DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SWAZILAND

C404 ELECTROANALYTICAL CHEMISTRY

MAY 2018 FINAL EXAMINATION

Time Allowed : Three (3) Hours

Instructions:

1. **This examination has five (5) questions and one data sheet. The total number of pages is five(5) including this page.**

2. **Answer any four (4) questions fully; diagrams should be clear, large and properly labeled. Marks will be deducted for improper units and lack of procedural steps in calculations.**

3. **Each question is worth 25 marks.**

Special Requirements

1. Data sheet.

YOU ARE NOT SUPPOSED TO OPEN THIS PAPER UNTIL PERMISSION TO DO SO HAS BEEN GIVEN BY THE CHIEF INVIGILATOR.

QUESTION 1 [25]

a) i) With the aid of a diagram, use ion exchange theory to explain how a pH glass membrane electrode works. [3]

ii) Write the Nernst expression for an ideal pH glass electrode, and show that unit calibrations in the readout are in increments of 59mV. [3]

iii) Explain, using diagrams and equations, how the selectivity coefficient and ion exchange principles enable fabrication of a pNa electrode. [3]

b) i) With the aid of a diagram, explain how an SCE electrode is fabricated, and explain the role of each component in the electrode. [4]

ii) Write down its half cell reaction and Nernst expression. [2]

iii) State the standard electrode potential for the SCE. [2]

iv) Under what conditions will the SCE not work. [2]

c) In the analysis of fluoride ion in tap water using the LaF_3 solid state electrode, TISAB is almost always added to both standards and unknown samples. List all the components that make up "TISAB" and explain briefly the role of each. [6]

QUESTION 2 [25]

b) What is the role of a reference electrode in potentiometry? [1]

c) Discuss each of the two (2) main requirements of reference electrodes in potentiometry. [2]

d) i) With the aid of a diagram, explain how an AgCl/Ag electrode is fabricated, and explain the role of each component in the electrode. [4]

ii) Write down its half cell reaction and Nernst expression. [2]

iii) State its standard electrode potential and typical input impendance. [2]

iv) Under what experimental conditions will this electrode not work? [2]

e) For the $Cr_2\ O_7^{2+}$ / Cr^{3+} system in acid, calculate the concentration of $Cr_2\ O_7^{2-}$ at pH=3 if the potential measured for a 0.0625M Cr^{3+} solution is 0.562V. vs SCE [6]

f) The data below were obtained when a Ca^{2+} ion-selective electrode was immersed in a series of standard solutions whose ionic strength was constant a 2.0M.

[Ca2+] (M)	E (mV)
3.4×10^{-5}	-74.8
3.6×10^{-4}	-48.4
3.2×10^{-3}	-18.7
3.0×10^{-2}	-10.0
3.5×10^{-1}	+37.7

What is the reading concentration of Ca^{2+} in the sample if it gave a reading of -22.5mV [6]

QUESTION 3 [25]

a) In the coulometric titration of Fe^{3+}, describe the role of Ti^{4+} intermediate added at the beginning of the analysis. [2]

b) i) Use diagrams and equations to describe how an amperometric titration of Pb^{2+} can be carried out with a one-polarized electrode system using SO_4^{2-} as titrant (Pb^{2+} is electroreducible at potentials more negative than -1.0V vs SCE). [3]

ii) Plot the titration curve expected for an amperometric titration with one polarized electrode for each of the following:

- SO_4^{2-} (non-electroreducible at -1.0V vs SCE) with Pb^{2+} as titrant. [2]
- Pb^{2+} titrated with a ligand that is also electroreducible at -1.0V vs SCE. [2]

c) i) Describe how an amperometric titration of Fe^{2+} with Ce^{4+} can be carried out with two indicator electrodes. [2]

ii) Draw the current-voltage curve for the Fe^{2+} / Ce^{4+} system mentioned in c (i) above at the following stages of titration. [4]

f = 0; f = 0.5; f = 1.0; f = 1.5

iii) Draw the expected titration curve for the Fe^{2+} / Ce^{4+} system described in c (i) and c (ii) above. [2]

d) Consider the voltametric titration of Tl^+ with electrochemically generated Br_2 according to the reaction

