Chem 400
Inorganic Chemistry
Practice Exam 1

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Name ________________________
(please print)
1. a. Predict the structure of SF₄ using the VSEPR model. (2 points)

   ![SF₄ structure diagram]

   b. Explain the fact that at 298 K and in solution the¹⁹F NMR spectrum of SF₄ exhibits a singlet but that at 175 K, two equal intensity triplets are observed. (3 points)

   Temperature dependent ¹⁹F NMR spectrum indicates that SF₄ is stereochemically non-rigid (fluxional). There is more thermal energy at 298 K than at 175 K. At 298 K, a singlet is observed, therefore all F atoms must be equivalent, and the axial and equatorial positions are exchanging over the Berry pseudo-rotation.

   At 175 K, two equal intensity triplets are observed. This arises as follows. There are two F environments (axial and equatorial) as shown above. Each axial F couples to 2 equatorial F’s to give a binominal triplet (and vice versa). The two triplets occur at different chemical shifts.

2. Does VB (valence bond) theory indicate that the diatomic molecule He₂ is a viable species? Rationalize your answer using arguments derived from VB theory only. (5 points)

   Ground state electron configuration of He (Z = 2) is 1s². Within VB theory, the resonance structures that could be drawn (remembering that electrons are paired so far as possible) are:

   \[ \text{He}=\text{He} \leftrightarrow \text{He}^{2+} \quad \text{He}^{2-} \leftrightarrow \text{He}^{2-} \quad \text{He}^{2+} \]

   The double bond formation is not possible with only the 1s orbital per He atom, and the ionic form is unreasonable (look at ionization energies for He). It is concluded that He₂ is not a viable species. (The real question is “What is the stability of He₂ with respect to 2 He?” and VB theory does not give an answer to this.)
3. Draw Lewis structures for each of the following molecules. (2 points each)

a. SeCl$_4$

b. XeO$_3$

c. VOCl$_3$

d. ClO$_3^-$

e. SOF$_4$
4. Draw three-dimensional structures for each of the compounds in problem 3 using VSEPR theory. (2 points each)

a.

\[ \text{Se} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{disphenoidal molecular shape} \]

b.

\[ \text{O} \quad \text{Xe} \quad \text{O} \quad \text{O} \quad \text{Trigonal pyramidal shape, similar to NH}_3, \text{ but with Xe-O double bonds.} \]

c.

\[ \text{Cl} \quad \text{O} \quad \text{V} \quad \text{Cl} \quad \text{Cl} \quad \text{Distorted tetrahedral shape, with Cl-V-Cl angles of 111°, and Cl-V-O angles of 108°.} \]

d.

\[ \text{ClO}_3^- \quad \text{has a trigonal pyramidal shape, with one lone pair and three principal resonance structures.} \]

e.

\[ \text{SOF}_4 \quad \text{has a distorted trigonal bipyramidal shape. The axial fluorine atoms are nearly linear with the S atom.} \]
5. Determine the appropriate point group for each of the compounds in problem 4. (2 points each)

a) \( \text{SeCl}_4 \) has \( C_{2v} \) symmetry

b) \( \text{XeO}_3 \) has \( C_{3v} \) symmetry

c) \( \text{VOCl}_3 \) has \( C_{3v} \) symmetry

d) \( \text{ClO}_3^- \) has \( C_{3v} \) symmetry

e) \( \text{SOF}_4 \) has \( C_{2v} \) symmetry
6. Zinc sulfide has two crystalline forms (shown below). Describe these two structures in terms of closest packed spheres, interstitial occupancy, and coordination number. (10 points)

**Zinc-blende**

- A cubic closest packed (ccp) array of sulfide anions with zinc cations occupying \( \frac{1}{2} \) of the tetrahedral holes.
- \( \text{CN (Zn}^{2+}) = 4 \)
- \( \text{CN (S}^{2-}) = 4 \)

**Wurtzite**

- A hexagonal closest packed (hcp) array of sulfide anions with zinc cations occupying \( \frac{1}{2} \) of the tetrahedral holes.
- \( \text{CN (Zn}^{2+}) = 4 \)
- \( \text{CN (S}^{2-}) = 4 \)
7. a. Derive a set of diagrams using 3s, 3p$_x$, 3p$_y$ and 3d$_{x^2-y^2}$ atomic orbitals to describe the formation of sp$^2$d hybrid orbitals. (8 points)

