UNIVERSITY OF SWAZILAND
FINAL/SEMESTER EXAMINATION, 2012/2013

TITLE OF PAPER	:	Advanced Analytical Chemistry
COURSE NUMBER	:	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.

REQUIRED: GRAPH PAPER

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Question 1 (25 marks) 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 : (M)	$\Lambda(S\ cm^2\ mol^{-1})$	
	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 $\frac{1}{2}CaCl_2$ and $\frac{1}{2}CaSO_4$ 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). State specifically the measures you would take so as to maximize accuracy of data during a conductometric titration experiment. [4]

(b). Summarize the procedure for end point determination during a conductometric titration. Why are measurements near equivalent points unnecessary? [3]

©. The titration of a weak acid with a weak base is preferred to the titration of a weak acid with a strong base. Justify this statement, using specific examples with illustrative diagrams. [4]

(d). For the conductometric titrations of HCl with 0.50 M NaOH and of HCl with 0.50 M NH_4OH:
(i). Give a sketch of the expected shape of the titration curve in each case.
(ii). Indicate the equivalent point in each case. [4]

(e), On titrating a solution containing a mixture of an aliphatic acid and an aromatic sulphonic acid conductometrically with a 0.200M NH_3 solution (as titrant), the following data (after correcting for the titrant volume), were obtained:

Burette Reading (mL)	0.00	1.00	2.00	2.50	3.00	3.20	3.50	4.20	5.00	6.00	8.00
Λ (Scm^2equiv^{-1})	2.01	1.75	1.47	1.33	1.19	1.19	1.26	1.51	1.51	1.52	1.53

(i). Calculate the number of equivalents of each acid present in the mixture.
(ii) Comment briefly on the shape of the titration curve. [10]

Question 3 (25 marks)

(a). Give two favourable features associated with electrochemical methods and give an illustrative example in each case. [3]

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

© (i) Employing a real or hypothetical reaction, obtain the Nernst equation for the estimation of the potential for an electrode half reaction.
(ii) Under what condition is the Nernst equation applicable to a reaction at equilibrium? [6]

(d).   For the following half – cell reactions:

$PtCl^{2-}_6$ + $2e^-$ = $PtSl^{2-}_4$ + $2Cl^-$ E^o =   0.68 V

V^{3+} + e^- = V^{2+} E^o =   -0.225V
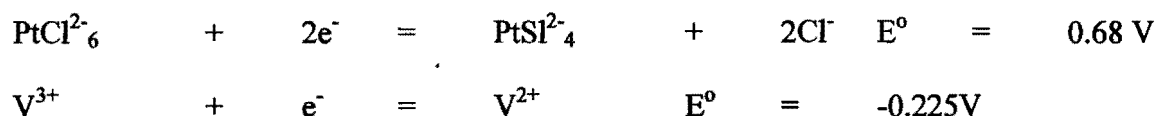
(i).   Write the overall cell reaction and calculate the corresponding cell voltage.
(ii).   Identify the anode, the cathode and the direction of spontaneous reaction.
(iii)   Calculate ΔG and K (the equilibrium constant) for the overall reaction.   [10]

Question 4(25 marks)

(a).   Define a reference electrode and state the salient characteristics of an ideal one.   [5]

(b).   Give a brief discussion of the make up, the half – cell line notation and the half cell reaction of a saturated calomel electrode.   [5]

©.   The potential (in volts), of some reference electrodes vs SHE, as a function of temperature are as tabulated below:

Temp (^{o}C)	Calomel (0.1 M KCl)	Calomel (Saturated KCl)	Ag/AgCl (Saturated KCl)
10	0.3362	0.2543	0.2138
20	0.3359	0.2479	0.2040
25	0.3356	0.2444	0.1989
30	0.3351	0.2411	0.1939
40	0.3336	0.2340	0.1835

(i).   Which of the electrodes has the poorest potential stability towards temperature variation, and how does this affect its performance as a reference electrode?
(ii).   Arrange the electrodes in the increasing order of their potential – temperature coefficient(or gradient).
(iii). Which would you choose for an analysis: a saturated calomel electrode or a 0.1M KCl calomel electrode? Explain.   [8]

(d).   State the advantages of Ag/AgCl reference electrode over a SCE.   [2]

(e).   A cell consisting of a SCE (E = 0.25 V), and an electrode of unknown potential, has a cell potential of 0.62V. Calculate the potential of the unknown electrode if the polarity of he SCE is: (i) positive,   (ii).   Negative   [5]

Question 5 (25 marks)

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

(b)   (i)   Explain the term 'concentration polarization'
        (ii)   How can it be minimized during an electrogravimetric analysis?
                (iii)   Demonstrate graphically the effects of concentration polarization
        on the current – potential behaviour of galvanic and electrolytic cells.
                [9]

©   A Na_2PtCl_6 sample weighing 247.90mg was   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 $AgNO_3$ using a
        Ag indicator electrode and a SCE reference electrode. The data obtained
        are tabulated below:

Vol. of AgNO3 (mL)	E vs SCE (V)
0.00	0.072
13.00	0.140
13.20	0.145
13.40	0.152
13.60	0.160
13.80	o.172
14.80	o.196
14.20	0.290
14.40	0.326
14.60	0.340

(i)   Employing 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 6 (25 marks)

    (a)   Differentiate between the following:
    (i)   Voltametry and coulometry.
    (ii)   Voltametry and potentiometry.   [4]

    (b) Discuss, very briefly, the salient features and the working principles of the
        dropping mercury electrode (DME).   [6]

© (i) Account for the use of a supporting electrolyte during polarographic analysis. Give two examples of such electrolytes. [3]
(ii) Why should the concentration of the supporting electrolyte be at least a 1000 – fold greater than that of the analyte ion? [2]

(d) (i) State the Ilkovic equation and define all the terms involved in it. [4]
(ii) A TeO_3^{2-} sample was reduced polarographically in a 1.0000M NaOH solution. The DME used for the analysis has the following parameters: $m = 1.50$ mg/s, $i_d = 61.9\mu A$, $t = 3.15s$, $D = 0.75 \times 10^{-5} cm^2 s^{-1}$ for a $4.0 \times 10^{-3}M$ tellurium ion solution. What is the oxidation state to which the tellurium has been reduced during this analysis? [6]

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	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	20.18(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								

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

TRANSITION ELEMENTS

*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
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

**Actinide Series

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

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

f	p	n	μ	m	c	d	k	M	G	Prefixes
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

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