Name KEY

1) {9 pts} For each of the following pairs of complexes, identify the one that has the larger LFSE and **EXPLAIN** your choice:

a. $[Fe(CN)_6]^{3-}$ or $[Ru(CN)_6]^{3-}$

LFSE increase as you down a group

b. $[Mn(H_2O)]^{2+}$ or $[Fe(H_2O)]^{3+}$

Fe^{3+} splits more, higher charge

c. $[Fe(CN)_6]^{3-}$ or $[FeCl_6]^{3-}$

Cl is weak field, CN is strong field

2) {5 pts} $[Cu(phen)_2]^+$ is an intensely orange colored compound. What kind of electronic transition (d-d, LMCT, MLCT, fluorescence, phosphorescence, etc.) gives rise to this color? $K[MnO_4]$ is a deep purple color (as those of you have used it to oxidize organic molecules will recall). What kind of electronic transition gives rise to this color? **EXPLAIN** your reasoning.

$[Cu(phen)_2]^+ \rightarrow Cu^+ \rightarrow d^{10} \rightarrow MLCT$

$K[MnO_4] \rightarrow Mn^{7+} \rightarrow d^0 \rightarrow LMCT$

3) {2 pts} Will Pu(IV) disproportionate to Pu(III) and Pu(V) in acidic solutions?

No. $E^\circ(R)$ is not greater than $E^\circ(L)$

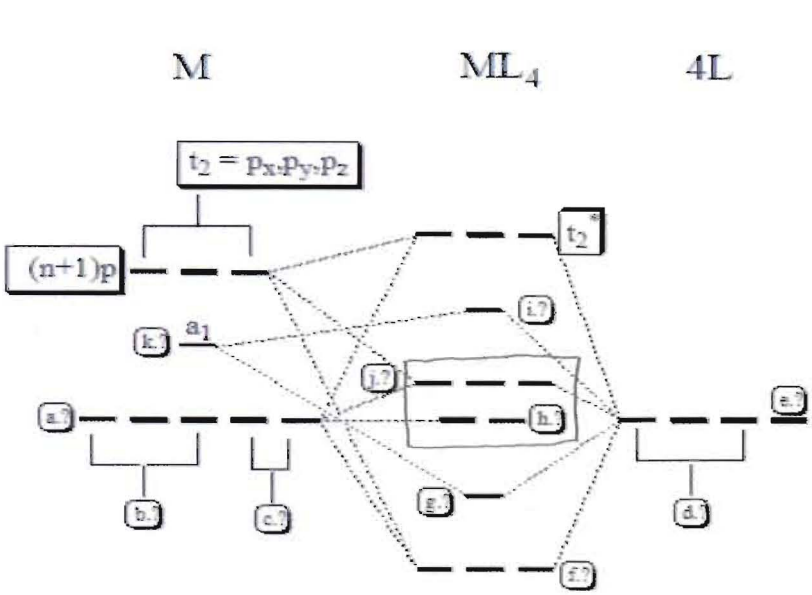
4) {4 pts} The rate constants for the formation of $[CoX(NH_3)_5]^{2+}$ from $[Co(NH_3)_6]^{3+}$ for X= Cl^-, Br^-, N_3^-, SCN^-, differs by no more than a factor of two. What is the mechanism of substitution? **EXPLAIN** your choice.

Dissociative. Rate is independant of incoming ligand

5) {4 pts} When $[Ni(CN)_4]^{2-}$ is reacted with labeled cyanide, $^{14}CN^-$, it predominately gives rise to products that have the formula $[Ni(CN_4)_x(^{14}CN)_y]$, where (x+y) = 4. However, there is a very small percentage of products where (x+y) = 5. What is the mechanism of substitution for $[Ni(CN)_4]^{2-}$ going to $[Ni(CN_4)_x(^{14}CN)_y]$, where (x+y) = 4? **EXPLAIN** your choice.

Associative. (x+y) = 5 = intermediate one can isolate. It is the Y-M-X. Also 4-coordinate tend to be a.

