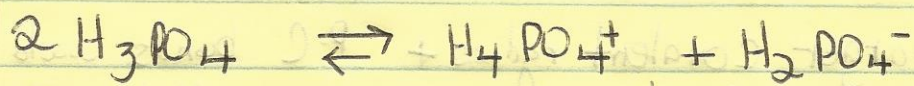
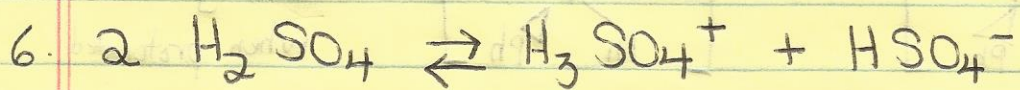


Ch. 6 HW

1.

	Acid	Base	Definition
a.	$AlBr_3$	Br^-	Lewis
b.	$HClO_4$	CH_3CN	Lewis, Brønsted-Lowry
c.	Ni^{2+}	NH_3	Lewis
d.	ClF	NH_3	Lewis
e.	SO_2	ClO_3^-	Lewis
f.	HF	C_3H_7COOH	Lewis, Brønsted-Lowry



form enough ions to allow conductance in the pure acids.

8. Basicity ranking

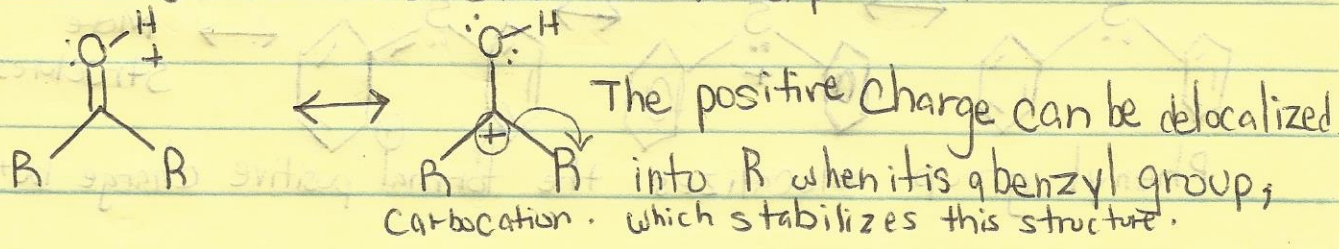
$CH_3COCH_3 < CH_3COCH_2CH_3 < PhCOPh$

proton affinities: 812.0 (kJ/mol) < 836.0 (kJ/mol) < 882.3 (kJ/mol)

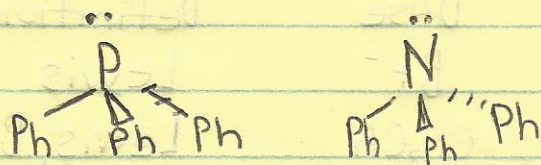
↑ proton affinity, ↑ basicity

The CH_2 group in $CH_3COCH_2CH_3$ donates e^- density to the carbonyl carbon, which stabilizes it.

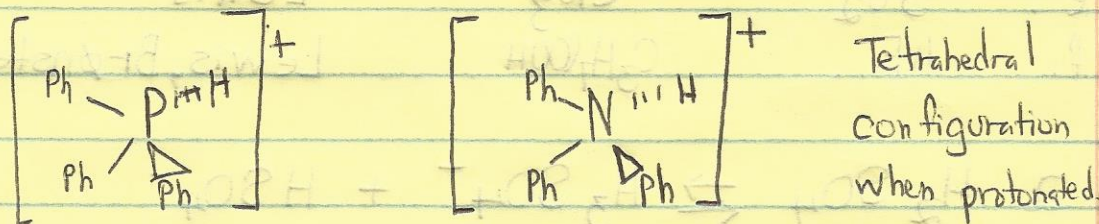
→ Look @ resonance structures to explain this.



9. Basicity ranking



$\chi_N > \chi_P$ and so you would expect the amine to be more basic. But sterics play a role here.

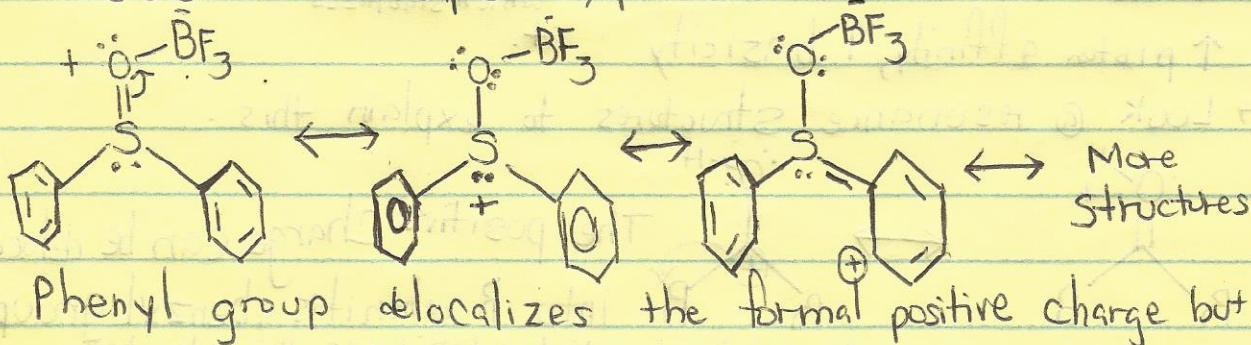


P has a larger covalent radius + P-C bonds would be longer than N-C. Therefore there would be less "back" strain in the Ph groups accommodating a tetrahedral geometry when the proton binds.

