UNIVERSITY OF SWAZILAND
FINAL EXAMINATION 2009/2010

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) State and briefly discuss the factors that influence the conductivity of an electrolyte. From the list of stated factors, pick the one you consider as the most important and state the factors that affect even its own value. [5]

(b) (i) Define the terms 'cell constant' and 'equivalent conductance'
(ii) State the S.I. units of the two terms and obtain an expression relating the two [5]

(c) Employing the concept of ionic atmosphere, discuss (with an illustrative example), the variation of limiting ionic conductance, λ°_{+}, of cations of elements from the same group in the periodic table. [5]

(d) A weak monobasic acid, HB, (F.W. 122), weighing 560.75mg was dissolved in 250 mL of dionized water at 25°C. If the measured resistance of the solution is 557Ω at 25°C, and the cell constant of the conductivity cell is 0.075 cm^{-1}, calculate the following for the acid:

(i) The molar conductance.
(ii) The degree of dissociation.
(iii) The ionization constant. 10]

$$(\lambda^{0}_{H^{+}} = 349.6, Scm^{3}mol^{-1},\ \lambda^{0}_{B^{-}} = 40.9Scm^{3}mol^{-1})$$

Question 2 (25 marks)

(a) What are the precautionary steps you would take in order to maximize accuracy of data during a conductometric titration? [4]

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

(c) Using specific examples with illustrative diagrams, explain why the titration of a weak acid with a weak base is preferred to the titration of a weak acid with a strong base. [4]

(d) Sketch the general forms of the titration curves for the following conductometric titrations and indicate the equivalent point in each case;

(i) Titration of HC1 with 0.50 M NaOH.

(e) A solution containing a mixture of an aliphatic acid and an aromatic sulphonic acid was titrated conductometrically with a 0.200 M NH_3 solution (as titrant). The conductance data obtained (after correction for the titrant volume) are as follows:

Burette Reading\mL	0.00	1.00	2.00	2.50	30..	3.20	3.50	4.20	4.50	5.00	6.00	8.00
\/S cm^{2}equiv^{-1}	2.01	1.75	1.47	1.33	1.19	1.19	1.26	1.47	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) 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 labeled 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 4 (25 marks)

(a) Give a brief discussion of the make up, the half – cell line notation and the half cell reaction of a saturated calomel electrode. [6]

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

Temp (°C)	Calomel(0.1MKU)	Calomel(Saturated KCL)	Ag/AgCI (Saturated KCI)
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	02340	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? [4]

(ii) Arrange the electrodes in the increasing order of their potential— temperature coefficient(or gradient). [2]

(iii) Which would you choose for an analysis: a saturated calomel electrode or a 0.1M KCI calomel electrode? Explain. [3]

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

(e) A cell consisting of a SCE (E = 0.25V), and an electrode of unknown potential, has a cell potential of 0.62 V. Calculate the potential of the unknown electrode if the polarity of the SCE is: (i) positive, (ii) Negative [8]

Question 5 (25 marks)

(a) Classify ion selective electrodes and give an example in each case. [6]

(b) State three favourable features of ion selective electrodes. [3]

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(c) Generally, H^+ ions interfere during the use of other types of glass membrane electrodes. What steps would you take to avoid serious H^+ ion interference during the measurement of other cations using a glass membrane electrode? [2]

(d) (i) With the aid of a diagram, describe the construction, the working mechanism, the electrode response and the major interfering ion of a fluoride ISE. [6]

(ii) State the class of the ISE to which it belongs. [1]

(iii) Explain why the membrane of this electrode is dopped with Eu(II). [2]

(e) A lithium ion – selective electrode has a selectivity coefficient, $K_{Li+, Ca2+} = 5.0 \times 10^{-5}$. On being laced in a 3.44×10^{-4}M Li^+ solution, its potential, versus SCE, was -0.333V. Calculate its potential when Ca^{2+} is added to give 0.100 M Ca^{2+}. [5]

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. [10]

(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. [11]

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	20.18 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	39.94 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	131.2 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	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e$	$5.291\,77 \times 10^{-11}$ 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 1*M* $HClO_4$)	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