Chem 370 / ENTS 369 **Spring Term 2003**
Assignment 4 Solution **Instructor: R. Rossi**

1. The device stipulated by the assumptions in this problem absorbs every photon that hits it with $E_{photon} \geq E_{gap}$, and none of those having $E_{photon} < E_{gap}$. Each absorbed photon delivers E_{gap} units of energy. The $J(\lambda)$ function given in the problem doesn't actually give us a numeric value for the number of photons hitting the device, because we don't know how big the device is or how far it is from the blackbody; nonetheless, the correction for that would be some cone angle correction factor ϕ, which will be independent of E_{gap} and $T_{blackbody}$ and which will have no effect on the external efficiency of the device, because that's defined as

$$\varepsilon = \text{external efficiency} = \frac{\text{total electric power out of device}}{\text{total solar power into device}}$$

The end result of any photon having $E_{photon} \geq E_{gap}$ impinging on a single-gap device of the sort considered here is the same: the electron-hole pair looses any energy in excess of the bandgap energy (as heat), and provides E_{gap} of electrical energy. We want to determine what bandgap energy in such a device will maximize the total electric power extracted from a given incident spectral distribution. Well, the total power such a device will deliver, $P_{\text{ideal single threshold device}}$, is

$$P_{ISTD} = \begin{pmatrix}\#\text{ of photons}\\ \text{collected}\end{pmatrix}\begin{pmatrix}\text{energy delivered}\\ \text{per photon}\end{pmatrix} = \begin{pmatrix}\text{collectable}\\ \text{photon flux}\end{pmatrix} E_{gap}$$

All the photons with $E \geq E_{gap}$ can be and are collected, and we can count them with an integral:

$$\begin{pmatrix}\text{collectable}\\ \text{photon flux}\end{pmatrix} = J_{cpf} = \phi\int_{\text{lower absorbtion limit}}^{\text{upper absorbtion limit}} J_{ph}(\lambda)d\lambda$$

To get the limits of integration to agree with the integrand, we can establish the limits as wavelengths:

$$\text{upper absorbtion wavelength limit} = \text{minimum photon energy} = \lambda_{gap} = \frac{hc}{E_{gap}}$$

$$\text{lower absorbtion wavelength limit} = \text{infinite photon energy} = \lambda_{min} = \frac{hc}{\infty} = 0$$

Then we would have $$J_{cpf} = \phi\int_0^{hc/E_{gap}} J_{ph}(\lambda)d\lambda = \phi\int_0^{hc/E_{gap}} \frac{2\pi c}{\lambda^4}\left(\frac{1}{e^{hc/\lambda kT}-1}\right)d\lambda$$

The other alternative is to convert the integrand into the energy regime. The latter approach is a bit tricky, because just like when you use a "u-substitution" in calculus, you have to convert both $J(\lambda)$ **and** $d\lambda$ to energy functions. But once you've pulled it off, I think it is much easier to think about:

$$\lambda = \frac{hc}{E_{ph}} \quad \Rightarrow \quad d\lambda = d\left(\frac{hc}{E_{ph}}\right) = hc\; d\left(\frac{1}{E_{ph}}\right) = hc\left(\frac{-1}{E_{ph}^2}dE_{ph}\right) = \frac{-hc}{E_{ph}^2}dE_{ph}$$

$$J_{cpf} = \phi\int_{\lambda=0}^{\lambda=\lambda_{gap}} \frac{2\pi c}{\left(\frac{hc}{E_{ph}}\right)^4}\left(\frac{1}{e^{\left[hc/kT\left(hc/E_{ph}\right)\right]}-1}\right)\frac{-hc}{E_{ph}^2}dE_{ph} = \phi\int_{E=\infty}^{E=E_{gap}} \frac{2\pi c E_{ph}^4}{h^4c^4}\left(\frac{1}{e^{hcE_{ph}/kThc}-1}\right)\frac{-hc}{E_{ph}^2}dE_{ph}$$

$$= -\phi\int_{\infty}^{E_{gap}} \frac{2\pi c E_{ph}^2}{h^3c^3}\left(\frac{1}{e^{E_{ph}/kT}-1}\right)dE_{ph} = \phi\int_{E_{gap}}^{\infty} \frac{2\pi E_{ph}^2}{h^3c^2}\left(\frac{1}{e^{E_{ph}/kT}-1}\right)dE_{ph}$$

This leaves us with two different, but equally valid expressions for the total collected power:

$$P_{ISTD} = E_{gap} \cdot J_{cpf} = E_{gap}\ \phi \int_0^{hc/E_{gap}} \frac{2\pi c}{\lambda^4}\left(\frac{1}{e^{hc/\lambda kT} - 1}\right) d\lambda = E_{gap}\ \phi \int_{E_{gap}}^{\infty} \frac{2\pi E_{ph}^2}{h^3 c^2}\left(\frac{1}{e^{E_{ph}/kT} - 1}\right) dE_{ph}$$

The other thing we are going to need is an expression for the total solar power hitting our little device. That's most easily calculated from an integral in energy: each photon provides E_{ph} of energy, and so

$$P_{blackbody} = \phi \int_{\text{all photons}} E_{ph} \cdot J_{ph} dE_{ph} = \phi \int_0^{\infty} E_{ph} \frac{2\pi E_{ph}^2}{h^3 c^2}\left(\frac{1}{e^{E_{ph}/kT} - 1}\right) dE_{ph} = \phi \int_0^{\infty} \frac{2\pi E_{ph}^3}{h^3 c^2}\left(\frac{1}{e^{E_{ph}/kT} - 1}\right) dE_{ph}$$

