Chemistry 331 **Assignment #2** (due Monday 05 October, in class)

Q1. Show that Planck's constant and angular momentum have the same SI units (J s). [1]

Q2. Gyroscopes illustrate an important application of angular momentum. Explain *briefly*. [1]

Q3. **a)** In Bohr's model of the hydrogen atom, the circumference of the electron orbit is an integer multiple of the electron's de Broglie wavelength: $2\pi r = \lambda, 2\lambda, 3\lambda, 4\lambda, \ldots$ Why?

[2] **b)** Lightning generates extremely low frequency (ELF) radio waves. These waves are reflected by the ionosphere (altitude $\approx$ 100 km) and circle the earth in the channel between the planet surface and the ionosphere. Resonance peaks in the ELF spectrum are observed at 7.8 Hz, 14.3 Hz, 20.8 Hz, 27.8 Hz, ... Why? *Hint*: use Bohr's model and 6,370 km for the radius of the earth.

Q4. **a)** Calculate the energy change for the **chemical reaction** of two moles of deuterium atoms forming one mole of molecular deuterium at 25 °C and 1 bar: $D(g) + D(g) \rightarrow D_2(g)$.

b) For comparison, calculate the energy change for the **nuclear reaction** where deuterium nuclei fuse to from one mole of alpha particles: $D^+(g) + D^{+\cdot}(g) \rightarrow He^{2+}(g)$. *Hint*: $E = mc^2$

[4] **c)** Why are very high temperatures (> 10^7 K) required for nuclear fusion reactions?

d) Use the answer to **b** to explain why huge international research projects are underway to develop controlled thermonuclear fusion technology for commercial energy production.

Data: $\Delta H_{fm}°(D, g) = 218\ kJ\ mol^{-1}$ $\quad m_{D+} = 3.343583772 \times 10^{-27}$ kg
$m_{He++} = 6.644657230 \times 10^{-27}$ kg

Q5. **a)** Incandescent light bulbs use electrically-heated tungsten filaments to produce visible light. Why is tungsten (a rare and expensive metal) used for bulb filaments?

[4] **b)** Assuming blackbody behavior (an excellent approximation at high temperatures), calculate the total energy radiated per unit surface area of tungsten heated to 3200 K.

c) A 0.200 mm diameter tungsten wire is heated to 3200 K. Calculate the length of wire required for a 60 W light bulb. *Hint*: the surface area of wire of radius r and length L is $2\pi rL$

Q6. Emissivity has units J m^{-2} s^{-1}, but $e(T,\nu)$ has units J m^{-2}. Explain this apparent contradiction. [1]

Q7. **a)** The aluminum used in mirrors is definitely not a blackbody! Explain.

[2] **b)** But grinding the aluminum into a powder produces an almost perfect blackbody. Why?

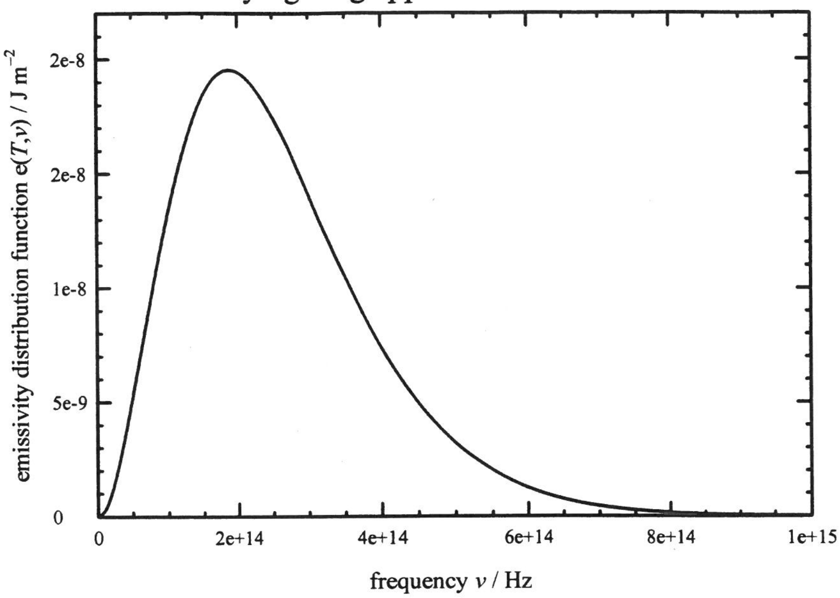
... page 2

Q8. The emissivity distribution function $e(T,\nu)$ is plotted below for a blackbody at 3200 K.

a) Sketch on the diagram the area that gives the emissivity in the visible region of the spectrum (wavelengths from 400 nm to 700 nm).

