UNIVERSITY OF SWAZILAND
SUPPLEMENTARY EXAMINATION 2013/2014

TITLE OF PAPER : **Advanced Analytical Chemistry**

COURSE CODE : **C404**

TIME ALLOWED : **Three (3) Hours.**

INSTRUCTIONS : **Answer any Four (4) Questions. Each Question Carries 25 Marks**

A periodic table and other useful data have been provided with this paper.

DO NOT OPEN THIS QUESTION PAPER UNTIL PERMISSION TO DO SO HAS BEEN GRANTED BY THE CHIEF INVIGILATOR.

Question 1 (25 marks)

(a) Account for the variation in the conductances of an electrolyte and that of a metallic conductor as temperature increases. [4]

(b) Given the following terms:
specific conductance k, conductance, G, and cell constant, K.
Define each of the terms and state their S.I units. Obtain an expression relating all the terms together. [6]

(c) Given the following table of limiting molar conductances of ions in water as 25^{0}C:

Cations	Li^+	Na^+	K^+	Rb^+	Mg^{2+}	C^{2+}	Ba^{2+}
Λ_+^0 /Scm^{2}mol^{-1}	38.6	50.1	73.5	77.8	53.1	59.5	63.6

Based on the concept of ionic atmosphere in solutions, account for the variation in λ^0 values of the cations. [3]

(d) Suppose that 0.5M solutions of HCl and CH_3COOH were diluted serially in several stages to 0.001M. If the molar conductance at each stage was recorded, show a plot of the expected variation of Λ with $\sqrt{c}$. Offer an explanation for the expected shapes and state how any useful information can be obtained from either of the curves. [7]

(e) During the determination of the solubility of AgCl, the specific conductance of the specially purified water used was found to be 8.1 x 10^{-7} Scm^{-1} at 25^{0}C. Solid AgCl was added to the same water unto saturation at 25^{0}C and the specific conductance was 26.2 x 10^{-7} Scm^{-1}. Calculate the solubility product of AgCl. [5]

$(\lambda^0_{Ag^+} = 61.9, and\ \lambda^0_{Cl^-} = 76.4\,\mathrm{Scm^2mol^{-1}})$

Question 2 (25 marks)

(a) What are the salient properties of an ideal reference electrode? [4]

(b) For the Ag/AgCl reference electrode:
  (i) Write the half-cell reaction and its shorthand notation. [2]
  (ii) Write the Nernst equation for its potential and show that the potential depends on the [KCl], the filling solution. [3]

  (iii) Draw a labelled schematic diagram of this electrode and briefly describe its preparation. [5]
  (iv) Give one advantage and one disadvantage of this electrode when compared with the saturated calomel electrode (SCE). [2]
  (v) Which is more temperature dependent – the one prepared using saturated KCl or the one prepared using 3.5M KCl? Explain. [4]

(c) A cell was prepared by dipping a Pt wire(indicator electrode), and a S.C.E into a solution containing a 0.2M Fe^{3+} and 0.1M Fe^{2+} and the two were connected to a potentiometer so that the Pt-wire is the cathode while the S.C.E is the anode.
Calculate the theoretical cell voltage, given that:
$Fe^{3+} + e^{-} = Fe^{2+}$: $E^{o} = +0.771V$
$E_{ref} = 0.245V$(i.e. $E_{sce} = 0.245V$)
$E_{ij} = 0$, and Activity Coefficient = 1.0 [5]

Question 3 (25 marks)

(a) Which would you prefer for the analysis of iron in a sample – an electrochemical or a spectrophotometric method, and why? [2]

(b) Discuss the function and working principles of a salt bridge in an electrochemical cell [3]

(c) What is ohmic potential? How does it affect:
  (i) The observed potential of a galvanic cell, and
  (ii) The potential required to operate an electrolytic cell? [3]

(d) Given the following reactions:

$CuI_{(s)} \quad = \quad Cu^{+}_{(aq)} + \quad I^{-}_{(aq)}$

$Cu^{2+} \quad + \quad e^{-} \quad = \quad Cu^{+} \quad : \quad E^{0} = +0.153V$

$Cu^{2+} \quad + \quad I^{-}_{(aq)} \quad + \quad e^{-} \quad = \quad Cu_{(s)} \quad + \quad ½I_2 \quad : \quad E^{0} = +0.86V$

Calculate the solubility product constant, K_{sp}, for $CuI_{(s)}$ [5]

(e) Given the following half – reactions of a cell:

$VO^{+}_{2} \; + 2H^{+} \; + \; e^{-} \quad = \quad VO^{2+} \; + H_2O \quad : \quad E^{0} = 1.00V$

$UO^{2+}_{2} \; + 4H^{+} \; + \; 2e^{-} \quad = \quad U^{4+} \; + 2H_2O \quad : \quad E^{0} = 0.334V$

