

UNIVERSITY OF SWAZILAND
SECOND SEMESTER EXAMINATION, 2007/2008

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

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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 $\frac{1}{2}\text{CaCl}_2$ and $\frac{1}{2}\text{CaSO}_4$ 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 $32.22 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate:
- (i) The degree of dissociation of acetic acid at this concentration.
- (ii) The ionization constant, K_i . [10]

$$(\lambda_{\text{H}^+}^0 = 349.6 \text{ S cm}^2 \text{ mol}^{-1}; \lambda_{\text{OAc}^-}^0 = 40.9 \text{ S cm}^2 \text{ mol}^{-1})$$

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.
- Titration of HCl with 1.0 M KOH
 - Titration of HCl with 1.0 M NH₄OH
- 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 a 0.10M solution of acetic acid was titrated with 1.0M solution of NaOH.

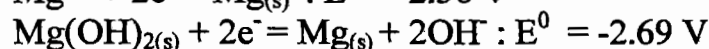
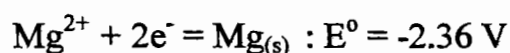
Buret Reading:(mL)	0.20	0.60	1.00	1.21	1.40	2.00	2.20	2.40	2.60	3.00
Λ : (S cm ² mol ⁻¹)	0.23	0.56	0.92	1.10	1.28	2.21	2.71	3.21	3.70	4.70

Determine the concentration of acid. [12]

$$(\lambda_{\text{H}^+}^0 = 349.6; \lambda_{\text{Cl}^-}^0 = 76.4; \lambda_{\text{K}^+}^0 = 73.5; \lambda_{\text{OH}^-}^0 = 198.6; \lambda_{\text{NH}_4^+}^0 = 73.3, \text{ S cm}^2 \text{ mol}^{-1})$$

Question 3 (25 marks)

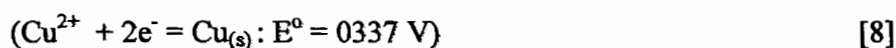
- (a) What are the main properties of an ideal reference electrode? [4]
- (b) (i) Describe the constructions of simple bottle-type saturated calomel electrode. Give the half-cell line notation and the reaction for the SCE. [6]
- (ii) Given a saturated calomel electrode and a 0.1M calomel Electrode,
- Which would you prefer for analysis and why?
 - Which has a higher cell potential at a given temperature?
- Justify your answer. [4]
- (c) State the advantages and disadvantages of a Ag/AgCl electrode over saturated calomel electrode. [4]
- (d) Given the following half reactions :



- 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.



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 $[\text{Ca}^{2+}]$ 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 $\beta = 100$)

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 polarographic 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

PERIODS	GROUPS																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIIIB	VIIIB	VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.008 H																	4.003 He
2	6.941 Li	9.012 Be																18.998 F
3	22.990 Na	24.305 Mg																39.948 Ar
4	39.098 K	40.078 Ca	44.956 Sc	47.88 Ti	50.942 V	51.996 Cr	54.938 Mn	55.847 Fe	58.933 Co	58.69 Ni	63.546 Cu	65.39 Zn	69.723 Ga	72.61 Ge	74.922 As	78.96 Se	79.904 Br	83.80 Kr
5	85.468 Rb	87.62 Sr	88.906 Y	91.224 Zr	92.906 Nb	95.94 Mo	98.907 Tc	101.07 Ru	102.91 Rh	106.42 Pd	107.87 Ag	112.41 Cd	114.82 In	118.71 Sn	121.75 Sb	127.60 Te	126.90 I	131.29 Xe
6	132.91 Cs	137.33 Ba	138.91 *La	178.49 Hf	180.95 Ta	183.85 W	186.21 Re	190.2 Os	192.22 Ir	195.08 Pt	196.97 Au	200.59 Hg	204.38 Tl	207.2 Pb	208.98 Bi	(209) Po	(210) At	(222) Rn
7	223 Fr	226.03 Ra	(227) **Ac	(261) Rf	(262) Ha	(263) Unh	(262) Uns	(265) Uno	(266) Uue	(267) Uun								

