Chem 4A, Fall 2006
Midterm Exam 1, September 22, 2006.
Prof. Head-Gordon, Prof. Moretto

Name: KEY TA: ______________

Grade:

1. (5 points) ______
2. (6 points) ______
3. (8 points) ______
4. (5 points) ______

Total: ______

Closed book exam. There are 6 pages. Calculators are OK. Set brains in high gear and go!
Use back side of pages for scribble paper

Some possibly useful facts and figures:

$R = 8.3145$ J mol^{-1} K^{-1}
$h = 6.6261 \times 10^{-34}$ J s
$c = 2.9979 \times 10^{8}$ m s^{-1}
$m_e = 9.1094 \times 10^{-31}$ kg
$N_0 = 6.0221 \times 10^{23}$ mol^{-1}

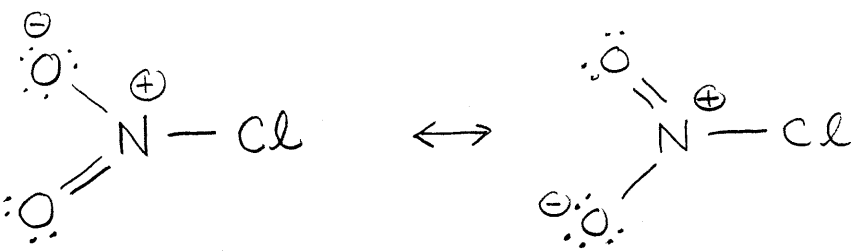
molar volume at STP = 22.4 L
$\hbar = h / 2\pi$

Some possibly relevant equations:

Planck relation:	$E = h\nu$	
de Broglie relation:	$p = h / \lambda$	
wave equation:	$c = \nu\lambda$	
uncertainty principle	$\Delta p \Delta x \geq \hbar / 2$	
particle-in-a-box	$E_n = \dfrac{n^2 \pi^2 \hbar^2}{2ma^2}$	$\Psi_n = \sqrt{\dfrac{2}{a}} \sin \dfrac{n\pi x}{a}$
hydrogen atom	$E_n = -\dfrac{Z^2}{n^2} R_\infty$	$R_\infty = 2.18 \times 10^{-18} J$
linear momentum	$p = mv$	
kinetic energy	$T = \frac{1}{2} mv^2$	

1. Nitryl chloride, NO_2Cl, is known to decompose to NO_2 and Cl_2.

(a) (2 points) Write Lewis structures for NO2Cl, given that the chlorine (7 valence electrons, atomic number Z=17, relative atomic mass M=35.453) atom and both oxygen (Z=8, M=15.999) atoms are bonded to the nitrogen (Z=7, M=14.007). Be sure to show the role of resonance structures if there is more than one plausible Lewis structure. Also show any formal charges.



octets (1)
formal charge (1/2)
resonance (1/2)

(b) (1 point) Write a balanced equation for the decomposition of nitryl chloride.

$$2NO_2Cl \longrightarrow 2NO_{2(g)} + Cl_{2(g)}$$ (1)

(c) (2 points) If 2.00g of nitryl chloride decomposes to yield NO_2 and Cl_2, calculate the volume of gaseous products under standard conditions.

$M(NO_2Cl) = 81.458$ g/mol
$\Rightarrow n(NO_2Cl) = 0.0246$ mol (1)

Both NO_2 and Cl_2 are gases

$n(\text{gas}) = n(NO_2) + n(Cl_2)$
$= \frac{3}{2} n(NO_2Cl) = 0.0368$ mol (1/2)

1 mol gas at STP = 22.4 L

$\Rightarrow V(\text{gas}) = 22.4 \times 0.0368 = 0.825$ L (1/2)

2. (a) (2 points) The work function of metallic sodium is 4.4×10^{-19} J. What is the longest wavelength of light that could be expected to cause electron emission from sodium?

longest wavelength ⟺ lowest frequency

$$h\nu_{min} = \frac{hc}{\lambda_{max}} = 4.4\times10^{-19}\text{ J}$$

$$\Rightarrow \lambda_{max} = \frac{6.6261\times10^{-34}\times 2.9979\times10^{8}}{4.4\times10^{-19}} = 4.5\times10^{-7}\text{ m}$$

