Spring 1997

Friday, June 13, 1997

Time: 2 hours

Prof. Ayssar Nahlé

Chemistry 215

Analytical Chemistry

Final

Name: ....

Family First name

I.D. number: ...._ ....

Grade

I	/ 14
II	/ 14
III	/ 14
IV	/ 20
V	/ 14
VI	/ 24
total	/100

Good luck

I. In each of two beakers 100 mL of a 0.100 M Fe^{2+}— 0.100 M Fe^{3+} solution is added, an electrode is immersed in each solution, and the two solutions are connected by a salt bridge. When 10.0 mL of a reducing solution is added to one of the two beakers, the voltage of the cell is changed from 0.0000 to +0.1183 V. Calculate the normality of the reducing solution.

Normality = ...

II. A 1.00×10^{-4} M solution of substance **B** has absorbances of 0.840 and 0.360 at 320 and 278 nm, respectively, whereas a 1.00×10^{-4} M solution of substance **C** has absorbances of 0.480 and 0.432 at these wavelengths, respectively. An unknown solution has $A_{320} = 0.386$ and $A_{278} = 0.347$. All measurements were carried out under the same experimental conditions.

a) Find which compound (**B** or **C**) exists in the unknown solution,

Compound .... exists in the unknown solution

and **b)** calculate its concentration.

Concentration = ... M

III. The nitrate concentration in an industrial effluent is determined using a nitrate ion-selective electrode. Standards and samples are diluted 20-fold with 0.1 M K_2SO_4 to maintain constant ionic strength. Nitrate standards of 0.0050 and 0.0100 M give potential readings of -108.6 and -125.2 mV, respectively. The sample gives a reading of -119.6 mV. What is the concentration of nitrate in the sample?

$[NO_3^-]$ in the sample = ... M

IV.

A) Find the absolute and the percent relative standard deviations (S_y and $\frac{S_y}{y}$) for the following expressions, and round the result to the appropriate significant figures.

a) $$y = \log_{10}\left(\frac{\sqrt{0.104(\pm 0.006)}}{0.0511(\pm 0.0009)}\right) = 0.800095.....$$

S_y = ...

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

y = ... ± ....

b) $$y = \frac{\left[2.698(\pm 0.007) + \log_{10} 13.5(\pm 0.3)\right]^3}{anti\log_{10} 1.73(\pm 0.05)} \times 2.179(\pm 0.004) = 2.276599378....$$

S_y = ...

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

y = ... ± ....

B) The Ti content (wt%) of two different ore samples was measured several times by the same method. Are the mean values significantly different at the 95% confidence level?

Sample 1	0.0134	0.0138	0.0128	0.0133	0.0137
Sample 2	0.0135	0.0142	0.0137	0.0141	0.0143

Answer: ....

C) Calculate the voltage of the following cell:

Pt | Sn^{4+} (8.0×10^{-4} M), Sn^{2+} (0.040 M) || $[Ag(CN)_2]^-$ (9.0×10^{-4} M), CN^- (0.030 M) | **Ag**

E_{cell} = ...

V. A 0.1455-g sample of sulfates was dissolved in water, the sulfates were precipitated as $BaSO_4$, the precipitate was dissolved in 25.00 mL of 0.02004 M EDTA solution and the excess of unreacted EDTA was titrated with 3.25 mL of $MgSO_4$ solution. A blank determination with the same volume of EDTA required 45.34 mL of $MgSO_4$ solution. Calculate:

a) the molarity of the $MgSO_4$ solution,

Molarity of $MgSO_4$ = ...

b) the percent of Na_2SO_4 in the sample.

% Na_2SO_4 = ...

VI. a) Derive the titration curve of 50.00 mL of a solution 0.1000 M in both hydrochloric acid and acetic acid with 0.2000 M NaOH solution. Calculate the pH of the solution after addition of each NaOH volume as indicated in the following table, and insert the calculated pH values in the appropriate column.

V_{NaOH}, mL	pH	$\frac{\Delta pH}{\Delta V}$	V'	$\frac{\Delta^2 pH}{\Delta V^2}$	V"
0.00					
5.00					
10.00					
15.00					
22.00					
25.00					
28.00					
30.00					
35.00					
40.00					
45.00					
50.00					
52.00					
56.00					
60.00					

b) On one graph paper plot the resulting titration curve.

c) Calculate the first and the second derivatives ($\frac{\Delta pH}{\Delta V}$ and $\frac{\Delta^2 pH}{\Delta V^2}$ respectively) and their corresponding volumes (V' and V"). Insert the values in the table above.

d) Plot the first derivative on the second provided graph paper.

