

# Chm 451 Fall 2007

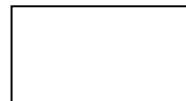
## Exam 3 27 November 2007

Name: \_\_\_\_\_

You may use the Study Guides from Days 14 – 19. Five point bonus for not using any of the guides. This exam has a point total of 105 points. You can skip 5 points or answer them all. Your score will be 105 – points missed + bonus. Maximum score = 100%. Suggestion: Work in pencil. You may ask me for one if you don't have one with you.

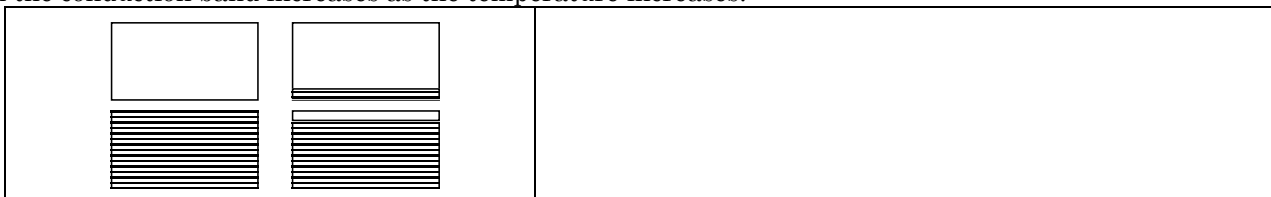
### MO theory for Network Covalents and Metals.

1. (12 pts) Using one or two boxes such as shown at right, sketch the MO diagrams for each of the following network covalent and metallic materials. Designate the band gap carefully in those cases where there is one. I will specifically look for the presence or absence of a band gap and the relative size of the gap from drawing to drawing, as well as the relative number of filled orbitals designated with lines or shading, your choice.

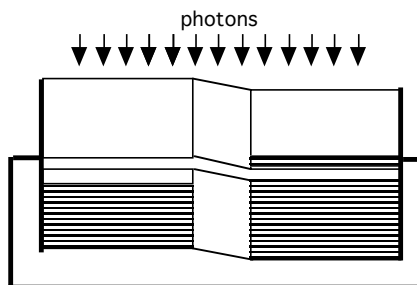
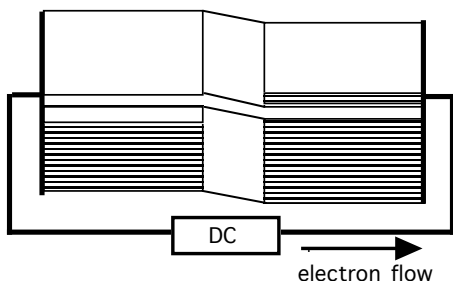


(a) Ti	(b) Cu	(c) Si
(a) C(diamond)	(d) C(graphite)	(e) Si containing 0.01% As

2. (2 pts) Sketch a Boltzmann distribution that shows how the population of electrons with suitable energy to be in the conduction band increases as the temperature increases.



3. (2 pts) Sketch the flow of electrons through the (a) semiconductor (left) and the photocell (right).



## Silicates

4. (6 pts) The two different silicates shown at right are each part of infinite "2-D" chains. What is the empirical formula of each silicate?

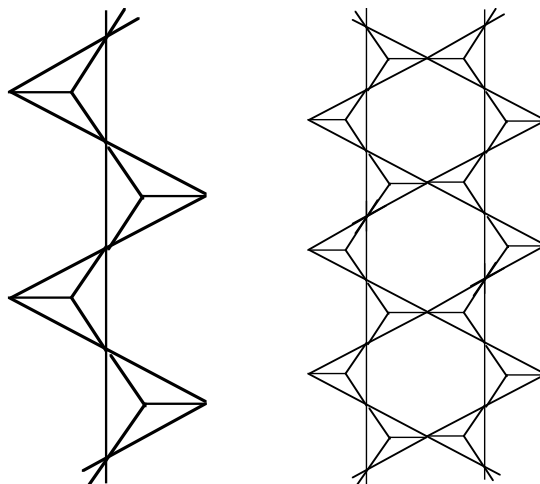
Left:

Right:

b. (2 pts) If the cation is iron(II), what is the formula for each silicate?

