60 minutes. Show all work, partial credit will be given. Supplemental information is provided on the last page.

1. What are the point groups for:
   (a) CH₂Cl₂ [6 pts]  
   (b) fac PCl₃F₃⁻ [6 pts]  
   (a) C₂ᵥ  
   (b) C₃ᵥ  
   (c) Are either (a) or (b) chiral? Explain using symmetry rules. [6 pts]
   Neither is chiral, both point groups have mirror planes.

2. The hexaaquairon(II) ion reacts above pH = 10 to form oligomers.
   (a) Write a balanced chemical reaction for the formation of the dimeric species. [7 pts]
   \[ 2 [\text{Fe(OH}_2\text{)}_6]^{2+} (aq) + \text{OH}^- (aq) \rightarrow [\text{Fe}_2(\text{OH}_2\text{)}_{10}(\text{OH})]^{3+} (aq) + 2 \text{H}_2\text{O} \]
   Or similar (oxo bridge OK, or additional hydroxo ligands).
   (b) Draw the dimeric species produced in (a), showing clearly the geometry and ligands around the metal cations. [7 pts]
   \[
   \begin{array}{c}
   \text{Fe} \\
   \text{H} \\
   \end{array}
   \quad \text{---} \quad
   \begin{array}{c}
   \text{O} \\
   \text{Fe} \\
   \end{array}
   \quad \text{---} \quad
   \begin{array}{c}
   \text{Fe} \\
   \text{H} \\
   \end{array}
   \quad 3^+ 
   
   (c) Which do you predict to be more acidic in aqueous solution, FeCl₃ or FeCl₂, and why? [7 pts]
   FeCl₃  
   More highly charge central ions are better H⁺ donors and therefore more acidic.  
   Fe³⁺ is therefore more acidic than Fe²⁺.
3. (a) Using the Pourbaix diagram for Fe provided, write a balanced half-reaction for reduction of Fe (III) to Fe (II) at pH = 5. [6 pts]

\[ \text{e}^- + \text{Fe(OH)}_3(s) + 3\text{H}^+ (\text{aq}) \rightarrow [\text{Fe(OH}_2)_6]^{2+} (\text{aq}) \]

(b) Based on your answer in part (a) and the Nernst equation below, if the Fe(III)/Fe(II) reduction potential is +0.45 V at pH = 5, what is the potential at pH = 7? [8 pts]

Nernst equation: \[ E = E^0 - \frac{(0.059 \text{ V})}{n} \log Q \]

\[ = E^0 - 3 \times (0.059 \text{ V}) \Delta \text{pH} = +0.45 \text{ V} - 3(0.059 \text{ V})(2) = +0.10 \text{ V} \]

(c) Why is the line to the right of Fe$^{3+}$ in the Pourbaix diagram exactly vertical (no slope)? [5 pts]

This is the conversion of the hexaaquametal cation into dimeric and oligomeric cations, and finally precipitation as Fe(OH)$_3$. It is not a redox reaction, purely acid/base reactions are vertical lines in Pourbaix diagrams.

(d) From the Pourbaix diagram, Fe(m) isn’t thermodynamically stable in aqueous solution. How can old iron objects (like treasure chests) survive 300 years under water? [5 pts]

Fe(m) is not thermodynamically stable, it does not appear anywhere in the Pourbaix diagram within the stability window for water. However, surface passivation of the metal with iron oxide occurs. This passivation layer is not as good a barrier as with Al, but can slow the thermodynamically-favored corrosion of Fe(m).

4. \( \text{Au}^+(\text{aq}) \rightarrow \text{Au}(\text{s}) \quad E^0 = +1.7 \text{ V at pH = 0} \).

\( \text{Au}^+ \) cannot exist in aqueous solution. Briefly explain why and also give a way to stabilize \( \text{Au(I)} \) in aqueous acid. [7 pts]

\[ \text{Au}^+ + \text{H}_2\text{O} \rightarrow \text{Au(s)} + \text{O}_2 \] (no need to balance) will have a potential of \( 1.7 - 1.23 = +0.47 \text{ V at pH=0 and therefore} \text{Au}^+ \text{ would be reduced to Au and oxidize water. However, addition of a ligand such as C}^- \text{ or C}N^- \text{ dramatically decreases} \]
the Au(I) reduction potential by forming the stable complexes $\text{AuCl}_2^-$ or $\text{Au(CN)}_2^-$. 

5. Sketch a molecule of chlorobenzene and show/explain the location of all mirror plane symmetry elements. [6 pts]

Two mirror planes, the first contains the C-Cl bond and bisects the molecule (vertical to the page), the other is the horizontal plane that contains the molecule. The figure shows the edges of the first plane as a line, and shows the horizontal plane as a rectangle.

![Chlorobenzene molecule with mirror planes](image)

Circle the one best answer for each question. [4 pts each]

6. What do Pauling’s rules predict for the $\text{pK}_{a1}$ of $\text{H}_3\text{PO}_4$?
   (a) -10    (b) -8    (c) -3    (d) 0    (e) 3    (f) 6    (g) 10

7. Which is not true about the reaction of $\text{Al}_2\text{S}_3$ in air?
   (a) $\text{Al}^{3+}$ is a hard Lewis acid and reacts with water to form an oxide and eliminate $\text{H}_2\text{S}$
   (b) $\text{Al}^{3+}$ is a harder Lewis acid than $\text{H}^+$
   (c) $\text{S}^{2-}$ is a softer Lewis base than $\text{O}^{2-}$
   (d) the complex $\text{Al}_2\text{O}_3$ is more stable than the complex $\text{Al}_2\text{S}_3$
   (e) $\text{S}^{2-}$ and $\text{O}^{2-}$ are both Lewis bases
   (f) the reaction to form $\text{H}_2\text{S}$ can be described as both an acid-base and a redox reaction

8. Which of the following is the strongest acid in aqueous solution?
   (a) $\text{Cr}^{2+}$    (b) $\text{Fe}^{2+}$    (c) $\text{Ni}^{2+}$    (d) $\text{Na}^+$    (e) $\text{Ca}^{2+}$
   (f) all of these have similar acidities in water due to solvent leveling

9. Under which conditions will nitrate be the strongest oxidant?
   (a) $\text{pH} = 0$    (b) $\text{pH} = 7$    (c) $\text{pH} = 14$
   (d) the oxidizing strength is independent of the solution pH

10. Using the Frost diagram below, for N at pH = 14, which species cannot disproportionate in aqueous base?
11. PF$_5$ shows fluxional behavior and a single sharp $^{19}$F NMR peak at room temperature, but at low temperatures the NMR spectra separates into which of the following?

(a) two singlets with a 2:1 intensity ratio  
(b) three singlets with a 3:1:1 intensity ratio  
(c) a triplet and quartet with a 3:2 intensity ratio  
(d) two triplets with equal intensities  
(e) two doublets with a 3:2 intensity ratio  
(f) a triplet, singlet and doublet with 3:1:2 intensity ratio