(i) Obtain the net cell reaction. [1]

(ii) Determine ΔG and the equilibrium constant, K. [6]

(iii) If $[VO^{+}_{2}] = 0.1M$; $[UO^{2+}_{2}] = 0.01M$ and $[U^{4+}] = 0.1M$.
Determine the E_{cell} ; write the cell notation and indicate the direction of spontaneous reaction. Assume that the Pt-electrodes are used in the half – cells. [5]

Question 4 (25 marks)

(a) Define the 'selectivity coefficient' of an Ion Selective Electrode (ISE). Suppose that an ISE designed for measuring A^{+} has the following selectivity coefficients for ions B, C, D, & E

$K_{A^+,B^+} = 0.01$: $K_{A^+,C^+} = 0.08$: $K_{A^+,D^+} = 0.04$; $K_{A^+,E^+} = 0.1$

Arrange the ions in an increasing order of the electrode's sensitivity to them. How is this interpreted in terms of their relative interference with the ion A^{+}, using this electrode? [4]

(b) If you were to determine H^{+}, Na^{+}, and K^{+} in separate solutions, which of the following glass electrodes would you employ for the measurement of each of them respectively: The pH type, the cation sensitive type, Sodium sensitive type. Why? [4]

(c) With a diagrammatic support, describe the construction, the working principles and the potential of a Ca^{2+} ion selective electrode. Give two interfering ions of this electrode. [9]

(d) When a Na^+- I.S.E with a selectivity coefficient, $k_{Na^+,H^+} = 36$, was immersed in 1.00×10^{-3} M NaCl at a pH 8, a potential of -38mV (vs)SCE was recorded. Assuming unit activity coefficients and that $\beta = 1$. Calculate the potential when

(i) The electrode was immersed in 5.00×10^{-3}M NaCl at a pH 8 [4]

(ii) [NaCl] $= 1.00 \times 10^{-3}$ at pH 3.87 [4]

(iii) From the results obtained in (i) & (ii), comment on the importance of pH in the use of a Na^+ ISE. [2]

Question 5 (25 marks)

(a) What are the requisite physical properties that assure adequate electrodeposition of a metal during an electrogravimetric analysis? What factors influence the physical characteristics of such deposits? [4]

(b) What is a potentiostat? Draw a well labeled diagram of a typical one. [6]

(c) Explain how controlled cathode electrolysis is more selective than constant cell-voltage electrolysis. Discuss the application of this unique feature (advantage) of controlled cathode potential electrolysis. [6]

(d) A solution containing Mn^{2+} and a second metal ion, M^{3+} was placed in an electrolysis cell in which the electrodes, Pt and Mn are connected to the power supply. The two reactions occurring in the cell are:

$$Mn_{(s)} \rightarrow Mn^{2+} + 2e^- \quad \text{and} \quad M^{3+} + 3e^- \rightarrow M_{(s)}$$

The initial volume of the filled cell was 1.00L, and the initial concentration of M^{2+} was 2.50×10^{-2}M.

(i) Identify the anode and the cathode among the electrodes. [2]

(ii) On passing a constant current of 2.60 A through the cell for 18.00min; 0.504g of the metal M was deposited on the Pt electrode. Determine the atomic weight of M. [4]

(iii) What will be the concentration of Mn^{2+} in the cell at the end of the experiment? [3]

Question 6 (25 marks)

(a) Distinguish between
  (i) Voltammetry and potentiometry,
  (ii) Voltammetry and coulometry. [4]

(b) Offer a brief but appropriate explanation for the following:
  (i) Highly reproducible current-potential data are usually obtained from polarographic analysis.
  (ii) H^+ reduction does not interfere with most reductions at the Hg electrode.
  (iii) Alkali metals (with lower standard potentials) can be reduced more easily than H^+ at a DME.
  (iv) A DME is preferred for cathodic reactions during amperometric titrations while a Pt electrode is preferred for anodic reactions. [8]

(c) The iodate ion undergoes the following reaction at the DME

$$IO^{-}_{3} + 6H^{+} + 6e^{-} = I^{-} + 3H_2O$$

When a 1.41mM solution of KIO_3 in a 0.1M perchloric acid was reduced polarographically at a DME with a drop time of 2.18s and Hg flow rate of 2.67mg/s, the diffusion current was 37.1µA.Determine the diffusion coefficient of the iodate ion in 0.1M perchloric acid. [13]

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.008 H 1																	4.003 He 2
2	6.941 Li 3	9.012 Be 4										Atomic mass → Symbol → Atomic No. →	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					TRANSITION ELEMENTS						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								

***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	$R_\infty = m_e e^4/8h^3c$	$1.097\,37 \times 10^{5}$ 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