UNIVERSITY OF SWAZILAND

Faculty of Science
Department of Chemistry
First Semester Examination, 2014/15

Title of paper: Thermal and Electroanalytical Methods

Course code: C613

Time allowed: 3 (THREE) HOURS

Instructions:
1) Answer any Four (4) questions
2) Each question is weighted 25 marks
3) Write neatly and clearly
4) A periodic table and other useful data have been provided with this paper.

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

Question 1 (25 marks)

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

(i) Draw a labeled 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 salient features that should be entrenched in its design to achieve these goals. [5]

(c) A 50mg sample of $C_aC_2O_4 \cdot H_2O$ was heated to 1200°C in a thermobalance furnace:

(i) Without being numerically or quantitatively exact, draw a fully labeled diagram of the expected TG curve. [2]

(ii) Show the equations for the decompositional stages involved. [3]

(iii) Calculate the magnitude of all weight losses involved. [5]

Question 2 (25 marks)

(a) With respect to the following features, differentiate between TG (thermogravimetric Analysis), and DTA (Differential Thermal Analysis):

- Their thermograms
- Quantity measured
- Instrument used
- Nature of sample and reference. [4]

(b) Why is atmospheric control 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 24.60 mg sample of $C_aC_2O_4 \cdot H_2O$ was heated from room temperature to 1,100°C at a rate of 5°C/min. The following mass changes with the corresponding temperature ranges were obtained:

Temp Range (°C)	Mass Loss. (mg)
100-250	3.03
400-500	4.72
700-850	7.41

Identify the gas evolved and the solid residue produced at each step of the thermal decomposition. [10]

Question 3 (25 marks)

(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) Distinguish between DTA and DSC with respect to their basic principles and instrumental setup. [3]

(b) Summarize 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 a DSC scan and how are they obtained from the curve/scan? [4]

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

(d) The heat of fusion of naphthalene is 4.63KCal/mole at 80°C. On using 0.100g sample, a DTA peak of $36.3cm^2$ was observed. At 0°C, the heat of fusion of water is 1.43KCal/mole. What is the peak area for 0.100g of ice under similar conditions?

[5]

Question 4 (25 marks)

(a) The evolved gas analysis (EGA) and evolved gas detection (EGD), are often coupled with TG, DTA and DSC.

(i) Briefly describe what is involved in each of these (EGA & EGD) methods.

[2]

(ii) Give three other examples of such hyphenated techniques and one application of any one of them. [2]

(b) For a typical thermometric experiment.

(i) Identify the components (parts) of a basic instrumental set up. [2]

(ii) Draw and label a schematic titration assembly for the TT. (2)

(c) Briefly discuss the temperature control requirements for a Thermometric Titration.

[2]

(d) The Thermistor is considered the ideal temperature sensing system for the TT and DIE. Discuss:

(i) Its nature and operational basis (principles). [3]

(ii) The factors that make it the ideal temperature sensing system for the TT and DIE.

[3]

(e) (i) Use a diagram to show the four major regions of an ideal Thermometric Titration curve. [4]

(ii) During the titration of an acid A with a base B, a curve similar to the one drawn in e(i) above was obtained with the following slopes for the four regions respectively: 1.0×10^{-5}, 8.0×10^{-4}, -1.0×10^{-5} and -0.5×10^{-5} °C/sec. The overall temperature change was 0.1000°C, and the cell's heat capacity is 1.000 Cal/°C.

The titration rate was 6.0×10^{-8} mole/s for B. Also, under similar experimental conditions, the titration of B into distilled water gave a slope of 2.0×10^{-5} °C/sec. Calculate ΔH, the heat of reaction for this titration. [5]

Question 5 (25 marks)

(a) (i) Explain the term: 'cathodic depolarizer'

(ii) Employing a given example, show how it is used during constant voltage electrolysis.

(iii) Discuss its mechanisms of action. [5]

(b) (i) What is a potentiostat? [1]

(ii) Compare and contrast the working principles of a constant voltage electrolysis and controlled potential (constant cathode/anode potential) electrolysis. Which of the two is more selective? Explain how the enhanced selectivity is achieved by this method. [7]

(c) (i) Enumerate the favourable and unfavourable features of potentiometric titration method of analysis. [4]

(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:-

Titration 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

Obtain plots of (i) E and (ii) $\Delta E/\Delta V$, against the titrant volume and determine the end point from each of the two curves. Compare the results and comment on them. [8]

Question 6 (25marks)

(a) Identify the difference/s between:

(i) A limiting current and residual current

(ii) Differential pulse polarography and square wave polarography. (4)

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

(c) Discuss the effects of the following factors on the polarographic shape and data during a DME polarographic experiment:

(i) Current maxima

(ii) Presence of Oxygen

Discuss steps usually taken to minimize their effects. (6)

(d) Discuss the working principles of differential pulse polarography. Account for its enhanced sensitivity over the conventional (d.c.) polarography. (6)

(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 -0.05V. If the diffusion coefficient, $D = 2.12 \times 10^{-5} cm^2s^{-1}$, calculate the oxygen level in the water in:

(i) mM (millimoles/L).

(ii) ppm. (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

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
PERIODS	IA	IIA	IIIB	IVB	VB	VIB	VIIB		VIIIB		IB	IIB	IIIA	IVA	VA	VIA	VIIA
1	1.008 H 1																
2	6.941 Li 3	9.012 Be 4										Atomic mass → Symbol → Atomic No. →	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					TRANSITION ELEMENTS						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							

*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.