Half reaction	E^0, volts	$E^{0'}$, volts	Conditions for the formal potentials
1. Acidic solutions			
$Pb^{2+} + 2e \rightleftharpoons Pb$	−0.126		
$Sn^{2+} + 2e \rightleftharpoons Sn$	−0.136		
$AgI + e \rightleftharpoons Ag + I^-$	−0.151		
$CuI + e \rightleftharpoons Cu + I^-$	−0.185		
$Ni^{2+} + 2e \rightleftharpoons Ni$	−0.250		
$V^{3+} + e \rightleftharpoons V^{2+}$	−0.255		
$Co^{2+} + 2e \rightleftharpoons Co$	−0.277		
$[Ag(CN)_2]^- + e \rightleftharpoons Ag + 2CN^-$	−0.31		
$PbSO_4 + 2e \rightleftharpoons Pb + SO_4^{2-}$	−0.356		
$Cd^{2+} + 2e \rightleftharpoons Cd$	−0.403		
$Cr^{3+} + e \rightleftharpoons Cr^{2+}$	−0.41		
$Fe^{2+} + 2e \rightleftharpoons Fe$	−0.440		
$Cr^{3+} + 3e \rightleftharpoons Cr$	−0.74		
$Zn^{2+} + 2e \rightleftharpoons Zn$	−0.763		
$Mn^{2+} + 2e \rightleftharpoons Mn$	−1.18		
$Al^{3+} + 3e \rightleftharpoons Al$	−1.66		
$Mg^{2+} + 2e \rightleftharpoons Mg$	−2.37		
$Na^+ + e \rightleftharpoons Na$	−2.71		
$Ca^{2+} + 2e \rightleftharpoons Ca$	−2.87		
$Sr^{2+} + 2e \rightleftharpoons Sr$	−2.89		
$Ba^{2+} + 2e \rightleftharpoons Ba$	−2.90		
$K^+ + e \rightleftharpoons K$	−2.92		
$Li^+ + e \rightleftharpoons Li$	−3.04		
2. Alkaline solutions			
$ClO^- + H_2O + 2e \rightleftharpoons Cl^- + 2OH^-$	+0.89		
$O_2^{2-} + 2H_2O + 2e \rightleftharpoons 4OH^-$	+0.88		
$BrO^- + H_2O + 2e \rightleftharpoons Br^- + 2OH^-$	+0.76		
$MnO_4^- + 2H_2O + 3e \rightleftharpoons MnO_2 + 4OH^-$	+0.59		
$O_2 + 2H_2O + 4e \rightleftharpoons 4OH^-$	+0.401		
$[Ag(NH_3)_2]^+ + e \rightleftharpoons Ag + 2NH_3$	+0.373		
$ClO_3^- + H_2O + 2e \rightleftharpoons ClO_2^- + 2OH^-$	+0.33		
$Co(OH)_3 + e \rightleftharpoons Co(OH)_2 + OH^-$	+0.17		
$[Co(NH_3)_6]^{3+} + e \rightleftharpoons [Co(NH_3)_6]^{2+}$	+0.1		
$NO_3^- + H_2O + 2e \rightleftharpoons NO_2^- + 2OH^-$	+0.01		
$MnO_2 + 2H_2O + 2e \rightleftharpoons Mn(OH)_2 + 2OH^-$	−0.05		
$[Cu(NH_3)_4]^{2+} + 2e \rightleftharpoons Cu + 4NH_3$	−0.11		
$NO_3^- + 6H_2O + 8e \rightleftharpoons NH_3 + 9OH^-$	−0.13		
$NO_2^- + 5H_2O + 6e \rightleftharpoons NH_3 + 7OH^-$	−0.18		
$[Ag(CN)_2]^- + e \rightleftharpoons Ag + 2CN^-$	−0.31		
$NO_2^- + H_2O + e \rightleftharpoons 2OH^- + NO$	−0.46		

