

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SWAZILAND

C 404

Electroanalytical Chemistry

May 2005 Final Examination

Time Allowed:

Three (3) Hours

Instructions:

1. This examination has six (6) questions and one data sheet. The total number of pages is four (4) excluding this page.
2. Answer any four (4) questions fully; diagrams should be clear, large and properly labeled. Marks will be deducted for improper units and lack of procedural steps in calculations.
3. Each question is worth 25 marks.

Special Requirements:

1. Data Sheet

YOU ARE NOT SUPPOSED TO OPEN THIS PAPER UNTIL PERMISSION TO DO SO HAS BEEN GIVEN BY THE CHIEF INVIGILATOR.

Some Useful Physical Constants:

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$c = 2.998 \times 10^8 \text{ m sec}^{-1}$$

$$N = 6.02 \times 10^{23}$$

$$k = 1.381 \times 10^{-23} \text{ JK}^{-1}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

Atomic weights: Fe = 55.85; S = 32.06; O = 16.00; H = 1.008; N = 14.01; C = 12.01

QUESTION 1 [25]

- (a) Calculate the input impedance of an electrochemical cell whose measured voltage is 10V allowing 30mA to flow through it [3]
- (b) In potentiometry, potentials are measured relative to the Standard Hydrogen Electrode (SHE) potential.
- Draw the SHE and label all its components [3]
 - Write down the electrochemical equation taking place within the SHE, and state its standard electrode potential [2]
- (c) With regards to the pH glass membrane electrode, describe:
- The structure of the electrode membrane with the aid of diagrams [3]
 - The concept of "selectivity coefficient" using equations to illustrate [3]
- (d) Consider a cell in which one electrode is composed of a cadmium wire dipped in a 0.0167M CdCl₂ solution, and the other composed of a silver wire coated with AgCl and dipped in a 0.0468M KCl solution. Both electrodes are separated by a salt bridge.
- Write down the cell notation assuming the reduction takes place in the Cd half cell. [2]
 - Calculate the potential of the Cd electrode [2]
 - Calculate the potential of the AgCl electrode [2]
 - Calculate the cell potential [2]
 - Would the cell be galvanic as written? Give a reason for your answer [2]
- (e) Calculate the concentration (in ppm) of Cu²⁺ solution in a 25-mL water sample, given that the voltage recorded in a cell made up of a Cu wire dipped in the sample was 0.241 V measured against the SCE, assuming the SCE is the anode [4]

QUESTION 2 [25]

- (a) When reference electrodes are used in potentiometry, electrical contact is made by slow leakage of electrolyte, and this introduces errors to the measured cell potential.
- Use diagrams to explain the origins of this error [3]
 - Comment on the magnitude and direction of this error [2]
 - How is this error eliminated? [1]
- (b) Discuss any four (4) disadvantages of using the pH glass electrode for pH measurements [4]
- (c) The fluoride ion electrode is probably the most selective solid state electrode.
- Draw and label the components of a fluoride ion electrode [3]
 - Write down the Nernst expression relating the measured voltage to the fluoride concentration in a sample measured by the fluoride ion electrode [2]
 - Describe any two (2) disadvantages of fluoride ion electrodes [2]
- (d) Draw and label an electrode suitable for measurements of NH₃. Use chemical equations to explain how it works [4]
- (e) Draw the first and second derivative plots of an indirect potentiometric measurement of a mixture of 3 weak acids [4]

QUESTION 3 [25]

- (a) Describe each of the three modes of mass transport in polarography, indicating if each is desired, and if not, what means are put in place to eliminate it [4]
- (b) Briefly discuss each of the four (4) advantages of performing voltammetry at the dropping mercury electrode [4]
- (c) In polarography, what is meant by
- the anodic limit? [2]
 - the cathodic limit? [2]
- (d) Use equations to describe what sets
- the anodic limit in polarography [2]
 - the cathodic limit in polarography [3]
- (e) Write down the Heyrovsky-Ilkovic equation of polarography and explain all terms appearing in it [3]
- (f) Use the Nernst equation to derive an equation that relates the dependence of the measured current i on the impressed voltage E on the rising portion of a polarographic wave, and show how it can yield values of n and E° [5]

