Analytical Chemistry

1. Find the conditions under which \( \text{Pb}^{2+} \) and \( \text{TI}^+ \) can be separated quantitatively by \( \text{H}_2\text{S} \) precipitation from a solution that is 0.1 \( F \) in each cation. (10%)

The equilibrium constants for the two important reactions are:

\[
\begin{align*}
\text{PbS(s)} & \rightleftharpoons \text{Pb}^{2+} + \text{S}^{2-} \quad [\text{Pb}^{2+}][\text{S}^{2-}] = 7 \times 10^{-28} \\
\text{TI} \text{S(s)} & \rightleftharpoons 2\text{TI}^+ + \text{S}^{2-} \quad [\text{TI}^+]^2[\text{S}^{2-}] = 1 \times 10^{-22}
\end{align*}
\]

2. Calculate the normality of an iodine solution if 37.34 ml were required to titrate a 0.2040 g sample of primary standard \( \text{Ag}_2\text{O}_3 \) (gfw = 197.8 g). The reaction is

\[
\text{I}_2 + \text{H}_2\text{AsO}_5^- + \text{H}_2\text{O} \rightarrow 2\text{I}^- + \text{H}_2\text{AsO}_4^- + 2\text{H}^+
\]

3. A 0.74-g sample containing chloride and iodide ions gave a silver halide precipitate (AgCl (fw 143g) and AgI (fw 235g)) weighting 0.51 g. The precipitate was then strongly heated in a stream of Cl\(_2\) to convert the AgI to AgCl

\[
2\text{AgI(s)} + \text{Cl}_2(g) \rightarrow 2\text{AgCl(s)} + \text{I}_2(g)
\]

After completion of this treatment, the precipitate weights 0.36g. Calculate the weight percentages of KI (fw 166 g) and NaCl (fw 58 g) in the sample. (15%)

4. A 1.000-g sample containing \( \text{Cl}^- \) and \( \text{ClO}_4^- \) sufficient water to give 125.0 ml of solution. A 25.00 ml aliquot required 7.05 ml of 0.04000M \( \text{AgNO}_3 \) to titrate the \( \text{Cl}^- \), A second 25.00 ml aliquot was treated with \( \text{AgNO}_3 \) to titrate \( \text{Cl}^- \), A second 25.00 ml aliquot was treated with \( \text{V}_2(\text{SO}_4)_3 \) to reduced the \( \text{ClO}_4^- \) to \( \text{Cl}^- \):

\[
\text{ClO}_4^- + 4\text{V}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} \rightarrow \text{Cl}^- + 12\text{SO}_4^{2-} + 8\text{VO}^{2+} + 8\text{H}^+
\]

Titration of the reduced sample required 20.25 ml of the \( \text{AgNO}_3 \) solution. Calculate the percentage of \( \text{Cl}^- \) and \( \text{ClO}_4^- \) in the sample. (Cl = 25.457 g/mole) (15%)

5. Calculate the pH change which takes place when 100 ml of 0.0500-\( F \) NaOH are added to 400 ml of a buffer solution that is 0.200 \( F \) in NH\(_3\) (NH\(_3\), dissociation constant = 1.76x10\(^{-5}\) at 25 °C) (15%)

6. Calculate pCd. When a 0.01M cadmium (II) solution is buffered with 0.10M \( \text{NH}_4^+ \) and 0.10M free \( \text{NH}_3 \), and 50 % of the cadmium (II) has been titrated with EDTA (neglecting any dilution from the EDTA titrant).

\[
\log K_{\text{cdy}^{2+}} = 16.46. \text{ Formation constants for the Cd(II)-ammonia complexes are: } \log k_1 =
\]
2.60, \( \log k_1k_2 = 4.65 \), \( \log k_1k_2k_3 = 6.04 \), and \( \log k_1k_2k_3k_4 = 6.92 \). (15%)