Reaction	Potential, V
$Co^{2+} + 2e = Co$	−0.28
$Co^{3+} + e = Co^{2+}$(3 *M* HNO_3)	1.842
$Cr^{2+} + 2e = Cr$	−0.557
$Cr^{3+} + e = Cr^{2+}$	−0.41
$Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O$	1.33
$Cu^+ + e = Cu$	0.522
$Cu^{2+} + 2CN^- + e = Cu(CN)_2^-$	1.12
$Cu^{2+} + e = Cu^+$	0.158
$Cu^{2+} + 2e = Cu$	0.3402
$Cu^{2+} + 2e = Cu(Hg)$	0.345
$Eu^{3+} + e = Eu^{2+}$	−0.43
$\frac{1}{2}F_2 + H^+ + e = HF$	3.03
$Fe^{2+} + 2e = Fe$	−0.409
$Fe^{3+} + e = Fe^{2+}$(1 *M* HCl)	0.770
$Fe(CN)_6^{3-} + e = Fe(CN)_6^{4-}$(1 *M* H_2SO_4)	0.69
$2H^+ + 2e = H_2$	0.0000
$2H_2O + 2e = H_2 + 2OH^-$	−0.8277
$H_2O_2 + 2H^+ + 2e = 2H_2O$	1.776
$2Hg^{2+} + 2e = Hg_2^{2+}$	0.905
$Hg_2^{2+} + 2e = 2Hg$	0.7961
$Hg_2Cl_2 + 2e = 2Hg + 2Cl^-$	0.2682
$Hg_2Cl_2 + 2e = 2Hg + 2Cl^-$(sat'd. KCl)	0.2415
$HgO + H_2O + 2e = Hg + 2OH^-$	0.0984
$Hg_2SO_4 + 2e = 2Hg + SO_4^{2-}$	0.6158
$I_2 + 2e = 2I^-$	0.535
$I_3^- + 2e^- = 3I^-$	0.5338
$K^+ + e = K$	−2.924
$Li^+ + e = Li$	−3.045
$Mg^{2+} + 2e = Mg$	−2.375
$Mn^{2+} + 2e = Mn$	−1.029
$Mn^{3+} + e = Mn^{2+}$	1.51
$MnO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O$	1.208
$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$	1.491
$Na^+ + e = Na$	−2.7109
$Ni^{2+} + 2e = Ni$	−0.23
$Ni(OH)_2 + 2e = Ni + 2OH^-$	−0.66
$O_2 + 2H^+ + 2e = H_2O_2$	0.682
$O_2 + 4H^+ + 4e = 2H_2O$	1.229
$O_2 + 2H_2O + 4e = 4OH^-$	0.401
$O_3 + 2H^+ + 2e = O_2 + H_2O$	2.07
$Pb^{2+} + 2e = Pb$	−0.1263
$Pb^{2+} + 2e = Pb(Hg)$	−0.1205
$PbO_2 + 4H^+ + 2e = Pb^{2+} + 2H_2O$	1.46
$PbO_2 + SO_4^{2-} + 4H^+ + 2e = PbSO_4 + 2H_2O$	1.685
$PbSO_4 + 2e = Pb + SO_4^{2-}$	−0.356
$Pd^{2+} + 2e = Pd$	0.83
$Pt^{2+} + 2e = Pt$	~1.2
$PtCl_4^{2-} + 2e = Pt + 4Cl^-$	0.73
$PtCl_6^{2-} + 2e = PtCl_4^{2-} + 2Cl^-$	0.74
$S + 2e = S^{2-}$	−0.508
$Sn^{2+} + 2e = Sn$	−0.1364

Reaction	Potential, V
$Sn^{4+} + 2e = Sn^{2+}$	0.15
$Tl^+ + e = Tl$	−0.3363
$Tl^+ + e = Tl(Hg)$	−0.3338
$Tl^{3+} + 2e = Tl^+$	1.247
$U^{3+} + 3e = U$	−1.8
$U^{4+} + e = U^{3+}$	−0.61
$UO_2^+ + 4H^+ + e = U^{4+} + 2H_2O$	0.62
$UO_2^{2+} + e = UO_2^+$	0.062
$V^{2+} + 2e = V$	−1.2
$V^{3+} + e = V^{2+}$	−0.255
$VO^{2+} + 2H^+ + e = V^{3+} + H_2O$	0.337
$VO_2^+ + 2H^+ + e = VO^{2+} + H_2O$	1.00
$Zn^{2+} + 2e = Zn$	−0.7628
$ZnO_2^{2-} + 2H_2O + 2e^- = Zn + 4OH^-$	−1.216

Values of t for Various Degrees of Freedom and Confidence Levels.

Confidence Level, % → D.F. = n-1 ↓	50	90	95	99	99.9
1	1.000	6.314	12.706	63.657	636.619
2	0.816	2.920	4.303	9.925	31.598
3	0.765	2.353	3.182	5.841	12.941
4	0.741	2.132	2.776	4.604	8.610
5	0.727	2.015	2.571	4.032	6.859
6	0.718	1.943	2.447	3.707	5.959
7	0.711	1.895	2.365	3.500	5.405
8	0.706	1.860	2.306	3.355	5.041
9	0.703	1.833	2.262	3.250	4.781
10	0.700	1.812	2.228	3.169	4.587
11	0.697	1.796	2.201	3.106	4.437
12	0.695	1.782	2.179	3.055	4.318
13	0.694	1.771	2.160	3.012	4.221
14	0.692	1.761	2.145	2.977	4.140
15	0.691	1.753	2.131	2.947	4.073
20	0.687	1.725	2.086	2.845	3.850
25	0.684	1.708	2.060	2.787	3.725
30	0.683	1.697	2.042	2.750	3.646
∞	0.674	1.645	1.960	2.576	3.291

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