Chapter 12
The Laws of Thermodynamics

Quick Quizzes

1. (b). The work done on a gas during a thermodynamic process is the **negative** of the area under the curve on a *PV* diagram. Processes in which the volume decreases do positive work on the gas, while processes in which the volume increases do negative work on the gas. The work done on the gas in each of the four processes shown is:

$$W_a = -4.00 \times 10^5 \text{ J},\ W_b = +3.00 \times 10^5 \text{ J},\ W_c = -3.00 \times 10^5 \text{ J}, \text{ and } W_d = +4.00 \times 10^5 \text{ J}$$

Thus, the correct ranking (from most negative to most positive) is a,c,b,d.

2. *A* is isovolumetric, *B* is adiabatic, *C* is isothermal, *D* is isobaric.

3. (c). The highest theoretical efficiency of an engine is the Carnot efficiency given by $e_c = 1 - T_c/T_h$. Hence, the theoretically possible efficiencies of the given engines are:

$$e_A = 1 - \frac{700 \text{ K}}{1\,000 \text{ K}} = 0.300,\ e_B = 1 - \frac{500 \text{ K}}{800 \text{ K}} = 0.375, \text{ and } e_C = 1 - \frac{300 \text{ K}}{600 \text{ K}} = 0.500$$

and the correct ranking (from highest to lowest) is C, B, A.

4. (b). $\Delta S = \dfrac{Q_r}{T} = 0$ and $Q = 0$ in an adiabatic process. If the process was reversible, but not adiabatic, the entropy of the system could undergo a non-zero change. However, in that case, the entropy of the system's surroundings would undergo a change of equal magnitude but opposite sign, and the total change of entropy in the universe would be zero. If the process was irreversible, the total entropy of the universe would increase.

5. The number 7 is the most probable outcome because there are six ways this could occur: 1-6, 2-5, 3-4, 4-3, 5-2, and 6-1. The numbers 2 and 12 are the least probable because they could only occur one way each: either 1-1, or 6-6. Thus, you are six times more likely to throw a 7 than a 2 or 12.

Answers to Even Numbered Conceptual Questions

2. Either statement can be considered an instructive analogy. We choose to take the first view. All processes require energy, either as energy content or as energy input. The kinetic energy which it possessed at its formation continues to make Earth go around. Energy released by nuclear reactions in the core of the Sun drives weather on Earth and essentially all processes in the biosphere. The energy intensity of sunlight controls how lush a forest or jungle can be and how warm a planet is. Continuous energy input is not required for the motion of the planet. Continuous energy input is required for life because energy tends to be continuously degraded, as energy is transferred by heat into lower-temperature sinks. The continuously increasing entropy of the Universe is the index to energy-transfers completed.

4. Shaking opens up spaces between the jelly beans. The smaller ones have a chance of falling down into spaces below them. The accumulation of larger ones on top and smaller ones on the bottom implies an increase in order and a decrease in one contribution to the total entropy. However, the second law is not violated and the total entropy of the system increases. The increase in the internal energy of the system comes from the work required to shake the jar of beans (that is, work your muscles must do, with an increase in entropy accompanying the biological process) and also from the small loss of gravitational potential energy as the beans settle together more compactly.

6. Temperature = A measure of molecular motion. Heat = the process through which energy is transferred between objects by means of random collisions of molecules. Internal energy = energy associated with random molecular motions plus chemical energy, strain potential energy, and an object's other energy not associated with center of mass motion or location.

8. A higher steam temperature means that more energy can be extracted from the steam. For a constant temperature heat sink at T_c and steam at T_h, the maximum efficiency of the power plant goes as $\frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h}$ and is maximized for high T_h.

10. $e_{\max} = \frac{\Delta T}{T_h} = \frac{80\text{ K}}{373\text{ K}} \approx 22\%$ (Assumes atmospheric temperature of 20°C.)

12. An analogy due to Carnot is instructive: A waterfall continuously converts mechanical energy into internal energy. It continuously creates entropy as the organized motion of the falling water turns into disorganized molecular motion. We humans put turbines into the waterfall, diverting some of the energy stream to our use. Water flows spontaneously from high to low elevation and energy is transferred spontaneously from high to low temperature by heat. Into the great flow of solar radiation from Sun to Earth, living things put themselves. They live on energy flow. A basking snake diverts high-temperature energy through itself temporarily, before it is inevitably lost as low-temperature energy radiated into outer space. A tree builds organized cellulose molecules and we build libraries and babies who look like their grandmothers, all out of a thin diverted stream in the universal flow of energy crashing down to disorder. We do not violate the second law, for we build local reductions in the entropy of one thing within the inexorable increase in the total entropy of the Universe. Your roommate's exercise increases random molecular motions within the room.

14. Even at essentially constant temperature, energy must be transferred by heat out of the solidifying sugar into the surroundings. This action will increase the entropy of the environment. The water molecules become less ordered as they leave the liquid in the container to mix with the entire atmosphere.

16. A slice of hot pizza cools off. Road friction brings a skidding car to a stop. A cup falls to the floor and shatters. Any process is irreversible if it looks funny or frightening when shown in a videotape running backward. At fairly low speeds, air resistance is small and the flight of a projectile is nearly reversible.

Answers to Even Numbered Problems

2. **(a)** 610 J **(b)** 0 **(c)** –410 J
(d) 0 **(e)** 200 J

4. **(a)** 31 m/s **(b)** 0.17

6. **(c)** More work is done in (a) because of higher pressure during the expansion.

8. -465 J

10. **(a)** –12.0 MJ **(b)** 12.0 MJ

12. $6P_0V_0$

14. $\Delta U = 0,\ Q<0,\ W>0$

16. **(a)** 12 kJ **(b)** –12 kJ

18. $Q_{AB}>0,\ W_{AB}<0,\ \Delta U_{AB}>0$
$Q_{BC}<0,\ W_{BC}=0,\ \Delta U_{BC}<0$
$Q_{CA}<0,\ W_{CA}>0,\ \Delta U_{CA}<0$

20. **(a)** 8.24 J **(b)** 12.4 J **(c)** 20.6 J

22. **(a)** $W_{IAF} = -76.0$ J, $W_{IBF} = -101$ J, $W_{IF} = -88.7$ J
(b) $Q_{IAF} = 165$ J, $Q_{IBF} = 190$ J, $Q_{IF} = 178$ J

24. 19.7%

26. **(a)** 10.7 kJ **(b)** 0.533 s

28. 13.7°C

30. **(a)** 0.0512 (or 5.12%) **(b)** 5.27×10^{12} J
(c) Such engines would be one way to harness solar energy as conventional energy sources become more expensive. However, this engine could produce unacceptable thermal pollution in the deep ocean waters.

32. **(a)** 9.10 kW **(b)** 11.9 kJ

34. 453 K

36. 6.06 kJ/K

38. 2.7 kJ/K

40. **(a)**

End Result	Possible Draws	Total Number of Same Result
All R	RRR	1
1G, 2R	RRG, RGR, GRR	3
2G, 1R	GGR, GRG, RGG	3
All G	GGG	1

(b)

End Result	Possible Draws	Total Number of Same Result
All R	RRRRR	1
1G, 4R	RRRRG, RRRGR, RRGRR, RGRRR, GRRRR	5
2G, 3R	RRRGG, RRGRG, RGRRG, GRRRG, RRGGR, RGRGR, GRRGR, RGGRR, GRGRR, GGRRR	10
3G, 2R	GGGRR, GGRGR, GRGGR, RGGGR, GGRRG, GRGRG, RGGRG, GRRGG, RGRGG, RRGGG	10
4G, 1R	GGGGR, GGGRG, GGRGG, GRGGG, RGGGG	5
All G	GGGGG	1

42. **(a)** 1/52 **(b)** 1/13 **(c)** 1/4

44. 3.0

46. $\Delta S_h = -16.0 \text{ J/K}$, $\Delta S_c = 26.7 \text{ J/K}$, $\Delta S_{Universe} = 10.7 \text{ J/K}$

48. 0.55 kg

50. **(a)** 251 J **(b)** 314 J **(c)** 104 J by the gas
(d) 104 J on the gas **(e)** zero in both cases

52. $5.97 \times 10^4 \text{ kg/s}$

54. **(a)** $4P_0V_0$ **(b)** $4P_0V_0$ **(c)** 9.07 kJ

56. **(a)** $-4.9 \times 10^{-2} \text{ J}$ **(b)** 16 kJ **(c)** 16 kJ

58. **(a)** $\frac{21}{2}nRT_0$ **(b)** $\frac{17}{2}nRT_0$
(c) 0.190 (or 19.0%) **(d)** 0.833 (or 83.3%)

60. **(a)** $+335 \text{ J}$ **(b)** $2.09 \times 10^3 \text{ J}$

62. **(a)** $2.4 \times 10^6 \text{ J}$ **(b)** $1.6 \times 10^6 \text{ J}$ **(c)** $2.8 \times 10^2 \text{ J}$

Problem Solutions

12.1 From kinetic theory, the average kinetic energy per molecule is

$$\overline{KE}_{molecule} = \frac{3}{2}k_{\mathrm{B}}T = \frac{3}{2}\left(\frac{R}{N_{\mathrm{A}}}\right)T$$

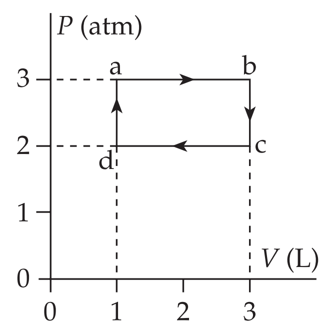
For a monatomic ideal gas containing N molecules, the total energy associated with random molecular motions is

$$U = N \cdot \overline{KE}_{molecule} = \frac{3}{2}\left(\frac{N}{N_{\mathrm{A}}}\right)RT = \frac{3}{2}nRT$$

Since $PV = nRT$ for an ideal gas, the internal energy of a monatomic ideal gas is found to be given by $\boxed{U = \frac{3}{2}PV}$.