TRANSITION ELEMENTS

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
26.982	Al	13
28.086	Si	14
30.974	P	15
32.06	S	16
35.453	Cl	17
39.948	Ar	18

*Lanthanide Series

**Actinide Series

140.12	140.91	144.24	(145)	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
58	59	60	61	62	63	64	65	66	67	68	69	70	71
232.04	231.04	238.03	237.05	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
90	91	92	93	94	95	96	97	98	99	100	101	102	103

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

Quantity	Symbol	Value	General data and fundamental constants
Speed of light†	c	$2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$	
Elementary charge	e	$1.602\,177 \times 10^{-19} \text{ C}$	
Faraday constant	$F = eN_A$	$9.6485 \times 10^4 \text{ C mol}^{-1}$	
Boltzmann constant	k	$1.380\,66 \times 10^{-23} \text{ J K}^{-1}$	
Gas constant	$R = kN_A$	$8.314\,51 \text{ J K}^{-1} \text{ mol}^{-1}$ $8.205\,78 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ $62.364 \text{ L Torr K}^{-1} \text{ mol}^{-1}$	
Planck constant	h $\hbar = h/2\pi$	$6.626\,08 \times 10^{-34} \text{ J s}$ $1.054\,57 \times 10^{-34} \text{ J s}$	
Avogadro constant	N_A	$6.022\,14 \times 10^{23} \text{ mol}^{-1}$	
Atomic mass unit	u	$1.660\,54 \times 10^{-27} \text{ kg}$	
Mass of electron	m_e	$9.109\,39 \times 10^{-31} \text{ kg}$	
proton	m_p	$1.672\,62 \times 10^{-27} \text{ kg}$	
neutron	m_n	$1.674\,93 \times 10^{-27} \text{ kg}$	
Vacuum permeability†	μ_0	$4\pi \times 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$ $4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^2$	
Vacuum permittivity	$\epsilon_0 = 1/c^2\mu_0$ $4\pi\epsilon_0$	$8.854\,19 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$ $1.112\,65 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$	
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24} \text{ J T}^{-1}$	
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27} \text{ J T}^{-1}$	
Electron g value	g_e	2.002 32	
Bohr radius	$a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$	$5.291\,77 \times 10^{-11} \text{ m}$	
Rydberg constant	$R_\infty = m_e e^4/8h^3 c$	$1.097\,37 \times 10^5 \text{ cm}^{-1}$	
Fine structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$	
Gravitational constant	G	$6.672\,59 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2}$	
Standard acceleration of free fall†	g	$9.806\,65 \text{ m s}^{-2}$	

