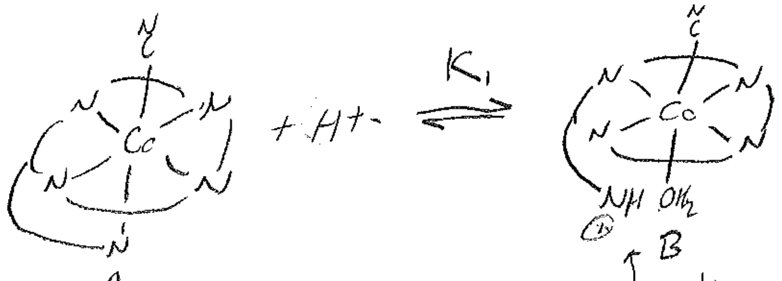
#1

a)



A + H^+ $\overset{K_1}{\rightleftharpoons}$ B

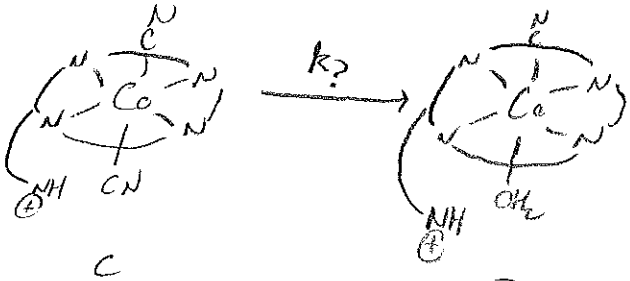
$pK_a = 0.38$ (B)

$K_a = 10^{-0.38} = 0.417\ M$

$$\boxed{K_1 = K_a^{-1} = \frac{1}{0.417M} = 2.40\ M^{-1}}$$

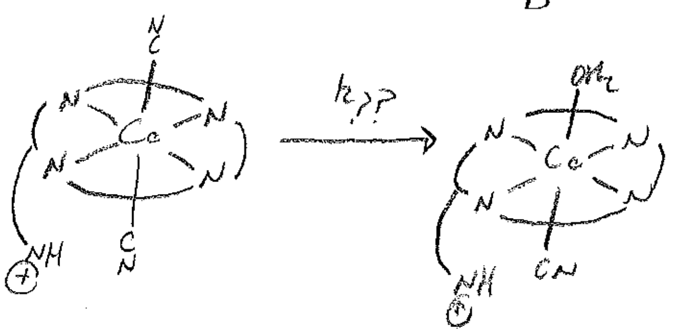
$$K_1 = \frac{[B]}{[A][H^+]} \qquad K_a = \frac{[A][H^+]}{[B]}$$

b)



C $\xrightarrow{k?}$ B

C → B IN SCHEME 1 IS k_{-2}



C $\xrightarrow{k??}$ D

C → D IN SCHEME 1 IS k_3

$$\boxed{k_{ov} = k_{-2} + k_3}$$

c) $0.042\ s^{-1} = k_{-2} + k_3$

RATIO OF B AND D REFLECTS RATIO OF k_{-2} AND k_3

$$\frac{B}{D} = 0.53 = \frac{k_{-2}}{k_3} \qquad k_{-2} = 0.53\ k_3$$

$0.042\ s^{-1} = 0.53 k_3 + k_3$ $\boxed{k_3 = 0.027\ s^{-1} \text{ AND } k_{-2} = 0.015\ s^{-1}}$

d)

