CHM 3411 – Problem Set 1
Due date: Wednesday, January 16th
Do all of the following problems. Show your work.

1) The Planck distribution law is

$$M(\lambda,T)\, d\lambda = \frac{2\pi hc^2}{\lambda^5 [\exp(hc/\lambda kT) - 1]}\, d\lambda \qquad (1.1)$$

a) Show that in the limit $\lambda \to \infty$ eq 1.1 reduces to the classical (Rayleigh-Jeans) expression for blackbody radiationd

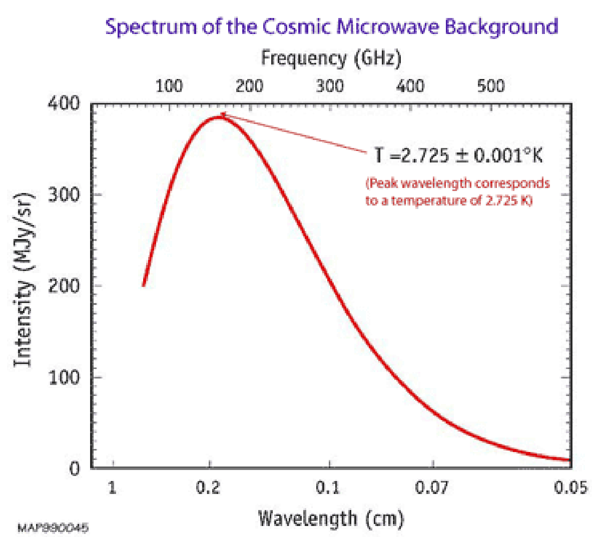
$$M_{RJ}(\lambda,T)\, d\lambda = \frac{2\pi ckT}{\lambda^4}\, d\lambda \qquad (1.2)$$

b) Starting with eq 1.1, derive Wien's law

$$\lambda_{max}T = A_W = \text{constant} \qquad (1.3)$$

and find the value predicted for A_W, the Wien's law constant (Note: If you do this problem correctly you will get a final expression for A_W that cannot be solved exactly, but can be used to find the value for A_W either by making a reasonable approximation or by numerical methods.)

2) The cosmic microwave spectrum believed to be the residual radiation from the "big bang" (as obtained by the COBE or COsmic Background Explorer satellite) is given below



a) Assuming that the background radiation is described by the Planck distribution law, find the location of the peak wavelength for the observed radiation. Give your answer in units of millimeters (mm). In what region of the electromagnetic spectrum does the peak occur?

b) Find the value for $\xi(T)$, the energy density of a blackbody at a temperature equal to that of the cosmic background radiation. (Recall that $M(T) = (c/4)\, \xi(T)$). Give your answer in units of J/m^3.

3) In 1897, Wilhelm Wien derived a formula for blackbody radiation (using thermodynamic arguments) that for a time was believed to be correct. His formula, the Wien distribution law, is

$$M_W(\lambda,T)\, d\lambda = \frac{2\pi hc^2}{\lambda^5} \exp(-hc/\lambda kT)\, d\lambda \qquad (3.1)$$

a) Starting with eq 3.1, find the expression for $M_W(\nu,T)\, d\nu$ (Hint: You will have to substitute both for λ and for $d\lambda$.)

b) Using your answer to part a, find an expression for the total intensity of light predicted to be emitted by a blackbody according to Wien's distribution law.

$$M_W(T) = \int_0^\infty M_W(\nu,T)\, d\nu \qquad (3.2)$$

Does your result agree with the Stefan-Boltzmann expression ($M(T) = \sigma T^4$)? If so, find the value predicted for σ (in units of $W/m^2 \cdot K^4$, recalling that W = watt = J/s). (Note: In principle we could find $M_W(T)$ by integrating eq 3.1, but in practice it is easier to do the integration over ν rather than over λ.)