But we can also obtain this value from an integration in λ. Because $E_{ph} = hc/\lambda$, the total power present in the photons emitted by a blackbody in a wavelength window of width $d\lambda$ centered around λ is given by $dP_{blackbody} = E_{ph}\ dJ_{ph}$, and we can integrate this over all wavelengths to get $P_{blackbody}$:

$$P_{blackbody} = \int_0^{\infty} \frac{hc}{\lambda} dJ_{ph} = \phi \int_0^{\infty} \frac{hc}{\lambda} \frac{2\pi c}{\lambda^4}\left(\frac{1}{e^{hc/\lambda kT} - 1}\right) d\lambda = \phi \int_0^{\infty} \frac{2\pi hc^2}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT} - 1}\right) d\lambda$$

The external efficiency of our device is thus

$$\varepsilon = \text{external efficiency} = \frac{\text{total electric power out of device}}{\text{total solar power into device}} = \frac{P_{ISTD}}{P_{blackbody}}$$

$$\varepsilon = \frac{E_{gap}\ \phi \int_0^{hc/E_{gap}} \frac{2\pi c}{\lambda^4}\left(\frac{1}{e^{hc/\lambda kT} - 1}\right) d\lambda}{\phi \int_0^{\infty} \frac{2\pi hc^2}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT} - 1}\right) d\lambda} = \frac{E_{gap}\ \phi \int_{E_{gap}}^{\infty} \frac{2\pi E_{ph}^2}{h^3 c^2}\left(\frac{1}{e^{E_{ph}/kT} - 1}\right) dE_{ph}}{\phi \int_0^{\infty} \frac{2\pi E_{ph}^3}{h^3 c^2}\left(\frac{1}{e^{E_{ph}/kT} - 1}\right) dE_{ph}} = f(E_{gap}, T_{blackbody})$$

Whichever nasty fraction we use, it is, at its root, just a function of E_{gap} and $T_{blackbody}$. Plug in a value for T and a value for E_{gap}, and this will give you a number. At least, it will if you can crunch it somehow!

Ok, so now, on to the solution for approach (a), the hand-wavy one:

i. To find the optimal bandgap, we want to maximize P_{ISTD} by varying E_{gap}, holding T constant. We can do this by either plotting P_{ISTD} vs. E_{gap} and picking out the maximum, or by finding the point where

$$\frac{\partial P_{ISTD}}{\partial E_{gap}} = 0 \quad \text{in} \quad E_{gap} = [0, \infty]$$

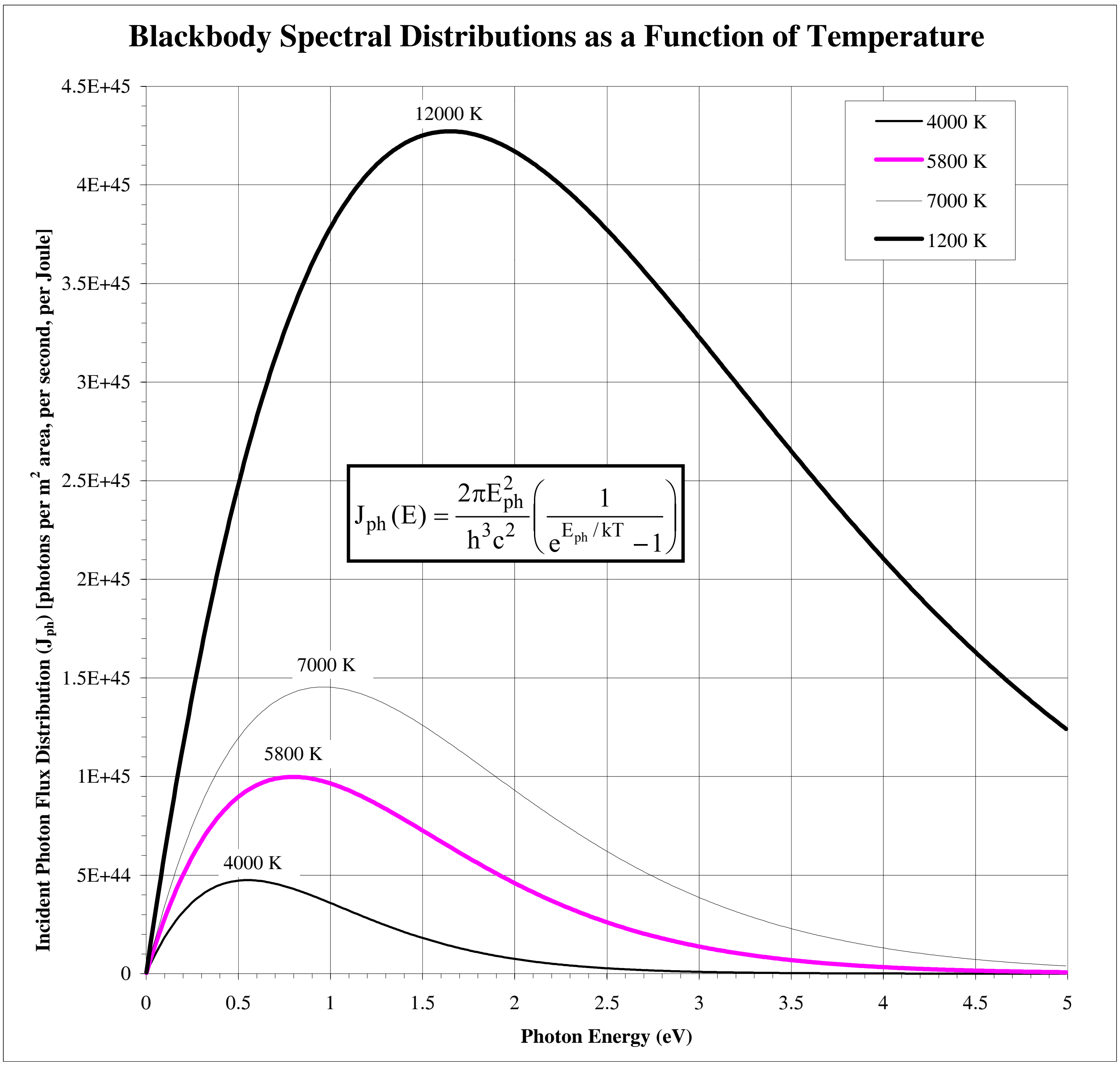
ii. The maximum efficiency attainable at a given solar source temperature will be that attained by a device having the optimal bandgap calculated in part (i). To determine the efficiency of such a device, we just plug the optimum E_{gap} value into the ε expression up above. Never mind that actually getting a number for it is darn hard, you don't have to do so. Note that in each case the unknown cone angle correction ϕ drops out, so we don't have to know what it is. What that tells us (and I hope this makes intuitive sense for you) is that the optimum bandgap for this idealized single-threshold device doesn't depend on how far from the blackbody it is, or on how large the device is.

