,\text{atm}\cdot\text{L} \times \dfrac{101.325\,\text{J}}{\text{atm}\cdot\text{L}}\right)}{4\,\text{kJ}} \right) = \boxed{313\,\text{K}}$$

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Picture the Problem We can use the definitions of the COP and ε_C to show that their relationship is $\text{COP} = T_c / (\varepsilon_C T_h)$.

Using the definition of the COP, relate the heat removed from the cold reservoir to the work done each cycle:

$$\text{COP} = \frac{Q_c}{W}$$

Apply energy conservation to relate Q_c, Q_h, and W:

$$Q_c = Q_h - W$$

Substitute to obtain:

$$\text{COP} = \frac{Q_h - W}{W}$$

Divide numerator and denominator by Q_h and simplify to obtain:

$$\text{COP} = \frac{Q_h - W}{W} = \frac{1 - \dfrac{W}{Q_h}}{\dfrac{W}{Q_h}}$$

Because $\varepsilon_C = W/Q_h$:

$$\text{COP} = \frac{1 - \varepsilon_C}{\varepsilon_C} = \frac{1 - \left(1 - \dfrac{T_c}{T_h}\right)}{\varepsilon_C} = \frac{\dfrac{T_c}{T_h}}{\varepsilon_C}$$

$$= \boxed{\frac{T_c}{\varepsilon_C T_h}}$$

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Picture the Problem We can use the definition of the COP to express the work the motor must do to maintain the temperature of the freezer in terms of the rate at which heat flows into the freezer. Differentiation of this expression with respect to time will yield an expression for the power of the motor that is needed to maintain the temperature in the freezer.

Using the definition of the COP, relate the heat that must be removed from the freezer to the work done by the motor:

$$\text{COP} = \frac{Q_c}{W}$$

Solve for W:

$$W = \frac{Q_c}{\text{COP}}$$

Differentiate this expression with respect to time to express the power of the motor:

$$P = \frac{dW}{dt} = \frac{dQ_c/dt}{\text{COP}}$$

Express the maximum COP of the motor:

$$\text{COP}_{max} = \frac{T_c}{\Delta T}$$

Substitute to obtain:

$$P = \frac{dQ_c}{dt}\frac{\Delta T}{T_c}$$

Substitute numerical values and evaluate P:

$$P = (50\,\text{W})\left(\frac{50\,\text{K}}{250\,\text{K}}\right) = \boxed{10.0\,\text{W}}$$

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Picture the Problem We can use the ideal-gas law to find the unknown temperatures, pressures, and volumes at points A, B, and C and then find the work done by the gas and the efficiency of the cycle by using the expressions for the work done on or by the gas and the heat that enters the system for the isobaric, adiabatic, and isothermal processes of the cycle.

(*a*) Apply the ideal-gas law to find the volume of the gas at A:

$$V_A = \frac{nRT_A}{P_A}$$
$$= \frac{(2\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})(600\,\text{K})}{5\,\text{atm} \times \dfrac{101.325\,\text{kPa}}{\text{atm}}}$$
$$= \boxed{19.7\,\text{L}}$$

(*b*) We're given that:

$$V_B = 2V_A = 2(19.7\,\text{L}) = \boxed{39.4\,\text{L}}$$

Apply the ideal-gas law to this isobaric process to obtain:

$$T_B = T_A\frac{V_B}{V_A} = (600\,\text{K})\frac{2V_A}{V_A} = \boxed{1200\,\text{K}}$$

