Spring 1998

Friday, June 19, 1998

Time: 90 minutes

Prof. Ayssar Nahlé

Chemistry 215

Analytical Chemistry

Final

Name: ....
Family First name

ID number: ...._ ....

Grade

I	/ 14
II	/ 14
III	/ 14
IV	/ 14
V	/ 14
VI	/ 16
VII	/ 14
total	/100

Good luck

I. The chloride in a 0.12-g sample of 95% pure $MgCl_2$ is to be precipitated as AgCl. Calculate the volume of 0.100 M $AgNO_3$ solution required to precipitate the chloride and give a 10% excess.

Volume = ... mL

II. The emf of the galvanic cell

(-)**Ag** | $[Ag(S_2O_3)_2]^{3-}$ (0.0100 M), $S_2O_3^{2-}$(1.00 M) || Ag^+ (0.100 M) | **Ag**(+)

is +0.828 V. Calculate the instability constant of the complex $[Ag(S_2O_3)_2]^{3-}$.

Instability constant = ...

III. Calcium in powdered milk is determined by ashing (ash is the powder remained after burning) a 1.50-g sample and then titrating the calcium with EDTA solution, 12.1 mL being required. The EDTA was standardized by titrating 10.0 mL of zinc solution prepared by dissolving 0.632 g zinc metal in acid and diluting to 1L (10.8 mL EDTA required for titration). What is the concentration of calcium in the powdered milk in parts per million?

Ca^{2+} concentration = ... ppm.

IV. Calculate the absolute and the relative standard deviations (S_y and $\frac{S_y}{y}$ respectively), and round the result to the appropriate number of significant figures. the numbers in parentheses are absolute standard deviations.

a) $$y = \frac{16.12(\pm 0.03) \times \log_{10}[57.3(\pm 0.5) - 49.75(\pm 0.06)]}{3.01(\pm 0.04) + \sqrt{9.12(\pm 0.06)}} = 2.347041508.........$$

S_y =....................................

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

y =.............................±..........................

b) $$y = \left\{3.64(\pm 0.05) - \log_{10}[5.6(\pm 0.2)]^2\right\}^3 = 9.85021703..............$$

S_y =....................................

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

y =.............................±............................

V. Given that the galvanic cell

Pt | Fe^{3+} (0.100M), Fe^{2+} (0.0100M) | | MnO_4^- (0.0100M), Mn^{2+} (0.00100M), H^+ (1.00M) | **Pt**

contains equal volumes of solutions in the two half-cells, calculate the potential of each half-cell and the voltage of the cell, before the reaction and at equilibrium.

Before reaction, E_{cell} = ... **V**

At equilibrium, E_{cell} = ... **V**

VI. A 100.0-mL aliquot of 0.100 M diprotic acid H_2A ($pK_1 = 4.00$, $pK_2 = 8.00$) was titrated with 1.00 M NaOH.

a) Find the pH at the volumes shown in the table below and plot a graph of pH versus volume of the base.

b) Calculate the first derivative ($\Delta pH / \Delta V$), and the corresponding volumes (v').

mL NaOH	pH	(ΔpH / ΔV)	V'
0			
5.0			
8.0			
10.0			
12.0			
15.0			
18.0			
20.0			
22.0			
25.0			

VII. A 0.2000-g sample that consists of only Na_2CO_3 and $NaHCO_3$ requires 24.25 mL of 0.1000 N HCl solution to reach the methyl orange end point. Calculate the percent Na_2CO_3 and $NaHCO_3$ in the sample.

