EXAM ONE PART ONE

CHM 451 (INORGANIC CHEMISTRY)

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Instructions: This exam has two parts. In Part One, only a pencil and molecular models may be used. When you have completed Part 1, turn it in and obtain Part Two. In Part Two, your data sheet (on the periodic table), a molecular model set, and a non-programmable calculator may be used.

1. (4 pts) Give the electron configuration for these species. You may use "core notation."

Sc	
I	
Fe^{3+}	
Pt^{2+}	

2. (2 pts) (a) Which 2+ ion has six 3d electrons?   (b)Which 3+ ion has three 3d electrons?

(a)	(b)

4. (6 pts) Which has the higher ionization energy within each pair?

    Ca or Sr   Mg or Al   Rb or I

    Cr or Mo   Si or P   Zn or Ga

5. (6 pts) Which has the higher electron affinity within each pair?

    B or C   C or N   Zn or Ga

    S or Cl   I or Br   Mg or Al

6. (6 pts) True or False.

    T F Electron affinities are generally exothermic.

    T F Ionization energies are generally exothermic.

    T F Anions are larger than cations in isoelectronic monatomic ions.

    T F Cations are generally paramagnetic, while anions are generally diamagnetic.

    T F Effective nuclear charge is used to explain periodic trends across the periodic table, but not used to explain periodic trends vertically within the table.

    T F Subsequent ionization energies become increasingly endothermic.

7. (2 pts) The energies for removal of an electron from Cl^-, Cl, and Cl^+ are 343, 1250, and 2300 kJ/mol, but not necessarily in that order. Is this order correct? If not, write the ionization energies in order for Cl^-, Cl, and Cl^+.

    [ ] Yes   OR [ ] No, the order is :

8. (4 pts) Circle the largest ion within each pair

       S^{2-} or Cl^- K^+ or Ca^{2+} Sc^{3+} or Ti^+ Fe^{2+} or Fe^{3+}

9. (12 pts) Sketch the Lewis dot structure for each of the following. Give the ABE formula and shape.

| Lewis dot structure	ABE formula	Geometric shape name
BrF_4^-		
PF_5		
PH_2^-		
NO_2^-		
ClO_4^-		
XeO_3		

10. (5 pts) The ion CNO⁻ could have any of these structures, all of which obey the octet rule. Assign formal charges to every atom in these nine structures in order to determine which drawings are most plausible. Circle the one(s) that meet with your approval.

:N:::C:Ö: :N̈::C::O̤:   :N̈:C:::O:

:C:::N:Ö: :C̈::N::O̤:   :C̈:N:::O:

:N:::O:C̤:   :N̈::O::C̤:   :N̈:O:::C:

11. (4 pts) The MO diagram for HCl is shown below.

   (a) Draw all necessary connecting lines between atomic and molecular orbitals

   (b) Populate atomic and molecular orbitals with the appropriate number of electrons.

   (c) Calculate the bond order for HCl.
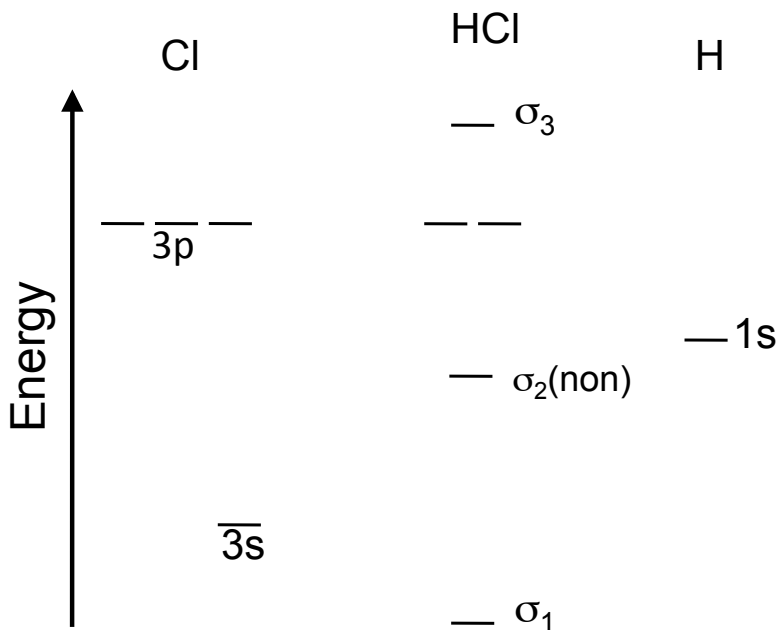
End of Part 1.