$rate_d = k_3[C]$

$rate_c = 0 = k_2[B][CN] - k_{-2}[C] - k_3[C]$;

$$[C] = \frac{k_2[CN]}{k_{-2}+k_3}[B]$$

$$rate_d = \frac{k_3 k_2 [CN]}{k_{-2}+k_3}[B] \qquad \boxed{k_f = \frac{k_3 k_2 [CN]}{k_{-2}+k_3}}$$

d cont

$rate_b = k_{-2}[C]$

$rate_c = 0 = k_{-3}[CN][D] - k_3[C] - k_{-2}[C]$

$$[C] = \frac{k_{-3}[CN]}{k_3 + k_{-2}}[D]$$

$$rate_b = \frac{k_{-3}k_{-2}[CN]}{k_3 + k_{-2}}[D]$$

$$\boxed{k_r = \frac{k_{-3}k_{-2}[CN]}{k_3 + k_{-2}}}$$

e) k_{obs} vs $[CN]$ slope is $2.83 \times 10^6\ s^{-1}M^{-1}$

$$\text{slope} = \frac{k_{-3}k_{-2}}{k_{-3}+k_{-2}} + \frac{k_3 k_2}{k_{-2}+k_3}$$

$$2.83\times10^6 = \frac{k_{-3}(0.015)}{(0.027+0.015)} + \frac{(0.027)k_2}{(0.027+0.015)}$$

$$2.83\times10^6 = \frac{(0.015)k_{-3} + (0.027)k_2}{0.042}$$

$$1.19\times10^5 = 0.015\,k_{-3} + 0.027\,k_2$$

and $K_{23} = \frac{k_f}{k_r} = 2.7$

$$2.7 = \frac{\frac{k_3 k_2[CN]}{k_{-2}+k_3}}{\frac{k_{-3}k_{-2}[CN]}{k_3+k_{-2}}} = \frac{k_3 k_2}{k_{-3}k_{-2}}$$

$$2.7 = \frac{(0.027)\,k_2}{k_{-3}\,(0.015)}$$

$$\frac{(2.7)(0.015)}{(0.027)}k_{-3} = k_2$$

$$1.5\,k_{-3} = k_2$$

$$1.19\times10^5 = 0.015\,k_{-3} + (0.027)(1.5)k_{-3}$$

$$1.19\times10^5 = 0.0555\,k_{-3}$$

$$\boxed{2.14\times10^6 = k_{-3}\ (s^{-1}M^{-1})}$$

$\Rightarrow$ $1.5(2.14\times10^6) = k_2$

$$\boxed{k_2 = 3.2\times10^6\ M^{-1}s^{-1}}$$

$$K_3 = \frac{k_3}{k_{-3}} = \frac{0.027\ s^{-1}}{2.14\times10^6\ M^{-1}s^{-1}}$$

$$\boxed{K_3 = 1.26\times10^{-8}\ M}$$

$$K_2 = \frac{k_2}{k_{-2}} = \frac{3.6\times10^6\ M^{-1}s^{-1}}{0.015\ s^{-1}}$$

$$\boxed{K_2 = 2.4\times10^8\ M^{-1}}$$

f) $[A] = 5\,mM$

$K_1 = \frac{[B]}{[A][H^+]}$ $\quad [B] = K_1[A][H^+]$ $\quad [B] = (2.4)(0.005)(10^{-2}) = 0.00012\,M$

$K_{23} = \frac{[D]}{[B]}$ $\quad [D] = K_{23}[B]$ $\quad [D] = 2.7[B]$

$[D] = 0.000324$

$K_2 = \frac{[C]}{[B][CN]}$

$[C] = K_2 K_1 [A][H^+][CN]$

$[C] = (2.4\times10^{8}\,M^{-1})(2.40\,M^{-1})[0.005\,M][10^{-2}\,M][10^{-8}\,M]$

$= 0.0288 \times 10^{-2}\,M$

$= 2.9\times10^{-4}\,M$

$\frac{[C]}{[A]+[B]+[C]+[D]} = \frac{2.9\times10^{-4}\,M}{5.7\times10^{-3}\,M} = 4.7\%$ AUTHORS STATES THIS VALIDATES S.S. APPROXIMATIO[N]

g) ^-CN EXERTS A STRONGER TRANS EFFECT THAN OH_2 FACILITATING SUBSTITUTION FROM DICYANOCOBALAMIN SPECIES

PROBLEM 2

a) $[Cr(OH_2)_5NCS]^{2+} + [V(OH_2)_6]^{2+} \xrightarrow[-NCS]{H_2O} [Cr(OH_2)_6]^{2+} + [V(OH_2)_6]^{3+}$

