1. Draw the molecular geometry with VSEPR and indicate any deviations from ideal coordination angles. Give the point group for each molecule.

(a) [10 pts] \( \text{ICl}_4^- \)

\[
\begin{array}{c}
\text{Cl} \\
\cdot \\
\text{I} \\
\cdot \\
\text{Cl}
\end{array}
\]

Square planar

\(< \text{Cl-I-Cl bond: } 90^\circ\)

\(\text{D}_{4h}\)

(b) [10 pts] \( \text{POCl}_3 \)

\[
\begin{array}{c}
\text{O} \\
\cdot \\
\text{P} \\
\cdot \\
\text{Cl}
\end{array}
\]

Trigonal pyramidal

\(< \text{Cl-P-Cl bond less than } 109.5^\circ\)

\(\text{C}_{3v}\)

(c) [8 pts] Is either of the above species polar? Explain using symmetry rules.

\(\text{ICl}_4^-\) is nonpolar due to its \(\text{D}_{4h}\) point group.

\(\text{POCl}_3\) is polar due to its \(\text{C}_{3v}\) point group.
2. (a) [12 pts] Write down a Born-Haber analysis (give all the reaction steps) needed to estimate $\Delta H_f$ for CaF$_2$ (s) from the elements in standard states. Label each reaction step with an appropriate energy term (such as I, $E_a$, $\Delta H_L$, etc). Clearly indicate the sign (+ or -) for each term.

$$\text{Ca}^{2+} (g) + 2e^- + 2 \text{ F} (g)$$

$\Delta H_{\text{sub}}$ (Ca)

Ca$^+$ (g) + e$^- + 2$ F(g) \quad \downarrow \quad \text{Ca}^{2+} (g) + 2$ F$^- (g)$

$\text{I}_1$ (Ca)

Ca (g) + 2 F(g) \quad \downarrow \quad \text{D}_0$ (F$_2$)

Ca (g) + F$_2$ (g) \quad \downarrow \quad \Delta H_{\text{sub}}$ (Ca)

Ca (s) + F$_2$ (g) \quad \downarrow \quad \Delta H_f$ (CaF$_2$)

CaF$_2$ (s)

(b) [10 pts] Sketch (draw a picture) and also describe in writing a unit cell for the fluorite CaF$_2$ structure.

Ca$^{2+}$ ions form the cubic close packing, and F$^-$ ions fill up the tetrahedral holes.
3. (a) [10 pts] Construct an MO diagram for the F₂ (g), including valence atomic and molecular orbitals, symmetry labels, and the electron filling of the MO's.

![MO diagram for F₂]

(b) [5 pts] Sketch a figure showing the geometry of the HOMO orbital on F₂.

![Sketch of HOMO orbital]

(c) [5 pts] Is the ionization energy of F₂ higher or lower than atomic F? Explain your answer.

It’s lower. The HOMO is an antibonding level and is therefore higher in E than the atomic p orbitals. This makes the ionization energy lower than for atomic F.
(d) [5 pts] Is F\textsubscript{2} paramagnetic? Explain your answer.

No. Because there are no unpaired electrons.

4. (a) [10 pts] Write a balanced equation for the half reduction reaction of Fe(OH)\textsubscript{3} to Fe\textsuperscript{2+} and use the Nernst equation to explain why the reduction potential for Fe(OH)\textsubscript{3} to Fe\textsuperscript{2+} is pH dependent.

\[ \text{Fe(OH)}_3 + 3\text{H}^+ + \text{e}^- \rightarrow \text{Fe}^{2+} + 6\text{H}_2\text{O} \]

\[ E = E^\circ - 0.059V/n \log Q \]

\[ E = E^\circ - 0.059V/n \log Q \]

\[ \log Q = \log\left\{ \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^3} \right\} \]
\[ = \log[\text{Fe}^{2+}] - 3\log[H^+] \]
\[ = \log[\text{Fe}^{2+}] + 3pH \]

(b) [5 pts] Is the reaction associated with the vertical line in 4(a) near pH=3 an acid/base reaction, a redox reaction, both, or neither?

It is an acid-base reaction.
5. **[10 pts]** Explain why the standard reduction potential for \([\text{Au(CN)}_2]^- (aq)\) to \(\text{Au} (m)\) is \(+0.6 \text{ V}\), compared to \(+1.69 \text{ V}\) for \(\text{Au}^+ (aq)\) to \(\text{Au}\).

Many ligands, such as \(\text{CN}^-\), dramatically lower the reduction potential of \(\text{Au}^+\) and many other TM cations. This is mainly due to the effects of pi interaction of \(t_{2g}\) TM orbitals with ligand pi orbitals, which stabilizes the TM cation complex. Aqua ligands, as available in aqueous acid, do not participate in pi interactions and are therefore less stabilizing. The more stable the TM complex, the lower the reduction potential to for the metal.

