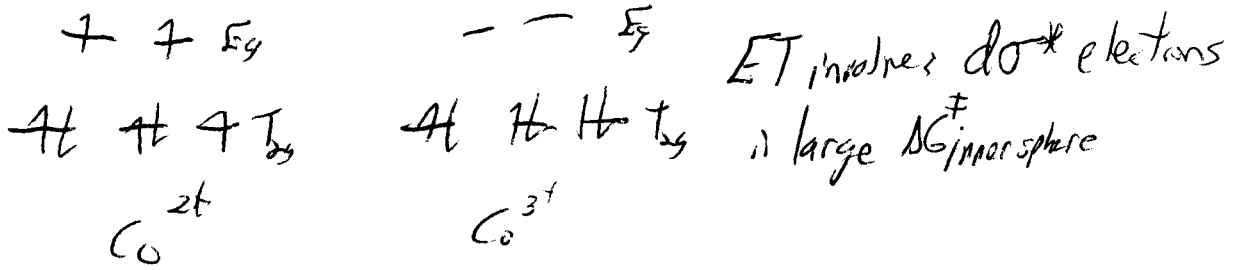
Chemistry 450 Exam 3. In-Class Part
Name Key

(1)(20 points) The following electron transfer reactions are arranged in order from slowest to fastest. Explain the order.

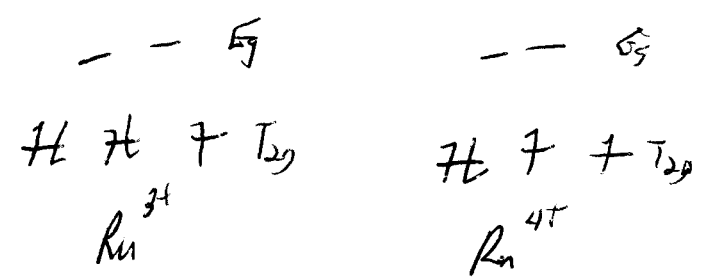
$[Co(H_2O)6]^{2+}(aq) + [Co(H_2O)6]^{3+}(aq)$ -------> $[Co(H_2O)6]^{3+}(aq) + [Co(H_2O)6]^{2+}(aq)$

$[Ru(NH_3)6]^{3+} + [Ru(NH_3)6]^{4+}$ -------> $[Ru(NH_3)6]^{4+} + [Ru(NH_3)6]^{3+}$

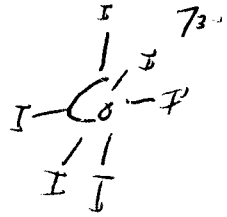
$[Co(H_2O)6]^{2+}(aq) + [Co(I)6]^{3-}(aq)$ -------> $[CoI(H_2O)5]^{2+}(aq) + [Co(H_2O)6]^{2+}(aq)$



ET involves $d\sigma^*$ electrons
⇒ large $\Delta G^{\ddagger}_{inner\ sphere}$



only T_{2g} ($d\pi$, nonbonding) electrons involved. ⇒ small $\Delta G^{\ddagger}_{inner\ sphere}$

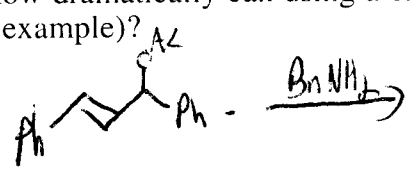


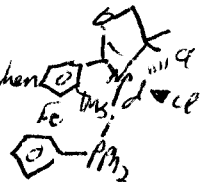
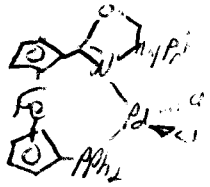
looks like an inner sphere mechanism, which is faster than outer sphere mechanisms.

(10)(30 pts) Read the paper "Asymmetric Catalysis with Chiral Ferrocene Ligands" , (Hou et al.*Acc. Chem. Res.* **2003**, *36*, 659-667) and answer the following questions.

