UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2006

TITLE OF PAPER	:	**THERMAL AND ELECTROANALYTICAL METHODS**
COURSE NUMBER	:	**C513**
TIME	:	**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.

SPECIAL REQUIREMENT : GRAPH PAPER

You are not supposed to open this paper until permission to do so has been granted by Chief Invigilator.

<u>Question 1</u> (25 marks)

(a). The thermobalance is the instrument employed for the TG analysis of a sample.

i) Draw a labelled schematic diagram of a modern type of this instrument.

ii) State the five main components of the instrument.

iii) Give six of the features you consider desirable in the design/construction of an ideal thermobalance. (10)

(b). The design and operation of the thermobalance furnace are critically important in obtaining accurate and reproducible thermograms: Discuss the features that should be entrenched in its design to achieve these goals. (5)

(c). A thermal analyst wanted to ascertain whether a given sample was MgO, $MgCO_3$ or MgC_2O_4. He then subjected a 350.0mg sample to a thermogravimetric analysis, for which the thermogram showed a loss of 182.0mg: If the following are the relevant possible reactions:

$MgO \rightarrow$ No reaction

$MgCO_3 \rightarrow MgO + CO_2$

and

$MgC_2O_4 \rightarrow MgO + CO_2 + CO$

Which of the three formulae represents the compound present in the sample? (10)

<u>Question 2</u> (25 marks)

(a) Compare and contrast the TG (thermogravimetric Analysis) and DTA (Differential Thermal Analysis) in terms of:
Their thermograms
Quantity measured
Instrument used
Nature of sample and reference. (4)

(b) Why is the atmospheric control a more critical factor in TG than in DTA analysis? (2)

(c) Discuss the effects and possible corrections of four of the factors that influence DTA heating curves (thermograms). (6)

(d) State the factors that determine the choice/nature of the following during a DTA experiment.

(i) Sample holder

(ii) Temperature measuring device. (3)

(e) A compound that consists of Cu(II), ammonia and chloride is subjected to TG analysis. A 50.0mg sample of the compound had a weight loss of 28.2mg. If all the loss is ammonia, what is the formula of the sample? (4)

(f) The solid lines in the figure (fig. 2.1) below depicts the simultaneous DTA and TGA thermograms of manganese hydrogen carbonate in a porous crucible;

(i) Identify the transitions involved at each peak on the DTA trace and the products at each TG plateau.

(ii) The dashed line/thermogram was obtained when a controlled atmosphere with 13 atm CO_2 was used. Why is the initial oxide of Mn formed from its carbonate different? (6)

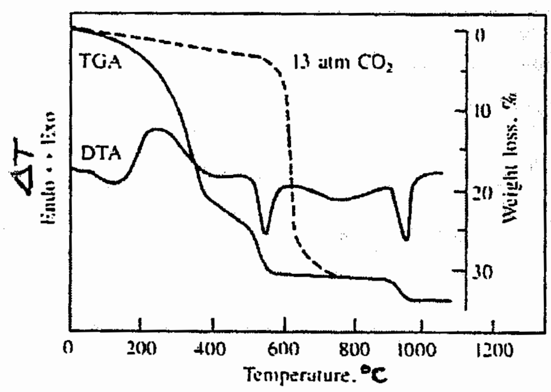

Fig 2.1

Question 3 (25marks)

(a) i) Briefly describe the principles in Differential Scanning Calorimetry (DSC) (3)

ii) Draw a schematic diagram of the setup of the temperature sensors and heaters in a DSC (2)

iii) State the differences between DTA and DSC with regard to the basic principles and instrumental setup. (3)

(b) Briefly discuss the functions of the following in the instrument setup on a DSC

i) The average temperature controller

ii) The differential temperature controller

(2)

(c) i) Draw a typical DSC Thermogram (i.e. a DSC curve/scan) (4)

ii) What information (data) are obtainable from the DSC scan and how are they obtained from the curve/scan? (4)

iii) What structural difference exists between a DTA and DSC thermogram (2)