11. ↑ BF₃ affinity, ↑ Lewis basicity

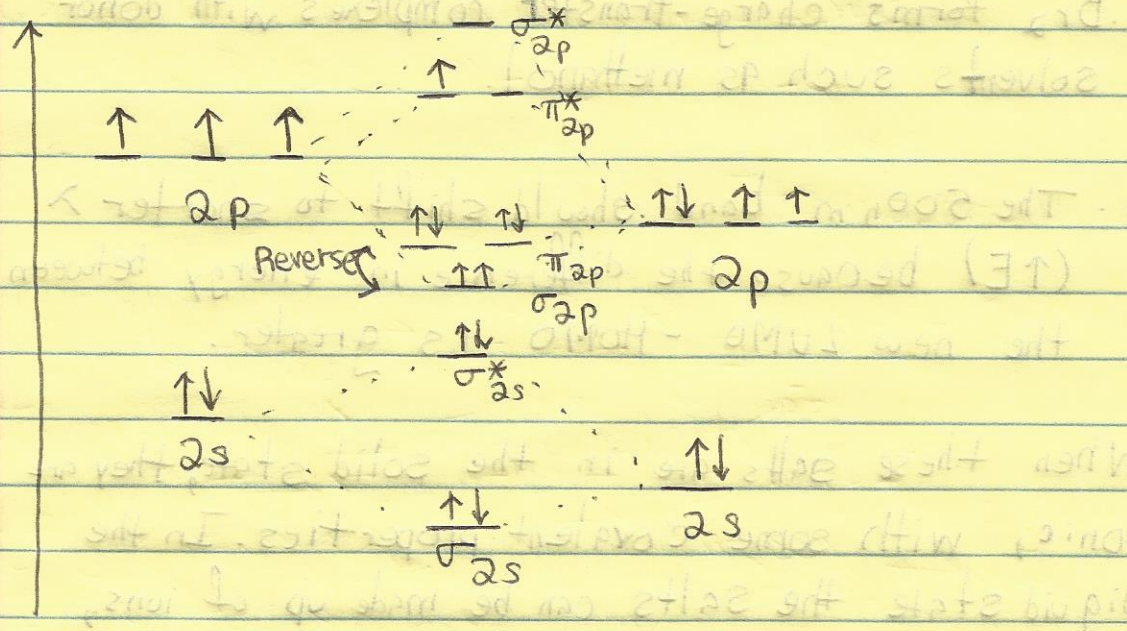
The electron-releasing ability of substituents in sulfoxides (R₂SO) increases in the order of R: Ph, Me < nBu < cyclo-(CH₂)

Resonance helps explain this.



the alkyl groups lower the formal positive charge.

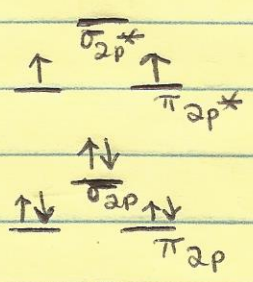
15. The N-O distance in the complex 2b is 129.6 pm, longer than the corresponding bond in free NO (115.1 pm).



LUMO is an antibonding orbital. Bond lengthening is expected since NO likely uses its π^* orbital (its LUMO) to accept e^- density from the phosphine. Population of an orbital that is antibonding with respect to the N-O bond will result in a longer bond distance.

21. See the MO diagram above

NO^-



(4)

Bonding with H^+ depends on which end of the π^* orbital carries more e^- density. It is likely N because it is less χ . This makes HNO more likely.

22. a. Br_2 forms charge-transfer complexes with donor solvents such as methanol.

b. The 500 nm band should shift to shorter λ ($\uparrow E$) because the difference in energy between the new LUMO - HOMO is greater.

26. When these salts are in the solid state, they are ionic, with some covalent properties. In the liquid state the salts can be made up of ions, covalent molecules, or something in between. If the liquid is molecular, vaporization should be easier. If the liquid is mostly ionic, vaporization is more difficult. The most ionic liquids should be ZnF_2 and CdF_2 and the most molecular liquids should be HgF_2 + $HgCl_2$. Hg, as the softest metal in the series, forms the more molecular compounds and zinc, as the hardest, forms the more ionic compounds.

27. a. pyridine + BF_3

$$\Delta H = -(E_{\text{py}} E_{\text{BF}_3} + C_{\text{py}} C_{\text{BF}_3})$$

$$= -[(1.17)(9.88) + (6.40)(1.62)] = -21.9 \text{ kcal/mol}$$

$$\downarrow$$
$$-91.6 \text{ kJ/mol}$$

Roughly 13% less exothermic than the experimental value of -105 kJ/mol .