iii. It is helpful to note that there are two types of "loss" in efficiency from (ii):

1) First, not all of the photons are collected by the device: the upper integral in ε does not include photons of energy less than E_{gap} (wavelengths longer than λ_{gap}).

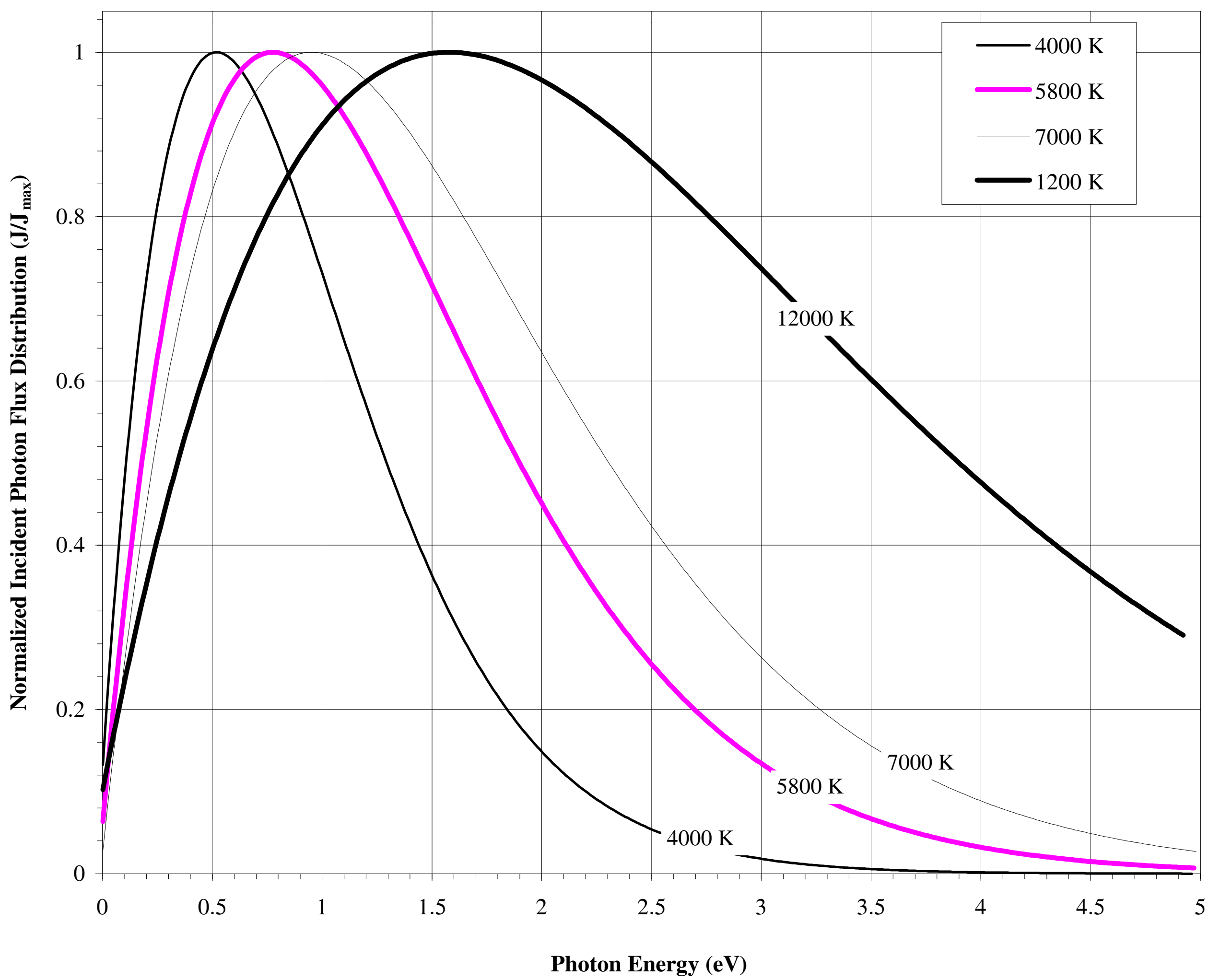
2) Second, the device only collects E_{gap} worth of energy from any given photon, regardless of how much energy the photon itself has. The (energy per photon) term in the denominator is variable, equal to E_{ph}, and appears inside integral, while the (energy per photon) term in the numerator is fixed, equal to E_{gap}, and less than or equal to E_{ph} for all of the photons that actually get absorbed.

