

**Chemistry 362 Mini-Exam V**  
**Fall 2019**

**Thursday November 14, 2019**

**Professor Kim R. Dunbar**

**NAME:** \_\_\_\_\_

**ID:** \_\_\_\_\_

**Total Points on Exam is 50 points**

1. (6 pts)  
 a. What are the three main bonding theories for transition metal complexes and the two main considerations that all three theories must take into account?

- 1) **Molecular orbital theory**
- 2) **Crystal Field Theory**
- 3) **Ligand Field theory**

**Considerations are**

- 1) **Geometry**
- 2) **Ligand type**

2. (10 pts)  
 For the molecules in the list below

- a) Choose the correct answers from I, II or III
- b) Classify the ligand as *strong field* or *weak field*

$W(CO)_6$                       **a) I b) strong field**

$[Co(NH_3)_6]^{2+}$                 **a) II b) strong field**

$[Cr(CN)_6]^{3-}$                 **a) I b) strong field**

$[Zn(H_2O)_6]^{2+}$                **a) II b) weak field**

$[Re_2Cl_8]^{2-}$                  **a) III b) weak field**

- I. the ligand type is a  $\pi$ -acceptor.
- II. the ligand type is a  $\sigma$ -donor.
- III. the ligand type is a  $\pi$ -donor

3. (4 points)  
 The magnitude of d-orbital splitting is affected by both the nature of the metal and the nature of the ligand.  
 For each parameter (metal dependence and ligand dependence) select the **correct** series (A or B, C or D) ordering in terms of *increasing* the ligand field splitting.

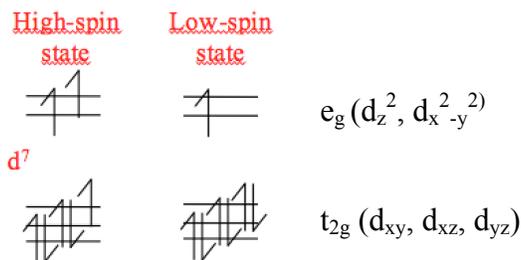
**Metal dependence**

- (A)  $Mn^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > V^{2+} > Fe^{3+} > Cr^{3+} > V^{3+} > Co^{3+} > Mn^{4+} > Mo^{3+} > Rh^{3+} > Pd^{4+} > Ir^{3+} > Re^{4+} > Pt^{4+}$   
 (B)  $Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+} < Mn^{4+} < Mo^{3+} < Rh^{3+} < Pd^{4+} < Ir^{3+} < Re^{4+} < Pt^{4+}$

**Ligand dependence - the Spectrochemical Series**

- (C)  $O_2^{2-} > I^- > Br^- > S^{2-} > SCN^-$  (S-bonded)  $> Cl^- > N_3^- > F^- > NCO^- > OH^- > C_2O_4^{2-} > H_2O > NCS^-$  (N-bonded)  $> CH_3CN > py$  (pyridine)  $> NH_3 > en$  (ethylenediamine)  $> bipy$  (2,2'-bipyridine)  $> phen$  (1,10-phenanthroline)  $> NO_2^- > PPh_3 > CN^- > CO$   
 (D)  $O_2^{2-} < I^- < Br^- < S^{2-} < SCN^-$  (S-bonded)  $< Cl^- < N_3^- < F^- < NCO^- < OH^- < C_2O_4^{2-} < H_2O < NCS^-$  (N-bonded)  $< CH_3CN < py$  (pyridine)  $< NH_3 < en$  (ethylenediamine)  $< bipy$  (2,2'-bipyridine)  $< phen$  (1,10-phenanthroline)  $< NO_2^- < PPh_3 < CN^- < CO$

4. (10points)  
 a) Sketch both a Low-Spin L.S. and a High-Spin H.S.  $d^7$  octahedral splitting diagram and put the electrons in. 4 pts



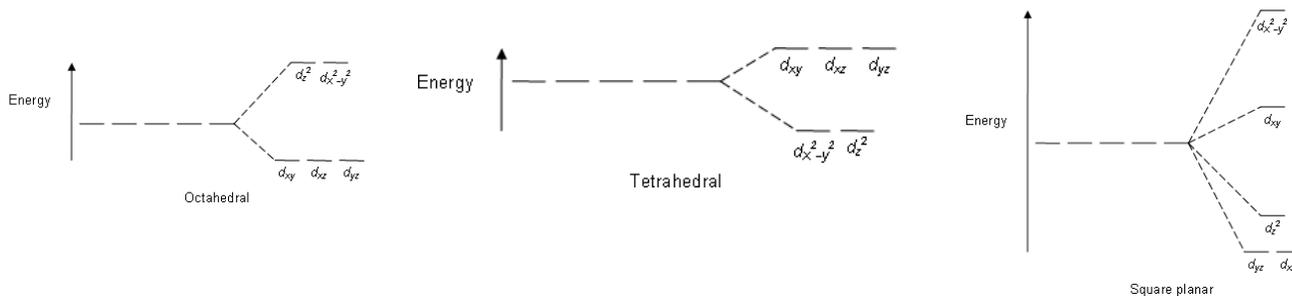
- b) Calculate the CFSE for each one. 2 pts

**LS  $d^7$ :  $6(-2/5 \Delta_o) + 1(3/5 \Delta_o) + 3P$**   
**HS  $d^7$ :  $5(-2/5 \Delta_o) + 2(3/5 \Delta_o) + 2P$**

- b) The adoption of one configuration over the other depends on what? 4 pts

**Depends on the relative magnitude of  $\Delta_o$  as compared to the electron pairing energy. If  $\Delta_o$  is greater than PE, then the configuration will be LS. If  $\Delta_o$  is less than PE, then the configuration will be high spin.**

6. (12 pts)  
 a) Draw the d-orbital splitting diagrams for octahedral, tetrahedral and square planar geometries 6 pts



- b) Why is the relative splitting energy larger for an octahedral field larger than that of a tetrahedral field? 3 pts

**Interactions are weaker in tetrahedral geometries as ligands do not point to orbitals on the metal. Therefore, the magnitude of stabilization/destabilization is decreased compared to octahedral geometries.**

- c) If a  $d^9$  metal was placed into the above ligand fields, would you expect paramagnetism or diamagnetism? 3 pts

**All three geometries would result in a paramagnetic configuration for a  $d^9$  metal**

5. Determine the ground state term symbols for the following free ions. Show ALL work (8 pts)

(a)  $\text{Fe}^{3+}$

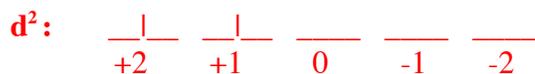


$$L=0 \rightarrow S$$

$$2S+1 = 2(2.5)+1 = 6$$

${}^6S$

(b)  $\text{Ti}^{2+}$

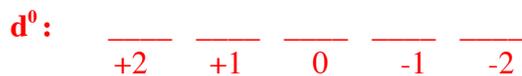


$$L=3 \rightarrow F$$

$$2S+1 = 2(1)+1 = 3$$

${}^3F$

(c)  $\text{Ti}^{4+}$



$$L=0 \rightarrow S$$

$$2S+1 = 2(0)+1 = 1$$

${}^1S$

(d)  $\text{Cu}^{2+}$



$$L=2 \rightarrow D$$

$$2S+1 = 2(0.5)+1 = 2$$

${}^2D$