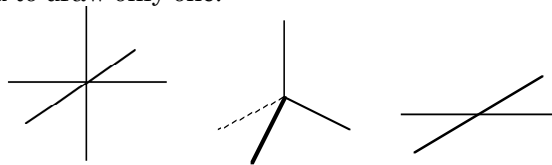
Left:

Right:



## Structure and Isomers

5. (12 pts) Sketch these transition metal complexes in 3-D. Use brackets and charges for ions. Use the following perspectives for octahedral, tetrahedral and square planar geometries, respectively. In cases where isomers exist, you need to draw only one.

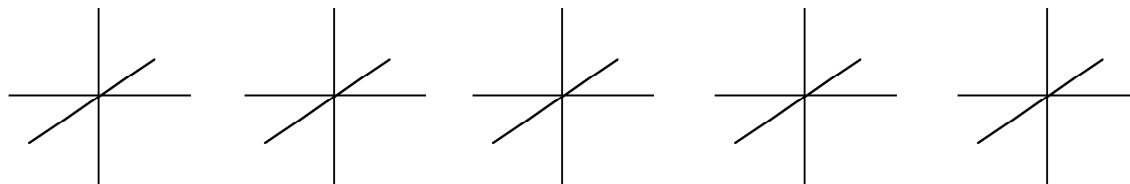


$\text{NH}_4[\text{FeCl}_4]$	$[\text{Cr}(\text{NH}_3)_6]\text{SO}_4$	$\text{Co}(\text{en})_2\text{Cl}_2$
$\text{K}_2[\text{Pt}(\text{CN})_4]$	$[\text{Co}(\text{P}(\text{CH}_3)_3)_4]_2(\text{SO}_4)_3$	$[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$

6. (20 pts) (a) The oxidation state on the transition metal, (b) Determine the d-electron configuration ( $d^n$ ), (c) predict if the complex is high spin or low spin and (d) how many unpaired electrons are present.

$[\text{Mn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$    (a)  (b)  (c)  (d)	$(\text{NH}_4)_4[\text{Fe}(\text{CN})_6]$    (a)  (b)  (c)  (d)	$[\text{Ru}(\text{py})_6]\text{Br}_3$    (a)  (b)  (c)  (d)
$\text{K}_4[\text{CrCl}_6]$    (a)  (b)  (c)  (d)	$[\text{Os}(\text{CO})_6]\text{Cl}_2$    (a)  (b)  (c)  (d)	Doodle space

7. (5 pts) How many stereoisomers (geometric) isomers are possible for  $\text{Rh}(\text{en})\text{Cl}_2(\text{NH}_3)_2$ ? Sketch them using these templates. Hint: There may be more templates than you actually need.



8. (3 pts) What are the three factors that determine if  $\Delta_o$  is large enough to be low spin? Assume that the complex has enough electrons to be either high or low spin.

