1. (10 points) 
To form a buffer solution with pH greater than 7 it is possible to mix a weak base with a salt of the base. Calculate the pOH of a solution of 0.020 moles of morphine (C_{17}H_{19}O_{3}N; call it Mp) and 0.016 moles of MpHCl (i.e., MpH^+ , Cl^-) in sufficient water to make 1.000 L of solution. Activity coefficients may be ignored for the purpose of this problem.

\[ \text{Mp} + \text{H}_2\text{O} = \text{MpH}^+ + \text{OH}^- \]

\[ 0.02 - x \quad 0.016 + x \quad x \]

\[ K_b = 16 \times 10^{-6} = \frac{x(0.016 + x)}{(0.020 - x)} \]

\[ x = 2.0 \times 10^{-6} \quad [\text{OH}^-] = 2.0 \times 10^{-6} \text{ mol L}^{-1} \]

\[ \text{pOH} = -\log_{10}\left(\frac{[\text{OH}^-]}{1 \text{ mol L}^{-1}}\right) = -\log_{10}(2.0 \times 10^{-6}) \]

\[ \text{pOH} = 5.70 \]
2. (10 points)
Identify the conjugate acid-base pairs for the following reaction:

\[ \text{C}_5\text{H}_5\text{NH}^+ + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{C}_5\text{H}_5\text{N} \]

Then, use the table of data attached to the equation sheet to give a numerical value for the equilibrium constant for this reaction.

Acid #1 \( \underline{\text{C}_5\text{H}_5\text{NH}^+} \); conjugate base #1 \( \underline{\text{C}_5\text{H}_5\text{N}} \)

Acid #2 \( \underline{\text{H}_3\text{O}^+} \); conjugate base #2 \( \underline{\text{H}_2\text{O}} \)

Equilibrium constant \( 5.6 \times 10^{-6} \)

3. (12 points: 6,6)

a) Some solid ZnS is added to a 0.02 M solution of ZnCl\(_2\) in water at 25 °C. Determine the mean ionic activity coefficient for Zn\(^{2+}\), S\(^{2-}\) in this solution. Assume that the ZnCl\(_2\) is completely dissociated into Zn\(^{2+}\) and Cl\(^-\) ions and that the amount of Zn\(^{2+}\) and S\(^{2-}\) from the dissociation of ZnS is negligible for the calculation of ionic strength.

\[
\begin{align*}
I &= \frac{1}{2} \left( 0.02(2)^2 + 0.04(1)^2 \right) = 0.06 \\
\ln \gamma_\pm &= -1.172 \log(2) - \log(2) \sqrt{0.06} \\
\gamma_\pm &= 0.317
\end{align*}
\]

b) Determine the concentration of S\(^{2-}\) in the solution in Part (a) given that the solubility constant for ZnS is \( 1.6 \times 10^{-24} \) at 25 °C. Include the effect of the activity coefficient determined in Part (a).

\[
\text{ZnS} = \text{Zn}^{2+} + \text{S}^{2-} \\
0.02 + S \\
K_S = 1.6 \times 10^{-24} = \gamma_\pm^2 (0.02 + S) S
\]

\[
S = \frac{1.6 \times 10^{-24}}{(0.02)(0.317)^2} \quad [\text{S}^{2-}] = 8 \times 10^{-22} \text{ mol L}^{-1}
\]
4. (12 points: 6,6)
25.0 mL of a solution of benzoic acid (HBz) in water is titrated with 0.016 M NaOH. The titration was stopped at the stoichiometric point, which required 20.0 mL of the NaOH solution.

a) What was the original molarity of the benzoic acid solution?

\[
\text{HBz} + \text{NaOH} \rightarrow \text{NaBz} + \text{H}_2\text{O}
\]

moles HBz = moles NaOH

\[ (0.025)[\text{HBz}] = (0.020)(0.016) \]

\[ [\text{HBz}] = 0.0128 \text{ mol L}^{-1} \]

b) What was the molarity of NaBz in the solution at the endpoint of the titration?

\[ [\text{NaBz}] = \frac{\text{moles NaBz}}{\text{liters of solution}} \]

moles NaBz = moles NaOH = (0.020)(0.016) = 3.2 \times 10^{-4}

\[ [\text{NaBz}] = \frac{3.2 \times 10^{-4}}{0.025 + 0.020} = 7.11 \times 10^{-3} \text{ mol L}^{-1} \]

5. (6 points)
An electric current passes through a solution of AgNO₃ and then through a solution of CrCl₃ so that the same current passes through each solution. After the current was turned off, it was found that 0.15 moles of Ag was deposited by reduction of Ag⁺ in the AgNO₃ solution. How many moles of Cr was deposited by reduction of Cr³⁺ in the CrCl₃ solution?