Turn this in and receive Part 2. In Part 2, you can use your data sheet, a molecular model set, and a non-programmable calculator.

EXAM ONE PART TWO

CHM 451 (INORGANIC CHEMISTRY)

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Instructions for Part 2: Show all work or provide complete explanations! You will receive credit for how you worked each problem as well as for the correct answer. Non-programmable calculators, your data sheet and a molecular model set are allowed during this portion of the exam. Illegible handwriting will not be graded. BOX YOUR ANSWERS!

12. (2 pts) Using Slater's rules, determine Z_{eff} for a 2p electron in:

N
Ne

13. (2 pts) Using Slater's rules, determine Z_{eff} for a 2p electron in:

O^{2-}
Mg^{2+}

14. (2 pts) Using Slater's rules, determine Z_{eff} for a:

4s electron of Cu
3d electron of Cu

15. (6 pts) Predict the physical state of the following substances at room temperature (s, l, or g), based on what you know about intermolecular forces, and types of compounds. Some explanation is required for credit.

SO_3 (MM = 80 g/mol)	$CH_2(NH_2)_2$ (MM = 45 g/mol)	SF_6 (MM = 146 g/mol)
K_2SO_4 (MM = 174 g/mol)	SiH_4 (MM = 32 g/mol)	P_4S_6 (MM = 316 g/mol)

16. (15 pts) Complete the table below.

|	Identify the primary rotation axis, (e.g. C_4)	Identify any other rotation axes, C_n, or enter "none"	Enter the number of vertical mirror planes, σ_v	Is there a horizontal mirror plane, σ_h	Is there an inversion center, i	Point group
NF_3 (AB_3E)				Yes No	Yes No	
SO_3 (AB_3)				Yes No	Yes No	
SO_2 (AB_2E)				Yes No	Yes No	
CS_2 (AB_2)				Yes No	Yes No	
PF_5^- (AB_5E)				Yes No	Yes No	

17. (10 pts) Sketch a molecular orbital diagram for the nitrosyl ion, NO^+. Label all of the atomic and molecular orbitals and populate it accordingly. You can ignore sp-mixing.

1. What is the bond order?

2. Is this species diamagnetic or paramagnetic?

   My checklist for awarding points:

      3. [ ] Are the atomic orbitals for N and O labeled?

      4. [ ] Do the atomic orbitals have appropriate relative energies?

      5. [ ] Are all molecular orbitals labeled (with σ and π designations)?

      6. [ ] Are the MOs linked to the appropriate atomic orbitals?

      7. [ ] Are there the correct number of electrons present?

      8. [ ] Are the MOs in correct order?

      9. [ ] Did you sketch the bonding MOs (with the lobe diagrams) correctly?

      10. [ ] Did you sketch the anti-bonding MOs (with the lobe diagrams) correctly?

