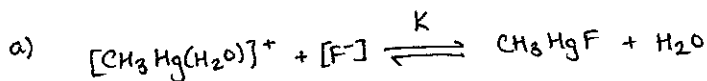


PROBLEM 1

PART A)



(7)
$$K_{eq7} = \frac{[CH_3HgF][H_2O]}{[CH_3Hg(H_2O)]^+[F^-]} = \underbrace{\left(\frac{[CH_3HgF][H_3O^+]}{[CH_3Hg(H_2O)]^+[HF]} \right)}_{K_{HF/CH_3Hg(H_2O)^+} \text{ eq 4}} \cdot \underbrace{\left(\frac{[HF][H_2O]}{[F^-][H_3O^+]} \right)}_{\frac{1}{K_{HF/H_2O}} \text{ eq 1}} = K_{eq1} \cdot \frac{1}{K_{eq1}} = \frac{4.5 \times 10^{-2}}{7.9 \times 10^{-4}} = 5.7 \times 10^1$$

this generally true for this

(8) $K_{eq8} = K_{eq5} \cdot \frac{1}{K_{eq2}} = \frac{1.8 \times 10^{12}}{1 \times 10^7} = 1.8 \times 10^5$

(9) $K_{eq9} = K_{eq6} \cdot \frac{1}{K_{eq3}} = \frac{4.2 \times 10^{15}}{1 \times 10^9} = 4.2 \times 10^6$

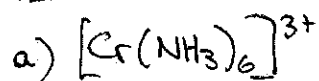
b) $K_{eq7} < K_{eq8} < K_{eq9}$ $K_I > K_{Br}$ since I^- even softer than Br^-
 Hg^{+2} soft better matched w/ larger softer anions meaning $Br > Cl > F$, which matches trend
 F^- hardest \therefore best solvated in aqueous environment $\therefore \Delta H_{soln} \Rightarrow F > Cl > Br$, which matches trend.

c) (i) $K_{eq10} = \frac{[CH_3HgBr][F^-]}{[CH_3HgF][Br^-]} = \underbrace{\left(\frac{[CH_3HgBr][H_2O]}{[CH_3Hg(H_2O)]^+[Br^-]} \right)}_{K_{eq9}} \cdot \underbrace{\left(\frac{[CH_3Hg(H_2O)]^+[F^-]}{[CH_3HgF][H_2O]} \right)}_{\frac{1}{K_{eq7}}} = \frac{K_{eq9}}{K_{eq7}} = 7.4 \times 10^4 = \left(\frac{4.2 \times 10^6}{5.7 \times 10^1} \right)$

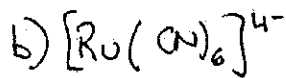
(ii) $K_{eq11} = \frac{[CH_3HgCl][Br^-]}{[CH_3HgBr][Cl^-]} = \underbrace{\left(\frac{[CH_3HgCl][H_2O]}{[CH_3Hg(H_2O)]^+[Cl^-]} \right)}_{K_{eq8}} \cdot \underbrace{\left(\frac{[CH_3Hg(H_2O)]^+[Br^-]}{[CH_3HgBr][H_2O]} \right)}_{\frac{1}{K_{eq9}}} = \frac{K_{eq8}}{K_{eq9}} = 4.3 \times 10^{-2} = \left(\frac{1.8 \times 10^5}{4.2 \times 10^6} \right)$

Problem 1 part B

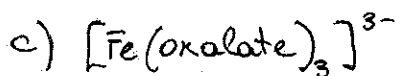
A



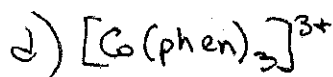
NH_3 is a stronger field ligand than H_2O as seen in the spectrochemical series



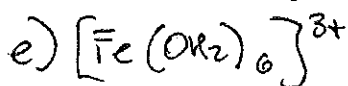
Ru is ~~low~~ below Fe in the periodic table - therefore it forms stronger bonds than Fe to ligands, and the d-d splitting will be larger as a consequence.



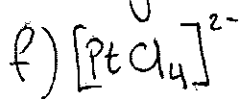
This is an octahedral complex, while $[\text{NiCl}_4]^{2-}$ is tetrahedral. The tetrahedral d-d splitting is much smaller than the octahedral one



