Chemistry 331 **Term Test #1** (14 October 2020)

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This is a **three-hour test**.

Please answer all **seven questions** in the spaces provided.

A calculator and the equation sheets provided can be used.

No books or notes are allowed. No marks for unreadable answers.

Q1. a) Briefly describe an experiment to show electromagnetic waves can behave like particles.

Photoelectric Experiment Electromagnetic radiation consists of "particles" (photon packets).

b) Briefly describe an experiment to show particles can behave like waves.

Electron Diffraction Electrons create wave-like diffraction patterns after passing through crystalline metal foils.

c) For an electron with deBroglie wavelength 1.70 × 10^{-15} m, calculate:

$\lambda = h/p$

i) the momentum of the electron

$$p = \frac{h}{\lambda} = \frac{6.626 \times 10^{-34}\ \mathrm{J\,s}}{1.70 \times 10^{-15}\ \mathrm{m}} = \boxed{3.90 \times 10^{-19}\ \mathrm{kg\ m\ s^{-1}}}$$

$$p = m_e v$$

[7] **ii)** the speed of the electron

$$v = \frac{p}{m_e} = \frac{3.90 \times 10^{-19}\ \mathrm{kg\,m\,s^{-1}}}{9.110 \times 10^{-31}\ \mathrm{kg}} = \boxed{4.28 \times 10^{11}\ \mathrm{m\,s^{-1}}}$$

(too fast! relativistic effects ignored)

iii) the kinetic energy of the electron

$$T = \frac{1}{2} m_e v^2 = \frac{p^2}{2m_e} = \frac{(3.90 \times 10^{-19}\ \mathrm{kg\,m\,s^{-1}})^2}{2(9.110 \times 10^{-31}\ \mathrm{kg})} = \boxed{8.34 \times 10^{-8}\ \mathrm{J}}$$

$$T = 5.20 \times 10^{11}\ \mathrm{eV} = \boxed{520\ \mathrm{GeV}}$$

d) The diameter of a proton is 1.70 × 10^{-15} m. Use the answers to **c** to explain the existence of atoms and molecules, and therefore *the existence of chemists*!

Under "normal" conditions, electron energies are <<< 520 GeV, and the electron de Broglie wavelength is >>> proton diameter.

Electron waves are "too big" to fit inside protons.

$\Rightarrow$ stable atoms and molecules (not subatomic particles, such as neutrons)

$(e^- + p^+ \rightarrow n^0)$

Q2. a) Show Planck's law $e(T,\nu) = \dfrac{2\pi h\nu^3}{c^2(e^{h\nu/kT} - 1)}$ for the blackbody emissivity spectrum reduces to the classical Rayleigh-Jeans law $e(T,\nu) = \dfrac{2\pi kT\nu^2}{c^2}$ in the limit $h\nu/kT \to 0$.

$$\lim_{\frac{h\nu}{kT}\to 0} \frac{2\pi h\nu^3}{c^2(e^{h\nu/kT}-1)} = \lim_{\frac{h\nu}{kT}\to 0} \frac{2\pi h\nu^3}{c^2(1+\frac{h\nu}{kT}-1)}$$

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

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

b) The surface of the sun closely resembles a blackbody radiation source at 5600 K. Calculate:

i) the total emissivity of sun in units of J m^{-2} s^{-1}

$$\int_0^\infty e(T,\nu)\,d\nu = \sigma T^4 = (5.670\times10^{-8})\,5600^4$$

$$= \boxed{55.8\times10^6 \text{ J m}^{-2}\text{ s}^{-1}}$$

[7] **ii)** the frequency for the maximum emissivity.

$$\nu_{max} = 2.821\frac{kT}{h} = 2.821\frac{1.381\times10^{-23}(5600)}{6.626\times10^{-34}} = \boxed{3.29\times10^{14}\text{ s}^{-1}}$$

c) **i)** Show the Rayleigh-Jeans law is accurate for the sun at radio frequencies (0 to 10^{12} Hz).

$$\left(\frac{h\nu}{kT}\right)_{\substack{\text{max at}\\ \text{radio freq.}}} = \frac{6.626\times10^{-34}(10^{12})}{1.381\times10^{-23}(5600)} = \boxed{0.00857 \ll 1}$$

ii) Use the Rayleigh-Jeans law to calculate the emissivity of the sun at radio frequencies (0 Hz to 10^{12} Hz).