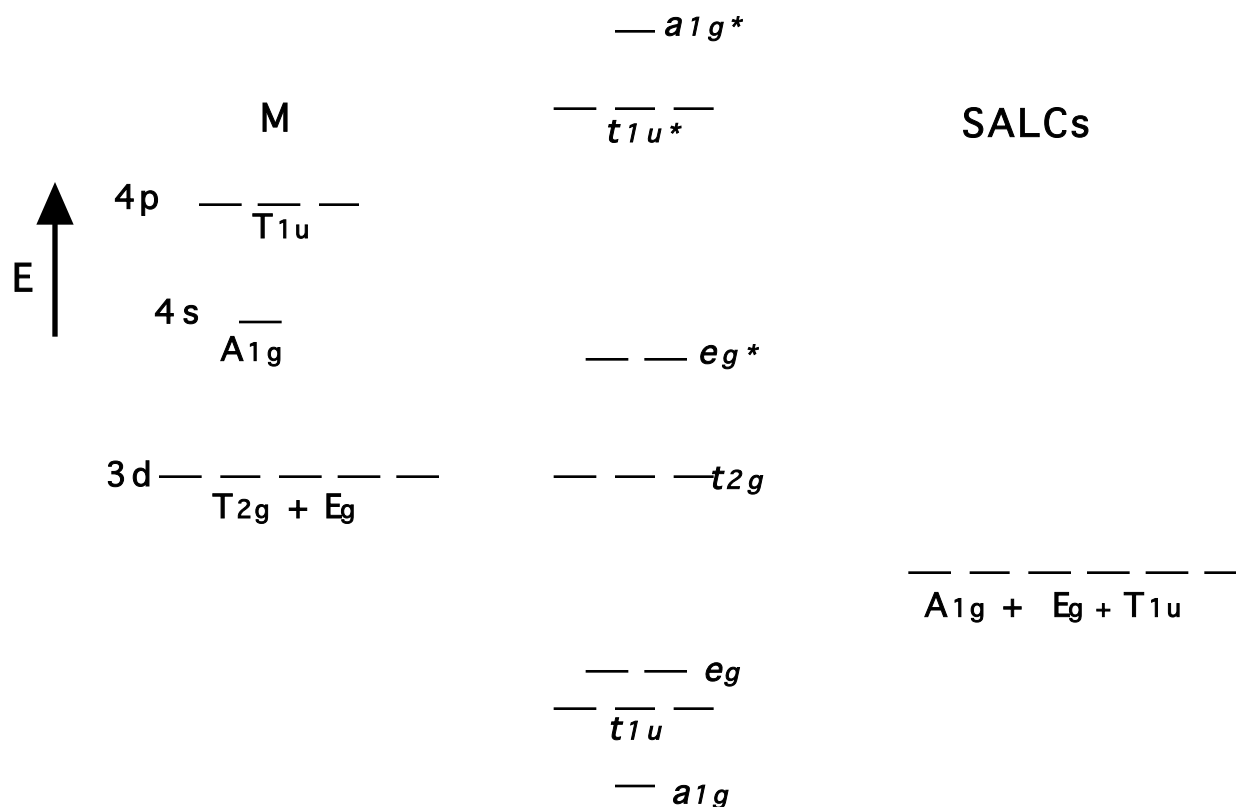
9. (5 pts) Sketch the crystal-field splitting pattern for the d-orbitals in an octahedral field of ligands. Label the amount of stabilization experienced by the lower and upper orbitals. Use your diagram to determine the CFSE for high-spin  $d^6$  and low spin  $d^6$ . Include pairing energies if appropriate.

10. (5 pts) Use Jorgensen's relationship to predict  $\Delta_o$  for  $\text{Co}(\text{bpy})_3^{+2}$  and  $\text{Co}(\text{bpy})_3^{+3}$ . Compare  $\Delta_o$  to the pairing energies for these two ions and predict if these complexes are high spin or low spin. [Those not using their notes can ask for the necessary values.]

11. (5 pts) What is the expected crystal field splitting energy pattern for square planar complexes? Label each orbital. Character table provided on the periodic table sheet.

12. The MO energy diagram for the octahedron is shown below.

(a) (3 pts) Connect up the lines between metal's atomic orbitals, the SALCs and the MOs.



(b) (6 pts) Sketch the following MOs. Character table provided on the periodic table sheet.

$a_{1g}$	$t_{1u}$	$e_g^*$
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(c) (3 pts) Populate the MO diagram for  $Fe(NH_3)_6^{+3}$ , a low-spin complex on the diagram above.

13. (6 pts) Use the method of microstates to determine the term symbols for p-orbital electron configuration  $p^2$ . Which is the ground state? What transitions between terms are spin-allowed, if any?

14. (4 pts) Using the Tanabe-Sugano diagrams, what absorption band(s) are expected for a high-spin octahedral  $d^4$  complex? Your answer should have the format:  ${}^nX \rightarrow {}^nX'$  where X means "term." Which one corresponds to  $\Delta_0$ ?

15. (4 pts) What Tanabe-Sugano diagram would you use to predict the allowed electronic transitions for a  $d^3$  tetrahedral complex? What transitions are expected and which one corresponds to  $\Delta_t$ ?