(d) A polymer sample weighing 15.4 mg was run on a DSC and the thermogram showed a baseline shift from 4.22 to 8.80 mCal/sec at a heating rate of 10.0 °C/min. Calculate:

i) The change in the heat capacity of the sample.

ii) The new heat capacity, given that the original heat capacity was 2.73 Cal/°Cg (6)

<u>Question 4</u> (25 marks)

(a) For both thermometric titration (TT) and direct injection enthalpimetry (DIE) experiment.

i) What parameters must be known prior to their successful application

ii) Discuss how relevant data are usually obtained from their respective curves/experiments (6)

(b) An adiabatic cell is an important component of a TT set up

i) Discuss its main functions

ii) Give a typical example

iii) How is its performance evaluated?

iv) What physical feature of the cell enhances its performance and how? (4)

(c) A thermometric titration was carried out at 25°C for the reaction.

$$M + L \leftrightarrows ML$$

The following data were obtained:

Time (s)	Heat Evolved (cal.)
5.0	1.95
10.0	3.87
15.0	5.73
20.0	7.42
25.0	8.68
30.0	9.30
35.0	9.56
40.0	9.69
50.0	9.89
60.0	9.97
70.0	10.0
80.0	10.0

Given that the initial sample concentration for both (M) and (L) was 0.01M, and that the titration rate was 0.04 mL/s.

i) Sketch the appropriate titration curve
ii) Calculate the equilibrium constant, K and $\triangle G$
iii) Identify the equivalence point and calculate the corresponding titrant volume. (10)

(Take Gas Constant, R = 1.9872 cal-$K^{-1}mol^{-1}$)

Question 5 (25 marks)

(a) What is a cathodic depolarizer?
Using a given example, show how it is employed during constant voltage electrolysis. Discuss its mechanisms of action. (5)

(b) i) What is a potertiostat? (1)
ii) Compare and contrast the working principles of a constant voltage electrolysis and controlled potential (constant cathode potential) electrolysis. Which of the two is more selective? Explain how the enhanced selection is achieved by this method. (8)

(c) i) Enumerate the favourable and unfavourable features of potentiometric titration method of analysis
ii) The following data were obtained near the end point of a potentiometric titration of a reducing solution with 0.1000 M oxidant, using a Pt-S.C.E electrode pair:-

Titrant Vol(mL)	E.(mV)
38.70	541.0
38.80	547.0
38.90	555.0
39.00	566.0
39.10	583.0
39.20	884.0
39.30	1104.0
39.40	1121.0
39.50	1133.0

Plot (i) E and (ii) $\Delta E/\Delta V$, against the titrant volume and obtain the end point from each of the curves. Compare the results and comment on them. (12)

Question 6 (25 marks)

a) Distinguish between
   i) A limiting current and residual current
   ii) Differential pulse polarography and square wave polarography.

b) Explain the occurrence a polarographic wave (i.e. the oscillating current), in a polarogram. (4)

c) Discuss the effects of the following factors on the polarogram's shape and hence on the polarographic data.
   i) Current maxima
   ii) Presence of Oxygen
   State steps usually taken to minimize their effects (8)

d) Briefly discuss the working principles of differential pulse polarography. Account for its enhanced sensitivity over the conventional (d.c.) polarography. (8)

e). In using the polarographic method for the estimation of the oxygen level in water, the limiting current for the first 2-electron oxygen reduction was 2.11 μA. The capillary used had m=2.0 mgs^{-1} and t=5.00s at –0.05 V. If the diffusion coefficient, D = 2.12 x $10^{-5}cm^2s^{-1}$, calculate the oxygen level in the water in
   i) mM (millimoles/L)
   ii) p.p.m. (5)

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	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	$R_\infty = m_e e^4/8h^3c\varepsilon_0^2$	$1.097\,37 \times 10^{5}$ 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}

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	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								

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	174.97 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.