Note: Lengthy numerical calculations using the trapezoidal rule are *not required* to answer this question.

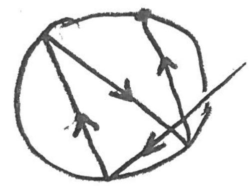
$$\int_0^{10^{12}\text{ Hz}} \frac{2\pi kT}{c^2}\nu^2\,d\nu = \frac{2\pi kT}{c^2}\int_0^{10^{12}\text{ Hz}}\nu^2\,d\nu = \frac{2\pi kT}{c^2}\left.\frac{\nu^3}{3}\right|_0^{10^{12}\text{ Hz}}$$

$$= \frac{2\pi(1.381\times10^{-23})(5600)}{(2.998\times10^8)^2}\left(\frac{(10^{12})^3}{3} - \frac{0^3}{3}\right)$$

$$= \boxed{1.80\text{ J m}^{-2}\text{ s}^{-1}}$$

Q3. **a)** A small hole in the wall of a hollow cavity is an excellent approximation to a blackbody radiation source. Why?

Even if the cavity material is slightly reflective, all photons entering the hole are absorbed: no reflected radiation leaves the hole



b) Because blackbodies are good **radiation absorbers**, they are also good **radiation emitters**. Explain.

At thermal equilibrium, emitted radiation = absorbed radiation

(otherwize, objects would spontaneously heat up or cool down) (violating the 2nd Law)

c) The **SR-71 Blackbird** is a supersonic (Mach 3.5) strategic reconnaissance aircraft. Why are SR-71s black?
Hint: Air friction causes aircraft surfaces to get dangerously hot at high speeds.

more thermal radiation is emitted (see part b), keeping the aircraft surfaces cooler compared to gray or shiny aluminum.

$\left(c = \lambda \nu \quad \nu = \frac{c}{\lambda}\right)$

d) This question refers to a laser emitting a 750 W beam of radiation at wavelength 1.06×10^{-5} m.

i) Calculate the number of photons emitted per second by the laser.

$$750\ \text{W} = 750\ \frac{\text{J}}{\text{s}} = \left(\begin{matrix}\text{number of photons}\\ \text{per second}\end{matrix}\right) h\nu = \left(\frac{dN}{dt}\right) h\nu$$

$$\frac{dN}{dt} = \frac{750\ \text{J s}^{-1}}{6.626\times10^{-34}\left(\frac{2.998\times10^{8}}{1.06\times10^{-5}}\right)} = \boxed{4.00\times10^{22}} \text{ photons per second}$$

[8] **ii)** Calculate the linear momentum of photons with wavelength 1.06×10^{-5} m.

$$p = \frac{h}{\lambda} = \frac{6.626\times10^{-34}\ \text{J s}}{1.06\times10^{-5}\ \text{m}} = \boxed{6.25\times10^{-29}\ \text{kg m s}^{-1}}$$

iii) Interstellar travel using "photonic sails" has been proposed. Calculate the force exerted on a sail that absorbs all of the photons from the laser. *Hint*: force = d(momentum)/d*t*.

$$\text{force} = \left(\begin{matrix}\text{number of photons}\\ \text{absorbed per second}\end{matrix}\right)\left(\begin{matrix}\text{momentum}\\ \text{per photon}\end{matrix}\right)$$

$$= (4.00\times10^{22}\ \text{s}^{-1})(6.25\times10^{-29}\ \text{kg m s}^{-1})$$

$$= \boxed{2.50\times10^{-6}\ \text{N}}$$

iv) Twice as much force can be generated using a sail that reflects photons. Explain.

absorb a photon: $\downarrow$ momentum change $= \frac{h}{\lambda}$ for the sail

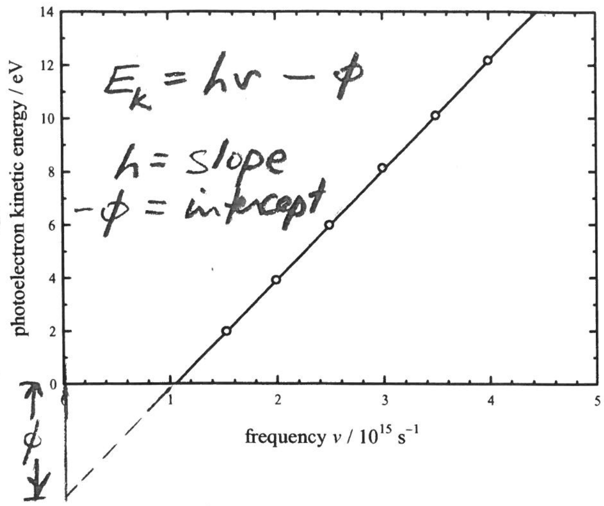
reflect a photon: $\downarrow\uparrow$ momentum change $= \frac{h}{\lambda} - \left(-\frac{h}{\lambda}\right) = \frac{2h}{\lambda}$