Because the shape of the blackbody spectral distribution changes with temperature, so does the optimal bandgap value. As can be seen from the plot below, the spectral distribution shifts toward higher energies at higher temperatures (this trend is reversed, but still quite clear, on a wavelength plot). The area under each curve equals the number of photons in that energy regime. It is pretty clear that if some reasonable value (say 0.5 eV) is optimal at 4000K, you can more than double the energy per photon to 1.0 eV and not lose more than half the collected photons when the solar source is at a flaming 12000K. Thus, the optimal bandgap should increase with temperature.



iv. An analysis similar to that described above gives us a handle on what happens to the maximum efficiency of a single-threshold device as a function of the local solar source temperature. Scaling the plot above to a consistent maximum, we see that the blackbody distribution becomes progressively broader in energy with increasing temperature, but retains a very similar shape:

Relative Blackbody Spectral Distributions as a Function of Temperature



In fact, if the photon energy scale for each temperature in the plot above is multiplied by the ratio $\frac{E_{photon} \text{ of maximum } J_{photon} \text{ at 4000 K}}{E_{photon} \text{ of maximum } J_{photon} \text{ at given temperature}}$, then the resulting curves all fall right on top of one another. (This is not shown, because it's not very exciting to look at. Visualize all of the curves above falling right on top of the 4000 K line in the plot above.) In other words, the J_{ph} functions are self-similar with temperature! When the temperature increases, both the position of the maximum in J_{ph} and the optimal E_{gap} value increase, but the fraction of the photons collected remains the same. What's more, the self-similar nature of J_{ph} implies that the "average photon energy" of the distribution will increase at the same rate as E_{gap}. The efficiency of an ideal-gap ISTD will be independent of the local blackbody source temperature, because both fractions in the expression below remain constant:

$$\text{External Efficiency} = \left(\frac{\text{ideal } E_{gap}}{\text{average } E_{photon}}\right)\left(\begin{array}{l}\text{Fraction of all incident} \\ \text{photons collected by device}\end{array}\right)$$

You didn't have to go to this extent in providing an explanation for this question, but I like this one.

b. To get at this problem numerically, I originally used an old-school DOS program called Derive. (You're probably asking, "What's DOS?" Never mind, I'm way old.) Any numerical crunch program can do this, provided you can figure out how to enter the equations [in such a way that they don't incur numeric overflows] and put the program into numeric (rather than analytic) mode. To make the numerical values friendlier, I used energies in eV and scaled the photon counts with constants:

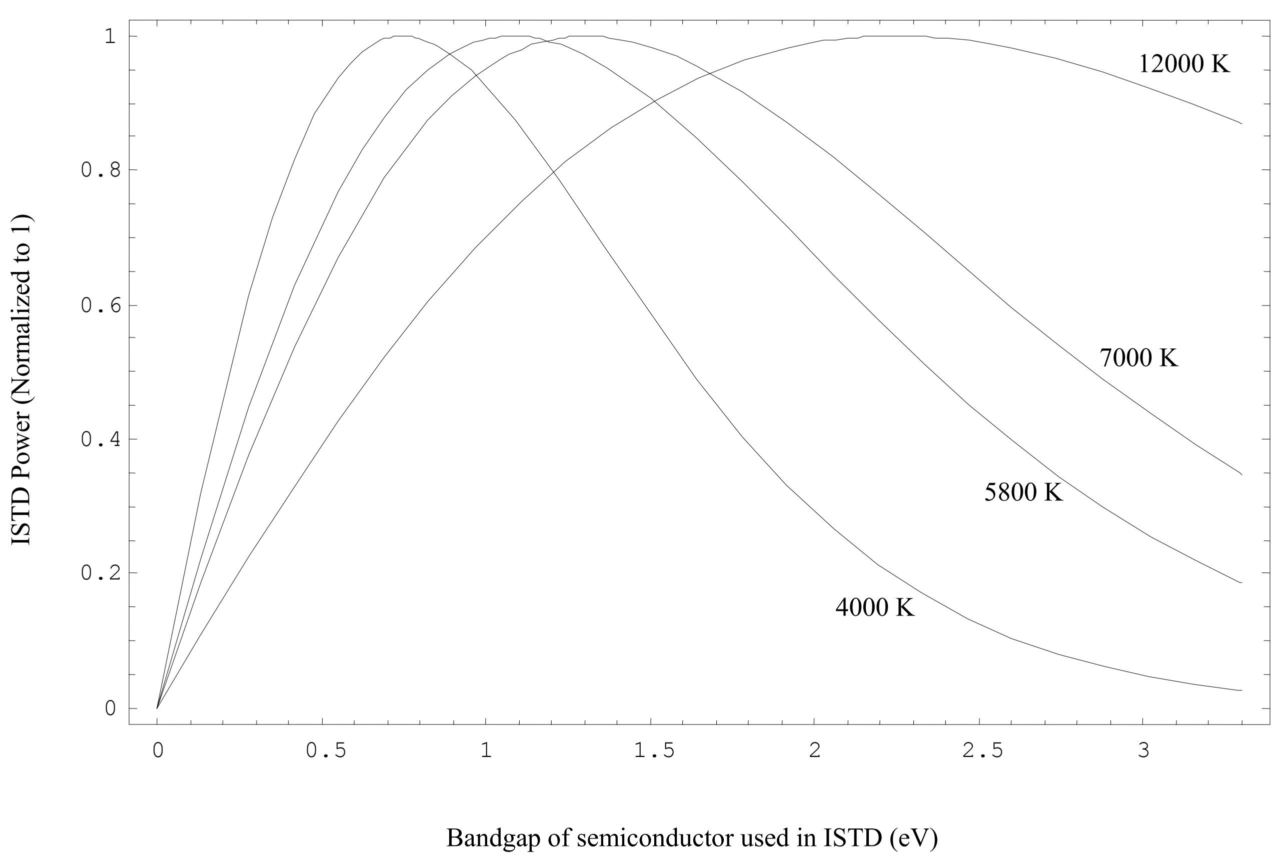
$$P_{ISTD} = E_{gap}\int_{E_{gap}}^{\infty} a\ E_{ph}^2 \left(\frac{1}{e^{E_{ph}/b}-1}\right) dE_{ph} \qquad \text{where}$$