$Tl^+ + Br_2 \Longleftrightarrow Tl^{3+} + 2Br^-$, where

$Tl^{3+} + 2e^- \Longleftrightarrow Tl^+$ $E^0 = -0.78V$ vs SCE

$Br_2 + 2e^- \Longleftrightarrow 2Br^-$ $E^0 = -1.08V$ vs SCE

i) Draw the current-voltage curves of this titration at the following stages of the titration: [4]

f = 0; f = 0.5; f = 1.0; f = 1.5

ii) Plot the titration curve expected for this system using a single indicator electrode. [2]

iii) Plot the titration curve expected for this system using a two-indicator electrode system. [2]

QUESTION 4 [25]

a) It takes 9.805 minutes to titrate a sample of Na_2CO_3 coulometrically in an electrolytic cell with electrogenerated hydrogen ions. The generating current is 191.95 mA in a system incorporating Pt electrodes. Assuming that the endpoint occurs when all CO_3^{2-} has been converted to H_2CO_3, calculate the weight of Na_2CO_3 in the sample. [6]

b) Use equations to explain the role of a depolarizer in electrogravimetry. [3]

c) Use equations to describe the anodic and cathodic reactions taking place during electrodeposition in the measurement of copper in an unknown solution. [4]

d) A solution of 0.200M Cu^{2+} in 1M H^+, resistance 0.5 Ω, is to be electrodeposited to 99.995% completion with 1A in an open cell (partial pressure of O_2 in air = 0.2 atm). In the equation $E_{app} = E_{cathode} + IR + \omega$ used to ascertain the potential at which electrodeposition will occur:

i) Calculate $E_{cathode.}$ [1]
ii) Calculate $E_{anode.}$ [1]
iii) Calculate the IR drop. [1]

iv) Describe the term ω, and explain its origins in electrogravimetry using suitable equations. [3]

d) i) Outline the steps involved in calibration of pH glass electrodes. [2]

ii) List two (2) sources of standards used in the calibration of pH glass electrodes. [2]

iii) Scratched membranes make electrodes difficult to calibrate. Explain how scratched membranes are regenerated in potentiometry. [2]

QUESTION 5 [25]

a) In voltammetry, what do the following acronyms stand for? [3]

i) HMDE ii) NPP iii) RDE

b) Describe the term "overpotential" in relation to the polarography technique, and explain why overpotential is desirable in this electroanalytical technique. [2]

c) Draw and label the electrode used in classical polarography, explain how it works, and use chemical equations to explain the shape of the polarogram of Pb^{2+}. [4]

d) Voltammetry in the upper right quadrant can be complicated by the presence of dissolved oxygen in solution.

g) Use chemical equations to explain the origin of oxygen waves. [3]

ii) How are oxygen waves eliminated in voltammetry? [1]

e) i) Use diagrams to explain the origins of "non-faradaic" current in polaragraphy. [2]

ii) Use a diagram to illustrate the dependence of "non-faradaic" current on time during the lifetime of a mercury drop in polaragraphy. [2]

iii) Use a diagram to illustrate the dependence of "faradaic" current on time during the lifetime of a mercury drop in polaragraphy. [2]

iv) Use a diagram to illustrate the effect of concentration on "non-faradiac" current during the lifetime of a mercury drop in polarography. [2]

f) Use equations to explain the processes that dictate the useful range of potentials in polarography. [4]