phen is a stronger-field ligand than NH_3 due to its being a better π acceptor



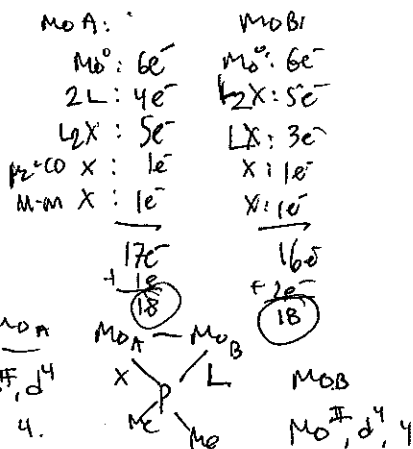
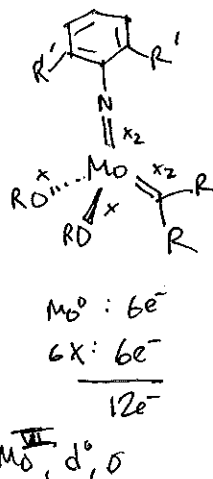
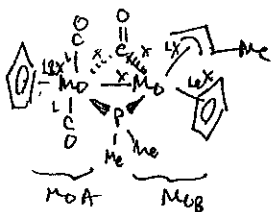
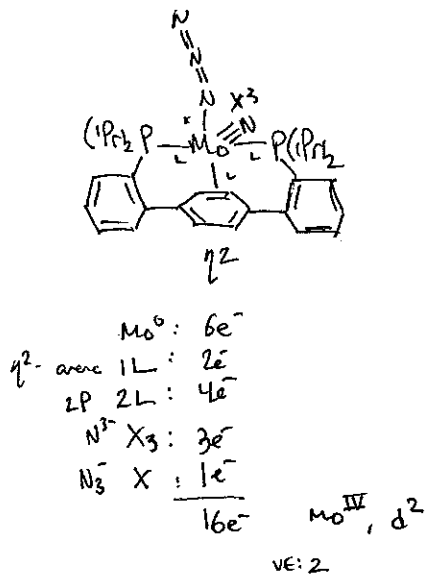
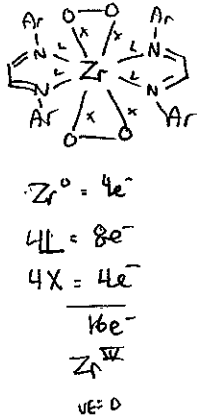
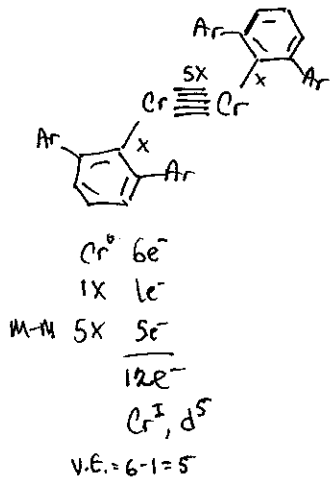
Iron in the higher oxidation state (III vs. II) has a larger d-d splitting due to stronger interaction with the ligand.



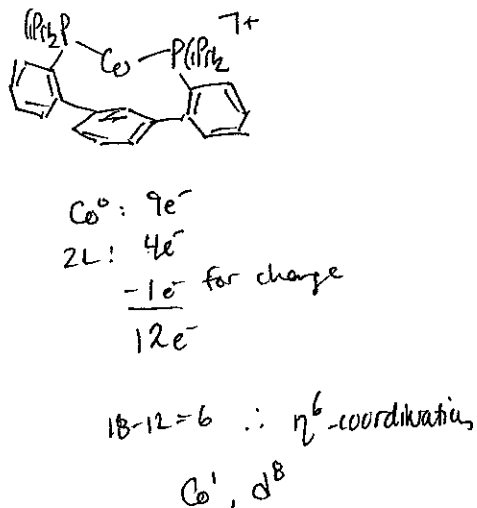
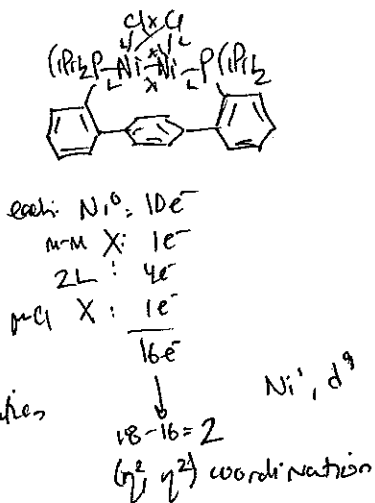
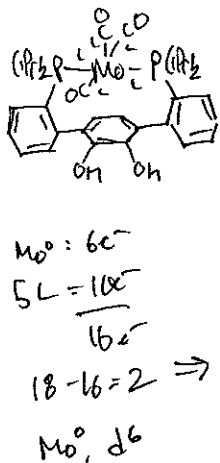
Pt is below Pd - same reasoning as in (b).

PROBLEM 2

PART A:

