Name _____

Student Number _____

Chem 241 Section 51 - Mid-term Exam - 1¼ hours

October 28th, 2009

Answer all the questions on this examination paper. Use the back of the periodic table for rough work or extra space: ***do not detach it****.*

1) (1 mark) Fluorine-19 is the only stable isotope of fluorine. All other are radioactive. Which mode of decay is most likely for Fluorine-18?

a) $^{18}F + \beta^- \rightarrow {}^{18}O$

b) $^{18}F \rightarrow {}^{18}Ne + \beta^-$

c) $^{18}F \rightarrow {}^{9}Be + {}^{9}B$

Answer a): Fluorine-19 is stable, so fluorine-18 must have a neutron/proton ratio which is "uncomfortably" low. Electron capture converts a proton into a neutron raising the ratio.

Comment: Oxygen-18 is a stable isotope of oxygen.

2) (1 mark) Consider the following orbitals: 4s, 5s, 6s, $4p_x$, $5p_x$, $6p_x$, $4d_{z^2}$, $5d_{z^2}$ and $6d_{z^2}$. Which orbitals feature 3 radial (spherical) nodes?

a) 4s, $5p_x$, $6d_{z^2}$

b) 5s, $6p_x$

c) $4d_{z^2}$ only

d) None of the above

Answer a): The number of spherical nodes is given by $n - \ell - 1$.

3) (1 mark) A rhodium atom in the gas phase has the configuration $[Kr]5s^14d^8$. In rhodium (I) compounds (Rh^+), the configuration of the ion is:

a) $[Kr]5s^24d^6$

b) $[Kr]5s^14d^7$

c) $[Kr]5s^04d^8$

d) $[Kr]5s^04d^6$

Answer c): For ions of the transition metals the ns orbital is above the (n – 1)d orbitals in energy, so the d orbitals are filled first, and the ns orbitals will always be empty.

4) (1 mark) A Xenon atom has configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$. Which of the following represents the valence shell and atomic ground state used in describing the bonding and structure of its compounds when using valence bond theory?

a) $4d^{10}5s^2 5p^6$

b) $5s^2 5p^6 5d^0$

c) $5s^2 5p^6 5d^{10}$

d) $4d^{10}5s^2 5p^6 5d^0$

Answer b): The orbitals considered as the valence shell of a main group element are the partially filled or filled ns and np orbitals, and the empty nd orbitals, if any. Filled (n – 1)d orbitals are part of the core.

5) (1 mark) Several different radii can be attributed to an element. For fluorine, which is the correct order for increasing radius:

a) F(covalent) < F^-(4-coordinate) < F^-(6-coordinate)

b) F(covalent) < F^-(6-coordinate) < F^-(4-coordinate)

c) F^-(6-coordinate) < F^-(4-coordinate) < F(covalent)

~~d) F^-(6-coordinate) < F^-(4-coordinate) < F(covalent)~~

e) None of the above

Answer a): Anions are always larger than the atoms from which they are derived so the choice is initially between a) and b). In addition, the effective anion sizes increase with the coordination number – the number of nearest neighbor anions.

6) (1 mark) Consider removal of the last electron from the ions Li^{2+} and Be^{3+}. Which of the following statements is true?

a) The ionization energy for the two ions are equal.

b) Li^{2+} is 1.33 times more difficult to ionize than Be^{3+}

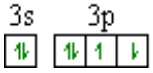
c) Be^{3+} is 1.33 times more difficult to ionize than Li^{2+}

d) Li^{2+} is 1.78 times more difficult to ionize than Be^{3+}

e) Be^{3+} is 1.78 times more difficult to ionize than Li^{2+}

Answer e): In this case the electron is excited from orbit or orbital n = to n = ∞. The energy associated with this, if there is just one electron (hydrogen or a hydrogenic cation, e.g. He^+) is directly proportional to the nuclear charge, Z, squared; 9 in the case of Li^{2+} and 16 in the case of Be^{3+}. The ratio 16/9 = 1.78.

7) (2 marks) The diagram below shows an electron configuration.



