Fall 1997-98 | Tues. February 10, 1998

Time: 2 hours | Prof. Ayssar Nahlé

Quantitative Analysis

Chemistry 206

Final Exam

Name: ....
Family First name

ID no.: ....

Section no.: 1 2 3 4 5
(Please circle)

Grades

I.	....	/ 16
II.	....	/ 16
III.	....	/ 20
IV.	....	/ 18
V.	....	/ 15
VI.	....	/ 15
Total	....	/ 100

Good Luck

I. A Mixture of Mn^{2+}, Mg^{2+}, and Zn^{2+} was analyzed as follows: The 25.00-mL sample was treated with 0.25 g of $NH_3OH^+Cl^-$ (hydroxylammonium chloride, a reducing agent that maintains manganese in the +2 state), 10 mL of ammonia buffer (pH 10), and a few drops of Eriochrome black T indicator and then diluted to 100 mL. It was warmed to 40°C and titrated with 39.98 mL of 0.04500 M EDTA to the blue end point. Then 2.5 g of NaF was added to displace Mg^{2+} from its EDTA complex. The liberated EDTA required 10.26 mL of standard 0.02065 M Mn^{2+} for complete titration. After this second end point was reached, 5 mL of 15 wt % aqueous KCN was added to displace Zn^{2+} from its EDTA complex. This time the liberated EDTA required 15.47 mL of standard 0.02065 M Mn^{2+}. Calculate the number of milligrams of each metal (Mn^{2+}, Zn^{2-}, and Mg^{2+}) in the 25.00-mL sample of unknown.

.... **mg Mg**

.... **mg Zn**

.... **mg Mn**

II. A 1.000-g sample consisting of $NaHCO_3$, Na_2CO_3, and impurities was analysed as follows: It was first titrated to the phenolphthalein end point, 25.00 mL of 0.1000 M HCl being required. To this solution was added a 50.00-mL portion of 0.1000 M NaOH. Then Ba^{2+} ions were added to precipitate $BaCO_3$. The precipitate was separated by filtration and the filtrate titrated with 0.1000 M HCl using phenolphthalein indicator. 10.00 mL of acid was required. Calculate the percentages of Na_2CO_3 and $NaHCO_3$ in the sample.

% Na_2CO_3 = ...

% $NaHCO_3$ = ...

III. a) Calculate the potential of the solution in the titration of 50.0 mL of 0.100 M Fe^{2+} in 1.00 M $HClO_4$ with 0.0167 M $Cr_2O_7^{2-}$ at the volume of added titrant as shown in the table below. ***(Enter the calculated potentials in the appropriate boxes)***

Volume of $Cr_2O_7^{2-}$ mL	Potential E mV	$\frac{\Delta E}{\Delta V}$	V'
0.00			
5.00			
10.00			
20.00			
25.00			
30.00			
40.0			
50.00			
55.00			
60.00			

b) Plot the resulting titration curve on the provided graph paper.

c) Calculate the first derivative ($\frac{\Delta E}{\Delta V}$) and the corresponding volume (V') and insert them in the table above.

d) On the same graph paper and using a different potential scale, plot the first derivative curve, and show the end point(s).

IV. The T, using a 1-cm cell, of a 5.0×10^{-4} M solution of substance **K** (MW 170) was 0.289 at 530 nm and 0.892 at 640 nm, and the T, using the same cell, of a 5.0×10^{-4} M solution of substance **L** (MW 234) was 0.933 at 530 nm and 0.240 at 640 nm. Using the same cell, the T of an unknown solution was 0.661 at 530 nm and 0.381 at 640 nm. Calculate:

a) the absorbances *(fillthe values in the table below)*;

	Absorbance at 530 nm	**Absorbance at 640 nm**
Solution of K		
Solution of L		
Unkown solution		

b) the molar absorptivities of **K** and L;

Molar absorptivity of K = ...

Molar absorptivity of L = ...

c) the molar concentrations of **K** and **L** in the unknown;

Concentration of K = ... **M**

Concentration of L = ... **M**

d) express these concentrations as ppm (mg/liter).

Concentration of K = ... **ppm**

Concentration of L = ... **ppm**

V. Calculate the voltage of the following cell:

Pt|Tl^+(0.100 M), Tl^{3+}(0.0100 M) || MnO_4^-(0.0100 M), Mn^{2+}(0.100 M), H^+(pH 2.00)|Pt

E_{cell} = ... V

VI. An analyst wishes to prepare 100 mL of a solution of pH 9.00 from 0.20 M ammonia and 0.050 M HCl. How many milliliters of each solution should be mixed to give the desired solution? Assume volumes additive.

