EXAM TWO PART ONE **CHM 451 (INORGANIC CHEMISTRY)**

DR. MATTSON 5 NOVEMBER 2014 NAME:

Instructions: This exam has two parts. In Part One, only a pencil and molecular models may be used. When you have completed Part One, 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.

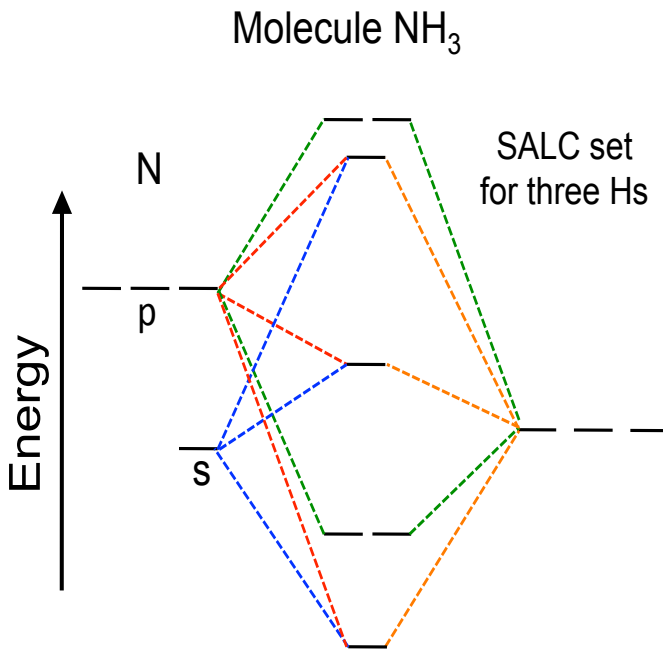
1. (1 pt) Ammonia has a trigonal pyramidal shape. What is its point group?

2. (1 pt) Sketch in one diagram using sticks-and-balls, the atomic orbitals that will form the SALCs (and only the SALCs).

3. (1 pt) How many SALCs are you expecting?

4. (3 pts) Using your character table provided, determine the reducible representation, Γ, for ammonia and the irreducible components.

5. (3 pts) On this partially completed MO diagram, add the appropriate symmetry labels (as obtained from the character table) to each molecular orbital in this diagram.



6. (1 pt) Fill the MO diagram with the appropriate number of electrons.

7. (2 pts) What atomic orbital(s) on nitrogen interact(s) with the SALC forming the lowest energy MO?

8a. (2 pts) Sulfur dioxide can function as a Lewis acid or Lewis base. Sketch a Lewis dot structure showing how it interacts with Ru^{+3} through the sulfur atom.

8b. (2 pts) Continuing with sulfur dioxide, sketch a Lewis dot structure showing how it interacts with OH^-, again through the sulfur atom.

9. (4 pts) Identify these as a Lewis acid, Lewis base or neither.

BF_3	Lewis acid	Lewis base	Neither
Cr^{+3}	Lewis acid	Lewis base	Neither
SiH_4	Lewis acid	Lewis base	Neither
H_2O	Lewis acid	Lewis base	Neither

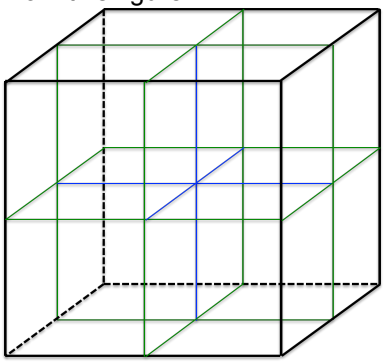
10. (3 pts) Identify these salts as acidic, basic or neutral when dissolved in water.

KF	acidic	basic	neutral
NH_4ClO_4	acidic	basic	neutral
$NaHSO_4$	acidic	basic	neutral

11. (1 pt) Which of these is not an acid anhydride?

SO_3 N_2O_5 NO_2 CO_2 CaO

This figure is provided as a reference in answering several of the following questions. Nothing is required from this figure.



