UNIVERSITY OF SWAZILAND
FINAL EXAMINATION 2014/2015

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.

REQUIREMENT: GRAPH PAPER

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

Question 1 (25 marks)

(a) Explain the observed difference in the variation of the conductivity of an electrolyte and that of a metallic conductor as temperature increases. [4]

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

The following table contains limiting molar conductances of ions in water at 25^0C:

Cations	Li^+	Na^+	K^+	Rb^+	Mg^{2+}	Ca^{2+}	Ba^{2+}
$\Lambda^0_+ /Scm^2mol^{-1}$	38.6	50.1	73.5	77.8	53.1	59.5	63.6

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

(c) Consider that 0.1M solutions of HCl and CH_3COOH were each 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 $\sqrt{c}$. Account for the respective shapes and state how any useful information can be obtained from either of the curves. [7]

(e) At 25^0C, the specific conductance of a saturated solution of AgCl was 26.2×10^{-7} Scm^{-1}. The specific conductance of the specially purified water used to prepare the solution was found to be 8.1×10^{-7} Scm^{-1} Calculate the solubility product of AgCl at 25^0C. [5]

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

Question 2 (25 marks)

(a) Give two favourable features of electrochemical methods of analysis. [2]

(b) Define and differentiate between the following terms:
(i) A galvanic cell and an electrolytic cell
(ii) A faradaic and a non-faradaic process,
(iii) A chemically reversible and an irreversible cell. [6]

(c) Using a specific cell set up and reactions as illustration, describe how a galvanic cell can be converted into an electrolytic cell. [5]

(d) For the following cell:

$Cu|Cu(NO_3)_2(0.2M)||Fe(NO_3)_2(0.05M)|Fe$

(i) Write the cell reaction
(ii) Determine the cell potential
(iii) Indicate the polarities of the electrode
(iv) Give the direction of spontaneous reaction
(v) Calculate the ΔG^0 and K

($Cu^{2+} + 2e^- = Cu(s)$) : $E^0 = 0.337V$
$F^{2+} + 2e^- = Fe(s)$: $E^0 = -0.44V$) [12]

Question 3 (25 marks)

(a). Define an indicator electrode. [1]

(b) Differentiate between an indicator electrode of the first kind and an indicator electrode of the second kind. Give an example and state the expression for the cell potential in each case. [7]

© Not all metals can be used as indicator electrodes of the first kind. Account for this observation and give four examples metals that cannot be so used. [5]

(d). Given the following reaction:

$CuSCN(s) + e^- = Cu(s) + SCN^-$

(i) Estimate the standard potential for this reaction.

(ii) Write the line notation for the cell in which the Cu indicator electrode is the cathode and a SCE as the anode that could be used fo the determination of SCN^-.

(iii) If there is no liquid junction potential, obtain an expression relating the observed potential in (ii) to pSCN.

(iv) With reference to the cell in (ii) above, calculate the pSCN for a solution saturated with CuSCN when the resulting cell potential is – 0.076V. [12]

($K_{sp} = 4.8 \times 10^{-15}$ for CuSCN)

Question 4 (25 marks)

(a) Give four favourable features of potentiometric titration. [2]

(b) (i) Explain the term 'concentration polarization'

(ii) How can it be minimized during an electrochemical analysis?

(iii) Demonstrate graphically the effects of concentration polarization on the current - potential behaviour of galvanic and electrolytic cells. [9]

(c) A 247.90mg sample of Na_2PtCl_6 was being analyzed for its chloride content. The Pt(IV) was reduced to Pt metal using hydrazine sulphate. The liberated Cl^- was titrated potentiometrically with 0.2314M $AgNO_3$ solution, using a Ag indicator electrode and a SCE reference electrode. The data obtained are tabulated below:

Vol. of $AgNO_3$ (mL)	E vs SCE (V)
00.00	0.072
13.00	0.140
13.20	0.14
13.40	0.152
13.60	0.160
13.80	0.172
14.00	0.196
14.20	0.290
14.40	0.326
14.60	0.340

(i) By using any of the conventional methods for 'end – point determination', estimate the end point of this titration. [7]

(ii) Calculate the apparent percent of the Cl^- in the sample, and the expected percent in a pure sample of this compound. [7]

Question 5 (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 or the 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. [7]

(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 and in [4]

(ii) [NaCl] = 1.00×10^{-3}M at pH 3.87 [4]

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

Question 6 (25 marks)

(a) Differentiate between the following methods:

(i) Voltammetry and coulometry.

(ii) Voltammetry and potentiometry [4]

(b) For the dropping mercury electrode (DME), polarographic method of analysis:

(i) Summarize its salient features and working principles. [7]

(ii) Why is the use of a supporting electrolyte essential when using it for the analysis of a sample? Give two examples of such electrolytes. [3]

(iii) Justify the use of greatly enhanced concentration of the supporting electrolyte (by at least 1000 – fold), relative to that of the analyte ion. [2]

© (i) Give the expression for the Ilkovic equation. Define all the terms in it. [3]

(ii) A TeO_3^{2-} sample was reduced polarographically in a 1.000M NaOH solution. The DME used for the analysis has the following parameters: m = 1.50mg/s, I_d = 61.9 μA, t = 3.15s, D = 0.75 x 10^{-5} cm^2s^{-1}, for a 4.0 x 10^{-3} M tellurium ion solution. Determine the oxidation state to which the tellurium has been reduced during this analysis? [6]

PERIODIC TABLE OF ELEMENTS

GROUPS

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

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											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)