

**UNIVERSITY OF SWAZILAND
SECOND SEMESTER EXAMINATION, 2006/2007**

TITLE OF PAPER : **Advanced Analytical Chemistry**
COURSE NUMBER : **C404**
TIME ALLOWED : **Three 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.

You are not supposed to open this 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]
- ©. 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 557 Ω 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]

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

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]
- ©. For the conductometric titration of HCl with 0.50M NaOH and of HCl with 0.50M NH₄OH:
(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 NH₃ solution (as titrant), the following data (after correction 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
Δ (Scm ² /quiv)	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)

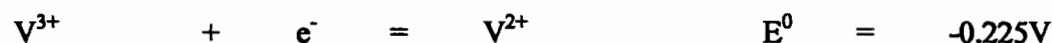
- (a). Give two favourable features associated with electrochemical methods and give an illustrative example in each case. [3]

(b). Distinguish 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 – reactions:



- (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.

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

Temp (°C)	Calomel (0.1M 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 ($E = 0.25V$), and an electrode of unknown potential, has a cell potential of 0.62V. Calculate the potential of the unknown electrode if the polarity of the 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 being analyzed for its chloride content. The Pt(IV) was reduced to Pt metal using hydrazine sulphate. The liberated Cl⁻ was titrated potentiometrically with 0.2314M $AgNO_3$ 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)
0.00	0.072
13.00	0.140
13.20	0.145
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

- (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. [4]
- (ii) Voltametry and potentiometry. [4]
- (b) Discuss, very briefly, the salient features and the working principles of the dropping mercury electrode (DME). [6]
- (c) (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 TeO₃ sample was reduced polarographically in a 1.0000M NaOH solution. The DME used for the analysis has the following parameters: $m = 1.50 \text{ mg/s}$, $i_d = 61.9 \mu\text{A}$, $t = 3.15\text{s}$, $D = 0.75 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for a $4.0 \times 10^{-3} \text{ M}$ 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	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	VII B	VIII B	VIII B	IB	IIB	IIIA	IVA	VA	VIA	VIA	VIIA	VIIIA
1	1.008 H																	2 He
2	6.941 Li	9.012 Be																10 Ne
3	22.990 Na	24.305 Mg																18 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) Une	(267) Uun								

TRANSITION ELEMENTS

Atomic mass	10.811	12.011	14.007	15.999	18.998	20.180
Symbol	B	C	N	O	F	Ne
Atomic No.	5	6	7	8	9	10

*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	$6.626\,08 \times 10^{-34} \text{ J s}$	
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34} \text{ J s}$	
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	$4\pi \times 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$ $4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^3$	
Vacuum permittivity	$\epsilon_0 = 1/c^2 \mu_0$	$8.854\,19 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$ $4\pi \epsilon_0$ $1.112\,65 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$	
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	$R_\infty = m_e e^4/8h^3c$	$1.097\,37 \times 10^5 \text{ cm}^{-1}$	
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
$Ag^2+ + e^- = Ag^+$	2.00
$H_2O_2 + 2H^+ + 2e^- = 2H_2O$	1.77
$MnO_4^- + 4H^+ + 3e^- = MnO_2(s) + 2H_2O$	1.70
$Ce(IV) + e^- = Ce(III) \text{ (in } 1M \text{ HClO}_4\text{)}$	1.61
$H_5IO_6 + H^+ + 2e^- = IO_3^- + 3H_2O$	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
$\text{CuCl}_2^- + \text{e}^-$	$= \text{Cu} + 3\text{Cl}^-$	0.178
$\text{SO}_2^- + 4\text{H}^+ + 2\text{e}^-$	$= \text{SO}_2(\text{aq}) + 2\text{H}_2\text{O}$	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
$\text{S}_2\text{O}_8^{2-} + 2\text{e}^-$	$= 2\text{S}_2\text{O}_3^{2-}$	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
$\text{N}_2 + 5\text{H}^+ + 4\text{e}^-$	$= \text{H}_2\text{NNH}_3^+$	-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