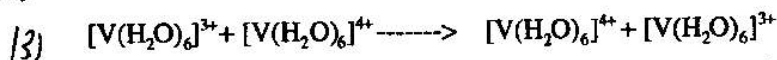
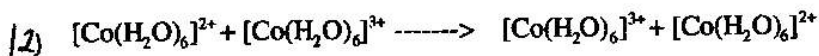
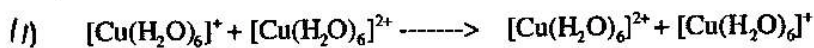


# Chem 450 Exam 3

Name Key

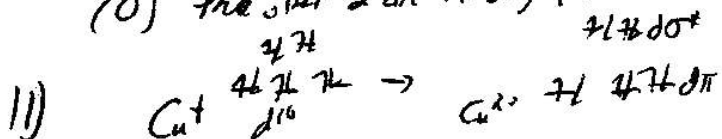
(1)(30 points) Place the following outer sphere electron transfer reactions in order from slowest to fastest. Explain your reasoning.



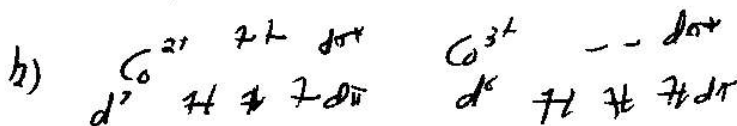
Factors that affect outer sphere  $e^-$  transfer rate include

$\Delta G_{\text{rxn}}$ ,  $\Delta G_{\text{inner}}^\ddagger + \Delta G_{\text{outer}}^\ddagger$ . Since  $\Delta G_{\text{rxn}}$  is the same for all of these

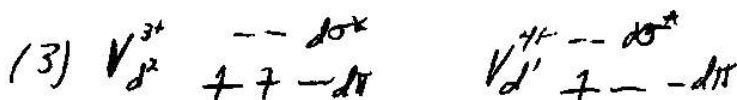
(0) the other 2 are the only factors.



This  $e^-$  transfer results in the addition or removal of an  $e^-$  from an antibonding orbital. This should result in a large  $\Delta G_{\text{inner}}^\ddagger$  (lots of bond length changes).



This  $e^-$  transfer results in a high spin to low spin transition resulting in a change of 2  $e^-$  in the  $d_{\text{orb}}$ . This should have a very large  $\Delta G_{\text{inner}}^\ddagger$ .

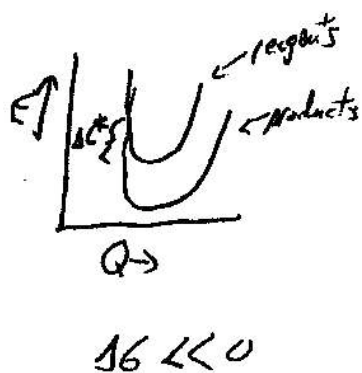
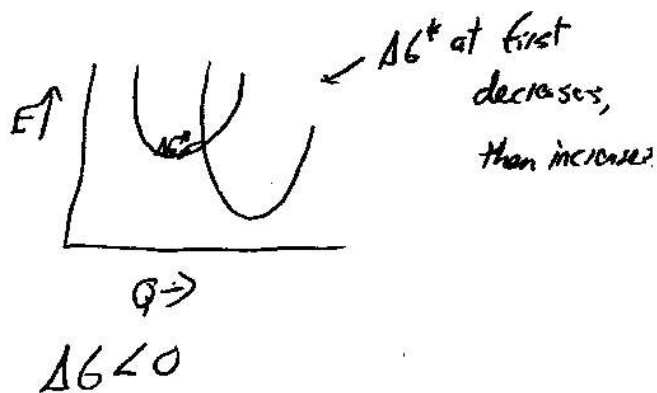
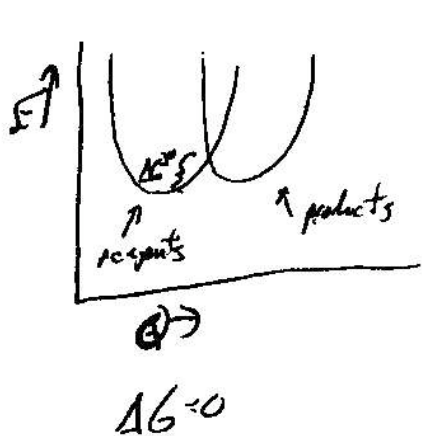
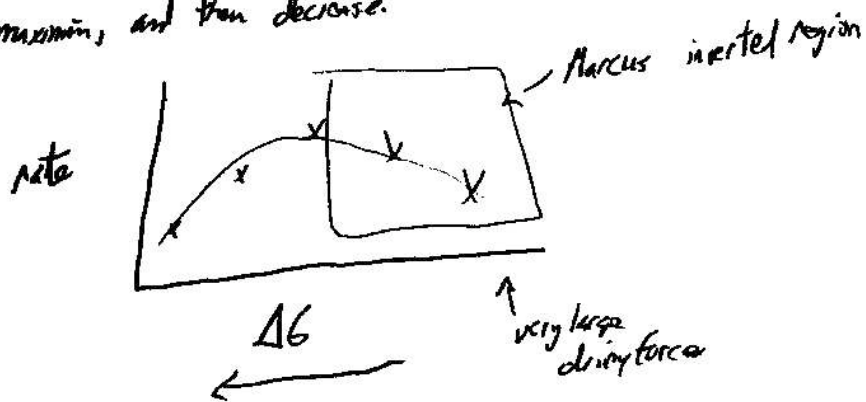


