

Inorganic Exam 1
Chm 451
22 September 2009

Name:

Instructions. Always show your work where required for full credit.

- (3 pts) Element 110 has finally been named darmstadtium. What do you predict for its periodic properties as compared to those of platinum?
 - Atomic size: Darmstadtium would be _____ than platinum.
 - First ionization energy: Darmstadtium would have a _____ first ionization energy than platinum.
 - Electron affinity: Darmstadtium would have an electron affinity that is _____ than that of platinum.
- (3 pts) One element in each group listed here has an electron affinity much lower than that of the other three. Circle this element in each group.
 - titanium, nickel, arsenic, krypton
 - sodium, calcium, yttrium, hafnium
 - nickel, copper, zinc, gallium
- (3 pts) In Period 2, circle each element that has a lower first ionization energy than the element before it:

Li Be B C N O F Ne
- (2 pts) A 3rd row element (Period 3) has the following successive ionization energies: 578, 1817, 2745, 11,575, 14,830, and 18,376 kJ/mol. What element is this?

Na Mg Al Si P S Cl Ar
- (1 pt) Which alkali metal was most reactive with water: Li, Na, or K?
- (2 pts) Lead often occurs as sulfides in nature, the most common mineral being galena, PbS. Lead, and other elements that also form sulfide and selenide minerals, are called (a) lithophiles, (b) siderophiles, or (c) chalcophiles. Circle a, b, or c.
- (3 pts) Which species in each sequence is the smallest?
 - Si, P, S, Cl
 - P, As, Sb, Bi
 - V⁺², V⁺³, V⁺⁵

8. (6 pts) Use Slater's rules to estimate the shielding felt by

a. a valence electron on phosphorus

b. a valence electron on calcium

a. a 3d electron on copper

9. (3 pts) Estimate the effective nuclear charge felt by a valence electron on fluorine.

10. (6 pts) Write the electron configuration using core notation for

a. arsenic

b. titanium

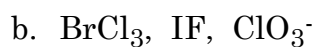
c. Mn^{+2}

11. (6 pts) Sketch the best Lewis dot structure and give the ABE formula for each of these species:

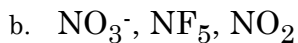
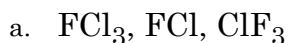


12. (4 pts) Sketch two Lewis dot structures for sulfite: (a) Sketch the best one in which all atoms obey the octet rule and (b) Modify the sketch so that formal charges are optimized.

13. (3 pts) One species (compound or polyatomic ion) in each group *must* expand the octet on the central atom in order to satisfy the octet rule. Circle this compound in each of these groups.



14. (3 pts) One member of each group does not exist. Circle it.



15. (8 pts) Predict the state of matter (solid, liquid or gas) for each of these species. The MM is given in each case:

SO_3 (MM = 80 g/mol)
LiNO_3 (MM = 69 g/mol)
t-butanol, $(\text{CH}_3)_3\text{COH}$ (MM = 74 g/mol)
NI_3 (MM = 395 g/mol)
BN (network covalent) (MM = 24.8 g/mol)
Os (AM = 190 g/mol)
TeH_2 (MM = 130 g/mol)
CS_2 (MM = 76 g/mol)

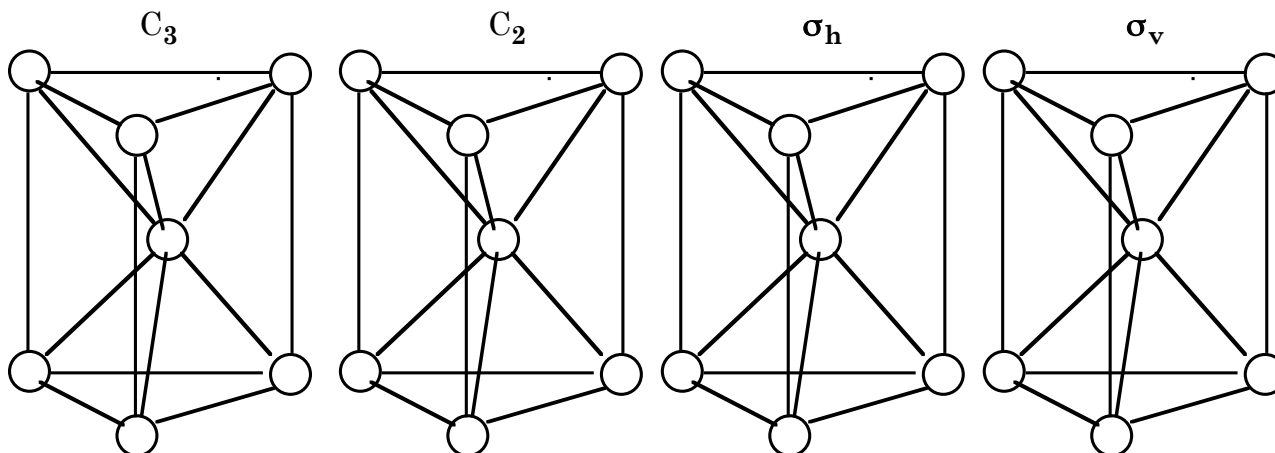
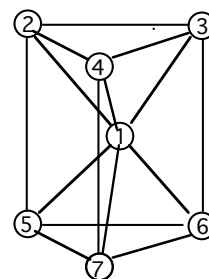
16. (18 pts) Consider the following common objects: a five petal flower (assume it is highly symmetric with the petals slightly directed towards viewer), an octagon, a 3-legged piano stool and a round-sided pencil.