6) {14 pts} Using Ligand Field Theory, complete the σ MO diagram of a complex with tetrahedral symmetry.

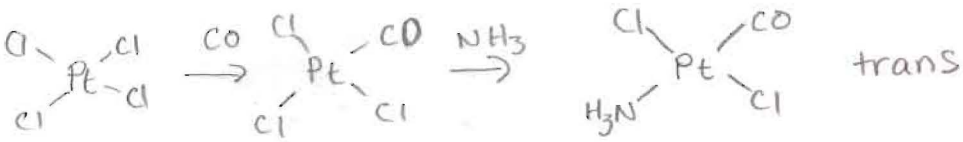


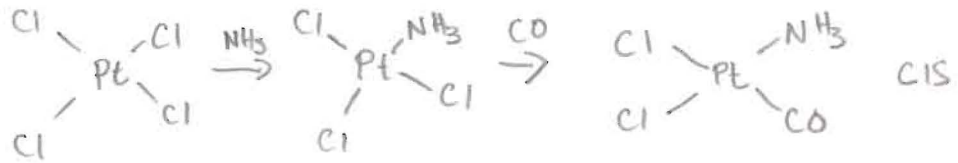
a. nd
b. $t_2 = d_{xy}, d_{yz}, d_{zx}$
c. $e = d_{z^2}, d_{x^2-y^2}$
d. t_2
e. a_1
f. t_2
g. a_1
h. e
i. a_1^*
j. t_2^*
k. (n+1)s

7) {1 pt} Draw a box around the orbitals considered by CFT.

8) {10 pts} Design a two-step syntheses for the *cis*- and *trans*- $[Pt_2Cl_2(CO)(NH_3)]^{2-}$ starting from $[PtCl_4]^{2-}$.

$CO > Cl^- > NH_3$





9) {5 pts} Calculate the value of E° for the PuO_2^{2+}/Pu couple in aqueous acidic solutions.

$$\frac{2(1.03) + 4(-1.25)}{6} = -0.49V$$

10) {9 pts} Assign an outer- or inner-sphere mechanism for each of the following. **EXPLAIN** your choice.

a. The main product of the reaction between $[Cr(H_2O)_4(NCS)F]^+$ and $[Cr(H_2O)_6]^{2+}$ is $[Cr(H_2O)_5F]^{2+}$.

Inner-sphere. Ligand got transferred.

b. When $[VO(edta)]^{2-}$ reacts with $[VO]^{2-}$, a transient red color is observed.

Inner-sphere. Transient red color = Transient bridged complex

c. The rates of reduction of $[Co(NH_3)_5py]^{3+}$ by $[Fe(CN)_6]^{3-}$ are insensitive to substitution of py.

Outer-sphere. Py substitution would effect bridge formation. Since it doesn't, no bridge formed

11) {6 pts} Calculate the cell emf produced by a fuel cell that combines hydrogen with oxygen under standard conditions.

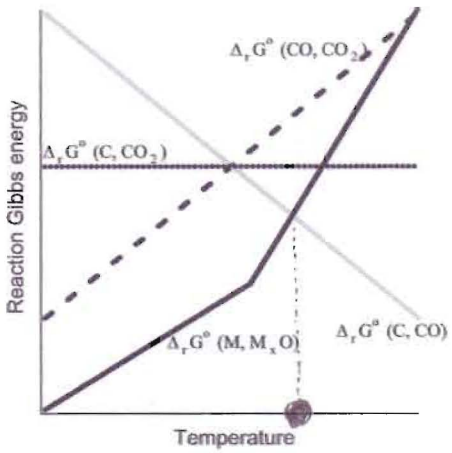
$2H_2 + O_2 \rightarrow 2H_2O$

$2\times (H_2 \rightarrow 2H^+ + 2e^-)$ $\quad E^\circ = 0$

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $\quad E^\circ = 1.229\,V$

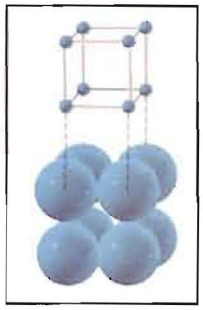
$E^\circ = 1.229\,V$

12) {5 pts} On the Ellingham diagram below, mark on the temperature axis the lowest temperature at which the metal oxide can be reduced to metal by carbon. What is the overall reaction at this temperature?