Volume of ammonia = ... mL

Volume of HCl = ... mL

Half-Reaction	E^0, V*	Formal Potential, V†
Aluminum		
$Al^{3+} + 3e^- \rightleftharpoons Al(s)$	−1.662	
Antimony		
$Sb_2O_5(s) + 6H^+ + 4e^- \rightleftharpoons 2SbO^+ + 3H_2O$	+0.581	
Arsenic		
$H_3AsO_4 + 2H^+ + 2e^- \rightleftharpoons H_3AsO_3 + H_2O$	+0.559	0.577 in 1 M HCl, $HClO_4$
Barium		
$Ba^{2+} + 2e^- \rightleftharpoons Ba(s)$	−2.906	
Bismuth		
$BiO^+ + 2H^+ + 3e^- \rightleftharpoons Bi(s) + H_2O$	+0.320	
$BiCl_4^- + 3e^- \rightleftharpoons Bi(s) + 4Cl^-$	+0.16	
Bromine		
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1.065	1.05 in 4 M HCl
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.087‡	
$BrO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}Br_2(l) + 3H_2O$	+1.52	
$BrO_3^- + 6H^+ + 6e^- \rightleftharpoons Br^- + 3H_2O$	+1.44	
Cadmium		
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	−0.403	
Calcium		
$Ca^{2+} + 2e^- \rightleftharpoons Ca(s)$	−2.866	
Carbon		
$C_6H_4O_2$ (quinone) $+ 2H^+ + 2e^- \rightleftharpoons C_6H_4(OH)_2$	+0.699	0.696 in 1 M HCl, $HClO_4$, H_2SO_4
$2CO_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2C_2O_4$	−0.49	
Cerium		
$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$		+1.70 in 1 M $HClO_4$; +1.61 in 1 M HNO_3; +1.44 in 1 M H_2SO_4
Chlorine		
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.359	
$HClO + H^+ + e^- \rightleftharpoons \frac{1}{2}Cl_2(g) + H_2O$	+1.63	
$ClO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}Cl_2(g) + 3H_2O$	+1.47	
Chromium		
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	−0.408	
$Cr^{3+} + 3e^- \rightleftharpoons Cr(s)$	−0.744	
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33	
Cobalt		
$Co^{2+} + 2e^- \rightleftharpoons Co(s)$	−0.277	
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1.808	
Copper		
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+0.337	
$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0.153	
$Cu^+ + e^- \rightleftharpoons Cu(s)$	+0.521	
$Cu^{2+} + I^- + e^- \rightleftharpoons CuI(s)$	+0.86	
$CuI(s) + e^- \rightleftharpoons Cu(s) + I^-$	−0.185	
Fluorine		
$F_2(g) + 2H^+ + 2e^- \rightleftharpoons 2HF(aq)$	+3.06	
Hydrogen		
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.000	−0.005 in 1 M HCl, $HClO_4$
Iodine		
$I_2(s) + 2e^- \rightleftharpoons 2I^-$	+0.5355	
$I_2(aq) + 2e^- \rightleftharpoons 2I^-$	+0.615‡	
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+0.536	
$ICl_2^- + e^- \rightleftharpoons \frac{1}{2}I_2(s) + 2Cl^-$	+1.056	
$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2(s) + 3H_2O$	+1.196	
$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2(aq) + 3H_2O$	+1.178‡	
$IO_3^- + 2Cl^- + 6H^+ + 4e^- \rightleftharpoons ICl_2^- + 3H_2O$	+1.24	
$H_5IO_6 + H^+ + 2e^- \rightleftharpoons IO_3^- + 3H_2O$	+1.601	

