CHEM 26100 (Quantum Mechanics) Problem Sets

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Contents

1 Blackbodies and the Photoelectric Effect

10/6:   1. The intensity (or emissive power) of solar radiation at the surface of the earth is 1.4×10^3 W/m^2, the distance from the center of the sun to the sun's surface is 7×10^8 m, and the distance from the center of the sun to the earth is 1.5×10^{11} m.

(a) Assuming that the sun is a black body, calculate the temperature at the surface of the sun in Kelvin. (Hint: The surface area of a sphere of radius r is $4\pi r^2$.)

Answer. Let

$$I = 1\,400\,\frac{\text{W}}{\text{m}^2} \qquad r_1 = 7 \times 10^8\,\text{m} \qquad r_2 = 1.5 \times 10^{11}\,\text{m}$$

and let $\sigma = 5.67 \times 10^{-8}\,\text{W}\,\text{m}^{-2}$ be Stefan's constant. If P is the total power radiated by the sun, we have from physics that

$$I = \frac{P}{4\pi r_2^2}$$
$$P = 4\pi r_2^2 I$$

and from quantum that

$$P = R \cdot 4\pi r_1^2$$
$$= \sigma T^4 \cdot 4\pi r_1^2$$

Thus, setting these two quantities equal to each other, we obtain

$$4\pi r_2^2 I = \sigma T^4 \cdot 4\pi r_1^2$$
$$r_2^2 I = \sigma T^4 r_1^2$$
$$T = \sqrt[4]{\frac{r_2^2 I}{\sigma r_1^2}}$$
$$\boxed{T = 5\,803\,\text{K}}$$

□

(b) Secondly, compute the wavelength at which the emissive power at the sun's surface has its maximum. In which region of the radiation spectrum does this wavelength lie, i.e., infrared (IR), visible, or ultraviolet (UV)?

Answer. If $b = 2.898 \times 10^{-3}\,\text{m}\,\text{K}$ is Wien's displacement constant and we plug in the temperature value T from part (a), then Wien's first law gives us

$$\lambda_{\max} T = b$$
$$\lambda_{\max} = \frac{b}{T}$$
$$\boxed{\lambda_{\max} = 4.99 \times 10^{-7}\,\text{m}}$$

This wavelength lies in the $\boxed{\text{visible}}$ spectrum. □

2. (a) Using Planck's formula for the energy density $\rho(\lambda, T)$, prove that the total energy density $\rho(T)$ is given by $\rho(T) = aT^4$, where $a = 8\pi^5 k^4/(15h^3 c^3)$. (Hint: Use the integral $\int_0^\infty x^3/(e^x - 1)\,\mathrm{d}x = \pi^4/15$.)

Proof. Planck's formula for the energy density is

$$\mathrm{d}\rho(\lambda, T) = \frac{8\pi hc}{\lambda^5} \cdot \frac{\mathrm{d}\lambda}{e^{hc/\lambda kT} - 1}$$

Thus, if we use the change of variables $x = hc/(\lambda kT)$ (also implying $\lambda = hc/(xkT)$ and $\mathrm{d}\lambda = -hc/(x^2 kT)\,\mathrm{d}x$), we have that

$$\int_0^\infty \mathrm{d}\rho(\lambda, T) = \int_{\lambda=0}^\infty \frac{8\pi hc}{\lambda^5} \cdot \frac{\mathrm{d}\lambda}{e^{hc/\lambda kT} - 1}$$

$$\int_0^\infty \rho_\lambda(T)\,\mathrm{d}\lambda = \int_{x=\infty}^0 \frac{8\pi hc}{\left(\frac{hc}{xkt}\right)^5} \cdot \frac{1}{e^x - 1} \cdot -\frac{hc}{x^2 kt}\,\mathrm{d}x$$

$$\rho(T) = \int_{x=\infty}^0 -\frac{8\pi (hc)^2 (kT)^5 x^5}{(hc)^5 (e^x - 1)(x^2)(kT)}$$

$$= \int_{x=0}^\infty \frac{8\pi (kT)^4 x^3}{(hc)^3 (e^x - 1)}$$

$$= \frac{8\pi (kT)^4}{(hc)^3} \int_0^\infty \frac{x^3}{e^x - 1}\,\mathrm{d}x$$

$$= \frac{8\pi (kT)^4}{(hc)^3} \cdot \frac{\pi^4}{15}$$

$$= \frac{8\pi^5 k^4}{15 h^3 c^3} T^4$$

$$= aT^4$$

as desired. □

(b) Does this agree with the Stefan-Boltzmann law for the total emissive power?

Answer. Yes — we are given the conversion factor $\rho(\lambda, T) = 4/c \cdot R(\lambda, T)$, so from the above, we should have

$$R(T) = \frac{c}{4} \cdot R(\lambda, T)$$

$$= \frac{c}{4} \cdot \frac{8\pi^5 k^4}{15 h^3 c^3} T^4$$

$$= \frac{2\pi^5 k^4}{15 h^3 c^2} T^4$$

But by plugging in the appropriate values, we can determine that

$$\frac{2\pi^5 k^4}{15 h^3 c^2} = \sigma$$

where σ is Stefan's constant, giving us

$$R(T) = \sigma T^4$$

as desired. □

3. The photoelectric work function for lithium is $2.3\,\mathrm{eV}$.

(a) Find the threshold frequency ν_t and the corresponding λ_t.

