UNIVERSITY OF SWAZILAND
FIRST SEMESTER EXAMINATION, 2009/2010

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

SPECIAL REQUIREMENT : GRAPH PAPER

DO NOT OPEN THIS QUESTION PAPER UNTL PERMISSION TO DO SO HAS BEEN GRANTED BY THE CHIEF INVIGILATOR.

Question 1 (25 marks)

(a) State and briefly explain the various types of available thermogravimetric analysis. Which of these is the most commonly used? [4]

(b)

(i) What are the basic information obtainable from a typical thermogravimetric analysis? [3]

(ii) With regard to the sample, what condition is required to obtain a meaningful result, using a TG? [1]

(iii) Using illustrative diagrams and basic equations differentiate between TG and DTG. Summarize the advantages of the later over the former. [7]

(c)

(i) Give 4 of the sample characteristics capable of influencing its TG analysis. [2]

(ii) Discuss how the following can negatively affect/influence a T.G analysis.

- Sample container air buoyancy. [5]
- Furnace convection currents and turbulence. [3]

Question 2 (25 marks)

(a) The analytical instrument during the TG analysis of a sample is the thermobalance:

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) In order to ascertain whether a given sample was MgO, $MgCO_3$ or MgC_2O_4. an analyst subjected a 350.0mg of the sample to a thermogravimetric analysis. The thermogram showed a loss of 182.0mg: Given the following relevant possible reactions:

$MgO \rightarrow$ No reaction

$MgCO_3 \rightarrow MgO + CO_2$

and

$MgC_2O_4 \rightarrow MgO + CO_2 + CO$

Identify the compound present in the sample? [10]

Question 3 (25 marks)

(a) Differentiate between TG (thermogravimetric Analysis), and DTA (Differential Thermal Analysis), with respect to:
Their thermograms
Quantity measured
Instrument used
Nature of sample and reference. [4]

(b) Explain why atmospheric control is a more critical factor in TG than in DTA analysis. [2]

(c) Discuss the effects and possible corrections of three of the factors that influence DTA thermograms. [6]

(d) What factors 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. 3.1) 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]

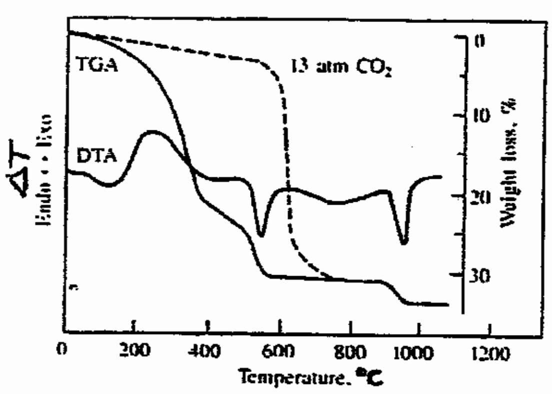

Fig 3.1

Question 4 (25marks)

(a)

(i) Discuss the principles involved 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) Distinquish between DTA and DSC with respect to their basic principles and instrumental setup. [3]

(b) Sumarize the functions of the following in the instrument setup of 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): [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]

Question 5 (25 marks)

(a) In using thermometric titration (TT) and direct injection enthalpimetry (DIE) for analysis:

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) For the adiabatic cell 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?

[6]

(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 ΔG
iii) Identify the equivalence point and calculate the corresponding titrant volume. [13]

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

Question 6 (25 marks)

(a) Explain the occurrence of a polarographic wave (i.e the oscillation current), in the polarogram when a dropping mercury electrode is used for analysis. [4]

(b) Discuss the effects of the following factors on the polarogram's shape and hence on the polarographic data:
(i) Current maxima. [4]
(ii) Presence of Oxygen.
What steps are usually taken to minimize their effects? [4]

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

(d) During the analysis of the oxygen level in water by the polarographic method, the limiting current for the first 2-electron oxygen reduction was 2.11μA. For the capillary used, m = 2.0 mgs^{-1} and t = 5.00s at -0.05V. Given that the difussion coefficient, D = 2.12 x $10^{-5}cm^2s^{-1}$, calculate the oxygen level in the water in:

(i) mM (millimoles/L)

(ii) ppm (i.e. mg/L) [5]

General data and fundamental constants

Quantity	Symbol	Value
Speed of light†	c	$2.997\,924\,58 \times 10^{8}\ \mathrm{m\ s^{-1}}$
Elementary charge	e	$1.602\,177 \times 10^{-19}\ \mathrm{C}$
Faraday constant	$F = eN_A$	$9.6485 \times 10^{4}\ \mathrm{C\ mol^{-1}}$
Boltzmann constant	k	$1.380\,66 \times 10^{-23}\ \mathrm{J\ K^{-1}}$
Gas constant	$R = kN_A$	$8.314\,51\ \mathrm{J\ K^{-1}\ mol^{-1}}$
		$8.205\,78 \times 10^{-2}\ \mathrm{dm^{3}\ atm\ K^{-1}\ mol^{-1}}$
		$62.364\ \mathrm{L\ Torr\ K^{-1}\ mol^{-1}}$
Planck constant	h	$6.626\,08 \times 10^{-34}\ \mathrm{J\ s}$
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34}\ \mathrm{J\ s}$
Avogadro constant	N_A	$6.022\,14 \times 10^{23}\ \mathrm{mol^{-1}}$
Atomic mass unit	u	$1.660\,54 \times 10^{-27}\ \mathrm{kg}$
Mass of		
electron	m_e	$9.109\,39 \times 10^{-31}\ \mathrm{kg}$
proton	m_p	$1.672\,62 \times 10^{-27}\ \mathrm{kg}$
neutron	m_n	$1.674\,93 \times 10^{-27}\ \mathrm{kg}$
Vacuum permeability†	μ_0	$4\pi \times 10^{-7}\ \mathrm{J\ s^{2}\ C^{-2}\ m^{-1}}$
		$4\pi \times 10^{-7}\ \mathrm{T^{2}\ J^{-1}\ m^{3}}$
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12}\ \mathrm{J^{-1}\ C^{2}\ m^{-1}}$
	$4\pi\varepsilon_0$	$1.112\,65 \times 10^{-10}\ \mathrm{J^{-1}\ C^{2}\ m^{-1}}$
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}\ \mathrm{J\ T^{-1}}$
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}\ \mathrm{J\ T^{-1}}$
Electron g value	g_e	$2.002\,32$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	$5.291\,77 \times 10^{-11}\ \mathrm{m}$
Rydberg constant	$R_\infty = m_e e^4/8h^3c\varepsilon_0^2$	$1.097\,37 \times 10^{5}\ \mathrm{cm^{-1}}$
Fine structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Gravitational constant	G	$6.672\,59 \times 10^{-11}\ \mathrm{N\ m^{2}\ kg^{-2}}$
Standard acceleration of free fall†	g	$9.806\,65\ \mathrm{m\ s^{-2}}$

† 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

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

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
1	1.008 H 1																
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
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
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
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
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
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

*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.