

Inorganic Chemistry 411/511

115 minutes; 200 points total

Show your work for partial credit.

Final Exam**KEY**

1. Draw the **molecular geometry** *and* give the **point group** for the following. Indicate any deviations from ideal VSEPR coordination angles.

- (a) [10 pts] ClO_3^- (chlorate anion)

C_{3v} O-Cl-O likely to be less than 109.5°

- (b) [10 pts] XeF_4

D_{4h} perfectly square planar

- (c) [7 pts] Is XeF_4 a polar molecule? Explain using symmetry rules.

No, D groups cannot be polar.

2. [14 pts] Write down a Born-Haber analysis (give all the reaction steps) needed to estimate ΔH_f for BaF_2 (s) from the elements in standard states.

Correct reactions steps 6

Correct label for energetics (I, E_a , ΔH_L , etc) 4

Correct summation and signs 4

- (b) [7 pts] Do you predict that BaF_3 (s) will be stable? Explain briefly.

No, 3rd IE for Ba will be too large

- (c) [7 pts] Which structure is likely for BaF_2 (s), rocksalt, fluorite, or sphalerite? Explain briefly.

Fluorite, this is an AB_2 type compound.

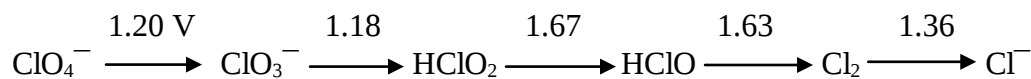
3. (a) [16 pts] Construct a molecular orbital diagram for carbon monoxide, CO (g), including valence atomic and molecular orbitals, with symmetry labels, and with the correct electron filling of the MO's.

See Fig 2.22 in text.

- (b) [7 pts] Draw the geometry of the orbital on CO that acts as a π -acceptor with transition metal cations.

This is the π^* orbital. See Fig 2.23 in text.

4. A Latimer diagram for Cl at pH=0 is:



- (a) [10 pts] What is the standard potential for reduction of ClO_4^- to Cl_2 at pH = 0 ?

$$E^0 = [2(1.20) + 2(1.18) + 2(1.67) + 1(1.63)] / 7 = +1.39 \text{ V}$$

- (b) [10 pts] Does HClO_2 disproportionate spontaneously in aqueous acid? Explain.

Yes, for example $\text{HClO}_2 \rightarrow \text{HClO} + \text{ClO}_3^-$ would have a potential of $+1.67 - 1.18 = +0.49 \text{ V}$

- (c) [10 pts] Write a balanced half-reaction for the reduction of ClO_4^- to ClO_3^- in acidic solution.



- (d) [12 pts] Calculate the potential for the half-reaction in part (c) at pH = 3. The Nernst equation is $E = E^0 - (0.059 \text{ V} / n) \log Q$

$$E = +1.20 - (3)(0.059) = +1.02 \text{ V}$$

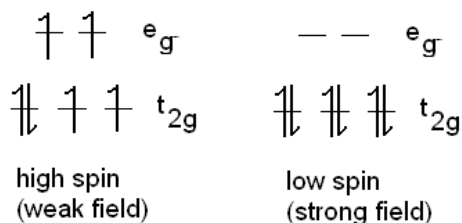
5. (a) [10 pts] Write out the full name of both isomers of $[\text{PtBr}_2\{\text{NH}_3\}_2]$

Cis and trans-diamminedibromoplatinum(II) or (0)

- (b) [10 pts] Give the d orbital energy level diagram for the complex in part (a), assuming an approximately square planar structure. Label the d-orbitals (z^2 , x^2-y^2 , xy , xz , yz).

See text Fig 20.10 (add 8 electrons)

6. (a) [10 pts] Draw the d-orbital energy levels and electron occupancies for both the strong-field (low spin) and weak-field (high spin) O_h complexes of Fe(II).



- (b) [10 pts] Calculate the ligand field stabilization energies (LFSE) relative to Δ_o for each of the two configurations in part (a).

Low spin LFSE = $2.4 \Delta_o$; high spin is LFSE = $0.4 \Delta_o$

- (c) [8 pts] How would you experimentally determine the actual configuration (high or low-spin) for an O_h complex of Fe(II)?

Magnetic moment should be proportional to $\sqrt{N(N+2)}$. [8 pts]
 Trying to measure LFSE by calorimetry is not a good method. [4 pts if this]

7. [4 pts each] Circle the ONE best choice.

- (a) MgO has the stacking sequence of (AcBaCb)_n. What is the coordination geometry around the cation in the lattice?
 (1) tetrahedral (2) square planar (3) **octahedral**
 (4) trigonal prismatic (5) linear (6) trigonal bipyramidal
- (b) Which of the following is the strongest acid?
 (1) HClO (2) HClO₂ (3) HClO₃ (4) **HClO₄** (5) ClO₄⁻ (6) H₂O
- (c) Which of the following will rapidly react with water to form H₂?
 (1) NH₃ (2) **KH** (3) HF (4) CH₄ (5) SF₆ (6) F₂
- (d) Which acts as a π -donor with a weak ligand field effect?
 (1) N(CH₃)₃ (2) H⁻ (3) CN⁻ (4) **Cl⁻** (5) NH₃ (6) CO

- (e) Which ligand will form the strongest complex with the soft acid Pd^{2+} ?
 (1) F^- (2) Cl^- (3) Br^- **(4) I^-** (5) all complexes will have the same K_f
- (f) Which statement is NOT true for transition metal complexes?
 (1) Td complexes are generally high spin
 (2) d^8 complexes are often square planar
 (3) 3rd row transition metal ions often show higher coordination than 1st row ions
 (4) Hg(I) often exists as the species Hg_2^{2+}
(5) the ligand-field splitting energy for Td complexes (Δ_T) is generally greater than the ligand-field splitting energy for octahedral complexes (Δ_O)
- (g) Which complex has the largest LFSE?
 (1) $[\text{Ti}(\text{OH}_2)_6]^{2+}$ **(2) $[\text{V}(\text{OH}_2)_6]^{2+}$** (3) $[\text{Cr}(\text{OH}_2)_6]^{2+}$
 (4) $[\text{Fe}(\text{OH}_2)_6]^{2+}$ (5) all these complexes have the same LFSE
- (h) Which of the following octahedral complexes has no geometric isomers?
(1) $[\text{FeCl}(\text{OH}_2)_5]^{2+}$ (2) $[\text{IrCl}_3\text{F}_3]^{2-}$ (3) $[\text{RuCl}_4(\text{bipy})]^{2-}$
 (4) $[\text{CoBr}_2\text{Cl}_2(\text{NH}_3)_2]^+$ (5) $[\text{W}(\text{CO})_4(\text{PMe}_3)_2]^0$ (6) $[\text{CrCl}_4(\text{NH}_3)_2]^{1-}$