QUESTION 4 [25]

- (a) Modern polarographic methods seek to reduce capacitive current in order to improve the detection limit.
- Define "signal-to-noise ratio" in electroanalytical techniques [2]
 - Define "detection limit" in electroanalytical techniques [2]
 - Define "resolution" in electroanalytical techniques [2]
 - For each of the following modern polarographic techniques, draw the shape of the current-voltage curve, state its detection limit, and state its resolution.
 - classic polarography (DC) [3]
 - differential pulse polarography (DPP) [3]
 - alternating current (AC) polarography [3]
- (b) Describe the principle behind amperometric titrations with one polarized electrode using diagrams to illustrate [4]
- (c) It takes 3.562 min to titrate a sample of Na_2CO_3 coulometrically in an electrolytic cell with electrogenerated hydrogen ions. The generating current is 248.32 mA in a system incorporating Pt electrodes. Assuming that the end point occurs when all CO_3^{2-} has been converted to H_2CO_3 , calculate the weight of Na_2CO_3 in the sample [6]

QUESTION 5 [25]

- (a) Cyclic voltammetry involves the application of a potential to a chemical system in the form of a triangular ramp.
- Write down the Randles-Sevcik equation for cyclic voltammetry, and explain all terms appearing in it [3]
 - Explain the difference between the Randles-Sevcik equation of cyclic voltammetry and the Ilkovic-Heyrovsky equation for polarography [2]
- (b) The cyclic voltammogram of the $\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}^0$ system shows that it is a reversible system.
- Draw the cyclic voltammogram of this system [2]
 - Use the Randles-Sevcik equation to explain the shape of voltammograms obtained for reversible systems [3]
 - Use equations to explain how the observed peak potentials in cyclic voltammetry of reversible systems are related to the polarographic half wave potentials [3]
 - Use equations to explain how the anodic and cathodic peak currents are separated by $57/z$ mV for a reversible system [4]
- (c) The cyclic voltammogram of the N, N-Dimethylaniline oxidation process on a glassy carbon electrode shows that it is an irreversible system.
- Draw the cyclic voltammogram of this system [2]
 - Write down the Randles-Sevcik equation for this irreversible system, and explain all terms appearing in it [3]
 - Use equations to explain how peak potentials in cyclic voltammetry of irreversible systems are dependent on the scan rate [3]

QUESTION 6 [25]

- (a) The measurement of electrical current passing through a solution is a very versatile and accurate analytical method known as coulometry.
- Describe the principle behind constant current coulometry [3]
 - Describe how the constant current coulometric titration of Fe^{3+} would result in a positive error, and how Tl^{4+} used as an intermediate would eliminate this error [4]
- (b) One variant of coulometry is when the potential is kept constant throughout the analysis.
- Use diagrams to describe the principle behind constant potential coulometry [3]
 - Using chemical equations, explain the process that takes place in the constant potential coulometric analysis of Br^- in a solution of bromide salt with Ag at +0.16V vs SCE as the anode, and Pt as the cathode [4]
 - Suppose the OH^- produced in part b(ii) is titrated with 0.0325M HCl after the coulometric reaction with bromide is complete, and that 10.68 mL were required to reach the end point. How much Br^- was in the sample? [3]
- (c) Amperometric titrations can also be conducted on a Rotating Disk Electrode (RDE). With regards to the RDE,
- Use diagrams to describe the hydrodynamic movement of solution in the vicinity of the electrode [3]
 - Explain how detection limits in the RDE are up to an order of magnitude higher as compared to stationary electrodes [2]
 - Write down the Levich equation of the RDE, and describe all the terms appearing in it [3]

