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1(a) we know that $V_A - V_B = 0.5L = 0.5 \times 10^{-3}\ m^3$ and $\frac{V_A}{V_B} = 9.5$.

So we can solve these equations simultaneously to get

$$9.5V_B - V_B = 0.5 \times 10^{-3}\ m^3.$$
$$8.5V_B = 0.5 \times 10^{-3}\ m^3$$
$$V_B = 5.88 \times 10^{-5}\ m^3$$
$$\therefore\ V_A = 9.5 \times 5.88 \times 10^{-5}\ m^3$$
$$= 5.59 \times 10^{-4}\ m^3$$

b. $n = \frac{P_A V_A}{R T_A} = \frac{100\ kPa \times 5.59 \times 10^{-4}\ m^3}{8.314 \times 300K}$

$= 0.0224\ mol$ Assume fuel-air is mostly air

$m = 6.49 \times 10^{-4}\ kg$ So molar mass = 29g

c. $P_B V_B^{\gamma} = P_A V_A^{\gamma} \Rightarrow P_B = P_A \left(\frac{V_A}{V_B}\right)^{\gamma} = 100\ kPa \times 9.5^{1.4}$

$= 2.34 \times 10^3\ kPa.$

then $T_B = \frac{P_B V_B}{nR} = \frac{2.34 \times 10^3\ kPa \times 0.588 \times 10^{-4}\ m^3}{0.0224 \times 8.314}$

$= 739K.$ (nb. Could also use $T_A V_A^{\gamma-1} = T_B V_B^{\gamma-1}$)

d. The process B -> C occurs at constant volume.

$T_C = 1350^\circ C = 1623K.$ $P_C = \frac{nRT_C}{V_C}$

$$= \frac{0.0224 \times 8.314 \times 1623K}{5.88 \times 10^{-5}\ m^3}$$

$$= 5.14 \times 10^3\ kPa.$$

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1e. $P_D = P_c \left(\frac{V_c}{V_D}\right)^{\gamma} = P_c \left(\frac{V_B}{V_A}\right)^{\gamma}$

$= 5.14 \times 10^3 \text{ kPa} \times \left(\frac{1}{9.5}\right)^{1.40}$

$= 219.8 \text{ kPa}.$

and $T_D = \frac{P_D V_D}{nR}$

$= \frac{219.8 \text{ kPa} \times 5.59 \times 10^{-4} \text{ m}^3}{0.0224 \times 8.314}$

$= 660\text{K}.$

F. $Q_h = nC_v(T_c - T_B) = 0.0224 \times 20.8 \text{ J/molK} \times (1623 - 739)\text{K}$

$= 412 \text{ J}.$

$Q_c = nC_v(T_D - T_A) = 0.0224 \times 20.8 \text{ J/mol.K} \times (660 - 300)\text{K}$

$= 168 \text{ J}$

$W = Q_h - Q_c = 412 - 168 \text{ J}$

$= 244 \text{ J}$

1g. $e = \frac{W}{Q_h} = \frac{2}{412} = 59.2\%.$

1h. Power is only produced on every other rotation of the crankshaft.

$P = \frac{1}{2} \times 6 \times (4000 \text{rev/min} \times 1\text{min}/60\text{s}) \times 244\text{J}$ (or 66.6 rev/sec)

$= 48.8 \text{ kW}.$ (= 65 horse. power)

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Q2. If you put an air conditioner in the middle of a building, then the only place it can dump the waste heat is into the building (rather than outside). Since the waste heat is always *greater* than the heat removed from the cold "reservoir," the net effect would be to raise the temperature inside the building rather than to lower it.

Q3.