(c) Because the process C→A is isothermal:

$$T_C = T_A = \boxed{600\,\text{K}}$$

(d) Apply the equation of state for an adiabatic process ($\gamma = 1.4$) to find the volume of the gas at C:

$$T_B V_B^{\gamma-1} = T_C V_C^{\gamma-1}$$

and

$$V_C = V_B \left(\frac{T_B}{T_C}\right)^{\frac{1}{\gamma-1}} = (39.4\,\text{L})\left(\frac{1200\,\text{K}}{600\,\text{K}}\right)^{\frac{1}{1.4-1}}$$

$$= \boxed{223\,\text{L}}$$

(e) Express and evaluate the work done by the gas during the isobaric process AB:

$$W_{A-B} = P_A(V_B - V_A) = P_A(2V_A - V_A)$$
$$= P_A V_A = (5\,\text{atm})(19.7\,\text{L})$$
$$= 98.50\,\text{atm}\cdot\text{L} \times \frac{101.325\,\text{J}}{\text{atm}\cdot\text{L}}$$
$$= \boxed{9.98\,\text{kJ}}$$

Apply the first law of thermodynamics to express the work done by the gas during the adiabatic expansion BC:

$$W_{\text{on, B-C}} = \Delta E_{\text{int,B-C}} - Q_{\text{in, B-C}} = \Delta E_{\text{int, B-C}} - 0$$
$$= \Delta E_{\text{int, B-C}} = -nc_V \Delta T_{\text{B-C}}$$
$$= -\tfrac{5}{2}nR\Delta T_{\text{B-C}}$$

Substitute numerical values and evaluate $W_{\text{B-C}}$:

$$W_{\text{B-C}} = -\tfrac{5}{2}(2\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})(600\,\text{K} - 1200\,\text{K}) = \boxed{24.9\,\text{kJ}}$$

The work done by the gas during the isothermal compression CA is:

$$W_{\text{C-A}} = nRT_C \ln\left(\frac{V_A}{V_C}\right) = (2\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})(600\,\text{K})\ln\left(\frac{19.7\,\text{L}}{223\,\text{L}}\right) = \boxed{-24.2\,\text{kJ}}$$

(f) The heat absorbed during the isobaric expansion AB is:

$$Q_{\text{A-B}} = nc_P\Delta T_{\text{A-B}} = \tfrac{7}{2}nR\Delta T_{\text{A-B}} = \tfrac{7}{2}(2\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})(1200\,\text{K} - 600\,\text{K})$$
$$= \boxed{34.9\,\text{kJ}}$$

The heat absorbed during the adiabatic expansion BC is:

$$Q_{\text{B-C}} = \boxed{0}$$

Use the first law of thermodynamics to find the heat absorbed during the isothermal compression CA:

$$Q_{C-A} = W_{C-A} + \Delta E_{int, C-A} = W_{C-A}$$
$$= \boxed{-24.2\,\text{kJ}}$$

because $\Delta E_{int,C-A} = 0$ for an isothermal process.

(g) The thermodynamic efficiency ε is:

$$\varepsilon = \frac{W}{Q_{in}} = \frac{W_{A-B} + W_{B-C} + W_{C-A}}{Q_{A-B}}$$

Substitute numerical values and evaluate ε:

$$\varepsilon = \frac{9.98\,\text{kJ} + 24.9\,\text{kJ} - 24.2\,\text{kJ}}{34.9\,\text{kJ}}$$
$$= \boxed{30.6\%}$$

75   ••

Picture the Problem We can use the ideal-gas law to find the unknown temperatures, pressures, and volumes at points B, C, and D and then find the work done by the gas and the efficiency of the cycle by using the expressions for the work done on or by the gas and the heat that enters the system for the various thermodynamic processes of the cycle.

(a) Apply the ideal-gas law for a fixed amount of gas to the isothermal process AB:

$$P_B = P_A \frac{V_A}{V_B} = (5\,\text{atm})\frac{V_A}{2V_A}$$
$$= 2.50\,\text{atm} \times \frac{101.325\,\text{kPa}}{1\,\text{atm}}$$
$$= \boxed{253\,\text{kPa}}$$

(b) Apply the ideal-gas law for a fixed amount of gas to the adiabatic process BC:

$$T_C = T_B \frac{P_C V_C}{P_B V_B}$$

Using the ideal-gas law, find the volume at B:

$$V_B = \frac{nRT_B}{P_B}$$
$$= \frac{(2\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})(600\,\text{K})}{253\,\text{kPa}}$$
$$= 39.43\,\text{L}$$