12.2 (a) $W_{ab} = P_a\left(V_b - V_a\right)$

$$= \left[3\left(1.013\times10^5\text{ Pa}\right)\right]\left(3.0\text{ L} - 1.0\text{ L}\right)\left(\frac{10^{-3}\text{ m}^3}{1\text{ L}}\right) = \boxed{610\text{ J}}$$



(b) $W_{bc} = P\left(V_c - V_b\right) = \boxed{0}$

(c) $W_{cd} = P_c\left(V_d - V_c\right)$

$$= \left[2\left(1.013\times10^5\text{ Pa}\right)\right]\left(1.0\text{ L} - 3.0\text{ L}\right)\left(\frac{10^{-3}\text{ m}^3}{1\text{ L}}\right) = \boxed{-410\text{ J}}$$

(d) $W_{da} = P\left(V_a - V_d\right) = \boxed{0}$

(e) $W_{net} = W_{ab} + W_{bc} + W_{cd} + W_{da} = +610\text{ J} + 0 - 410\text{ J} + 0 = \boxed{+200\text{ J}}$

12.3 The number of molecules in the gas is $N = nN_A$ and the total internal energy is

$$U = N\left(\overline{KE}\right) = nN_A\left(\frac{3}{2}k_B T\right) = \frac{3}{2}nRT$$

$$= \frac{3}{2}(3.0 \text{ mol})\left(8.31 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(303 \text{ K}) = \boxed{1.1\times 10^4 \text{ J}}$$

Alternatively, use the result of Problem 12.1,

$U = \frac{3}{2}PV = \frac{3}{2}nRT$, just as found above.

12.4 (a) The work done *by* the gas on the projectile is given by the area under the curve in the PV diagram. This is

$$W_{\text{by gas}} = (\text{triangular area}) + (\text{rectangular area})$$

$$= \frac{1}{2}\left(P_0 - P_f\right)\left(V_f - V_0\right) + P_f\left(V_f - V_0\right) = \frac{1}{2}\left(P_0 + P_f\right)\left(V_f - V_0\right)$$

$$= \frac{1}{2}\left[(11 + 1.0)\times 10^5 \text{ Pa}\right]\left[(40.0 - 8.0) \text{ cm}^3\right]\left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3}\right) = 19 \text{ J}$$

From the work-energy theorem, $W = \Delta KE = \frac{1}{2}mv^2 - 0$ where W is the work done on the projectile by the gas. Thus, the speed of the emerging projectile is

$$v = \sqrt{\frac{2W}{m}} = \sqrt{\frac{2(19 \text{ J})}{40.0\times 10^{-3} \text{ kg}}} = \boxed{31 \text{ m/s}}$$

(b) The air in front of the projectile would exert a retarding force of

$$F_r = P_{air}A = \left(1.0\times 10^5 \text{ Pa}\right)\left[\left(1.0 \text{ cm}^2\right)\left(1 \text{ m}^2/10^4 \text{ cm}^2\right)\right] = 10 \text{ N}$$

on the projectile as it moves down the launch tube. The energy spent overcoming this retarding force would be

$$W_{spent} = F_r \cdot s = (10 \text{ N})(0.32 \text{ m}) = 3.2 \text{ J}$$

and the needed fraction is $\frac{W_{spent}}{W} = \frac{3.2 \text{ J}}{19 \text{ J}} = \boxed{0.17}$

12.5 In each case, the work done *on* the gas is given by the negative of the area under the path on the PV diagram. Along those parts of the path where volume is constant, no work is done. Note that $1\text{ atm} = 1.013 \times 10^5\text{ Pa}$ and $1\text{ Liter} = 10^{-3}\text{ m}^3$.

(a) $W_{IAF} = W_{IA} + W_{AF} = -P_I\left(V_A - V_I\right) + 0$

$$= -\left[4.00\left(1.013 \times 10^5\text{ Pa}\right)\right]\left[\left(4.00 - 2.00\right) \times 10^{-3}\text{ m}^3\right] = \boxed{-810\text{ J}}$$

(b) $W_{IF} = -\left(\text{triangular area}\right) - \left(\text{rectangular area}\right)$

$$= -\frac{1}{2}\left(P_I - P_B\right)\left(V_F - V_B\right) - P_B\left(V_F - V_B\right) = -\frac{1}{2}\left(P_I + P_B\right)\left(V_F - V_B\right)$$

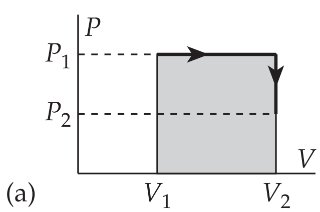
$$= -\frac{1}{2}\left[\left(4.00 + 1.00\right)\left(1.013 \times 10^5\text{ Pa}\right)\right]\left(4.00 - 2.00\right) \times 10^{-3}\text{ m}^3$$

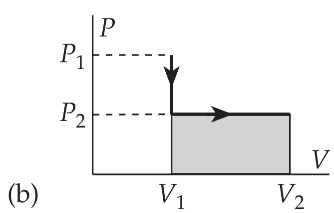
$$= \boxed{-507\text{ J}}$$

(c) $W_{IBF} = W_{IB} + W_{BF} = 0 - P_B\left(V_F - V_I\right)$

$$= -\left[1.00\left(1.013 \times 10^5\text{ Pa}\right)\right]\left[\left(4.00 - 2.00\right) \times 10^{-3}\text{ m}^3\right] = \boxed{-203\text{ J}}$$

12.6 The sketches for (a) and (b) are shown below:





(c) As seen from the areas under the paths in the PV diagrams above, the higher pressure during the expansion phase of the process results in more work done *by* the gas in (a) than in (b).

12.7 The constant pressure is $P = \left(1.5\text{ atm}\right)\left(1.013 \times 10^5\text{ Pa/atm}\right) = 1.52 \times 10^5\text{ Pa}$ and the work done on the gas is $W = -P\left(\Delta V\right)$.

(a) $\Delta V = +4.0\text{ m}^3$ and

$$W = -P\left(\Delta V\right) = -\left(1.52 \times 10^5\text{ Pa}\right)\left(+4.0\text{ m}^3\right) = \boxed{-6.1 \times 10^5\text{ J}}$$

(b) $\Delta V = -3.0 \text{ m}^3$, so

$$W = -P(\Delta V) = -\left(1.52 \times 10^5 \text{ Pa}\right)\left(-3.0 \text{ m}^3\right) = \boxed{+4.6 \times 10^5 \text{ J}}$$

12.8 As the temperature increases, while pressure is held constant, the volume increases by

$$\Delta V = V_f - V_i = \frac{nRT_f}{P} - \frac{nRT_i}{P} = \frac{nR(\Delta T)}{P}$$

where the change in absolute temperature is $\Delta T = \Delta T_C = 280 \text{ K}$. The work done on the gas is

$$W = -P(\Delta V) = -nR(\Delta T) = -(0.200 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K})(280 \text{ K}) = \boxed{-465 \text{ J}}$$

12.9 (a) From the ideal gas law, $nR = PV_f/T_f = PV_i/T_i$. With pressure constant this gives

$$T_f = T_i\left(\frac{V_f}{V_i}\right) = (273 \text{ K})(4) = \boxed{1.09 \times 10^3 \text{ K}}$$

(b) The work done on the gas is

$$W = -P(\Delta V) = -\left(PV_f - PV_i\right) = -nR\left(T_f - T_i\right)$$

$$= -(1.00 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K})(1\,092 \text{ J} - 273 \text{ K})$$

$$= -6.81 \times 10^3 \text{ J} = \boxed{-6.81 \text{ kJ}}$$

12.10 (a) The work done on the fluid is the negative of the area under the curve on the *PV* diagram. Thus,

$$W_{if} = -\Big\{\left(6.00 \times 10^6 \text{ Pa}\right)(2.00 - 1.00) \text{ m}^3 + \frac{1}{2}\left[(6.00 - 2.00) \times 10^6 \text{ Pa}\right](2.00 - 1.00) \text{ m}^3 + \left(2.00 \times 10^6 \text{ Pa}\right)(4.00 - 2.00) \text{ m}^3\Big\}$$

$$W_{if} = -1.20 \times 10^7 \text{ J} = \boxed{-12.0 \text{ MJ}}$$

(b) When the system follows the process curve in the reverse direction, the work done on the fluid is the negative of that computed in (a), or

$$W_{fi} = -W_{if} = \boxed{+12.0 \text{ MJ}}$$

12.11 (a) Because the volume is held constant, $\boxed{W = 0}$. Energy is transferred by heat *from* the burning mixture, so $\boxed{Q < 0}$. The first law then gives $\Delta U = Q + W = Q$, so $\boxed{\Delta U < 0}$.

