UNIVERSITY OF SWAZILAND
SECOND SEMESTER EXAMINATION, 2015/2016

TITLE OF PAPER	**:**	**Advanced Analytical Chemistry**
COURSE NUMBEER	**:**	**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

You are not supposed to open this paper until permission to do so has been granted by the Chief Invigilator.

Question 1(25 marks)

(a) For the following two terms: cell constant, K, and equivalent conductance, Λ, for a conductivity cell

(i) Define each of them and state their S.I. Units [3]

(ii) Derive a relationship between the two of them. [2]

(b) Account for the difference in the variation patterns of molar/equivalent conductances of strong and weak electrolytes with concentration. Show how this phenomenon is employed for the determination of Λ^0, (Equivalent conductance at infinite dilution), for strong electrolytes while it is not applicable in the case of weak electrolytes. [6]

(c) Given the Table below:

Conc^n : (Equiv/L)	Λ(S cm^2 mol^{-1})	
	HCl	NaCl
0.0005	422.74	124.50
0.001	421.36	123.74
0.005	415.80	120.65
0.010	412.00	118.51
0.020	407.24	115.76
0.050	399.09	116.06
0.100	391.32	106.74

(i) Comment on the general variation of Λ with concentration [1]

(ii) For which of these salt solutions does Λ vary more rapidly and why? [2]

(iii) If conductivity data of aqueous solutions of ½$CaCl_2$ and ½$CaSO_4$ of some concentrations were included in the above data, arrange the two salts in decreasing order of rapidity of variation of Λ with concentration [1]

(d) A given solution of acetic acid has a concentration of 2.414×10^{-3} M and molar conductance of 32.22 S cm^2 mol^{-1}. Calculate:

(i) The degree of dissociation of acetic acid at this concentration.

(ii) The ionization constant, K_i. [10]

($\lambda^0_{H^+} = 349.6$ S cm^2 mol^{-1} ; $\lambda^0_{OAC^-} = 40.9$ S cm^2 mol^{-1})

Question 2 (25 marks)

(a) In carrying out a conductometric titration, what are the necessary precautionary steps that need to be taken in order to maximize accuracy of data? [3]

(b) Give three advantages of conductometric titration and explain why measurements near equivalent points are not necessary. [4]

(c) Sketch the general form of the titration curve for the following conductometric titrations indicating the equivalent points.

(i) Titration of HCl with 1.0 M KOH

(ii) Titration of HCl with 1.0 NH_4OH

Briefly explain the difference in the shapes of the two curves. [6]

(d) The following relative conductance readings, corrected for titrant volume, were obtained when a100.00mLsolution of acetic acid was titrated with 1.0M solution of NaOH.

Buret Reading:(mL)	0.20	0.60	1.00	1.21	1.40	2.00	2.20	2.40	2.60	3.00
Λ: (Scm^2 mol^{-1})	0.23	0.56	0.92	1.10	1.28	2.21	2.71	3.21	3.70	4.70

Determine the concentration of the acid. [12]

($\lambda^0_{H+} = 349.6$; $\lambda^0_{Cl^-} = 76.4$; $\lambda^0_{K^+} = 73.5$; $\lambda^0_{OH^-} = 198.6$; $\lambda^0_{NH_4^+} = 73.3$, S cm^{2}mol^{-1})

Question 3 (25 marks)

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

(b) (i) Describe the constructions of simple bottle-type saturated calomel electrode. Give the half-cell line notation and the reaction for the SCE. [6]

(ii) Given a saturated calomel electrode and a 0.1M calomel Electrode,

- Which would you prefer for analysis and why?
- Which has a higher cell potential at a given temperature? Justify your answer. [4]

(c) Sate the advantages and disadvantages of a Ag/AgCl electrode over saturated calomel electrode. [4]

(d) Given the following half reactions :

$$Mg^{2+} + 2e^- = Mg_{(s)} : E^o = -2.36\ V$$
$$Mg(OH)_{2(s)} + 2e^- = Mg_{(s)} + 2OH^- : E^0 = -2.69\ V$$

Calculate : (i) ΔG^0

(ii) The solubility product, K_{sp}, of $Mg(OH)_{2(s)}$.
(F = 96485 Coul/mol). [7]

Question 4 (25 marks)

(a) What is an indicator electrode? Give the main features of an ideal indicator electrode. [2]

(b) For a metallic indicator electrode of the first kind, use a specific illustrative example to describe its :

(i) set up,
(ii) operating principles,
(iii) cell potential $E_{ind.}$,
(iv) variation of the E_{ind} with pX (where X is the activity of the ion being analyzed) [12]

(c) Explain why certain metals cannot be employed as electrodes of the first kind. Give two examples of such metals. [3]

(d) In preparing a cell, a copper wire and SCE were dipped into a 0.100 M $CuSO_4$ solution. The copper wire was connected to the positive terminal of a potentiometer while the SCE was connected to the negative terminal.

(i) Write the half-cell reaction for the Cu-electrode
(ii) Write the Nernst equation for the Cu-electrode.
(iii) Calculate the cell voltage.

$(Cu^{2+} + 2e^- = Cu_{(s)} : E^\circ = 0337\ V)$ [8]

Question 5 (25 marks)

(a) Give five favourable features of ion selective electrodes (ISE). [5]

(b) State the specific type and class of ISE you would employ for the determination of the following ions in solutions: H^+, K^+, Na^+ and Ca^{2+}. [4]

(c) I.S.E's are designed to respond to the activity of a solution (and not to concentration). How would you plan your experiment so that the electrode would measure the concentrations of your solutions directly? [1]

(d) For the fluoride ISE.
(i) Draw a labeled schematic diagram.
(ii) Give an outline of its working principles (including establishment of potential difference across the membrane).

(iii) State the major interfering ion and its selectivity coefficient. [7]

(e) A Ca^{2+} I.S.E was employed for the determination of $[Ca^{2+}]$ in a water sample. A 10.00-ml sample was transferred to 100-ml volumetric flask and diluted to volume. A 50.00-ml aliquot of the latter sample was placed in a beaker containing a Ca^{2+} - ISE and S.C.E, and the measured potential was -0.05290V. When a 1.00-ml aliquot of 5.00×10^{-2} M standard Ca^{2+} solution was added, the potential changed to -0.04417V. Calculate the molar concentration of Ca^{2+} in the original water sample. [8]
(Take $\beta = 1.00$)

Question 6 (25 marks)

(a) (i) What are the usual functions of a supporting electrolyte during polarographic analysis of an ion? Give three examples. [5]
(ii) Why should the concentration of a supporting electrolyte be at least 1000 – fold that of the analyte ion? [3]

(b) Enumerate the sources of residual current during linear scan polarography. [2]

(c)
(i) Discuss briefly how current maxima and oxygen affect polarographic data.
(ii) What steps should be taken to minimize their effects during a polarograpic analysis. [8]

(d). The half-wave potential, $E_{1/2}$, for the uncomplexed reduction of a metal ion, M^{2+} on a DME in 0.1M $NaClO_4$ was -0.74 V. On being complexed with a ligand, L with concentration $C_L = 2.0 \times 10^{-4}$ M, the half-wave potential shifted to -0.930 V. If both polarograms are reversible and given that the metal –to- ligand ratio of the complex is unity, calculate K_f for the complex. [7]

PERIODIC TABLE OF ELEMENTS

GROUPS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
PERIODS	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	$R_\infty = m_e e^4/8h^3 c\varepsilon_0^2$	$1.097\,37 \times 10^{5}$ 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