UNIVERSITY OF SWAZILAND
SECOND SEMESTER EXAMINATION, 2008/2009

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) Define the following terms, state their S.I units and differentiate between them:
   (i) Molar conductance
   (ii) Specific conductance   [4]

(b) Account for the difference in the variation of molar conductances of strong and weak electrolytes with dilution. How is this principle employed for the determination of Λ^0 for strong electrolytes? Explain why the same principle cannot be employed for the determination of Λ^0 for weak electrolytes.   [8]

(c) Given the following limiting Ionic equivalent conductances at 25°C

Ion	Li$^+$	Na$^+$	K$^+$	Rb$^+$
λ^0_+/Scm^2 equiv^{-1}	38.6	50.1	73.5	77.8

Ion	F$^-$	Cl$^-$	Br$^-$
λ^0_+/Scm^2 equiv^{-1}	55.4	76.4	78.1

Account for the variation of the limiting ionic conductances within each of the groups.   [3]

(d) At 25^{0}C, a saturated solution of barium sulphate has a specific conductance of 4.58×10^{-6} S cm^{-1} while that of the water used was 1.52×10^{-6} S cm^{-1} . Calculate :
   (i) The concentration of BaSO$_4$ at 25°C in equivalents/L, moles/L and g/L.
   (ii) The solubility product of BaSO$_4$ at 25°C

   (Λ_{BaSO4} = 143.6 Scm^{2}equiv^{-1}; Ba = 137.34; S = 32.06; O =16.00)
                                                                                   [10]

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 processs,
   (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 :

$$Cu|Cu(NO_3)_2(0.02M)||Fe(NO_3)_2(0.05M)|Fe.$$

(i) Write the cell reaction

(ii) Calculate the cell potential

(iii) Indicate the polarities of the electrodes

(iv) Give the direction of spontaneous reaction

(v) Calculate ΔG^0 and K

$(Cu^{2+} + 2e- = Cu(s) : E^0 = 0.337$ V
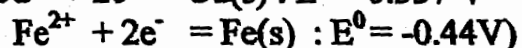
$\quad Fe^{2+} + 2e^- = Fe(s) : E^0 = -0.44V)$ [12]

Question 3 (25 marks)

(a) Draw the set up for a typical potentiometric titration and give a brief procedure for carrying it out. [3]

(b) Give five advantages (favourable features) and two disadvantages of potentiometric titration method of analysis. [7]

(c) Using a silver wire indicator electrode and a S.C.E Ref. Electrode, the following data were obtained during the potentiometric titration of an aqueous solution of KCl(50.00ml) with 0.09603M $AgNO_3$:

Vol. of $AgNO_3$ ml	E vs SCE, V
10.00	+0.062
20.00	0.085
25.00	0.107
27.00	0.123
28.00	0.138
28.50	0.161
29.10	0.180
29.20	0.192
29.30	0.221
29.40	0.288
29.50	0.304
29.60	0.314
29.70	0.321
30.00	0.336
30.50	0.348
31.00	0.359
33.00	0.389

(i) Plot $\Delta E/\Delta V$ vs. Titrant volume and locate the equivalence point. [4]

(ii) Plot $\Delta V/\Delta E$ vs. Titrant volume, and estimate the equivalence pint by extrapolating the point of intersection of the two linear curves to the titrant volume axis. [4]

(iii) Compare the two results. Which do you suppose is better and why? [2]

(iv) Calculate the [Cl⁻] in the sample using the result from (i) or (ii) [5]

Question 4 (25 marks)

(a) (i) State the expression for the operational definition of pH

(ii) Define all terms in the above pH expression.

(iii) Give two reasons why this definition is better than the more common definition of a pH (i.e pH $= \log_{10}[H^+]$) [4]

(b) For the glass pH- electrode:

(i) State six of its properties/advantages. [5]

(ii) Discuss what occurs when a newly manufactured one is soaked in water prior to use and give reason/s for the necessity of this step. [3]

(iii) Describe the necessary precautionary measures that need to be taken to assure accurate data collection while using this electrode. [3]

(iv) Draw and label the schematic/line diagram of this electrode. [4]

(v) Discuss the cause, the effects and the correction of the alkaline error often associated with the use of this electrode. Why is it called a negative error in pH?

[6]

Question 5 (25 marks)

(a) What are the salient features of electrogravimetric and coulometric methods of analysis? [4]

(b) (i) What are the causes of kinetic and concentration polarization? [2]
(ii) Show graphically the effects of concentration polarization on the output voltage of a galvanic cell and applied voltage needed to drive an electrolysis cell. [6]
(iii) State four steps you would take to decrease concentration polarization. [2]

(c) Assuming no concentration polarization occurs, calculate the cathode potential (versus S.H.E), needed to reduce the $[Sn^{2+}]$ in a solution to 1.0×10^{-8} during electrolysis aimed at reducing Sn^{2+} to $Sn(s)$.
(i) What would be the potential if the S.H.E is now replaced with S.C.E?
(ii) Would the potential become more negative or positive if concentration polarization occurs?

$$\text{For SCE}: \quad E^0 = +0.241V, \text{ and}$$
$$\text{For (i)}: \quad Sn^{2+} + 2e^- = Sn(s) \; ; \quad E^0 = -0.141 \qquad [5]$$

(d) A substance weighing 0.654g was made up of lead lactate, $Pb(CH_3CHO\ HCO_2)_2$, plus another inert material. On being electrolyzed, 0.222g of PbO_2 was deposited on one of the electrodes.
(i) Identify the electrode (anode or cathode) on which the PbO_2 was deposited. [2]
(ii) Calculate the percent of the lactate in the unknown. [4]