Half-Reaction	E^0, V*	Formal Potential, V†
Iron		
$Fe^{2+} + 2e^- \rightleftharpoons Fe(s)$	−0.440	
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771	0.700 in 1 M HCl; 0.732 in 1 M $HClO_4$; 0.68 in 1 M H_2SO_4
$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$	+0.36	0.71 in 1 M HCl; 0.72 in 1 M $HClO_4$, H_2SO_4
Lead		
$Pb^{2+} + 2e^- \rightleftharpoons Pb(s)$	−0.126	−0.14 in 1 M $HClO_4$; −0.29 in 1 M H_2SO_4
$PbO_2(s) + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$	+1.455	
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	−0.350	
Lithium		
$Li^+ + e^- \rightleftharpoons Li(s)$	−3.045	
Magnesium		
$Mg^{2+} + 2e^- \rightleftharpoons Mg(s)$	−2.363	
Manganese		
$Mn^{2+} + 2e^- \rightleftharpoons Mn(s)$	−1.180	
$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$		1.51 in 7.5 M H_2SO_4
$MnO_2(s) + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	+1.23	
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.51	
$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2(s) + 2H_2O$	+1.695	
$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$	+0.564	
Mercury		
$Hg_2^{2+} + 2e^- \rightleftharpoons Hg(l)$	+0.788	0.274 in 1 M HCl; 0.776 in 1 M $HClO_4$; 0.674 in 1 M H_2SO_4
$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$	+0.920	0.907 in 1 M $HClO_4$
$Hg^{2+} + 2e^- \rightleftharpoons 2Hg(l)$	+0.854	
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	+0.268	0.244 in sat'd KCl; 0.282 in 1 M KCl; 0.334 in 0.1 M KCl
$Hg_2SO_4(s) + 2e^- \rightleftharpoons 2Hg(l) + SO_4^{2-}$	+0.615	
Nickel		
$Ni^{2+} + 2e^- \rightleftharpoons Ni(s)$	−0.250	
Nitrogen		
$N_2(g) + 5H^+ + 4e^- \rightleftharpoons N_2H_5^+$	−0.23	
$HNO_2 + H^+ + e^- \rightleftharpoons NO(g) + H_2O$	+1.00	
$NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O$	+0.94	0.92 in 1 M HNO_3
Oxygen		
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.776	
$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^-$	+0.88	
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229	
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.682	
$O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O$	+2.07	
Palladium		
$Pd^{2+} + 2e^- \rightleftharpoons Pd(s)$	+0.987	
Platinum		
$PtCl_4^{2-} + 2e^- \rightleftharpoons Pt(s) + 4Cl^-$	+0.73	
$PtCl_6^{2-} + 2e^- \rightleftharpoons PtCl_4^{2-} + 2Cl^-$	+0.68	
Potassium		
$K^+ + e^- \rightleftharpoons K(s)$	−2.925	
Selenium		
$H_2SeO_3 + 4H^+ + 2e^- \rightleftharpoons Se(s) + 3H_2O$	+0.740	
$SeO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons H_2SeO_3 + H_2O$	+1.15	

Half-Reaction	E^0, V*	Formal Potential, V†
Silver		
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.799	0.228 in 1 M HCl; 0.792 in 1 M $HClO_4$; 0.77 in 1 M H_2SO_4
$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-$	+0.073	
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+0.222	0.228 in 1 M KCl
$Ag(CN)_2^- + e^- \rightleftharpoons Ag(s) + 2\,CN^-$	−0.31	
$Ag_2CrO_4(s) + 2\,e^- \rightleftharpoons 2\,Ag(s) + CrO_4^{2-}$	+0.446	
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	−0.151	
$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2\,S_2O_3^{2-}$	+0.017	
Sodium		
$Na^+ + e^- \rightleftharpoons Na(s)$	−2.714	
Sulfur		
$S(s) + 2\,H^+ + 2\,e^- \rightleftharpoons H_2S(g)$	+0.141	
$H_2SO_3 + 4\,H^+ + 4\,e^- \rightleftharpoons S(s) + 3\,H_2O$	+0.450	
$SO_4^{2-} + 4\,H^+ + 2\,e^- \rightleftharpoons H_2SO_3 + H_2O$	+0.172	
$S_4O_6^{2-} + 2\,e^- \rightleftharpoons 2\,S_2O_3^{2-}$	+0.08	
$S_2O_8^{2-} + 2\,e^- \rightleftharpoons 2\,SO_4^{2-}$	+2.01	
Thallium		
$Tl^+ + e^- \rightleftharpoons Tl(s)$	−0.336	−0.551 in 1 M HCl; −0.33 in 1 M $HClO_4$, H_2SO_4
$Tl^{3+} + 2\,e^- \rightleftharpoons Tl^+$	+1.25	0.77 in 1 M HCl
Tin		
$Sn^{2+} + 2\,e^- \rightleftharpoons Sn(s)$	−0.136	−0.16 in 1 M $HClO_4$
$Sn^{4+} + 2\,e^- \rightleftharpoons Sn^{2+}$	+0.154	0.14 in 1 M HCl
Titanium		
$Ti^{3+} + e^- \rightleftharpoons Ti^{2+}$	−0.369	
$TiO^{2+} + 2\,H^+ + e^- \rightleftharpoons Ti^{3+} + H_2O$	+0.099	0.04 in 1 M H_2SO_4
Uranium		
$UO_2^{2+} + 4\,H^+ + 2\,e^- \rightleftharpoons U^{4+} + 2\,H_2O$	+0.334	
Vanadium		
$V^{3+} + e^- \rightleftharpoons V^{2+}$	−0.256	−0.21 in 1 M $HClO_4$
$VO^{2+} + 2\,H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.359	
$V(OH)_4^+ + 2\,H^+ + e^- \rightleftharpoons VO^{2+} + 3\,H_2O$	+1.00	1.02 in 1 M HCl, $HClO_4$
Zinc		
$Zn^{2+} + 2\,e^- \rightleftharpoons Zn(s)$	−0.763	

