Chemistry 331 **Assignment #1** (due Monday, September 28, in class)

Q1. Planck's law $\rho(T,v) = \dfrac{8\pi h v^3}{c^3 (e^{hv/kT} - 1)}$ for thermal radiation gives the energy density

[2] distribution as function of frequency v. Show $\rho(T,v)$ reaches a maximum at the frequency

$$v_{\text{max}} = 2.821\frac{kT}{h} \qquad \textbf{(Wien's law)}$$

Q2. **a)** At room temperature ($\approx$ 300 K), use Wein's law to show that v_{max} is in the infrared region of the electromagnetic spectrum (wavelengths from about 700 nm to 1 mm).

[2] **b)** An object glows "red hot". Use Wein's law and $\lambda \approx 700$ nm for red light to estimate the temperature of the object. *Hint*: $c = \lambda v$.

Q3. As $hv/kT \to 0$, the energy spacing hv of thermal oscillators becomes negligibly small compared

[2] to thermal energy kT. In this limit, show Planck's expression for $\rho(T,v)$ reduces to the

classical Rayleigh-Jeans spectrum $\rho(T,v) = \dfrac{8\pi kT v^2}{c^3}$. *Hint*: $e^x \approx 1 + x$ for $|x| << 1$.

Q4. How many photons per second are emitted by a 2.00 mW green LED (light-emitting diode)?
[1] Use $\lambda = 554$ nm. *Hint*: 2.00 mW = 0.00200 J s^{-1}.

Q5. **a)** Give the key assumption made by Einstein to derive $E_{\text{m}}(T) = 3RT\dfrac{hv}{kT}\dfrac{1}{e^{hv/kT} - 1}$

for the molar vibrational energy of monatomic crystals.

[3] **b)** Show $E_{\text{m}}(T) \longrightarrow 3RT$ in the limit $T \longrightarrow \infty$.

c) Show $E_{\text{m}}(T) \longrightarrow 0$ in the limit $T \longrightarrow 0$.

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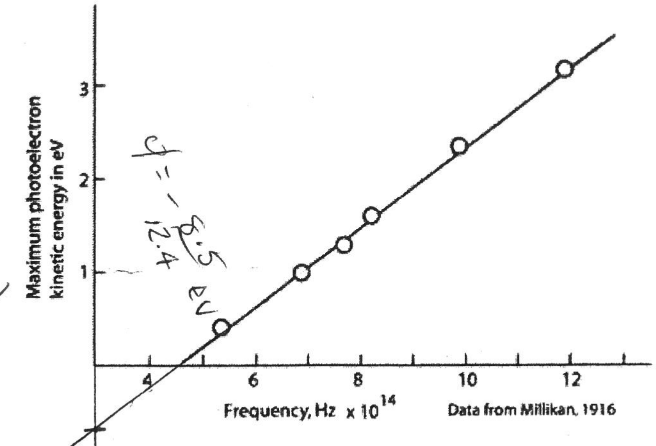
Q6. **a)** Use the photolectric data for sodium plotted below to calculate Planck's constant h.

$\phi = 0.68$ eV



[3] **b)** Calculate the work function (ϕ) of sodium.

c) Give the maximum photoelectron energy if sodium is irradiated with red light ($\lambda = 700$ nm).

Q7. In class we derived $\mu v^2 = \dfrac{e^2}{4\pi\varepsilon_0 r}$ for a hydrogen atom. Use this result to show the kinetic

[1] energy of a hydrogen atom ($\mu v^2/2$) is one-half as large as the electric potential energy.

Q8. **a)** For a ground-state hydrogen atom ($n = 1$), calculate the kinetic energy, electric potential energy, and the total energy E_1.

b) Calculate the de Broglie wavelength λ of an electron in a ground-state hydrogen atom.

[5] **c)** Use the value of λ to estimate the diameter of a hydrogen atom.

d) Use the value of λ to explain why the electrons and protons in atoms and molecules do not merge to form neutrons (a subatomic particles), which would put chemists out of business!

Q9. The rate of rotation of a pirouetting ice skater is reduced if the skater outstretches their arms.
[1] Explain.