(b) Again, since volume is constant, $\boxed{W = 0}$. Energy is transferred by heat from the burning mixture to the water, so $\boxed{Q > 0}$. Then, $\Delta U = Q + W = Q$ gives $\boxed{\Delta U > 0}$.

12.12 The work done on the gas is the negative of the area under the curve on the PV diagram, or

$$W = -\left[P_0(2V_0 - V_0) + \frac{1}{2}(2P_0 - P_0)(2V_0 - V_0)\right] = -\frac{3}{2}P_0V_0$$

From the result of Problem 1,

$$\Delta U = \frac{3}{2}P_fV_f - \frac{3}{2}P_iV_i = \frac{3}{2}(2P_0)(2V_0) - \frac{3}{2}P_0V_0 = \frac{9}{2}P_0V_0$$

Thus, from the first law, $Q = \Delta U - W = \frac{9}{2}P_0V_0 - \left(-\frac{3}{2}P_0V_0\right) = \boxed{6P_0V_0}$

12.13 (a) $W = -P(\Delta V) = -(0.800 \text{ atm})(-7.00 \text{ L})\left(\frac{1.013 \times 10^5 \text{ Pa}}{1 \text{ atm}}\right)\left(\frac{10^{-3} \text{ m}^3}{1 \text{ L}}\right) = \boxed{567 \text{ J}}$

(b) $\Delta U = Q + W = -400 \text{ J} + 567 \text{ J} = \boxed{167 \text{ J}}$

12.14 The work done on the gas is the negative of the area under the curve on the PV diagram,

so $$W = -\left[P_0\left(V_0 - 2V_0\right) + \frac{1}{2}\left(2P_0 - P_0\right)\left(V_0 - 2V_0\right)\right] = +\frac{3}{2}P_0V_0\text{, or } \boxed{W > 0}$$

From the result of Problem 1,

$$\Delta U = \frac{3}{2}P_fV_f - \frac{3}{2}P_iV_i = \frac{3}{2}\left(2P_0\right)\left(V_0\right) - \frac{3}{2}\left(P_0\right)\left(2V_0\right) = \boxed{0}$$

Then, from the first law, $Q = \Delta U - W = 0 - \frac{3}{2}P_0V_0 = -\frac{3}{2}P_0V_0$, or $\boxed{Q < 0}$

12.15 (a) Along the direct path *IF*, the work done on the gas is

$$W = -\left(\textit{area under curve}\right)$$

$$= -\left[\left(1.00\text{ atm}\right)\left(4.00\text{ L} - 2.00\text{ L}\right) + \frac{1}{2}\left(4.00\text{ atm} - 1.00\text{ atm}\right)\left(4.00\text{ L} - 2.00\text{ L}\right)\right]$$

$$W = -\left(5.00\text{ atm}\cdot\text{L}\right)\left(\frac{1.013\times10^5\text{ Pa}}{1\text{ atm}}\right)\left(\frac{10^{-3}\text{ m}^3}{1\text{ L}}\right) = -506.5\text{ J}$$

Thus, $\Delta U = Q + W = 418\text{ J} - 506.5\text{ J} = \boxed{-88.5\text{ J}}$

(b) Along path *IAF*, the work done on the gas is

$$W = -\left(4.00\text{ atm}\right)\left(4.00\text{ L} - 2.00\text{ L}\right)\left(\frac{1.013\times10^5\text{ Pa}}{1\text{ atm}}\right)\left(\frac{10^{-3}\text{ m}^3}{1\text{ L}}\right) = -810\text{ J}$$

From the first law, $Q = \Delta U - W = -88.5\text{ J} - \left(-810\text{ J}\right) = \boxed{722\text{ J}}$

12.16 (a) In a cyclic process, $\Delta U = 0$ and the first law gives

$$\Delta U = Q + W = 0\text{, or } Q = -W$$

The total work done on the gas is $W_{ABC} = W_{AB} + W_{BC} + W_{CA}$, and on each step the work is the negative of the area under the curve on the PV diagram, or

$$W_{AB} = -\Big[(2.0\text{ kPa})(10\text{ m}^3 - 6.0\text{ m}^3) + \frac{1}{2}(8.00\text{ kPa} - 2.0\text{ kPa})(10\text{ m}^3 - 6.0\text{ m}^3)\Big] = -20\text{ kJ}$$

$$W_{BC} = 0\text{, and } W_{cA} - (2.0\text{ kPa})(6.0\text{ m}^3 - 10\text{ m}^3) = +8.0\text{ kJ}$$

Thus, $W_{ABC} = -20\text{ kJ} + 0 + 8.0\text{ kJ} = -12\text{ kJ}$, and $Q = -W = \boxed{12\text{ kJ}}$

(b) If the cycle is reversed,

$$W_{CBA} = -W_{ABC} = -(-12\text{ kJ}) = 12\text{ kJ} \text{ and } Q = -W = \boxed{-12\text{ kJ}}$$

12.17 (a) The change in the volume occupied by the gas is

$$\Delta V = V_f - V_i = A(L_f - L_i) = (0.150\text{ m}^2)(-0.200\text{ m}) = -3.00\times 10^{-2}\text{ m}^3$$

and the work done by the gas is

$$W_{\text{by gas}} = +P(\Delta V) = (6\,000\text{ Pa})(-3.00\times 10^{-2}\text{ m}^3) = \boxed{-180\text{ J}}$$

(b) The first law of thermodynamics is $\Delta U = Q_{\text{input}} + W_{\text{on gas}} = -Q_{\text{output}} - W_{\text{by gas}}$. Thus, if $\Delta U = -8.00\text{ J}$, the energy transferred out of the system by heat is

$$Q_{\text{output}} = -\Delta U - W_{\text{by gas}} = -(-8.00\text{ J}) - (-180\text{ J}) = \boxed{+188\text{ J}}$$

12.18 Volume is constant in process BC, so $\boxed{W_{BC} = 0}$. Given that $\boxed{Q_{BC} < 0}$, the first law shows that $\Delta U_{BC} = Q_{BC} + W_{BC} = Q_{BC} + 0$. Thus, $\boxed{\Delta U_{BC} < 0}$.

For process CA, $\Delta V_{CA} = V_A - V_C < 0$, so $W = -P(\Delta V)$ shows that $\boxed{W_{CA} > 0}$. Then, given that $\boxed{\Delta U_{CA} < 0}$, the first law gives $Q_{CA} = \Delta U_{CA} - W_{CA}$ and $\boxed{Q_{CA} < 0}$.

In process AB, the work done on the system is $W = -(\text{area under curve } AB)$ where

$$(\text{area under curve } AB) = P_A\left(V_B - V_A\right) + \frac{1}{2}\left(P_B - P_A\right)\left(V_B - V_A\right) > 0$$

Hence, $\boxed{W_{AB} < 0}$. For the cyclic process, $\Delta U = \Delta U_{AB} + \Delta U_{BC} + \Delta U_{CA} = 0$, so, $\Delta U_{AB} = -\left(\Delta U_{BC} + \Delta U_{CA}\right)$. This gives $\boxed{\Delta U_{AB} > 0}$, since both ΔU_{BC} and ΔU_{CA} are negative. Finally, from the first law, $Q = \Delta U - W$ shows that $\boxed{Q_{AB} > 0}$ since both ΔU_{AB} and $-\mathrm{W}_{AB}$ are positive.

12.19 (a) $W = -P(\Delta V)$

$$= -\left(1.013\times10^{5}\ \text{Pa}\right)\left[\left(1.09\ \text{cm}^3 - 1.00\ \text{cm}^3\right)\left(\frac{1\ \text{m}^3}{10^6\ \text{cm}^3}\right)\right] = \boxed{-9.12\times10^{-3}\ \text{J}}$$

(b) To freeze the water, the required energy transfer by heat is

$$Q = -mL_f = -\left(1.00\times10^{-3}\ \text{kg}\right)\left(3.33\times10^{5}\ \text{J/kg}\right) = -333\ \text{J}$$

The first law then gives

$$\Delta U = Q + W = -333\ \text{J} - 9.12\times10^{-3}\ \text{J} = \boxed{-333\ \text{J}}$$

12.20 Treating the air as an ideal gas at constant pressure, the final volume is

$V_f = V_i\left(T_f/T_i\right)$, or the change in volume is

$$\Delta V = V_f - V_i = V_i\left(\frac{T_f - T_i}{T_i}\right)$$

$$= \left[\left(0.600\ \text{L}\right)\left(\frac{10^{-3}\ \text{m}^3}{1\ \text{L}}\right)\right]\left(\frac{310\ \text{K} - 273\ \text{K}}{273\ \text{K}}\right) = 8.13\times10^{-5}\ \text{m}^3$$

(a) The work done on the lungs *by* the air is

$$W_{\text{by gas}} = +P(\Delta V) = \left(1.013\times10^{5}\ \text{Pa}\right)\left(8.13\times10^{-5}\ \text{m}^3\right) = \boxed{8.24\ \text{J}}$$

(b) Using the result of Problem 1, the change in the internal energy of the air is

$$\Delta U = \frac{3}{2}P(\Delta V) = \frac{3}{2}\left(1.013\times10^{5}\ \text{Pa}\right)\left(8.13\times10^{-5}\ \text{m}^3\right) = \boxed{12.4\ \text{J}}$$