$$a = \frac{2\pi}{h^3c^2} = 9.88\times10^{26}\ \frac{J^3/eV^3}{J^3s^3m^2s^{-2}} = 9.88\times10^{26}\ \frac{eV^3}{m^2s}$$

$$\text{and} \quad b = kT \begin{cases} 0.3447 \text{ eV at } 4000 \text{ K} \\ 0.4998 \text{ eV at } 5800 \text{ K} \\ 0.6032 \text{ eV at } 7000 \text{ K} \\ 1.0341 \text{ eV at } 12000 \text{ K} \end{cases}$$

Since it's hard to get Derive to put its output into a readily printable format, I broke down and tried to do the same thing with My Buddy™ Mathematica. It was a lot harder for me, but by peeking at Ben Luey's work from last term, I finally got it. So this is actually Mathematica output, but it matches what I originally got on my trusty old 386 back in 1993:

Determination of Optimal Bandgaps for Ideal Single Threshold Devices Exposed to Simple Blackbody Sources at 4000, 5800, 7000, and 12000 K



The maximum efficiency at each temperature can be calculated using the formula

$$\varepsilon_{ISTD} = \frac{E_{gap,\,optimal}\displaystyle\int_{E_{gap,\,optimal}}^{\infty}\frac{a\,E_{ph}^2}{e^{E_{ph}/b}-1}\,dE_{ph}}{\displaystyle\int_0^{\infty}\frac{a\,E_{ph}^3}{e^{E_{ph}/b}-1}\,dE_{ph}} = \frac{E_{gap,\,optimal}\displaystyle\int_{E_{gap,\,optimal}}^{\infty}\frac{a\,E_{ph}^2}{e^{E_{ph}/b}-1}\,dE_{ph}}{\dfrac{\pi^4 a k^4}{15}T^4}$$

(The denominator can actually be solved analytically: see Tipler's Modern Physics, p.107.)

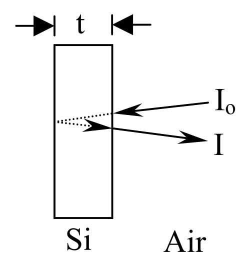
The "exact" numerical results I obtained with Mathematica appear in the table below:

Blackbody Temperature (K)	4000.	5800.	7000.	12000.
Optimal Bandgap for an ISTD (eV)	0.74_6	1.08_2	1.30_6	2.23_9
Maximum Efficiency at Optimal Bandgap	43.8_8%	43.8_8%	43.8_8%	43.8_8%

Your values may show slight variations if you employed a discrete integral or a numerical method to get your results, but as long as you estimated this uncertainty, no worries! Those of you who read that paper by C. H. Henry may be saying "Whoa! Those aren't the same values he got!" (I said it, anyway…) But Henry's work differs from what we are doing in this problem in two important respects:

1. Henry considers a few additional loss mechanisms, such as radiative recombination
2. Henry uses the AM1.5 solar spectrum, which has sizable chunks cut out of it due to the greenhouse (IR absorbing) gasses in the atmosphere, like H_2O and CO_2. This reduces the spectral density in the infrared portion of the spectrum and shifts the optimal bandgap values upward appreciably.

2. Here's the anticipated light path and model:
The effective pathlength for the light within the Si is 2t, and we want to absorb 99% of the incident light, which means we want I to be 1%, or 0.01, of the incident intensity I_o. Applying Beer's law for solids, we find



$$A = -\ln\frac{I}{I_o} = \varepsilon bc = \alpha\ell \quad \text{for solids} \quad \Rightarrow$$

$$\frac{I}{I_o} = 1\% = 0.01, \text{ so we need } \alpha\ell = -\ln\frac{I}{I_o} = -\ln(0.01) = +2.3$$

Our pathlength, ℓ, is 2t, so $2\alpha t = 2.3 \quad \Rightarrow \quad t = \dfrac{2.3}{\alpha}$

Now all we need is the value of α at 800 nm for Si and GaAs. We can read this off of Figure 7 on p. 41 in the chapter by Lewis and Rosenbluth, once we calculate what photon energy it corresponds to:

$$E_{photon} = \frac{hc}{\lambda} = \frac{1.986\times10^{-25}\ \text{J}\cdot\text{s}\cdot\text{m/s}}{800\times10^{-9}\ \text{m}} \times \frac{1\ \text{eV}}{1.602\times10^{-19}\ \text{J}} = 1.55\ \text{eV} \quad \Rightarrow \quad \alpha = \begin{cases} 10^{2.8}\,\text{cm}^{-1} & \text{for Si} \\ 10^{4.1}\,\text{cm}^{-1} & \text{for Ga As} \end{cases}$$

$$t_{Si} = \frac{2.3}{\alpha} = \frac{2.3}{10^{2.8}\,\text{cm}^{-1}} = 0.0036_5\ \text{cm} = 36._5\ \mu\text{m} \qquad t_{GaAs} = \frac{2.3}{\alpha} = \frac{2.3}{10^{4.1}\,\text{cm}^{-1}} = 0.00018\ \text{cm} = 1.8\ \mu\text{m}$$

Notice how at 800 nm, a GaAs solar device could be about one tenth the thickness of a Si device and still absorb the same fraction of the incident light. This is because Si is indirect-gap, while GaAs is direct gap.