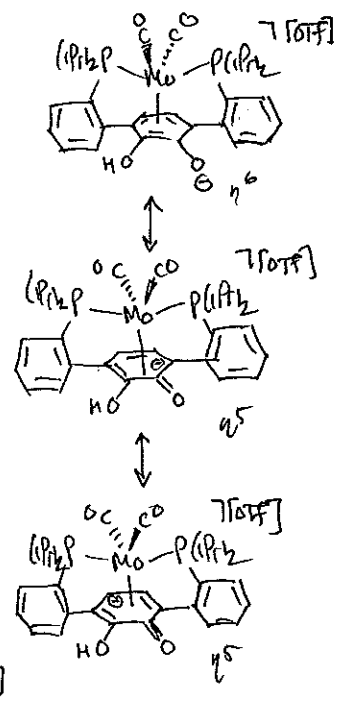
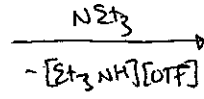
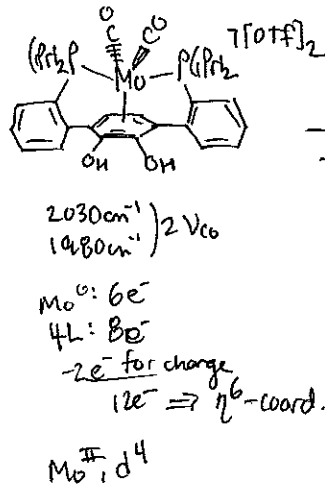
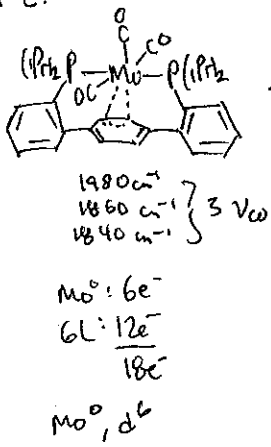


PART B

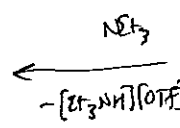
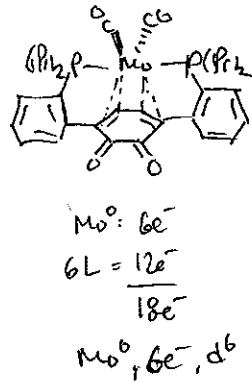


PART C:

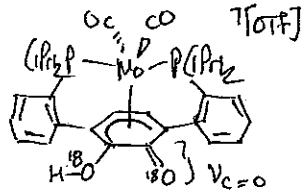
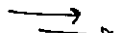
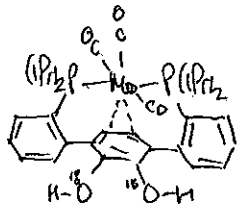
(i+ii)



$\text{Mo}^0: 6e^-$
 $7L: 14e^-$
 $-2e^-$
 $\frac{18e^-}{\text{Mo}^{\text{II}}}$
 $\nu_{\text{CO}}: 1940\text{cm}^{-1}$
 1920cm^{-1}
 $\nu_{\text{C=O}}: 1620\text{cm}^{-1}$



iii)

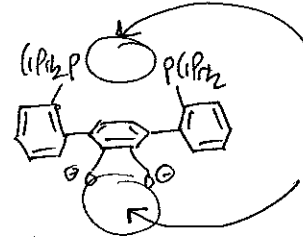


ν_{CO} : not affected
 significant $\begin{matrix} 1940\text{cm}^{-1} \\ 1920\text{cm}^{-1} \end{matrix}$

$$\mu = \frac{M_a A_b}{(M_a + M_b)} \quad \nu_{\text{C=O}} = \sqrt{\frac{M_{\text{C=O}}}{M_{\text{C}}}} = \sqrt{\frac{17.999}{12}} = 1.024 \frac{\nu_{\text{C=O}}}{\nu_{\text{C=O}}}$$

$$\nu_{\text{C=O}} = \frac{\nu_{\text{C=O}}}{1.024} = 1620\text{cm}^{-1}$$

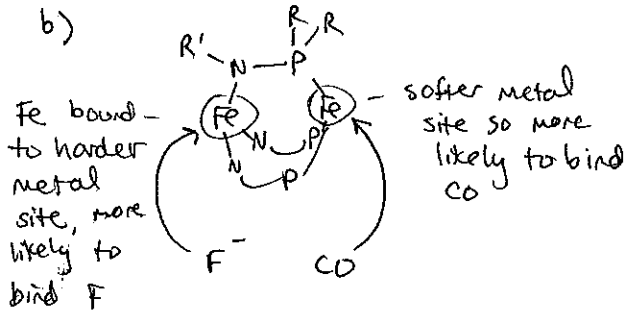
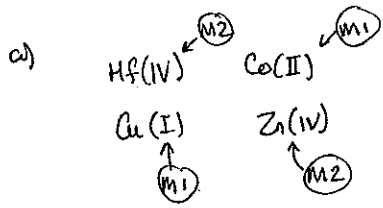
iv)

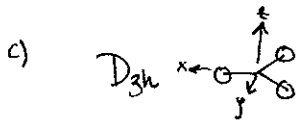


Pd^0 - soft phosphine and arene binding
 AlEt_3 - hard Lewis acid prefers dianionic oxygen pocket.