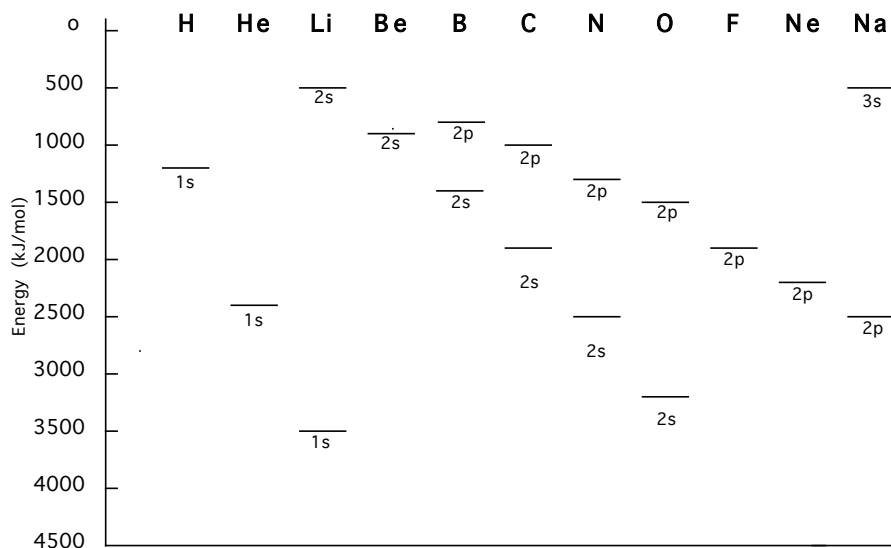


Complete the table regarding the symmetry properties of these objects. Given that the point groups are all of the type C_{nv} or D_{nh} , provide the point group for each object.

Object	Principle rotation axis	Other rotation axes (list)	σ_h mirror plane	How many σ_v mirror planes?	How many σ_d mirror planes	Point group
Flower			Yes or No			
Hexagon			Yes or No			
Stool			Yes or No			
Pencil			Yes or No			

17. (8 pts) An unusual alternative to the octahedron is the trigonal bipyramid, shown at right. Molecules of this structure belong to the D_{3h} point group. Perform the following symmetry operations on the molecule by indicating by number the result of each operation. Perform each of these operations on the numbered version shown at right, not on your previous answer!





18. (9 pts) The first preparation of the diazide ion, N_2^{-2} , was reported in 2001. Sketch its molecular orbital energy diagram showing all of the atomic orbitals and the resulting molecular orbitals. You can ignore sp-mixing. Populate the MO diagram with the appropriate number of electrons. *Label all of the molecular orbitals with labels such as σ_{2s} , etc.*

18 (continued) How many unpaired electrons, if any, does the diazide ion possess?

19. (9 pts) Sketch the molecular orbital energy diagram for carbon monoxide. Show all of the atomic orbitals and the resulting molecular orbitals. Again, you can ignore sp-mixing. Populate the MO diagram with the appropriate number of electrons.

On your MO energy diagram for CO, sketch a picture of the various molecular orbitals (using the little balloon shapes, some shaded, some open) for each bonding and antibonding MO.

2-point bonus: In the book, you encountered numerous MO energy diagrams. Along the right-hand sides of several of these diagrams were funny looking spectra plotted vertically and used to indicate the approximate energies of the molecular orbitals created. What is the name of the spectroscopy that gives us this information?

Answers:

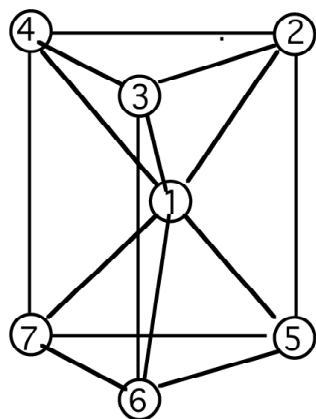
1. Atomic size: Darmstadtium would be larger than platinum. Its first ionization energy would be lower than platinum. Darmstadtium would have an electron affinity that is less than that of platinum.
2. (a) krypton; (b) calcium; (c) zinc
3. Lithium, boron and oxygen. I did not count off if Li was not circled because the question could be interpreted to mean "among those listed." Lithium does, however, have a lower first ionization energy than helium, not shown.
4. aluminum; 5. K (recall demo in class); 6. (c) chalcophile
7. (a) Cl; (b) P; (c) V⁺⁵
8. (a) P (1s)² (2s2p)⁸ (3s3p)⁵; S = 2 x 1 + 8 x 0.85 + 4 * 0.35 = 10.2
 (b) Ca (1s)² (2s2p)⁸ (3s3p)⁸ (3d)⁰ (4s4p)²; S = 10 x 1 + 8 x 0.85 + 1 * 0.35 = 17.15
 (c) Cu (1s)² (2s2p)⁸ (3s3p)⁸ (3d)¹⁰ (4s4p)¹ (recall that copper's ground state is an exception); S = 18 x 1 + 9 x 0.35 = 21.15
9. F (1s)² (2s2p)⁷; S = 2 x 0.85 + 6 * 0.35 = 3.8; Z* = 9 - 3.8 = 5.2
10. (a) Arsenic [Ar] 4s² 3d¹⁰ 4p³; (b) Titanium [Ar] 4s² 3d²; (c) Mn⁺² [Ar] 4s⁰ 3d⁵
11. (a) NO₃⁻ AB₃ and note that nitrogen must have 8 electrons! It cannot have 10 or 6. Your structure should have one double bond between N and O and the other two are single bonded; (b) PF₃O AB₄; (c) SF₄O AB₅ In both (b) and (c) you have a choice as to whether or not to double bond the oxygen or to "snap" in onto the lone pair. The latter is generally preferred due to Period 3's reluctance to form double bonds, even though the double-bonded version satisfies formal charge arguments better. I accepted either form because both predict the correct ABE formula.
12. (a) Sulfite in which all atoms obey the octet rule calls for three single-bonded oxygen atoms to sulfur which has the AB₃E geometry. Each oxygen has a formal charge of -1 and the sulfur has a formal charge of +1. (b) To modify the sketch so that formal charges are optimized, simply make one of the oxygen atoms double bonded to the sulfur, thus reducing the formal charge on sulfur from +1 to 0. Any further double-bonding of oxygen-to-sulfur would be inappropriate as the FC on sulfur would become negative.
13. (a) AsF₅; (b) BrCl₃; (c) SF₄
14. (a) FCl₃; (b) NF₅; (c) SeO₄

15. (a) SO_3 gas; (b) LiNO_3 is ionic therefore a solid; (c) t-butanol, $(\text{CH}_3)_3\text{COH}$ has hydrogen bonding and therefore a liquid despite its $\text{MM} < 100$; (d) NI_3 is a solid; (e) BN is a network covalent and therefore a solid; (f) the element osmium is a solid as are all metals except Hg ; (g) TeH_2 ($\text{MM} = 130 \text{ g/mol}$) is polar covalent and with a relatively low MM , so we predict probably a gas but maybe a liquid (actually, it is a gas at room temperature, $\text{bp} = -2.2 \text{ }^\circ\text{C}$); (h) carbon disulfide has a $\text{MM} < 100$ and is non-polar leading us to predict it is a gas. It is, however, a liquid with a $\text{bp} = 46 \text{ }^\circ\text{C}$. I accepted either gas or liquid for both (g) and (h)

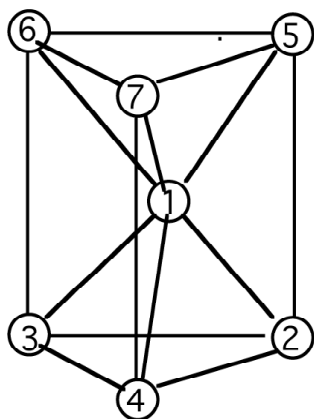
16.

Object	Principle rotation axis (0.5 pt per box)	Other rotation axes (list) (0.5 pt per box)	σ_h mirror plane (0.5 pt per box)	How many σ_v mirror planes? (0.5 pt per box)	How many σ_d mirror planes (0.5 pt per box)	Point group (2 pts per box)
Flower	C_5	None	No	5	0	C_{5v}
Octagon	C_8	4 C_2 and 4 C_2'	Yes	4	4	D_{8h}
Stool	C_3	None	No	3	0	C_{3v}
Pencil	C_{inf}	none	No	infinity	0	$C_{\text{inf-v}}$

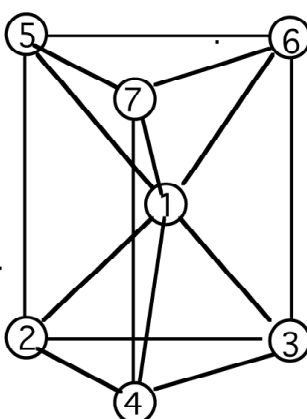
17. C_3



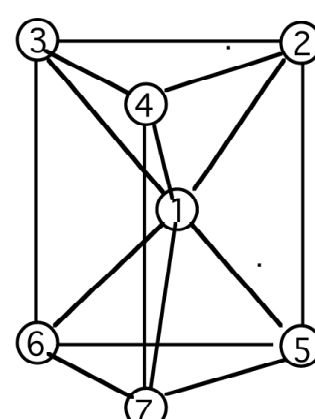
C_2



σ_h



σ_v



18. (9 pts) Looks much like that of dioxygen, O_2 . The diazide ion possess two unpaired electrons.

19. See book and homework assignment;

2-point bonus: photoelectron spectroscopy