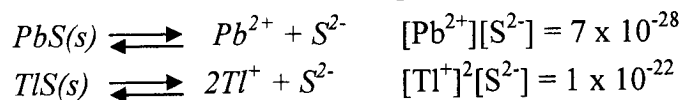


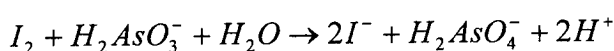
## Analytical Chemistry

- 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%)

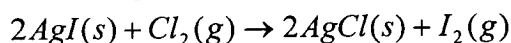
The equilibrium constants for the two important reactions are :



- 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%)

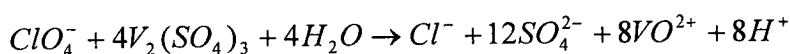


- 3 · A 0.74-g sample containing chloride and iodide ions gave a silver halide precipitate ( $AgCl$  (fw 143g) and  $AgI$  (fw 235g)) weighting 0.51 g . The precipitate was then strongly heated in a stream of  $Cl_2$  to convert the  $AgI$  to  $AgCl$



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  $Cl^-$  :



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%)

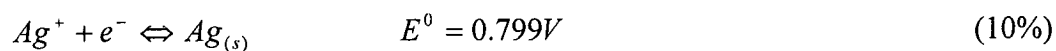
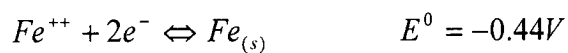
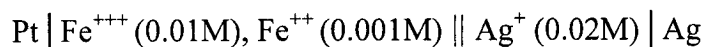
- 5 · Calculate the pH change which takes place when 100 ml of 0.0500- $F$   $NaOH$  are added to 400 ml of a buffer solution that is 0.200  $F$  in  $NH_3$  ( $NH_3$ , dissociation constant =  $1.76 \times 10^{-5}$  at 25 °C) (15%)

- 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) has been titrated with EDTA (neglecting any dilution from the EDTA titrant).

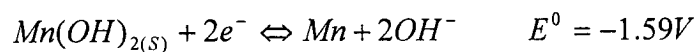
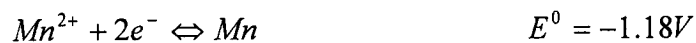
$\log K_{cdY}^{2-} = 16.46$ . Formation constants for the Cd(II)-ammonia complexes are :  $\log k_1 =$

$$2.60, \log k_1 k_2 = 4.65, \log k_1 k_2 k_3 = 6.04, \text{ and } \log k_1 k_2 k_3 k_4 = 6.92. \quad (15\%)$$

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



8 · Give the single electrode potentials

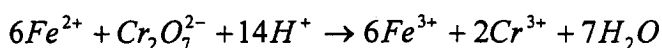


Calculate the  $K_{\text{sp}}$  of  $\text{Mn}(\text{OH})_2$ . (10%)

## Analytical Chemistry

1. Iron is determined in a sample by precipitation of the hydrous oxide and ignition to  $\text{Fe}_2\text{O}_3$ . How many milligrams of sample should be taken for analysis so that each 10 mg of  $\text{Fe}_2\text{O}_3$  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  $\text{Fe}^{2+}$ . A 25.00 mL aliquot of a 0.002107M solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  was added, which resulted in the reaction



The excess  $\text{K}_2\text{Cr}_2\text{O}_7$ , was back-titrated with 10.00 mL 0.01000M  $\text{Fe}^{2+}$ , calculate the part per million of iron in the sample ( $\text{Fe}=55.847\text{g/mol}$ ). (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  $\text{H}_2\text{SO}_3$ .

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

(3) Write the reaction that occurs when  $\text{H}_2\text{SO}_3$  and  $\text{Na}_2\text{SO}_3$  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 in a 500 mL mineral water sample was precipitated with sodium tetraphenyl 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  $\text{Mg}^{2+}$

(1) Write balanced 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.  $\text{RNH}_2$ :  
 $\text{Pt}, \text{H}_2 (1.00 \text{ atm}) | \text{RNH}_2 (0.054\text{M}), \text{RNH}_3\text{Cl} (0.0750\text{M}) || \text{SHE}$ , where  $\text{RNH}_3\text{Cl}$  is the chloride salt of the amine, The potential of the cell was 0.481 V. Calculate  $K_b$ , the dissociation constant for the  $\text{RNH}_2$ . (20%)

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

(1) at the equivalence point and

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

6. Selenium in a 10.0g soil sample is distilled as the tetrabromide, which is collected in aqueous solution where it is hydrolyzed to  $\text{SeO}_3^{2-}$ . The  $\text{SeO}_3^{2-}$  is determined iodometrically. Requiring 4.5 ml of standard thiosulfate solution for the titration.

(1) If the thiosulfate titer is 0.049 mg  $\text{K}_2\text{Cr}_2\text{O}_7$  /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) (15%)