

**DEPARTMENT OF CHEMISTRY**  
**UNIVERSITY OF SWAZILAND**

**C612**

**SPECTRO CHEMICAL ANALYSIS**

**MAY 2013**

**FINAL EXAMINATION**

**Time Allowed:**

**Three (3) Hours**

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**Instructions:**

- 1. This examination has six (6) questions and one (1) data sheet. The total number of pages is five (5), including 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.**
- 2. Graph paper.**

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

### QUESTION 1 [25]

- a) The Globar is one of the most widely used sources in infra red spectroscopy.
- (i) Give a brief description of the Globar. (1)
  - (ii) Calculate  $\lambda_{\max}$  in  $\text{cm}^{-1}$ , for the Globar heated to 500K, given its Wein's Displacement constant of  $2.9 \times 10^{-3} \text{mK}$ . (2)
  - (iii) Explain why the Globar heated to 500 K is at the ideal temperature for use as an IR source compared to 10,000K. (2)
- b) Infra-red instruments operating in the dispersive mode are widely used for qualitative and semi-quantitative measurements.
- (i) Why in dispersive IR the sample is placed before the monochromator and not after it? (2)
  - (ii) How does quantum mechanics explain the appearance of a fundamental vibration band of HCl at approximately  $1800 \text{ cm}^{-1}$ . (3)
  - (iii) Explain why dispersive IR instruments suffer from poor resolution. (3)
- c) With regard to IR utilizing a Michaelson interferometer,
- (i) Use diagrams to explain how the interferometer works. (4)
  - (ii) Explain the role of the He-Ne laser used in FT-IR. (2)
  - (iii) What is meant by the "Jacquinot Advantage" in FT-IR? (3)
  - (iv) How does quantum mechanics explain the hyperfine appearance of the H-Cl fundamental vibration band, i.e., the equally-spaced lines making up this band being separated by  $10 \text{ cm}^{-1}$ ? (3)

### QUESTION 2 [25]

- a. A typical monochromator using a grating is a rectangular block of glass with 1180 lines etched on every mm of its surface. It is 4.6 cm wide.
- (i) State the Bragg's equation for the grating acting as a monochromator, and calculate the primary angle at which radiation of  $300 \text{ nm}$  is diffracted when it hits the grating. (3)
  - (ii) Calculate the first order resolving power of this grating, and calculate the resolution at  $750 \text{ nm}$ . (3)
- b. Prisms are widely used in uv-visible spectrometers as monochromators. The base length of a prism is typically  $5 \text{ cm}$ , and the prism material has a dispersion of  $2.7 \times 10^{-5}$ .
- (i) State Snell's law for a prism. (1)
  - (ii) Calculate the resolution power of the prism, and the resolution at  $5268 \text{ \AA}$ . (3)
  - (iii) Use diagrams to explain the principle of "Resolution As Limited by the Exit Slit" (2)

- c. Draw the circular type Photo Multiplier Tube (PMT) and explain how it works. (3)
- d. Use the photon counting experiment to demonstrate the nature of a PMT signal. (3)
- e. There are many applications of uv-visible spectroscopy today.
- Describe how uv-visible spectroscopy can be used to determine the dissociation constant,  $K_a$ , for a weak acid HA. (3)
  - Describe the "Jobs Method of Continuous Variation", and explain how it was used to arrive at the conclusion that the stoichiometry of the palladium-Thio Mickler's Ketone complex is 1:1 at low ligand concentrations, and 1:4 at high ligand concentrations. (4)