NO

N

O

Energy

__ __ __
2p

__ __ __
2p

__
2s

__
2s
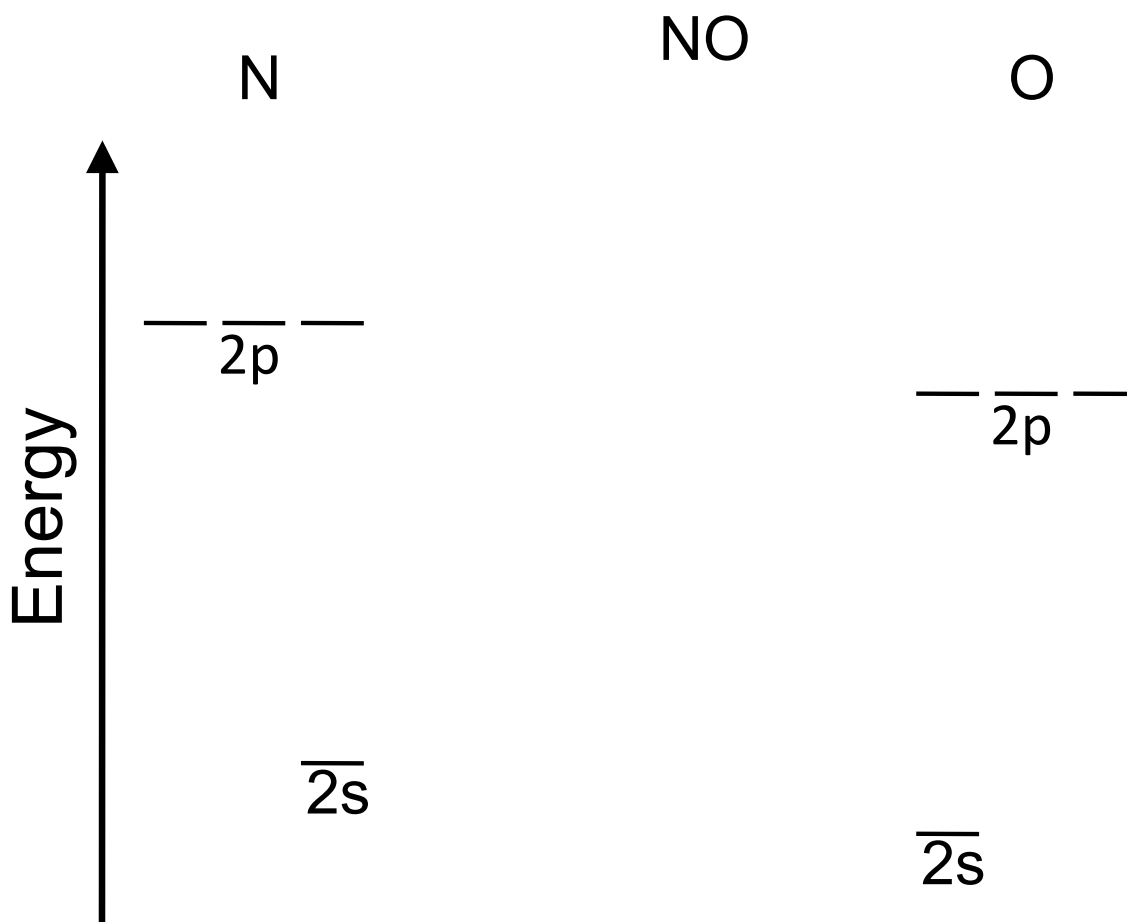
18. (10 pts) If you were to construct a MO diagram for PF_5, you would start by creating a SALC set or orbitals for the fluorine atoms. Then you would use the D_{3h} character table to generate a reducible representation, Γ. You would next determine the irreducible components. The trigonal bipyramid is unusual in that the axial and equatorial positions are separate entities and you can work this problem as if it were two separate problems.

D_{3h}	E	$2C_3$	$3 C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$(x^2 + y^2, z^2)$
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	R_x, R_y	(xz, yz)

(a) (3 pts) First, start with the two axial positions, determine Γ_{axial} and then resolve them into their irreducible components.

(b) (2 pts) What atomic orbitals on phosphorus would transform the same as the axial SALCs?

(c) (3 pts) Then repeat the process for the three equatorial positions, determining $\Gamma_{equitorial}$ and then resolving them into their irreducible components. You will find that one of the irreducible representations is used twice – once for the axial SALCs and once for the equatorial SALCs!

(d) (2 pts) What atomic orbitals on phosphorus would transform the same as the equatorial SALCs?

5 pt Bonus: Given that the atomic orbitals of fluorine are similar in energy to the 3s orbitals on P, and that the 3p and 3d orbitals on P are a bit higher in energy, construct a MO diagram for PF_5. No partial credit.

Answers:

1. Sc [Ar] $4s^2 3d^1$; I [Kr] $5s^2 4d^{10} 5p^5$; Fe^{3+} [Ar] $4s^0 3d^5$; Pt^{2+} [Xe] $6s^0 4f^{14} 5d^8$

2. (a) Fe^{+2}; (b) Cr^{+3}; 4. first row: Ca, Mg, I; second row: Cr, P, Zn ; 5. first row: C, C, Ga; second row: Cl, Br, Al

6. T F T F T T; 7. Yes, the order is correct; 8. S^{2-}, K^+, Ti^+, Fe^{2+}

9. Lewis dot structure	ABE formula	Geometric shape name
BrF_4^-	AB_4E_2	Square plane
PF_5	AB_5	Trigonal bipyramid
PH_2^-	AB_2E_2	Bent
NO_2^-	AB_2E	Bent
ClO_4^-	AB_4	tetrahedral
XeO_3	AB_3E	trigonal pyramid

10. the first two across the top row have the most favorable formal charges. The first one has FC = 0, 0, and -1 for N, C, and O, respectively. The second one (across the top) has FC = -1, 0, and 0 for N, C, and O, respectively. All of the other structures have at least one atom with a + or -2, which is not favorable compared to those with lower formal charges.