(c) The energy added to the air by heat is

$$Q = \Delta U - W = \frac{3}{2}P(\Delta V) - \left[-P(\Delta V)\right] = \frac{5}{2}P(\Delta V)$$

or, $Q = \frac{5}{2}\left(1.013\times10^{5}\ \text{Pa}\right)\left(8.13\times10^{-5}\ \text{m}^3\right) = \boxed{20.6\ \text{J}}$

12.21 (a) The original volume of the aluminum is

$$V_0 = \frac{m}{\rho} = \frac{5.0\ \text{kg}}{2.70\times10^{3}\ \text{kg/m}^3} = 1.85\times10^{-3}\ \text{m}^3$$

and the change in volume is $\Delta V = \beta V_0(\Delta T) = (3\alpha)V_0(\Delta T)$, or

$$\Delta V = 3\left[24\times10^{-6}\ (°\text{C})^{-1}\right]\left(1.85\times10^{-3}\right)(70°\text{C}) = 9.3\times10^{-6}\ \text{m}^3$$

The work done *by* the aluminum is then

$$W_{\text{by system}} = +P(\Delta V) = \left(1.013\times10^{5}\ \text{Pa}\right)\left(9.3\times10^{-6}\ \text{m}^3\right) = \boxed{0.95\ \text{J}}$$

(b) The energy transferred by heat to the aluminum is

$$Q = mc_{\text{Al}}(\Delta T) = (5.0\ \text{kg})(900\ \text{J/kg}\cdot°\text{C})(70°\text{C}) = \boxed{3.2\times10^{5}\ \text{J}}$$

(c) The work done on the aluminum is $W = -W_{\text{by system}} = -0.95\ \text{J}$, so the first law gives

$$\Delta U = Q + W = 3.2\times10^{5}\ \text{J} - 0.95\ \text{J} = \boxed{3.2\times10^{5}\ \text{J}}$$

12.22 (a) The work done on the gas in each process is the negative of the area under the process curve on the *PV* diagram.

For path *IAF*, $W_{IAF} = W_{IA} + W_{AF} = 0 + W_{AF}$, or

$$W_{IAF} = -\left[(1.50\ \text{atm})\left(1.013\times10^{5}\ \frac{\text{Pa}}{\text{atm}}\right)\right]\left[(0.500\ \text{L})\left(\frac{10^{-3}\ \text{m}^3}{1\ \text{L}}\right)\right]$$

$$= \boxed{-76.0\ \text{J}}$$

For path *IBF*, $W_{IBF} = W_{IB} + W_{BF} = W_{IB} + 0$, or

$$W_{IBF} = -\left[(2.00\ \text{atm})\left(1.013\times 10^{5}\ \frac{\text{Pa}}{\text{atm}}\right)\right]\left[(0.500\ \text{L})\left(\frac{10^{-3}\ \text{m}^{3}}{1\ \text{L}}\right)\right]$$

$$= \boxed{-101\ \text{J}}$$

For path *IF*, $W_{IF} = W_{AF} - (\textit{triangular area})$, or

$$W_{IF} = -76.0\ \text{J} - \frac{1}{2}\left[(0.500\ \text{atm})\left(1.013\times 10^{5}\ \frac{\text{Pa}}{\text{atm}}\right)\right]\left[(0.500\ \text{L})\left(\frac{10^{-3}\ \text{m}^{3}}{1\ \text{L}}\right)\right]$$

$$= \boxed{-88.7\ \text{J}}$$

(b) Using the first law, with $\Delta U = U_F - U_A = (180 - 91.0)\ \text{J} = 89.0\ \text{J}$, for each process gives

$$Q_{IAF} = \Delta U - W_{IAF} = 89.0\ \text{J} - (-76.0\ \text{J}) = \boxed{165\ \text{J}}$$

$$Q_{IBF} = \Delta U - W_{IBF} = 89.0\ \text{J} - (-101\ \text{J}) = \boxed{190\ \text{J}}$$

$$Q_{IF} = \Delta U - W_{IF} = 89.0\ \text{J} - (-88.7\ \text{J}) = \boxed{178\ \text{J}}$$

12.23 The maximum efficiency possible is that of a Carnot engine operating between the given reservoirs.

$$e_c = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h} = 1 - \frac{293\ \text{K}}{573\ \text{K}} = \boxed{0.489\ \ (\text{or } 48.9\%)}$$

12.24 The maximum possible efficiency of an engine is the Carnot efficiency, $e_c = \dfrac{T_h - T_c}{T_h} = 1 - \dfrac{T_c}{T_h}$, where T_h and T_c are the absolute temperatures of the reservoirs the engine operates between. For the given engine, the temperatures of the reservoirs are $300°\text{F} = 149°\text{C} = 422\ \text{K}$ and $150°\text{F} = 65.6°\text{C} = 339\ \text{K}$ so the maximum efficiency is

$$e_c == 1 - \frac{339\ \text{K}}{422\ \text{K}} = \boxed{0.197 \text{ or } 19.7\%}$$

12.25 (a) $e \equiv \dfrac{W_{\text{eng}}}{|Q_h|} = \dfrac{W_{\text{eng}}}{3W_{\text{eng}}} = \dfrac{1}{3} = \boxed{0.333 \text{ or } 33.3\%}$

(b) $e \equiv \dfrac{W_{\text{eng}}}{|Q_h|} = 1 - \dfrac{|Q_c|}{|Q_h|}$, so $\dfrac{|Q_c|}{|Q_h|} = 1 - e = 1 - \dfrac{1}{3} = \boxed{\dfrac{2}{3}}$

12.26 (a) From $e \equiv \dfrac{W_{\text{eng}}}{|Q_h|} = 1 - \dfrac{|Q_c|}{|Q_h|}$, the energy intake each cycle is

$$|Q_h| = \frac{|Q_c|}{1-e} = \frac{8\,000 \text{ J}}{1-0.250} = 10\,667 \text{ J} = \boxed{10.7 \text{ kJ}}$$

(b) From $\mathcal{P} = \dfrac{W_{\text{eng}}}{t} = \dfrac{e|Q_c|}{t}$, the time for one cycle is

$$t = \frac{e|Q_c|}{\mathcal{P}} = \frac{(0.250)(10\,667 \text{ J})}{5.00 \times 10^3 \text{ W}} = \boxed{0.533 \text{ s}}$$

12.27 (a) The maximum efficiency possible is that of a Carnot engine operating between the specified reservoirs.

$$e_c = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h} = 1 - \frac{703 \text{ K}}{2\,143 \text{ K}} = \boxed{0.672 \ \ (\text{or } 67.2\%)}$$

(b) From $e = \dfrac{W_{\text{eng}}}{|Q_h|}$, we find $W_{\text{eng}} = e|Q_h| = 0.420\left(1.40 \times 10^5 \text{ J}\right) = 5.88 \times 10^4 \text{ J}$

so $\mathcal{P} = \dfrac{W_{\text{eng}}}{t} = \dfrac{5.88 \times 10^4 \text{ J}}{1.00 \text{ s}} = 5.88 \times 10^4 \text{ W} = \boxed{58.8 \text{ kW}}$

12.28 The work done by the engine equals the change in the kinetic energy of the bullet, or

$$W_{\text{eng}} = \frac{1}{2}m_b v_f^2 - 0 = \frac{1}{2}\left(2.40\times10^{-3}\ \text{kg}\right)\left(320\ \text{m/s}\right)^2 = 123\ \text{J}$$

Since the efficiency of an engine may be written as $e = \dfrac{W_{\text{eng}}}{|Q_h|} = \dfrac{W_{\text{eng}}}{W_{\text{eng}}+|Q_c|}$ where $|Q_c|$ is the exhaust energy from the engine, we find that

$$|Q_c| = W_{\text{eng}}\left(\frac{1}{e}-1\right) = (123\ \text{J})\left(\frac{1}{0.0110}-1\right) = 1.10\times10^{4}\ \text{J}$$

This exhaust energy is absorbed by the 1.80-kg iron body of the gun, so the rise in temperature is

$$\Delta T = \frac{|Q_c|}{m_{gun}c_{iron}} = \frac{1.10\times10^{4}\ \text{J}}{(1.80\ \text{kg})(448\ \text{J/kg}\cdot{}^\circ\text{C})} = \boxed{13.7\,^\circ\text{C}}$$

12.29 (a) $e \equiv \dfrac{W_{\text{eng}}}{|Q_h|} = 1 - \dfrac{|Q_c|}{|Q_h|} = 1 - \dfrac{1\,200\ \text{J}}{1\,700\ \text{J}} = \boxed{0.294\ \ (\text{or } 29.4\%)}$

(b) $W_{\text{eng}} = |Q_h| - |Q_c| = 1\,700\ \text{J} - 1\,200\ \text{J} = \boxed{500\ \text{J}}$

(c) $\mathcal{P} = \dfrac{W_{\text{eng}}}{t} = \dfrac{500\ \text{J}}{0.300\ \text{s}} = 1.67\times10^{3}\ \text{W} = \boxed{1.67\ \text{kW}}$

12.30 (a) The Carnot efficiency represents the maximum possible efficiency. With $T_h = 20.0^\circ\text{C} = 293\ \text{K}$ and $T_c = 5.00^\circ\text{C} = 278\ \text{K}$, this efficiency is given by

$$e_c = 1 - \frac{T_c}{T_h} = 1 - \frac{278\ \text{K}}{293\ \text{K}} = \boxed{0.0512\ \ (\text{or } 5.12\%)}$$

(b) The efficiency of an engine is $e = W_{\text{eng}}/|Q_h|$, so the minimum energy input by heat each hour is

$$|Q_h|_{\min} = \frac{W_{\text{eng}}}{e_{\max}} = \frac{\mathcal{P}\cdot\Delta t}{e_{\max}} = \frac{(75.0\times10^{6}\ \text{J/s})(3\,600\ \text{s})}{0.0512} = \boxed{5.27\times10^{12}\ \text{J}}$$

(c) As fossil-fuel prices rise, this could be an attractive way to use solar energy. However, the potential environmental impact of such an engine would require serious study. The energy output, $|Q_c| = |Q_h| - W_{\text{eng}} = |Q_h|(1-e)$, to the low temperature reservoir (cool water deep in the ocean) could raise the temperature of over a million cubic meters of water by 1 °C every hour.