(Pb = 207.2; C = 12..01; H = 1.008; O = 16.00)

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.
      [3]
(iii) Alkali metals (with lower standard potentials), can be reduced more easily
      than H$^+$ at a DME.   [3]
(iv) A DME is preferred for cathodic reactions during amperometric titrations
      while a Pt electrode is preferred for anodic reactions.   [2]

©.   The iodate ion undergoes the following reaction at the DME:

     $$IO_3^- \quad + \quad 6H^+ \quad + \quad e^- \quad = \quad I^- \quad + \quad 3H_2O$$

     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 2.67
     mg/s, the diffusion current was 37.1 μA. Determine the diffusion coefficient of
     the iodate ion in 0.1M perchloric acid.   [13]

QUESTION ONE

(a) Discuss the use of inorganic elements in the following fields of medicine:
    (i)   chelation therapy
    (ii)   cancer treatment
    (iii) anti-arthritis drugs
    (iv) imaging agents   [12]

(b) Discuss the roles of the ions of the major elements K^+, Na^+ and Ca^{2+} in metabolic processes? In the discussion identify which ions are found within and outside the cells and their relative concentrations.   [6]

(c) Describe the origin of CO toxicity in mammals, including a consideration of the nature of metal-CO bonding.   [3]

(d) Why might Cu sensors be 'designed' to bind Cu(I) rather than Cu(II)?   [4]

QUESTION TWO

(a) Discuss the structure of the zinc metalloenzyme carboxypeptidase and outline the mechanism of its function.   [5]

(b) (i)   Draw the structure of the porphine ligand
    (ii)   Show how the structure of the porphine ligand
        (1)   has been modified in the chlorophyll molecule
        (2)   differs from the corrin ring ligand in vitamin B_{12}
        (3)   is related to the heme structure
    (ii)   Describe the characteristics of the ligands that are adopted for binding Ca^{2+} to proteins and those used to bind Fe^{2+} in the oxygen-carrying protein hemoglobin.   [10]

(c) (i)   What is the shape and makeup of the manganese complexes utilised in PSII?
    (ii)   Which features of manganese suit it to function as a redox center in PSII, as opposed to metals such as copper or nickel?   [4]

(d) (i)   What is meant by the term *zwitterion*?
    (ii)   Describe what is meant by the term *primary structure of proteins*?
    (iii) What type of bonding between amino acid residues is most important in holding a protein or polypeptide in a specific secondary configuration.
    (iv) A globular protein in aqueous surroundings contains the following amino acid residues: methionine, lysine, and alanine. Which amino acid side chains would be directed toward the inside of the protein and which would be directed toward the aqueous surroundings?   [6]

QUESTION THREE

(a) Describe the characteristics of zinc that make it an important element in biochemistry? Compare these characteristics to those of the other metals found in biological systems. [6]

(b) (i) The O–O bond lengths in O_2, KO_2 (O_2^-), and BaO_2 (O_2^{2-}) are 1.21, and 1.49 Å, respectively. These values provide reference data on the relation 1.34, between bond length and oxidation state. For the complexes $[Co(CN)_5(O_2)]^{3-}$, $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+}$, and $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$, the O–O bond lengths are 1.24, 1.47, and 1.30 Å, respectively. Comment on the extent of Co to O_2 electron transfer (state number of electrons transferred) in each complex.

(ii) Early attempts to synthesise O_2-carrying iron-porphyrin models were prevented by the formation of oxidized porphyrin dimers having a μ–O bridge between the iron atoms. Outline three approaches that have been successfully employed to circumvent this problem. [9]

(c) Why are iron-sulphur proteins employed in redox catalysis? [3]

(d) (i) What functional groups are found in all amino acids?
(ii) Draw the structure of the amino acid leucine in acidic solution at a pH below the isoelectric point. [3]

(e) Provide an explanation for why the toxicity of mercury is greatly increased by the action of enzymes containing cobalamin. [4]

QUESTION FOUR

(a) Discuss the uptake of O_2 by myoglobin and hemoglobin and its
(i) pH dependency   (ii) cooperative mechanism
(iii) effect of partial pressure of O_2 [9]

(b) (i) What is the function of the metallo-biomolecule, nitrogenase?
(ii) Identify the metal(s) that are at the active centres of nitrogenase.
(iii) Describe the essential features of the structure of nitrogenase.
(iv) Describe the essential steps in the mechanism of the function of nitrogenase. [8]

(c) One of the problems that has plagued synthetic chemists in their attempts to prepare model compounds for cysteine-complexed metal ions in metalloproteins is the easy oxidation of the thiolate anions (RS^-) to RS—SR. Simple complexes with Cu^{2+}—SR and Fe^{3+}—SR bonds that might serve as models for cytochrome P-450 and the ferredoxins are labile because of this reaction. Write balanced equations for the decomposition of $[Cu^{(II)}L_n(SR)]$ and $[Fe^{(III)}L_n(SR)]$. [2]

(d) Discuss three factors that illuminate the difference between Ca^{2+} and Mg^{2+}. [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	18 VIIIA
1	1.008 **H** 1																	4.003 **He** 2
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	18.998 **F** 9	20.180 **Ne** 10
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	35.453 **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								

TRANSITION ELEMENTS

Atomic mass → 10.811
Symbol → **B**
Atomic No. → 5

*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.