QUESTION 6 **[25]**

a) For each of the following modern variants of the polarographic technique, draw the shape of the voltammogram:

i) Alternating current polarography. [1]
ii) Fast linear sweep polarography. [1]
iii) Cyclic sweep voltammetry. [1]

b) For each of the following techniques, indicate, on a voltage-time plot, when sampling of the signal is carried out. Draw the shape of the resultant voltammogram, and indicate the typical resolution (in Volts) and detection limit (in mol/L).

i) Tast polarography. [3]
ii) Normal pulse polarography. [3]
iii) Differential Pulse Polarography [3]

c) i) Draw a schematic diagram of the apparatus used in Anodic Stripping Voltametry (ASV). [3]

ii) Assume that ASV is being carried out on an environmental sample containing the toxic element cadmium. Use equations to describe the chemical processes taking place at each of the three steps involved in the ASV of the sample. [4]

iii) Explain why ASV is considered superior over most analytical techniques in terms of detection limits. [2]

d) Cyclic voltametry is a very useful analytical tool in thermodynamic studies. Explain how you would differentiate between reversible and irreversible systems on the basis of the peak current and peak potentials observed in cyclic voltametry? [4]

PERIODIC TABLE OF ELEMENTS

GROUPS

Atomic mass → 10.811 | Symbol → B | Atomic No. → 5

TRANSITION ELEMENTS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1.008 H 1																	4.003 He 2
2	6.941 Li 3	9.012 Be 4											10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9	20.180 Ne 10
3	22.990 Na 11	24.305 Mg 12											26.982 Al 13	28.086 Si 14	30.974 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
4	39.098 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.942 V 23	51.996 Cr 24	54.938 Mn 25	55.847 Fe 26	58.933 Co 27	58.69 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.922 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36
5	85.468 Rb 37	87.62 Sr 38	88.906 Y 39	91.224 Zr 40	92.906 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.91 Rh 45	106.42 Pd 46	107.87 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.90 I 53	131.29 Xe 54
6	132.91 Cs 55	137.33 Ba 56	138.91 *La 57	178.49 Hf 72	180.95 Ta 73	183.85 W 74	186.21 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.97 Au 79	200.59 Hg 80	204.38 Tl 81	207.2 Pb 82	208.98 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	223 Fr 87	226.03 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109	(267) Uun 110								

Series														
*Lanthanide Series	140.12 Ce 58	140.91 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.96 Eu 63	157.25 Gd 64	158.93 Tb 65	162.50 Dy 66	164.93 Ho 67	167.26 Er 68	168.93 Tm 69	173.04 Yb 70	174.97 Lu 71
**Actinide Series	232.04 Th 90	231.04 Pa 91	238.03 U 92	237.05 Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103

( ) indicates the mass number of the isotope with the longest half-life.

General data and fundamental constants

Quantity	Symbol	Value
Speed of light†	c	$2.997\,924\,58 \times 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\,177 \times 10^{-19}$ C
Faraday constant	$F = eN_A$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = kN_A$	8.314 51 J K^{-1} mol^{-1}
		$8.205\,78 \times 10^{-2}$ dm^3 atm K^{-1} mol^{-1}
		62.364 L Torr K^{-1} mol^{-1}
Planck constant	h	$6.626\,08 \times 10^{-34}$ J s
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34}$ J s
Avogadro constant	N_A	$6.022\,14 \times 10^{23}$ mol^{-1}
Atomic mass unit	u	$1.660\,54 \times 10^{-27}$ kg
Mass of electron	m_e	$9.109\,39 \times 10^{-31}$ kg
proton	m_p	$1.672\,62 \times 10^{-27}$ kg
neutron	m_n	$1.674\,93 \times 10^{-27}$ kg
Vacuum permeability†	μ_0	$4\pi \times 10^{-7}$ J s^2 C^{-2} m^{-1}
		$4\pi \times 10^{-7}$ T^2 J^{-1} m^3
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12}$ J^{-1} C^2 m^{-1}
	$4\pi\varepsilon_0$	$1.112\,65 \times 10^{-10}$ J^{-1} C^2 m^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}$ J T^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}$ J T^{-1}
Electron g value	g_e	2.002 32
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Rydberg constant	$R_\infty = m_e e^4/8h^3 c$	$1.097\,37 \times 10^{5}$ cm^{-1}
Fine structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ N m^2 kg^{-2}
Standard acceleration of free fall†	g	9.806 65 m s^{-2}