$\approx 1582.0\text{cm}^{-1}$

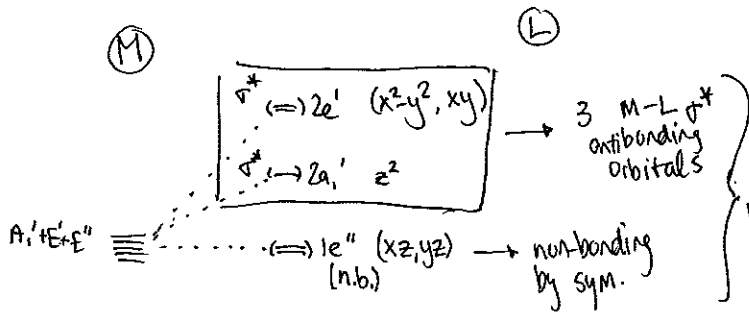
PROBLEM 3





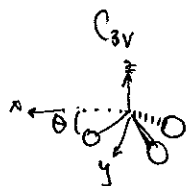
- σ -sym. ligand orbitals transform as A_1' and E'

- M-d-orbitals transform as A_1', E', E''
 $z^2 \downarrow (xz, yz)$
 (x^2-y^2, xy)



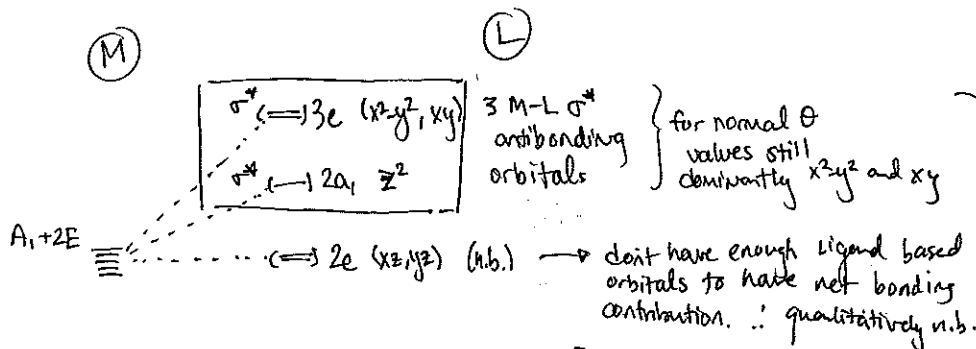
limited to using M d-orbitals, not s and p orbitals

for most metal complexes, these orbitals are the most important as they represent the FMO's of most metal complexes

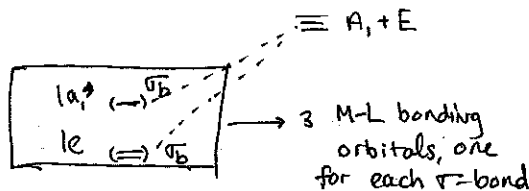


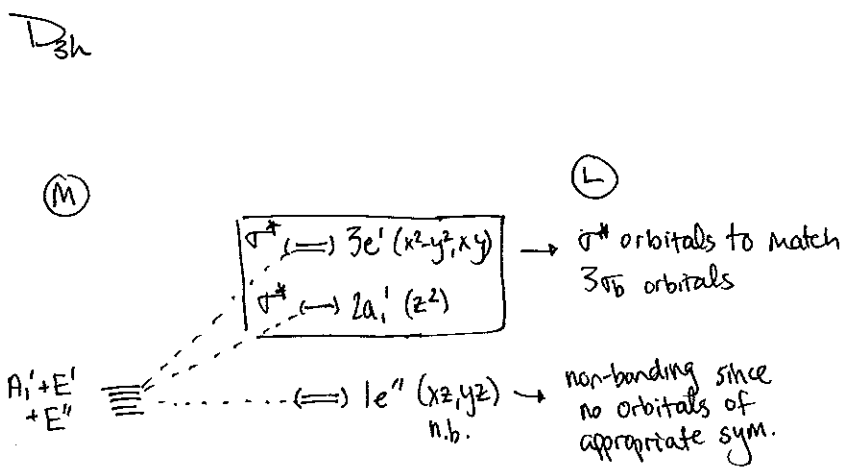
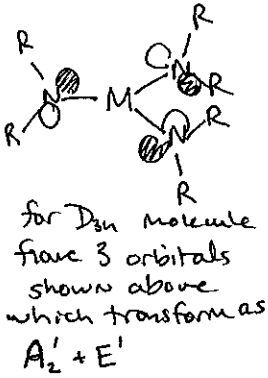
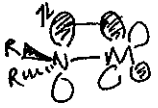
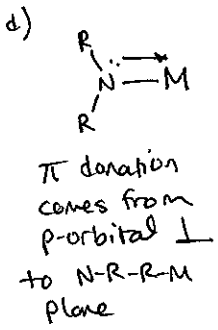
- σ -sym ligand orbitals transform as E and A_1