O <sub>h</sub>	E	8C <sub>3</sub>	6C <sub>2</sub>	6C <sub>4</sub>	3C <sub>2</sub>	i	6S <sub>4</sub>	8S <sub>6</sub>	3σ <sub>h</sub>	6σ <sub>d</sub>		
A <sub>1g</sub>	1	1	1	1	1	1	1	1	1	1	(R <sub>x</sub> , R <sub>y</sub> , R <sub>z</sub> )	x <sup>2</sup> + y <sup>2</sup> + z <sup>2</sup>
A <sub>2g</sub>	1	1	-1	-1	1	1	-1	1	1	-1		z <sup>2</sup> , x <sup>2</sup> - y <sup>2</sup>
E <sub>g</sub>	2	-1	0	0	2	2	0	-1	2	0		(xy, xz, yz)
T <sub>1g</sub>	3	0	-1	1	-1	3	1	0	-1	-1		
T <sub>2g</sub>	3	0	1	-1	-1	3	-1	0	-1	1		
A <sub>1u</sub>	1	1	1	1	1	-1	-1	-1	-1	-1	(x, y, z)	
A <sub>2u</sub>	1	1	-1	-1	1	-1	1	-1	-1	1		
E <sub>u</sub>	2	-1	0	0	2	-2	0	1	-2	0		
T <sub>1u</sub>	3	0	-1	1	-1	-3	-1	0	1	1		
T <sub>2u</sub>	3	0	1	-1	-1	-3	1	0	1	-1		

D <sub>4h</sub>	E	2C <sub>4</sub>	C <sub>2</sub>	2C' <sub>2</sub>	2C'' <sub>2</sub>	i	2S <sub>4</sub>	σ <sub>h</sub>	2σ <sub>v</sub>	2σ <sub>d</sub>		
A <sub>1g</sub>	1	1	1	1	1	1	1	1	1	1	R <sub>z</sub>	x <sup>2</sup> + y <sup>2</sup> , z <sup>2</sup>
A <sub>2g</sub>	1	1	1	-1	-1	1	1	1	-1	-1		x <sup>2</sup> - y <sup>2</sup>
B <sub>1g</sub>	1	-1	1	1	-1	1	-1	1	1	-1	(R <sub>x</sub> , R <sub>y</sub> )	xy
B <sub>2g</sub>	1	-1	1	-1	1	1	-1	1	-1	1		(xz, yz)
E <sub>g</sub>	2	0	-2	0	0	2	0	-2	0	0		
A <sub>1u</sub>	1	1	1	1	1	-1	-1	-1	-1	-1	z	
A <sub>2u</sub>	1	1	1	-1	-1	-1	-1	-1	1	1		
B <sub>1u</sub>	1	-1	1	1	-1	-1	1	-1	-1	1	(x, y)	
B <sub>2u</sub>	1	-1	1	-1	1	-1	1	-1	1	-1		
E <sub>u</sub>	2	0	-2	0	0	-2	0	2	0	0		

## Answers

- Ti: no band gap (metals are conductors) and less than half filled because Ti is an early transition metal.
  - Cu: no band gap (metals are conductors) and more than half filled because Cu is a late transition metal.
  - Si: definite band gap (semi-metal) and exactly half filled.
  - C(diamond) large band gap (non-conductor) and exactly half filled.
  - C(graphite) no band gap (graphite is a conductor) and half filled
  - Si containing 0.01% As: definite band gap (semi-metal) and valence band fully filled and conduction band partially filled.
- Plot of population on y-axis and KE on x-axis. The curve rises sharply starting at  $x = 0$  and peaks and then decreases slowly as KE increases.
- (2 pts) (a) counterclockwise with electrons flowing through wire; (b) clockwise with electrons flowing through wire.

4. (a) Left:  $\text{SiO}_3^{-2}$  ; Right:  $\text{Si}_4\text{O}_{11}^{-6}$

b. Left:  $\text{FeSiO}_3$ ; Right:  $\text{Fe}_3\text{Si}_4\text{O}_{11}$

## Structure and Isomers

5.

$\text{NH}_4[\text{FeCl}_4]$  tetrahedron of  $\text{FeCl}_4^{-1}$

$[\text{Cr}(\text{NH}_3)_6]\text{SO}_4$  octahedron of  $\text{Cr}(\text{NH}_3)_6^{+2}$

$\text{Co}(\text{en})_2\text{Cl}_2$  octahedron of neutral  $\text{Co}(\text{en})_2\text{Cl}_2$

$\text{K}_2[\text{Pt}(\text{CN})_4]$  aquare plane of  $\text{Pt}(\text{CN})_4^{-2}$

$[\text{Co}(\text{P}(\text{CH}_3)_3)_4]_2(\text{SO}_4)_3$  tetrahedron of  $\text{Co}(\text{P}(\text{CH}_3)_3)_4^{+3}$

$[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$  octahedron of  $\text{Ti}(\text{H}_2\text{O})_6^{+3}$

6. (20 pts) (a) The oxidation state on the transition metal, (b) Determine the d-electron configuration ( $d^n$ ), (c) predict if the complex is high spin or low spin and (d) how many unpaired electrons are present.

