Analytical Chemistry

1、Find the conditions under which Pb^{2+} and Tl^{+} can be separated quantitatively by H_2S precipitation from a solution that is 0.1 *F* in each cation. (10%)

The equilibrium constants for the two important reactions are：

$PbS(s) \rightleftharpoons Pb^{2+} + S^{2-}$ $\quad [Pb^{2+}][S^{2-}] = 7 \times 10^{-28}$

$TlS(s) \rightleftharpoons 2Tl^{+} + S^{2-}$ $\quad [Tl^{+}]^2[S^{2-}] = 1 \times 10^{-22}$

2、Calculate the normality of an iodine solution if 37.34 ml were required to titrate a 0.2040 g sample of primary standard Ag_2O_3 (gfw = 197.8 g). The reaction is (10%)

$$I_2 + H_2AsO_3^- + H_2O \rightarrow 2I^- + H_2AsO_4^- + 2H^+$$

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

$$2AgI(s) + Cl_2(g) \rightarrow 2AgCl(s) + I_2(g)$$

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 Cl^- and ClO_4^- sufficient water to give 125.0 ml of solution. A 25.00 ml aliquot required 7.05 ml of 0.04000M $AgNO_3$ to titrate the Cl^-, A second 25.00 ml aliquote was treated with $AgNO_3$ to titrate Cl^-, A second 25.00 ml aliquote was treated with $V_2(SO_4)_3$ to reduced the ClO_4^- to Cl^- ：

$$ClO_4^- + 4V_2(SO_4)_3 + 4H_2O \rightarrow Cl^- + 12SO_4^{2-} + 8VO^{2+} + 8H^+$$

Titration of the reduced sample required 20.25 ml of the $AgNO_3$ solution. Calculate the percentage of Cl^- and 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 = 1.76×10^{-5} at 25 ℃) (15%)

6、Calculate pCd. When a 0.01M cadmium (II) solution is buffered with 0.10M NH_4^+ and 0.10M free NH_3 , and 50 % of the cadmium (II) bas been titrated with EDTA (neglecting any dilution from the EDTA titrant).

$\log K_{CdY^{2-}} = 16.46$. 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,
Pt | Fe^{+++} (0.01M), Fe^{++} (0.001M) || Ag^{+} (0.02M) | Ag

$$Fe^{++} + 2e^{-} \Leftrightarrow Fe_{(s)} \qquad E^0 = -0.44V$$

$$Fe^{+++} + e^{-} \Leftrightarrow Fe^{++} \qquad E^0 = 0.771V$$

$$Ag^{+} + e^{-} \Leftrightarrow Ag_{(s)} \qquad E^0 = 0.799V$$ (10%)

8、Give the single electrode potentials

$$Mn^{2+} + 2e^{-} \Leftrightarrow Mn \qquad E^0 = -1.18V$$

$$Mn(OH)_{2(S)} + 2e^{-} \Leftrightarrow Mn + 2OH^{-} \qquad E^0 = -1.59V$$

Calculate the K_{sp} of $Mn(OH)_2$. (10%)

Analytical Chemistry

1. Iron is determined in a sample by precipitation of the hydrous oxide and ignition to Fe_2O_3. How many milligrams of sample should be taken for analysis so that each 10 mg of Fe_2O_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 $K_2Cr_2O_7$ was added, which resulted in the reaction

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

The excess $K_2Cr_2O_7$, 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:
$K_{a1} = 1.2\text{x}10^{-2}$ and $K_{a2} = 6.6\text{x}10^{-8}$.
(1) Calculate the pH of a solution of 0.100M H_2SO_3.
(2) Calculate the pH of a solution of 0.100M Na_2SO_3.
(3) Write the reaction that occurs when H_2SO_3 an Na_2SO_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 precipited with sodium tetraphenyl boron. The pretipitate 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_3Cl (0.0750M) || SHE, where RNH_3Cl 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_2SO_4, calculate the electrode potential
(1) at the equivalence point and

The formal potentials of Ce^{4+} an Sn^{4+} are 1.44V and 0.15V, respectively. (10%)

6. Selenium in a 10.0g soil sample is disrilles as the tetrabromide, which is collected in aqueous solution where it is hydrolyzed to SeO_3^{2-}. The SeO_3^{2-} is determined iodometrically. Requiring 4.5 ml of standard thiosulfate solution for the titration.

(1) If the thiosulfate titer is 0.049 mg $K_2Cr_2O_7$ /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) (15%)