12.31 The actual efficiency of the engine is $e = 1 - \dfrac{|Q_c|}{|Q_h|} = 1 - \dfrac{300 \text{ J}}{500 \text{ J}} = 0.400$

If this is 60.0% of the Carnot efficiency, then $e_c = \dfrac{e}{0.600} = \dfrac{0.400}{0.600} = \dfrac{2}{3}$

Thus, from $e_c = 1 - \dfrac{T_c}{T_h}$, we find $\dfrac{T_c}{T_h} = 1 - e_c = 1 - \dfrac{2}{3} = \boxed{\dfrac{1}{3}}$

12.32 (a) The Carnot efficiency is $e_c = 1 - \dfrac{T_c}{T_h} = 1 - \dfrac{353 \text{ K}}{623 \text{ K}} = 0.433$, so the maximum power output is

$$\mathcal{P}_{\text{max}} = \frac{(W_{\text{eng}})_{\text{max}}}{t} = \frac{e_c|Q_h|}{t} = \frac{0.433(21.0 \text{ kJ})}{1.00 \text{ s}} = \boxed{9.10 \text{ kW}}$$

(b) From $e = 1 - \dfrac{|Q_c|}{|Q_h|}$, the energy expelled by heat each cycle is

$$|Q_c| = |Q_h|(1-e) = (21.0 \text{ kJ})(1 - 0.433) = \boxed{11.9 \text{ kJ}}$$

12.33 From $\mathcal{P} = \dfrac{W_{\text{eng}}}{t} = \dfrac{e|Q_h|}{t}$, the energy input by heat in time t is $|Q_h| = \dfrac{\mathcal{P} \cdot t}{e}$

Thus, from $e = \dfrac{|Q_h| - |Q_c|}{|Q_h|}$, the energy expelled in time t is

$$|Q_c| = |Q_h|(1-e) = \left(\frac{\mathcal{P} \cdot t}{e}\right)(1-e) = \mathcal{P} \cdot t\left(\frac{1}{e} - 1\right)$$

In time t, the mass of cooling water used is $m = \left(1.0\times10^{6}\ \text{kg/s}\right)\cdot t$, and its rise in temperature is

$$\Delta T = \frac{|Q_c|}{mc} = \frac{\mathcal{P}\cdot t}{\left(1.0\times10^{6}\ \text{kg/s}\right)\cdot t\cdot c}\left(\frac{1}{e}-1\right)$$

$$= \frac{\left(1\,000\times10^{6}\ \text{J/s}\right)}{\left(1.0\times10^{6}\ \text{kg/s}\right)\left(4\,186\ \text{J/kg}\cdot{}^\circ\text{C}\right)}\left(\frac{1}{0.33}-1\right)$$

or $\qquad \Delta T = \boxed{0.49^\circ\text{C}}$

12.34 The actual efficiency of the engine is

$$e_{actual} = \frac{\left(W_{\text{eng}}\right)_{actual}}{|Q_h|} = \frac{\frac{1}{2}m_{train}v_{actual}^2}{|Q_h|}$$

while the theoretically possible efficiency (the Carnot efficiency) is

$$e_c = \frac{\left(W_{\text{eng}}\right)_{theoretical}}{|Q_h|} = \frac{\frac{1}{2}m_{train}v_{theoretical}^2}{|Q_h|}$$

The energy input from the high temperature reservoir is the same in the two cases since it is specified that the same amount of fuel is consumed in both cases. Thus, we find

$$\frac{e_c}{e_{actual}} = \frac{\left(W_{\text{eng}}\right)_{theoretical}}{\left(W_{\text{eng}}\right)_{actual}} = \left(\frac{v_{theoretical}}{v_{actual}}\right)^2 \text{ or } e_c = e_{actual}\left(\frac{v_{theoretical}}{v_{actual}}\right)^2 = (0.200)\left(\frac{6.50\ \text{m/s}}{5.00\ \text{m/s}}\right)^2 = 0.338$$

But, we also know that $e_c = 1-\dfrac{T_c}{T_h}$, giving $T_h = \dfrac{T_c}{1-e_c} = \dfrac{300\ \text{K}}{1-0.338} = \boxed{453\ \text{K}}$

12.35 The energy transferred from the water by heat, and absorbed by the freezer, is

$$Q = mL_f = (\rho V)L_f = \left[\left(10^{3}\ \text{kg/m}^3\right)\left(1.0\times10^{-3}\ \text{m}^3\right)\right]\left(3.33\times10^{5}\ \frac{\text{J}}{\text{kg}}\right) = 3.3\times10^{5}\ \text{J}$$

Thus, the change in entropy of the water is

(a) $$\Delta S_{water} = \frac{(\Delta Q_r)_{water}}{T} = \frac{-3.3 \times 10^5 \text{ J}}{273 \text{ K}} = -1.2 \times 10^3 \ \frac{\text{J}}{\text{K}} = \boxed{-1.2 \text{ kJ/K}}$$

and that of the freezer is

(b) $$\Delta S_{freezer} = \frac{(\Delta Q_r)_{freezer}}{T} = \frac{+3.3 \times 10^5 \text{ J}}{273 \text{ K}} = \boxed{+1.2 \text{ kJ/K}}$$

12.36 The energy added to the water by heat is

$$\Delta Q_r = mL_v = (1.00 \text{ kg})(2.26 \times 10^6 \text{ J/kg}) = 2.26 \times 10^6 \text{ J}$$

so the change in entropy is

$$\Delta S = \frac{\Delta Q_r}{T} = \frac{2.26 \times 10^6 \text{ J}}{373 \text{ K}} = 6.06 \times 10^3 \ \frac{\text{J}}{\text{K}} = \boxed{6.06 \text{ kJ/K}}$$

12.37 The potential energy lost by the log is transferred away by heat, so

$$Q = mgh = (70 \text{ kg})(9.80 \text{ m/s}^2)(25 \text{ m}) = 1.7 \times 10^4 \text{ J}$$

and the change in entropy is $\Delta S = \frac{\Delta Q_r}{T} = \frac{1.7 \times 10^4 \text{ J}}{300 \text{ K}} = \boxed{57 \text{ J/K}}$

12.38 The total momentum before collision is zero, so the combined mass must be at rest after the collision. The energy dissipated by heat equals the total initial kinetic energy, of

$$Q = 2\left(\frac{1}{2}mv^2\right) = (2\,000 \text{ kg})(20 \text{ m/s})^2 = 8.0 \times 10^5 \text{ J} = 800 \text{ kJ}$$

The change in entropy is then $\Delta S = \frac{\Delta Q_r}{T} = \frac{800 \text{ kJ}}{296 \text{ K}} = \boxed{2.7 \text{ kJ/K}}$

12.39 A quantity of energy, of magnitude Q, is transferred from the Sun and added to Earth. Thus, $\Delta S_{Sun} = \dfrac{-Q}{T_{Sun}}$ and $\Delta S_{Earth} = \dfrac{+Q}{T_{Earth}}$, so the total change in entropy is

$$\Delta S_{total} = \Delta S_{Earth} + \Delta S_{Sun} = \frac{Q}{T_{Earth}} - \frac{Q}{T_{Sun}}$$

$$= (1\,000 \text{ J})\left(\frac{1}{290 \text{ K}} - \frac{1}{5\,700 \text{ K}}\right) = \boxed{3.27 \text{ J/K}}$$

12.40 (a)

End Result	Possible Draws	Total Number of Same Result
All R	RRR	1
1G, 2R	RRG, RGR, GRR	3
2G, 1R	GGR, GRG, RGG	3
All G	GGG	1

(b)

End Result	Possible Draws	Total Number of Same Result
All R	RRRRR	1
1G, 4R	RRRRG, RRRGR, RRGRR, RGRRR, GRRRR	5
2G, 3R	RRRGG, RRGRG, RGRRG, GRRRG, RRGGR, RGRGR, GRRGR, RGGRR, GRGRR, GGRRR	10
3G, 2R	GGGRR, GGRGR, GRGGR, RGGGR, GGRRG, GRGRG, RGGRG, GRRGG, RGRGG, RRGGG	10
4G, 1R	GGGGR, GGGRG, GGRGG, GRGGG, RGGGG	5
All G	GGGGG	1

12.41 (a) The table is shown below. On the basis of the table, the most probable result of a toss is $\boxed{2\text{ H and }2\text{ T}}$.