1. PERIODIC CHART OF THE ELEMENTS

1												18							
1A 2A												2							
3 4												10							
Li Be												He							
6.941 9.012												4.00260							
11 12		3		4		5		6		7		8		9		17			
Na Mg		3B 4B		5B 6B		7B		8B		9B		10B		11B		12B			
22.98977 24.305		39.0983 40.08		44.9559 47.88		50.9415 51.996		54.9380 55.847		58.932 58.69		63.546 65.38		69.72 72.59		74.9216 78.96		79.904 83.80	
13 14 15 16 17												18							
B C N O F												Ne							
10.81 12.011 14.0067 15.9994 18.9984												20.1797							
19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36												18							
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr												Ar							
39.0983 40.08 44.9559 47.88 50.9415 51.996 54.9380 55.847 58.932 58.69 63.546 65.38 69.72 72.59 74.9216 78.96 79.904 83.80												39.948							
37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54												18							
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe												Ar							
85.4678 87.62 88.9059 91.22 92.9064 95.94 (98) 101.07, 102.9055 106.42 107.8682 (124) 114.82 118.69 121.75 127.60 126.9045 131.29												131.29							
55 56 57 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86												18							
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn												Ar							
132.9055 137.33 138.9055 178.49 180.9479 183.85 186.207 190.2 192.22 195.08 196.9665 200.59 204.383 207.2 208.9804 (209) (210) (223)												223							
87 88 89 104 105 106 107 108 109												18							
Fr Ra Ac Unq Unp Unh Uns Uno Uue												Ar							
(223) 226.0254 227.0279 (281) (282) (283) (284) (285) (286)												223							

A value in brackets denotes the mass number of the longest lived or best known isotope.

4. NET STABILITY CONSTANTS

Ag(CN) ₂ ⁻	5 × 10
Ag(NH ₃) ₂ ⁺	1.6 × 10
Ag(S ₂ O ₃) ₂ ⁻³	4.7 × 10
Al(OH) ₄ ⁻	1.0 × 10
Ca(EDTA)	1.0 × 10
Cd(CN) ₄	8.3 × 10
Cd(NH ₃) ₄ ²⁺	5.5 × 10
Co(NH ₃) ₆ ³⁺	2 × 10
Cr(OH) ₄ ⁻	4 × 10
Cu(CN) ₄ ⁻³	1 × 10
Cu(NH ₃) ₄ ²⁺	1.2 × 10
Fe(CN) ₆ ⁻³	4.0 × 10
Fe(CN) ₆ ⁻⁴	2.5 × 10
Fe(SCN) ₂ ⁺	1.0 × 10
HgCl ₄	1.3 × 10
Hg(CN) ₄	8.3 × 10
Hg(SCN) ₄	5.0 × 10
HgI ₄	6.3 × 10
Mg(EDTA)	1.3 × 10
Ni(NH ₃) ₆ ²⁺	4.7 × 10
Pb(OH) ₃ ⁻	7.9 × 10
Zn(CN) ₄	4.2 × 10
Zn(NH ₃) ₄ ²⁺	7.8 × 10
Zn(OH) ₄ ²⁻	6.3 × 10

★ Lanthanide series

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.9077	144.24	(145)	150.36	151.96	157.25	158.9254	162.50	164.9304	167.26	168.9342	173.04	174.967

▲ Actinide series

90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.0381	231.0359	238.0289	237.0482	(249)	(249)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)

