UNIVERSITY OF SWAZILAND
FIRST SEMESTER EXAMINATION, 2012/2013

TITLE OF PAPER	:	**THERMAL AND ELECTROANALYTICAL METHODS**
COURSE CODE	:	**C613**
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) Briefly discuss the various types of thermogravimetric analytical methods. Identify the most commonly used among them. [4]

(b)

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

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

(iii) With the help of diagrams and relevant equations differentiate between TG and DTG. What are 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 the negative affect/influence of the following a T.G analysis (Use a diagram where necessary).

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

Question 2 (25 marks)

(a) The thermobalance is the analytical instrument during the TG analysis. For it:

i) Draw a labelled schematic diagram of a modern type.
ii) Identify its five main components.
iii) Give six of the features you consider desirable in the design/construction of an ideal thermobalance. [10]

(b) To obtain accurate and reproducible thermograms, the design and operation of the thermobalance furnace are critically important.Discuss the features that should be entrenched in its design to achieve these goals. [5]

(c) During the analysis to confirm whether a given sample was MgO, $MgCO_3$ or MgC_2O_4. a 350.0 mg of the sample was subjected to a thermogravimetric analysis. The thermogram showed a loss of 182.0 mg: 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) Identify the factors that determine the choice/nature of the following during a DTA analysis.
(i) Sample holder.
(ii) Temperature measuring device. [3]

(d) A 28.2 mg mass loss was observed when 50.0 mg of a compound that consists of Cu(II), ammonia and chloride is subjected to TG analysis. 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 broken 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]

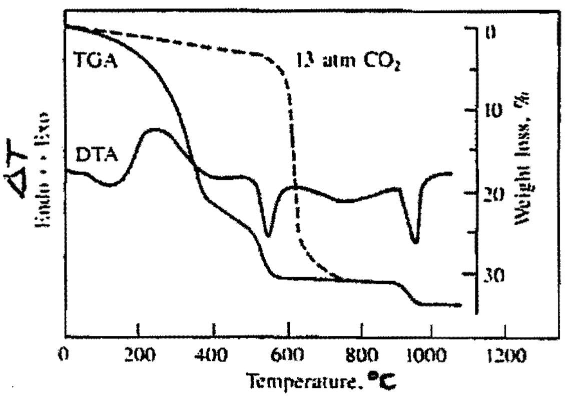

Fig 3.1

Question 4 (25marks)

(a)

(i) Describe the basic principles of Differential Scanning Calorimetry (DSC) [3]

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

(iii) Differentiate DTA from DSC based on their basic principles and instrumental setup. [3]

(b) Enumerate 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 labeled typical DSC curve. [4]

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

iii) Identify the structural difference between a DTA and a DSC thermogram? [2]

(c) On using a heating rate of 10.0 °C/min,the DSC thermogram of a polymer sample weighing 15.4 mg showed a baseline shift from 4.22 to 8.80 mCal/sec. 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) On carrying out a thermometric titration at 25°C for the reaction:

$$M + L \leftrightarrows ML$$

The data obtained are tabulated below:

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

If the titration rate was 0.04 mL/s and the initial sample concentration for both was 0.01 M,

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) Account for the occurrence of a polarographic wave (i.e the oscillation current), in the polarogram of a conventional dropping mercury electrode. [4]

(b) What are the effects of the following factors on both the polarographic shape and data:

(i) Current maxima. [4]

(ii) Presence of Oxygen.

What steps are usually taken to minimize their effects? [4]

(c) Briefly 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 2.11 μA. For the capillary used, m = 2.0 mgs^{-1} and t = 5.00 s at -0.05 V. 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	$1.390\,66 \times 10^{-23}\ \mathrm{J\ K^{-1}}$
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	μ_N [illegible] $\hbar/2m_p$	$5.050\,79 \times 10^{-27}\ \mathrm{J\ T^{-1}}$
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	$R_\infty = m_e e^4/8h^3 c$	$1.097\,37 \times 10^{5}\ \mathrm{cm^{-1}}$
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

TRANSITION ELEMENTS

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	VIIB		VIIIB		IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1.008 H 1																	4.003 He 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
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
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
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
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
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								

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.