Which ***two*** of the following statements are true?

a) The configuration is forbidden by Hund's rule

b) The configuration represents an excited state as defined by Hund's rule

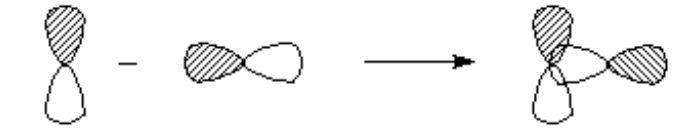
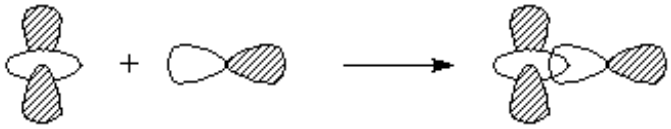
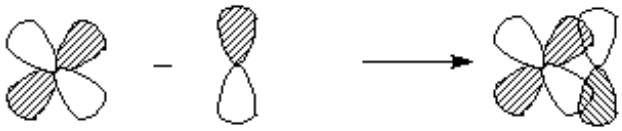
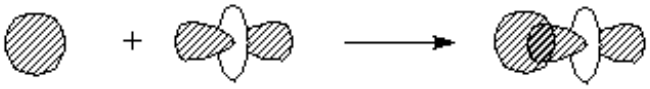
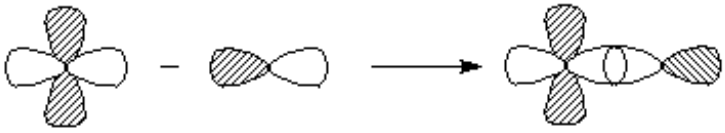
c) The diagram could be showing the valence electrons of Se

d) The configuration is not forbidden by the Pauli principle

Answers b) and d): According to Hund's rule, the electrons in degenerate (same energy) half-filled orbitals should have their spins parallel, in order to have the lowest energy. Otherwise, the atom is in an excited, but not impossible (forbidden) state. The excited state configuration shown has no electrons in the same orbital with parallel spins, so it is not forbidden by the Pauli principle.

Comment: Se has its valence electrons in the 4s and 4p orbitals!

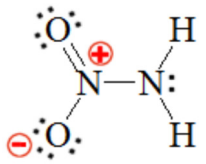
8) (5 marks) Five linear combinations of atomic orbitals to make molecular orbitals are depicted below. Mark whether the resulting molecular orbital is classified as bonding, antibonding, or non-bonding, and if they are bonding or antibonding, indicate whether the molecular orbitals are σ or π. (The shading is indicative of the *relative* signs of ψ, that is, unshaded means positive ψ, shaded means negative ψ (or the reverse).

Combination	Bonding, antibonding or nonbonding?	σ or π?
	Non-bonding	N/A
	Bonding	σ
	Antibonding	π
	Bonding	σ
	Bonding	σ

9) Nitramide, NH_2NO_2, an lesser known nitrogen compound with a nitrogen – nitrogen single bond, can be made from hydrazine and ammonia:

$$N_2O_5 + 2NH_3 \rightarrow O_2NNH_2 + NH_4NO_3$$

a) (3 marks) Draw a Lewis structure for the compound, and give the geometry and hybridization at each of the nitrogen atoms.

Left-hand Nitrogen: Basic shape: trigonal Observed shape: trigonal Hybridization: sp^2		Right-hand Nitrogen: Basic shape: tetrahedral Observed shape: trigonal pyramidal Hybridization: sp^3

b) (1 mark) For your Lewis structure and any equivalent canonical (resonance) structures, what is the average nitrogen – oxygen bond order, and (average) charges on individual atoms.

Left-hand Nitrogen:
Average nitrogen – oxygen bond order: 1½
Average charge on oxygens: -½

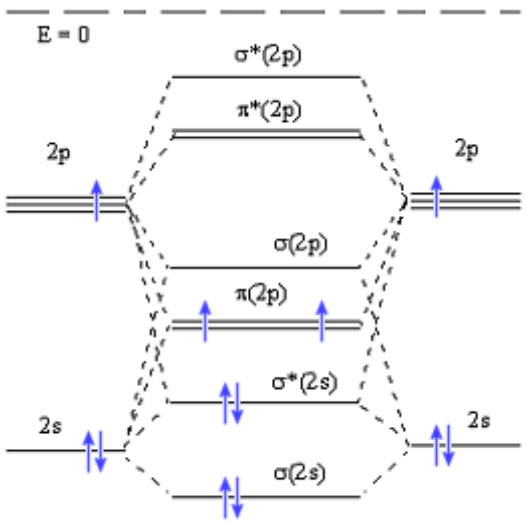
10) (2 marks) Using box diagrams of their electron configurations, explain why the electron affinity of phosphorus is *smaller* than that of silicon, although in general, electron affinities *increase* across a period.

The electron affinity is related to the electron capture enthalpy, the energy released when an electron is added to an atom.

Using Slater's rules it appears that the effective nuclear charge of silicon is lower than that of phosphorus, so it might be expected that the electron affinity would also be lower.

