

Spring 1998

Monday, June 8, 1998

Time: 60 minutes

Prof. Avssar Nahlé

Quantitative Analysis

Chem. 206

Lab. Final

Name: .....

Family

First name

ID. number: .....

Section:      1                      2                      3                      4  
(Please circle)

Grades

I. .... / 16  
II. .... / 16  
III. .... / 16  
IV. .... / 16  
V. .... / 20  
VI. .... / 16

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Total ..... / 100

Good luck

- I. The ion  $M^{n+}$  and the ligand  $L$  form the complex  $[ML_n]^{n-}$ . At the wavelength of maximum absorption by the complex, where  $M^{n+}$  and  $L$  do not absorb, the absorbance of solution B, which has  $C_M = 3.60 \times 10^{-4} \text{ M}$  and  $C_L = 2.48 \times 10^{-2} \text{ M}$ , is exactly equal to that of solution D, which has  $C_M = 2.80 \times 10^{-4} \text{ M}$  and  $C_L = 2.62 \times 10^{-2} \text{ M}$ . Calculate the instability constant of the complex.

Instability constant = .....

- II. a) How many milliliters of 1.00 M NaOH solution should be mixed with 60.0 mL of 0.100 M NaHCO<sub>3</sub> solution to prepare a buffer containing 2.00 mol HCO<sub>3</sub><sup>-</sup>/mol CO<sub>3</sub><sup>2-</sup>?

Volume of NaOH = ..... mL

- b) What is the pH of the buffer?

pH = .....

- III. A 50.0-mL solution containing  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  was treated with 25.0 mL of 0.0452 M EDTA to bind all the metal. The excess of unreacted EDTA required 12.4 mL of 0.0123 M  $\text{Mg}^{2+}$  for complete reaction. An excess of the reagent 2,3-dimercapto-1-propanol was then added to displace the EDTA from zinc. Another 29.2 mL of  $\text{Mg}^{2+}$  was required for reaction with the liberated EDTA. Calculate the molarities of  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  in the original solution.

$$[\text{Ni}^{2+}] = \dots\dots\dots \text{M}$$

$$[\text{Zn}^{2+}] = \dots\dots\dots \text{M}$$

IV. A solution was known to contain only sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ), and its initial pH was found to be 10.63. When a 25.00-mL aliquot of this solution was titrated with 0.1000 F hydrochloric acid, the pH of the solution after the addition of 21.00 mL of the acid was 9.35. What were the molar concentrations of sodium carbonate and sodium bicarbonate in the original solution?

Molar concentration of sodium carbonate = ..... M

Molar concentration of sodium bicarbonate = ..... M

- V. A mixture of dichromate and permanganate ions in 1F sulfuric acid was analyzed spectrophotometrically at 440 and 545 nm as a means for the simultaneous determination of these two species, and the observed values of the absorbances were 0.385 and 0.653, respectively, at each wavelength for a 1-cm cell. Independently, the absorbance in a 1-cm cell of an  $8.33 \times 10^{-4}$  M solution of dichromate in 1F sulfuric acid was found to be 0.308 at 440 nm and only 0.009 at 545 nm. Similarly, a  $3.77 \times 10^{-4}$  M solution of permanganate, placed in a 1-cm cell, exhibited an absorbance of 0.035 at 440 nm and 0.886 at 545 nm. Calculate the molar absorptivity of dichromate at 440 nm, the molar absorptivity of permanganate at 545 nm, and the concentrations of dichromate and permanganate in the unknown mixture.

Molar absorptivity of dichromate at 440 nm = .....

Molar absorptivity of permanganate at 545 nm = .....

Concentration of dichromate = .....

Concentration of permanganate = .....

- VI. A hydrochloric acid solution was standardized against sodium carbonate in the presence of methyl orange as indicator. Just 37.66 mL of the acid was required to titrate a 0.3663-g sample of the sodium carbonate. Later, it was discovered that the sodium carbonate was really the hydrated compound,  $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ , and not the anhydrous compound as expected. What were the reported and the corrected concentrations of the hydrochloric acid solution?

Reported concentration of HCl = ..... M

Corrected concentration of HCl = ..... M

Dissociation constants for acids.