3. a. This is straightforward, the given information is pretty much all you need:

$$P_{\text{solar device}} = (\text{Total power in from sun})(\text{External efficiency of device})$$

$$P_{\text{ideal single-gap device at AM1}} = (P_{\text{total, AM1}})(\varepsilon_{\text{external, ISTD in AM1}})$$

$$= \left(\frac{925\text{ W}}{\text{m}^2\text{ of exposed area}}\right)(2\text{ m}^2\text{ exposed area})(31\%)$$

$$= 5_{73.5}\text{ W from an ideal single-gap device covering the surface of a vehicle}$$

(Note: Whoops! Henry's study is actually based on AM1.5, not AM1! I've fixed that for the future, and I apologize if that led to any confusion. The big idea you get from this certainly still holds.)

b. This is a unit conversion, nothing more, though you have to dig up the conversion factor:

$$5_{73.5}\text{ W}\left(\frac{1\text{ horsepower}}{0.7457\text{ kW}}\right)\left(\frac{1\text{ kW}}{1000\text{ W}}\right) = 0.7_{69}\text{ horsepower (HP)}$$

Keep in mind that a Geo Metro's 3-cylinder combustion engine packs 55 HP; a solar cell does *not* provide a lot of oomph! It's for this reason that any remotely practical solar-powered vehicle needs to carry some sort of energy storage device, like a battery. As you'll learn below, even this small amount of power can maintain a meaningful speed, but getting up to speed would take an eternity if you couldn't even draw a single horse out of your powerplant.

c. Now we'll have to put our thinking caps back on! This part of the problem requires we learn a few new tricks from the fine folks at New Mexico Tech. For starters, the aerodynamic drag force (viscous + static) acting on an object moving relative to a fluid is equal to

$$F_D = \text{Aerodynamic drag force} = C_D A(\text{KE}_{\text{fluid hitting object}}\text{ per unit length of fluid}) = C_D A\left(\tfrac{1}{2}\rho v^2\right)$$

$$[=]\ \text{m}^2\left(\frac{\text{kg}}{\text{m}^3}\right)\left(\frac{\text{m}}{\text{s}}\right)^2\ [=]\ \text{m}^2\left(\frac{\text{m}^2\cdot\text{kg}}{\text{m}^3\cdot\text{s}^2}\right)\left(\frac{1\text{ N}}{1\frac{\text{kg}\cdot\text{m}}{\text{s}^2}}\right)\ [=]\ \text{m}^2\left(\frac{\text{N}}{\text{m}^2}\right)\ [=]\ \text{m}^2\left(\frac{\text{N}\cdot\text{m}}{\text{m}}\right)\ [=]\ \text{m}^2\left(\frac{\text{J}}{\text{m}}\right)\ [=]\ \text{N}$$

where C_D is an empirically-determined coefficient describing how aerodynamic the shape of the object is, ρ is the density of the fluid, v is the velocity of the fluid relative to the object, and A is the projected surface area of the object perpendicular to the flow (what would the area of the object's shadow be on a wall behind it and perpendicular to the flow, if the fluid were actually light?). Assuming this to be the only force preventing the object from moving through the fluid, the work required to overcome it and maintain a constant relative flow would be

$$\text{Power} = P = \frac{\text{work}}{\text{unit time}} = \frac{\text{Force}\cdot\text{distance}}{\text{time}}\ [=]\ \text{N}\frac{\text{m}}{\text{s}} = F_D\cdot v = C_D A\left(\tfrac{1}{2}\rho\cdot v^2\right)v = \tfrac{1}{2}C_D\cdot A\cdot\rho\cdot v^3$$

(We'll see this equation repeatedly in our wind unit!!!) Alrighty, so now we need to pick out a specific C_D and A pair for a specific vehicle, a fluid density for air, and solve for the velocity we can maintain for a given power. I'm keen to know about the Honda Civic Hybrid, so I'll use its characteristics: namely, $C_D = 0.28$ and $A = 1.7\text{ m}^2$ (the latter is estimated based on data for an older Civic model, from http://www.teknett.com/pwp/drmayf/dragcd~1.htm). The density of air varies with humidity, temperature, and elevation, but according to the Danish Wind Industry Association, it is 1.225 kg/m^3 for dry air at 15ºC, at sea level. I'll use 1.2_{25}, which should cover most dry air:

$$P = \tfrac{1}{2}C_D\cdot A\cdot\rho\cdot v^3 = 5_{73.5}\text{ W} = \tfrac{1}{2}(0.28)(1.7\text{ m}^2)\left(1.2_{25}\frac{\text{kg}}{\text{m}^3}\right)v^3 \quad\Rightarrow$$

$$v^3 = \frac{2\cdot 5_{73.5}\text{ W}}{(0.28)(1.7\text{ m}^2)\left(1.2_{25}\frac{\text{kg}}{\text{m}^3}\right)}\left(\frac{1\text{ J}\cdot\text{s}^{-1}}{1\text{ W}}\right)\left(\frac{\text{kg}\cdot\text{m}^2\cdot\text{s}^{-2}}{1\text{ J}}\right) = 1_{967}\left(\frac{\text{m}^3}{\text{s}^3}\right)$$