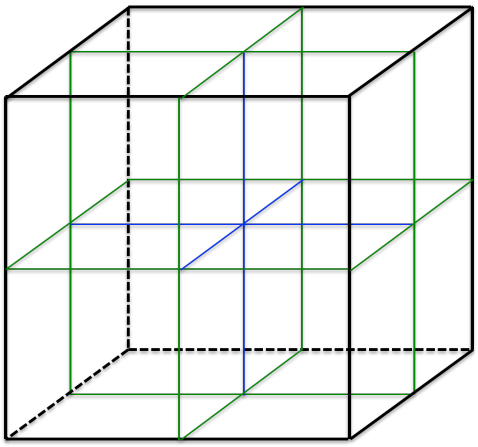
12. What is the relationship between the radius of the space-filling spheres, r, and the length of the edge, e, for:

12a. (1 pt) the simple cube

12b. (1 pt) the body-centered cube

12c. (1 pt) the face-centered cube

13a. (2 pts) Using the template below, indicate the location of all of the octahedral holes for a fcc lattice using open circles, ○. Be careful! Your answer must be unambiguous!



13b. (1 pt) Using a filled circle, ●, indicate on the template above, the location of just one of the tetrahedral holes for a fcc lattice.

13c. (1 pt) How many tetrahedral holes are enclosed within a fcc unit cell?

14. (2 pts) Calcium silicate, Ca_2SiO_4, crystallizes with oxygen ions in a fcc sublattice. The calcium ions occupy octahedral holes and the silicon atoms are in tetrahedral holes. What fraction of each type of hole is occupied?

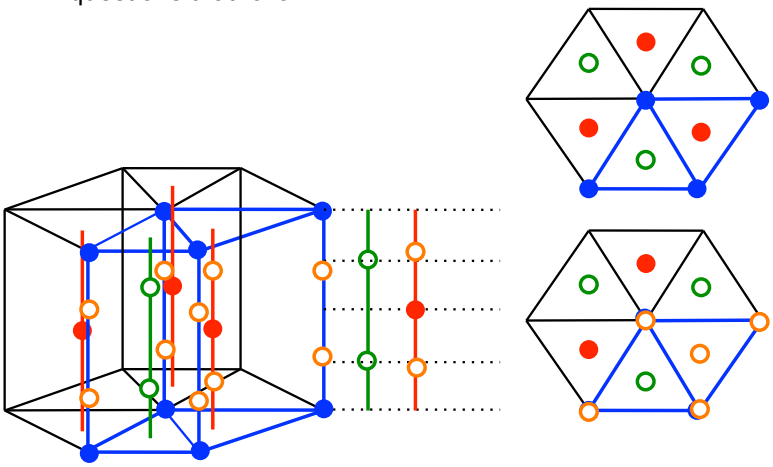
Octahedral holes:

$^1/_8$ $^1/_4$ $^3/_8$ $^1/_3$ $^1/_2$ $^5/_8$ $^2/_3$ $^3/_4$ $^7/_8$

Tetrahedral holes:

$^1/_8$ $^1/_4$ $^3/_8$ $^1/_3$ $^1/_2$ $^5/_8$ $^2/_3$ $^3/_4$ $^7/_8$

15. Consider the drawing below to answer the questions that follow.



15a. (1 pt) The locations of the space-filling atoms/ions are shown in (may be more than one):

Blue Orange Red Green

15b. (1 pt) The locations of the octahedral holes are shown in (may be more than one):

Blue Orange Red Green

15c. (1 pt) The locations of the tetrahedral holes are shown in (may be more than one):

Blue Orange Red Green

16. (1 pt) Perovskite contains titanium and calcium cations and oxide anions. The Ca^{+2} ions occupy the corner positions, the titanium ion occupies the body-center position and the oxides occupy all of the face-centered positions of a cubic unit cell. What is the formula of perovskite?

17. (1 pt) Which of these statements in not true?