$C(s) + M_xO(s) \rightarrow xM(s \text{ or } l) + CO(g)$

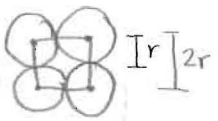
13) {12 pts} Use the diagrams of the primitive cubic unit cell shown on the right. (Be careful when calculating an edge – look at where the spheres are touching and where they are not – this is different from the closed packed one we covered.)



a. Calculate the number of atoms in the unit cell.

$8 \times \frac{1}{8} = 1$

b. Calculate the fraction of the cell that is empty space.



volume of sphere $= 4/3\pi r^3$

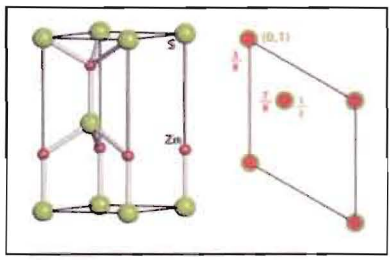
volume of cube $= (2r^3) = 8r^3$

fraction of empty space $= \frac{8r^3 - 4/3\pi r^3}{8r^3} = 0.48$ or 48% free

c. What is the "coordination number" of the atoms in the solid? In other words how many atoms is each atom touching?

6

14) {12 pts} Use the diagram of a zinc sulfur unit cell shown on the right.



a. Calculate the formula unit.

S: $8 \times \frac{1}{8} = 1 > 2$
1

Zn: $4 \times \frac{1}{4} = 1 > 2$
1

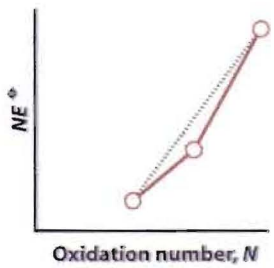
$Zn_2S_2 \rightarrow \boxed{ZnS}$

b. How many formula units are in the unit cell?

2

c. This unit cell can be viewed as an expanded hexagonal closed packed unit cell in S^{2-} with Zn^{2+} in ½ the tetrahedral holes.

15) {2 pts} The species depicted in the Frost diagram will tend to go under what kind of reaction?



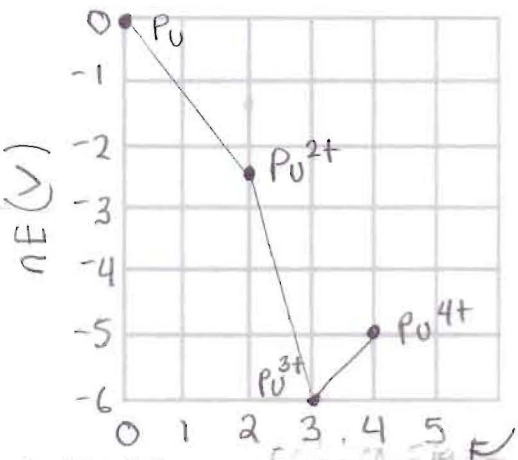
Tends to comproportionate

BONUS:

1) {2 pts} What is the name of the crystal structure in question 14?

Wurtzite

2) {5 pts} Using the grid below, construct a Frost diagram for plutonium(0) to plutonium(IV). Be sure to label your axes.



oxidation state	E	nE
0	0	0
2	-1.2	-2.4
3	-2.00	-6
4	-1.25	-5

3) {3 pts} Common glass used for windows and bottles appears colorless, but when viewed through the edge it appears faintly green. Fe^{3+} causes the color. Why it is so faintly colored and why does looking at the edge reveal the color?

d-d transition not as intense as CT, especially high spin. Viewing on edge increases path length thus absorption

$$A = \epsilon b c$$