End Result	Possible Tosses	Total Number of Same Result
All H	HHHH	1
1T, 3H	HHHT, HHTH, HTHH, THHH	4
2T, 2H	HHTT, HTHT, THHT, HTTH, THTH, TTHH	6
3T, 1H	TTTH, TTHT, THTT, HTTT	4
All T	TTTT	1

(b) The most ordered state is the least likely. This is seen to be $\boxed{\text{all H or all T}}$.

(c) The least ordered state is the most likely. This is seen to be $\boxed{\text{2H and 2T}}$.

12.42 (a) There is only one ace of spades out of 52 cards, so the probability is $\boxed{\dfrac{1}{52}}$

(b) There are four aces out of 52 cards, so the probability is $\dfrac{4}{52} = \boxed{\dfrac{1}{13}}$

(c) There are 13 spades out of 52 cards, so the probability is $\dfrac{13}{52} = \boxed{\dfrac{1}{4}}$

12.43 The maximum efficiency is that of a Carnot engine and is given by

$$e_c = 1 - \frac{T_c}{T_h} = 1 - \frac{100\text{ K}}{200\text{ K}} = 0.50\text{ , or } e_{\max} = \boxed{50\%}\text{. The }\boxed{\text{claim is invalid}}$$

12.44 Operating between reservoirs having temperatures of $T_h = 100°\text{C} = 373\ \text{K}$ and $T_c = 20°\text{C} = 293\ \text{K}$, the theoretical efficiency of a Carnot engine is

$$e_c = 1 - \frac{T_c}{T_h} = 1 - \frac{293\ \text{K}}{373\ \text{K}} = 0.21$$

If the temperature of the hotter reservoir is changed to $T_h' = 550°\text{C} = 823\ \text{K}$, the theoretical efficiency of the Carnot engine increases to

$$e_c' = 1 - \frac{T_c}{T_h'} = 1 - \frac{293\ \text{K}}{823\ \text{K}} = 0.64$$

The factor by which the efficiency has increased is

$$\frac{e_c'}{e_c} = \frac{0.64}{0.21} = \boxed{3.0}$$

12.45 (a) The entropy change of the hot reservoir, with an energy output of magnitude $|Q_h|$, is

$$\Delta S_h = \frac{\Delta Q_r}{T_h} = \boxed{\frac{-|Q_h|}{T_h}}$$

(b) For the cold reservoir, with an energy input of magnitude $|Q_c|$, the change in entropy is

$$\Delta S_c = \frac{\Delta Q_r}{T_c} = \boxed{\frac{+|Q_c|}{T_c}}$$

(c) The engine has an energy input of magnitude $|Q_h|$ from a reservoir at temperature T_h and an energy output of magnitude $|Q_c|$ to a reservoir at temperature T_c. The net change in entropy for the engine is

$$\Delta S_{\text{eng}} = \sum\left(\frac{\Delta Q_r}{T}\right) = \boxed{\frac{|Q_h|}{T_h} - \frac{|Q_c|}{T_c}}$$

(d) For the isolated system consisting of the engine and the two reservoirs, the change in entropy is

$$\Delta S_{\substack{isolated\\system}} = \Delta S_h + \Delta S_{\text{eng}} + \Delta S_c = -\frac{|Q_h|}{T_h} + \left(\frac{|Q_h|}{T_h} - \frac{|Q_c|}{T_c}\right) + \frac{|Q_c|}{T_c} = \boxed{0}$$

12.46 In this case, $|Q_h| = |Q_c| = 8\,000\text{ J}$. The change in entropy of the hot reservoir is

$$\Delta S_h = \frac{-|Q_h|}{T_h} = \frac{-8\,000\text{ J}}{500\text{ K}} = \boxed{-16.0\text{ J/K}}$$

For the cold reservoir, $\Delta S_c = \dfrac{+|Q_c|}{T_c} = \dfrac{8\,000\text{ J}}{300\text{ K}} = \boxed{26.7\text{ J/K}}$

The net entropy change for this irreversible process is

$$\Delta S_{universe} = \Delta S_h + \Delta S_c = (-16.0+26.7)\text{ J/K} = \boxed{10.7\text{ J/K}} > 0$$

12.47 The energy output to the river each minute has magnitude

$$|Q_c| = (1-e)|Q_h| = (1-e)\left(\frac{|Q_h|}{t}\right)\cdot t = (1-0.30)\left(25\times10^8\ \frac{\text{J}}{\text{s}}\right)(60\text{ s}) = 1.05\times10^{11}\text{ J}$$

so the rise in temperature of the $9.0\times10^6\text{ kg}$ of cooling water used in one minute is

$$\Delta T = \frac{|Q_c|}{mc} = \frac{1.05\times10^{11}\text{ J}}{(9.0\times10^6\text{ kg})(4\,186\text{ J/kg}\cdot{}^\circ\text{C})} = \boxed{2.8{}^\circ\text{C}}$$

12.48 The energy exhausted from a heat engine is

$$Q_c = Q_h - W_{\text{eng}} = \frac{W_{\text{eng}}}{e} - W_{\text{eng}} = W_{\text{eng}}\left(\frac{1}{e}-1\right)$$

where Q_h is the energy input from the high temperature reservoir, W_{eng} is the useful work done, and $e = W_{\text{eng}}/Q_h$ is the efficiency of the engine.

For a Carnot engine, the efficiency is $e_c = 1 - T_c/T_h = (T_h - T_c)/T_h$

so we now have $$Q_c = W_{\text{eng}}\left(\frac{T_h}{T_h - T_c} - 1\right) = W_{\text{eng}}\left(\frac{T_c}{T_h - T_c}\right)$$

Thus, if $T_h = 100°\text{C} = 373\text{ K}$ and $T_c = 20°\text{C}=293\text{ K}$, the energy exhausted when the engine has done $5.0\times10^4\text{ J}$ of work is

$$Q_c = \left(5.0\times10^4\text{ J}\right)\left(\frac{293\text{ K}}{373\text{ K}-293\text{ K}}\right) = 1.83\times10^5\text{ J}$$

The mass of ice (at 0°C) this exhaust energy could melt is

$$m = \frac{Q_c}{L_{f,\text{ water}}} = \frac{1.83\times10^5\text{ J}}{3.33\times10^5\text{ J/kg}} = \boxed{0.55\text{ kg}}$$

12.49 The work output from the engine in an interval of one second is $W_{\text{eng}} = 1\,500\text{ kJ}$. Since the efficiency of an engine may be expressed as

$$e = \frac{W_{\text{eng}}}{|Q_h|} = \frac{W_{\text{eng}}}{W_{\text{eng}} + |Q_c|}$$

the exhaust energy each second is $|Q_c| = W_{\text{eng}}\left(\frac{1}{e}-1\right) = \left(1\,500\text{ kJ}\right)\left(\frac{1}{0.25}-1\right) = 4.5\times10^3\text{ kJ}$

The mass of water flowing through the cooling coils each second is

$$m = \rho V = \left(10^3\text{ kg/m}^3\right)\left(60\text{ L}\right)\left(10^{-3}\text{ m}^3/1\text{ L}\right) = 60\text{ kg}$$

so the rise in the temperature of the water is

$$\Delta T = \frac{|Q_c|}{mc_{water}} = \frac{4.5\times10^6\text{ J}}{\left(60\text{ kg}\right)\left(4\,186\text{ J/kg}\cdot°\text{C}\right)} = \boxed{18°\text{C}}$$

12.50 (a) From the first law, $\Delta U_{1\to3} = Q_{123} + W_{123} = +418\text{ J} + \left(-167\text{ J}\right) = \boxed{251\text{ J}}$

(b) The difference in internal energy between states 1 and 3 is independent of the path used to get from state 1 to state 3.

Thus, $\Delta U_{1\to3} = Q_{143} + W_{143} = 251\text{ J}$,

and $Q_{143} = 251\text{ J} - W_{143} = 251\text{ J} - \left(-63.0\text{ J}\right) = \boxed{314\text{ J}}$

(c) $W_{12341} = W_{123} + W_{341} = W_{123} + \left(-W_{143}\right) = -167 \text{ J} - \left(-63.0 \text{ J}\right) = -104 \text{ J}$

or $\boxed{\text{104 J of work is done } by \text{ the gas}}$ in the cyclic process 12341.

(d) $W_{14321} = W_{143} + W_{321} = W_{143} + \left(-W_{123}\right) = -63.0 \text{ J} - \left(-167 \text{ J}\right) = +104 \text{ J}$

or $\boxed{\text{104 J of work is done } on \text{ the gas}}$ in the cyclic process 14321.

(e) The change in internal energy is $\boxed{\text{zero}}$ for both parts (c) and (d) since both are cyclic processes.

12.51 (a) The work done *by* the system in process *AB* equals the area under this curve on the *PV* diagram. Thus,

$$W_{\text{by system}} = \left(\text{triangular area}\right) + \left(\text{rectangular area}\right)\text{, or}$$

$$W_{\substack{\text{by}\\\text{system}}} = \left[\frac{1}{2}\left(4.00 \text{ atm}\right)\left(40.0 \text{ L}\right) + \left(1.00 \text{ atm}\right)\left(40.0 \text{ L}\right)\right]\left(1.013 \times 10^5 \ \frac{\text{Pa}}{\text{atm}}\right)\left(\frac{10^{-3} \text{ m}^3}{\text{L}}\right)$$

$$= 1.22 \times 10^4 \text{ J} = \boxed{12.2 \text{ kJ}}$$

Note that the work done on the system is $W_{AB} = -W_{\substack{\text{by}\\\text{system}}} = -12.2 \text{ kJ}$ for this process.