† Exact (defined) values

Prefixes

f	p	n	μ	m	c	d	k	M	G
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

APPENDIX C POTENTIALS OF SELECTED HALF-REACTIONS AT 25 °C

A summary of oxidation/reduction half-reactions arranged in order of decreasing oxidation strength and useful for selecting reagent systems.

Half-reaction		E° (V)
$F_2(g) + 2H^+ + 2e^-$	$= 2HF$	3.06
$O_3 + 2H^+ + 2e^-$	$= O_2 + H_2O$	2.07
$S_2O_8^{2-} + 2e^-$	$= 2SO_4^{2-}$	2.01
$Ag^{2+} + e^-$	$= Ag^+$	2.00
$H_2O_2 + 2H^+ + 2e^-$	$= 2H_2O$	1.77
$MnO_4^- + 4H^+ + 3e^-$	$= MnO_2(s) + 2H_2O$	1.70
$Ce(IV) + e^-$	$= Ce(III)$ (in 1M $HClO_4$)	1.61
$H_5IO_6 + H^+ + 2e^-$	$= IO_3^- + 3H_2O$	1.6
Bi_2O_4 (bismuthate) $+ 4H^+ + 2e^-$	$= 2BiO^+ + 2H_2O$	1.59
$BrO_3^- + 6H^+ + 5e^-$	$= \frac{1}{2}Br_2 + 3H_2O$	1.52
$MnO_4^- + 8H^+ + 5e^-$	$= Mn^{2+} + 4H_2O$	1.51
$PbO_2 + 4H^+ + 2e^-$	$= Pb^{2+} + 2H_2O$	1.455
$Cl_2 + 2e^-$	$= 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$= 2Cr^{3+} + 7H_2O$	1.33
$MnO_2(s) + 4H^+ + 2e^-$	$= Mn^{2+} + 2H_2O$	1.23
$O_2(g) + 4H^+ + 4e^-$	$= 2H_2O$	1.229
$IO_3^- + 6H^+ + 5e^-$	$= \frac{1}{2}I_2 + 3H_2O$	1.20
$Br_2(l) + 2e^-$	$= 2Br^-$	1.065
$ICl_2^- + e^-$	$= \frac{1}{2}I_2 + 2Cl^-$	1.06
$VO_2^+ + 2H^+ + e^-$	$= VO^{2+} + H_2O$	1.00
$HNO_2 + H^+ + e^-$	$= NO(g) + H_2O$	1.00
$NO_3^- + 3H^+ + 2e^-$	$= HNO_2 + H_2O$	0.94
$2Hg^{2+} + 2e^-$	$= Hg_2^{2+}$	0.92
$Cu^{2+} + I^- + e^-$	$= CuI(s)$	0.86
$Ag^+ + e^-$	$= Ag$	0.799
$Hg_2^{2+} + 2e^-$	$= 2Hg$	0.79
$Fe^{3+} + e^-$	$= Fe^{2+}$	0.771
$O_2(g) + 2H^+ + 2e^-$	$= H_2O_2$	0.682
$2HgCl_2 + 2e^-$	$= Hg_2Cl_2(s) + 2Cl^-$	0.63
$Hg_2SO_4(s) + 2e^-$	$= 2Hg + SO_4^{2-}$	0.615
$Sb_2O_5 + 6H^+ + 4e^-$	$= 2SbO^+ + 3H_2O$	0.581
$H_3AsO_4 + 2H^+ + 2e^-$	$= HAsO_2 + 2H_2O$	0.559
$I_3^- + 2e^-$	$= 3I^-$	0.545
$Cu^+ + e^-$	$= Cu$	0.52
$VO^{2+} + 2H^+ + e^-$	$= V^{3+} + H_2O$	0.337
$Fe(CN)_6^{3-} + e^-$	$= Fe(CN)_6^{4-}$	0.36
$Cu^{2+} + 2e^-$	$= Cu$	0.337
$UO_2^{2+} + 4H^+ + 2e^-$	$= U^{4+} + 2H_2O$	0.334