pyridine + $\text{B}(\text{CH}_3)_3$

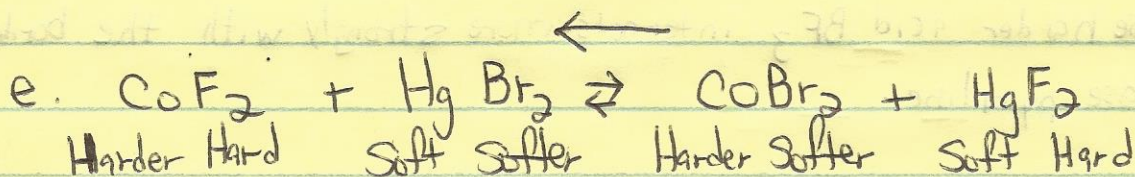
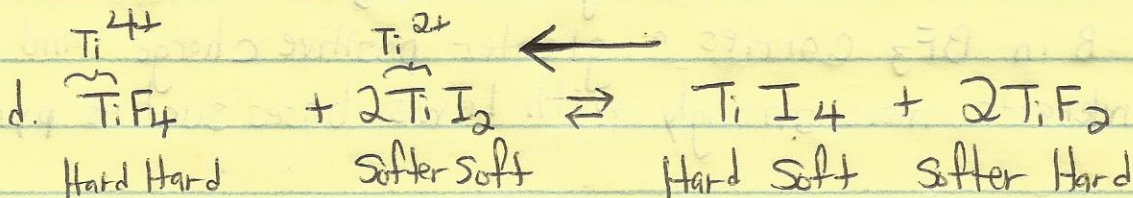
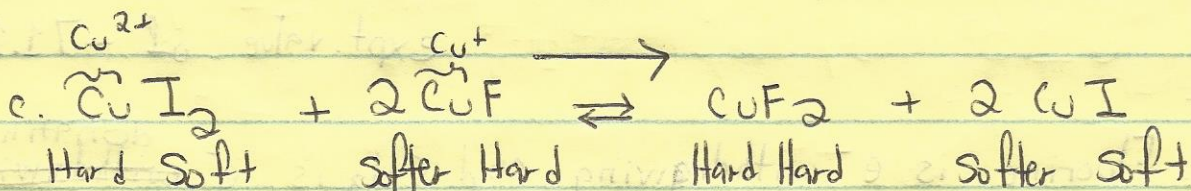
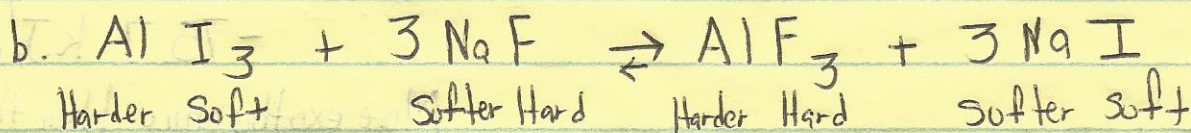
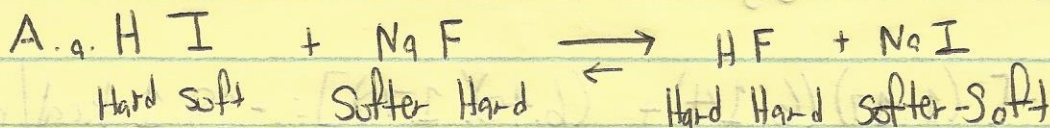
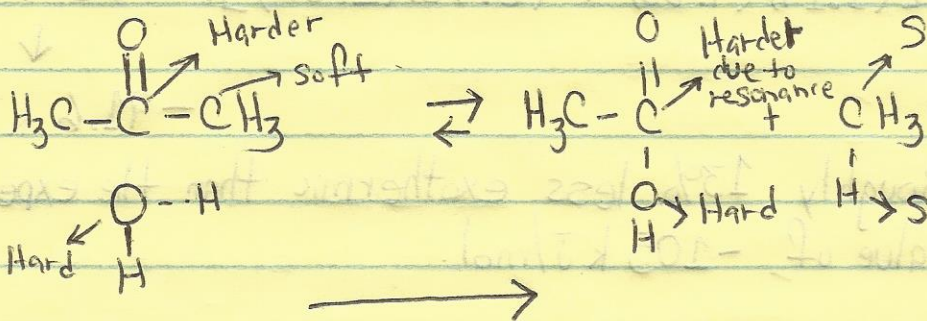
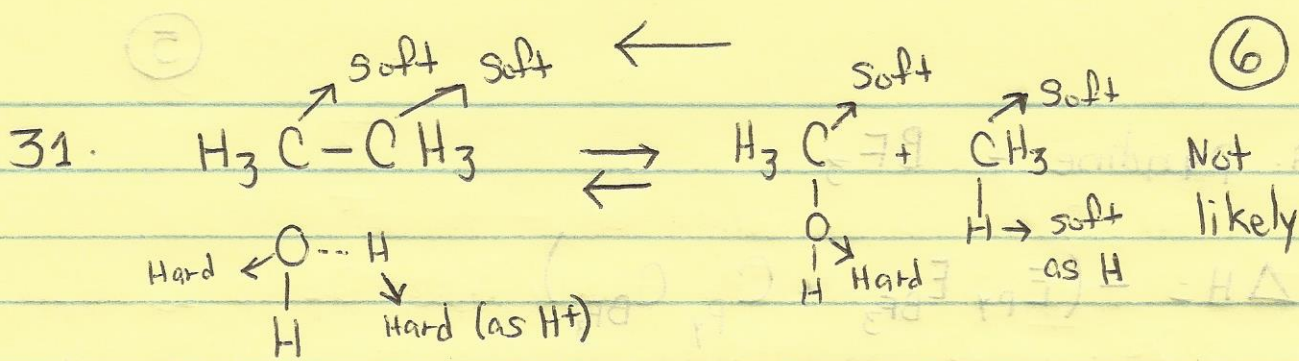
$$\Delta H = -[(1.17)(6.14) + (6.40)(1.70)] = -18.1 \text{ kcal/mol}$$

$$\downarrow$$
$$-75.7 \text{ kJ/mol}$$

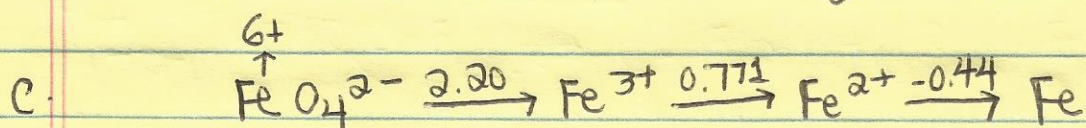
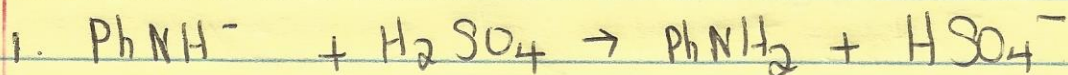
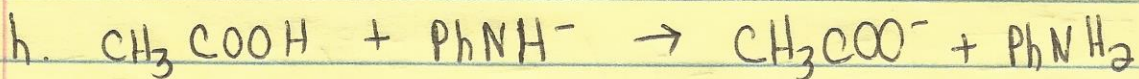
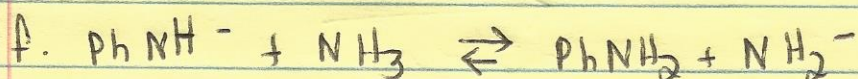
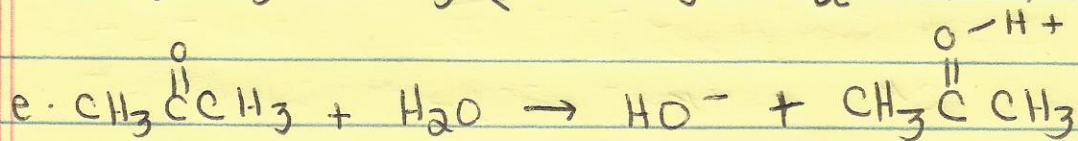
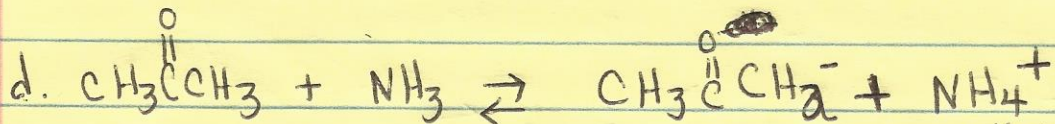
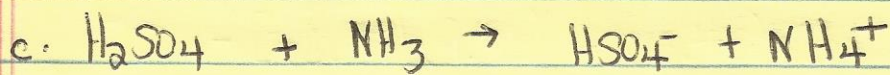
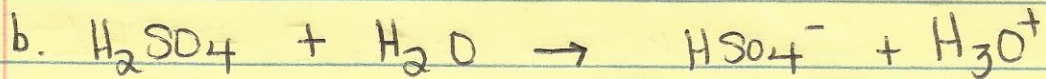
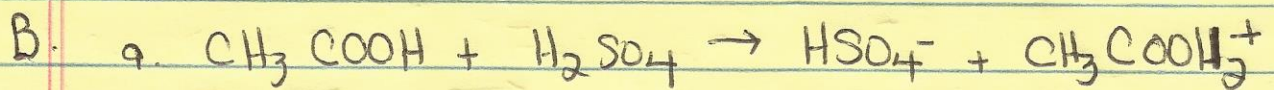
More exothermic than the expt. value of -71.1 kJ/mol

b. Fluorine is e^- withdrawing and CH_3 is e^- donating.
 \therefore B in BF_3 carries a greater positive charge and interacts more strongly with Lewis bases such as pyridine.

c. The harder acid BF_3 interacts more strongly with the borderline base pyridine.