(a) How and why are ferrocene's used in asymmetric catalysis? Ferrocene can be easily ~~[illegible]~~ molded to form chiral ligands. It is easy to modify, cheap and stable.

(b) How dramatically can using a chiral ferrocene affect the products in a chemical reaction (with example)?



The product is formed with 89.5% ee in S configuration when  but when the catalyst is changed to  the product is 96.5% ee in R.

(c) In the article, tuning the electronic properties of the polymer was discussed. What were they talking about? How do sterics and electronics affect the products of the reactions discussed?

Sterics allow the substrate to bind more favorably in one orientation preferentially. Electronics can change what reaction steps occur. In the reaction to form  , one orientation was favored with an electron donating ligand, while the opposite was preferred with an electron withdrawing substituent.

(9)(20 points) Carbon monoxide does not bind well to either early transition metals or late transition metals. It does bind well to transition metals in the middle of the d-block. Use Ligand-field theory and HSAB theory to explain these observations.

CO needs the metal to have dπ electrons to participate in back bonding. Early TMs have no dπ electrons, so CO can only bind through σ donation. CO is a hard ligand, but not to hard or lower TMs or hard (for Zn^{2+}) late TMs are rather soft. The TMs in the middle have some dπ e⁻s and are of similar hardness as CO, striking the best balance.

(2)(15 points) Explain what the Marcus Inverted region of electron transfer is.

When ΔG° becomes large enough (negative) the rate of electron transfer actually decreases if ΔG is made more negative.

(3)(10 points) Why do hard acids bond better to hard bases than soft acids?

Because hard acids aren't polarizable, They bond best through ionic bonding Hard bases form good ionic bonds as well. Soft bases, don't form good ionic bonds but good covalent bonds.

(4)(20 points) Give an example of each of the following and use it in an appropriate acid-base reaction

(a) Usanovich acid Fe^{3+}

$$Fe^{3+} + Na \rightarrow Fe^{2+} + Na^{+}$$

(b) Lewis base $:NH_3$

$$NH_3 + Fe^{3+} \rightarrow Fe^{2+}(NH_3)$$

(c) Brønsted-Lowry Acid HCl

$$HCl + OH^{-} \rightarrow H_2O + Cl^{-}$$

(d) Arrhenius Base

$NaOH$

$$NaOH_{(s)} \xrightarrow{H_2O} Na^{+}_{(aq)} + OH^{-}_{(aq)}$$

Chem 450 Exam 3. Take-Home Part Due Tuesday, December 4
Name Key

(7)(20 points) How can electrons transfer across large distances in biological systems (such as respiration) when the only path is through saturated organic chains?

By using inner sphere electron transport the two metals can be held together until electron transfer occurs.

(8)(20 points) For the following outer sphere electron transfer reactions, arrange them in order of increasing rate. You may use the table of standard reduction potentials from your analytical or general chemistry book. Explain your ordering.

Reaction

$[Fe(H_2O)_6]^{2+} + [V(H_2O)_6]^{2+} \longrightarrow Fe(H_2O)_6]^{3+} + [V(H_2O)_6]^{3+}$

$[Fe(H_2O)_6]^{2+} + [Ti(H_2O)_6]^{2+} \longrightarrow Fe(H_2O)_6]^{3+} + [Ti(H_2O)_6]^{3+}$

$[Fe(H_2O)_6]^{2+} + [Ce(H_2O)_6]^{4+} \longrightarrow Fe(H_2O)_6]^{3+} + [Ce(H_2O)_6]^{3+}$

(5)(25 points) Describe at least two systems of oxygen transport found in animals.

Describe 2 of the 3

Hb/Mb

hemerythrin

hemocyanin

(6)(15 points) Describe at least one system your body uses to remove toxins.

Metallothioneins are small proteins containing lots of cysteine residues that bind heavy metals well. When the protein binds enough Pb^{2+}, Hg^{2+}, Cd^{2+}, etc, it is excreted from the body.

Cytochrome P450 adds -OH groups to nonpolar molecules to make them more water soluble. Water soluble toxins can be excreted more easily