$Cr^{III}\ d^3$ $\quad V^{II}\ d^3$ $\quad Cr^{II}\ d^4$ $\quad V^{III}\ d^2$

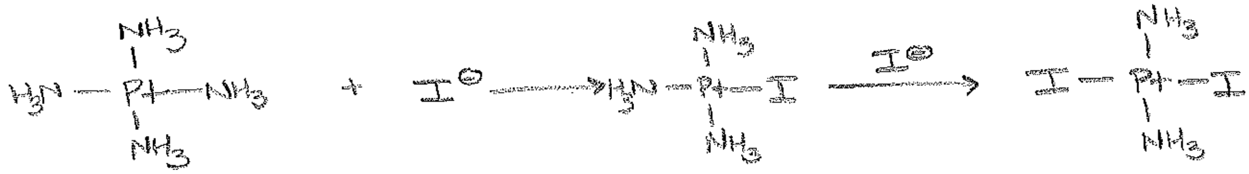
b&c) $k_{obs} = k_1 + \frac{k_2}{[H^+]}$

- $k_1 = 4.0\times10^{-5}\,M^{-1}s^{-1}$
- $k_2 = 3.7\times10^{-4}\,s^{-1}$ ← FROM SLOPE OF k_{obs} VS $\frac{1}{[H^+]}$ PART b)
- → SLOPE PART a)

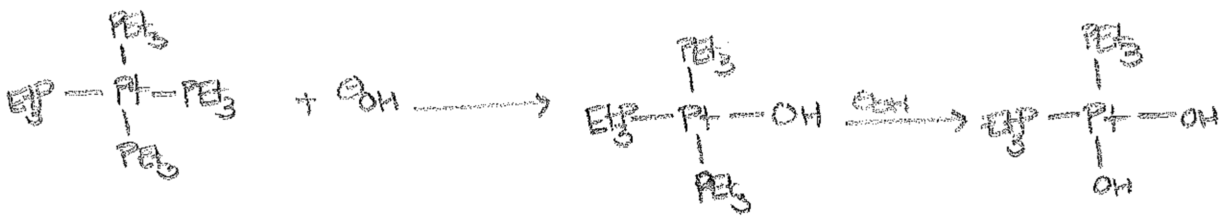
4.1×10^{-4}
$-\,3.7\times10^{-4}$
$\sim 4.0\times10^{-5} = k_1$

d) N IS A HARD BASE WHEREAS S IS A SOFT BASE. N-BOUND NCS^- THEREFORE MATCHES V^{2+} (HARD ACID) BETTER THAN S-BOUND SCN^-, STABILIZING $[V(H_2O)_5NCS]^{2+}$ RELATIVE TO $[V(H_2O)_5SCN]$