(b) (2 points) Suppose electrons have been accelerated to a kinetic energy of 1×10^{6} J/mol. What is their effective de Broglie wavelength?

$$E = p^2/2m \Rightarrow p = \sqrt{2mE} = \sqrt{\frac{2\times9.1\times10^{-31}\times1\times10^{6}}{6.0\times10^{23}}}$$

i.e. $p = 1.7\times10^{-24}$ kg m s^{-1} (1)

$$\lambda = h/p = \frac{6.6\times10^{-34}}{1.7\times10^{-24}} = 3.81\times10^{-10}\text{ m}$$ (1)

(c) (2 points) Estimate the de Broglie wavelength of a spilled pea as it hits the floor. Show your assumptions clearly.

height ~ 1 m ; mass ~ 1 g ~ 10^{-3} kg

speed ~ 1 m s^{-1}

} reasonable assumptions (1)

$\Rightarrow p \sim 10^{-3}$ kg m s^{-1}

$$\Rightarrow \lambda = \frac{h}{p} = \frac{10^{-33}}{10^{-3}} \sim 10^{-30}\text{ m}$$

} within 3 order of magnitude (1)

3. Suppose an electron is known to be within a 2 Å distance (something like a chemical bond).
   (a) (1 point) What is the minimum uncertainty in its momentum?

$$\Delta p \Delta x \geq h/4\pi$$

$$\Delta p \geq \frac{h}{4\pi \Delta x} = \frac{6.6\times10^{-34}}{4\pi \times 2\times10^{-10}} = 2.6\times10^{-25}\ \text{kg m s}^{-1}$$ (½) (½)

(particle in a 3-d box is OK too)

   (b) (3 points) Calculate the wavelength of light necessary to excite this electron from its ground state to its first excited state, assuming that these states can be described as the lowest and next to lowest energy levels of the particle in a box.

$$E_n = \frac{\hbar^2}{2m}\frac{n^2\pi^2}{a^2} = \left(\frac{h^2}{4\pi^2}\right)\frac{n^2\pi^2}{2ma^2} = \frac{h^2n^2}{8ma^2}$$

n=1 is the ground state
n=2 is the 1st excited state

$$\Delta E = E_2 - E_1 = \frac{h^2}{8ma^2}(4-1) = \frac{(6.626\times10^{-34})^2 \times 3}{8\times 9.109\times10^{-31}\times(2\times10^{-10})^2}$$

$$= 4.52\times10^{-18}\ \text{J}$$ (2)