A. Lattice energies increase with the magnitude of the charge on the ions.

B. Lattice energies are always exothermic.

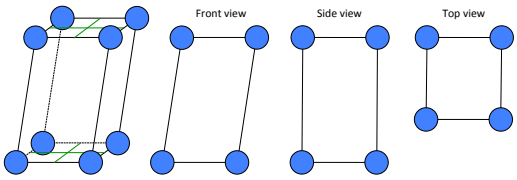
C. Lattice energy always exceeds ΔH_f.

D. Lattice energy refers to: n $E^{m+}(g)$ + m $X^{n-}(g)$ → $E_nX_m(s)$.

18. For the next four questions, identify the Bravais unit cell type.

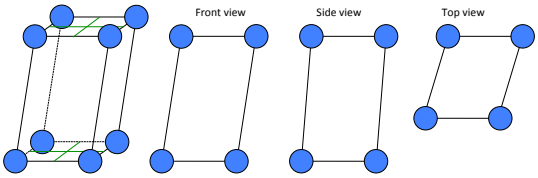
18a. (1 pt) Circle your choice for the drawing that follows:

Cubic Hexagonal Monoclinic Orthorhombic Rhombohedral (trigonal) Tetragonal Triclinic



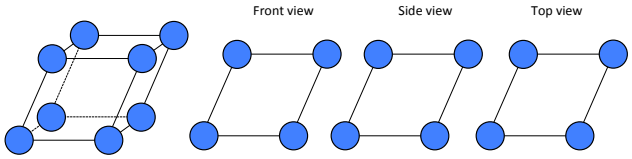
18b. (1 pt) Circle your choice for the drawing that follows:

Cubic Hexagonal Monoclinic Orthorhombic Rhombohedral (trigonal) Tetragonal Triclinic



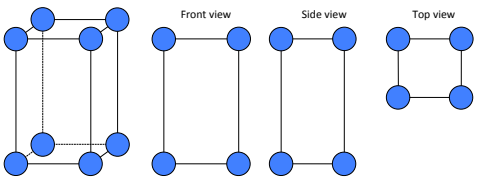
18c. (1 pt) Circle your choice for the drawing that follows:

Cubic Hexagonal Monoclinic Orthorhombic Rhombohedral (trigonal) Tetragonal Triclinic

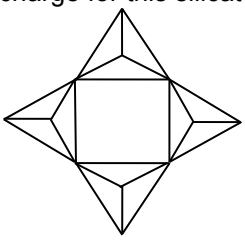


18d. (1 pt) Circle your choice for the drawing that follows:

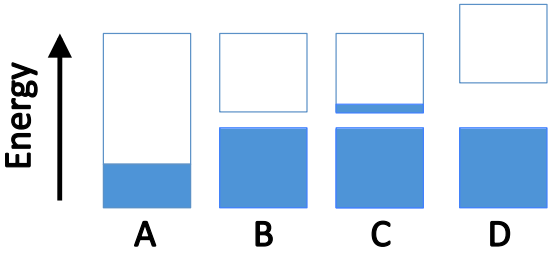
Cubic Hexagonal Monoclinic Orthorhombic Rhombohedral (trigonal) Tetragonal Triclinic



19. (1 pt) What is the formula and charge for this silicate?



20. Consider figures A – D below to answer the questions that follow.



20a. (1 pt) Which figure represents a n-type semiconductor?

Fig A Fig B Fig C Fig D None of these

20b. (1 pt) Which figure represents an insulator?

Fig A Fig B Fig C Fig D None of these

20c. (1 pt) Which figure represents an early transition metal such as vanadium?

Fig A Fig B Fig C Fig D None of these

20d. (1 pt) Which figure represents an p-type semiconductor?

Fig A Fig B Fig C Fig D None of these

20e. (1 pt) Which figure represents a semi-metal such as silicon?

Fig A Fig B Fig C Fig D None of these

21. (4 pts) Determine the oxidation state on the transition metal in the following compounds.

