Name ______________________________

Student Number ______________________

Chem 241 Section 01 - Mid-term Exam - 1¼ hours

October 22nd, 2013

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) Iodine-127 decays radioactively to give xenon-127, which then decays to give cesium-127. Which of the following statement is correct:

   a) Iodine-127 decays by γ decay, and then xenon-127 decays by β decay.

   b) Iodine-127 decays by α decay, and then Xenon-127 decays by β decay.

   c) Both iodine-127 and xenon-127 decay by β decay.

   Answer c): The mass number does not change, and the atomic number goes up by 1 at each step, so neutrons must be converted to protons by β^- emission (β decay).

2) (1 mark) Consider the following orbitals: 3s, 4s, 5s, $3p_x$, $4p_x$, $5p_x$, $3d_{xy}$, $4d_{xy}$ and $5d_{xy}$. Which orbital(s) feature 2 radial (spherical) nodes **and** 1 planar node?

   a) 2s, $3p_x$ and $4d_{xy}$

   b) 5s, $4p_x$ and $3d_{xy}$

   c) $4p_x$ only

   d) None of the above

   Answer c): There is 1 planar node so it has to be a p orbital ($\ell = 1$). (The number of spherical nodes = $n - \ell - 1$, so $2 = n - 1 - 1$, therefore $n = 4$, matching a 4p orbital which could be the $4p_x$.)

3) (1 mark) A copper atom (in the gas phase) has the configuration $[Ar]4s^1 3d^{10}$. In cuprous *compounds* (Cu^+), the configuration of the ion is:

   a) $[Ar]4s^2 3d^8$

   b) $[Ar]4s^2 3d^{10}$

   c) $[Ar]4s^1 3d^9$

   d) $[Ar]4s^0 3d^{10}$

   Answer d): 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) An Antimony atom has configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^3$. 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) $4d^{10} 5s^2 5p^3$

b) $5s^2 5p^3 5d^0$

c) $5s^2 5p^3 5d^{10}$

d) $4d^{10} 5s^2 5p^3 5d^0$

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 potassium, which is the correct order for increasing radius:

a) K(metallic) < K^+ (6-coordinate) < K^+(8-coordinate)

b) K^+(6-coordinate) < K^+(8-coordinate) < K(metallic)

c) K(metallic) < K^+(8-coordinate) < K^+(6-coordinate)

d) K^+(8-coordinate) < K(metallic) < K^+(6-coordinate)

Answer b): Cations are always smaller than the atoms from which they are derived. (The effective cation sizes increase with the coordination number – the number of nearest neighbor anions. This information is not needed to answer this particular question)

6) (1 mark) Consider the ionization of the remaining electron of He^+. Compared with ionization from the ground state (n = 1), which of the following is true?

a) It is 9 times more difficult to remove the last electron if, instead, it starts out in the n = 3 level.

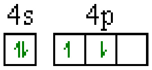
b) It is 3 times more difficult to remove the last electron if, instead, it starts out in the n = 3 level.

c) It is 9 times easier to remove the last electron if, instead, it starts out in the n = 3 level.

d) It is 3 times easier to remove the last electron if, instead, it starts out in the n = 3 level.

Answer c): The energy associated with an electronic transition from one orbit or orbital to another, if there is just one electron (hydrogen or a hydrogenic cation, e.g. He^+) is given by $(1/n_1^2 - 1/n_2^2)$ where n_1 and n_2 are the initial and final values of the principal quantum number, n. For ionization, $n_2 = \infty$, so the energy is proportional to $(1/n_1^2 - 1/\infty^2)$. That will be 9 times less is $n_1 = 3$ than if $n_3 = 1$.