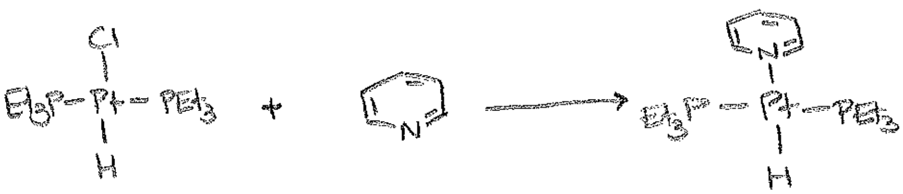
PART 2



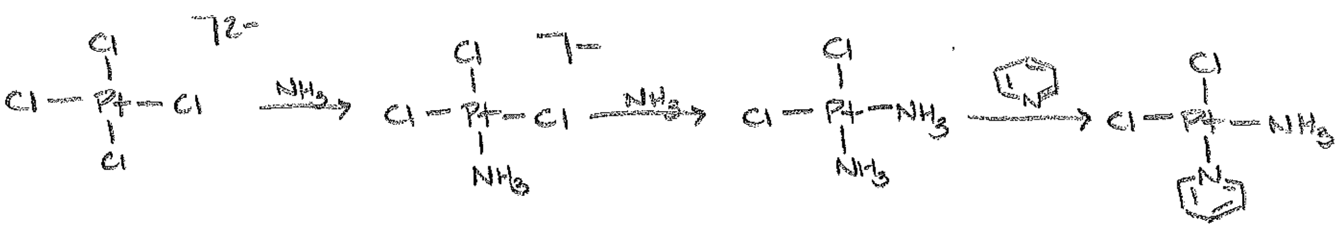
$I^{\ominus}$ EXERTS A STRONGER TRANS EFFECT THAN NH_3