- M d-orbitals transform as $A_1 + 2E$

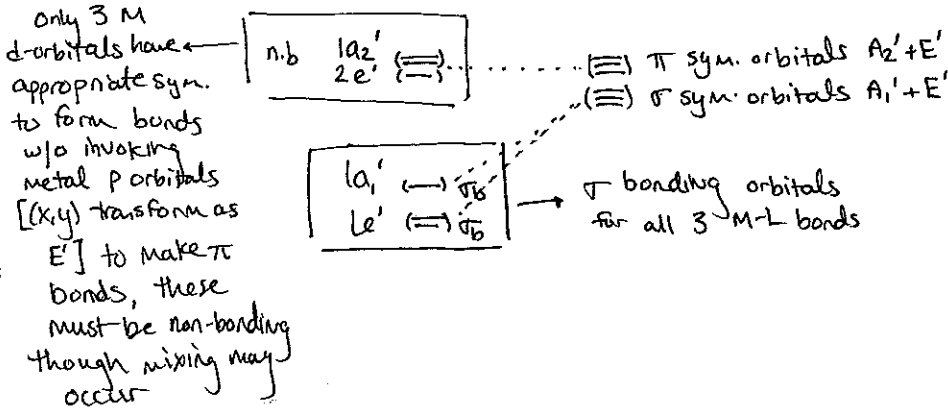


for normal θ values still dominantly x^2y^2 and xy

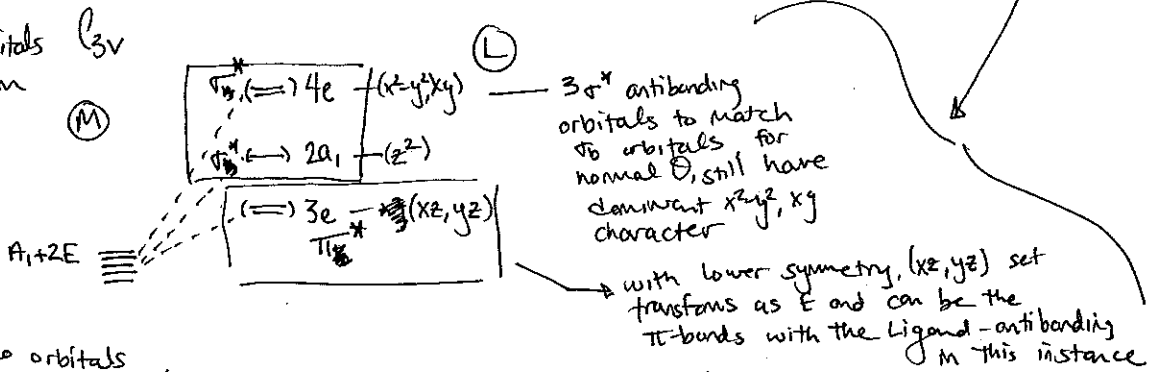




FMOs important to d-orbital splitting diagram



in C_{3v} , π sym. orbitals of ligand transform as $E + A_2$



no orbitals of same sym. to mix with

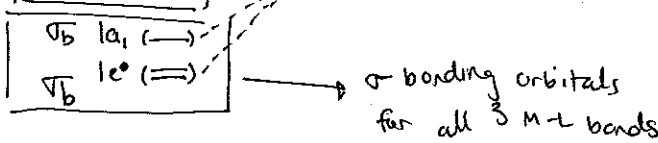
n.b. $\rightarrow 1a_2' (e')$

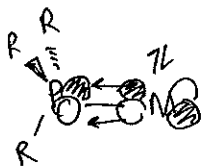
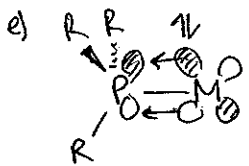
$\pi_b 2e' (e')$

π -sym. orbitals $A_2 + E$

σ sym. orbitals $A_1 + E$

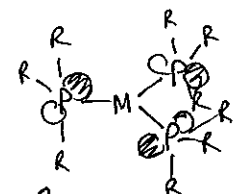
in C_{3v} sym have appropriate sym. to make 5 ~~max~~ M-L bonds ($3\sigma + 2\pi$) \therefore unlike D_{3h} where p-orbitals are needed for π -bonds, can have max B.O. of 5 with just d-orbitals



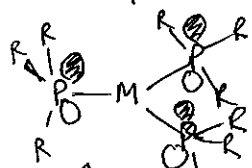


phosphine can act as a π -acid in two orthogonal directions (shown above)