[3] **b)** Sketch on the diagram the area that gives the emissivity in the infrared (700 nm to 1 mm).

c) Use the answers for parts **a** and **b** to explain why light emitting diodes are replacing incandescent bulbs in many lighting applications.



Q9. Planck's radiation law gives $\langle h\nu \rangle = \dfrac{h\nu}{e^{h\nu/kT} - 1}$ for the average photon energy.

[1] At high temperatures ($kT \gg h\nu$), show $\langle h\nu \rangle = kT$.

10. The ideal gas law shows the number of moles of gas molecules per unit volume is

$$\frac{n}{V} = \frac{p}{RT}$$

What is the corresponding number of moles of photons per unit volume of thermal radiation?

The pressure of a photon gas is one third of the energy density. In the high-temperature limit where $\langle h\nu \rangle = kT$, show the number of moles of photons per unit volume is

$$\frac{n}{V} = 3\frac{p}{RT} = \frac{4\sigma T^3}{cR}$$

Chem 331 <u>Assignment #2</u>

(Q1) It's difficult to overestimate the importance of <u>angular momentum</u> in quantum chemistry!

An object of mass m rotating at angular velocity ω at radius r from the axis of rotation has

$$\text{angular momentum } L = mr^2\omega$$

mass $m \sim$ kg
radius $r \sim$ m
angular velocity $\omega \sim s^{-1}$

> ω = radians of rotation per second
>
> 1 radian = 2π (dimensionless)
>
> so ω has units s^{-1}

SI angular momentum units $\sim mr^2\omega$

$$\sim (kg)(m)^2(s^{-1})$$

$$\sim \boxed{kg\ m^2\ s^{-1}}$$

Planck constant h has SI units J s

$$\sim [\text{energy}][\text{time}] \sim [(\text{mass})(\text{acceleration})(\text{distance})][\text{time}]$$

$$\sim [(kg)(m\ s^{-2})(m)][s]$$

$$\sim \boxed{kg\ m^2\ s^{-1}}\ (= \text{angular momentum units})$$

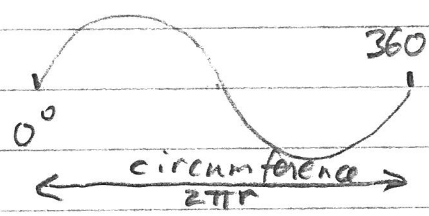
(Q2) A gyroscope is a mechanical device with a rapidly rotating disc (or spindle) in a frame (a set of "gimbals") allowing the spinning rotor to assume any axis of rotation. Conservation of angular momentum keeps the rotor spining about the same axis — useful for ship, aircraft, sub navigation

> similarly, a compass "points" North

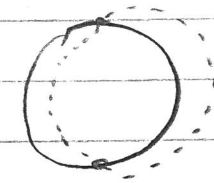
Q3

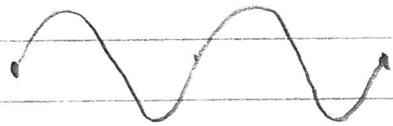
a) In Bohr's model of the hydrogen atom, the electron is a wave (not a particle) with wavelength $\lambda = h/mv$ from de Broglie's relation.

For a stable, resonant, standing wave: the electron wave must be in phase with itself after completing each 360° orbit. This is possible only if the circumference of the electron orbit = 1 wavelength, 2 wavelengths, 3 wavelengths, ...

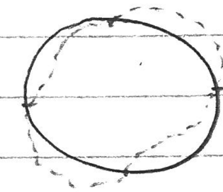


$2\pi r = \lambda$





$2\pi r = 2\lambda$



etc.

google: Schumann resonances

b) The average radius of the waveguide between the surface of the earth and the ionosphere is

$r = (6370 + 50)\ \text{km} = 6420\ \text{km} = 6.42 \times 10^6\ \text{m}$

$\boxed{\lambda_n = n\,2\pi r \quad n = 1, 2, 3, \ldots}$

for the lowest energy wave $(n = 1)$: $2\pi r = \lambda_1$

frequency $\nu_1 = \dfrac{c}{\lambda_1} = \dfrac{c}{2\pi r} = \dfrac{2.998 \times 10^8\ \text{ms}^{-1}}{2\pi (6.42 \times 10^6\ \text{m})}$