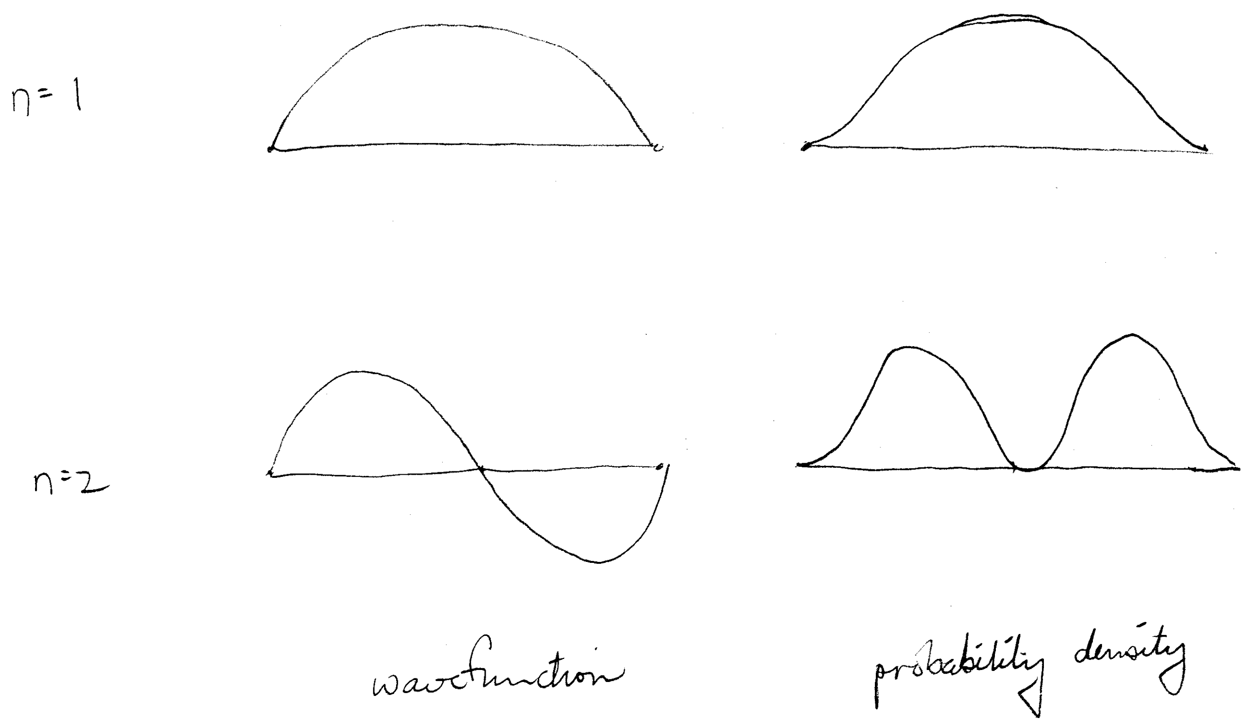
$$\Delta E = h\nu = hc/\lambda$$

$$\rightarrow \lambda = \frac{hc}{\Delta E} = \frac{(6.626\times10^{-34})\times(2.998\times10^{8})}{4.52\times10^{-18}} = 4.39\times10^{-8}\ \text{m}$$ (1

(particle in a 3-d box is OK too)

(c) (2 points) Make a sketch of the wavefunction and the probability density associated with the ground state and the first excited state of the particle in a box.

($\frac{1}{2}$ each)



(d) (1 point) How many nodes does the state of the particle in a box with quantum number n have?

$(n-1)$

(e) (1 point) Give a reason why the energy increases with the number of nodes (not based on classical waves)

- suppose there are n nodes in a box of length a
- then $\lambda \sim a/(n+1)$
- but $p = h/\lambda \sim h(n+1)/a$
- & $E = p^2/2m \sim \dfrac{h^2(n+1)^2}{2ma^2}$

other reasons that are OK too...
*curvature of wavefunction

i.e. shorter de Broglie wavelength follows from more nodes.
shorter $\lambda \Rightarrow$ higher $p \Rightarrow$ increasing energy.

4. Atomic energy levels

(a) (1 point) Ionization is the process of removing an electron from an atom or a molecule. Does this process give off energy or require energy? Explain your answer carefully.

Ionizing an electron from a stable atom requires energy because the electron is initially bound. Energy is required to enable it to be removed. (0/1)

0, 1

(b) (1 point) Evaluate the energy change associated with removing the electron from He^+.

$$\Delta E = E_{free} - E(n=1\ He^+)$$

$$= 0 - -\frac{Z^2 R_\infty}{n^2} = \frac{2^2 \times 2.18\times10^{-18}}{1} = 8.72\times10^{-18}\ J$$

0, 0.5, 1

($\frac{1}{2}$ point for n or Z wrong).

(c) (1 point) Would you expect the ionization energy of the first electron from He to be larger or smaller than the answer you obtained in (b)? Explain carefully.

Ionizing the first electron from He

$$\Delta E = -E(n=1\ He) = -Z_{eff}^2 R_\infty$$

Z_{eff} for the 1s electrons in He will be smaller than Z=2 for He^+ due to screening. Hence I.E. is smaller.

(d) (2 points) The ionization energy of the potassium atom (K: Z=19; 1 valence electron) is about one third smaller than the ionization energy of a calcium atom (Ca: Z=20; 2 valence electrons). However the ionization energy of K+ is nearly 3 times as large as Ca+. Can you explain these results?

- Z_{eff}(3s of Ca) > Z_{eff}(3s of K) because K has $Z_{eff} \sim 1$ while Ca has $1 < Z_{eff} < 2$ due to 2 outer electrons (1)

(1/1)

- For $K^{\oplus}$ ionization is from the 2p levels (large Z_{eff}) while for $Ca^{\oplus}$ it is still from 3s ($Z_{eff} \sim 1$) (1)

(1/1)