(b) The work done on the system (that is, the work input) for process *BC* is the negative of the area under the curve on the *PV* diagram, or

$$W_{BC} = -\left[\left(1.00 \text{ atm}\right)\left(10.0 \text{ L} - 50.0 \text{ L}\right)\right]\left(1.013 \times 10^5 \ \frac{\text{Pa}}{\text{atm}}\right)\left(\frac{10^{-3} \text{ m}^3}{1 \text{ L}}\right)$$

$$= \boxed{4.05 \text{ kJ}}$$

(c) The change in internal energy is zero for any full cycle, so the first law gives

$$Q_{cycle} = \Delta U_{cycle} - W_{cycle} = 0 - \left(W_{AB} + W_{BC} + W_{CA}\right)$$

$$= 0 - \left(-12.2 \text{ kJ} + 4.05 \text{ kJ} + 0\right) = \boxed{8.15 \text{ kJ}}$$

12.52 The efficiency of the plant is $e = e_c = 1 - \dfrac{T_c}{T_h} = 1 - \dfrac{300\text{ K}}{500\text{ K}} = 0.400$

Also, $e = 1 - \dfrac{|Q_c|}{|Q_h|}$, so $|Q_h| = \dfrac{|Q_c|}{1-e} = \dfrac{|Q_c|}{0.600}$

From $\mathcal{P} = \dfrac{W_{\text{eng}}}{t} = \dfrac{e|Q_h|}{t} = \left(\dfrac{0.400}{0.600}\right)\dfrac{|Q_c|}{t}$,

the rate of energy transfer to the river by heat is

$$|Q_c|/t = 1.50\mathcal{P} = 1.50(1\,000\text{ MW}) = 1.50\times10^{9}\text{ J/s}$$

The flow rate in the river is then

$$\frac{m}{t} = \frac{\left(|Q_c|/t\right)}{c_{water}(\Delta T)_{river}} = \frac{1.50\times10^{9}\text{ J/s}}{(4\,186\text{ J/kg}\cdot{}^{\circ}\text{C})(6.00^{\circ}\text{C})} = \boxed{5.97\times10^{4}\text{ kg/s}}$$

12.53 (a) The change in length, due to linear expansion, of the rod is

$$\Delta L = \alpha L_0(\Delta T) = \left[11\times10^{-6}\ ({}^{\circ}\text{C})^{-1}\right](2.0\text{ m})(40^{\circ}\text{C} - 20^{\circ}\text{C}) = 4.4\times10^{-4}\text{ m}$$

The load exerts a force $F = mg = (6\,000\text{ kg})(9.80\text{ m/s}^2) = 5.88\times10^{4}\text{ N}$ on the end of the rod in the direction of movement of that end. Thus, the work done on the rod is

$$W = F\cdot\Delta L = (5.88\times10^{4}\text{ N})(4.4\times10^{-4}\text{ m}) = \boxed{26\text{ J}}$$

(b) The energy added by heat is

$$Q = mc(\Delta T) = (100\text{ kg})\left(448\ \frac{\text{J}}{\text{kg}\cdot{}^{\circ}\text{C}}\right)(20^{\circ}\text{C}) = \boxed{9.0\times10^{5}\text{ J}}$$

(c) From the first law, $\Delta U = Q + W = 9.0\times10^{5}\text{ J} + 26\text{ J} = \boxed{9.0\times10^{5}\text{ J}}$

12.54 (a) The work done *by* the gas during each full cycle equals the area enclosed by the cycle on the PV diagram. Thus

$$W_{\text{by gas}} = (3P_0 - P_0)(3V_0 - V_0) = \boxed{4P_0V_0}$$

(b) Since the work done on the gas is $W = -W_{\text{by gas}} = -4P_0V_0$ and $\Delta U = 0$ for any cyclic process, the first law gives

$$Q = \Delta U - W = 0 - \left(-4P_0V_0\right) = \boxed{4P_0V_0}$$

(c) From the ideal gas law, $P_0V_0 = nRT_0$, so the work done by the gas each cycle is

$$W_{\text{by gas}} = 4nRT_0 = 4(1.00\text{ mol})\left(8.31\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(273\text{ K})$$

$$= 9.07\times10^3\text{ J} = \boxed{9.07\text{ kJ}}$$

12.55 (a) The energy transferred to the gas by heat is

$$Q = mc(\Delta T) = (1.00\text{ mol})\left(20.79\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(120\text{ K})$$

$$= 2.49\times10^3\text{ J} = \boxed{2.49\text{ kJ}}$$

(b) Treating the neon as an ideal gas, the result of Problem 1 gives the change in internal energy as

$$\Delta U = \frac{3}{2}\left(P_fV_f - P_iV_i\right) = \frac{3}{2}\left(nRT_f - nRT_i\right) = \frac{3}{2}nR(\Delta T)\text{, or}$$

$$\Delta U = \frac{3}{2}(1.00\text{ mol})\left(8.31\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(120\text{ K}) = 1.50\times10^3\text{ J} = \boxed{1.50\text{ kJ}}$$

(c) From the first law, the work done *on* the gas is

$$W = \Delta U - Q = 1.50\times10^3\text{ J} - 2.49\times10^3\text{ J} = \boxed{-990\text{ J}}$$

12.56 (a) The change in volume of the aluminum is

$$\Delta V = \beta V_0(\Delta T) = (3\alpha)(m/\rho)(\Delta T)\text{, or}$$

$$\Delta V = 3\left[24\times10^{-6}\ (^\circ\text{C})^{-1}\right]\left(\frac{1.0\text{ kg}}{2.70\times10^{3}\text{ kg/m}^3}\right)(18\,^\circ\text{C}) = 4.8\times10^{-7}\text{ m}^3$$

so the work done on the aluminum is

$$W = -P(\Delta V) = -(1.013\times10^{5}\text{ Pa})(4.8\times10^{-7}\text{ m}^3) = \boxed{-4.9\times10^{-2}\text{ J}}$$

(b) The energy added by heat is

$$Q = mc(\Delta T) = (1.0\text{ kg})(900\text{ J/kg}\cdot{}^\circ\text{C})(18\,^\circ\text{C}) = 1.6\times10^{4}\text{ J} = \boxed{16\text{ kJ}}$$

(c) The first law gives the change in internal energy as

$$\Delta U = Q + W = 1.6\times10^{4}\text{ J} - 4.9\times10^{-2}\text{ J}=1.6\times10^{4}\text{ J} = \boxed{16\text{ kJ}}$$

12.57 (a) The energy input by heat from the molten aluminum is

$$|Q_h| = m_{\text{Al}}L_f = (1.00\times10^{-3}\text{ kg})(3.97\times10^{5}\text{ J/kg}) = 397\text{ J}$$

and the energy output to the frozen mercury is

$$|Q_c| = m_{\text{Hg}}L_f = (15.0\times10^{-3}\text{ kg})(1.18\times10^{4}\text{ J/kg}) = 177\text{ J}$$

The efficiency of the heat engine is given by

$$e = \frac{W_{\text{eng}}}{|Q_h|} = \frac{|Q_h|-|Q_c|}{|Q_h|} = 1-\frac{|Q_c|}{|Q_h|} = 1-\frac{177\text{ J}}{397\text{ J}} = \boxed{0.554\text{ or }55.4\%}$$

(b) $T_h = 660\,^\circ\text{C} = 933\text{ K}$ and $T_c = -38.9\,^\circ\text{C} = 234\text{ K}$. The Carnot efficiency for a heat engine operating between these two reservoirs is

$$e_c = 1-\frac{T_c}{T_h} = 1-\frac{234\text{ K}}{933\text{ K}} = \boxed{0.749\text{ or }74.9\%}$$

12.58 (a) From the result of Problem 1,

$$\Delta U_{A\to C} = \frac{3}{2}\left(P_C V_C - P_A V_A\right) = \frac{3}{2}\left[\left(3P_0\right)\left(2V_0\right) - P_0 V_0\right] = \frac{15}{2}P_0 V_0 = \frac{15}{2}nRT_0$$

The work done on the gas in process *ABC* equals the negative of the area under the process curve on the *PV* diagram, or

$$W_{ABC} = -\left[\left(3P_0\right)\left(2V_0 - V_0\right)\right] = -3P_0 V_0 = -3nRT_0$$

The total energy input by heat, $Q_{ABC} = Q_1 + Q_2$, is found from the first law as

$$Q_{ABC} = \Delta U_{A\to C} - W_{ABC} = \frac{15}{2}nRT_0 - \left(-3nRT_0\right) = \boxed{\frac{21}{2}nRT_0}$$

(b) For process *CDA*, the work done on the gas is the negative of the area under curve *CDA*, or $W_{CDA} = -\left[\left(P_0\right)\left(V_0 - 2V_0\right)\right] = +P_0 V_0 = +nRT_0$. The change in internal energy is $\Delta U_{C\to A} = -\Delta U_{A\to C} = -\frac{15}{2}nRT_0$. Thus, the energy *input* by heat for this process is

$$Q_{CDA} = \Delta U_{C\to A} - W_{CDA} = -\frac{15}{2}nRT_0 - nRT_0 = -\frac{17}{2}nRT_0$$