PEt_3 EXERTS A STRONGER TRANS EFFECT THAN $^{\ominus}OH$

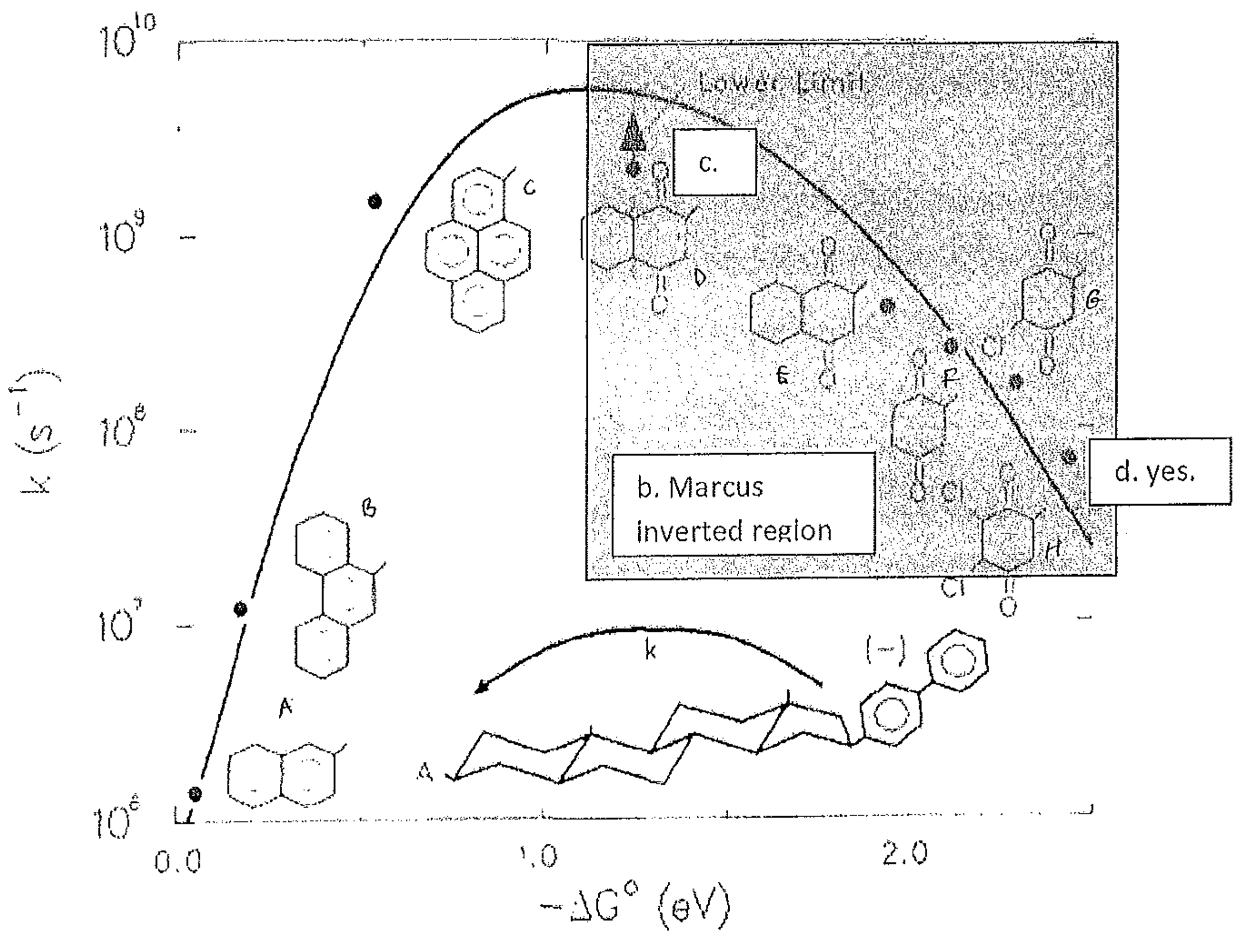


$H^{\ominus}$ EXERTS A STRONGER TRANS EFFECT THAN Cl



$Cl^{\ominus}$ STRONGER TRANS EFFECT THAN NH_3

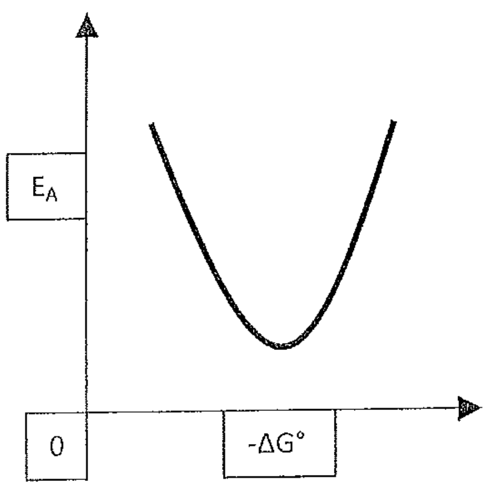
Problem 3



10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
k (s⁻¹)
Lower Limit
c.
d. yes.
b. Marcus inverted region
A
B
C
D
E
F
G
H
k
(–)
0.0
1.0
2.0
–ΔG° (eV)

a.

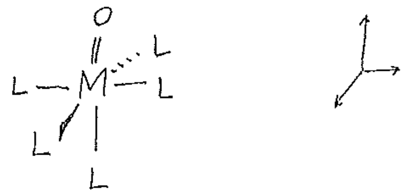
e.



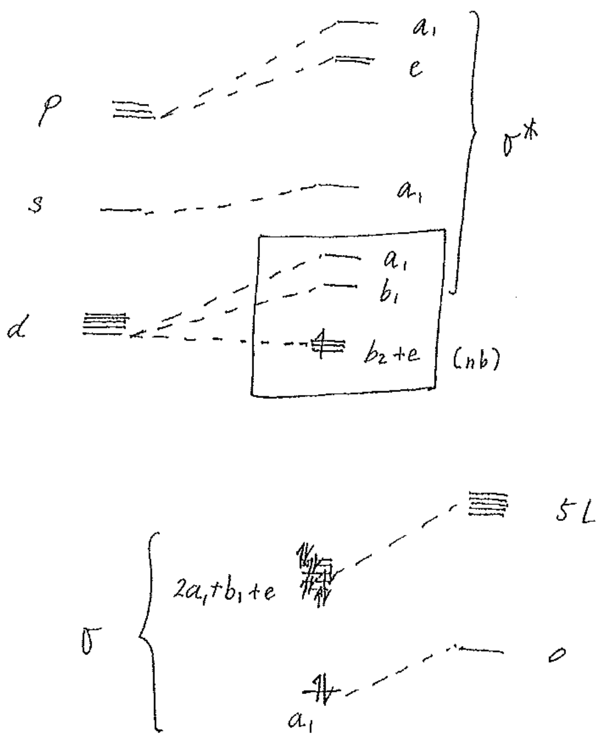
E_A
0
-ΔG°

Problem 4

1)