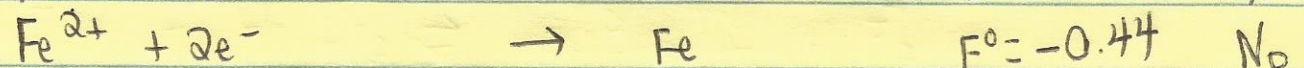
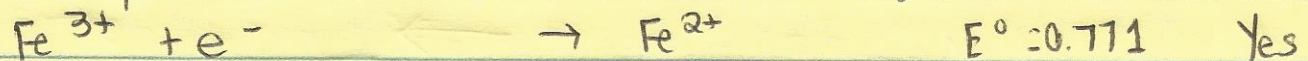
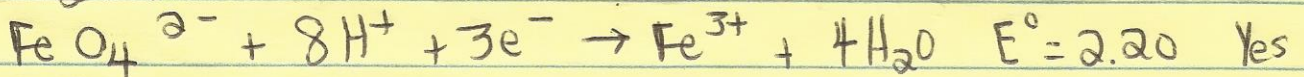


(7)



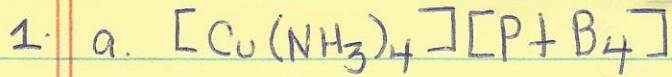
~~FeO₄²⁻~~

Spontaneous?

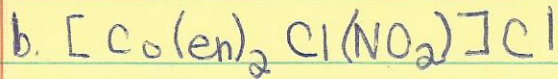


Problem Set #4

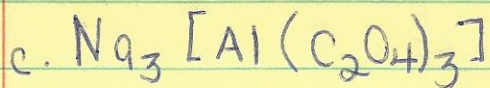
1



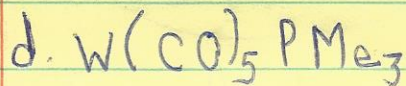
tetraamminecopper(II) tetrabromoplatinate(II)



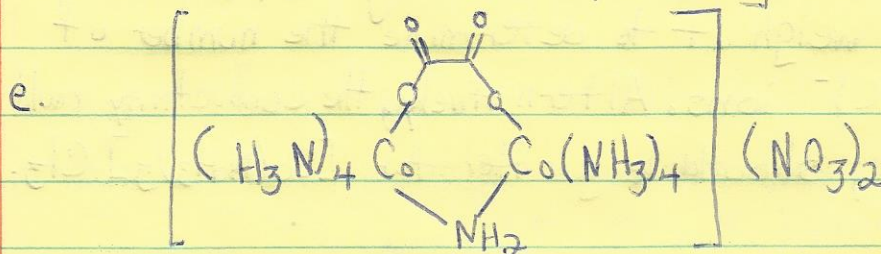
chlorobis(ethylenediamine)nitritocobalt(II) chloride



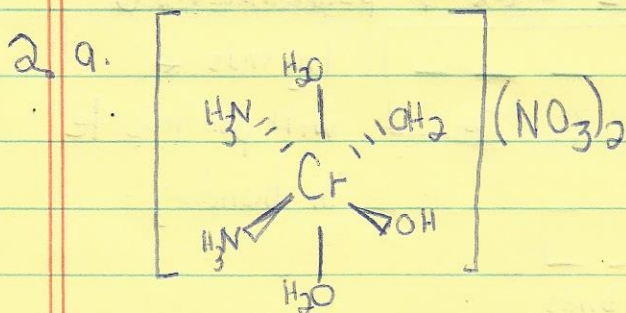
sodium tris(oxalato)aluminate(III)

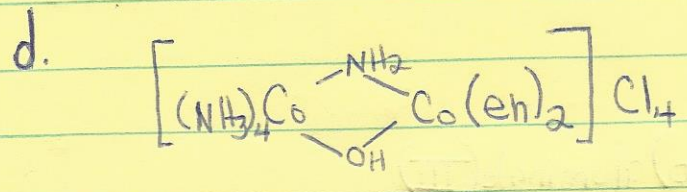
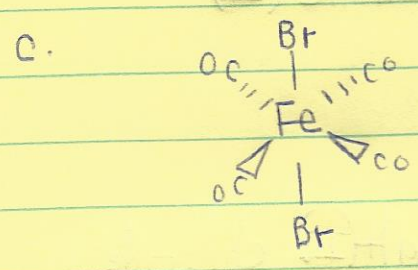
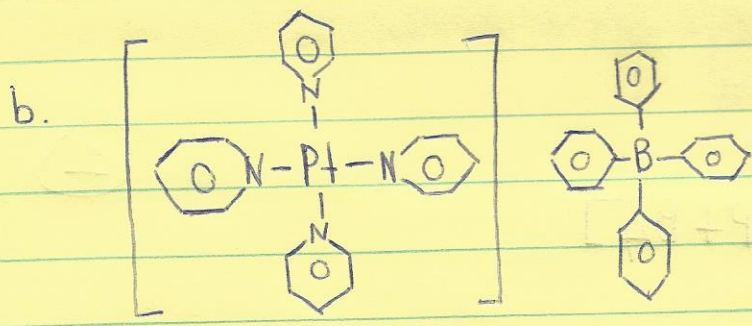


pentacarbonyltrimethylphosphine tungsten(0)



μ -amido- μ -oxalato bis(tetraamminecobalt(II)) nitrate



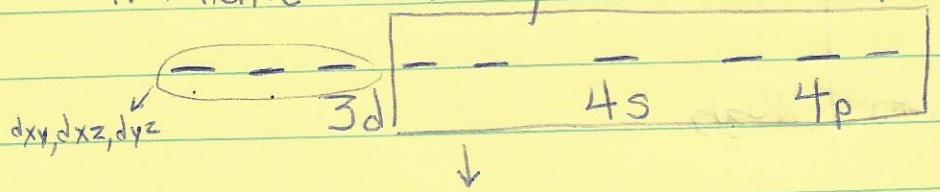


3. The number of free Cl^- ions would be different for the two complexes (3 vs 2). Add AgNO_3 , precipitate AgCl , and weigh it to determine the number of dissociable Cl^- ions. Alternatively, the conductivity could be measured; should be greater for $[\text{Co}(\text{NH}_3)_5]\text{Cl}_3$.