Therefore must consider P-based orbitals as shown below

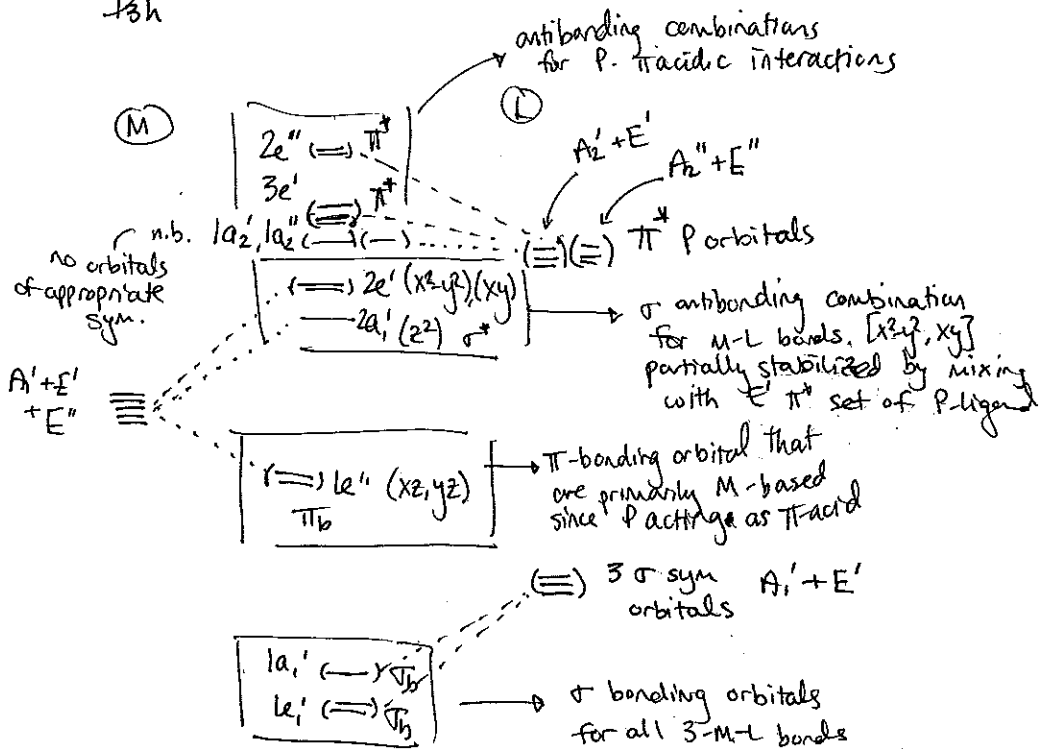


transforms as $A_1' + E'$



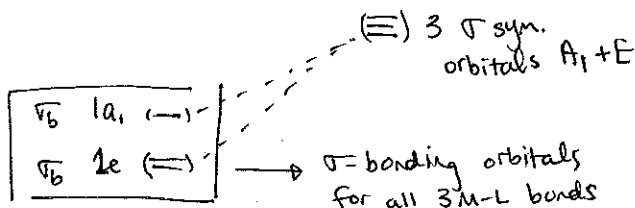
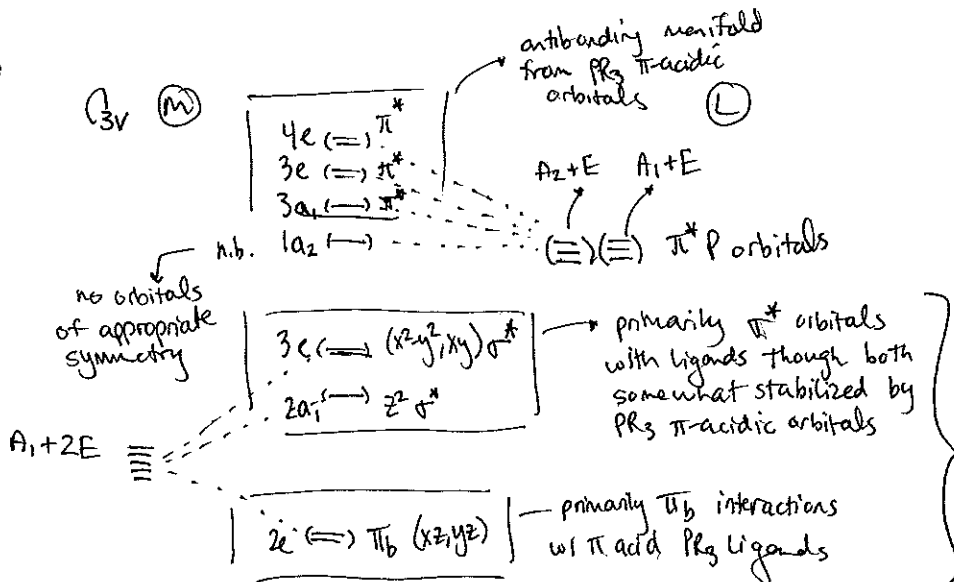
transforms as $A_2'' + E''$

D_{3h}

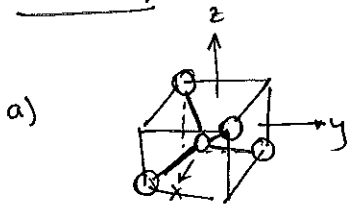


FNOS important to d-orbital splitting diagram

D_{3v}

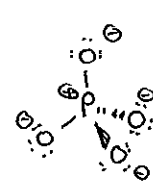
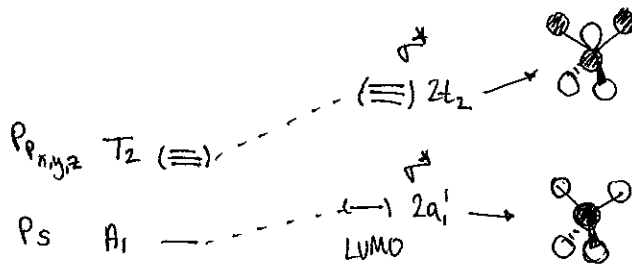