4) Experimental data from a study of the photoelectric effect for potassium metal are given below. Based on the data, find the following:

a) λ_0, the critical wavelength for potassium (in units of nm).
b) Φ, the value for the work function for potassium metal (in units of eV).
b) h, the experimental value for the Planck constant obtained from the data (in units of J•s).

Wavelength (nm)	E_{Kmax} (eV)	Wavelength (nm)	E_{Kmax} (eV)
350.	1.44	509.	0.30
385.	1.09	553.	0.08
455.	0.56	608.	n/a

5) The observation by Dulong and Petit (1819) that the molar heat capacity of solid metals at room temperature is approximately C = 3R = 24.9 J/mol•K was useful in finding the correct value for atomic mass for a number of different metallic elements, as shown in this problem.

a) 76.47 g of a sample of pure metal (M) will completely react with 11.81 g of oxygen gas (O_2) to form a pure metal oxide. Find the atomic mass of the metal assuming the following for the chemical formula of the metal oxide – MO, MO_2, M_2O, M_2O_3.

b) The specific heat of the metal, measured at room temperature, was found to be s = 0.128 J/g•K. Based on this value for s, the Dulong-Petit law, and your answer to part a of this problem, find the atomic mass of the metal.

6) A typical wavelength used in X-ray crystallography is λ = 0.100 nm (approximately the size of the spacing between atoms in a crystal).

a) Find the velocity of a beam of monoenergetic electrons and a beam of monoenergetic neutrons that has a de Broglie wavelength λ_{dB} = 0.100 nm.

b) It is usually easier to generate a beam of monoenergetic electrons than it is a beam of monoenergetic neutrons. Suggest a reason why this is true.

Solutions.

1) a) The Planck distribution law says

$$M(\lambda,T) = (2\pi hc^2/\lambda^5)\,[\exp(hc/\lambda kT) - 1]^{-1}$$

Since $\exp(x) = 1 + x + (x^2/2!) + \ldots$, then, using $x = hc/\lambda kT$, we may say

$$\exp(hc/\lambda kT) = 1 + hc/\lambda kT + \ldots \cong 1 + hc/\lambda kT$$

Substituting into the expression for $M(\lambda,T)$ gives

$$M(\lambda,T) = (2\pi hc^2/\lambda^5)\,[\exp(hc/\lambda kT) - 1]^{-1} = (2\pi hc^2/\lambda^5)\,[1 + hc/\lambda kT + \ldots - 1]^{-1}$$

$$= (2\pi hc^2/\lambda^5)\,[1 + hc/\lambda kT + \ldots - 1]^{-1}$$

$$\cong (2\pi hc^2/\lambda^5)\,[\ hc/\lambda kT\ ]^{-1}$$

$$= (2\pi hc^2/\lambda^5)\,(\lambda kT/hc) = (2\pi ckT/\lambda^4)$$

the classical (Rayleigh-Jeans) result.

How do we know how many terms in the expansion for $M(\lambda,T)$ to keep? Since we are looking at a particular limit ($\lambda \to \infty$) we keep terms up to the first non-zero term that results.

b) To find λ_{max} we use the condition for an extreme point

$$d/d\lambda\ (2\pi hc^2/\lambda^5)\,[\exp(hc/\lambda kT) - 1]^{-1} = 0$$

$$= d/d\lambda\ (2\pi hc^2)\,\lambda^{-5}\,[\exp(hc/\lambda kT) - 1]^{-1}$$

$$= (2\pi hc^2)\,\{(-5)\,\lambda^{-6}\,[\exp(hc/\lambda kT) - 1]^{-1} + \lambda^{-5}\,(-1)\,[\exp(hc/\lambda kT) - 1]^{-2}\exp(hc/\lambda kT)\,(-\,hc/\lambda^2 kT)\} = 0$$