2. IONIZATION CONSTANTS (K_a) FOR WEAK ACIDS

Acetic	1.9 × 10 ⁻⁵	Hypochlorous	3.7 × 10 ⁻⁸
2-Amino-pyridinium Ion	2 × 10 ⁻⁷	H ₂ S	K ₁ 9 × 10 ⁻⁸ K ₂ 1 × 10 ⁻¹⁵
Ammonium Ion	5.6 × 10 ⁻¹⁰	Imidazolium Ion	1.1 × 10 ⁻⁷
Anilinium Ion	2.3 × 10 ⁻⁵	Lactic	1.4 × 10 ⁻⁴
Arsenic	K ₁ 5.6 × 10 ⁻³	Methylammonium Ion	2.7 × 10 ⁻¹¹
Benzoic	K ₁ 6.7 × 10 ⁻⁵	Monoethanol-ammonium Ion	3 × 10 ⁻¹⁰
Boric	K ₁ 5 × 10 ⁻¹⁰	Nicotinium Ion	9.6 × 10 ⁻⁹
Carbonic	K ₁ 4.3 × 10 ⁻⁷ K ₂ 5.6 × 10 ⁻¹¹	Oxalic	K ₁ 6 × 10 ⁻² K ₂ 6 × 10 ⁻⁵
Chloroacetic	K ₁ 1.5 × 10 ⁻³ K ₂ 3.2 × 10 ⁻⁷	Phenol	1.3 × 10 ⁻¹⁰
Chromic	K ₁ 8.7 × 10 ⁻⁴ K ₂ 1.8 × 10 ⁻⁵ K ₃ 4 × 10 ⁻⁶	Phthalic	K ₁ 7.5 × 10 ⁻³ K ₂ 6.2 × 10 ⁻⁸
Citric	K ₁ 8.7 × 10 ⁻⁴ K ₂ 1.8 × 10 ⁻⁵ K ₃ 4 × 10 ⁻⁶	Phosphoric	K ₁ 7.5 × 10 ⁻³ K ₂ 6.2 × 10 ⁻⁸ K ₃ 4.7 × 10 ⁻¹³
Dichloroacetic	5 × 10 ⁻²	Phosphorous	K ₁ 1.0 × 10 ⁻² K ₂ 2.6 × 10 ⁻⁷
EDTA	K ₁ 7 × 10 ⁻³ K ₂ 2 × 10 ⁻³ K ₃ 7 × 10 ⁻⁷ K ₄ 6 × 10 ⁻¹¹	Pyridinium Ion	1 × 10 ⁻⁵
Formic	2 × 10 ⁻⁴	Succinic	K ₁ 7 × 10 ⁻⁵ K ₂ 2.5 × 10 ⁻⁶
α-D(+)-Glucose	5.2 × 10 ⁻¹³	Sulfuric	K ₁ 1.2 × 10 ⁻² K ₂ 2 × 10 ⁻²
Glycinium Ion	K ₁ 4.6 × 10 ⁻³ K ₂ 2.5 × 10 ⁻¹⁰	Sulfurous	K ₁ 2 × 10 ⁻² K ₂ 6 × 10 ⁻⁸
Hydrazinium Ion	5.9 × 10 ⁻⁹	Trimethyl-ammonium Ion	1.6 × 10 ⁻¹⁰
Hydrocyanic	7 × 10 ⁻¹⁰	Uric	1.3 × 10 ⁻⁴
Hydrofluoric	7 × 10 ⁻⁴	Water, K _w , 24°C	1.0 × 10 ⁻¹⁴
Hydroxyl-ammonium Ion	9.1 × 10 ⁻⁷		

3. SOLUBILITY PRODUCT CONSTANTS

AgBr	4 × 10 ⁻¹³	BaC ₂ O ₄	2 × 10 ⁻⁸	KClO ₄	2 × 10 ⁻²
Ag ₂ CO ₃	6 × 10 ⁻¹²	BaSO ₄	1 × 10 ⁻¹⁰	MgCO ₃	1 × 10 ⁻⁵
AgCl	1 × 10 ⁻¹⁰	CaCO ₃	5 × 10 ⁻⁹	MgC ₂ O ₄	9 × 10 ⁻⁵
Ag ₂ CrO ₄	2 × 10 ⁻¹²	CaF ₂	4 × 10 ⁻¹¹	MgNH ₄ PO ₄	2 × 10 ⁻¹³
Ag ₂ [Ag(CN) ₂] ₄	2 × 10 ⁻¹²	CaC ₂ O ₄	2 × 10 ⁻⁹	Mg(OH) ₂	1 × 10 ⁻¹¹
AgI	1 × 10 ⁻¹⁶	CdS	1 × 10 ⁻²⁸	MnS	1 × 10 ⁻¹⁵
Ag ₃ PO ₄	1 × 10 ⁻¹⁹	Cu(OH) ₂	2 × 10 ⁻²⁰	PbCrO ₄	2 × 10 ⁻¹⁴
Ag ₂ S	1 × 10 ⁻⁵⁰	CuS	1 × 10 ⁻³⁶	PbS	1 × 10 ⁻²⁸
AgCNS	1 × 10 ⁻¹²	Fe(OH) ₃	1 × 10 ⁻³⁶	PbSO ₄	2 × 10 ⁻⁸
Al(OH) ₃	2 × 10 ⁻³²	Hg ₂ Br ₂	3 × 10 ⁻²³	SrCrO ₄	4 × 10 ⁻⁵
BaCO ₃	5 × 10 ⁻⁹	Hg ₂ Cl ₂	6 × 10 ⁻¹⁹	Zn(OH) ₂	3.6 × 10 ⁻¹⁶
BaCrO ₄	1 × 10 ⁻¹⁰	HgS	1 × 10 ⁻⁵²	ZnS	1 × 10 ⁻²⁴

