Spring 1996

Thursday , June 27, 1996

Time: 2 hours

Prof. Ayssar Nahlé

Chemistry 206

Quantitative Analysis

Final Exam

Name: .....
Family First name

I.D. number: ....

Section number: 1 2 3
(Please circle)

Grade

I	/ 14
II	/ 15
III	/ 15
IV	/ 14
V	/ 15
VI	/ 20
VII	/ 7
total	/100

Good luck

I. In the potentiometric titration of $KMnO_4$ with a $FeSO_4$ solution in acid medium using a Pt-saturated calomel pair of electrodes, the pH of the solution at the point 50% to the equivalence point was 1.00. **a)** What is the emf of the cell, E_{cell}, at this point? **b)** What is the value of E_{cell}, when a 40% excess of $FeSO_4$ solution has been added?

a) $\mathbf{E_{cell}}$ = ...

b) $\mathbf{E_{cell}}$ = ...

II. Each of the following solutions contains one or more of the following substances: NaOH, Na_3PO_4, Na_2HPO_4. The volumes of 0.1000 M HCl required for the titration of 25.00 mL of each of the four solutions to reach the methyl orange and the phenolphthalein end points are given below. Which compound or compounds and in what amounts, in **milligrams**, are contained in each of the four solutions?
(Cross the box corresponding to the compound(s) not contained in each solution; and fill the rest of the boxes with the appropriate amount(s))

Sample	V_{HCl}, mL		Composition, milligrams		
	Methyl orange (V_m)	Phenolphthalein (V_p)	NaOH	Na_3PO_4	Na_2HPO_4
a	41.30	17.09			
b	40.92	24.33			
c	37.44	18.72			
d	29.08	0.00			

III. 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, and **b)** Calculate its concentration.

Compound = ...

Concentration of compound = ...

IV. The potential of a fluoride selective electrode against a SCE in a 1.00×10^{-5} M NaF solution is +0.1300 V. Solid NaF is added to 100 mL of this solution until the measured potential becomes +0.0120 V. Calculate the new concentration of F^- ions and the amount of NaF added (in mg). Assume no change in the volume of the solution and $a_{F^-} = [F^-]$.

New $[F^-]$ = ...

Amount of NaF added = ... mg

V. How many milliliters of 1.00 M NaOH solution should be added to 0.9004 g of oxalic acid to give a buffer of pH 4.43 when diluted to 100 mL?

Volume of NaOH added = ... mL

VI. **a)** Construct a potentiometric titration curve for the titration of 50.00 mL of 0.0500 N Fe(II) solution with 0.1000 N $KMnO_4$ solution. Both solutions are 1.0 M in H_2SO_4 (neglect the change in $[H^+]$ during the titration).
In the table below, calculate the platinum electrode potential versus SHE (E) after each addition of the oxidant.(Fill the results in the table).

b) Calculate the first and the second derivatives ($\frac{\Delta E}{\Delta V}$ and $\frac{\Delta^2 E}{\Delta V^2}$) and the corresponding volumes V' and V".

c) Plot the second derivative on the provided graph paper and show graphically the end point.

V_{KMnO4}	E, V	$\frac{\Delta E}{\Delta V}$	V'	$\frac{\Delta^2 E}{\Delta V^2}$	V"
5.00					
10.00					
12.50					
20.00					
24.00					
24.95					
25.00					
25.05					
25.50					
30.00					
50.00					

VII. Calculate the absolute and the relative standard deviations (S_y and $\frac{S_y}{y}$) for the following expression, and round the result to the appropriate significant figures.

$$y = \frac{12.163(\pm 0.003) + 0.971(\pm 0.004) \times \sqrt{\frac{72.321(\pm 0.006)}{13.97(\pm 0.05)}}}{5 \times \left[\log 73.14(\pm 0.08)\right]^3 - 21.317(\pm 0.001)} = 1.297913872....$$

S_y = ...

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

y = ... ± .....

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
1. Acidic solutions			
$F_2 + 2H^+ + 2e \rightleftharpoons 2HF$	+3.06		
$F_2 + 2e \rightleftharpoons 2F^-$	+2.85		
$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$	+2.01		
$Co^{3+} + e \rightleftharpoons Co^{2+}$	+1.82		
$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O$	+1.77		
$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$	+1.695		
$Ce^{4+} + e \rightleftharpoons Ce^{3+}$		+1.70	1 M $HClO_4$
		+1.61	1 M HNO_3
		+1.44	1 M H_2SO_4
		+1.28	1 M HCl
$2HClO + 2H^+ + 2e \rightleftharpoons Cl_2 + 2H_2O$	+1.63		
$NaBiO_3 + 6H^+ + 2e \rightleftharpoons Na^+ + Bi^{3+} + 3H_2O$	+1.6		
$H_5IO_6 + H^+ + 2e \rightleftharpoons IO_3^- + 3H_2O$	+1.6		
$2BrO_3^- + 12H^+ + 10e \rightleftharpoons Br_2 + 6H_2O$	+1.52		
$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$	+1.51		
$Mn^{3+} + e \rightleftharpoons Mn^{2+}$	+1.51		
$PbO_2 + 4H^+ + 2e \rightleftharpoons Pb^{2+} + 2H_2O$	+1.455		
$Cl_2 + 2e \rightleftharpoons 2Cl^-$	+1.359		
$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33		
		+1.09	1 M HCl
$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O$	+1.23		
		+1.24	1 M $HClO_4$
$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$	+1.229		
$2IO_3^- + 12H^+ + 10e \rightleftharpoons I_2 + 6H_2O$	+1.195		
$Br_{2(aq)} + 2e \rightleftharpoons 2Br^-$	+1.087[a]		
$Br_2(l) + 2e \rightleftharpoons 2Br^-$	+1.065[a]		