(a) For these extreme temperatures the maximum efficiency would be

$$e = 1 - \frac{T_c}{T_h} = 1 - \frac{293\text{ K}}{773\text{ K}} = 62.1\%.$$

(b) With the higher steam temperature the maximum efficiency would be

$$e = 1 - \frac{T_c}{T_h} = 1 - \frac{293\text{ K}}{873\text{ K}} = 66.4\%.$$

If this efficiency is actually attained, then for a given Q_h we would get more work output than before by a factor of

$$\frac{.664}{.621} = 1.069,$$

that is, we get an additional .069 GW of power. To compute the additional profit, multiply the extra energy by the price charged:

$$\Delta\$ = (.069 \times 10^9\text{ J/s})(3.16 \times 10^7\text{ s/yr})\left(\frac{1\text{ kw-hr}}{3.6 \times 10^6\text{ J}}\right)\left(\frac{.05\ \$}{1\text{ kw-hr}}\right) = 3 \times 10^7\ \$.$$

Not bad: we make 30 megabucks!

(c) An efficiency of 40% means that the other 60% of the energy consumed ends up as waste heat. That's 1.5 times as much as the amount that ends up as work. More generally, by the definition of efficiency and the first law,

$$e = \frac{W}{Q_h} = \frac{W}{Q_c + W},$$

so the waste heat is

$$Q_c = W\left(\frac{1}{e} - 1\right) = 1.5\,W = 1.5\text{ GW}.$$

(d) In one second, the waste heat dumped to the river is 1.5×10^9 J, and this heat is spread among 10^5 kg of water, so each kilogram gets 15 kJ. With a heat capacity of 4186 J/°C, the water's temperature increases by $\Delta T = Q/C = 15000\text{ J}/4186\text{ J/°C} = 3.6$°C.

(e) The latent heat to evaporate water is 2260 J/g (at 100°C). At room temperature it's about 8% more, as mentioned in Problem 1.54 and Figure 5.11; so I'll take $L =$ 2400 J/g. The total amount of water that must evaporate each second is then

$$\frac{1.5 \times 10^9\text{ J}}{2400\text{ J/g}} = 6 \times 10^5\text{ g} = 600\text{ kg}.$$

That's only 0.6 m^3, or only 0.6% of the water in the river.

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Q4. As computed in the text, an ideal kitchen refrigerator could have a COP of about

$$\mathrm{COP} = \frac{T_c}{T_h - T_c} = \frac{255\ \mathrm{K}}{298\ \mathrm{K} - 255\ \mathrm{K}} = 5.9.$$

Therefore, by the definition of COP, $Q_c = 5.9W$ or $W = Q_c/5.9$. In each second, this refrigerator must remove 300 J of heat from the inside, so the work required is $W = 300\ \mathrm{J}/5.9 = 50$ J. In other words, the power drawn from the wall could be as little as 50 W. (In practice the operation won't be ideal, of course.)

Q5. The probability of finding any particular gas molecule in the leftmost 99% of a container is 99%. So the probability of finding all 100 molecules in the leftmost 99% would be

$$(0.99)^{100} = 0.366;$$

in other words, the rightmost 1% of the container will be empty about a third of the time. If instead there are 10,000 molecules, however, the probability drops to

$$(0.99)^{10{,}000} = (0.366)^{100} = 2.25 \times 10^{-44};$$

so this will "never" happen. And if there are 10^{23} molecules, the probability would be unimaginably small,

$$(0.99)^{10^{23}} = 10^{-4.4\times 10^{20}}.$$

Q6. (*) For argon at room temperature and atmospheric pressure, the volume per molecule is

$$\frac{V}{N} = \frac{kT}{P} = \frac{(1.38 \times 10^{-23}\ \mathrm{J/K})(300\ \mathrm{K})}{10^5\ \mathrm{N/m^2}} = 4.14 \times 10^{-26}\ \mathrm{m}^3,$$

while the energy per molecule is

$$\frac{U}{N} = \frac{3}{2}kT = \frac{3}{2}(1.38 \times 10^{-23}\ \mathrm{J/K})(300\ \mathrm{K}) = 6.21 \times 10^{-21}\ \mathrm{J}.$$

The mass of an argon atom is 40 u or 6.64×10^{-26} kg, so the argument of the logarithm in the Sackur-Tetrode equation is

$$\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2} = (4.14 \times 10^{-26}\ \mathrm{m}^3)\left(\frac{4\pi(6.64 \times 10^{-26}\ \mathrm{kg})(6.21 \times 10^{-21}\ \mathrm{J})}{3(6.63 \times 10^{-34}\ \mathrm{J\,s})^2}\right)^{3/2} = 1.02 \times 10^7.$$