4. $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $\text{Ni}^{2+} \cdot d^8$

a. Valence bond theory

$d_{z^2} + d_{x^2-y^2}$ point directly @



ligands + will participate in bonding.

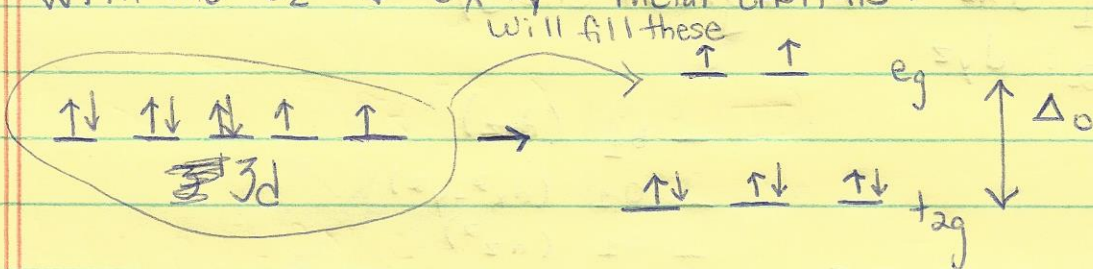


Ligand e^- fill the d^2sp^3 orbitals and metal e^- fill the 3d orbitals. However, there are more metal d e^- than can fill the 3d orbitals.

→ Limitation of VBT.

b. Crystal field theory

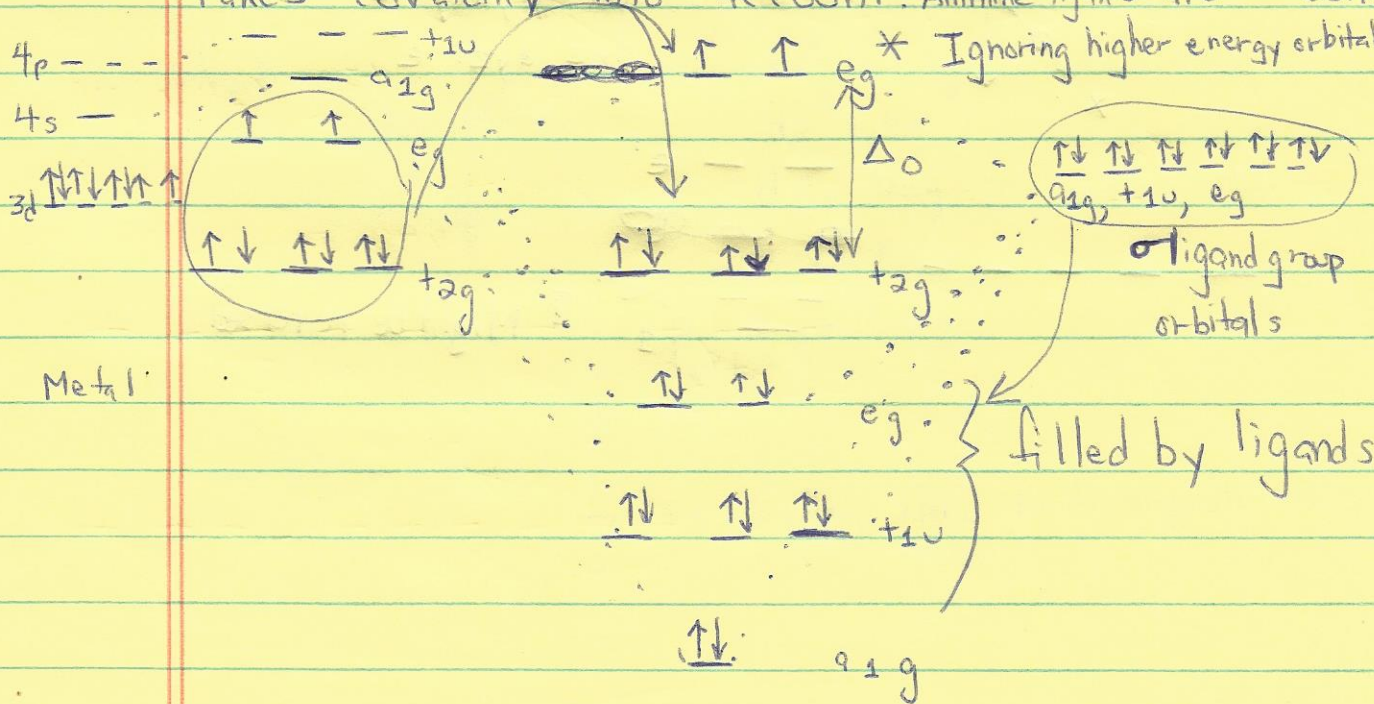
The ammine ligands are point charges that interact with the $d_{z^2} + d_{x^2-y^2}$ metal orbitals.



High-field, low-field not important here

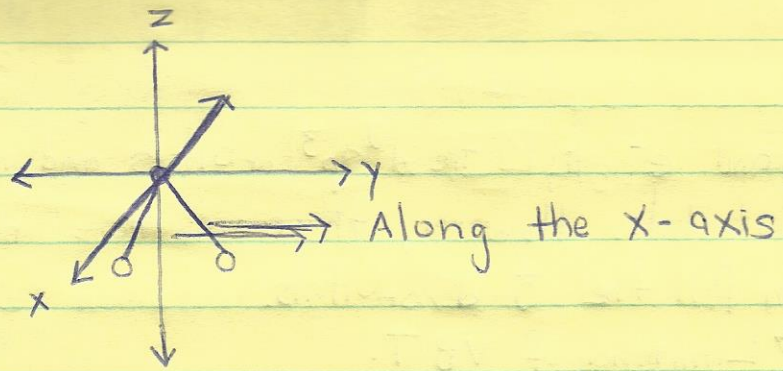
c. Ligand field (molecular orbital) theory

Takes covalency into account. Ammine ligands are σ donors.