(twice as large)

Q4. **a)** Part **a** refers to the photoelectric data for chromium plotted below.

i) The data cannot be explained by using classical physics. Why?

kinetic energy of the ejected electrons should increase with light intensity (not frequency)



ii) No photoelectrons are produced at frequencies below 1.09×10^{15} Hz. Why?

photon energy $h\nu$ insufficient to overcome electron binding energy to the metal ($= \phi$)

iii) Evaluate Planck's constant from the data.

$$\text{slope } h \approx \frac{\Delta \text{ kinetic energy}}{\Delta \text{ frequency}} \approx \frac{14.0 \text{ eV}}{(4.42 - 1.06)10^{-15} \text{ s}} = 4.17 \times 10^{-15} \text{ eV s}$$

$$= (4.17 \times 10^{-15} \text{ eV s})(1.602 \times 10^{-19} \text{ J eV}) = 6.68 \times 10^{-34} \text{ Js}$$

[7] **iv)** Evaluate the work function for chromium.

$$-\phi = \text{intercept} \cong -4.3 \text{ eV}$$

$$\boxed{\phi = 4.3 \text{ eV} \qquad (6.9 \times 10^{-19} \text{ J})}$$

b) Part **b** refers to the molar vibrational energy (E_m) of lead crystals ($\nu = 6.21 \times 10^{10}$ s^{-1}).

i) Calculate E_m for lead at 2.00 K assuming classical behavior.

$$E_m(\text{classical}) = \lim_{h\nu/kT \to 0} 3RT \frac{h\nu}{kT} \frac{1}{1 + \frac{h\nu}{kT} - 1} = 3RT \frac{h\nu/kT}{h\nu/kT} = 3RT$$

$$= 3(8.314)2.00 = 49.9 \text{ J mol}^{-1}$$

ii) Calculate E_m for lead at 2.00 K using Einstein's theory.

$$\frac{h\nu}{kT} = \frac{(6.626 \times 10^{-34})(6.21 \times 10^{10})}{(1.381 \times 10^{-23})(2.00)} = 1.49$$

$$E_m = 3RT \frac{h\nu}{kT} \frac{1}{e^{h\nu/kT} - 1} = 3RT(1.49)\frac{1}{e^{1.49} - 1} = 0.434 \, RT$$

$$= 0.434(49.9 \text{ J mol}^{-1}) = \boxed{21.6 \text{ J mol}^{-1}}$$

iii) Why is the value of E_m predicted by Einstein much smaller than the classical value?

Vibrations are "frozen" out. Most lead atoms are in the ground vibrational level ($E = 0$) at 2.00 K.

Q5. **a)** Prove z^*z is always real for the complex number $z = x + yi$.

$$z^* z = (x+yi)^*(x+yi) = (x-yi)(x+yi)$$
$$= x^2 - xyi + xyi - yi^2 = x^2 - y^2(-1) = \underbrace{x^2+y^2}_{\text{(positive real number)}}$$

b) Give the solutions of the equation $0 = \frac{1}{2}x^2 + 6x + 50$.

Hint: The equation $ax^2 + bx + c = 0$ has solutions $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$.

$a = \frac{1}{2}$ $b = 6$ $c = 50$

$$x = \frac{-6 \pm \sqrt{36 - 4(\frac{1}{2})50}}{2(\frac{1}{2})} = \frac{-6 \pm \sqrt{36-100}}{1} = -6 \pm \sqrt{-64}$$

$$= -6 \pm 8\sqrt{-1} = -6 \pm 8i = \boxed{-6-8i,\ -6+8i}$$

c) For the function $f(x,y) = 5e^x\cos(y)$, derive expressions for

i) $\vec{\nabla} f(x,y) = \hat{i}\frac{\partial f}{\partial x} + \hat{j}\frac{\partial f}{\partial y}$

$$= \hat{i}\,5e^x\cos(y) + \hat{j}\,5e^x(-\sin y)$$
$$= \boxed{\hat{i}\,5e^x\cos(y) - \hat{j}\,5e^x\sin(y)} \quad \text{(a vector)}$$