PROBLEM 4



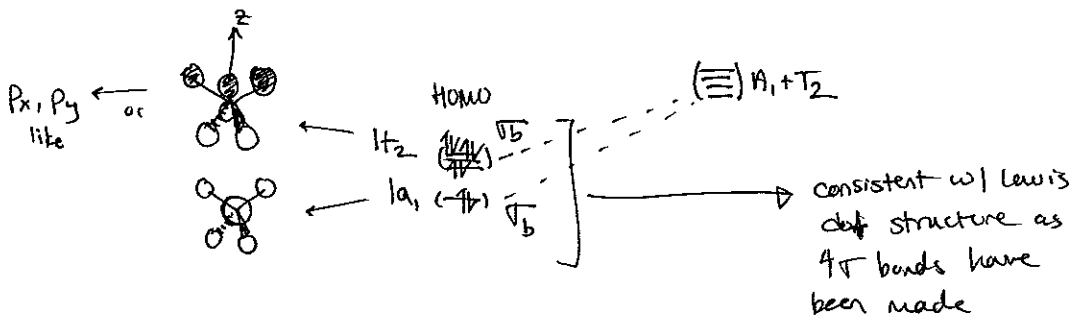
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
Γ_{40}	4	1	0	0	2	$\Rightarrow A_1 + T_2$
Γ_M	$A_1 + T_2 + E + T_2$					
	s	3p orbitals	(z^2, x^2-y^2)	(xz, yz, xy)		
Γ_P	$A_1 + T_2$					
	s	3p orbitals				

b) PO_4^{3-} - P-only



73-

think Lewis dot structure. Expect 4 σ bonds

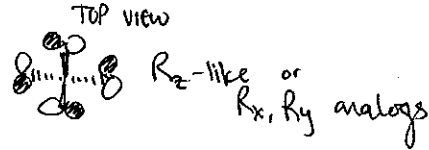
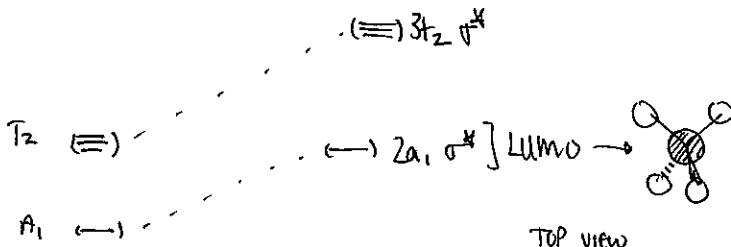


c)

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
$\Gamma_{\text{oxygen } p_{x,y}}$	8	-1	0	0	0	$= T_1 + T_2 + E$

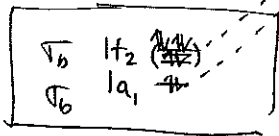
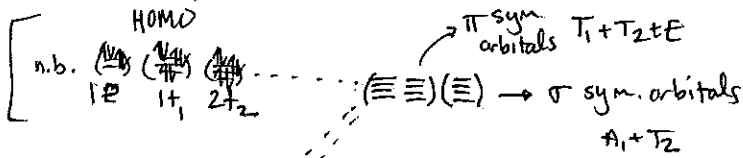
d)

(P)



12 pairs of e^-

oxygen-based lone pairs. $2t_2$ is net non-bonding since only 3 T_2 sym. bonds can be formed because P only has one T_2 set. Consequently π bonding comes at the expense of σ -bonding

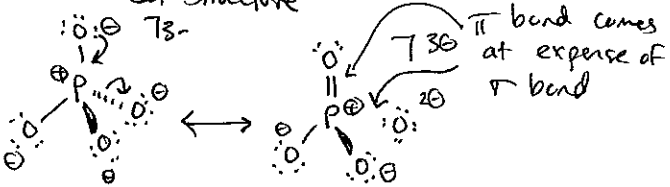


orbitals contributing to σ -bonding framework has contribution from $2t_2$ π -sym. orbitals, but still dominated by σ -bonding picture

(by this count 4 σ sym. orbitals for $4 \times 2 e^-$ total of 8e)

can make π -bonds or σ bonds but can't have both since only one t_2 set can be bonding energywise.

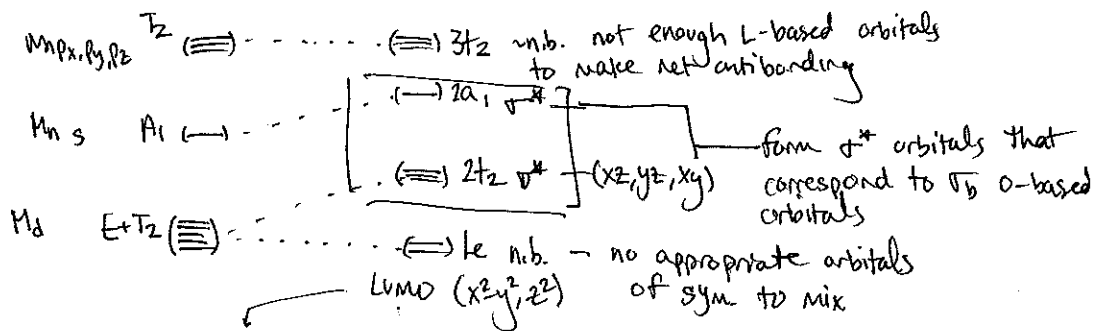
\Rightarrow consistent w/ Lewis dot structure