Acid	Equilibrium equation	$K_a$	$pK_a$
Acetic	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	$1.8 \times 10^{-5}$	4.74
Aluminum hydroxide	$Al(OH)_3 \rightleftharpoons H^+ + AlO_2^- + H_2O$	$4 \times 10^{-13}$	12.4
Aluminum ion	$[Al(H_2O)_6]^{3+} \rightleftharpoons H^+ + [Al(H_2O)_5(OH)]^{2+}$	$1.1 \times 10^{-5}$	4.96
Ammonium ion	$NH_4^+ \rightleftharpoons H^+ + NH_3$	$5.6 \times 10^{-10}$	9.25
Antimony(III) hydroxide	$Sb(OH)_3 \rightleftharpoons H^+ + SbO_2^- + H_2O$	$1 \times 10^{-11}$	11.0
Arsenic	$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^-$	$6.0 \times 10^{-3} (K_{a1})$	2.22
	$H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^{2-}$	$1 \times 10^{-7} (K_{a2})$	7.0
	$HAsO_4^{2-} \rightleftharpoons H^+ + AsO_4^{3-}$	$3 \times 10^{-12} (K_{a3})$	11.5
Benzoic	$C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-$	$6.6 \times 10^{-5}$	4.18
Boric	$H_3BO_3 \rightleftharpoons H^+ + H_2BO_3^-$	$6.0 \times 10^{-10}$	9.22
Carbonic	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	$4.2 \times 10^{-7} (K_{a1})$	6.38
	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	$4.8 \times 10^{-11} (K_{a2})$	10.32
Chloroacetic	$ClCH_2COOH \rightleftharpoons H^+ + ClCH_2COO^-$	$1.4 \times 10^{-3}$	2.85
Chromic	$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^-$	$\approx 10^{-1} (K_{a1})$	1.0
	$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-}$	$3.2 \times 10^{-7} (K_{a2})$	6.49
Copper(II) hydroxide	$Cu(OH)_2 \rightleftharpoons H^+ + HCuO_2^-$	$1.5 \times 10^{-16} (K_{a1})$	15.82
	$HCuO_2^- \rightleftharpoons H^+ + CuO_2^{2-}$	$8 \times 10^{-14} (K_{a2})$	13.1
Dichloroacetic	$Cl_2CHCOOH \rightleftharpoons H^+ + Cl_2CHCOO^-$	$5.5 \times 10^{-2}$	1.26
Formic	$HCOOH \rightleftharpoons H^+ + HCOO^-$	$2.1 \times 10^{-4}$	3.68
Hydrocyanic	$HCN \rightleftharpoons H^+ + CN^-$	$4 \times 10^{-10}$	9.4
Hydrofluoric	$HF \rightleftharpoons H^+ + F^-$	$6.9 \times 10^{-4}$	3.16
Hydrogen peroxide	$H_2O_2 \rightleftharpoons H^+ + HO_2^-$	$2.4 \times 10^{-12}$	11.52

## Dissociation Constants for Bases

Base	Formula	Dissociation Constant at 25°C
Ammonia	$NH_3$	$1.76 \times 10^{-5}$
Aniline	$C_6H_5NH_2$	$3.94 \times 10^{-10}$
1-Butylamine	$CH_3(CH_2)_2CH_2NH_2$	$4.0 \times 10^{-4}$
Dimethylamine	$(CH_3)_2NH$	$5.9 \times 10^{-4}$
Ethanolamine	$HOC_2H_4NH_2$	$3.18 \times 10^{-5}$
Ethylamine	$CH_3CH_2NH_2$	$4.28 \times 10^{-4}$
Ethylenediamine	$NH_2C_2H_4NH_2$	$K_1 = 8.5 \times 10^{-5}$
		$K_2 = 7.1 \times 10^{-8}$
Hydrazine	$H_2NNH_2$	$1.3 \times 10^{-6}$
Hydroxylamine	$HONH_2$	$1.07 \times 10^{-6}$
Methylamine	$CH_3NH_2$	$4.8 \times 10^{-4}$
Piperidine	$C_5H_{11}N$	$1.3 \times 10^{-2}$
Pyridine	$C_5H_5N$	$1.7 \times 10^{-9}$
Trimethylamine	$(CH_3)_3N$	$6.25 \times 10^{-5}$

From L. Meites, *Handbook of Analytical Chemistry*, p. 1-21. New York: McGraw-Hill, 1963. With permission.