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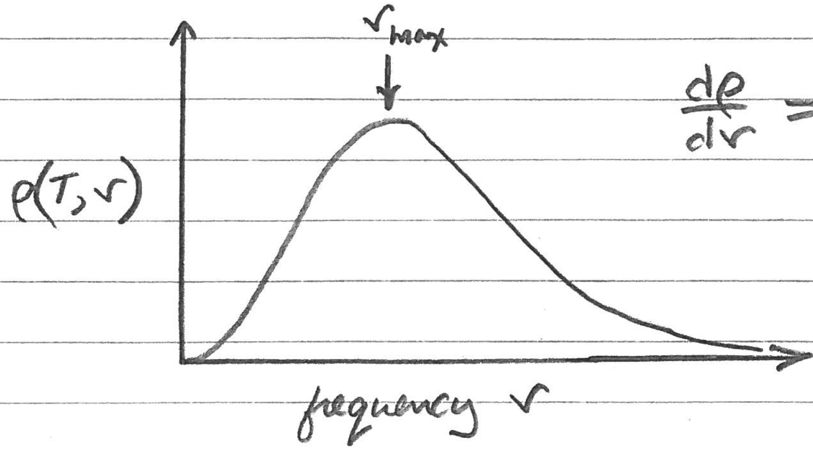
Q1



$\frac{d\rho}{d\nu} = 0$ at ν_{max}

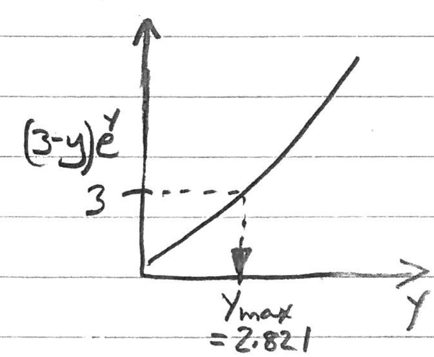
to simplify the math, use $y = h\nu/kT$

and notice $\rho(T,\nu)$ is proportional to $\frac{y^3}{e^y - 1}$

$$\left[\frac{8\pi h\nu^3}{c^3(e^{h\nu/kT}-1)} = \frac{8\pi}{c^3}\frac{h^3\nu^3}{(kT)^3}\frac{(kT)^3}{h^2}\frac{1}{e^{h\nu/kT}-1} \propto \frac{y^3}{e^y-1}\right]$$

$$\frac{d}{dy}\left(\frac{y^3}{e^y-1}\right) = \frac{(e^y-1)3y^2 - y^3e^y}{(e^y-1)^2} = \frac{y^2}{(e^y-1)^2}\left[(3-y)e^y - 3\right]$$

$$= 0 \text{ when } (3-y)e^y = 3$$



solve numerically for $y_{max} = 2.821 = \frac{h\nu_{max}}{kT}$

$$\boxed{\nu_{max} = 2.821\frac{kT}{h}}$$

Wein's law

Q2 a) at 300 K: $\nu_{max} = 2.821 \dfrac{kT}{h}$

$$\nu_{max} = 2.821 \frac{1.381\times10^{-23}(300)}{6.626\times10^{-34}} = 1.76\times10^{13}\ s^{-1}$$

$$\lambda_{max} = \frac{c}{\nu_{max}} = \frac{2.998\times10^{8}}{1.76\times10^{13}} = \boxed{1.70\times10^{-5}\ m}$$

(in the infrared 7×10^{-9} m to 10^{-3} m)

b) for red light with $\lambda = 700$ nm:

$$\nu = c/\lambda = (2.998\times10^{8})/(7\times10^{-7}) = 4.28\times10^{14}\ s^{-1}$$

$$T = \frac{h\nu_{max}}{2.821\,k} = \frac{(6.626\times10^{-34})(4.28\times10^{14})}{2.821\,(1.381\times10^{-23})}$$

$$\boxed{T = 7280\ K}$$

(assumed to be ν_{max})

