UNIVERSITY OF SWAZILAND
SECOND SEMESTER EXAMINATION, 2013/2014

TITLE OF PAPER	**:**	**Advanced Analytical Chemistry**
COURSE CODE	**:**	**C404**
TIME ALLOWED	**:**	**Three (3) Hours.**
INSTRUCTIONS	**:**	**Answer any <u>Four</u> (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) Briefly discuss the factors that influence the conductivity of an electrolyte. From these factors. identify the one you consider as the most important and state the factors that affect its own value. [5]

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

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

(d) A 560.75mg sample of a weak monobasic acid, HB, with a formula weight of 122g/mol 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]

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

Question 2 (25 marks)

(a) Discuss the measures you would take in order to maximize accuracy of data when carrying out a conductometric titration . [3]

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

© Sketch the general form of the titration curve for the following conductometric titration indicating the equivalent points.

(i) Titration of HCl with 0.1 M NåOH solution

(ii) Titration of HCI with 0.1 M NH_4OH solution.

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

(d) The table below contains relative conductance readings, corrected for the titrant volume, obtained when a 100.00Ml solution 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^2mo^{-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]

(λ^o_{H+}=349.6; $\lambda^o_{CI^-}$=76.4; $\lambda^o_{K^+}$=73.5; $\lambda^o_{OH^-}$=198.6; $\lambda^o_{NH4^+}$=73.3 S cm^2 mol^{-1})

Question 3 (25 marks)

(a) State the ideal properties of a reference electrode? [4]

(b) (i) Describe the construction of simple bottle –type saturated calomel electrodeGive 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 of them would you prefer for analysis and why?
- Which has a higher cell potential at a given temperature?

Justify your answer. [4]

© What are the advantages and disadvantages of a Ag/AgCI electrode over saturated calomel electrode? [4]

(d) Given the following half reactions:

$Mg^{2+} + 2e^- = Mg_{(s)}$ $E^o = -2.36V$

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

Calculate:

(i) ΔG^0

(i) 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? Enumerate the ideal features of an 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 molar concentration of the ion being analyzed. [12]

© Give reasons 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 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.

($Cu^{2+} + 2e^- = Cu_{(s)}$ $E^o = 0.337V$) [8]

Question 5 (25 marks)

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

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

© 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 of it.

(ii) Briefly discuss its working principles (including the establishment of potential difference across the membrane). [7]

(e) A Ca^{2+} ISE was employed for the determination of $[Ca^{2+}]$ in a water sample. A 10.00-ml sample was transferred into a 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 -0.05290 V. When a 1.00-ml aliquot of 5.00×10^{-2}M standard Ca^{2+} solution was added, the potential changes to -0.04417V. Calculate the molar concentration of Ca^{2+} in the original water sample. [8]

(Take β =100)

Question 6 (25marks)

(a) (i) Summarize 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). Identify the usual sources of residual currents during linear scan plarographic analysis. [2]

© (i) Discuss briefly how current maxima and oxygen influence polargraphic data. [4]

(ii) What steps are usually taken to minimize their effects during a polarographic analysis? [4]

(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=2.0×10^{-4} M , the half-wave potential shifted to -0.930V. If both polarograms are reversible and given that the metal –to- ligand ratio of the complex is unity, calculate K_f for then complex. [7]

PERIODIC TABLE OF ELEMENTS

GROUPS

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										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	$R_\infty = m_e e^4/8h^3 c$	$1.097\,37 \times 10^{5}$ 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