### QUESTION 3 [25]

- a. (i) Use the molecular orbital diagram of  $\text{CH}_2\text{O}$ , formaldehyde, to explain the origin of the  $n \rightarrow \pi^*$  transition, and explain why it appears as a spectroscopic band. (4)
- (ii) State the difference between "bathochromic" and "hypsochromic" shift in uv-visible spectroscopy. (2)
- b. Use equations to explain why:
- The optical components of spectrometers are always kept in a darkened compartment. (3)
  - uv-visible spectroscopic measurements are always taken at  $\lambda_{\text{max}}$  rather than at shoulders of molecular spectra. (4)
- c. Photodiode arrays (PDA's) are widely used as detectors in uv-visible spectroscopy.
- Use a diagram to explain how a PDA works. (4)
  - What is the major advantage of the PDA over the phototube? (2)
  - Given that the signals from a photodiode array detector are in the form of current, which must be converted to voltage for input into a computer for electronic display, draw the operational amplifier that must be used at this stage of signal processing, and state its output. (3)
  - After computing the voltage ratio from the reference and sample channels in the PDA, and given that the voltage ratio (transmittance) must be converted to absorbance, draw the operational amplifier that must be used at this stage of signal processing, and state its output. (3)

### QUESTION 4 [25]

- a. In the table below,

Spectral Region	Energy (J)	Type of Transition	Wavelength (nm)	Frequency ( $\text{sec}^{-1}$ )	Wavenumber ( $\text{cm}^{-1}$ )	Energy (eV)
gamma rays				$10^{20}$		A
x-ray		B				120
uv-visible			700			
infra-red		D			4,000	
micro-wave			G	$10^8$	F	

- (i) Use a diagram to describe the transition labelled "B". (3)

- (ii) Calculate "A" in MeV. (3)
  - (iii) Use a diagram to describe the transition labelled "D". (3)
  - (iv) Calculate "G" (3)
  - (v) Calculate "F" (1)
- b. Matrix effects are problematic in atomic spectroscopy. For each of the following spectroscopic techniques discuss how matrix effects arise, and state how they can be eliminated in each case.
- (i) ICP-OES (3)
  - (ii) DC Spark (3)
  - (iii) Flame Atomic Absorption Spectroscopy (3)
  - (iv) Electrothermal Vaporization Atomic Absorption Spectroscopy (3)

#### **QUESTION 5 [25]**

- a.
- (i) Use the hydrogen Grotrian diagram and Bohr-Rydberg equation to explain the atomic lines of hydrogen spectra. (3)
  - (ii) Explain why ultrasonic digestion of a biological sample is faster than a conventional digestion. (3)
  - (iii) Use diagrams and equations to show why atomic absorption measurements are most sensitive when carried out using the resonance line of an atom. (3)
  - (iv) Starting with the sample before aspiration, trace the path of Ca in a solution in flame atomic absorption spectroscopy, up until the final number of absorbing atoms per unit volume in a flame. (4)
- b. The DC Arc emission spectroscopic technique is one of the oldest of such techniques, but the mining industry is now seeing its resurgence in metal analysis.
- (i) Discuss the principles of DC Arc emission spectroscopy using a circuit diagram to illustrate. (3)
  - (ii) What are the three (3) main advantages of DC Arc emission spectroscopy over the more recent flame atomic absorption spectroscopy? (3)
  - (iii) Discuss the problem of fractional volatilization in the DC Arc method, and explain how it is overcome. (3)
  - (iv) Fully quantitative DC Arc emission measurements are achieved by means of an internal standard, an old but useful concept for this purpose (Gerlach, *ZAnorg Allem. Chem.*, 142, 383, (1925)). What are the three (3) desirable characteristics of an internal standard, and how are analytes quantified using it? (3)

#### **QUESTION 6 [25]**

- a. The AC Spark electrothermal method is widely used in the steel industry.
- (i) Discuss the principles of AC Spark emission spectroscopy using a circuit diagram to illustrate. (4)
  - (ii) What are the six (6) events that take place in the analytical gap of an AC Spark spectrometer (6)
  - (iii) Discuss any three (3) advantages of AC Spark over DC Arc emission spectroscopy in the determination of Al in steels. (3)