11. (c) The bond order for HCl = 2/2 = 1

12. (2 pts) Using Slater's rules, determine Z_{eff} for a 2p electron in:

N $(1s)^2 (2s2p)^5$ S = 0.85 x 2 + 0.35 x 4 = 3.1; Z_{eff} = 7 – 3.10 = 3.90

Ne $(1s)^2 (2s2p)^8$ S = 0.85 x 2 + 0.35 x 7 = 4.15; Z_{eff} = 10 – 4.15 = 5.85

O^{2-} $(1s)^2 (2s2p)^8$ S = 0.85 x 2 + 0.35 x 7 = 4.15; Z_{eff} = 8 – 4.15 = 3.85

Mg^{2+} $(1s)^2 (2s2p)^8$ S = 0.85 x 2 + 0.35 x 7 = 4.15; Z_{eff} = 12 – 4.15 = 7.85

Molecular HCl

4s electron of Cu $(1s)^2 (2s2p)^8 (3s3p)^8 (3d)^{10} (4s4p)^1$; S = 1.0 x 10 + 0.85 x 18 = 25.30 ; Z_{eff} = 29 – 25.3 = 3.70

3d electron of Cu $(1s)^2 (2s2p)^8 (3s3p)^8 (3d)^{10} (4s4p)^1$; S = 1.0 x 18 + 0.35 x 9 = 21.15 ; Z_{eff} = 29 – 21.15 = 7.85

15.

SO_3 (MM = 80 g/mol)	$CH_2(NH_2)_2$ (MM = 45 g/mol)	SF_6 (MM = 146 g/mol)
Non-polar, MM close to 100 g/mol; predict: gas or liquid mp 17 ºC bp = 45 ºC	Strong H-bonding (Predict: liquid) mp ? bp = 83 ºC	Non-polar; predict gas or liquid Non-polar, bp = -64 ºC
K_2SO_4 (MM = 174 g/mol) Ionic; predict solid	SiH_4 (MM = 32 g/mol) Non-polar covalent-molecular Predict gas; bp = -112 ºC	P_4S_6 (MM = 316 g/mol) High MM, predict solid, mp = 173 ºC

6.						
NF_3 (AB_3E)	C_3	none	$3\ \sigma_v$	No	No	C_{3v}
SO_3 (AB_3)	C_3	C_2	$3\ \sigma_v$	Yes	No	D_{3h}
SO_2 (AB_2E)	C_2	none	$2\ \sigma_v$ or $\sigma_v + \sigma_d$	No	No	C_{2v}
CS_2 (AB_2)	C_∞	C_2	$\infty\ \sigma_v$	Yes	Yes	$D_{\infty h}$
PF_5^- (AB_5E)	C_4	C_2	$2\ \sigma_v + 2\ \sigma_d$	No	No	C_{4v}

17. 1. Bond order = 3; 2. Diamagnetic;   2. Is this species diamagnetic or paramagnetic?

NO^+
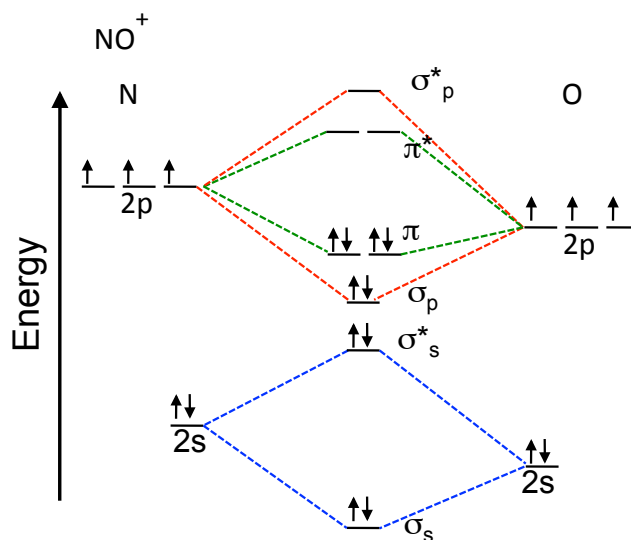
18. (a) and (b)

D_{3h}	E	$2C_3$	$3 C_2$	σ_h	$2S_3$	$3\sigma_v$		
Γ	2	2	0	0	2	2		

$\Gamma = A_1' + A_2''$. In terms of orbitals on the phosphorus, the 3s and $3d_{z^2}$ transform as A_1', and the $3p_z$ transforms as A_2''.

(c) and (d)

D_{3h}	E	$2C_3$	$3 C_2$	σ_h	$2S_3$	$3\sigma_v$		
Γ	3	0	1	3	0	1		

$\Gamma = E' + A_1'$. In terms of orbitals on the phosphorus, the 3s and $3d_{z^2}$ transform as A_1' (as above), and the doubly degenerate $(3p_x, 3p_x)$ transforms as E', as does the doubly degenerate $(3d_{xy}, 3d_{x^2-y^2})$.