Use the equation of state for an adiabatic process and $\gamma = 1.4$ to find the volume occupied by the gas at C:

$$V_C = V_B \left(\frac{P_B}{P_C}\right)^{1/\gamma} = (39.43\,\text{L})\left(\frac{2.5\,\text{atm}}{1\,\text{atm}}\right)^{1/1.4}$$
$$= 75.87\,\text{L}$$

Substitute and evaluate T_C:

$$T_C = (600\,\text{K})\frac{(1\,\text{atm})(75.87\,\text{L})}{(2.5\,\text{atm})(39.43\,\text{L})}$$

$$= \boxed{462\,\text{K}}$$

(c) Express the work done by the gas in one cycle:

$$W = W_{A-B} + W_{B-C} + W_{C-D} + W_{D-A}$$

The work done during the isothermal expansion AB is:

$$W_{A-B} = nRT_A \ln\left(\frac{V_B}{V_A}\right) = (2\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})(600\,\text{K})\ln\left(\frac{2V_A}{V_A}\right) = 6.915\,\text{kJ}$$

The work done during the adiabatic expansion BC is:

$$W_{B-C} = -C_V\Delta T_{B-C} = -\tfrac{5}{2}nR\Delta T_{B-C} = -\tfrac{5}{2}(2\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})(462\,\text{K} - 600\,\text{K})$$
$$= 5.737\,\text{kJ}$$

The work done during the isobaric compression CD is:

$$W_{C-D} = P_C(V_D - V_C) = (1\,\text{atm})(19.7\,\text{L} - 75.87\,\text{L}) = -56.17\,\text{atm}\cdot\text{L} \times \frac{101.325\,\text{J}}{\text{atm}\cdot\text{L}}$$
$$= -5.690\,\text{kJ}$$

Express and evaluate the work done during the constant-volume process DA:

$$W_{D-A} = 0$$

Substitute numerical values and evaluate W:

$$W = 6.915\,\text{kJ} + 5.737\,\text{kJ} - 5.690\,\text{kJ} + 0$$

$$= \boxed{6.96\,\text{kJ}}$$

Using its definition, express the thermodynamic efficiency of the cycle:

$$\varepsilon = \frac{W}{Q_{in}} = \frac{W}{Q_{A-B} + Q_{D-A}} \qquad (1)$$

Express and evaluate the heat entering the system during the isothermal process AB:

$$Q_{A-B} = W_{A-B} + \Delta E_{int,\,A-B} = W_{A-B} = 6.915\,\text{kJ}$$

Because $\Delta E_{int} = 0$ for an isothermal process.

Express the heat entering the system

$$Q_{D-A} = C_V\Delta T_{D-A} = \tfrac{5}{2}nR\Delta T_{D-A}$$

during the constant-volume process DA:

Apply the ideal-gas law to the constant-volume process DA to obtain:

$$T_D = T_A \frac{P_D}{P_A} = (600\,\text{K})\frac{1\,\text{atm}}{5\,\text{atm}} = 120\,\text{K}$$

The heat entering the system during the process DA is:

$$Q_{D\text{-}A} = \tfrac{5}{2}(2\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})(600\,\text{K}-120\,\text{K}) = 20.0\,\text{kJ}$$

Substitute numerical values in equation (1) and evaluate the efficiency of the cycle:

$$\varepsilon = \frac{6.975\,\text{kJ}}{6.915\,\text{kJ}+20.0\,\text{kJ}} = \boxed{25.9\%}$$

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Picture the Problem We can use the ideal-gas law to find the unknown temperatures, pressures, and volumes at points A, B, and C and then find the work done by the gas and the efficiency of the cycle by using the expressions for the work done on or by the gas and the heat that enters the system for the isobaric, adiabatic, and isothermal processes of the cycle.