Take the shaded lobes of the p$_x$ and d$_{x^2-y^2}$ orbital to point along the +x axis, and the shaded lob of the p$_y$ orbital to point along the +y axis. In the xy plane, the orbital combinations to give 4 sp$^2$d hybrid orbital are:

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b. What is the percentage character of each sp$^2$d hybrid orbital in terms of constituent atomic orbitals? (2 points)

Available for hybridization are one s, two p and one d orbital. Each hybrid orbital must contain the same amount of s character; since there are 4 hybrid orbitals, each contains 25% s character. Each hybrid orbital also must contain the same amount of p character, i.e. 50% p character. Each hybrid orbital contains 25% d character.
8. Sketch out the molecular orbital energy level diagram for \( \text{NH}_3 \) applying the LGO approach. Define the spatial orientation of \( \text{NH}_3 \) using \( x, y, z \) directions and identify all atomic and ligand group orbitals involved in bonding. (10 points)
9. Draw schematic representations for all of the bonding molecular orbitals (MO’s) of \( \text{NH}_3 \) (use the information derived in Problem 8). (10 points)
10. How many normal modes of vibration are IR active for (2 points each):

a. H₂O
H₂O is polar and possesses a bent molecular shape. All three modes of vibration are IR active.
b. SiF₄
SiF₄ is tetrahedral and non-polar; T₄ symmetry. 4 modes of vibrational freedom (2 degenerate pairs) are IR active and give rise to 2 bands in the IR spectrum.
c. HCN
HCN is linear and polar. Thus, both symmetric and asymmetric stretches as well as the doubly degenerate deformation are IR active. Three fundamental absorptions are seen in the IR spectrum.
d. AlCl₃
AlCl₃ has a trigonal planar structure and is non-polar. Therefore, the symmetric stretch is IR inactive. The IR active modes are the symmetric deformation, doubly degenerate stretch and doubly degenerate deformation − 5 modes of vibrational freedom giving rise to 3 bands in the IR spectrum.
e. PBr₃
PBr₃ has a trigonal pyramidal structure and is polar. Both symmetric stretch and symmetric deformation are IR active, the doubly degenerate (asymmetric stretch and the doubly degenerate deformation are also IR active. In summary, there are 6 modes of vibrational freedom giving rise to 4 bands in the IR spectrum.

11. B₂O₃ is acidic, Al₂O₃ is amphoteric, and Sc₂O₃ is basic. Why? Give a detailed explanation writing down the equations describing the reaction of these compounds with water. (10 points)

In general, oxide ion reacts with water to form hydroxide:

\[ \text{O}^{2-} + \text{H}_2\text{O} \rightarrow 2 \text{OH}^- \]

unless other factors prevent it.

In B₂O₃, the small, hard B³⁺ holds on the oxide ions strongly. As a result:

\[ \text{B}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2 \text{B(OH)}_3 \leftrightarrow \text{H}^+ + \text{H}_2\text{BO}_3^- \]

and the solution is very weakly acidic (pKₐ = 9.25).

In Al₂O₃, the Al³⁺ ion is larger and softer. It can form either [Al(OH)₄]⁻ (acting as an acid) or [Al(H₂O)₆]³⁺ (acting as a base), depending on the other species in solution.

\[ \gamma\text{-Al}_2\text{O}_3(s) + 3\text{H}_2\text{O(l)} + 6\text{[H}_3\text{O}]^+(aq) \rightarrow 2[\text{Al(H}_2\text{O})_6]^{3+}(aq) \]

\[ \gamma\text{-Al}_2\text{O}_3(s) + 3\text{H}_2\text{O(l)} + 3\text{[OH}]^- (aq) \rightarrow 2[\text{Al(OH)}_4]^- (aq) \]

Sc³⁺ is still larger and softer, so it combines better with water than with hydroxide ion. As a result:

\[ \text{Sc}_2\text{O}_3 + 15 \text{H}_2\text{O} \rightarrow 2 [\text{Sc(H}_2\text{O})_6]^{3+} + 6 \text{OH}^- \]

is possible.