This changes the  $e^-$  count in the  $d_{\text{orb}}$  (nonbonding) set only. It should not result in much of a bond length change. Small  $\Delta G_{\text{inner}}^\ddagger$ .

$\therefore 2 < 1 < 3$

(2)(20 points) What is the Marcus inverted region and under what conditions is it observed?

as  $\Delta G$  decreases, electron transfer rates increase, reach a maximum, and then decrease.



(3)(30 points) Use ligand field theory and hard and soft acid base theory (separately) to explain why CO binds well to low valent transition metals such as  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  but do not bond well to high valent early transition metals such as  $\text{Sc}^{3+}$ . What type of bonding is this (explain with ionic/covalent and hard-soft acid base arguments)?

$$\text{CO } \chi = 7.9 \quad \text{Fe}^{2+} \chi = 7.3 \quad \text{Mn}^{2+} \chi = 9.3$$

$$\text{Sc}^{3+} \chi = 29.6$$

$\text{Sc}^{3+}$  is a hard acid,  $\text{Fe}^{2+}$  +  $\text{Mn}^{2+}$  are soft acids  
 CO is a soft base, so it should bind more strongly to  
 the soft acids like  $\text{Fe}^{2+}$  +  $\text{Mn}^{2+}$  than the hard acids such as ~~the~~  $\text{Sc}^{3+}$ .

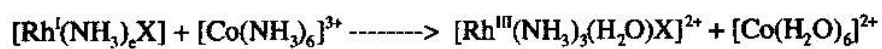
Soft acids always form covalent bonds well and hard acids + bases  
 form strong ionic bonds.

CO will form covalent bonds (bind to soft acids).

High valent early transition metals have very few d-electrons  
 (low  $\epsilon$  density) therefore backbond poorly. CO ~~very~~ does not  
 bond strongly to a metal unless it can back bond.

Metals such as  $\text{Fe}^{2+}$  +  $\text{Mn}^{2+}$  have quite a bit of d-electron  
 density & can backbond well.

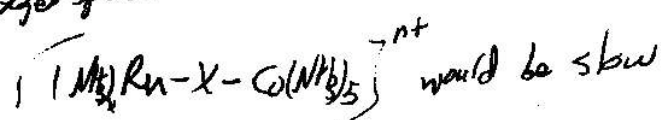
(4)(20 points) Do you think the following is an inner sphere or outer sphere electron transfer reaction? Explain your answer.



↑

X	relative rate
Cl <sup>-</sup>	4
CN <sup>-</sup>	9
Ph <sup>-</sup>	2
I <sup>-</sup>	7

1) Co<sup>3+</sup> is inert, it substitutes slowly, so the formation of a bridged species



2) Ph<sup>-</sup> cannot bridge  $\text{Ph}-\text{C}_6\text{H}_5$ , and the rate of e<sup>-</sup> transfer with X=Ph<sup>-</sup> & X=bridging ligands is ~ the same.

It is outer sphere.

(6)(16 points) Which of the following are acids? Which are bases? Which definition(s) of acid or base apply(ies)?

(a)  $\text{Fe}^{2+}$  acid, Lewis acid, Arrhenius acid

(b)  $\text{NH}_3$  Arrhenius, Lewis, Brønsted-Lowry, Arrhenius base

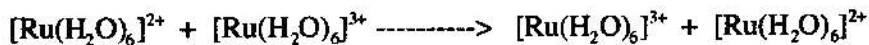
(c)  $\text{SO}_3$  <sup>Arrhenius</sup> Lux-Flood, Lewis acid

(d)  $\text{BF}_3$  Lewis base, Arrhenius base

✓ (30 points) The outer sphere electron transfer reaction:



is 200 times faster than a similar outer sphere electron transfer reaction



Using the factors for the activation energy for the above reactions, explain this difference.

In both, the metal & oxidation states are the same.

$$\Delta G^\ddagger = \Delta G_{\text{coulomb}}^\ddagger + \Delta G_{\text{inner}}^\ddagger + \Delta G_{\text{outer}}^\ddagger$$

Since the ox states are the same (+ charges)  $\Delta G_{\text{coulomb}}^\ddagger$  should be ~ the same

Same in both it is a  $\text{Ru}^{2+} \rightleftharpoons \text{Ru}^{3+}$  transition,  $\Delta G_{\text{inner}}^\ddagger$  should be similar.