The entropy of a mole of argon under these conditions is therefore

$$S = R[\ln(1.02 \times 10^7) + \tfrac{5}{2}] = R[18.64] = 155\ \mathrm{J/K}.$$

The only relevant difference between argon and helium in this calculation is the larger mass of the argon atom, which increases the argument of the logarithm by a factor of $(40/4)^{3/2} = 31.6$. The reason why m matters is because for a given energy, a molecule with more mass has more momentum, resulting in a larger "hypersphere" of allowed momentum states for the gas and hence a larger multiplicity.

Q7

(a) When you stir salt into a pot of soup, the sodium and chlorine ions can roam throughout the entire volume of the liquid. They can then have many more possible arrangements than when they are locked into crystals. More arrangements means higher multiplicity and hence higher entropy. And as we all know, it's not at all easy to reverse the process and get the salt out of the soup.

(b) Scrambling an egg mixes the yolk with the white, so that creates mixing entropy as the "yolk molecules" and "white molecules" can mix among each other. In addition, cooking the egg "denatures" the protein molecules, undoing their special folded patterns and stretching them out into long chains that can flop around randomly.

(c) Humpty Dumpty's fall itself is reversible (to a good approximation, neglecting air resistance), but when he lands and breaks into many pieces, his entropy suddenly increases because there are many more ways for him to be broken than whole. If the king's horses and the king's men just knew the second law of thermodynamics, they wouldn't have wasted their time trying to put him back together again!

(d) There are many more ways for the sand to be scattered about than for it to be sculpted into a sand castle, so the action of the wave most definitely increases the multiplicity and entropy of the sand.

(e) You can cut the tree in many places, at many angles, and it can fall in many directions, so there are many more ways for it to be cut down than for it to remain standing. Hence its entropy has increased. And of course, we all know that it's pretty much impossible to undo the cutting.

(f) When you burn gasoline, not only do you convert a smaller number of relatively large hydrocarbon molecules into a larger number of relatively small exhaust gas molecules, but you also release a great deal of thermal energy (converted from chemical energy) into the environment. This energy can arrange itself in many ways among the surrounding atoms, so the entropy of the environment increases a great deal as this thermal energy spreads farther and farther.

Q8.

(a) Assuming an average of eight hours of high-quality sunlight per day, a square meter of earth's surface receives in one year a total energy of

$$(1000 \text{ J/s})(3600 \text{ s/hr})(8 \text{ hrs/day})(365 \text{ days}) = 1.05 \times 10^{10} \text{ J}.$$

The entropy gained by the earth upon receiving this much energy is

$$\Delta S_{\text{earth}} = \frac{Q}{T} = \frac{1.05 \times 10^{10} \text{ J}}{300 \text{ K}} = 3.5 \times 10^{7} \text{ J/K}.$$

The entropy lost by the sun upon emitting this much energy is 20 times smaller than this, since the sun's surface is 20 times hotter than the earth's. The net change in entropy due to this process is therefore 19/20 of the preceding result; I'll just round it down to 3×10^{7} J/K.

(b) On a square meter of earth, in one year, you might be able to grow a few kilograms of grass, containing perhaps 1000 moles of carbon and other atoms. Even if this grass has *zero* entropy, the net reduction in entropy upon assembling it out of smaller molecules would only be of order

$$Nk = nR \approx (1000 \text{ moles})(8.3 \text{ J/mol}\cdot\text{K}) \sim 10^{4} \text{ J/K},$$

about 3000 times less than the entropy created by sunlight warming this patch of ground. So there's no violation of the second law here: The growth of the grass merely reduces the *increase* in entropy by a small fraction of a percent. A similar analysis could be applied to the growth of any other living thing, as well as to the process of evolution, which is claimed (by the so-called "scientific creationists") to violate the second law.