UNIVERSITY OF SWAZILAND
FIRST SEMESTER EXAMINATION, 2010/2011

TITLE OF PAPER : **Thermal And Electroanalytical Methods**

COURSE NUMBER : **C613**

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**

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

1

Question 1 (25 marks)

(a)   For the thermobalance :
    (i)   Draw and label a schematic diagram of a modern type of this instrument.
    (ii)   Which are 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)   Discuss the features that should be entrenched in the design of the
thermoblance furnace that would enhance obtaining accurate and reproducible
thermograms.   [5]

(c)   A thermal analyst wanted to ascertain whether a given sample was MgO,
$MgCO_3$ or MgC_2O_4. He then subjected a 350.0 mg sample to a
thermogravimetric analysis, for which the thermogram showed a loss of 182.0
mg: 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 $+CO$
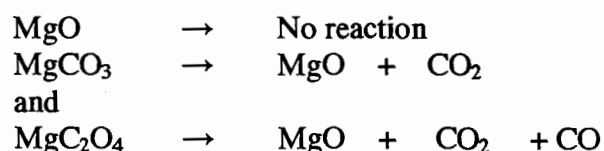
Which of the three formulae represents the compound present in the sample?
                                                                                                          [10]

Question 2 (25 marks)

(a)   With reference to the items listed below, compare and contrast the TG
(thermogravimetric Analysis) and DTA (Differential Thermal Analysis).
Their thermograms
Quantity measured
Instrument used
Nature of sample and reference.   [4]

(b)   Explain 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 thermograms.   [6]

(d)   What are the factors that influence the choice/nature of the following during a
DTA experiment.
    (i)   Sample holder
    (ii)   Temperature measuring device.   [3]

2

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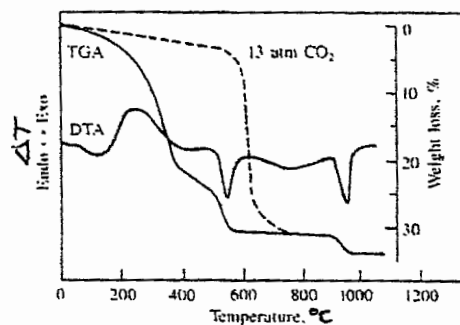

Fig 2.1

Question 3 (25marks)

   (a)
       (i)   Summarize the principles involved in the Differential Scanning Calorimetry   (DSC)   [3]

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

       (iii)   What are the differences between DTA and DSC with regard to the basic principles and instrumental setup.   [3]

   (b) State the functions of the following in the instrument setup on a DSC
       (i)   The average temperature controller
       (ii)   The differential temperature controller

                                                                                  [2]

3

(c)
   (i)   Draw and label typical DSC Thermogram .   [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 15.4 mg polymer sample was analyzed using a DSC. 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 4 (25 marks)

   (a) For both thermometric titration (TT) and direct injection enthalpimetry (DIE)
       experiment discuss :
       (i)   The parameters that must be known prior to their successful application
       (ii)   How relevant data are usually obtained from their respective
              Curves.   [6]

   (b) For the adiabatic cell of a TT experimental 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   ⇄   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)   Compare and contrast the following :
       (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.
       (iii) Alkali metals (with lower standard potentials) can be reduced more easily than
             H^+ at a DME.
       (iv) A DME is preferred for cathodic reactions during amperometric titrations while
             a Pt electrode is preferred for anodic reactions.   [10]

5

(c)   The iodate ion undergoes the following reaction at the DME

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

When a 1.41 mM solution of KIO_3 in a 0.1 M perchloric acid was
reduced polarographically at a DME with a drop time of 2.18 s 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 0.1 M perchloric acid.   [11]

Question 6 (25 marks)

(a)   (i)   What are the usual functions of a supporting electrolyte during
                polarographic analysis of an ion? Give three examples.   [5]
        (ii)   Why should the concentration of a supporting electrolyte be at least
                1000 – fold that of the analyte ion?   [3]

(b)   Enumerate the sources of residual current during linear scan polarography.   [2]

(c)
        (i)   Discuss briefly how current maxima and oxygen affect polarographic data.
        (ii)   What steps should be taken to minimize their effects during a polarograpic
                analysis.   [8]

(d).   The half-wave potential, $E_{1/2}$, for the uncomplexed reduction of a metal ion, M^{2+}
        on a DME in 0.1 M $NaClO_4$ was -0.74 V. On being complexed with a ligand, L
        with concentration $C_L = 2.0 \times 10^{-4}$ M, the half-wave potential shifted to -0.930 V. If
        both polarograms are reversible and given that the metal –to- ligand ratio of the
        complex is unity, calculate K_f for the complex.   [7]

6