$[Cr(H_2O)_6](NO_3)_3$	$NH_4[RuCl_4]$
$K_3[Fe(CN)_6]$	$[Co(P(CH_3)_3)_4]SO_4$

22. (4 pts) Determine the geometry around the central metal in the following compounds.

$[Cr(H_2O)_6](NO_3)_3$	$(NH_4)_2[CoCl_4]$
$K_3[Fe(CN)_6]$	$[Pt(P(C_6H_5)_3)_4]SO_4$

23. (4 pts) How many diastereomers are possible for the octahedral formula $MA_2B_2C_2$? Sketch all. One of these is enantiomeric. Circle it.

24. (8 pts) Show the crystal field energy diagram in the spaces provided. Correctly populate each diagram with electrons.

$[Cr(NH_3)_6](NO_3)_3$	$PtCl_2(NH_3)_2$
$K_4[Fe(CN)_6]$	$[Co(H_2O)_6]SO_4$

End of Part One.

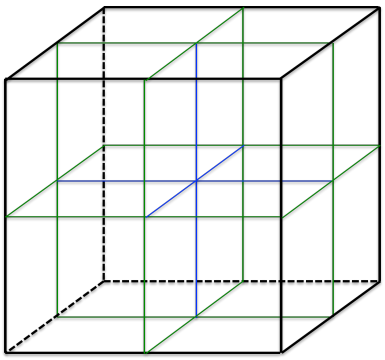
Turn this in and receive Part Two. In Part Two, you can use your data sheet, a molecular model set, and a non-programmable calculator.

EXAM TWO PART TWO

CHM 451 (INORGANIC CHEMISTRY)

DR. MATTSON 6 NOVEMBER 2014 NAME:

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!



25. (3 pts) Sodium exhibits a body-centered unit cell and a density of 0.971 g/cm^3. What is the atomic radius of sodium? You must show work for credit.

26. (3 pts) What is the percent occupancy for a simple cubic unit cell? Show work for credit.

27. (3 pts) What is the radius of an octahedral hole in a fcc lattice, expressed in terms of r, the radius of the space-filling atom/ion? Show work for credit.

28. (3 pts) Hydrogen shares some physical characteristics with the alkali metals and others with the halogens. Mark a check in one box or the other to indicate which group H is most like.

Property of hydrogen:	**Like Group 1**	**Like Group 7**
Ionization energy		
Electron affinity		
Stable molecular form		

29. (1 pt) Which of the following is NOT a reaction of the alkali metals (possibly unbalanced):

A. $Na(s) + H_2O(l) \rightarrow NaH(aq) + NaOH(aq)$

B. $Na(s) + H_2(g) \rightarrow NaH(s)$

C. $K(s) + O_2(g) \rightarrow KO_2(s)$

D. $Rb(s) + Cl_2(g) \rightarrow RbCl(s)$

E. $Li(s) + O_2(g) \rightarrow Li_2O(s)$

30. (1 pt) Which of the following is NOT a reaction of the alkaline earth metals (possibly unbalanced):

A. $Ca(s) + H_2(g) \rightarrow CaH_2(s)$

B. $Ca(s) + C(s) \rightarrow Ca_2C(s)$

C. $Mg(s) + O_2(g) \rightarrow MgO(s)$

D. $Mg(s) + N_2 \rightarrow Mg_3N_2(s)$

E. $Ca(s) + S_8(s) \rightarrow CaS(s)$

31. (1 pt) Aluminum reacts with acid as follows:

$2\ Al(s) + 6\ H_3O^+(aq) \rightarrow 3\ H_2(g) + Al^{+3}(aq) + H_2O(l)$

The $Al^{+3}(aq)$ is actually $[Al(H_2O)_6]^{+3}(aq)$ which is a weak acid with a $K_a = 1.4 \times 10^{-5}$. Which of the following equilibria describes the acidic nature of $[Al(H_2O)_6]^{+3}(aq)$? (possibly unbalanced)