Answer. From Einstein's annus mirabilis papers, we have that

$$\nu_t = \frac{W}{h} \qquad\qquad \lambda_t = \frac{c}{\nu_t} = \frac{ch}{W}$$

Plugging in $W = 3.685 \times 10^{-19}$ J and $h = 6.626 \times 10^{-34}$ J s^{-1}, we have that

$$\boxed{\nu_t = 5.56 \times 10^{14}\text{ Hz}} \qquad\qquad \boxed{\lambda_t = 5.39 \times 10^{-7}\text{ m}}$$

$\square$

(b) If UV light of wavelength $\lambda = 3\,000$ Å is incident on the Li surface, calculate the maximum kinetic energy of the electrons.

Answer. From Einstein's annus mirabilis papers, we have that

$$KE_{\max} = h\nu - W$$
$$= \frac{hc}{\lambda} - W$$
$$\boxed{KE_{\max} = 2.941 \times 10^{-19}\text{ J}}$$

$\square$

4. (a) Using the Bohr model, compute the ionization energies for He$^+$ and Li^{2+}.

Answer. From the Bohr model, we have that

$$IE = E_\infty - E_1$$
$$= -\frac{m_e e^4 Z^2}{8\epsilon_0^2 h^2} \cdot \frac{1}{\infty^2} + \frac{m_e e^4 Z^2}{8\epsilon_0^2 h^2} \cdot \frac{1}{1^2}$$
$$= \frac{m_e e^4 Z^2}{8\epsilon_0^2 h^2}$$

It follows since $Z = 2$ for He$^+$ and $Z = 3$ for Li^{2+} that

$$\boxed{IE(\text{He}^+) = 8.72 \times 10^{-18}} \qquad\qquad \boxed{IE(\text{Li}^{2+}) = 1.962 \times 10^{-19}}$$

in units of Joules per electron. $\square$

(b) Can the Bohr model be employed to compute the first ionization energy for He and Li? Explain briefly.

Answer. No — the Bohr model is only valid for single electron systems as it does not take into account electron-electron interactions. $\square$

5. (a) An electron is confined within a region of atomic dimensions on the order of 1×10^{-10} m. Compute the uncertainty in its momentum.

Answer. From the Heisenberg uncertainty principle, we have that

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$
$$\Delta p \geq \frac{h}{4\pi \Delta x}$$
$$\boxed{\Delta p \geq 5.273 \times 10^{-25}\ \frac{\text{kg m}}{\text{s}}}$$

$\square$

(b) Repeat the calculation for a proton confined to a region of nuclear dimensions on the order of 1×10^{-14} m.

Answer. From the Heisenberg uncertainty principle, we have that

$$\Delta p \geq \frac{h}{4\pi \Delta x}$$

$$\boxed{\Delta p \geq 5.273 \times 10^{-21}\, \frac{\text{kg m}}{\text{s}}}$$

□

6. Use the Quantum Chemistry Toolbox in Maple to complete the worksheet "Blackbody Radiation" on Canvas and answer the following questions.

   (a) Using the interactive graph of the spectral energy density $\rho(\nu, T)$ as a function of the frequency ν and temperature T, determine the frequency in Hz at which the spectral energy density peaks at a temperature of $700\,\text{K}$.

   Answer.
   $$\boxed{5 \times 10^{13}\,\text{Hz}}$$

   □

   (b) The cosmic background radiation, discovered in 1964 by Penzias and Wilson, can be explained by treating the universe as a blackbody. Using the interactive plot, determine the frequency (in Hz) and wavelength (in m) at which the cosmic background radiation peaks.

   Answer.

   $$\boxed{\nu = 2 \times 10^{11}\,\text{Hz}} \qquad\qquad \lambda = \frac{c}{\nu}$$

   $$\boxed{\lambda = 1.5 \times 10^{-3}\,\text{m}}$$

   □

   (c) In which region of the electromagnetic spectrum does the peak cosmic background radiation lie?

   Answer. In the $\boxed{\text{microwave}}$ region.   □

7. Use the Quantum Chemistry Toolbox in Maple to complete the worksheet "Photoelectric Effect" on Canvas and answer the following questions.

   (a) Copy and complete Table 1 of the worksheet.

   Answer.   □

	Au	Mg	Pb	Na	Average value of h:
Threshold frequency (ν_0)	$1.084 \times 10^{15}\,\text{Hz}$	$8.793 \times 10^{14}\,\text{Hz}$	$1.034 \times 10^{15}\,\text{Hz}$	$5.684 \times 10^{14}\,\text{Hz}$	
Planck's constant (h)	$6.681 \times 10^{-34}\,\text{J s}$	$6.553 \times 10^{-34}\,\text{J s}$	$6.717 \times 10^{-34}\,\text{J s}$	$6.522 \times 10^{-34}\,\text{J s}$	$6.618 \times 10^{-34}\,\text{J s}$

Table 1: Photoelectric data for Au, Mg, Pb, and Na.

   (b) What is the computed average value of Planck's constant, and how does this value compare to its experimental value?

   Answer. The computed average value of Planck's constant is $\boxed{6.618 \times 10^{-34}\,\text{J s}}$. It is $\boxed{0.12\%\ \text{off}}$ from the true value of $6.626 \times 10^{-34}\,\text{J s}$.   □

   (c) For which element is it *least* difficult to eject an electron?

   Answer. $\boxed{\text{Sodium}}$ — lowest threshold frequency means least energy required to excite an electron to the infinite energy level.   □