Chemistry 448/548 Key 1 Fall 2014

Very Short Answer Questions: (3 points each)

1. What is the electron configuration of Ir^+? [Xe] $4f^{14}$ $5d^8$
2. Which of the following is not isoelectronic to the others? Al^-, Cl^{3+}, As^+, S^{2+}, Si^0 (circle your choice)
3. The German word *gerade* means “even.” What does it mean when applied to an orbital? The wave function does not change sign on moving to the opposite side of the nucleus.
4. The outermost electrons on an atom are called the valence electrons.
5. Atoms with no unpaired electrons are called diamagnetic
6. The first electron affinity of open subshell atoms is exothermic.
7. The probability of finding an electron at a given point equals ψ^2.
8. The presence of which symmetry element requires that a molecule be non-polar? i
9. Give a point group to which a chiral molecule may belong. C_1, C_n, D_n
10. Boron is the one element from Groups I-IIIA that is physically hard.

Discussion Questions: (You must show work to receive credit!)

1. What is the difference between a kinetically controlled reaction and a thermodynamically controlled reaction? (5 points)

   A kinetically controlled reaction yields the product produced most rapidly, that is, the product with the lowest activation barrier. A thermodynamically controlled reaction generates the energetically most stable product. These can be the same if the energy barrier to the most stable product is smallest.

2. Give preparations of 3 of the following 4: Al_2O_3, $(BN)_x$, $Mg(OH)_2$, or Na_2O_2? (9 points)

   See handouts.

3. Discuss atomic size and ionization energy and the forces that affect them. (10 points)

   Ionization energy (IE) is the energy required to remove an e^- from a gas phase atom or ion.

   IE increases up and right across the periodic table while atomic size (AS) decreases in those directions.

   Electrons added to atoms in the same shells and subshells shield each other poorly or not at all. Thus on moving right across a period, the added e^- do not effectively shield the added positive charge well and the effective nuclear charge (Z_{eff}) experienced by each e^- increases. Greater Z_{eff} results in greater nuclear-e^- electrostatic attraction pulls the e^- closer to the nucleus and the AS decreases. For the same reason it is more difficult to remove an e^- and easier to added one.

   Going down a group the principle q.n., n, increases. Electrons in these orbitals are more energetic and lie further from the nucleus. Because of effective shielding Z_{eff} remains relatively constant but increased distance results in lower electrostatic attraction. This causes larger AS, but reduced IE.

4. When solving the Schrödinger equation for the particle-in-a-box three “interesting things” were found in the results. What were they? (10 points)

   Energy is a function of position and momentum. In classical mechanics only momentum has an effect.

   Only certain energies are allowed and they are related by whole number values. Thus, quantization is a result of the math. It does not have to be assumed.

   Regions of zero electron density called nodes occur. This is not allowed by classical mechanics.

5. The wave functions for a 2*s* orbital are: $R = K_{2s}(2 - Zr/a_o)e^{-Zr/a_o}$ and $\Theta\Phi = [(1/4\pi)]^{1/2}$. Describe how these functions correspond to a physically real picture of this orbital. Be as specific as you can. (10 points)

   There are two notable features of the radial function. When $Zr/a_o = 2$, $R = 0$. This is a place of zero electron density or a nodal surface. The second major feature is the exponential term e^{-Zr/a_o}. The negative sign in the exponential means that the function will trail off to zero at increasing distance from the nucleus.

   The angular function is a constant. Since there are no variables (θ, ϕ) there is no angular dependence. This means that the probability of finding an e^- at any distance r from the nucleus is everywhere the same. This is a sphere.

6. Give point groups for each of the following (no work required): (16 points)

   PH_3: C_{3v} $OSCl_2$: C_s *trans*-$Co(NH_3)_4Cl_2$: D_{4h} BeF_2: $D_{\infty h}$

7. The molecule benzene has numerous resonance forms. One of the most common shows it with 3 localized double bonds. This form has D_{3h} symmetry. Given the character table below: How many double bond absorptions would you expect to see in the IR if this localized structure were real? In the Raman? Give the irreducible representations of each. (10 points)

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E’	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E″	2	-1	0	-2	1	0
$\mathbf{\Gamma_{red}}$	**3**	**0**	**1**	**3**	**0**	**1**

$A_1' = 1/12[1(1)(3) + 2(1)(0) + 3(1)(1) + 1(1)(3) + 2(1)(0) + 3(1)(1)] = 1$

$E' = 1/12[1(2)(3) + 2(-1)(0) + 3(0)(1) + 1(2)(3) + 2(-1)(0) + 3(0)(1)] = 1$

E′ is IR active, so one IR stretch.

A_1' and E′ are Raman active, so two Raman stretches.