A. $[Al(H_2O)_6]^{+3}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + [Al(H_2O)_5(OH)]^{+2}(aq)$

B. $[Al(H_2O)_6]^{+3}(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + [HAl(H_2O)_6]^{+4}(aq)$

C. $[Al(H_2O)_6]^{+3}(aq) + H_3O^+(aq) \rightleftharpoons H_2O(aq) + [HAl(H_2O)_6]^{+4}(aq)$

D. $[Al(H_2O)_6]^{+3}(aq) + H_3O^+(aq) \rightleftharpoons [HAl(H_2O)_7]^{+4}(aq)$

E. $[Al(H_2O)_6]^{+3}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_7]^{+3}(aq)$

32. (1 pt) Aluminum also reacts with bases such as NaOH(aq). Which of these is the net ionic equation? (possibly unbalanced)

A. $Al(s) + OH^-(aq) \rightarrow Al_2O_3(s) + H_2(g)$

B. $Al(s) + H_2O \rightarrow Al^{3+}(aq) + OH^-(aq)$

C. $Al(s) + OH^-(aq) + H_2O(l) \rightarrow [Al(OH)_4]^-(aq) + H_2(g)$

D. $Al(s) + OH^-(aq) \rightarrow Al(OH)_3(aq)$

E. $Al(s) + OH^-(aq) + H_2O \rightarrow [Al(H_2O)_6]^{3+}(aq) + H^+(aq)$

33. The Ostwald is summarized as follows:

$4\ NH_3(g) + 5\ O_2(g) \xrightarrow{Pt\ cat, 820^o} 4\ NO(g) + 6\ H_2O(g)\quad \Delta H = -905\ kJ$

$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)\quad \Delta H = -114\ kJ$

$3\ NO_2(g) + H_2O(l) \rightarrow 2\ HNO_3(aq) + NO(g)\quad \Delta H = -117\ kJ$

33. (1 pt) Is the second step entropy-favored? Are there temperature conditions for this reaction to take place?

	Entropy-favored?	Spontaneous?
A.	No	Low temps only
B.	No	High temps only
C.	No	All temperatures
D.	Yes	All temperatures
E.	Yes	High temps only

34. (3 pts) The third step is an example of disproportionation. Assign oxidation numbers to the nitrogen atom in each of these compounds.

NO_2	HNO_3	NO

35. (3 pts) Sketch the structure of white phosphorus, P_4, and indicate the hybridization and predicted P-P-P bond angles.

36. (3 pts) As a solid, PCl_5 actually has an ionic structure consisting of $PCl_4^?$ and $PCl_6^?$ ions. Rewrite these ions with appropriate charges and sketch their structures, giving the ABE formula and geometric shape for each.

37. (3 pts) As a solid, sulfur has the molecular formula S_8. Sketch or describe this structure, giving the ABE formula and geometric shape for each sulfur atom that is unique from the others.

38. (1 pt) What of the following is not true for fluorine chemistry?

A. Fluoride compounds are generally less soluble.

B. Fluorine makes stronger covalent bonds.

C. Fluorine compounds are generally more volatile.

D. The F-F bond in F_2 is among the strongest of all covalent bonds.

E. HF(aq) is a weak acid, unlike the rest of the hydrohalic acids.

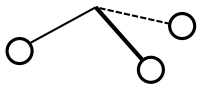
End of Part 2.

Turn this in and you are free to leave. You do NOT have to submit your periodic table.