1 mol e⁻ deposits 1 mol Ag from Ag⁺

0.15 mol e⁻ deposits 0.15 mol Ag from Ag⁺

1 mol e⁻ deposits 1/3 mol Cr from Cr³⁺

\[ 0.15 \text{ mol e}^{-} \text{ deposits } \frac{0.15}{3} = 0.05 \text{ mol Cr from Cr}^{3+} \]
5. (12 points)
Use the table of reduction half reactions and reduction potentials attached to the equation sheet to write half reactions and a balanced chemical equation and then predict the direction of reaction for a mixture made up from all of the following in approximately unit activity in water solution: Mn\(^{2+}\), MnO\(_4^-\), O\(_2\), H\(^+\).

(1) \[ 4 \times [ \text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^- = \text{Mn}^{2+} + 4 \text{H}_2\text{O} ] \]

(2) \[ 5 \times [ \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- = 2 \text{H}_2\text{O} ] \]

*Reaction (1) has a higher standard reduction potential than Reaction (2). The fact that a reaction with a higher reduction potential will oxidize the substances at the right in a reaction below it means that the overall reaction, which is derived by subtracting 5 × reaction 2 from 4 × reaction 1, will proceed spontaneously to the right. The overall reaction is*

\[ 4 \text{MnO}_4^- + 32 \text{H}^+ + 10 \text{H}_2\text{O} = 4 \text{Mn}^{2+} + 16 \text{H}_2\text{O} + 5 \text{O}_2 + 20 \text{H}^+ \]

Cancel species that appear on both sides of the equation:

\[ 4 \text{MnO}_4^- + 12 \text{H}^+ = 4 \text{Mn}^{2+} + 6 \text{H}_2\text{O} + 5 \text{O}_2 \]

This reaction is spontaneous to the right.

6. (8 points: 4,4)
For each of the following, use the metal activity series attached to the equation sheet and assume unit activity for all species. Circle the appropriate species.

a) Predict which of the following species will be oxidized by Cu\(^{2+}\) in water.

\[ \text{Zn}^{2+} \quad (\text{Fe}) \quad (\text{Pb}) \]

b) Predict which of the following species will be reduced by Cr in water.

\[ \text{Al}^{3+} \quad (\text{Pb}^{2+}) \quad \text{Ag} \]
7. (30 points: 5,9,8,8)
Consider the following galvanic cell and cell reaction for which $E^\circ = -0.07 \text{ V}$. (A short table of reduction potentials is attached to the equation sheets.)

$$\text{Cu(s)}|\text{Cu}^{2+}(aq),\text{Cl}^-(aq)|\text{Hg}_2\text{Cl}_2(s)|\text{Hg(l)}$$

$$\text{Hg}_2\text{Cl}_2(s) + \text{Cu(s)} = 2 \text{Hg(l)} + \text{Cu}^{2+}(aq) + 2 \text{Cl}^-(aq)$$

a) Determine the standard reduction potential for the calomel electrode.

$$E^\circ = E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

$$E^\circ = E^\circ_{\text{calomel}} - E^\circ_{\text{Cu, Cu}^{2+}}$$

$$-0.07 \text{ V} = E^\circ_{\text{calomel}} - 0.34 \text{ V}$$

$$E^\circ_{\text{calomel}} = 0.027 \text{ V}$$

b) Identify the cathode, anode, and direction of the flow of electrons in the outer circuit if all of the cell reactants are at unit activity.

Since for the cell, $E^\circ = -0.07 \text{ V} < 0$,

Right electrode (Hg(l)) is the anode

Left electrode (Cu(s)) is the cathode

Electrons flow from anode to cathode (i.e., from right to left) in the outer circuit
7. (cont.) Consider the following galvanic cell and cell reaction for which $E^o = -0.07$ V at 25 °C.

$$\text{Cu(s)}|\text{Cu}^{2+}(aq),\text{Cl}^- (aq)|\text{Hg}_2\text{Cl}_2(s)|\text{Hg}(l)$$

$$\text{Hg}_2\text{Cl}_2(s) + \text{Cu(s)} = 2 \text{Hg}(l) + \text{Cu}^{2+}(aq) + 2 \text{Cl}^-(aq)$$

c) Calculate the activity quotient $Q$ for this cell if $a(\text{Cu}^{2+}) = 0.05$ and $a(\text{Cl}^-) = 0.10$.

$$Q = a(\text{Cu}^{2+})a(\text{Cl}^-)^2$$

$$Q = (0.05)(0.10)^2$$

$$Q = 5 \times 10^{-4}$$

d) Calculate the potential for this cell at 25 °C for the conditions in part (c).

$$E = E^o - \frac{0.0257 \text{ V}}{\text{V}} \ln Q$$

$$E = -0.07 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln(5 \times 10^{-4})$$

$$E = 0.028 \text{ V}$$