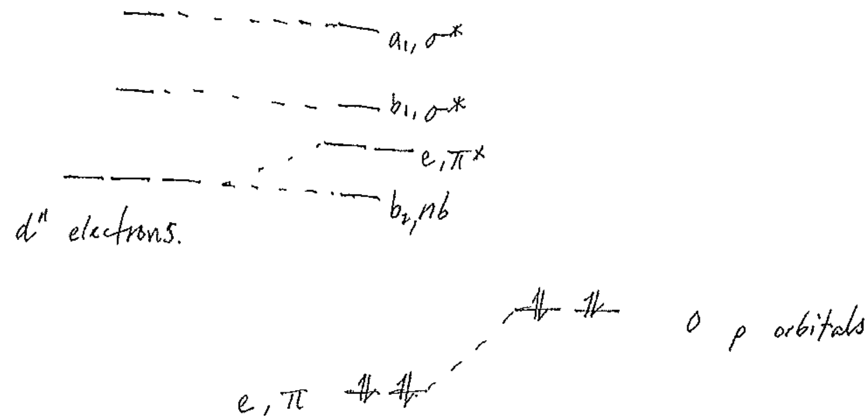
C_{4v}

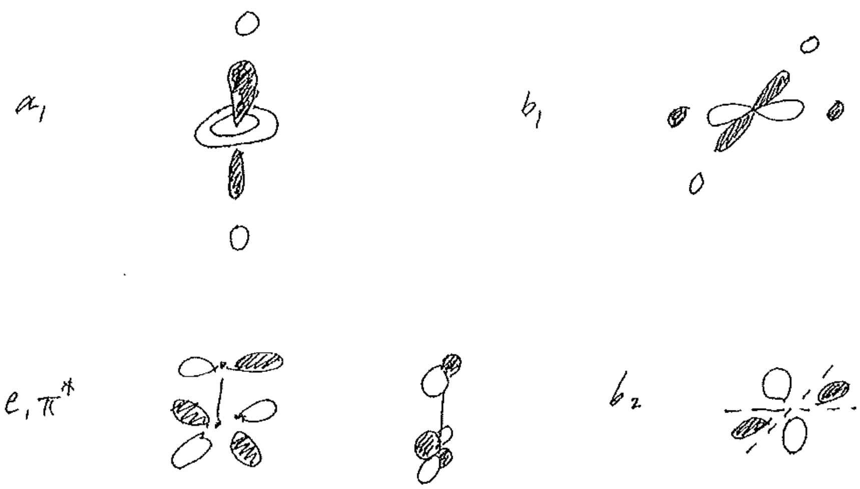


2) $(b_2+e) \longrightarrow b_1$

$(b_2+e) \longrightarrow a_1$

3)





4)