filled by ligands

5. C_{2v}



From character table, d-orbitals transform as

$a_1: dz^2, dx^2-y^2$ → Not degenerate because A is singly degenerate

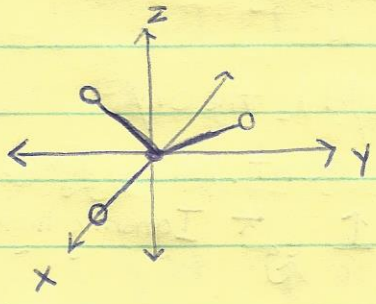
$a_2: dxy$

$b_1: dxz$ → highest energy

$b_2: dyz$

- $b_1 (dxz)$
- $a_1 (dx^2-y^2)$
- $a_1 (dz^2)$
- $b_2 (dxy)$
- $b_2 (dyz)$

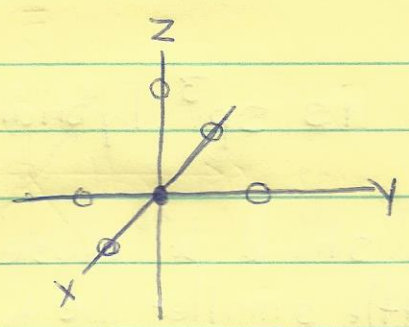
D_{3h}



$dz^2: a_1'$
 $dx^2-y^2, dxy: e'$
 $dxz, dyz: e''$

- - - e'
- - - $a_1' e''$ ⚡ Might be reversed

C_{4v}



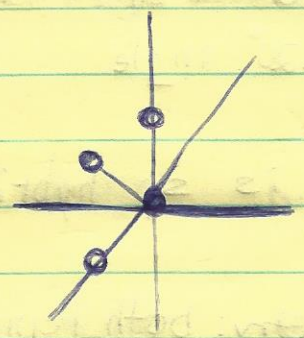
$dz^2: a_1$
 $dx^2-y^2: b_1$
 $dxy: b_2$
 $dxz, dyz: e$

- b_1
 - a_1



— b_2
 - - e

C_{3v}

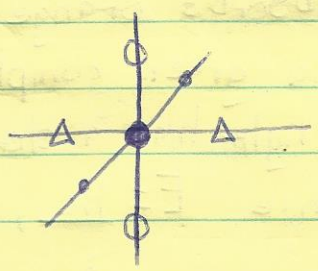


$dz^2: a_1$
 $dx^2-y^2, dxy: e$
 $dxz, dyz: e$

— — dx^2-y^2, dxy
 — a_1
 — — dxz, dyz



D_{2h}



$dx^2-y^2: a_g$
 $dz^2: a_g$
 $dxy: b_{1g}$
 $dxz: b_{2g}$
 $dyz: b_{3g}$

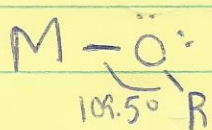
— dx^2-y^2
 — dz^2



— b_{1g}, b_{2g}, b_{3g} Hard to distinguish the order.

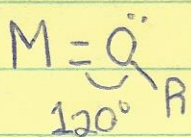
(6)

6.a. No π bonding: O is sp^3 hybridized



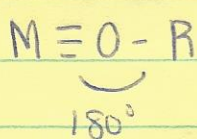
Angle should be close to 109.5°
(a little smaller due to distortion from lone pairs on O).

b. $2\pi e^-$ from $-\text{OR}$: O is sp^2 hybridized



Remaining p orbital on O forms π bond for a 120° angle

c. $4\pi e^-$ from $-\text{OR}$: O is sp hybridized

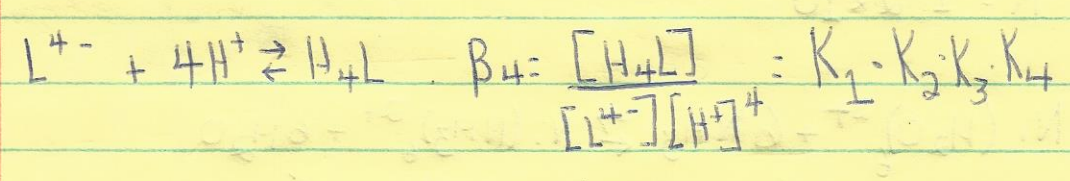
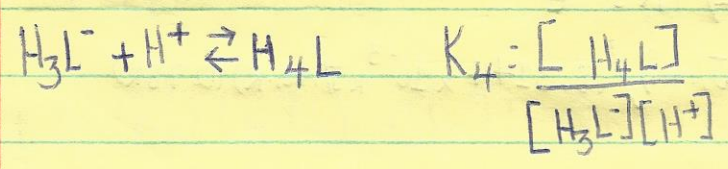
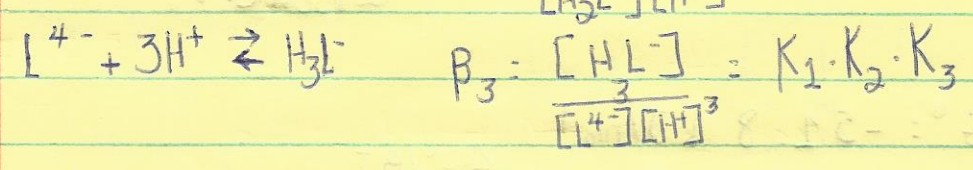
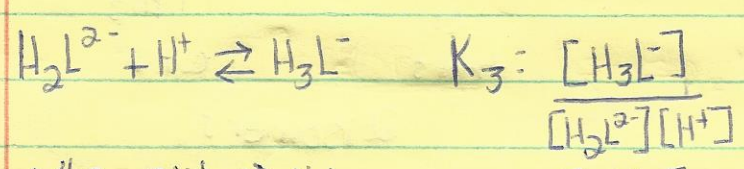
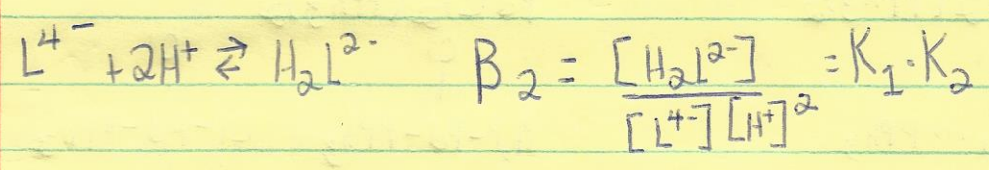
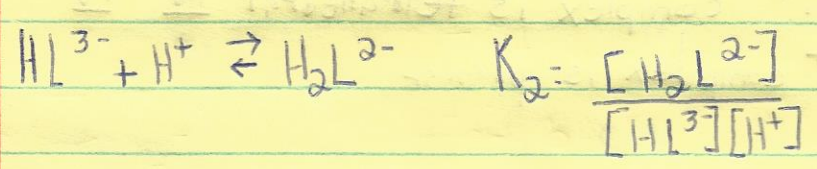
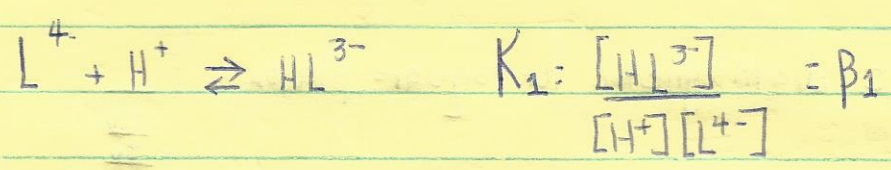


Linear geometry: both remaining p orbitals on O form π bonds.
Angle is 180° .