Solving for the velocity (and converting into yucky, yet familiar units) yields our desired result:

$$v = \sqrt[3]{1_{967}\,\frac{m^3}{s^3}} = 1_{2.53}\,\frac{m}{s}\left(\frac{1\text{ km}}{1000\text{ m}}\right)\left(\frac{3600\text{ s}}{1\text{hr}}\right)\left(\frac{1\text{ mile}}{1.609\text{ km}}\right) = 2_{8.0}\,\frac{\text{miles}}{\text{hour}} = 30\text{ mph}$$

The Honda Civic Hybrid is reasonably svelte and small for a modern car, so your calculated maintainable speed will probably be a bit smaller than this. (Much less if you analyzed an SUV…)

All of these speeds are actually over-estimates, because the "rolling resistance" of a car dominates at these low speeds, as explained on the Humanpower website. Aerodynamic drag becomes the dominant resistance at higher speeds, though, because it increases with the cube of the "airspeed."

4. Well, now we are told what speed we want to maintain, and have to determine how to get the power needed to do so! Let's figure out how much we need, first:

$$P = \tfrac{1}{2}C_D\cdot A\cdot\rho\cdot v^3 = \tfrac{1}{2}(0.28)(1.7\text{ m}^2)\left(1.2_{25}\,\frac{kg}{m^3}\right)\left[\left(70\,\frac{\text{miles}}{\text{hour}}\right)\left(\frac{1.609\text{ km}}{1\text{ mile}}\right)\left(\frac{1000\text{ m}}{1\text{ km}}\right)\left(\frac{1\text{hour}}{3600\text{ s}}\right)\right]^3$$

$$= \tfrac{1}{2}(0.28)(1.7\text{ m}^2)\left(1.2_{25}\,\frac{kg}{m^3}\right)\left(3_{1.3}\,\frac{m}{s}\right)^3 = 8_{934}\,\frac{m^2\cdot kg\cdot m^3}{m^3\cdot s^3} = 8_{934}\,\frac{m^2\cdot kg}{s^3}\left(\frac{1\text{ W}}{1\text{ J}\cdot s^{-1}}\right)\left(\frac{1\text{ J}}{kg\cdot m^2\cdot s^{-2}}\right)$$

$$= 8_{934}\,W\left(\frac{1\text{ horsepower}}{0.7457\text{ kW}}\right)\left(\frac{1\text{ kW}}{1000\text{ W}}\right) = 1_{1.98} = 1_2\text{ HP}$$

Sooooo, it takes about 12 HP for a Civic Hybrid to overcome aerodynamic drag in dry air at 70 MPH. (We'll use the more convenient 9 kW number in subsequent calculations, but I wanted to put this number in context and make sure that it was reasonable.) What if it was a Fuel Cell Civic Hybrid?!? To work that out, we need to determine how much energy can be obtained by combining hydrogen and oxygen in a fuel cell. To really determine this correctly, we'd have to take free energy into account, but we can much more readily get a pretty good estimate from enthalpies. (This is the effective difference between Henry calculating and using a W value in his paper, and our use of E_{gap} in problem 1!) I'll do it both ways, or at least try to! In either case, we are considering the chemical reaction

$$H_{2(g)} + \tfrac{1}{2}\,O_{2(g)} \rightarrow H_2O_{(\ell)}$$

and we want to determine how much energy a gram of H_2 will be able to provide a fuel cell that's 100% efficient (and thus how much power it can provide toward actually moving the vehicle, as it feeds a 100% efficient motor, through a magical, frictionless drivetrain.)

Enthalpy Approach: (Approximate)

The enthalpy change of the reaction above (ΔH_{rxn}) is actually the heat released when the reactants are combined at constant pressure. We are hoping to carry out this reaction in such a way that instead of producing heat, it produces only electric power. Since *most* of the energy released comes out as heat when H_2 is burned in the atmosphere, ΔH provides a pretty good surrogate for the energy available from this reaction. (However, it convolves in the ΔPV work and ignores the effect of entropy, so it's not at all rock-solid.) To get ΔH_{rxn}, we utilize a table of ΔH_f^o values, like the one in the back of Zumdahl[1]. Since the reaction above actually *is* the formation reaction for liquid water, its ΔH_{rxn} is simply $\Delta H_f^o[H_2O_{(\ell)}]$:

$$\Delta H_{rxn} = \Delta H_f^o[H_2O_{(\ell)}] = -286\,\frac{kJ}{\text{mole of }H_2O_{(\ell)}\text{ produced}} = \frac{286\text{ kJ of heat released}}{\text{mole of }H_{2(g)}\text{ consumed}}$$

With the energy available to the fuel cell assumed to be equal to the heat released in the situation above,

$$\text{Electric energy produced by the fuel cell} = \frac{286\text{ kJ}}{\text{mol }H_2}\left(\frac{1\text{ mol }H_2}{2\text{ mol H}}\right)\left(\frac{1\text{ mol of H}}{1.00794\text{ g of H}}\right) = 141_{.87}\,\frac{kJ}{\text{g of }H_2}$$

[1]S. S. Zumdahl and S. A. Zumdahl, *Chemistry*, 5th ed., Houghton Mifflin: Boston (2000), pp. A21-A24.