(continued)

APPENDIX C *(continued)*

Half-reaction		$E°$ (V)
$Hg_2Cl_2(s) + 2e^-$	$= 2Hg + 2Cl^-$	0.2676
$BiO^+ + 2H^+ + 3e^-$	$= Bi + H_2O$	0.32
$AgCl(s) + e^-$	$= Ag + Cl^-$	0.2222
$SbO^+ + 2H^+ + 3e^-$	$= Sb + H_2O$	0.212
$CuCl_3^{2-} + e^-$	$= Cu + 3Cl^-$	0.178
$SO_4^{2-} + 4H^+ + 2e^-$	$= SO_2(aq) + 2H_2O$	0.17
$Sn^{4+} + 2e^-$	$= Sn^{2+}$	0.15
$S + 2H^+ + 2e^-$	$= H_2S(g)$	0.14
$TiO^{2+} + 2H^+ + e^-$	$= Ti^{3+} + H_2O$	0.10
$S_4O_6^{2-} + 2e^-$	$= 2S_2O_3^{2-}$	0.08
$AgBr(s) + e^-$	$= Ag + Br^-$	0.071
$2H^+ + 2e^-$	$= H_2$	0.0000
$Pb^{2+} + 2e^-$	$= Pb$	−0.126
$Sn^{2+} + 2e^-$	$= Sn$	−0.136
$AgI(s) + e^-$	$= Ag + I^-$	−0.152
$Mo^{3+} + 3e^-$	$= Mo$	*approx.* −0.2
$N_2 + 5H^+ + 4e^-$	$= H_2NNH_3^+$	−0.23
$Ni^{2+} + 2e^-$	$= Ni$	−0.246
$V^{3+} + e^-$	$= V^{2+}$	−0.255
$Co^{2+} + 2e^-$	$= Co$	−0.277
$Ag(CN)_2^- + e^-$	$= Ag + 2CN^-$	−0.31
$Cd^{2+} + 2e^-$	$= Cd$	−0.403
$Cr^{3+} + e^-$	$= Cr^{2+}$	−0.41
$Fe^{2+} + 2e^-$	$= Fe$	−0.440
$2CO_2 + 2H^+ + 2e^-$	$= H_2C_2O_4$	−0.49
$H_3PO_3 + 2H^+ + 2e^-$	$= HPH_2O_2 + H_2O$	−0.50
$U^{4+} + e^-$	$= U^{3+}$	−0.61
$Zn^{2+} + 2e^-$	$= Zn$	−0.763
$Cr^{2+} + 2e^-$	$= Cr$	−0.91
$Mn^{2+} + 2e^-$	$= Mn$	−1.18
$Zr^{4+} + 4e^-$	$= Zr$	−1.53
$Ti^{3+} + 3e^-$	$= Ti$	−1.63
$Al^{3+} + 3e^-$	$= Al$	−1.66
$Th^{4+} + 4e^-$	$= Th$	−1.90
$Mg^{2+} + 2e^-$	$= Mg$	−2.37
$La^{3+} + 3e^-$	$= La$	−2.52
$Na^+ + e^-$	$= Na$	−2.714
$Ca^{2+} + 2e^-$	$= Ca$	−2.87
$Sr^{2+} + 2e^-$	$= Sr$	−2.89
$K^+ + e^-$	$= K$	−2.925
$Li^+ + e^-$	$= Li$	−3.045