Q3 as $\dfrac{h\nu}{kT} \to 0$, notice $e^{h\nu/kT} \longrightarrow 1 + \dfrac{h\nu}{kT}$

and
$$\frac{8\pi h\nu^3}{c^3(e^{h\nu/kT}-1)} \longrightarrow \frac{8\pi h\nu^3}{c^3\left(1+\frac{h\nu}{kT}-1\right)} = \frac{8\pi h\nu^3}{c^3}\,\frac{1}{\frac{h\nu}{kT}}$$

$$= \frac{8\pi kT\nu^2}{c^3}$$

classical energy density distribution

[predicts $\rho_{classical} \to \infty$ as $\nu \to \infty$ IMPOSSIBLE! "ultraviolet catastrophe"]

Q4 one green photon has energy $h\nu = \frac{hc}{\lambda}$

$$\frac{hc}{\lambda} = \frac{6.626\times10^{-34}(2.998\times10^{8})}{554\times10^{-9}} = 3.58\times10^{-19}\,J$$

$$\begin{array}{l}\text{number of photons}\\ \text{emitted per second}\end{array} = \frac{0.002\,J}{3.58\times10^{-19}} = \boxed{5.58\times10^{15}\,s^{-1}}$$

Q5 a) Einstein developed the quantum mechanical expression for the heat capacity of monatomic crystals by assuming the energies of the vibrating atoms are "quantized":

$$0,\ h\nu,\ 2h\nu,\ 3h\nu, \ldots$$

b) $$E_m = 3RT\,y\,\frac{1}{e^{y}-1} \qquad \left(y = \frac{h\nu}{kT}\right)$$

as $T \to \infty$, $y \to 0$ and $e^{y} \to 1+y$

$$E_m \longrightarrow 3RT\,y\,\frac{1}{1+y-1} = \boxed{3RT}$$

l'Hopital's rule

c) as $T \to 0$, $y \to \infty$ and

$$\lim_{y\to\infty} = \lim_{y\to\infty} 3RT\,\frac{y}{e^{y}-1} = \lim_{y\to\infty} 3RT\left(\frac{\frac{dy}{dy}}{\frac{d}{dy}(e^{y}-1)}\right)$$

$$= \lim_{y\to\infty} 3RT\,\frac{1}{e^{y}} = \boxed{0}$$

(Q6) a) maximum photoelectron kinetic energy

$$E_{max} = h\nu - \phi$$

$$\frac{dE_{max}}{d\nu} = h = \text{slope of the plot}$$

$$\approx \frac{\text{rise}}{\text{run}} = \frac{\Delta E_{max}}{\Delta \nu}$$

$$\approx \frac{3.0\ \text{eV}}{(11.5 - 4.7)\times 10^{14}\ \text{Hz}}$$

$$= \frac{(3.0\ \text{eV})(1.602\times 10^{-19}\ \text{J eV}^{-1})}{6.8\times 10^{14}\ \text{s}^{-1}}$$

$$\boxed{\text{slope } h = 7.07\times 10^{-34}\ \text{J s}}$$

b) at the "threshold" frequency ν^*, the electron kinetic energy is zero and $0 \overset{?}{=} h\nu^* - \phi$

from the graph, read $\nu^* = 4.7\times 10^{14}\ \text{s}^{-1}$
and $\phi = (6.626\times 10^{-34}\ \text{J s})(4.7\times 10^{14}\ \text{s}^{-1})$
$= 3.11\times 10^{-19}\ \text{J} = \boxed{1.94\ \text{eV}}$

c) for red light with $\lambda = 700$ nm :

$$\nu = \frac{c}{\lambda} = \frac{2.998\times 10^{8}\ \text{m s}^{-1}}{700\times 10^{-9}\ \text{m}} = 4.28\times 10^{14}\ \text{Hz}$$

ν is below the threshold frequency ν^*, so $E_{kin} = 0$
(no photoelectrons emitted)

