For the long answer questions (problems 6 –12) you must show all your working for full credit.

The following data may be of use:

\[ T_C = T_K - 273.15 \]
\[ R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ N_A = 6.02 \times 10^{23} \]

**Acid – Base Equilibria:**

\[ K_w = 1.0 \times 10^{-14} \text{ @ 25 °C} \]
\[ \text{pH} = - \log_{10} [H_3O^+] \]
\[ \text{pOH} = - \log_{10} [OH^-] \]

The Henderson-Hasselbalch Equation:

\[ \text{pH} = \text{pK}_a + \log_{10} \left( \frac{[A^-]}{[HA]} \right) \]

**Thermodynamics:**

\[ \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \]
\[ \Delta S_{\text{surr}} = - \frac{\Delta H}{T} \]
\[ \Delta G = \Delta H - T \Delta S \]

**Electrochemistry:**

\[ \Delta G^o = - n F E^o \]

Faraday Constant (F) = 96,485 C / mole of electrons

Definition of an Ampere: 1 A = 1 C / s

**Spectrochemical Series:**

\[ \text{CN}^- > \text{NO}_2^- > \text{en} > \text{NH}_3 > \text{H}_2\text{O} > \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^- \]

The solution of the quadratic equation \( ax^2 + bx + c = 0 \) is given by:

\[ x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]
Multiple Choice and Short Answer Problems.

1) Which of the following salts shows the lowest solubility in water.
   \( K_{sp} \) values: \( \text{Ag}_2\text{S} = 1.6 \times 10^{-49} \); \( \text{Bi}_2\text{S}_3 = 1.0 \times 10^{-72} \); \( \text{HgS} = 1.6 \times 10^{-54} \);
   \( \text{Mg(OH)}_2 = 8.9 \times 10^{-12} \); \( \text{MnS} = 2.3 \times 10^{-13} \)
   (a) \( \text{Bi}_2\text{S}_3 \)
   (b) \( \text{Ag}_2\text{S} \)
   (c) \( \text{HgS} \)

2) Consider the following electrochemical reactions:

\[
\text{Zn}^{2+} + 2 \text{e}^- \rightarrow \text{Zn} \quad E^0 = -0.76 \text{ V}
\]

\[
\text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu} \quad E^0 = 0.34 \text{ V}
\]

An electrolysis cell is set up with a solution of \( \text{ZnSO}_4 \) and \( \text{CuSO}_4 \) as well as zinc and copper electrodes. The cell is run with an electrolysis current of 3.00 amperes for 1.00 hour. Which of the following statements is true?

a) The Cu electrode will be 3.56 g heavier.

b) The Cu electrode will be 3.56 g lighter.

c) The Cu electrode will be 7.12 g heavier.

d) The Zn electrode will be 3.66 g lighter.

e) The Zn electrode will be 7.32 g heavier.
3) Draw the structures for the following compounds, including all reasonable isomers.

\[
\text{Co(NH}_3\text{)}_5\text{ClBr} \quad \text{Ni(H}_2\text{O)}_2\text{I}_2
\]
4) Circle each of the functional groups in the following molecule and identify by name each group you have circled. Give the approximate bond angles for $\alpha$, $\beta$ and $\gamma$. 

(10 points)
5) Carbon exists in two common forms, diamond and graphite. Silicon on the other hand exists only in a diamond like structure. Which of the following best accounts for this observation?

a) Si is softer than C
b) C makes strong multiple bonds, while Si does not
c) the ionization potential of Si is less than that of C
d) the lanthanide contraction is greater for Si than for C

(5 points)

6) The rusting of iron involves:

a) the initial dissolution of Fe in water to form Fe$^{2+}$
b) the direct reaction of oxygen with Fe(s) to give iron oxide
c) the formation of Fe(OH)$_2$
d) none of the above

(5 points)
Long Answers. You must show all your working to receive full credit.

7) (a) Show all the distinct tripeptides that can be formed from a single alanine (ala) and two glycine (gly) amino acid building blocks? Use the Ala and Gly labels in your answer.

(b) Draw the molecular structure for one of the tripeptides in your answer to (a) (and identify which one you are drawing) using the following information:

(c) Would you expect a long polypeptide composed of just glycine and alanine residues to be soluble in a hydrocarbon solvent? Why?