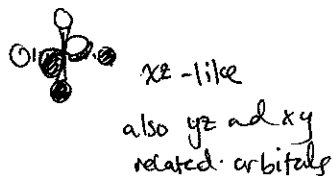
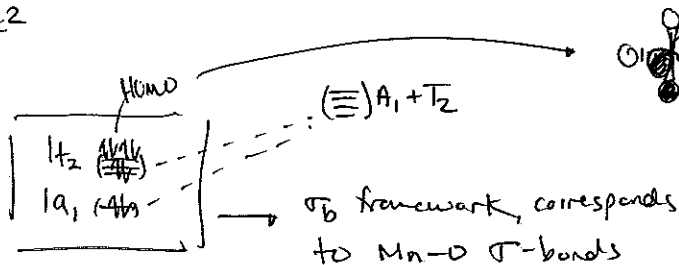
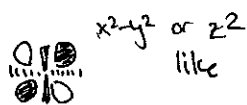
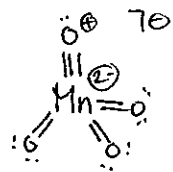
e) MnO_4^-

σ -only

Mn

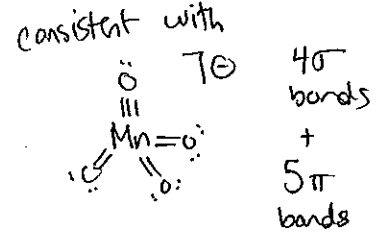
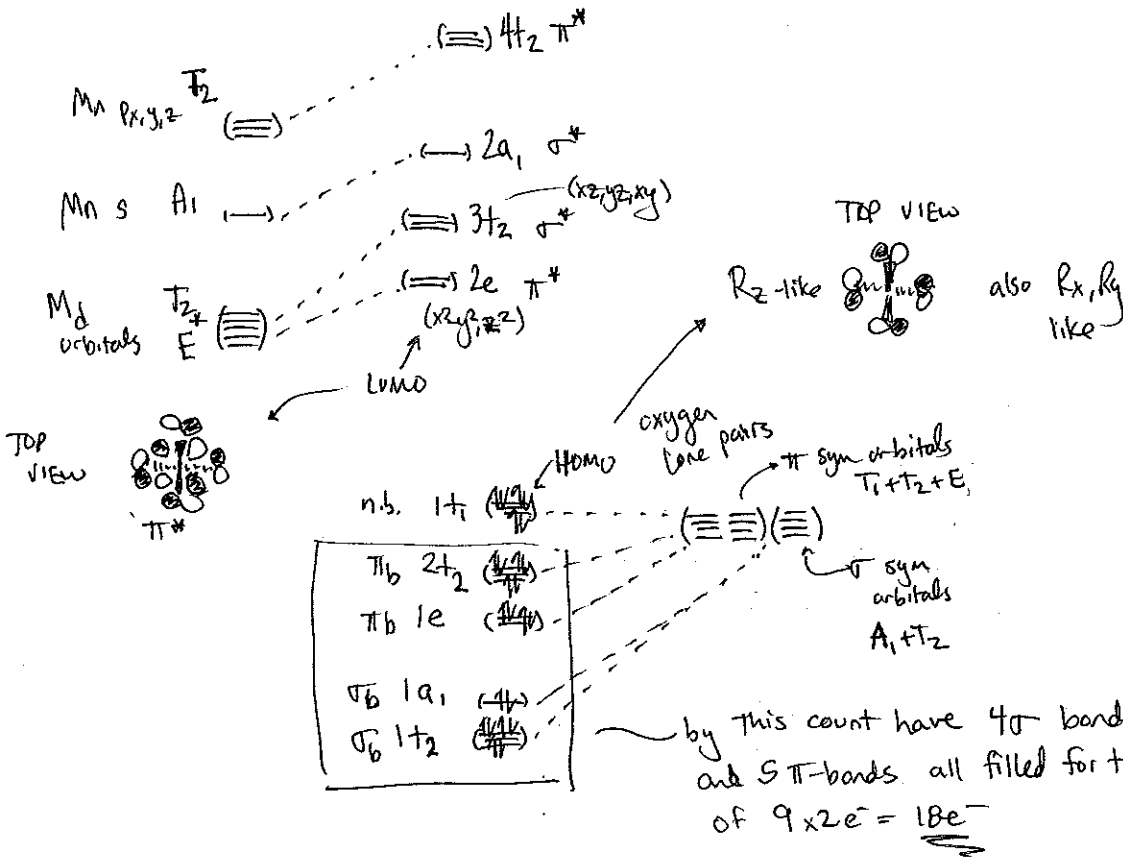


Lewis dot structure of MnO_4^-



f) π -sym allowed MnO_4^-

Mn



by this count have 4 σ bonds and 5 π -bonds all filled for total of $9 \times 2e^- = 18e^-$

g) PO_4^{3-} have 4 σ bonding orbitals for total of $8e^-$ shared at P valence shell $\therefore 8e^-$ which is consistent with octet rule.

no also consistent with resonance structure that obeys octet rule

MnO_4^- have 4 σ bonding and 5 π bonding orbitals for total of $18e^-$ in valence shell $\therefore 18e^-$ is consistent w/ $18e^-$ rule for metal complexes

no also consistent w/ Lewis dot structure.