Q7 From Coulomb's law, the electric potential energy of an electron (charge $-e$) and a proton (charge e) a distance r apart is

$$E_{pot.} = \frac{(-e)(e)}{4\pi\varepsilon_0 r} = -\frac{e^2}{4\pi\varepsilon_0 r}$$

notice $$\mu v^2 = 2\frac{\mu v^2}{2} = 2E_{kin} = \frac{e^2}{4\pi\varepsilon_0 r}$$

$$\therefore \ 2E_{kin} = -E_{pot}$$

Q8 a) ground-state energy of the H atom (a fundamental natural unit of energy):

$$E_1 = -\frac{\mu e^4}{8h^2\varepsilon_0^2} \qquad \mu = \frac{m_e m_p}{m_e + m_p} \ \text{(reduced mass)}$$

$$\mu = \frac{(9.109\times10^{-31})(1.673\times10^{-27})}{(9.109\times10^{-31})+(1.673\times10^{-27})}\ \text{kg} = 9.104\times10^{-31}\ \text{kg}\ (\approx m_e)$$

$$E_1 = -\frac{(9.104\times10^{-31})(1.602\times10^{-19})^4}{8(6.626\times10^{-34})^2(8.854\times10^{-12})^2} = -2.178\times10^{-18}\ \text{J}$$

$$= -\frac{2.178\times10^{-18}\ \text{J}}{1.602\times10^{-19}\ \text{J eV}^{-1}} = -13.59\ \text{eV}$$

(Q 8a cont.)

total energy $= E_1 = E_{pot.} + E_{kin.}$

$$E_1 = E_{pot.} - \frac{E_{pot.}}{2} = \frac{E_{pot.}}{2}$$

$$E_{pot.} = 2E_1 = -27.18 \text{ eV}$$

$$E_{kin} = E_1 - E_{pot.} = E_1 - 2E_1 = -E_1 = +13.59 \text{ eV}$$

always positive (or zero)

(reduced mass $\mu \simeq m_e$)

b) de Broglie wavelength $= \frac{h}{p}$ (so $E_{kin} \simeq \frac{1}{2} m_e v_e^2$)

momentum $p = m_e v_e$ $\quad \lambda = \frac{h}{m_e v_e}$

$$-E_1 = E_{kin} = 13.59 \text{ eV} = 2.178 \times 10^{-18} \text{ J} \cong \frac{1}{2} m_e v_e^2$$

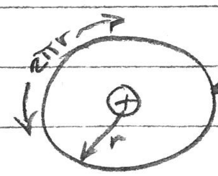
$$v_e = \sqrt{\frac{-2E_1}{m_e}} = \sqrt{\frac{2(2.178 \times 10^{-18})}{9.109 \times 10^{-31}}} = 2.187 \times 10^{6} \frac{m}{s}$$

$$\lambda = \frac{h}{m_e v_e} = \boxed{3.326 \times 10^{-10} \text{ m}} \simeq \text{H atom circumference}$$

c)

$$\lambda = 2\pi r_H \qquad r_H = \frac{3.326 \times 10^{-10} \text{ m}}{2\pi} = 5.29 \times 10^{-11} \text{ m}$$

H atom diameter $= 2r_H = 1.06 \times 10^{-10}$ m $= 0.106$ nm



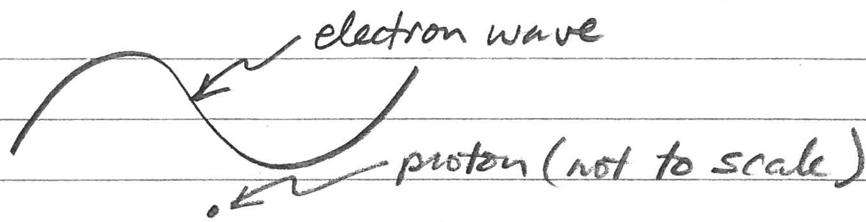
circumference $= \lambda = 2\pi r$

(Q8 cont.)

d) electron wavelength $\simeq$ 0.333 nm

proton diameter $\simeq$ 0.0001 nm

the electron is "too big" to fit inside a proton to form a subatomic particle



Q9 the angular momentum of the spinning skater (ignoring very small frictional effects) is constant.

$$\text{angular momentum} = I\,\omega$$

moment of inertia (mr^2)

angular velocity

$I = mr^2 \Rightarrow$ extending arms increases the moment of inertia
(mass at larger radius of rotation)

if $I\omega$ is constant, then increasing I must reduce ω

lower $\omega \rightarrow$ lower rate of rotation