If we multiply both sides of this equation by $-\dfrac{\lambda^6\,[\exp(hc/\lambda kT) - 1]}{5\,(2\pi hc^2)}$, we get

$$1 - \frac{(hc/\lambda kT)\exp(hc/\lambda kT)}{5\,[\ \exp(hc/\lambda kT) - 1]} = 0$$

$$5 = \frac{(hc/\lambda kT)\exp(hc/\lambda kT)}{[\ \exp(hc/\lambda kT) - 1]}$$

Let $x = (hc/\lambda kT)$. The above equation can then be written as

$$5 = \frac{x\,e^x}{(e^x - 1)}$$

Since $e^x/(e^x - 1) \cong 1$, we could simply say $x \cong 5$ and solve for λ_{max} without significant error. If we do this, we get

$$\lambda_{max} = \frac{hc}{5\,kT} = \frac{(6.626 \times 10^{-34}\ J{\bullet}s)\,(2.998 \times 10^{8}\ m/s)}{5\,(1.381 \times 10^{-23}\ J/K)\,T} = \frac{2.877 \times 10^{-3}\ m{\bullet}K}{T}$$

or $(\lambda_{max})T = 2.877 \times 10^{-3}\ m{\bullet}K = 2.877 \times 10^{6}\ nm{\bullet}K$

For a more accurate value for x we can use trial and error (by guessing values for x), noting that the correct value of x will give f(x) = 5.

x	$f(x) = \frac{x e^x}{(e^x - 1)}$
5.000	5.0339
4.966	5.0009
4.965	4.9999

So x = (hc/λkT) ≅ 4.965, and so

$$\lambda_{max} = \frac{hc}{(4.965)\ kT} = \frac{(6.626 \times 10^{-34}\ J \cdot s)\ (2.998 \times 10^{8}\ m/s)}{(4.965)\ (1.381 \times 10^{-23}\ J/K)\ T} = \frac{2.897 \times 10^{-3}\ m \cdot K}{T}$$

or $(\lambda_{max})T = 2.897 \times 10^{-3}$ m/s $= 2.897 \times 10^{6}$ nm•K

the value appearing in Wien's law (eq 7.3.3 of the Chapter 7 handout).

Notice that assuming x = 5 gives an error of only 0.7%.

2) a) From Wien's law

$\lambda_{max}\ T = A_W$,

and so $\lambda_{max} = A_W/T = (2.898 \times 10^{6}$ nm•K)/(2.725 K) $= 1.06 \times 10^{6}$ nm $(10^{-7}$ cm/nm) = 0.106 cm. This occurs in the microwave region of the spectrum. (NOTE: This answer does not seem to agree well with the figure in the problem set. This is because the figure is a plot of M(ν) dν instead of M(λ) dλ. Plotting in these two ways will affect where the maximum in the curve occurs, since the magnitude of dν and dλ are different.)

b) (c/4) ξ(T) = M(T) , and so ξ(T) = (4/c) M(T) = (4/c) σT^4 , where M(T) = σT^4 is from the Stefan-Boltzmann law.

So $\xi(T) = [\ 4/(2.998 \times 10^{8}\ m/s)\ ]\ (5.67 \times 10^{-8}\ W/m^2 \cdot K^4)\ (2.725\ K)^4$

$= 4.17 \times 10^{-14}\ J/m^3$

That doesn't seem like a lot of energy, but remember that the universe is big (this works out to about 4×10^{65} J of energy for the observed universe).

3) a) Since λν = c, then λ= cν, and $d\lambda = (d\lambda/d\nu)\ d\nu = -\ (c/\nu^2)\ d\nu$

If we substitute into eq 3.1, we get

$$M(\nu,T)\ d\nu = (2\pi hc^2)\ (\nu^5/c^5)\ \exp(-h\nu/kT)\ (-\ c/\nu^2)\ d\nu$$

$$= \frac{2\pi h\nu^3}{c^2} \exp(-h\nu/kT)\ d\nu$$

You might wonder what happened to the negative sign. Well, when λ increases, ν decreases. To change things so that we are looking at increasing values for ν introduces a second negative sign which cancels the one from the substitution for dλ.