(*a*) Apply the ideal-gas law to find the volume of the gas at A:

$$V_A = \frac{nRT_A}{P_A}$$
$$= \frac{(2\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})(600\,\text{K})}{5\,\text{atm}\times\dfrac{101.325\,\text{kPa}}{\text{atm}}}$$
$$= \boxed{19.7\,\text{L}}$$

(*b*) We're given that:

$$V_B = 2V_A = 2(19.7\,\text{L}) = \boxed{39.4\,\text{L}}$$

Apply the ideal-gas law to this isobaric process to obtain:

$$T_B = T_A \frac{V_B}{V_A} = (600\,\text{K})\frac{2V_A}{V_A} = \boxed{1200\,\text{K}}$$

(*c*) Because the process CA is isothermal:

$$T_C = T_A = \boxed{600\,\text{K}}$$

(*d*) Apply the equation of state for an adiabatic process ($\gamma = 5/3$) to find the volume of the gas at C:

$$T_B V_B^{\gamma-1} = T_C V_C^{\gamma-1}$$

and

$$V_C = V_B \left(\frac{T_B}{T_C} \right)^{\frac{1}{\gamma - 1}} = (39.4 \, L) \left(\frac{1200 \, K}{600 \, K} \right)^{\frac{3}{2}}$$

$$= \boxed{111 \, L}$$

(*e*) Express and evaluate the work done by the gas during the isobaric process AB:

$$W_{A-B} = P_A (V_B - V_A) = P_A (2V_A - V_A)$$
$$= P_A V_A = (5 \, atm)(19.7 \, L)$$
$$= 98.50 \, atm \cdot L \times \frac{101.325 \, J}{atm \cdot L}$$
$$= \boxed{9.98 \, kJ}$$

Apply the first law of thermodynamics to express the work done by the gas during the adiabatic expansion BC:

$$W_{on, B-C} = \Delta E_{int, B-C} - Q_{in, B-C}$$
$$= \Delta E_{int, B-C} - 0$$
$$= \Delta E_{int, B-C} = -(nc_V \Delta T_{B-C})$$
$$= -\tfrac{3}{2} nR\Delta T_{B-C}$$

Substitute numerical values and evaluate W_{B-C}:

$$W_{on, B-C} = -\tfrac{3}{2}(2 \, mol)(8.314 \, J/mol \cdot K)(600 \, K - 1200 \, K) = \boxed{14.9 \, kJ}$$

The work done by the gas during the isothermal compression CA is:

$$W_{C-A} = nRT_C \ln \left(\frac{V_A}{V_C} \right) = (2 \, mol)(8.314 \, J/mol \cdot K)(600 \, K) \ln \left(\frac{19.7 \, L}{111 \, L} \right)$$
$$= \boxed{-17.2 \, kJ}$$

(*f*) The heat absorbed during the isobaric expansion AB is:

$$Q_{in, A-B} = nc_P \Delta T_{A-B} = \tfrac{5}{2} nR\Delta T_{A-B} = \tfrac{5}{2}(2 \, mol)(8.314 \, J/mol \cdot K)(1200 \, K - 600 \, K)$$
$$= \boxed{24.9 \, kJ}$$

Express and evaluate the heat absorbed during the adiabatic expansion BC:

$$Q_{B-C} = \boxed{0}$$

Use the first law of thermodynamics to express and evaluate the heat absorbed during the isothermal compression CA:

$$Q_{C-A} = W_{C-A} + \Delta E_{int,\, C-A} = W_{C-A}$$
$$= \boxed{-17.2\,kJ}$$

because $\Delta E_{int} = 0$ for an isothermal process.

