UNIVERSITY OF SWAZILAND
FINAL EXAMINATION 2010/2011

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 at 25 ^{0}C:

Cation	Li^+	Na^+	K^+	Rb^+	Mg^{2+}	Ca^{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 0.5 M solutions of HCl and CH_3COOH were diluted serially in several stages to 0.001 M. 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]

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

Question 2 (25 marks)

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

(b) Distinguish 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 reaction as illustration, show how a galvanic cell can be converted into an electrolytic cell. [5]

(d) Given the following cell:

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

(i) Write the cell reaction

(ii) Calculate 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). What is an indicator electrode? [1]

(b) Distinguish 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 voltage in each case. [7]

(c) Some metals cannot be used as indicator electrodes of the first kind. Account for this observation and give four examples of such metals. [5]

(d). For the following reaction:

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

(i) Calculate the standard potential for this reaction.

(continued)

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

(iv) Using the cell in (ii), 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) 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]

(c) A Na_2PtCl_6 sample weighing 247.90 mg 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 0.2314 M $AgNO_3$ 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
14.80	0.196
14.20	0.290
14.40	0.326
14.60	0.340

(continued)

(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 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 -38 mV (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] = 1.00×10^{-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) Distinguish between
(i) Voltammetry and coulometry.
(ii) Voltammetry and potentiometry [4]

(b) For the dropping mercury electrode (DME), polarographic method of analysis:
(i) Discuss very briefly its salient features and working principles. [7]
(ii) Account for the use of a supporting electrolyte when using it for the analysis of a sample. Give two examples of such electrolytes. [3]
(iii) Why should the concentration of the supporting electrolyte be at least 1000 – fold higher than that of the analyte ion? [2]

(c) (i) State the Ilkovic equation and 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 = 1.50 mg/s, $I_d = 61.9\ \mu A$, t = 3.15 s, $D = 0.75 \times 10^{-5}\ cm^2s^{-1}$, for a 4.0×10^{-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 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA
1	1.008 H 1																
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	18.99 F 9
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	35.45 Cl 17
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	79.90 Br 35
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	126.9 I 53
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
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	174.9 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 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