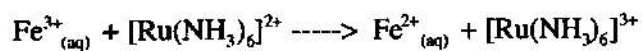
$\text{Ru}-\text{NH}_3$  &  $\text{Ru}-\text{OH}_2$  groups should have a different interaction with the solvent, however.  $\text{OH}_2$  can act as both an H-bond donor & acceptor

while  $\text{NH}_3$  can only be an acceptor as a ligand. It should take more

energy to rearrange the  $[\text{Ru}(\text{H}_2\text{O})_6]^{n+}$  outer sphere interactions

i.e.  $\Delta G_{\text{outer}}^\ddagger$  should be highest &  $[\text{Ru}(\text{H}_2\text{O})_6]^{2+/3+}$  rxn should be slower

Ⓞ (20 points) Calculate  $k_{12}$  for the following reaction



Self-exchange rates for the oxidant and reductant are  $4.2 \text{ M}^{-1}\text{s}^{-1}$  and  $4000 \text{ M}^{-1}\text{s}^{-1}$ .  $K_{12} = 2.0 \times 10^{11}$  and  $f_{12} = 0.85$ .

$$k_{12} = \sqrt{k_1 k_2 K_{12} f_{12}}$$

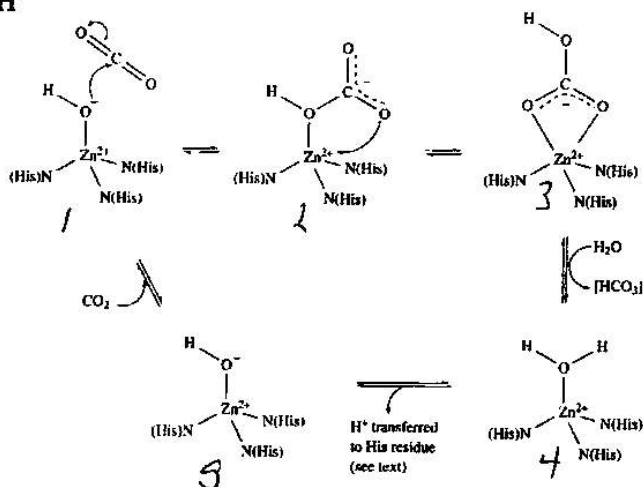
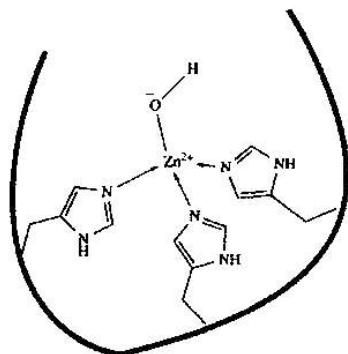
$$k_{12} = \sqrt{(4.2 \text{ M}^{-1}\text{s}^{-1})(4000 \text{ M}^{-1}\text{s}^{-1})(2.0 \times 10^{11})(0.85)}$$

$$k_{12} = 5.34 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$$

(9)(15 pts) Carbonic Anhydrase II catalyzes the reaction

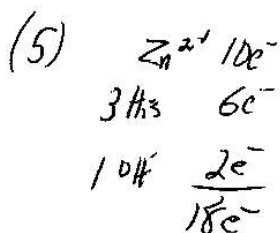
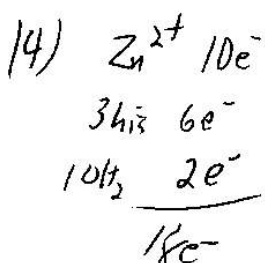
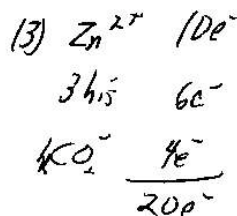
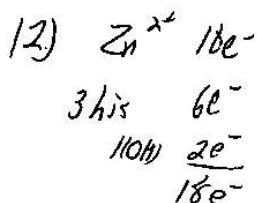
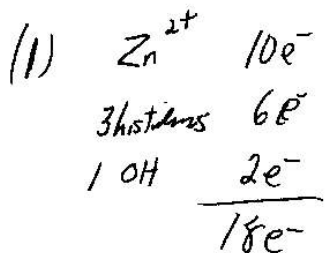


by the mechanism shown below.



Count the electrons around the  $\text{Zn}^{2+}$  at each step in the cycle.

Other 2+ metal ions can substitute for  $\text{Zn}^{2+}$  in these proteins, such as  $\text{Co}^{2+}$ . Why are high levels of many metals toxic?



Another metal would not allow this catalytic cycle to proceed. The  $e^-$  counts would not be right (not 18e for most species). For  $\text{Co}^{2+}$ , most of the electron counts would be  $15e^-$ , not good with backbonding imidazole groups



(10) Ferredoxins, Rubredoxins, and cytochromes are iron containing proteins that transfer electrons. Why are such a wide range of structures needed for electron transfer in living organisms? Why isn't a single electron transfer structure sufficient (hint: think of respiration and photosynthesis).

Electron transfer agents are needed with a wide range of potentials for  $e^-$  cascades such as respiration.