(g) The definition of thermodynamic efficiency ε is:

$$\varepsilon = \frac{W}{Q_{in}} = \frac{W_{A-B} + W_{B-C} + W_{C-A}}{Q_{A-B}}$$

Substitute numerical values and evaluate ε:

$$\varepsilon = \frac{9.98\,kJ + 14.9\,kJ - 17.2\,kJ}{24.9\,kJ}$$
$$= \boxed{30.8\%}$$

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Picture the Problem We can use the ideal-gas law to find the unknown temperatures, pressures, and volumes at points B, C, and D and then find the work done by the gas and the efficiency of the cycle by using the expressions for the work done on or by the gas and the heat that enters the system for the various thermodynamic processes of the cycle.

(a) Apply the ideal-gas law for a fixed amount of gas to the isothermal process AB:

$$P_B = P_A \frac{V_A}{V_B} = (5\,atm)\frac{V_A}{2V_A}$$
$$= 2.50\,atm \times \frac{101.3\,kPa}{1\,atm} = \boxed{253\,kPa}$$

(b) Apply the ideal-gas law for a fixed amount of gas to the adiabatic process BC:

$$T_C = T_B \frac{P_C V_C}{P_B V_B}$$

Using the ideal-gas law, find the volume at B:

$$V_B = \frac{nRT_B}{P_B}$$
$$= \frac{(2\,mol)(8.314\,J/mol \cdot K)(600\,K)}{253\,kPa}$$
$$= 39.43\,L$$

Use the equation of state for an adiabatic process and $\gamma = 5/3$ to find the volume occupied by the gas at C:

$$V_C = V_B \left(\frac{P_B}{P_C}\right)^{1/\gamma} = (39.43\,L)\left(\frac{2.5\,atm}{1\,atm}\right)^{3/5}$$
$$= 68.33\,L$$

Substitute and evaluate T_C:

$$T_C = (600\,\text{K})\frac{(1\,\text{atm})(68.33\,\text{L})}{(2.5\,\text{atm})(39.43\,\text{L})}$$

$$= \boxed{416\,\text{K}}$$

(c) Express the work done by the gas in one cycle:

$$W = W_{A-B} + W_{B-C} + W_{C-D} + W_{D-A} \quad (1)$$

The work done during the isothermal expansion AB is:

$$W_{A-B} = nRT_A \ln\left(\frac{V_B}{V_A}\right) = (2\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})(600\,\text{K})\ln\left(\frac{2V_A}{V_A}\right) = 6.915\,\text{kJ}$$

The work done during the adiabatic expansion BC is:

$$W_{B-C} = -C_V \Delta T_{B-C} = -\tfrac{5}{2}nR\Delta T_{B-C} = -\tfrac{3}{2}(2\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})(416\,\text{K} - 600\,\text{K})$$

$$= 4.589\,\text{kJ}$$

The work done during the isobaric compression CD is:

$$W_{C-D} = P_C(V_D - V_C) = (1\,\text{atm})(19.7\,\text{L} - 68.33\,\text{L}) = -48.63\,\text{atm}\cdot\text{L} \times \frac{101.3\,\text{J}}{\text{atm}\cdot\text{L}}$$

$$= -4.926\,\text{kJ}$$

The work done during the constant-volume process DA is:

$$W_{D-A} = 0$$

Substitute numerical values in equation (1) to obtain:

$$W = 6.915\,\text{kJ} + 4.589\,\text{kJ} - 4.926\,\text{kJ} + 0$$

$$= \boxed{6.58\,\text{kJ}}$$

The thermodynamic efficiency of the cycle is given by:

$$\varepsilon = \frac{W}{Q_{\text{in}}} = \frac{W}{Q_{A-B} + Q_{D-A}} \quad (2)$$

The heat entering the system during the isothermal process AB is:

$$Q_{A-B} = W_{A-B} + \Delta E_{\text{int}, A-B} = W_{A-B}$$

$$= 6.915\,\text{kJ}$$

because $\Delta E_{\text{int}} = 0$ for an isothermal process.