7. Calculate the theoretic Cell potential for the following Cell,

\[
\text{Pt} | \text{Fe}^{3+} (0.01M), \text{Fe}^{2+} (0.001M) || \text{Ag}^+ (0.02M) | \text{Ag}
\]

\[
\begin{align*}
\text{Fe}^{2+} + 2e^- & \Leftrightarrow \text{Fe}_{(s)} & E^0 &= -0.44V \\
\text{Fe}^{3+} + e^- & \Leftrightarrow \text{Fe}^{2+} & E^0 &= 0.77V \\
\text{Ag}^+ + e^- & \Leftrightarrow \text{Ag}_{(s)} & E^0 &= 0.79V
\end{align*}
\] (10%)

8. Give the single electrode potentials

\[
\begin{align*}
\text{Mn}^{2+} + 2e^- & \Leftrightarrow \text{Mn} & E^0 &= -1.18V \\
\text{Mn(OH)}_{2(s)} + 2e^- & \Leftrightarrow \text{Mn} + 2\text{OH}^- & E^0 &= -1.59V
\end{align*}
\]

Calculate the \( K_{sp} \) of \( \text{Mn(OH)}_2 \). (10%)
Analytical Chemistry

1. Iron is determined in a sample by precipitation of the hydrous oxide and ignition to Fe$_2$O$_3$. How many milligrams of sample should be taken for analysis so that each 10 mg of Fe$_2$O$_3$ represents 2.00% Fe in the sample? (Atomic weight of Fe is 55.487). (10%) 

2. A 100.0 mL sample of a spring water was analyzed for its iron content by acidifying and reducing all the iron present to Fe$^{2+}$. A 25.00 mL aliquot of a 0.002107M solution of K$_2$Cr$_2$O$_7$ was added, which resulted in the reaction

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

The excess K$_2$Cr$_2$O$_7$, was back-titrated with 10.00 mL 0.01000M Fe$^{2+}$, calculate the part per million of iron in the sample (Fe=55.847g/mol). (10%) 

3. The acid dissociation constants for sulfurous acid are:

$$K_{a1} = 1.2 \times 10^{-2} \text{ and } K_{a2} = 6.6 \times 10^{-8}.$$  

(1) Calculate the pH of a solution of 0.100M H$_2$SO$_3$.

(2) Calculate the pH of a solution of 0.100M Na$_2$SO$_3$.

(3) Write the reaction that occurs when H$_2$SO$_3$ an Na$_2$SO$_3$ are mixed.

(4) Calculate the pH of the solution resulting when equal volumes of the solution described in parts (1) and (2) are mixed. (20%) 

4. The potassium ion a 500 mL mineral water sample was precipitated with sodium tetrphenyl boron. The precipitate was filtered, washed, and then redissolved in an organic solution. An excess of mercury-(II)-EDTA chelate was added. The liberated EDTA was titrated with 28.65 mL of 0.516M Mg$^{2+}$

(1) Write balances equations for the reactions involved in the method.

(2) Calculate the potassium ion concentration in ppm. K = 39.7 (15%) 

5. The following cell was employed to determine the dissociation constant of the amine. RNH$_2$ : Pt, H$_2$ (1.00 atm) | RNH$_2$ (0.054M), RNH$_3$Cl (0.0750M) || SHE, where RNH$_3$Cl is the chloride salt of the amine, The potential of the cell was 0.481 V. Calculate $K_b$, the dissociation constant for the RNH$_2$. (20%) 

6. For the titration of 25.0 ml of Sn$^{2+}$ (0.0100M) with Ce$^{4+}$ (0.0100M) in 1 M H$_2$SO$_4$, calculate the electrode potential

(1) at the equivalence point and
6. Selenium in a 10.0g soil sample is disrilles as the tetrabromide, which is collected in aqueous solution where it is hydrolyzed to $\text{SeO}_4^{2-}$. The $\text{SeO}_4^{2-}$ is determined iodometrically. Requiring 4.5 ml of standard thiosulfate solution for the titration.

(1) If the thiosulfate titer is 0.049 mg $\text{K}_2\text{Cr}_2\text{O}_7$/ml, what is the concentration of selenium in the soil in ppm?

(2) Write balanced equations for all of the reactions involved in this problem.

(A.W.: O=16, K=39, Cr=52, Se=78.96)