Dissociation constants for acids.

Acid	Equilibrium equation	K_a	pK_a
Acetic	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.8×10^{-5}	4.74
Aluminum hydroxide	$Al(OH)_3 \rightleftharpoons H^+ + AlO_2^- + H_2O$	4×10^{-13}	12.4
Aluminum ion	$[Al(H_2O)_6]^{3+} \rightleftharpoons H^+ + [Al(H_2O)_5(OH)]^{2+}$	1.1×10^{-5}	4.96
Ammonium ion	$NH_4^+ \rightleftharpoons H^+ + NH_3$	5.6×10^{-10}	9.25
Antimony(III) hydroxide	$Sb(OH)_3 \rightleftharpoons H^+ + SbO_2^- + H_2O$	1×10^{-11}	11.0
Arsenic	$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^-$	6.0×10^{-3} (K_{a_1})	2.22
	$H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^{2-}$	1×10^{-7} (K_{a_2})	7.0
	$HAsO_4^{2-} \rightleftharpoons H^+ + AsO_4^{3-}$	3×10^{-12} (K_{a_3})	11.5
Benzoic	$C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-$	6.6×10^{-5}	4.18
Boric	$H_3BO_3 \rightleftharpoons H^+ + H_2BO_3^-$	6.0×10^{-10}	9.22
Carbonic	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	4.2×10^{-7} (K_{a_1})	6.38
	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	4.8×10^{-11} (K_{a_2})	10.32
Chloroacetic	$ClCH_2COOH \rightleftharpoons H^+ + ClCH_2COO^-$	1.4×10^{-3}	2.85
Chromic	$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^-$	$\simeq 10^{-1}$ (K_{a_1})	1.0
	$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-}$	3.2×10^{-7} (K_{a_2})	6.49
Copper(II) hydroxide	$Cu(OH)_2 \rightleftharpoons H^+ + HCuO_2^-$	1.5×10^{-16} (K_{a_1})	15.82
	$HCuO_2^- \rightleftharpoons H^+ + CuO_2^{2-}$	8×10^{-14} (K_{a_2})	13.1
Dichloroacetic	$Cl_2CHCOOH \rightleftharpoons H^+ + Cl_2CHCOO^-$	5.5×10^{-2}	1.26
Formic	$HCOOH \rightleftharpoons H^+ + HCOO^-$	2.1×10^{-4}	3.68
Hydrocyanic	$HCN \rightleftharpoons H^+ + CN^-$	4×10^{-10}	9.4
Hydrofluoric	$HF \rightleftharpoons H^+ + F^-$	6.9×10^{-4}	3.16
Hydrogen peroxide	$H_2O_2 \rightleftharpoons H^+ + HO_2^-$	2.4×10^{-12}	11.62

Dissociation Constants for Bases

Base	Formula	Dissociation Constant at 25°C
Ammonia	NH_3	1.76×10^{-5}
Aniline	$C_6H_5NH_2$	3.94×10^{-10}
1-Butylamine	$CH_3(CH_2)_2CH_2NH_2$	4.0×10^{-4}
Dimethylamine	$(CH_3)_2NH$	5.9×10^{-4}
Ethanolamine	$HOC_2H_4NH_2$	3.18×10^{-5}
Ethylamine	$CH_3CH_2NH_2$	4.28×10^{-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	1.3×10^{-6}
Hydroxylamine	$HONH_2$	1.07×10^{-8}
Methylamine	CH_3NH_2	4.8×10^{-4}
Piperidine	$C_5H_{11}N$	1.3×10^{-3}
Pyridine	C_5H_5N	1.7×10^{-9}
Trimethylamine	$(CH_3)_3N$	6.25×10^{-5}

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