6. (a) **[6 pts]** Write out the full name of the octahedral complex \([\text{Cr(NH}_3)_6]^{3+}\)

(hexaamminechromium(III) or hexaamminechromium(3+))

(b) **[10 pts]** Write a d orbital energy level diagram for the complex in part (a). Label the d-orbitals with \((z^2, x^2-y^2, xy, xz, \text{and } yz)\) and also give the orbital symmetry labels.

\[\begin{array}{c}
\text{dx}^2-\text{y}^2, \text{dz}^2 \\
\text{e}_g \quad \text{eg} \\
\text{f} \quad \text{t}_{2g} \\
\text{dxy, dyz and dxz}
\end{array}\]

(c) **[10 pts]** Calculate the ligand field stabilization energies (LFSE) in terms of \(\Delta_0\) for the electron configuration in part (b).

\[\text{LFSE} = 3 \times 0.4 \Delta_0 = 1.2 \Delta_0\]

(d) **[8 pts]** How could a chemistry researcher experimentally confirm that a Cr(III) complex has three unpaired electrons?

Magnetic moment should be proportional to \(\sqrt{N(N+2)}\). **[8 pts]**

Trying to measure LFSE by calorimetry is not a good method. **[4 pts if this]**

7. **[10 pts]** For a specific ligand \(X^-\), which has a negative charge, which of the following complexes is the most likely to be low spin? Explain your reasoning.

\([\text{CoX}_6]^{4-}\quad [\text{CoX}_6]^{3-}\quad [\text{IrX}_6]^{3-}\quad [\text{IrX}_6]^{2-}\)
\( \Delta \) increases with charge on the TM cation, and is also larger for the more extended d orbitals in TM rows 2 and 3. Therefore, we expect the largest \( \Delta \) for \([\text{IrX}_6]^{2-}\), and this is most likely to be low spin for a given ligand X.

8. (a) [10 pts] Write a balanced reaction showing how \( \text{H}_2 \) is generated on an industrial scale.

\[
\text{CH}_4 (\text{g}) + \text{H}_2\text{O} (\text{g}) \rightarrow \text{CO} (\text{g}) + 3 \text{H}_2 (\text{g})
\]

Or

\[
\text{C} (\text{s}) + 2 \text{H}_2\text{O} (\text{g}) \rightarrow \text{CO}_2 (\text{g}) + 2 \text{H}_2 (\text{g})
\]

Or, electrolysis is OK

(b) [10 pts] Describe briefly 2 important ways that hydrogen bonding affects our daily lives.

1. Lower density of ice than water
2. DNA replication
3. High bp of liquid water.

9. [12 pts] Predict the form of both the \(^{77}\text{Se}-\text{NMR}\) and the \(^{19}\text{F}-\text{NMR}\) spectra for \(^{77}\text{SeF}_6\) (both \(^{77}\text{Se}\) and \(^{19}\text{F}\) have \( I = \frac{1}{2} \))

This is an Oh molecule, all F are equivalent. Therefore the Se-NMR spectrum will be one septet (Se split by 6 F) and the F-NMR will be a doublet (one type of F split by 1 Se).

10. [4 pts each] Circle the ONE best choice.

(a) Wurtzite structure has the stacking sequence of \((\text{AaBb})_n\), where uppercase letters are anions and lowercase are cations. What is the coordination geometry around anions in the lattice?

(1) tetrahedral \hspace{1cm} (2) square planar \hspace{1cm} (3) octahedral
(4) trigonal prismatic \hspace{1cm} (5) linear \hspace{1cm} (6) trigonal bipyramidal
(b) Which of the following octahedral complexes has more than two geometric isomers?
(1) \([\text{FeBr(OH}_2\text{)}_3]^{2+}\) (2) \([\text{RhCl}_3\text{F}_3]^{-}\) (3) \([\text{RuCl}_4(\text{acac})]^{4+}\)
(4) \([\text{CoBr}_2\text{Cl}_2(\text{NH}_3)_2]^+\) (5) \([\text{Re(CO)}_6]^{-}\) (6) \([\text{CrCl}_5(\text{NH}_3)]^{2-}\)

(c) Which cation will form the strongest complex with the base iodide?
(1) \(\text{Li}^+\) (2) \(\text{K}^+\) (3) \(\text{Rb}^+\) (4) \(\text{Cs}^+\)
(5) all these complexes will have the same \(K_f\)

(d) Which ligand is a \(\pi\)-donor with a weak ligand field effect?
(1) \(\text{N(CH}_3\text{)}_3\) (2) \(\text{H}^-\) (3) \(\text{CN}^-\) (4) \(\text{Cl}^-\) (5) \(\text{NH}_3\) (6) \(\text{en}\)

(e) Which of the following is NOT square planar?

(f) Which of the following will react to reduce water?
(1) \(\text{O}_2\) (2) \(\text{H}_2\text{O}_2\) (3) \(\text{HF}_2^-\) (4) \(\text{SiBr}_4\) (5) \(\text{Ca(m)}\) (6) \(\text{Ni(m)}\)
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![Diagram](image)

**Molecule**

- Linear?
  - Y
  - Linear?
    - N
    - Two or more $C_n$? N
  - N
- N

**Linear groups**

- $D_n$
- $C_n$
- $I_n$
- $T_n$

**Cubic groups**

- $D_{nd}$
- $D_{gd}$
- $D_{hd}$
- $O_h$
- $T_d$

**Select C, with highest $n$; then, is nC, perpendicular to C**?
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