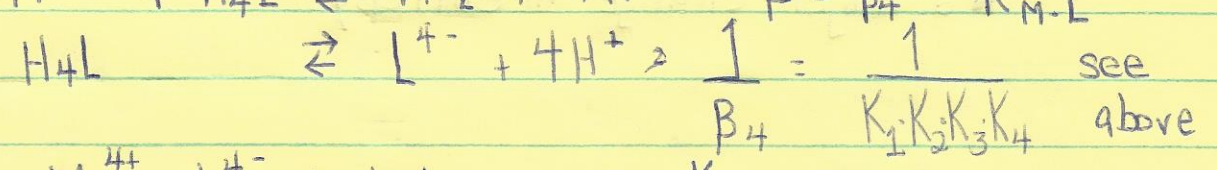
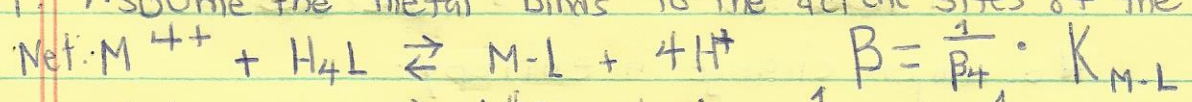
7. A blue-appearing complex absorbs orange light (the complementary color), while a green complex absorbs red light. Orange light has a shorter wavelength than red, so since $E = \frac{hc}{\lambda}$, the

blue complex has the higher value of Δ_o .

8. H₄L



9. Assume the metal binds to the acidic sites of the ligand.

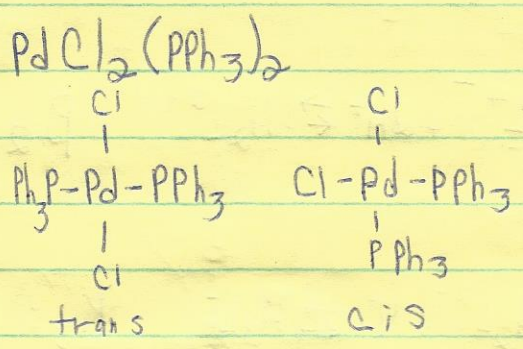
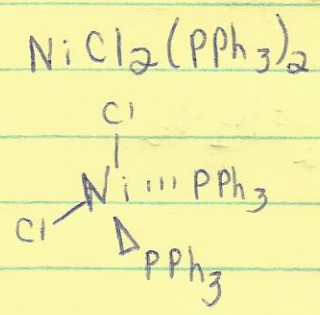


10. Ni²⁺ and Pd²⁺ are d⁸ ions

For T_d geometry, d⁸ is paramagnetic. $\uparrow\downarrow \uparrow \uparrow$
 $\uparrow\downarrow \uparrow\downarrow$

but it is diamagnetic for square planar.

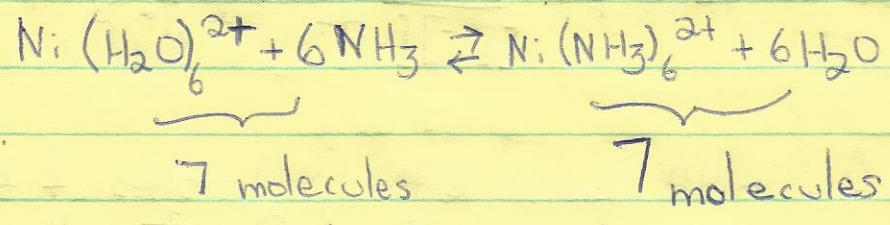
Thus, the Ni²⁺ complex is tetrahedral $\uparrow\downarrow \uparrow\downarrow$
and the Pd²⁺ complex is planar $\uparrow\downarrow \uparrow\downarrow$



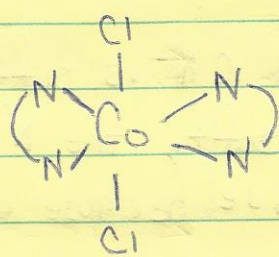
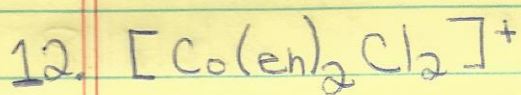
2 isomers

11. $\Delta G^\circ = -51.8 \text{ kJ/mol}$
 $\Delta G^\circ = -RT \ln K \Rightarrow K = e^{-\Delta G^\circ/RT}$

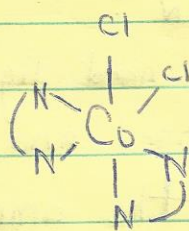
$K = e^{-(-51.8 \text{ kJ/mol}) / (8.3144 \times 10^{-3} \text{ kJ/mol}\cdot\text{K})(298\text{K})}$
 $K = 1.2 \times 10^9$



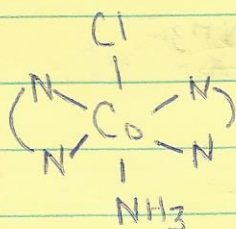
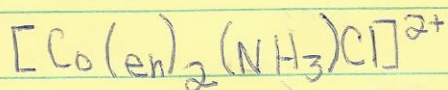
No major change in entropy.



