Problem 7.10. The 2 effects thought to contribute to the Irving-Williams series are the greater Lewis acidity (higher $Z_{\text{eff}}$) and the greater CFSE found across the series; these show up as higher $K_1$ and $K_2$ values for $\text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+}$. The decrease in $K$ value with each successive en ligand for $\text{Co}^{2+}$ and $\text{Ni}^{2+}$ is also expected on statistical grounds (see text p. 242 for discussion; in general $K_n > K_{n+1}$).

The major anomaly, of course, is $K_3$ for $\text{Cu}^{2+}$; this can be explained by the Jahn-Teller distortion of the coordination of this $d^9$ metal ion. Two en ligands coordinate in an equatorial plane, but addition of a third requires axial coordination, and this is noticeably weaker for $\text{Cu}^{2+}$. Hence the formation constant for the tris(en) complex is much smaller than expected.

Problem 14.1. Below are PMe$_3$ exchange pathways for both isomers.

- Observation of the 5-coordinate intermediate is consistent with the expected associative pathway for ligand substitution in these square planar complexes.
- Since the trans isomer (with PMe$_3$ trans to the leaving group) exchanges PMe$_3$ more rapidly than the cis one (which has hydride trans to the leaving group), this suggests PMe$_3$ is higher on the trans effect series than $\text{H}^-$.
- I have drawn distinct 5-coordinate intermediates formed from cis and trans starting materials, but, since this material is observed by NMR, both likely rearrange by Berry pseudorotation to form a common trigonal bipyramidal intermediate with the 3 bulky PMe$_3$ ligands in equatorial positions.

Problem 14.6.
You can't have a negative activation enthalpy for an elementary step in a reaction mechanism, so the experimental observation must be the result of a composite of 2 or more elementary steps. Thus a "negative activation enthalpy" means that the overall reaction slows down with increasing temperature. A common way for this to happen is if one step is an equilibrium for which the equilibrium constant is temperature-dependent.

Here, the mechanism probably looks like

\[
[\text{Cr(H}_2\text{O)}_{3}]^{2+} + [\text{Co(en)}_2\text{Cl}]^2- = [\text{Cr(H}_2\text{O)}_{3}(\mu-\text{Cl})\text{Co(en)}_2\text{Cl}]^{3+} + \text{H}_2\text{O}
\]

\[
[\text{Cr(H}_2\text{O)}_{3}(\mu-\text{Cl})\text{Co(en)}_2\text{Cl}]^{3+} \longrightarrow \text{electron transfer, then formation of products (where the first step has been oversimplified as an equilibrium to avoid the question of the mechanism of ligand substitution).}
\]

For the first step above, \( \text{K}_{eq} = \frac{[\text{Cr(H}_2\text{O)}_{3}(\mu-\text{Cl})\text{Co(en)}_2\text{Cl}]^{3+}[\text{H}_2\text{O}]}{[\text{Cr(H}_2\text{O)}_{3}]^{2+}[\text{Co(en)}_2\text{Cl}]^{2-}} \)

So \( [\text{Cr(H}_2\text{O)}_{3}(\mu-\text{Cl})\text{Co(en)}_2\text{Cl}]^{3+} = \text{K}[\text{Cr(H}_2\text{O)}_{3}]^{2+}[\text{Co(en)}_2\text{Cl}]^{2-} \)

Where \( \text{K} = \frac{\text{K}_{eq}}{[\text{H}_2\text{O}]} \)

If the rate-determining step is the electron transfer, then

\[
\text{Rate} = k_2 [\text{Cr(H}_2\text{O)}_{3}(\mu-\text{Cl})\text{Co(en)}_2\text{Cl}]^{3+} = k_2 \text{K}[\text{Cr(H}_2\text{O)}_{3}]^{2+}[\text{Co(en)}_2\text{Cl}]^{2-}
\]

The idea here is that the rate constant \( k_2 \) and the equilibrium constant \( \text{K} \) may have different temperature dependence. In particular, \( \text{K} \) may become smaller with increasing temperature, which would slow down the overall reaction and thus give an apparent negative activation enthalpy.

**Problem 14.7**

For the reductions of the Co complex, the much faster rate with the hydroxide is due to the inner-sphere, hydroxide-bridged intermediate in that process -- \( \text{OH}^- \) is a much better bridging ligand than water. These reactions work since the Cr(II) aquo complex (d\(^4\), high-spin) is labile and can readily undergo ligand substitution. When the same electron transfers are attempted with the Ru(II) reductant, there is not much difference between the \( \text{OH}^- \) and the \( \text{OH}_2 \) rates. This is because the Ru(II) complex is low-spin d\(^5\) and hence inert to ligand substitution. Therefore an inner-sphere pathway with a bridging ligand is not available and both reductions must go by the slower outer-sphere pathway.

2. (a) Why do Au(III) complexes react faster in ligand substitution than Pt(II)?

   **Answer:** both are square planar, so it's probably associative. Then, the **bigger formal charge** on Au(III) vs Pt(II) would make the Au more electrophilic, and it will react faster with an incoming nucleophile (ligand).

   (b) Since hydroxide gives the slowest ligand substitution, it's a poor nucleophile toward these Au(III) and Pt(II) centers. This makes sense, since they're soft, and it's hard. It could act as a base (base hydrolysis mechanism). But then you'd
expect **fast** ligand substitution; since it's observed to be slow, then base hydrolysis must not be happening.

(c) The fact that the substitution rate of the Et₄dien complexes is orders of magnitude smaller than for dien complexes and **independent** of [Y⁻] shows that rate-determining very slow dissociation of Cl⁻ must be occurring in this sterically crowded complex (D mechanism).

The pH dependence shows the rate increases as [OH⁻] goes up. Since hydroxide is a poor nucleophile (from part b) then **this must be a base hydrolysis effect**. In particular, deprotonation of the Et₄dien by hydroxide is the first step in a SN1CB mechanism by which the leaving group chloride dissociates -- as usual in base hydrolysis this is faster than the dissociation which occurs without this base assistance.

From these results, it appears that base hydrolysis in square planar complexes is not as common as in octahedral ones – apparently it only happened in (c) since the other 2 possibilities were slower.

3. (a) Inner sphere since F⁻ is transferred; if outer sphere then Cr(III) and Cr(II) would be found.
(b) The red color is likely due to an oxo-bridged dimer (edta)V-O-V(edta)³⁻; inner sphere.
(c) The lack of substituent effect suggests that the py is not a bridging ligand, so outer sphere.
(d) Azide appears to provide a better inner sphere pathway; inner sphere.
(e) A negative activation entropy implies a bimolecular RDS; likely inner sphere.

4. (a) The observation that the 4,4'-bipyridine ligand ends up bound to the substitution inert low-spin Fe(III) product is good evidence that it is a bridging ligand during electron transfer through an inner sphere mechanism:
(b) Although the Fe(II) reactant is labile, the Co(III) reactant does not have a potentially bridging ligand. Further, the substitutionally inert \([\text{Fe(CN)}_5(\text{H}_2\text{O})]^{2-}\) product has the same ligands as the Fe(II) reactant. Therefore, there is no evidence for an inner sphere mechanism and outer sphere is expected.

\[
[\text{Co(NH}_3)_6]^{3+} + [\text{Fe(CN)}_5(\text{H}_2\text{O})]^{3-} \xrightarrow{\text{outer sphere e- transfer}} [\text{Co(NH}_3)_6]^{2+} + [\text{Fe(CN)}_5(\text{H}_2\text{O})]^{2-} \\
[\text{Co(OH}_2)_6]^{2+} + 6\text{NH}_3
\]