

Fall 1995-96  
Time = 2 hours

Saturday Feb. 3, 1996  
Professor Ayssar Nahlé

Chemistry 215

Quantitative Analysis

Final

Student's name: .....  
Family First name

I.D. no.: ..... - .....

Grade

I.....	/ 14
II.....	/ 16
III.....	/ 16
IV.....	/ 18
V.....	/ 16
VI.....	/ 20

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Total: /100

Good Luck

I. a) Calculate the volumes of 0.500 M  $\text{NH}_4\text{Cl}$  and 0.500 M  $\text{NH}_3$  required for the preparation of 200 mL of a buffer of pH 8.00. (dissociation constant for ammonia =  $1.8 \times 10^{-5}$ )

$$V_{\text{NH}_4\text{Cl}} = \dots\dots\dots$$

$$V_{\text{NH}_3} = \dots\dots\dots$$

b) Estimate the absolute and the relative standard deviations ( $S_y$ ) and ( $\frac{S_y}{y}$ ) respectively in the results of the accompanying calculation (the numbers in parentheses are absolute standard deviations for the numbers they follow). Round the result to the appropriate number of significant figures. (Fill in the blank).

$$y = \frac{\log 12.321 (\pm 0.004) + 14.03 (\pm 0.06)}{[1.74 (\pm 0.03) - 0.211 (\pm 0.002)]^3} = 4.2171189 (\pm ??)$$

$$\frac{S_y}{y} = \dots\dots\dots$$

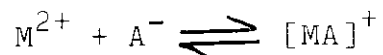
$$S_y = \dots\dots\dots$$

$$y = \dots\dots\dots \pm \dots\dots\dots$$

II. The transmittance of solutions B and D of substance X is 15.85% and 50.12%, respectively. At what volume ratio ( $V_B/V_D$ ) should solutions B and D be mixed so that the transmittance of the resulting solution would be 21.13% (all measurements are made in the same cell, and at the same wavelength)?

$$V_B/V_D = \dots\dots\dots$$

III. The complex  $[MA]^+$  is formed according to the reaction:



When a mixture of forty five milliliters of 0.0110 M  $M^{2+}$  solution and 45.0 ml of 0.0110 M  $A^-$  solution is placed in the left-hand half-cell of the galvanic cell

(-)  $M / M^{2+}$  (xM),  $[MA]^+$  (0.00550 M) //  $KCl$  (1.00 M),  $Hg_2Cl_2/Hg$  (+)

The emf of the cell was +0.259 V. Calculate the instability constant of the complex  $[MA]^+$  ( $E_{M^{2+}, M}^\circ = +0.178$  V)

$K_{inst.} = \dots\dots\dots$

IV. Each of the samples listed below contains the indicated number of millimoles of NaOH, NaHCO<sub>3</sub>, and Na<sub>2</sub>CO<sub>3</sub>. Calculate the volumes of 0.1000 M HCl solution which would be consumed for each sample, in the presence of a) phenolphthalein (V<sub>p</sub>) , b) Methyl orange (V<sub>m</sub>) as indicators.

Solution	mmol			V <sub>p</sub>	V <sub>m</sub>
	NaOH	NaHCO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>		
a	0	1.42	0		
b	0	0	2.15		
c	2.48	1.48	0		
d	0	0.83	1.19		
e	2.56	0	1.00		

V. The potential of a nitrate-selective electrode in a  $2.50 \times 10^{-3} \text{ M}$   $\text{NaNO}_3$  solution is  $+0.1194 \text{ V}$  vs. SCE. If solid  $\text{NaNO}_3$  is added to  $500 \text{ ml}$  of this solution until the potential becomes  $+0.0826 \text{ V}$ , what the new nitrate concentration be and what is the quantity of  $\text{NaNO}_3$  added? Assume negligible volume change upon the addition of  $\text{NaNO}_3$ .

$[\text{NO}_3^-]$  after adding  $\text{NaNO}_3 = \dots\dots\dots \text{ M}$

Weight of  $\text{NaNO}_3$  added =  $\dots\dots\dots \text{ g}$

- VI. a) Derive the titration curve of 25.00 ml of 0.100 M acetic acid solution titrated with 0.100 M NaOH solution. The pH of the resulting solution should be calculated according to the NaOH volumes shown in the table below, and must be inserted in the appropriate column.
- b) Plot the resulting titration curve on one of the graph papers provided and show graphically the volume of NaOH at the end point(s).
- c) Calculate the first derivative ( $\Delta \text{pH}/\Delta V$ ) and the corresponding volume ( $V'$ ) (fill the values in the table). Do the same with the second derivative ( $\Delta^2 \text{pH}/\Delta V^2$ ) and the corresponding volume ( $V''$ ).
- d) Plot the first and the second derivative on the other provided graph papers and show graphically the end points.
- (dissociation constant for acetic acid =  $1.75 \times 10^{-5}$ )