Critical Values for Rejection Quotient Q

Number of Observations	Q_{crit} 90% Confidence	96% Confidence	99% Confidence
3	0.94	0.98	0.99
4	0.76	0.85	0.93
5	0.64	0.73	0.82
6	0.56	0.64	0.74
7	0.51	0.59	0.68
8	0.47	0.54	0.63
9	0.44	0.51	0.60
10	0.41	0.48	0.57

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
1. Acidic solutions			
$2ICl_2^- + 2e \rightleftharpoons I_2 + 4Cl^-$	+1.06		
$HNO_2 + H^+ + e \rightleftharpoons NO + H_2O$	+1.00		
$NO_3^- + 4H^+ + 3e \rightleftharpoons NO + 2H_2O$	+0.96		
$NO_3^- + 3H^+ + 2e \rightleftharpoons HNO_2 + H_2O$	+0.94		
$NO_3^- + 10H^+ + 8e \rightleftharpoons NH_4^+ + 3H_2O$	+0.87		
$2Hg^{2+} + 2e \rightleftharpoons Hg_2^{2+}$	+0.920		
$Cu^{2+} + I^- + e \rightleftharpoons CuI$	+0.86		
$Ag^+ + e \rightleftharpoons Ag$	+0.7994		
$Hg_2^{2+} + 2e \rightleftharpoons 2Hg$	+0.789		
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	+0.771		
		+0.732	1 M $HClO_4$
		+0.700	1 M HCl
		+0.674	1 M H_2SO_4
		+0.46	2 M H_3PO_4
$O_2 + 2H^+ + 2e \rightleftharpoons H_2O_2$	+0.682		
$I_2(aq) + 2e \rightleftharpoons 2I^-$	+0.6197[b]		
$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$	+0.564		
$H_3AsO_4 + 2H^+ + 2e \rightleftharpoons H_3AsO_3 + H_2O$	+0.559		
		+0.577	1 M HCl, 1 M $HClO_4$
$[I_3]^- + 2e \rightleftharpoons 3I^-$	+0.536		
$I_2 + 2e \rightleftharpoons 2I^-$	+0.5355[b]		
$Cu^+ + e \rightleftharpoons Cu$	+0.521		
$H_2SO_3 + 4H^+ + 4e \rightleftharpoons S + 3H_2O$	+0.45		
$Ag_2CrO_4 + 2e \rightleftharpoons 2Ag + CrO_4^{2-}$	+0.446		
$2H_2SO_3 + 2H^+ + 4e \rightleftharpoons S_2O_3^{2-} + 3H_2O$	+0.40		
$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-}$	+0.356		
		+0.71	1 M HCl
$Cu^{2+} + 2e \rightleftharpoons Cu$	+0.337		
$Hg_2Cl_2 + 2e \rightleftharpoons 2Hg + 2Cl^-$	+0.2680		
		+0.3337	0.1 M KCl
		+0.2801	1 M KCl
		+0.2412	KCl satur.
$AgCl + e \rightleftharpoons Ag + Cl^-$	+0.2224		
$SO_4^{2-} + 4H^+ + 2e \rightleftharpoons H_2SO_3 + H_2O$	+0.17		
$Cu^{2+} + e \rightleftharpoons Cu^+$	+0.153		
$Sn^{4+} + 2e \rightleftharpoons Sn^{2+}$	+0.15		
$[SnCl_6]^{2-} + 2e \rightleftharpoons [SnCl_4]^{2-} + 2Cl^-$		+0.14	1 M HCl
$S + 2H^+ + 2e \rightleftharpoons H_2S$	+0.141		
$AgBr + e \rightleftharpoons Ag + Br^-$	+0.095		
$S_4O_6^{2-} + 2e \rightleftharpoons 2S_2O_3^{2-}$	+0.08		
$[Ag(S_2O_3)_2]^{3-} + e \rightleftharpoons Ag + 2S_2O_3^{2-}$	+0.01		
$2H^+ + 2e \rightleftharpoons H_2$	0.000		

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})	11.80
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 $\times 10^{-2}$(K_{a_1})	
	$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$	6.43 $\times 10^{-8}$(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