The heat entering the system during the constant-volume process DA is:

$$Q_{D-A} = C_V \Delta T_{D-A} = \tfrac{3}{2}nR\Delta T_{D-A}$$

Apply the ideal-gas law to the constant-volume process DA to obtain:	$T_D = T_A \dfrac{P_D}{P_A} = (600\,\text{K})\dfrac{1\,\text{atm}}{5\,\text{atm}} = 120\,\text{K}$

The heat entering the system during the process DA is:

$$Q_{D-A} = \tfrac{3}{2}(2\,\text{mol})(8.314\,\text{J/mol}\cdot\text{K})(600\,\text{K} - 120\,\text{K}) = 12.0\,\text{kJ}$$

Substitute numerical values in equation (2) and evaluate the efficiency of the cycle:	$\varepsilon = \dfrac{6.58\,\text{kJ}}{6.915\,\text{kJ} + 12.0\,\text{kJ}} = \boxed{34.8\%}$

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Picture the Problem We can express the efficiency of the Otto cycle using the result from Example 19-2. We can apply the relation $TV^{\gamma-1} = $ constant to the adiabatic processes of the Otto cycle to relate the end-point temperatures to the volumes occupied by the gas at these points and eliminate the temperatures at c and d. We can use the ideal-gas law to find the highest temperature of the gas during its cycle and use this temperature to express the efficiency of a Carnot engine. Finally, we can compare the efficiencies by examining their ratio.

The efficiency of the Otto engine is given in Example 19-2:	$\varepsilon_O = 1 - \dfrac{T_d - T_a}{T_c - T_b}$ (1)
	where the subscripts refer to the various points of the cycle as shown in Figure 19-3.
Apply the relation $TV^{\gamma-1} = $ constant to the adiabatic process $a \to b$ to obtain:	$T_b = T_a\left(\dfrac{V_a}{V_b}\right)^{\gamma-1}$
Apply the relation $TV^{\gamma-1} = $ constant to the adiabatic process $c \to d$ to obtain:	$T_c = T_d\left(\dfrac{V_d}{V_c}\right)^{\gamma-1}$
Subtract the first of these equations from the second to obtain:	$T_c - T_b = T_d\left(\dfrac{V_d}{V_c}\right)^{\gamma-1} - T_a\left(\dfrac{V_a}{V_b}\right)^{\gamma-1}$

In the Otto cycle, $V_a = V_d$ and
$V_c = V_b$. Substitute to obtain:

$$T_c - T_b = T_d \left(\frac{V_a}{V_b} \right)^{\gamma-1} - T_a \left(\frac{V_a}{V_b} \right)^{\gamma-1}$$

$$= (T_d - T_a) \left(\frac{V_a}{V_b} \right)^{\gamma-1}$$

Substitute in equation (1) and
simplify to obtain:

$$\varepsilon_O = 1 - \frac{T_d - T_a}{(T_d - T_a) \left(\dfrac{V_a}{V_b} \right)^{\gamma-1}}$$

$$= 1 - \left(\frac{V_b}{V_a} \right)^{\gamma-1} = 1 - \frac{T_a}{T_b}$$

Note that, while T_a is the lowest
temperature of the cycle, T_b is not the
highest temperature.

Apply the ideal-gas law to c and b to
obtain an expression for the cycle's
highest temperature T_c:

$$\frac{P_c}{T_c} = \frac{P_b}{T_b} \Rightarrow T_c = T_b \frac{P_c}{P_b} > T_b$$

Express the efficiency of a Carnot
engine operating between the
maximum and minimum
temperatures of the Otto cycle:

$$\varepsilon_C = 1 - \frac{T_a}{T_c}$$

Express the ratio of the efficiency of
a Carnot engine to the efficiency of
an Otto engine operating between
the same temperatures:

$$\frac{\varepsilon_C}{\varepsilon_O} = \frac{1 - \dfrac{T_a}{T_c}}{1 - \dfrac{T_a}{T_b}} > \boxed{1} \text{ because } T_c > T_b.$$

*79   •••
Picture the Problem We can use $nR = C_P - C_V$, $\gamma = C_P / C_V$, and $TV^{\gamma-1} = $ a constant
to show that the entropy change for a quasi-static adiabatic expansion that proceeds from
state (V_1, T_1) to state (V_2, T_2) is zero.