With these assumptions, the rate of hydrogen consumption would be

$$P_{\text{required to maintain 70 mph}} = 8_{934}\,\text{W}\left(\frac{1\ \text{J}\cdot\text{s}^{-1}}{1\ \text{W}}\right)\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)\left(\frac{1\ \text{g of H}_2}{141._{87}\ \text{kJ}}\right) = 0.06_{2973}\,\frac{\text{g of H}_2}{\text{second}}$$

$$= 0.06_{2973}\,\frac{\text{g of H}_2}{\text{second}}\left(\frac{3600\ \text{s}}{1\ \text{hr}}\right) = \frac{2_{27}\ \text{grams of H}_2}{\text{hour of travel}}$$

$$= \frac{2_{27}\ \text{grams of H}_2}{\text{hour of travel}}\left(\frac{1\ \text{mol of H}_2}{2.01588\ \text{g of H}_2}\right)\left(\frac{1\ \text{mol of H}_2\text{O}}{1\ \text{mol of H}_2}\right)\left(\frac{18.0152_8\ \text{g of H}_2\text{O}}{1\ \text{mol of H}_2\text{O}}\right)$$

$$= \frac{2_{026}\ \text{g of H}_2\text{O}}{\text{hour of travel}}$$

So, this method indicates that it would require about 200 g of $H_{2(g)}$ to maintain 70 mph for one hour, and that about two kilograms of water would emerge from the car's tailpipe over that period of time.

Free Energy Approach: (Technically correct)

In reality, even with a 100% efficient fuel cell, the amount of energy I can actually extract from the reaction above is the *free energy*, and that depends on the activity of the reagents, which in this case means the partial pressure of the gaseous reactants (assuming the water produced is a pure liquid). To really do this right, I'll have to make some assumptions. Namely, let's assume that the H_2 for this fuel cell comes from a storage tank employing a metal hydride technology, such that the fuel cell is fed with pure $H_{2(g)}$ at 6.0 atm. Most fuel cells obtain their oxygen from unpressurized air, so let's assume that's the case. Since air is $21\%_{mol}$ O_2, and assuming a pressure of 1 atm, the partial pressure of the oxygen fed to the reaction is 0.21 atm. Let's further assume that this is a PEM fuel cell, and thus operates at room temperature, 300 K. (Actual PEM's operate at about 80ºC, but that's because they aren't 100% efficient, and release some heat as they operate!) The standard free energy change (ΔG^o_{rxn}) for the reaction of interest is just the standard free energy of formation for liquid water, because the reaction above actually *is* the formation reaction for liquid water: its ΔG^o_{rxn} is simply $\Delta G_f^o[H_2O_{(\ell)}]$. To determine the actual free energy change, we use the following equation, realizing that the actual activity of a pure liquid is one and that the activity of a gas is the numerical value of its partial pressure in bar (or, approximately, atm):

$$\Delta G_{rxn} = \Delta G^o_{rxn} + R\,T\ln(Q)$$

$$= \Delta G^o_f[H_2O_{(\ell)}] + \left(8.31451\frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(300\,\text{K})\ln\left[\frac{\alpha_{H_2O_{(\ell)}}}{\left(\alpha_{H_{2(g)}}\right)\left(\alpha_{O_{2(g)}}\right)^{1/2}}\right]$$

$$= -237\frac{\text{kJ}}{\text{mol}} + \left(2_{494}\frac{\text{J}}{\text{mol}}\right)\ln\left[\frac{1}{(6)(.21)}\right] = -237\frac{\text{kJ}}{\text{mol}} + -5_{76.5}\frac{\text{J}}{\text{mol}}\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)$$

$$= -237\frac{\text{kJ}}{\text{mol}} - 0.5_{765}\frac{\text{kJ}}{\text{mol}} = -237._6\frac{\text{kJ}}{\text{mol}}$$

Ok, well, the effect of the pressure turned out to be nearly negligible, but you get the idea. In truth, rather than 286 kJ/mol, we can actually only extract $237._6$ kJ/mol of reaction. This is mostly because the entropy change involved in making a liquid from two gases is quite unfavorable. Carrying through the same calculations as I did above, but with this new number, I get:

$$\text{Electric energy produced by the fuel cell} = \frac{237._6\ \text{kJ}}{\text{mol H}_2}\left(\frac{1\ \text{mol H}_2}{2\ \text{mol H}}\right)\left(\frac{1\ \text{mol of H}}{1.00794\ \text{g of H}}\right) = 117._{865}\ \frac{\text{kJ}}{\text{g of H}_2}$$

With these assumptions, the rate of hydrogen consumption would be

$$P_{\text{required to maintain 70 mph}} = 8_{934}\ \text{W}\left(\frac{1\ \text{J}\cdot\text{s}^{-1}}{1\ \text{W}}\right)\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)\left(\frac{1\ \text{g of H}_2}{117._{865}\ \text{kJ}}\right) = 0.07_{58}\ \frac{\text{g of H}_2}{\text{second}}$$

$$= 0.07_{58}\ \frac{\text{g of H}_2}{\text{second}}\left(\frac{3600\ \text{s}}{1\ \text{hr}}\right) = \frac{2_{73}\ \text{grams of H}_2}{\text{hour of travel}}$$

$$= \frac{2_{73}\ \text{grams of H}_2}{\text{hour of travel}}\left(\frac{1\ \text{mol of H}_2}{2.01588\ \text{g of H}_2}\right)\left(\frac{1\ \text{mol of H}_2\text{O}}{1\ \text{mol of H}_2}\right)\left(\frac{18.0152_8\ \text{g of H}_2\text{O}}{1\ \text{mol of H}_2\text{O}}\right)$$

$$= \frac{2_{438.6}\ \text{g of H}_2\text{O}}{\text{hour of travel}}$$

All told, these results are the same as those obtained above, at least to a single sig fig. But in practice, I hope it gives you some idea of what the W deal was all about in the Henry paper, if you were wondering.