$\nu_1 = 7.43\ \text{s}^{-1} = 7.43\ \text{Hz}$

$\nu_2 = 2\nu_1 = 14.9\ \text{Hz}$ ⟵ twice λ_1, half ν_1

$\nu_3 = 3\nu_1 = 22.3\ \text{Hz}$ etc. ⟵ three times λ_1, one-third ν_1

$$\Delta n_g = -1\,\text{mol} \qquad \Delta V = -\frac{RT}{P}$$

Q4 a) $D(g) + D(g) \rightarrow D_2(g)$ $(25°C,\ 1\,\text{bar})$

$\boxed{\text{chemical reaction}}$

$$\Delta H = \Delta H^\circ_{fm}(D_2, g) - 2\Delta H^\circ_{fm}(D, g)$$

$$= 0 - 2(218\ \text{kJ mol}^{-1}) = -436\ \text{kJ mol}^{-1}$$

$$\Delta H = \Delta(U + pV) = \Delta U + \Delta(pV) = \Delta U + p\Delta V$$

energy change

$$\Delta U = \Delta H - p\Delta V = \Delta H - p\left(-\frac{RT}{P}\right)$$

$$= \Delta H + RT$$

$$= -436{,}000\ \text{J mol}^{-1} + \left(8.314\ \frac{\text{J K}}{\text{mol}}\right)(298.15\,\text{K})$$

$$= (-436{,}000 + 2500)\ \text{J mol}^{-1}$$

$$\boxed{\Delta U_m = -4.335 \times 10^5\,\text{J} \quad (\text{chemical})}$$

b) $D^+(g) + D^+(g) \rightarrow He^{2+}(g)$

$\boxed{\text{nuclear reaction}}$

$$E = mc^2 \Rightarrow \Delta E = c^2 \Delta m$$

$\Delta m = 4.251 \times 10^{-29}\,\text{kg}$

$$\Delta E = c^2 (m_{He2+} - 2m_{D+})$$

$$= (2.998 \times 10^8\ \text{m s}^{-1})^2 \underbrace{[6.644657230 - 2(3.343583772)]}_{\Delta m = 4.251\times10^{-29}\,\text{kg}} 10^{-27}\,\text{kg}$$

$$\Delta E = -3.820 \times 10^{-12}\,\text{J} \quad (\text{for one } He^{2+} \text{ nucleus})$$

$$\Delta E_m = N_A \Delta E = (6.022 \times 10^{23}\ \text{mol}^{-1})(-3.820 \times 10^{-12}\,\text{J})$$

$$\boxed{\Delta E_m = -2.301 \times 10^{12}\ \text{J mol}^{-1} \quad (\text{nuclear})}$$

yikes!

(Q4 cont.)

c) $D^+ + D^+ \rightarrow He^{2+}$

the deuterium nuclei are positively charged and strongly repel each other at close range

high temperatures and therefore high kinetic energies of the nuclei are required to overcome the Coulomb repulsion to get the nuclei close enough for attractive strong nuclear forces (also quantized) to take over and fuse two D^+ nuclei to form He^{2+}

d) The nuclear reaction of deuterium releases

$$\frac{2.301 \times 10^{12}}{4.335 \times 10^5} = \boxed{5.31 \times 10^6 \text{ more energy}}$$

than the chemical reaction, and hydrogen isotopes are widely available

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Q5

a) Tungsten-wire filaments are used for the filaments in incandescent light bulbs because tungsten has the highest melting point of any element (3695 K). (Can get hotter = more light!)

Tungsten filaments can therefore be heated to high temperatures (without melting the metal) and produce more light.

(Q5 cont.)

b) $T = 3200$ K

total energy radiated per square meter per second $= \int_0^\infty e(T,\nu)\,d\nu = \sigma T^4$

$= (5.670 \times 10^{-8}\ J\ m^{-2} s^{-1} K^{-4})(3200\ K)^4$

$= \boxed{5.94 \times 10^{6}\ J\ m^{-2}\ s^{-1}} = 5.94 \times 10^{6}\ W\ m^{-2}$

$(1\ \text{Watt} = 1\ W = 1\ J\ s^{-1})$

c) One square meter of tungsten radiates 5.94×10^6 W

For a 60 W light bulb, the surface area of tungsten is

$$A = (1\ m^2)\frac{60\ W}{5.94 \times 10^6\ W} = 1.01 \times 10^{-5}\ m^2 = 2\pi r L$$

length of the wire $\quad L = \dfrac{A}{2\pi r} = \dfrac{1.01 \times 10^{-5}\ m^2}{2\pi\ \frac{0.100}{1000}\ m} = 0.0161\ m$