b) $M(T) = \int_0^\infty M(\nu,T)\, d\nu = \int_0^\infty (2\pi h\nu^3/c^2) \exp(-h\nu/kT)\, d\nu$

$= (2\pi h/c^2) \int_0^\infty \nu^3 \exp(-h\nu/kT)\, d\nu$

The above is a definite integral that appears in our integral tables

$$\int_0^\infty x^n \exp(-ax)\, dx = \frac{n!}{a^{n+1}}$$

If we let n = 3 and a = h/kT, we can use this to evaluate our integral, to get

$$M(T) = (2\pi h/c^2)\, 3!\, (kT/h)^4 = \frac{12\pi k^4}{c^2h^3} T^4$$

This has the same form as the Stefan-Boltzmann law ($M(T) = \sigma T^4$) , and would predict that the value for σ would be

$$\sigma = \frac{12\pi k^4}{c^2h^3} = \frac{12\pi\,(1.381 \times 10^{-23}\ \mathrm{J/K})^4}{(2.998 \times 10^8\ \mathrm{m/s})^2\,(6.626 \times 10^{-34}\ \mathrm{J{\bullet}s})^3} = 5.24 \times 10^{-8}\ \mathrm{J/m^2{\bullet}s{\bullet}K^4}$$

The actual value for the constant is $\sigma = 5.67 \times 10^{-8}\ \mathrm{J/m^2{\bullet}s{\bullet}K^4}$, so the Wien distribution gives a value for σ that is about 8% lower than the correct value. This is close enough that for a time people believed Wien's distribution law was correct, but careful experimental measurements eventually showed that the Wien distribution is off at short wavelengths (where quantization of the oscillators becomes important).

4) To do this problem we can plot maximum kinetic energy (in eV) vs frequency of light. (Note $\nu = c/\lambda$, $c = 2.998 \times 10^8$ m/s)

Wavelength (nm)	Frequency (s^{-1})	E_{Kmax} (eV)
350.	8.566×10^{14}	1.44
385.	7.787×10^{14}	1.09
455.	6.589×10^{14}	0.56
509.	5.890×10^{14}	0.30
553.	5.421×10^{14}	0.08

The data are plotted on the next page.

a) The critical wavelength for potassium can be found from the value for the x-intercept in the plot.

$(0.4285 \times 10^{-14}\ \mathrm{eV{\bullet}s})\,(\nu_0) = 2.241$ eV

So ν_0 = critical frequency = $(2.241\ \mathrm{eV})/(0.4285 \times 10^{-14}\ \mathrm{eV{\bullet}s}) = 5.23 \times 10^{14}\ \mathrm{s^{-1}}$

