(35) I. 1. Predict the products for each of the following reactions in aqueous solution.
   2. Put the five reactions in order of reaction rate, from slowest to fastest. Explain your answer.

   a. $V^{3+} + V^{2+} \rightarrow V^{5+} + V^{3+}$

   b. $Fe^{3+} + V^{2+} \rightarrow Fe^{2+} + V^{3+}$

   c. $[Co(NH_3)_5Br]^2+ + V^{2+} \rightarrow [V(H_2O)_5Br]^2+ + [Co(H_2O)_6]^{3+} + 5NH_3$

   d. $[Co(NH_3)_5Br]^2+ + Cr^{2+} \rightarrow [Cr(H_2O)_5Br]^2+ + [Co(H_2O)_6]^{3+} + 5NH_3$

   e. $Cr^{2+} + Cr^{2+} \rightarrow Cr^{2+} + Cr^{3+}$

Reactions a, b, and c are outer sphere electron transfer, because there are no bridging ligands. Reactions c and d have Br⁻ as a potential bridging ligand, therefore probably proceed via an inner sphere mechanism. i.e., a, b, e are slower than c, d

$\underline{c, d}$

$V^{2+}$ is substitutionally inert, while $Cr^{2+}$ is labile.

i.e. d is faster than c

$\underline{a, b, e}$

a and b are $\pi \rightarrow \pi$, while c is $\pi \rightarrow \sigma$

i.e. a and b are faster than c

a has $\Delta\delta = 0$, while b has $\Delta\delta > 0$, i.e. b is faster

$\text{Rates: } e \leq a < b < c < d$
(30) II. Consider the reaction listed below between hydroxide ion and pentaamminechlorocobalt(2+).

1. Predict the final products for the reaction.
2. By what mechanism does the reaction proceed?
3. Write out the mechanism and indicate the rate-determining step.
4. The rate expression for this reaction is
   \[
   -d\left[\text{Co(NH}_3\text{)}_5\text{Cl}\right]^2^+ / dt = k_{obs} \left[\text{Co(NH}_3\text{)}_5\text{Cl}\right]^2^+ [\text{OH}^-]
   \]
   Is this consistent with your proposed mechanism? Why or why not?

1. \[
   \text{[Co(NH}_3\text{)}_5\text{Cl]}^2^+ + \text{OH}^- \rightarrow \text{[Co(NH}_3\text{)}_5\text{OH]}^2^+ + \text{Cl}^-\n   \]

2. Dissociative conjugate base mechanism

3. \[
   \text{[Co(NH}_3\text{)}_5\text{Cl]}^2^+ + \text{OH}^- \xrightleftharpoons[K_{eq}]{k_{eq}} \text{[Co(NH}_3\text{)}_4\text{(NH}_2\text{)}\text{Cl]}^+ + \text{H}_2\text{O}\n   \]

   Rate-determining step

4. \[
   \text{Rate } p_{II} = k_{eq} \left[\text{Co(NH}_3\text{)}_4\text{(NH}_2\text{)}\text{Cl}\right]^+\n   \]

   From first step

   \[
   \text{but } \text{[Co(NH}_3\text{)}_4\text{(NH}_2\text{)}\text{Cl]}^+ = K_{eq} \left[\text{Co(NH}_3\text{)}_5\text{Cl}^2^+] [\text{OH}^-]\n   \]

   Substituting,

   \[
   \text{Rate} = k_{eq} K_{eq} \left[\text{Co(NH}_3\text{)}_5\text{Cl}^2^+] [\text{OH}^-]\n   \]

   Which is consistent with the observed rate law.
III. The reaction below (where Pr = n-propyl) can be carried out in either hexane or methanol.

\[ \text{trans-PtCl}_2(\text{PPr}_3)(\text{NHEt}_2) + \text{NHEt}_2 \rightarrow \text{trans-PtCl}_2(\text{PPr}_3)(\text{*NHEt}_2) + \text{NHEt}_2 \]

The observed rate constants obtained are plotted against the concentration of \text{*NHEt}_2 in the following figure.

1. Why is the NHEt_group replaced in the molecule instead of Cl\(^-\) or PPr\(_3\)\(^-\)?

   \text{PPr}_3 is a stronger trans director than the other ligands.

2. Explain the plots above for each of the solvents used.

   Substitution of square planar complexes normally involves competing reactions — 1) direct attack by the entering ligand and attack by the solvent.

   Therefore, the rate expression is of the form:

   \[ \text{rate} = (k_1 + k_2 [\text{Et}_2\text{NH}]) [\text{trans-PtCl}_2(\text{PPr}_3)(\text{NHEt}_2)] \]

   Hexane is not very effective at coordinating to the metal, so the reaction proceeds entirely by the direct attack of the ammine (as indicated by the y-intercept of 0).

   Methanol is so effective at coordinating to the metal, that there is no contribution from attack by ammine (as indicated by slope = 0).