$[\text{Mn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ (a) +2 (b) $d^5$ (c) hs (d) 5	$(\text{NH}_4)_4[\text{Fe}(\text{CN})_6]$ (a) +2 (b) $d^6$ (c) ls (d) 0	$[\text{Ru}(\text{py})_6]\text{Br}_3$ (a) +3 (b) $d^5$ (c) ls (d) 1
$\text{K}_4[\text{CrCl}_6]$ (a) +2 (b) $d^4$ (c) hs (d) 4	$[\text{Os}(\text{CO})_6]\text{Cl}_2$ (a) +2 (b) $d^6$ (c) ls (d) 0	

7. There are three stereoisomers (geometric) possible for  $\text{Rh(en)Cl}_2(\text{NH}_3)_2$ . One has trans chlorides, one has trans ammonias and one has a chloride trans to an ammonia.

8. Low-spin complexes ( $d^4 - d^7$  octahedral) have one or more of the following going for them: 2<sup>nd</sup> or 3<sup>rd</sup> row transition metal, strong field ligand, first row metal in high oxidation state.

9. The CFSE for high-spin  $d^6$  is  $-4 \Delta_o + P$  and for low spin  $d^6$  it is  $-2.4 \Delta_o + 3P$ .

10.

$$\Delta_o = f \times g = 9 \times 1.33 \times 1000 \text{ cm}^{-1} = \text{for } \text{Co}(\text{bpy})_3^{+2} = 11,970 \text{ cm}^{-1}$$

$$\Delta_o = f \times g = 18.2 \times 1.33 \times 1000 \text{ cm}^{-1} = \text{for } \text{Co}(\text{bpy})_3^{+3} = 24,210 \text{ cm}^{-1}$$

The pairing energies for  $\text{Co}^{+2}$  is  $20,800 \text{ cm}^{-1}$  so we predict that  $\text{Co}(\text{bpy})_3^{+2}$  is high-spin.

The pairing energies for  $\text{Co}^{+3}$  is  $23,625 \text{ cm}^{-1}$  so we predict that  $\text{Co}(\text{bpy})_3^{+3}$  is low-spin (although it is close!)

11. (5 pts) What is the expected crystal field splitting energy pattern for square planar complexes? Label each orbital. Character table provided on the periodic table sheet.

Two degenerate orbitals,  $d_{xz}$  and  $d_{yz}$  are the lowest in energy, followed by  $d_{xy}$  and then by  $d_{z^2}$ . The highest orbital in terms of energy is  $d_{x^2-y^2}$ .

12. (a) Sketch lines of identical symmetry only. So the metal's  $a_{1g}$  orbitals and the SALC- $a_{1g}$  are connected to the bonding and anti-bonding  $a_{1g}$  molecular orbitals. Repeat the process for the  $t_{1u}$  orbitals and then for the  $e_g$  orbitals.

(c) There are 17 electrons total with the highest occupied molecular orbital being the  $(t_{2g})^5$ .

13.  $^3P$ ,  $^1D$ , and  $^1S$  with the  $^3P$  being the ground state. The only spin-allowed transition is between terms  $^1D$ , and  $^1S$ .

14.  $^5E \rightarrow ^5T$  is the only one allowed and it corresponds to  $\Delta_o$

15. Use the octahedral  $d^3$  Tanabe-Sugano diagram predict the allowed electronic transitions for a  $d^3$  tetrahedral complex. The transitions expected are

$$^4T_1 (\text{F}) \rightarrow ^4T_2 (\text{corresponding to } \Delta_t)$$

$$^4T_1 (\text{F}) \rightarrow ^4A_2$$

$$^4T_1 (\text{F}) \rightarrow ^4T_1 (\text{P})$$