Percent Na_2CO_3 = ... %

Percent $NaHCO_3$ = ... %

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	

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
Hydrogen sulfide	$H_2S \rightleftharpoons H^+ + HS^-$	1.0×10^{-7} (K_{a_1})	7.00
	$HS^- \rightleftharpoons H^+ + S^{2-}$	1.0×10^{-14} (K_{a_2})	14.00
Hypochlorous	$HClO \rightleftharpoons H^+ + ClO^-$	3.2×10^{-8}	7.49
Iron(III) ion	$[Fe(H_2O)_6]^{3+} \rightleftharpoons H^+ + [Fe(H_2O)_5(OH)]^{2+}$	8.9×10^{-4}	3.05
Lead(II) hydroxide	$Pb(OH)_2 \rightleftharpoons H^+ + HPbO_2^-$	2×10^{-16}	15.7
Nitrous	$HNO_2 \rightleftharpoons H^+ + NO_2^-$	4.5×10^{-4}	3.35
Oxalic	$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^-$	3.8×10^{-2} (K_{a_1})	1.42
	$HC_2O_4^- \rightleftharpoons H^+ + C_2O_4^{2-}$	5.0×10^{-5} (K_{a_2})	4.30
Periodic	$HIO_4 \rightleftharpoons H^+ + IO_4^-$	2.3×10^{-2}	1.64
Phenol	$C_6H_5OH \rightleftharpoons H^+ + C_6H_5O^-$	1×10^{-10}	10.0
Phosphoric	$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	7.5×10^{-3} (K_{a_1})	2.12
	$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$	6.2×10^{-8} (K_{a_2})	7.21
	$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$	1×10^{-12} (K_{a_3})	12.0
Phosphorous	$H_3PO_3 \rightleftharpoons H^+ + H_2PO_3^-$	1.6×10^{-2} (K_{a_1})	1.80
	$H_2PO_3^- \rightleftharpoons H^+ + HPO_3^{2-}$	7×10^{-7} (K_{a_2})	6.2
Silicic (meta)	$H_2SiO_3 \rightleftharpoons H^+ + HSiO_3^-$	3.2×10^{-10} (K_{a_1})	9.49
	$HSiO_3^- \rightleftharpoons H^+ + SiO_3^{2-}$	6.3×10^{-12} (K_{a_2})	11.30
Sulfamic	$HNH_2SO_3 \rightleftharpoons H^+ + NH_2SO_3^-$	1.1×10^{-1}	0.96
Sulfuric	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	1.0×10^{2} (K_{a_1})	−2.00
	$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	1.2×10^{-2} (K_{a_2})	1.92
Sulfurous	$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$	1.72×10^{-2} (K_{a_1})	
	$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$	6.43×10^{-8} (K_{a_2})	
Tartaric	$H_2C_4H_4O_6 \rightleftharpoons H^+ + HC_4H_4O_6^-$	1.1×10^{-3} (K_{a_1})	2.96
	$HC_4H_4O_6^- \rightleftharpoons H^+ + C_4H_4O_6^{2-}$	6.9×10^{-5} (K_{a_2})	4.16
Thiocyanic	$HSCN \rightleftharpoons H^+ + SCN^-$	1.4×10^{-1}	0.85
Thiosulfuric	$H_2S_2O_3 \rightleftharpoons H^+ + HS_2O_3^-$	2.0×10^{-2} (K_{a_1})	1.70
	$HS_2O_3^- \rightleftharpoons H^+ + S_2O_3^{2-}$	3.2×10^{-3} (K_{a_2})	2.49
Tin(II) hydroxide	$Sn(OH)_2 \rightleftharpoons H^+ + HSnO_2^-$	4×10^{-15}	14.4
Trichloroacetic	$Cl_3CCOOH \rightleftharpoons H^+ + Cl_3CCOO^-$	1.3×10^{-1}	0.89
Zinc hydroxide	$Zn(OH)_2 \rightleftharpoons H^+ + HZnO_2^-$	1×10^{-17} (K_{a_1})	17.0
	$HZnO_2^- \rightleftharpoons H^+ + ZnO_2^{2-}$	2×10^{-13} (K_{a_2})	12.7
Zinc ion	$[Zn(H_2O)_4]^{2+} \rightleftharpoons H^+ + [Zn(H_2O)_3(OH)]^+$	2.5×10^{-10}	9.60

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	