(d) A protein, in general, has a mixture of interactions that hold the overall structure together. When proteins are heated, the hydrogen bonding in the secondary structure breaks apart. This process is called denaturation. What are the algebraic signs of ΔH and ΔS for denaturation? Why?

(25 points)
In the gas phase, nitrogen dioxide (NO₂) is produced from nitric oxide and oxygen according to the following mechanism:

\[
\text{NO} + \text{NO} \xleftrightarrow{\text{Keq}} \text{N}_2\text{O}_2 \quad \text{Fast equilibrium}
\]

\[
\text{N}_2\text{O}_2 + \text{O}_2 \xrightarrow{k_2} 2 \text{NO}_2 \quad \text{Slow}
\]

Each step is an elementary reaction.

(a) What is the overall balanced equation for the reaction?

(b) Identify the intermediate(s) and catalysts, if any, in this reaction mechanism?

(c) Write an expression for the steady state (equilibrium) concentration of N₂O₂:

(d) If the form of the rate law for the overall reaction is \( \text{Rate} = k \left[\text{NO}\right]^x \left[\text{O}_2\right]^y \), find \( k \), \( x \) and \( y \) based on the mechanism above. Show your working.
9) (a) When MoCl$_3$ is dissolved in ammonia solution a complex results with a single unpaired spin. Is this observation more consistent with low-spin tetrahedral Mo(NH$_3$)$_4^{5+}$ or octahedral Mo(NH$_3$)$_6^{3+}$? Explain your answer. (15 points)
9 continued)

(b) If an identical complex were formed on dissolving MoCl$_3$ in water do you expect the wavelength of light absorbed by the complex to be longer or shorter than that absorbed by the complex in ammonia solution? Justify your answer.

(10 points)
10) For the following polymer:

(a) Define the polymer repeating unit by *carefully* circling a unit on the above structure.

(b) What monomer, or monomers, could be used to prepare this polymer.

(c) What is the product of oxidation of the following alcohol?

\[
\begin{align*}
\text{H}_3\text{C}-&\text{H} - \text{OH} \\
\text{CH}_3
\end{align*}
\]
11) The amount of manganese (Mn metal) in steel is determined by changing it to permanganate ion. The steel is first dissolved in nitric acid, producing Mn$^{2+}$ ions. These ions are then oxidized to the deeply colored MnO$_4^-$ permanganate ions by IO$_4^-$ in acid solution.

(a) Complete and balance an equation describing the reaction converting Mn$^{2+}$ to MnO$_4^-$ by IO$_4^-$:

(b) Calculate $E^o$, and $\Delta G^o$ for the formation of MnO$_4^-$ from Mn$^{2+}$ and IO$_4^-$ under standard conditions.

(20 points)
12) The nature of an aqueous solution of an unknown weak acid (HA) is determined by the following titration experiment. A starting volume of 100.0 mL of the weak acid is placed in a reaction flask and titrated versus a 1.00 mol L\(^{-1}\) NaOH solution. A pH meter is used to determine the course of the titration. The following data is obtained:

50.0 mL of NaOH solution is required to reach the equivalence point as determined by the steepest rise in the pH over the course of the titration.

(a) At the equivalence point, what are the principal species in the reaction flask?

(b) How many moles of HA were present in the initial acid solution? (Assume HA is monoprotic)
The pH of the solution was also measured when 25.0 mL of NaOH had been added to the original solution (i.e. halfway to the equivalence point)

(c) At the halfway to equivalence point, what are the concentrations of HA and A^- in the reaction flask?

(d) At the halfway to equivalence point the pH is measured to be 5.05. Pick the most likely identity for the unknown acid from the table of organic carboxylic acids below and explain your answer.

<table>
<thead>
<tr>
<th>Molecular Formula of acid</th>
<th>$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOOH</td>
<td>$1.78 \times 10^{-4}$</td>
</tr>
<tr>
<td>CH$_3$CH$_2$COOH</td>
<td>$1.35 \times 10^{-5}$</td>
</tr>
<tr>
<td>(CH$_3$)$_3$CCOOH</td>
<td>$8.91 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

(e) Draw the molecular structure of the acid you determined in part (d), indicating the acidic hydrogen.

(30 points total)