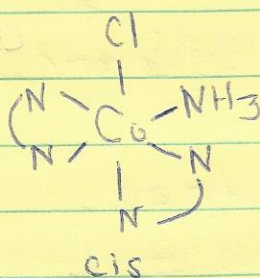
trans
(achiral)



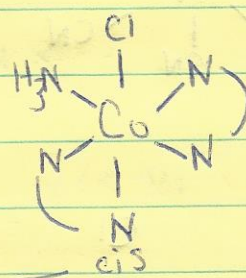
cis
(chiral)



trans
(achiral)

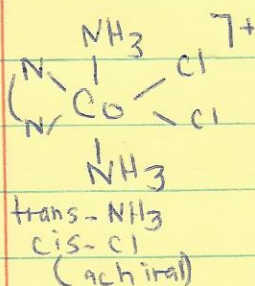
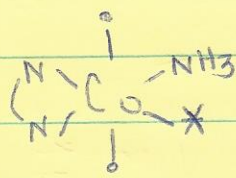
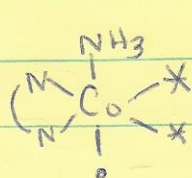
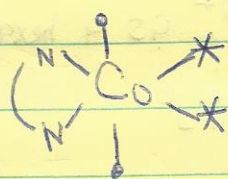
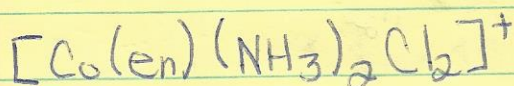


cis

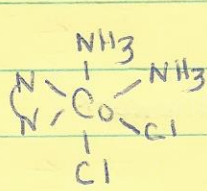


cis

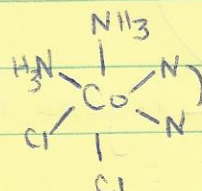
Optical isomers



trans-NH₃
cis-Cl
(achiral)

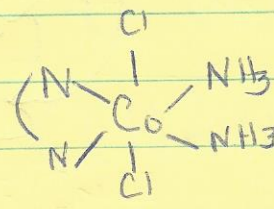


cis-NH₃
cis-Cl

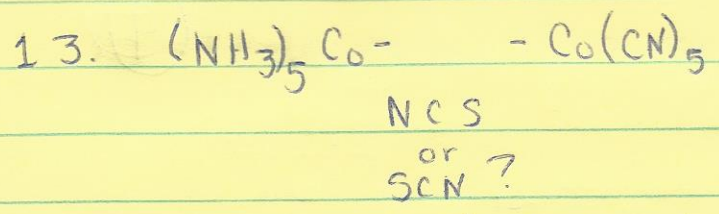


cis-NH₃
cis-Cl

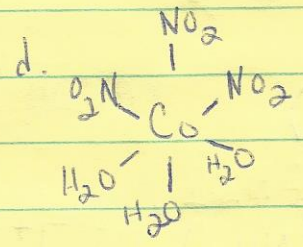
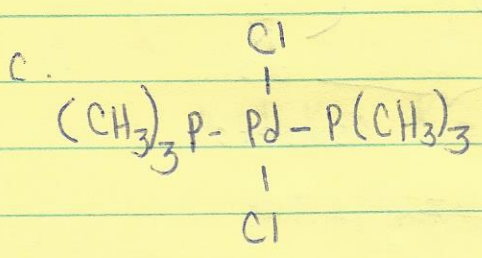
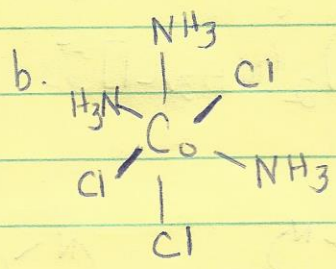
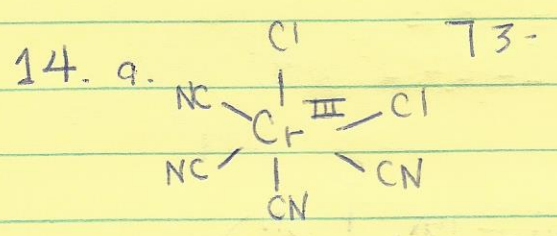
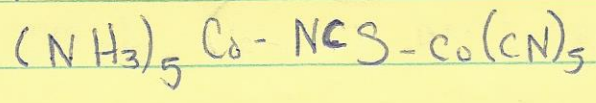
Optical isomers



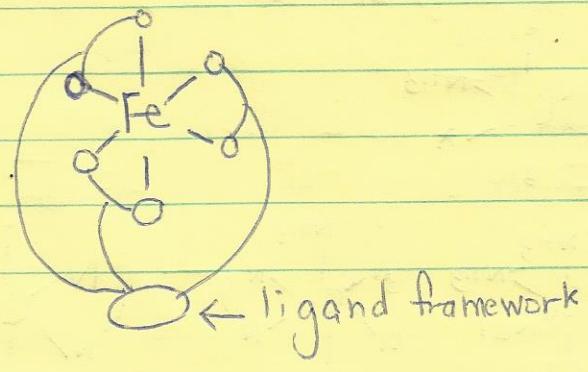
cis-NH₃
trans-Cl
(achiral)



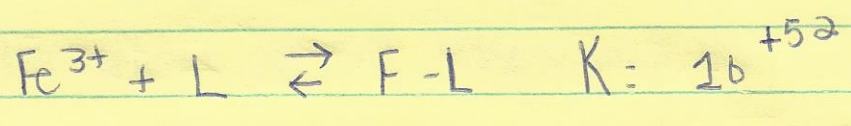
Since NH_3 is a hard ligand and CN^- is soft, and since N is hard and S is soft, the N should bond to the ammonia side because a hard-hard and a soft-soft interaction would result:



15. a. Enterobactin could coordinate Fe^{3+} as a hexadentate ligand through the phenolic oxygen



b. $[Fe-L] = 10^{-7} \text{ mol/L}$



$K = \frac{[Fe-L]}{[Fe^{3+}][L]}$

Easier to think of this as a dissociation.

	$Fe-L$	\rightleftharpoons	Fe^{3+}	+	L	$K = 10^{-52} = \frac{[Fe^{3+}][L]}{[Fe-L]}$
Initial	10^{-7}		0		0	
	-x		+x		+x	
Eq	$10^{-7} - x$		+x		+x	

$10^{-52} = \frac{x^2}{10^{-7} - x}$ Assume $x \ll 10^{-7}$

$10^{-52} = \frac{x^2}{10^{-7}} \quad x^2 = 10^{-59} \quad x = 3.16 \times 10^{-30}$

$[Fe^{3+}] = 3.16 \times 10^{-30} \frac{\text{mol}}{\text{L}}$

$1 \text{ Fe}^{3+} \text{ ion} \times \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ ion}} \times \frac{1 \text{ L}}{3.16 \times 10^{-30} \text{ mol}} = 52,530 \text{ L}$

MUY LOCO!!!
(CRAZY!!!)