$\boxed{\text{wire length} = 16.1\ mm}$

Q6 The emissivity of a blackbody at frequencies from ν_1 to ν_2 is

$$\int_{\nu_1}^{\nu_2} \underbrace{e(T,\nu)}_{\text{units } J\,m^{-2}}\ \underbrace{d\nu}_{\text{units } s^{-1}}$$

which has units $\overbrace{J\ m^{-2}}^{\text{from } e(T,\nu)}\ \underbrace{s^{-1}}_{\text{from } d\nu}$

(Q7) a) Aluminum in mirrors is bright and shiny with a very high reflectance.
(most of the incident radiation is reflected, not absorbed)

A blackbody – in contrast – absorbs all incident radiation at all frequencies, and reflects none.

b) If a sheet of shiny, polished aluminum is ground into a fine powder, the free electrons in the metal powder grains can travel only a few nm before hitting a boundary. The electrons are no longer free to travel hundreds of nm when accelerated by the electric field from the incoming light.

∴ finely powdered aluminum looks black

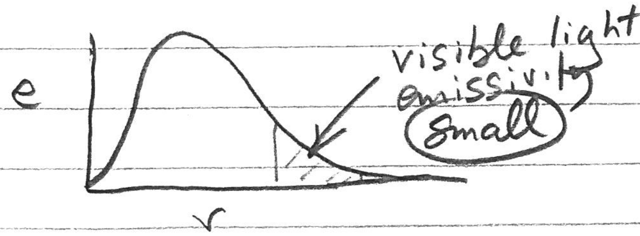
(Q8) a) emissivity for visible light (λ_1 400 to λ_2 700 nm)

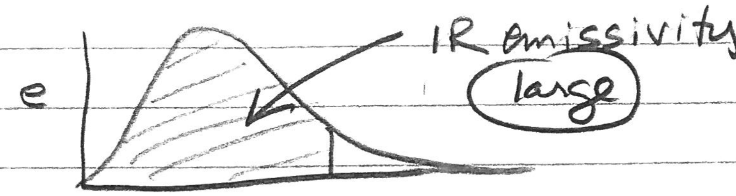
$= $ area under the plotted curve from $\nu_1 = \frac{c}{\lambda_1}$ to $\nu_2 = \frac{c}{\lambda_2}$

$= $ area under the curve from 4.28×10^{14} to $7.50 \times 10^{14}\ s^{-1}$

b) emissivity for infrared radiation (700 nm to 1 mm)

$= $ area under $e(T, \nu)$ from 3.00×10^{11} to 4.28×10^{14} Hz





c) most of the radiation emitted by incandescent bulbs is "invisible" IR radiation (useless for illumination)
LEDs emit more visible light than IR (heat)

Q9 Planck's radiation law gives

$$\langle h\nu \rangle = \frac{h\nu}{e^{h\nu/KT}-1}$$ for the average photon energy

define $y = h\nu/KT$, then $\langle h\nu \rangle = \dfrac{h\nu}{e^{y}-1}$

as $y \to 0$ $\left(\frac{h\nu}{KT} \to 0\right)$, $e^{y} \to 1+y$ and

$$\lim_{y\to 0} \langle h\nu \rangle = \lim_{y\to 0} \frac{h\nu}{e^{h\nu/KT}-1} = \lim_{y\to 0} \frac{h\nu}{1+y-1}$$

$$= \frac{h\nu}{y} = \frac{h\nu}{\frac{h\nu}{KT}} = KT$$

Q10 we know $p = \frac{1}{3}\frac{U}{V}$

for N photons with average energy KT:

$$p = \frac{1}{3}\frac{NKT}{V} \quad \text{so} \quad \frac{n}{V} = \frac{1}{N_A}\frac{N}{V} = \frac{1}{N_A}\frac{3p}{KT} = \frac{3p}{RT}$$

$$\frac{NKT}{V} = \frac{n}{V}RT = \frac{U}{V} = \int_0^\infty e(T,\nu)\,d\nu = \frac{4}{c}\int_0^\infty e(T,\nu)\,d\nu = \frac{4}{c}\sigma T^4$$

$$\frac{n}{V} = \frac{4\sigma T^3}{cR}$$