$[VOL_5]^{3+} \longrightarrow V^{5+} \longrightarrow d^0$ BO = 3

$[CrOL_5]^{3+} \longrightarrow Cr^{5+} \longrightarrow d^1$ BO = 3

$[MnOL_5]^{3+} \longrightarrow Mn^{5+} \longrightarrow d^2$ BO = 3

$[MnOL_5]^{2+} \longrightarrow Mn^{4+} \longrightarrow d^3$ BO = 2.5

$[FeOL_5]^{2+} \longrightarrow Fe^{4+} \longrightarrow d^4$ BO = 2

5) $Fe^{IV}-O$ B.O = 2

$V^{IV}-O$ B.O. = 3

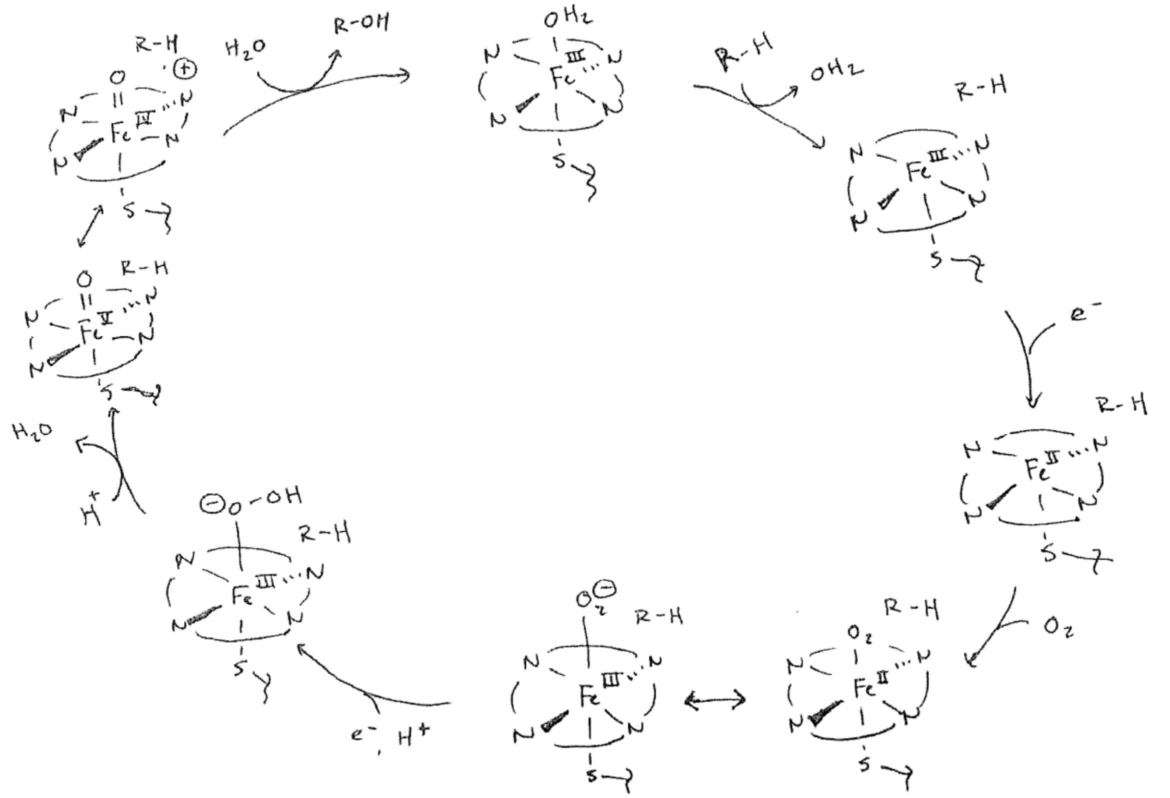
Hence, the $Fe^{IV}-O$ bond is more reactive and the oxygen atom is more basic.

6) $CoOL_5^{?2+} \longrightarrow d^5 \longrightarrow$ B.O = 1.5

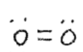
the oxo group becomes too basic and hence is very reactive. Bridging oxo species are more common for Co.

Problem 5.

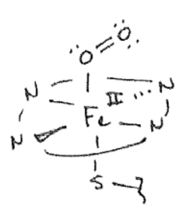
1.)



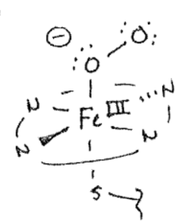
2.) O_2 $6(2) = 12\ e^-$



3.)

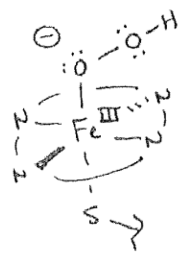


4.)



Note that this (-) charge is implicit much like the charge on any "X-type" ligand. However, for the purpose of following the flow of electrons around the cycle, drawing it explicitly can be helpful.

5.) Superoxide (O_2^-)

6.) 

7.) Hydroperoxide (HOO^-)

8.) NADPH is the ultimate e^- source for cytochrome P450