5. FIRST IONIZATION ENERGIES, e.v.

1A 2A											14		
5.4 9.3											8.3 11 15 14 17		
5.1 7.6	3B 4B 5B 6B 7B											18 2B	
4.3 6.1 6.6 6.8 6.7 6.8 7.4 7.9 7.9 7.6 7.7 9.4	6.0 8.1 11 10 13											6.0 8.1 10 9.8 12	
4.2 5.7 6.6 7.0 6.8 7.2	7.5 7.7 8.3 7.6 9.0 5.8 7.3 8.6 9.0 10												
3.9 5.2 5.0 6.9	3.5 6 8.0 7.9 8.7 9.2 9.0 9.2 10 4.1 7.4 8												

6. ELECTRONEGATIVITIES, Pauling

1A 2A											21		
1.0 1.5											2.0 2.5 3.0 3.5 4.0		
0.9 1.2	3B 4B 5B 6B 7B											18 2B	
0.8 1.0 1.3 1.5 1.6 1.6 1.5 1.8 1.8 1.8 1.9 1.6 1.8 1.8	1.5 1.8 2.1 2.5 3.0											2.0 2.4 2.8	
0.8 1.0 1.2 1.4 1.6 1.8 1.9 2.2 2.2 2.2 1.9 1.7 1.7 1.8 1.9	2.1 2.5											2.1 2.5	
0.7 0.9 1.1 1.3 1.5 1.7 1.9 2.2 2.2 2.2 2.4 1.9 1.8 1.8 1.9	2.0 2.2											2.0 2.2	

7. ATOMIC RADII picometers

1A 2A											37		
155 112											98 91 92 73 71		
190 160	3B 4B 5B 6B 7B											18 2B	
235 197 182 147 134 130 138 126 125 124 128 138 141 137 139 140 114	143 132 128 127 98											248 215 178 160 148 139 136 134 134 137 144 154 166 162 159 180 133	
267 228 187 167 149 141 137 135 136 139 146 167 171 175 170 176													

8. IONIC RADII pm

Li ⁺	60	Sr ²⁺	113	S ⁻²	184
Na ⁺	95	Ba ²⁺	135	Se ⁻²	198
K ⁺	133	B ³⁺	20	Te ⁻²	221
Rb ⁺	148	Al ³⁺	50	F ⁻	136
Be ²⁺	31	N ³⁺	171	Cl ⁻	181
Mg ²⁺	65	P ³⁺	212	Br ⁻	195
Ca ²⁺	99	O ²⁻	140	I ⁻	216

9. LATTICE ENERGIES

(All negative) kJ/n

	F	Cl	Br	I
Li	1030	840	781	717
Na	914	770	728	671
K	812	701	671	616
Rb	780	682	654	600
Cs	744	630	613	564

10. HALF LIVES

H ³	12.3 years	K ⁴⁰	1.28 × 10 ⁹ y	I ¹³¹	8.1 day
F ²⁰	11.4 secs	Ca ⁴⁵	165 days	Cs ¹³⁷	30 yea
C ¹⁴	5730 years	Fe ⁵⁹	45 days	Au ¹⁹⁸	2.69 da
Na ²⁴	15.0 hours	Co ⁶⁰	5.26 y	Ra ²²⁶	1620 y
P ³²	14.3 days	Br ⁸²	35.5 hours	U ²³⁵	7.1 × 10
S ³⁵	88 days	Sr ⁹⁰	28 years	U ²³⁸	4.51 × 10
Cl ³⁶	3.1 × 10 ⁵ y	I ¹²⁹	1.7 × 10 ⁷ y	Pu ²³⁹	24,400