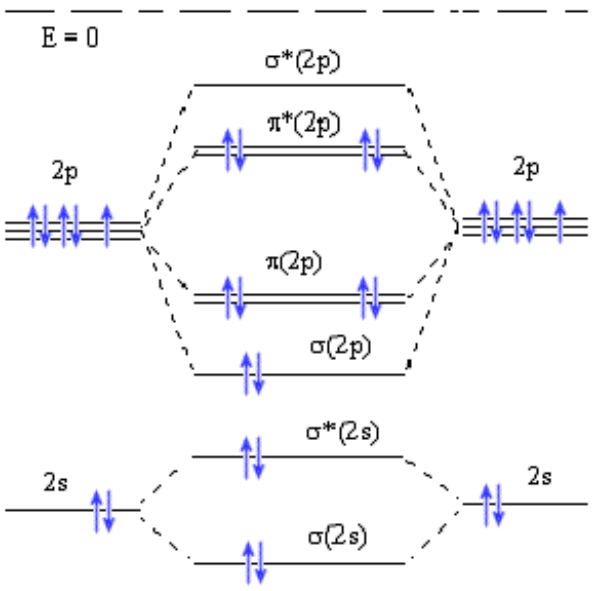
However, silicon has a vacant 3p orbital which can more easily accommodate the additional electron than the half-filled 3p orbitals of phosphorus. (Adding a second electron to one of the phosphorus 3p orbitals requires overcoming the electron – electron repulsion, and also leads to a loss of quantum mechanical "exchange energy".)

11) (3 marks) Three molecular orbital energy level diagrams are shown below. Using the correct diagram for each case, show the electrons on the molecular orbital levels for B_2, O_2^{2-}, and CN^-. Please make sure to distinguish which molecule or ion you are putting on which diagram by completing the labels below the diagrams. Give the bond order of each species. (Answers in blue.)



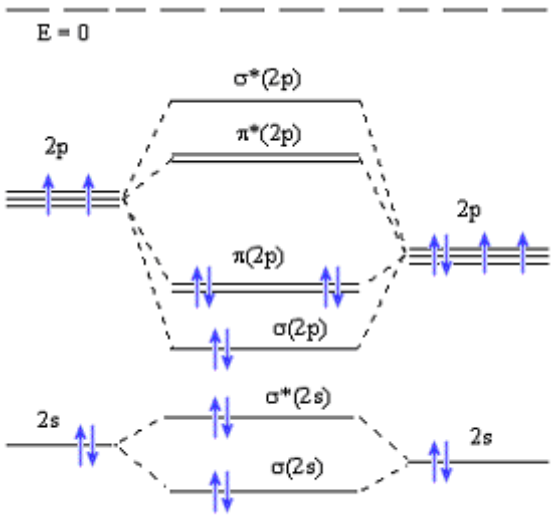
Atom = B Molecule = B_2 Atom = B

Bond Order = (4 bonding electrons – 2 antibonding electrons)/2 = 1



Atom = O^- Molecule = O_2^{2-} Atom = O^-

Bond order = (8 – 6)/2 = 1



Atom = C Molecule = CN^- Atom = N^-

Bond order = (8 – 2)/2 = 3

Comments:

The question did not ask for the atomic configurations, but it is probably a good idea to include them in order to avoid miscounting the electrons.

Molecular levels are filled, just as are atomic levels, using the aufbau principle and Hund's rule.

12) (3 marks) The H-N-H angle in ammonia is about 107°, and as one goes down the pnictogen group (Group 15), the equivalent angle decreases so that the H-Sb-H angle is about 90° in stibine, SbH_3. What effect causes this decrease in bond angle.

The energy difference between the ns and np orbitals increases such that sp^3 hybridization becomes less favorable over using pure p orbitals to form the pnictogen – hydrogen bonds. The angle therefore drops from close to the tetrahedral ideal to the 90° angle between the p orbitals.

(What was the stereochemically active (sticking out) lone pair becomes spherically symmetrical about the nucleus, part of the core and chemically inactive.)

Reasonable attempts to explain this effect invoking lone pair – bond pair repulsion variations also received marks. However, just mentioning bond polarity, without explanation of how it influences the angle was not enough.

Periodic Table of the Elements

1																	18
1 **H** 1.008	2											13	14	15	16	17	2 **He** 4.00
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31	3	4	5	6	7	8	9	10	11	12	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.87	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (97.91)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	**La-Lu**	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** 208.98	85 **At** 209.99	86 **Rn** 222.02
87 **Fr** 223	88 **Ra** 226.03	**Ac-Lr**	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (262)	108 **Hs** (265)	109 **Mt** (266)									

57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.35	63 **Eu** 151.97	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
89 **Ac** 227.03	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** (237)	94 **Pu** (245)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)