Express the entropy change for a
general process that proceeds from
state 1 to state 2:

$$\Delta S = C_V \ln \left(\frac{T_2}{T_1} \right) + nR \ln \left(\frac{V_2}{V_1} \right)$$

For an adiabatic process:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

Substitute and simplify to obtain:

$$\Delta S = C_V \ln\left(\frac{V_1}{V_2}\right)^{\gamma-1} + nR \ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{V_2}{V_1}\right)\left[nR + \frac{C_V \ln\left(\frac{V_1}{V_2}\right)^{\gamma-1}}{\ln\frac{V_2}{V_1}}\right]$$

$$= \ln\left(\frac{V_2}{V_1}\right)\left[nR + \frac{(\gamma-1)C_V \ln\left(\frac{V_1}{V_2}\right)}{-\ln\frac{V_1}{V_2}}\right] = \ln\left(\frac{V_2}{V_1}\right)\left[nR - (\gamma-1)C_V\right]$$

Use the relationship between C_P and C_V to obtain: $nR = C_P - C_V$

Substitute for nR and γ and simplify:

$$\Delta S = \ln\left(\frac{V_2}{V_1}\right)\left[C_P - C_V - \left(\frac{C_P}{C_V} - 1\right)C_V\right]$$

$$= \boxed{0}$$

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Picture the Problem

(*a*) Suppose the refrigerator statement of the second law is violated in the sense that heat Q_c is taken from the cold reservoir and an equal mount of heat is transferred to the hot reservoir and $W = 0$. The entropy change of the universe is then $\Delta S_u = Q_c/T_h - Q_c/T_c$. Because $T_h > T_c$, $S_u < 0$, i.e., the entropy of the universe would decrease.

(*b*) In this case, is heat Q_h is taken from the hot reservoir and no heat is rejected to the cold reservoir, i.e., $Q_c = 0$, then the entropy change of the universe is $\Delta S_u = -Q_h/T_h + 0$, which is negative. Again, the entropy of the universe would decrease.

(*c*) The heat-engine and refrigerator statements of the second law only state that *some* heat must be rejected to a cold reservoir and *some* work must be done to transfer heat from the cold to the hot reservoir, but these statements do not specify the minimum amount of heat rejected or work that must be done. The statement $\Delta S_u \geq 0$ is more restrictive. The heat-engine and refrigerator statements in conjunction with the Carnot efficiency are equivalent to $\Delta S_u \geq 0$.

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Picture the Problem We can express the net efficiency of the two engines in terms of W_1, W_2, and Q_h and then use $\varepsilon_1 = W_1/Q_h$ and $\varepsilon_2 = W_2/Q_m$ to eliminate W_1, W_2, Q_h, and Q_m.

Express the net efficiency of the two engines connected in series:	$$\varepsilon_{net} = \frac{W_1 + W_2}{Q_h}$$
Express the efficiencies of engines 1 and 2:	$$\varepsilon_1 = \frac{W_1}{Q_h}$$ and $$\varepsilon_2 = \frac{W_2}{Q_m}$$
Solve for W_1 and W_2 and substitute to obtain:	$$\varepsilon_{net} = \frac{\varepsilon_1 Q_h + \varepsilon_2 Q_m}{Q_h} = \varepsilon_1 + \frac{Q_m}{Q_h}\varepsilon_2$$
Express the efficiency of engine 1 in terms of Q_m and Q_h:	$$\varepsilon_1 = 1 - \frac{Q_m}{Q_h}$$
Solve for Q_m/Q_h:	$$\frac{Q_m}{Q_h} = 1 - \varepsilon_1$$
Substitute to obtain:	$$\varepsilon_{net} = \boxed{\varepsilon_1 + \left(1 - \varepsilon_1\right)\varepsilon_2}$$

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Picture the Problem We can express the net efficiency of the two engines in terms of W_1, W_2, and Q_h and then use $\varepsilon_1 = W_1/Q_h$ and $\varepsilon_2 = W_2/Q_m$ to eliminate W_1, W_2, Q_h, and Q_m. Finally, we can substitute the expressions for the efficiencies of the ideal reversible engines to obtain $\varepsilon_{net} = 1 - T_c/T_h$.