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

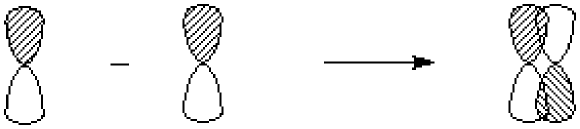
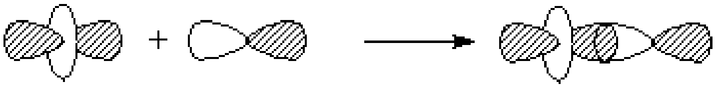
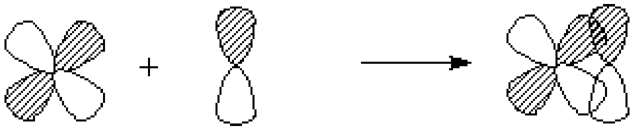
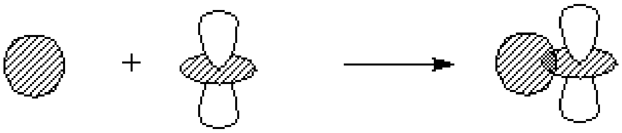
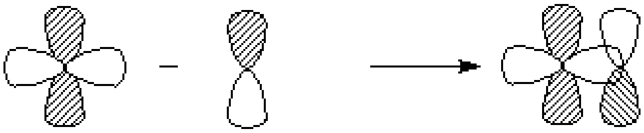
b) The configuration represents an excited state as defined by Hund’s rule

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

d) The configuration is forbidden by the Pauli principle

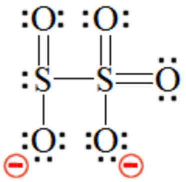
Answers b) and c): According to Hund’s rule, the electrons in degenerate (same energy) half-filled orbitals should have their spins parallel, in order to have the lowest energy. Otherwise, the atom is in an excited but not impossible (forbidden) state. The excited state configuration shown could be a Ge atom.

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 neither, 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?
	Antibonding	π
	Antibonding	σ
	bonding	π
	bonding	σ
	Non-bonding	N/A

9) The chemistry of the oxy-acids and their salts of sulphur is quite complicated: be thankful we do not ask you to memorize them all! One ion is the disulphite ion, which can be isolated as $Na_2S_2O_5$. The anion contains a sulphur – sulphur single bond.

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

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

b) (1 mark) In your Lewis structure and any equivalent canonical (resonance) structures, what are the sulphur – oxygen bond orders, and (average) charges on the individual atoms.

Left-hand Sulphur: Average sulphur – oxygen bond order: 1½ Average charge on oxygens: -½	Right-hand Sulphur: Average sulphur – oxygen bond order: 1⅔ Average charge on oxygens: -⅓

Comments: Read the question!

There is a S – S bond: NO bridging oxygen, S – O – S

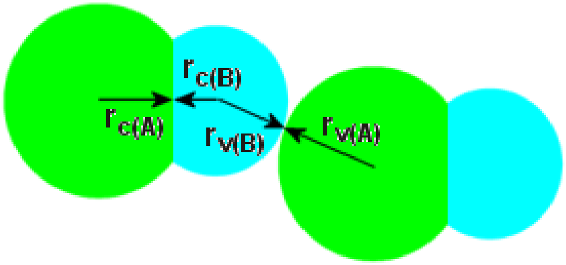
The question is about the anion. Na does not form covalent bonds: it is present as Na^+.

The formal charges must be shown, and must add up to the total charge on the ion.

10) (2 marks) Explain the difference between the covalent radius, and the van der Waals radius of an atom.

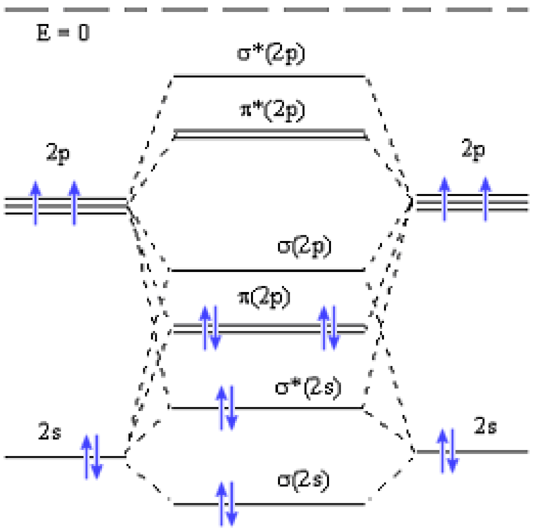
The covalent radius (r_c on the diagram) can be estimated as half the distance between the nuclei of two *identical* atoms *bonded together covalently*. By adding their covalent radii it is possible to predict bond distances between *dissimilar* elements.