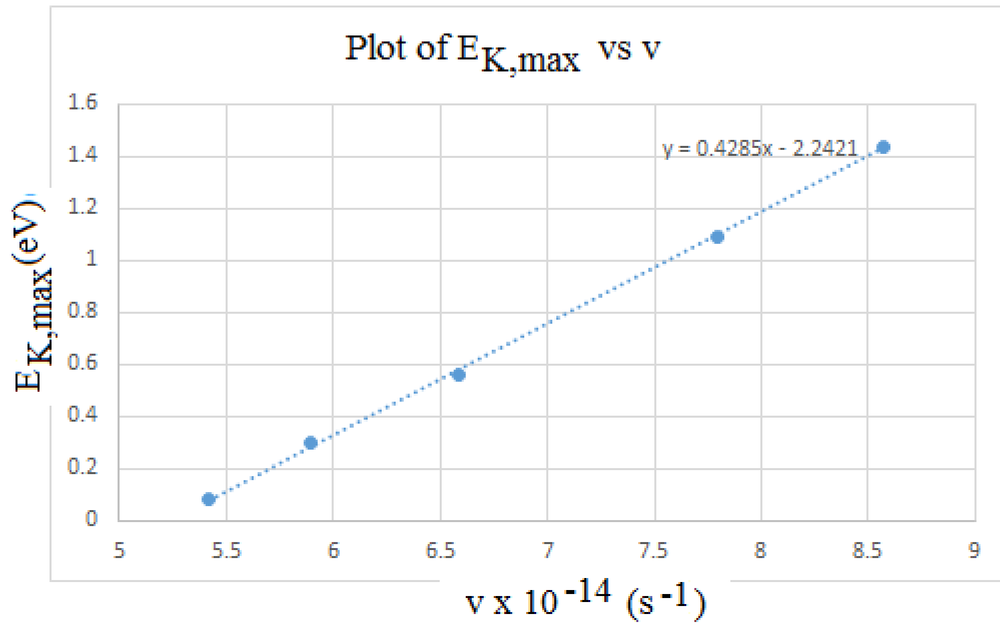
Since $\lambda\nu = c$, $\lambda_0 = c/\nu_0 = (2.998 \times 10^8\ \mathrm{m/s})/(5.23 \times 10^{14}\ \mathrm{s^{-1}}) = 5.73 \times 10^{-7}\ \mathrm{m} = 573.$ nm

b) The work function is equal to (-b), where b is the intercept in the plot of $E_{K,max}$ vs ν.

So Φ= 2.24 eV.

c) The slope of the plot should be equal to the value for the Planck constant. I get

$h = (0.4285 \times 10^{-14}\ \mathrm{eV{\bullet}s})\,(1.602 \times 10^{-19}\ \mathrm{J/eV}) = 6.86 \times 10^{-34}\ \mathrm{J{\bullet}s}$, in reasonable agreement with the currently accepted value $h = 6.626 \times 10^{-34}$ J•s.



5) Based on the chemical form of the oxide and the atomic mass of oxygen (MW = 16.00 g/mol) we can find the moles of metal atoms, and them the molecular mass of the metal

Formula	Moles O	Moles M	MW M (g/mol)	s_{DP} (J/g•K)
MO	0.7381	0.7381	103.6	0.240
MO_2	0.7381	0.3691	207.2	0.121
M_2O	0.7381	1.4762	51.8	0.481
M_2O_3	0.7381	0.4921	155.4	0.160

The value for molecular mass for the metal is MW = grams M/moles M.

If we assume that the molar heat capacity of the metal is C = 3R = 24.9 J/mol•K (as expected from the observation of Dulong and Petit) then the value for the specific heat of the metal is s_{DP} = (24.9 J/mol•K)/(MW), where MW is the molecular mass.

The value for s_{DP} that is closest to the experimental value for s is for the formula MO_2. Therefore, the experimental value for the atomic mass of the metal is 207.2 g/mol. (Note that this suggests the metal was lead, which has this value for atomic mass).

6) a) Since $\lambda_{dB} = h/mv$, then $v = h/m\lambda_{dB}$. We want λ_{dB} = 0.100 nm, and so

For an electron ($m_e = 9.11 \times 10^{-31}$ kg)

$$v = \frac{(6.626 \times 10^{-34}\ \text{J·s})}{(9.11 \times 10^{-31}\ \text{kg})\ (0.100 \times 10^{-9}\ \text{m})} = 7.27 \times 10^{6}\ \text{m/s}$$

For a neutron ($m_n = 1.675 \times 10^{-27}$ kg)

$$v = \frac{(6.626 \times 10^{-34}\ \text{J·s})}{(1.675 \times 10^{-27}\ \text{kg})\ (0.100 \times 10^{-9}\ \text{m})} = 3.96 \times 10^{3}\ \text{m/s}$$

b) It is easier to move electrons around than it is to move neutrons around because an electron has a charge. You can accelerate or move electrons from place to place by using charged plates, which will attract or repel the electrons in a known manner. Neutrons have no charge, and so are more difficult to manipulate.