† 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
$Ag^+ + e^- = Ag$	2.00
$H_2O_2 + 2H^+ + 2e^- = 2H_2O$	1.77
$MnO_4^- + 4H^+ + 3e^- = MnO_2(s) + 2H_2O$	1.70
$Ce(IV) + e^- = Ce(III) \text{ (in } 1M \text{ HClO}_4\text{)}$	1.61
$H_2IO_6 + H^+ + 2e^- = IO_3^- + 3H_2O$	1.6
$Bi_2O_4 \text{ (bismuthate)} + 4H^+ + 2e^- = 2BiO^+ + 2H_2O$	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)
$\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^-$	$= 2\text{Hg} + 2\text{Cl}^-$	0.2676
$\text{BiO}^+ + 2\text{H}^+ + 3\text{e}^-$	$= \text{Bi} + \text{H}_2\text{O}$	0.32
$\text{AgCl}(\text{s}) + \text{e}^-$	$= \text{Ag} + \text{Cl}^-$	0.2222
$\text{SbO}^+ + 2\text{H}^+ + 3\text{e}^-$	$= \text{Sb} + \text{H}_2\text{O}$	0.212
$\text{CuCl}_2 + \text{e}^-$	$= \text{Cu} + 2\text{Cl}^-$	0.178
$\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$	$= \text{SO}_2(\text{aq}) + 2\text{H}_2\text{O}$	0.17
$\text{Sn}^{4+} + 2\text{e}^-$	$= \text{Sn}^{2+}$	0.15
$\text{S} + 2\text{H}^+ + 2\text{e}^-$	$= \text{H}_2\text{S}(\text{g})$	0.14
$\text{TiO}^{2+} + 2\text{H}^+ + \text{e}^-$	$= \text{Ti}^{3+} + \text{H}_2\text{O}$	0.10
$\text{S}_4\text{O}_6^{2-} + 2\text{e}^-$	$= 2\text{S}_2\text{O}_3^{2-}$	0.08
$\text{AgBr}(\text{s}) + \text{e}^-$	$= \text{Ag} + \text{Br}^-$	0.071
$2\text{H}^+ + 2\text{e}^-$	$= \text{H}_2$	0.0000
$\text{Pb}^{2+} + 2\text{e}^-$	$= \text{Pb}$	-0.126
$\text{Sn}^{2+} + 2\text{e}^-$	$= \text{Sn}$	-0.136
$\text{AgI}(\text{s}) + \text{e}^-$	$= \text{Ag} + \text{I}^-$	-0.152
$\text{Mo}^{3+} + 3\text{e}^-$	$= \text{Mo}$	approx. -0.2
$\text{N}_2 + 5\text{H}^+ + 4\text{e}^-$	$= \text{H}_2\text{NNH}_2^+$	-0.23
$\text{Ni}^{2+} + 2\text{e}^-$	$= \text{Ni}$	-0.246
$\text{V}^{3+} + \text{e}^-$	$= \text{V}^{2+}$	-0.255
$\text{Co}^{2+} + 2\text{e}^-$	$= \text{Co}$	-0.277
$\text{Ag}(\text{CN})_2 + \text{e}^-$	$= \text{Ag} + 2\text{CN}^-$	-0.31
$\text{Cd}^{2+} + 2\text{e}^-$	$= \text{Cd}$	-0.403
$\text{Cr}^{3+} + \text{e}^-$	$= \text{Cr}^{2+}$	-0.41
$\text{Fe}^{2+} + 2\text{e}^-$	$= \text{Fe}$	-0.440
$2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$	$= \text{H}_2\text{C}_2\text{O}_4$	-0.49
$\text{H}_3\text{PO}_3 + 2\text{H}^+ + 2\text{e}^-$	$= \text{H}_2\text{P}_2\text{O}_5 + \text{H}_2\text{O}$	-0.50
$\text{U}^{4+} + \text{e}^-$	$= \text{U}^{3+}$	-0.61
$\text{Zn}^{2+} + 2\text{e}^-$	$= \text{Zn}$	-0.763
$\text{Cr}^{2+} + 2\text{e}^-$	$= \text{Cr}$	-0.91
$\text{Mn}^{2+} + 2\text{e}^-$	$= \text{Mn}$	-1.18
$\text{Zr}^{4+} + 4\text{e}^-$	$= \text{Zr}$	-1.53
$\text{Ti}^{3+} + 3\text{e}^-$	$= \text{Ti}$	-1.63
$\text{Al}^{3+} + 3\text{e}^-$	$= \text{Al}$	-1.66
$\text{Th}^{4+} + 4\text{e}^-$	$= \text{Th}$	-1.90
$\text{Mg}^{2+} + 2\text{e}^-$	$= \text{Mg}$	-2.37
$\text{La}^{3+} + 3\text{e}^-$	$= \text{La}$	-2.52
$\text{Na}^+ + \text{e}^-$	$= \text{Na}$	-2.714
$\text{Ca}^{2+} + 2\text{e}^-$	$= \text{Ca}$	-2.87
$\text{Sr}^{2+} + 2\text{e}^-$	$= \text{Sr}$	-2.89
$\text{K}^+ + \text{e}^-$	$= \text{K}$	-2.925
$\text{Li}^+ + \text{e}^-$	$= \text{Li}$	-3.045