$V_{\text{NaOH}}$	PH	$\Delta \text{pH}/\Delta V$	$V'$	$\Delta^2 \text{pH}/\Delta V^2$	$V''$
0.00					
5.00					
10.00					
12.50					
15.00					
20.00					
24.00					
24.90					
25.00					
26.00					
30.00					
40.00					

Standard and formal potentials,  $E^0$  and  $E^{0'}$ , at 25° C

Half reaction	$E^0$ , volts	$E^{0'}$ , volts	Conditions for the formal potentials
<i>1. Acidic solutions</i>			
$2\text{Cl}_2 + 2e \rightleftharpoons \text{I}_2 + 4\text{Cl}^-$	+1.06		
$2\text{Hg}_2^{2+} + 2e \rightleftharpoons \text{Hg}_2^{2+}$	+0.920		
$\text{Cu}^{2+} + \text{I}^- + e \rightleftharpoons \text{CuI}$	+0.86		
$\text{Ag}^+ + e \rightleftharpoons \text{Ag}$	+0.7994		
$\text{Hg}_2^{2+} + 2e \rightleftharpoons 2\text{Hg}$	+0.789		
$\text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+}$	+0.771		
		+0.732	1 M $\text{HClO}_4$
		+0.700	1 M $\text{HCl}$
		+0.674	1 M $\text{H}_2\text{SO}_4$
		+0.46	2 M $\text{H}_3\text{PO}_4$
$\text{O}_2 + 2\text{H}^+ + 2e \rightleftharpoons \text{H}_2\text{O}_2$	+0.682		
$\text{I}_2(\text{aq}) + 2e \rightleftharpoons 2\text{I}^-$	+0.6197 <sup>b</sup>		
$\text{MnO}_4^- + e \rightleftharpoons \text{MnO}_4^{2-}$	+0.564		
$\text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2e \rightleftharpoons \text{H}_3\text{AsO}_3 + \text{H}_2\text{O}$	+0.559		
		+0.577	1 M $\text{HCl}$ , 1 M $\text{HClO}_4$
$[\text{I}_3]^- + 2e \rightleftharpoons 3\text{I}^-$	+0.536		
$\text{I}_2 + 2e \rightleftharpoons 2\text{I}^-$	+0.5355 <sup>b</sup>		
$\text{Cu}^+ + e \rightleftharpoons \text{Cu}$	+0.521		
$\text{H}_2\text{SO}_3 + 4\text{H}^+ + 4e \rightleftharpoons \text{S} + 3\text{H}_2\text{O}$	+0.45		
$\text{Ag}_2\text{CrO}_4 + 2e \rightleftharpoons 2\text{Ag} + \text{CrO}_4^{2-}$	+0.446		
$2\text{H}_2\text{SO}_3 + 2\text{H}^+ + 4e \rightleftharpoons \text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O}$	+0.40		
$[\text{Fe}(\text{CN})_6]^{3-} + e \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$	+0.356		
		+0.71	1 M $\text{HCl}$
$\text{Cu}^{2+} + 2e \rightleftharpoons \text{Cu}$	+0.337		
$\text{Hg}_2\text{Cl}_2 + 2e \rightleftharpoons 2\text{Hg} + 2\text{Cl}^-$	+0.2680		
		+0.3337	0.1 M $\text{KCl}$
		+0.2801	1 M $\text{KCl}$
		+0.2412	$\text{KCl}$ satur.
$\text{AgCl} + e \rightleftharpoons \text{Ag} + \text{Cl}^-$	+0.2224		
$\text{SO}_4^{2-} + 4\text{H}^+ + 2e \rightleftharpoons \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	+0.17		
$\text{Cu}^{2+} + e \rightleftharpoons \text{Cu}^+$	+0.153		
$\text{Sn}^{4+} + 2e \rightleftharpoons \text{Sn}^{2+}$	+0.15		
$[\text{SnCl}_6]^{2-} + 2e \rightleftharpoons [\text{SnCl}_4]^{2-} + 2\text{Cl}^-$		+0.14	1 M $\text{HCl}$
$\text{S} + 2\text{H}^+ + 2e \rightleftharpoons \text{H}_2\text{S}$	+0.141		
$\text{AgBr} + e \rightleftharpoons \text{Ag} + \text{Br}^-$	+0.095		
$\text{S}_4\text{O}_6^{2-} + 2e \rightleftharpoons 2\text{S}_2\text{O}_3^{2-}$	+0.08		
$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-} + e \rightleftharpoons \text{Ag} + 2\text{S}_2\text{O}_3^{2-}$	+0.01		
$2\text{H}^+ + 2e \rightleftharpoons \text{H}_2$	0.000		