The total energy *output* by heat for the cycle is

$$Q_3 + Q_4 = -Q_{CDA} = -\left(-\frac{17}{2}nRT_0\right) = \boxed{\frac{17}{2}nRT_0}$$

(c) The efficiency of a heat engine using this cycle is

$$e = 1 - \frac{\left|Q_{output}\right|}{\left|Q_{input}\right|} = 1 - \frac{\left(17nRT_0/2\right)}{\left(21nRT_0/2\right)} = 1 - \frac{17}{21} = \boxed{0.190 \text{ or } 19.0\%}$$

(d) $$e_c = 1 - \frac{T_A}{T_C} = 1 - \frac{\left(P_A V_A/nR\right)}{\left(P_C V_C/nR\right)} = 1 - \frac{P_0 V_0}{\left(3P_0\right)\left(2V_0\right)} = \frac{5}{6} = \boxed{0.833 \text{ or } 83.3\%}$$

12.59 The mass of coal consumed in time t is given by $\Delta M = \left|Q_h\right|/Q_{coal}$ where $\left|Q_h\right|$ is the required energy input and Q_{coal} is the heat of combustion of coal. Thus, if $\mathcal{P}$ is the power output and e is the efficiency of the plant,

$$\Delta M = \frac{\left|Q_h\right|}{Q_{coal}} = \frac{\left(W_{eng}/e\right)}{Q_{coal}} = \frac{\mathcal{P}\cdot t}{e\cdot Q_{coal}}$$

(a) The coal used each day is

$$\Delta M = \frac{\mathcal{P}\cdot t}{e\cdot Q_{coal}} = \frac{\left(150\times10^{6}\ \text{J/s}\right)\left(86\,400\ \text{s/d}\right)}{(0.15)\left[\left(7.8\times10^{3}\ \dfrac{\text{cal}}{\text{g}}\right)\left(\dfrac{10^{3}\ \text{g}}{1\ \text{kg}}\right)\left(\dfrac{4.186\ \text{J}}{1\ \text{cal}}\right)\right]}$$

$$= 2.6\times10^{6}\ \text{kg/d} = \boxed{2.6\times10^{3}\ \text{metric ton/d}}$$

(b) The annual fuel cost is: $cost = \left(coal\ used\ yearly\right)\cdot\left(rate\right)$, or

$$cost = \left(\frac{\mathcal{P}\cdot t}{e\cdot Q_{coal}}\right)\cdot\left(\$8.0/\text{ton}\right)$$

$$= \frac{\left(150\times10^{6}\ \text{J/s}\right)\left(3.156\times10^{7}\ \text{s/yr}\right)}{(0.15)\left[\left(7.8\times10^{3}\ \dfrac{\text{cal}}{\text{g}}\right)\left(\dfrac{10^{3}\ \text{g}}{1\ \text{kg}}\right)\left(\dfrac{4.186\ \text{J}}{1\ \text{cal}}\right)\right]}\left(\frac{1\ \text{ton}}{10^{3}\ \text{kg}}\right)\left(\frac{\$8.0}{\text{ton}}\right) = \boxed{\$7.7\times10^{6}/\text{yr}}$$

(c) The rate of energy transfer to the river by heat is

$$\frac{|Q_c|}{t} = \frac{|Q_h| - W_{\text{eng}}}{t} = \frac{\left(W_{\text{eng}}/e\right) - W_{\text{eng}}}{t} = \mathcal{P}\cdot\left(\frac{1}{e} - 1\right)$$

Thus, the flow required is

$$\frac{m}{t} = \frac{|Q_c|/t}{c_{water}\left(\Delta T\right)} = \frac{\mathcal{P}}{c_{water}\left(\Delta T\right)}\left(\frac{1}{e} - 1\right)$$

$$= \frac{150\times10^{6}\ \text{J/s}}{\left(4186\ \text{J/kg}\cdot{}^{\circ}\text{C}\right)\left(5.0^{\circ}\text{C}\right)}\left(\frac{1}{0.15} - 1\right) = \boxed{4.1\times10^{4}\ \text{kg/s}}$$

12.60 (a) The energy transfer by heat required to raise the temperature of the water to the boiling point is

$$Q = mc\left(\Delta T\right) = \left(1.00\times10^{-3}\ \text{kg}\right)\left(4\,186\ \text{J/kg}\cdot{}^{\circ}\text{C}\right)\left(100^{\circ}\text{C} - 20.0^{\circ}\text{C}\right) = 335\ \text{J}$$

We neglect the very small volume expansion (and associated work done) by the water while in the liquid state. The first law of thermodynamics then gives the change in internal energy as

$$\Delta U = Q + W = 335\ \text{J} + 0 = \boxed{335\ \text{J}}$$

(b) To completely evaporate the water, the required energy input by heat is

$$Q = mL_v = \left(1.00 \times 10^{-3} \text{ kg}\right)\left(2.26 \times 10^{6} \text{ J/kg}\right) = 2.26 \times 10^{3} \text{ J}$$

The work done on the water in this process is

$$W = -P\left(V_f - V_i\right) = -\left(1.013 \times 10^{5} \text{ Pa}\right)\left(1\,671 \text{ cm}^3 - 1.00 \text{ cm}^3\right)\left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3}\right) = -169 \text{ J}$$

so the change in internal energy is

$$\Delta U = Q + W = 2.26 \times 10^{3} \text{ J} - 169 \text{ J} = \boxed{2.09 \times 10^{3} \text{ J}}$$

12.61. (a) The work done on the gas during this isobaric expansion process is

$$W = -P(\Delta V) = -P\left[A(\Delta x)\right] = -\left(8\,000 \text{ Pa}\right)\left[\left(0.10 \text{ m}^2\right)\left(+4.0 \times 10^{-2} \text{ m}\right)\right] = -32 \text{ J}$$

The first law of thermodynamics then gives the change in the internal energy of the system as

$$\Delta U = Q + W = 42 \text{ J} - 32 \text{ J} = \boxed{10 \text{ J}}$$

(b) If the piston is clamped in a fixed position, then $\Delta V = 0$ and

$$\boxed{\text{the work done on the gas is zero}}$$

In this case, the first law gives $\Delta U = Q + W = 42 \text{ J} + 0 = \; 42 \text{ J}$

12.62. (a) The energy transferred from the water by heat as it cools is

$$\left|Q_h\right| = mc\left|\Delta T\right| = \left(\rho V\right)c\left|\Delta T\right|$$

$$= \left[\left(1.0 \; \frac{\text{g}}{\text{cm}^3}\right)(1.0 \text{ L})\left(\frac{10^3 \text{ cm}^3}{1 \text{ L}}\right)\right]\left(1.0 \; \frac{\text{cal}}{\text{g} \cdot {}^\circ\text{C}}\right)\left(\frac{4.186 \text{ J}}{1 \text{ cal}}\right)(570^\circ\text{C} - 4.0^\circ\text{C})$$

or $\left|Q_h\right| = \boxed{2.4 \times 10^{6} \text{ J}}$

(b) The maximum efficiency of a heat engine is the Carnot efficiency. Thus,

$$e_c = 1 - \frac{T_c}{T_h} = 1 - \frac{(4.0 + 273)\ \text{K}}{(570+273)\ \text{K}} = 1 - \frac{277\ \text{K}}{843\ \text{K}} = 0.67$$

The maximum useful work output is then

$$\left(W_{\text{eng}}\right)_{\text{max}} = e_c\left|Q_h\right| = (0.67)\left(2.4\times10^6\ \text{J}\right) = \boxed{1.6\times10^6\ \text{J}}$$

(c) The energy available from oxidation of the hydrogen sulfide in 1.0 L of this water is

$$U = n(310\ \text{kJ/mol}) = \left[\left(0.90\times10^{-3}\ \frac{\text{mol}}{\text{L}}\right)(1.0\ \text{L})\right]\left(310\times10^3\ \frac{\text{J}}{\text{mol}}\right) = \boxed{2.8\times10^2\ \text{J}}$$

12.63. The work that you have done is

$$W_{\text{eng}} = mg(\Delta h) = \left[(150\ \text{lb})\left(\frac{4.448\text{N}}{1\ \text{lb}}\right)\right]\left[\left(90.0\ \frac{\text{step}}{\text{min}}\right)(30.0\ \text{min})\left(8.00\ \frac{\text{in}}{\text{step}}\right)\left(\frac{2.54\times10^{-2}\ \text{m}}{1\ \text{in}}\right)\right]$$

or $\quad W_{\text{eng}} = 3.66\times10^5\ \text{J}$

If the energy input by heat was $\left|Q_h\right| = (600\ \text{kcal})\left(\frac{4\,186\ \text{J}}{1\ \text{kcal}}\right) = 2.51\times10^6\ \text{J}$, your efficiency has been

$$e = \frac{W_{eng}}{\left|Q_h\right|} = \frac{3.66\times10^5\ \text{J}}{2.51\times10^6\ \text{J}} = \boxed{0.146\text{ or }14.6\%}$$

If the actual efficiency was $e = 0.180\text{ or }18.0\%$, the actual energy input was

$$\left|Q_h\right|_{actual} = \frac{W_{eng}}{e_{actual}} = \frac{3.66\times10^5\ \text{J}}{0.180} = \left(2.03\times10^6\ \text{J}\right)\left(\frac{1\ \text{kcal}}{4\,186\ \text{J}}\right) = \boxed{486\ \text{kcal}}$$