The van der Waals radius (r_v on the diagram) of an atom determines how close another atom can come *if there is not a covalent bond between them*. The closest possible approach of the nuclei would be the sum of their individual van der Waals radii.



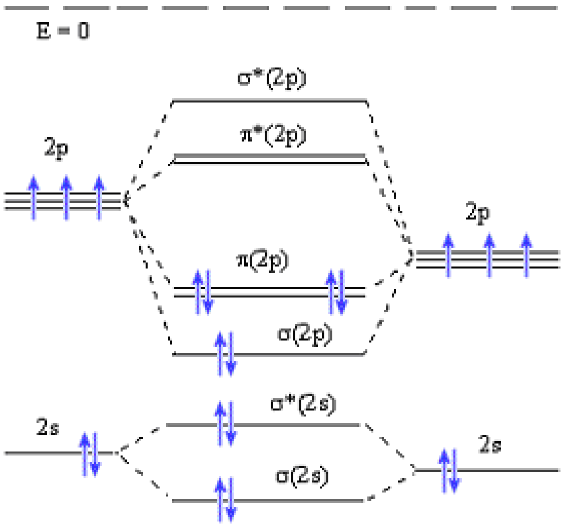
Comment: Please do not confuse the words “radius” and “distance”.

(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 C_2, O_2, and NO^+. 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.)



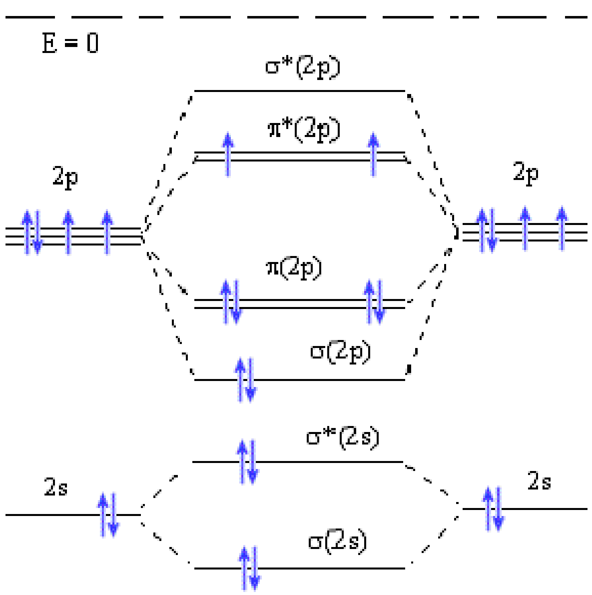
Atom = C Molecule = C_2 Atom = C

Bond Order = (6 bonding electrons – 2 antibonding electrons)/2 = 2



Atom = N Molecule = NO^+ Atom = O^+

Bond order = (8 – 2)/2 = 3



Atom = O   Molecule = O_2 Atom = O

Bond order = (8 – 4)/2 = 2

Comments:

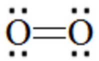
The question did not ask for the atomic configurations, but it is probably a good idea to include them in order to avoid miscounting the electrons. Only the valence electrons should appear because the 1s orbitals and derived molecular orbitals are not shown.

Molecular levels are filled, just as are atomic levels, using the aufbau principle and Hund’s rule. No violations of the Pauli principle.

11) (3 marks) Molecular orbital theory is more successful at describing the molecule O_2 than Valence Bond (Lewis) theory. Briefly explain this statement.

Dioxygen is found experimentally to be paramagnetic, that is, it is attracted into a magnetic field, which means it has some unpaired electrons:

The Lewis structure (below) for dioxygen has no unpaired electrons, so it cannot be correct.


$\underset{..}{\ddot{O}}=\underset{..}{\ddot{O}}$

The molecular orbital diagram for oxygen (in Q11, above) shows 2 unpaired electrons.

(Both theories correctly predict the observed bond order, that is, an O=O double bond.)

Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 1.008																	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											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)