[7] **ii)** $\nabla^2 f(x,y)$

$$\nabla^2 f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} = \frac{\partial}{\partial x}\left(5e^x\cos(y)\right) + \frac{\partial}{\partial y}\left(-5e^x\sin(y)\right)$$

$$= \boxed{5e^x\cos(y) - 5e^x\cos(y) = 0} \quad \text{(a scalar)}$$

d) A particle with de Broglie wavelength λ is described by the wave function $\psi(x) = Ae^{-i2\pi x/\lambda}$. Show $\psi(x)$ is an eigenfunction of the $\hat{p}_x$ operator with an eigenvalue equal to the momentum of the particle. (A is a constant.)

$$\hat{P}_x \psi(x) = -\frac{ih}{2\pi}\frac{\partial}{\partial x}Ae^{-i2\pi x/\lambda} = \left(-\frac{ih}{\cancel{2\pi}}\right)A\left(-\frac{i\cancel{2\pi}}{\lambda}\right)e^{-i2\pi x/\lambda}$$

$$= (-i)(-i)\frac{h}{\lambda}Ae^{-i2\pi x/\lambda} = ii\frac{h}{\lambda}\psi(x)$$

$$= \boxed{-\frac{h}{\lambda}\psi(x)}$$

the eigenvalue $-\frac{h}{\lambda}$ is the particle momentum

de Broglie relation

(imaginary probabilities — not defined)

Q6. **a)** The wave function for a hydrogen 2p orbital is $\psi_{2p} = \dfrac{1}{\sqrt{32\pi}}\left(\dfrac{1}{a_0}\right)^{3/2} \dfrac{r}{a_0} e^{-r/2a_0} \sin\theta\, e^{-i\phi}$.

i) $\psi^*\psi$ must be a real function. Why?

$\psi^*\psi$ = probability distribution function, must be real

ii) Show $\psi^*\psi$ is a real function.

$$\psi^*\psi = \left[\frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\sin\theta\, e^{+i\phi}\right]\left[\frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\sin\theta\, e^{-i\phi}\right]$$

$$= \frac{1}{32\pi}\frac{1}{a_0^3}\frac{r^2}{a_0^2}e^{-r/a_0}\sin^2\theta \qquad \text{(why? because } e^{i\phi}e^{-i\phi} = e^0 = 1\text{)}$$

b) The wave function for a ground-state hydrogen atom is $\psi_{1s} = \dfrac{1}{\sqrt{\pi}}\left(\dfrac{1}{a_0}\right)^{3/2} e^{-r/a_0}$. Calculate the most probable value of r for the electron.

$$P(r) = \psi_{1s}(r)^*\psi_{1s}(r) = \left(\frac{1}{\sqrt{\pi}}\frac{1}{a_0^{3/2}}e^{-r/a_0}\right)^*\left(\frac{1}{\sqrt{\pi}}\frac{1}{a_0^{3/2}}e^{-r/a_0}\right)$$

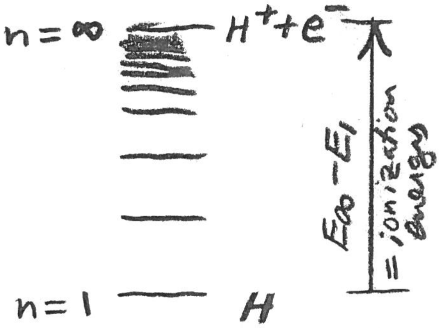
$$= \frac{1}{\pi a_0^3}e^{-2r/a_0} \qquad \text{max. } P(r) \text{ at } \boxed{r = 0}$$

c) Calculate the ionization energy for one mole of ground-state ($n = 1$) hydrogen atoms. To simplify the calculations, assume the reduced mass equals the electron mass.

ionization energy for one ground-state H atom:

[8]

$$E_\infty - E_1 = -\frac{m_e e^4}{8\varepsilon_0^2 h^2}\frac{1}{\infty^2} - \left(-\frac{m_e e^4}{8\varepsilon_0^2 h^2}\frac{1}{1^2}\right)$$



$$= \frac{m_e e^4}{8\varepsilon_0^2 h^2} = \frac{(9.110\times10^{-31})(1.602\times10^{-19})^4}{8(8.854\times10^{-12})^2(6.626\times10^{-34})^2}$$

$$= 2.179\times10^{-18}\text{ J} \quad \text{(for one H atom)}$$

for one mole of H atoms:

$$\text{molar ionization energy} = (6.022\times10^{23}\text{ mol}^{-1})(2.179\times10^{-18}\text{ J}) = \boxed{1.31\times10^{6}\text{ J mol}^{-1}}$$

d) The line spectra observed for deuterium atoms (D) are shifted to frequencies that are slightly higher (by 0.027%) relative to those for hydrogen (H) atoms. Explain.

The reduced mass of the D atom $\mu_D = \dfrac{m_e m_D}{m_e + m_D} = \dfrac{m_e}{1 + \frac{m_e}{m_D}}$

is slightly larger than $\mu_H = \dfrac{m_e m_H}{m_e + m_H} = \dfrac{m_e}{1 + \frac{m_e}{m_H}}$ (and $E_n \propto \mu$)

e) Infrared spectroscopy is widely used to study molecular vibrations. Can hydrogen atoms absorb or emit infrared radiation? Justify your answer.

yes! $\Delta E = h\nu = E_f - E_i = Q\left(\dfrac{-1}{n_f^2} - \dfrac{-1}{n_i^2}\right)$

$$= Q\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad n_i, n_f = 1, 2, 3, 4, \ldots$$

all photon energies from radio waves to ultraviolet allowed

$$g = 9.81 \text{ m s}^{-2}$$

Q7. This question refers to the classical mechanics of mass m moving the vertical x-direction.

a) The gravitational potential energy is $V(x) = mgx$. Show the force F_x acting on the mass is $-mg$.

$$F_x = -(\text{gradient of the potential energy}) = -\frac{d}{dx}(mgx) = -mg$$

b) Show $x(t) = c_0 + c_1 t - (\cancel{m}g/2)t^2$ is a solution of Newton's equation of motion $F_x = m d^2x(t)/dt^2$.

LS RS

$$F_x = -mg \quad \text{LS}$$

$$\text{RS} \quad m\frac{d^2x(t)}{dt^2} = m\frac{d}{dt}\frac{d}{dt}\left(c_0 + c_1 t - \frac{\cancel{m}g}{2}t^2\right)$$

$$= m\frac{d}{dt}(c_1 - \cancel{m}gt) = -mg$$

c) Show the constant c_0 is the position of the mass at time $t = 0$.

$$x(0) = c_0 + c_1(0) - \frac{g}{2}(0)^2 = c_0 = 0$$

[6]

d) Show constant c_1 is the velocity v_x of the mass at time $t = 0$.

$$\frac{dx(t)}{dt} = v(t) = \frac{d}{dt}\left(c_0 + c_1 t - \frac{g}{2}t^2\right) = c_1 - \frac{g}{2}2t = c_1 - gt$$

$$v(0) = c_1 - g(0) = c_1$$

e) A 150 gram baseball thrown upward has initial velocity $v_x(0) = 15 \text{ m s}^{-1}$ and initial position $x(0) = 0$. Ignoring air friction, calculate:

i) the maximum height of the baseball

$$x(t) = x(0) + v(0)t - \frac{g}{2}t^2$$

$$v(t) = \frac{dx(t)}{dt} = v(0) - gt = 0 \text{ at maximum height}$$

$$t_{max\,x} = \frac{v(0)}{g} = \frac{15 \text{ m s}^{-1}}{9.8 \text{ m s}^{-2}} = \boxed{1.53 \text{ s}}$$

$$x_{max} = v(0)t_{max\,x} - \frac{g}{2}t_{max\,x}^2 = 11.5 \text{ m}$$

ii) the time it takes for the baseball to return to $x = 0$.

$$x(t) = v(0)t - \frac{g}{2}t^2 = t\left(v(0) - \frac{g}{2}t\right)$$

$$= 0 \text{ when } v(0) = \frac{g}{2}t \qquad t = \frac{2v(0)}{g}$$

$$= \frac{2(15.0 \text{ m s}^{-1})}{9.80 \text{ m s}^{-2}} = \boxed{3.06 \text{ s}}$$

$$= 2(t_{max\,x})$$

Q1
Q2
Q3
Q4
Q5
Q6