Express the efficiencies of ideal reversible engines 1 and 2:	$$\varepsilon_1 = 1 - \frac{T_m}{T_h}$$ and $$\varepsilon_2 = 1 - \frac{T_c}{T_m}$$	(1) (2)
Express the net efficiency of the two engines connected in series:	$$\varepsilon_{net} = \frac{W_1 + W_2}{Q_h}$$	(3)

Express the efficiencies of engines 1 and 2:	$\varepsilon_1 = \dfrac{W_1}{Q_h}$ and $\varepsilon_2 = \dfrac{W_2}{Q_m}$
Solve for W_1 and W_2 and substitute in equation (3) to obtain:	$\varepsilon_{net} = \dfrac{\varepsilon_1 Q_h + \varepsilon_2 Q_m}{Q_h} = \varepsilon_1 + \dfrac{Q_m}{Q_h}\varepsilon_2$
Express the efficiency of engine 1 in terms of Q_m and Q_h:	$\varepsilon_1 = 1 - \dfrac{Q_m}{Q_h}$
Solve for Q_m / Q_h:	$\dfrac{Q_m}{Q_h} = 1 - \varepsilon_1$
Substitute to obtain:	$\varepsilon_{net} = \varepsilon_1 + (1 - \varepsilon_1)\varepsilon_2$
Substitute for ε_1 and ε_2 and simplify to obtain:	$\varepsilon_{net} = 1 - \dfrac{T_m}{T_h} + \left(\dfrac{T_m}{T_h}\right)\left(1 - \dfrac{T_c}{T_m}\right)$
	$= 1 - \dfrac{T_m}{T_h} + \dfrac{T_m}{T_h} - \dfrac{T_c}{T_h} = \boxed{1 - \dfrac{T_c}{T_h}}$

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Picture the Problem There are 26 letters and four punctuation marks (space, comma, period, and exclamation point) used in the English language, disregarding capitalization, so we have a grand total of 30 characters to choose from. This fragment is 330 characters (including spaces) long; there are then 30^{330} different possible arrangements of the character set to form a fragment this long. We can use this number of possible arrangements to express the probability that one monkey will write out this passage and then an estimate of a monkey's typing speed to approximate the time required for one million monkeys to type the passage from Shakespeare.

Assuming the monkeys type at random, express the probability P that one monkey will write out this passage:	$P = \dfrac{1}{30^{330}}$
Use the approximation $30 \approx \sqrt{1000} = 10^{1.5}$ to obtain:	$P = \dfrac{1}{10^{(1.5)(330)}} = \dfrac{1}{10^{495}} = 10^{-495}$
Assuming the monkeys can type at a rate of 1 character per second, it would take about 330 s to write a passage of length equal to the quotation from Shakespeare. Find the time T required for a million monkeys to type this particular passage by accident:	$T = \dfrac{(330\,\text{s})(10^{495})}{10^6}$ $= (3.30 \times 10^{491}\,\text{s})\left(\dfrac{1\,\text{y}}{3.16 \times 10^7\,\text{s}}\right)$ $\approx \boxed{10^{484}\,\text{y}}$

Express the ratio of T to Russell's estimate:

$$\frac{T}{T_{\text{Russell}}} = \frac{10^{484} \text{ y}}{10^{6} \text{ y}} = 10^{478}$$

or

$$T \approx \boxed{10^{478} T_{\text{Russell}}}$$