ANSWERS – PART ONE

1. C_{3v}

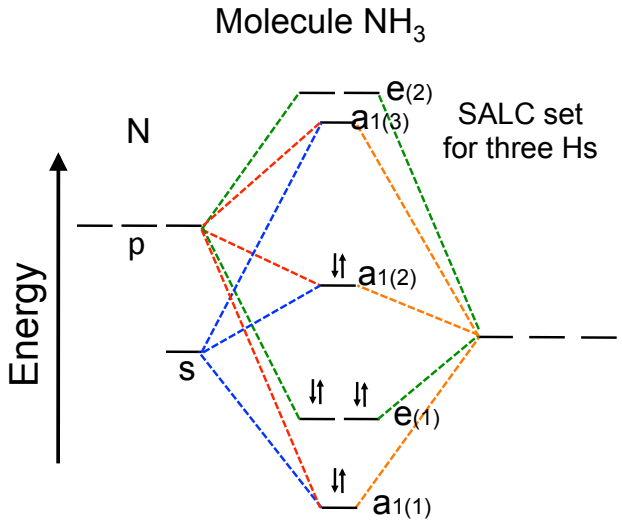
2.



3. three

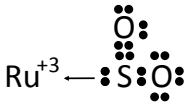
4. A_1 + E

5 and 6.

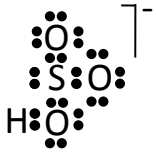


7. s and p_z

8a.



8b.



9.

BF_3	Lewis acid
Cr^{+3}	Lewis acid
SiH_4	Neither
H_2O	Lewis base

10.

KF	basic
NH_4ClO_4	acidic
$NaHSO_4$	acidic

11. CaO

12a. e = 2r; 12b. e = 4 r $3^{½}$; 12c. e = 2 r $2^{½}$

13a. All twelve of the of the edge centers plus the body-center position.

13b. At the center of any one of the eight mini-cubes

13c. 8

14. $^1/_2$ of the octahedral holes and $^1/_8$ of the tetrahedral holes

15. Consider the drawing below to answer the questions that follow.

15a. Blue Red

15b. Green

15c. Orange

16. $CaTiO_3$

17. C

18a. Monoclinic

18b. Triclinic

18c. Rhombohedral (trigonal

18d. Orthorhombic

19. $Si_4O_{12}^{8-}$

20a. Fig C; 20b. Fig D; 20c. Fig A; 20d. None; 20e. Fig B

21. Cr^{3+}; Ru^{3+}; Fe^{3+}; Co^{2+}

22.

$[Cr(H_2O)_6](NO_3)_3$ is octahedral

$(NH_4)_2[CoCl_4]$ is tetrahedral

$K_3[Fe(CN)_6]$ is octahedral

$[Pt(P(C_6H_5)_3)_4]SO_4$ is square planer

23. Five diastereomers for $MA_2B_2C_2$. The second one below is also enantiomeric.

1. A trans to A, B trans to B, C trans to C
2. A cis to A, B cis to B, C cis to C
3. A trans to A, B cis to B, C cis to C
4. A cis to A, B trans to B, C cis to C
5. A cis to A, B cis to B, C trans to C

24. Cr^{3+} is d^3 and the configuration is $t_{2g}^3\ e_g^0$;

Pt^{2+} is square planer d^8 with the d_{x2-y2} empty and highest in energy

Fe^{2+} is d^6 and with strong-field ligands is low-spin with the configuration is $t_{2g}^6\ e_g^0$;

Co^{2+} is d^7 and with waters as ligands, either high spin or low spin might occur. High spin configuration is $t_{2g}^5\ e_g^2$; low spin configuration is $t_{2g}^6\ e_g^1$

25. 186 pm

26. 52.4%

27. 0.414 r

28.

Property of hydrogen:	**Like Group 1**	**Like Group 7**
Ionization energy		X
Electron affinity	X	
Stable molecular form		X

29. A

30. B

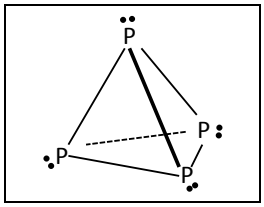
31. A

32. C

33. A

34. +4; +5; +2

35. (3 pts) Sketch the structure of white phosphorus, P_4, and indicate the hybridization and predicted P-P-P bond angles.



36. PCl_4^+ is AB_4 and PCl_6^- is AB_6.

37. S_8 forms an 8-member puckered ring with sp^3-sulfur atoms (AB_2E_2)

38. D