- b. Discuss any three (3) advantages of using a photographic plate as a detector in AC Spark emission over a photomultiplier tube. (3)
- c. The inductively Coupled Plasma (ICP) optical emission is now the widely preferred atomic spectroscopic technique.
- (i) Give a brief description of the ICP as a source of emission signals. (3)
  - (ii) Use a diagram to show why it is possible for the ICP to measure up to 35 elements simultaneously. (3)
  - (iii) How does the "order of magnitude" of the ICP compare with that of the atomic absorption techniques, and what are the implications of this? (3)

1. PERIODIC CHART OF THE ELEMENTS

1 1A 2 2A												13 3A	14 4A	15 5A	16 6A	17 7A	18 8 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.81	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.99840	10 Ne 20.1797
11 Na 22.98977	12 Mg 24.305	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9	10	11 1B	12 2B	13 Al 26.98154	14 Si 28.0855	15 P 30.97376	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.0983	20 Ca 40.08	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9058	40 Zr 91.22	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.42	47 Ag 107.8682	48 Cd (112.4)	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.9045	54 Xe 131.29
55 Cs 132.9055	56 Ba 137.33	57 La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.85	75 Re 186.207	76 Os 196.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.9665	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.9804	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Unq (260)	105 Unp (262)	106 Unh (263)	107 Uns (265)	108 Uno (266)	109 Une (267)	A value in brackets denotes the mass number of the longest lived or best known isotope.								

4. NET STABILITY CONSTANTS

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

★ Lanthanide series  
▲ Actinide series

58 Ce 140.12	59 Pr 140.9077	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.9254	66 Dy 162.50	67 Ho 164.9304	68 Er 167.26	69 Tm 168.9342	70 Yb 173.04	71 Lu 174.967
90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np 237.0482	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

2. IONIZATION CONSTANTS (K<sub>a</sub>) FOR WEAK ACIDS

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

5. FIRST IONIZATION ENERGIES, e.v.

1A	2A											14	15	16	17	18
5.4	9.3											8.3	11	15	14	
5.1	7.6	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	6.0	8.1	11	10	9.8
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	10	9.8	
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	
3.9	5.2	5.9	5.5	6	8.0	7.9	8.7	9.2	9.0	9.2	10	6.1	7.4	8		

6. ELECTRONEGATIVITIES, Pauling

1A	2A											14	15	16	17	18
1.0	1.5											2.0	2.5	3.0	3.5	4.0
0.9	1.2	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	1.5	1.8	2.1	2.5	3.0
0.8	1.0	1.3	1.5	1.6	1.6	1.9	1.8	1.8	1.9	1.6	1.8	1.8	1.8	2.0	2.4	3.0
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	3.0
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	3.0

7. ATOMIC RADII picometers

1A	2A											14	15	16	17	18
155	112											98	91	92	73	71
190	160	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	143	132	128	127	96
235	197	182	147	134	130	135	126	125	124	128	138	141	137	139	140	111
248	216	178	160	146	139	136	134	134	137	144	154	166	162	159	160	133
287	222	187	167	149	141	137	135	136	139	146	157	171	175	170	176	

8. IONIC RADII pm

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

9. LATTICE ENERGY

(All negative) kJ

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

10. HALF LIVES

H <sup>3</sup>	12.3 years	K <sup>40</sup>	1.28 × 10 <sup>9</sup> y	H <sup>31</sup>	8.1 d
F <sup>20</sup>	11.4 secs	Ca <sup>45</sup>	165 days	Cs <sup>137</sup>	30 y
C <sup>14</sup>	5730 years	Fe <sup>59</sup>	45 days	Au <sup>198</sup>	2.69 d
Na <sup>24</sup>	15.0 hours	Co <sup>60</sup>	5.26 y	Ra <sup>226</sup>	1620 y
P <sup>32</sup>	14.3 days	Br <sup>82</sup>	35.5 hours	U <sup>235</sup>	7.1 × 10 <sup>8</sup> y
S <sup>35</sup>	88 days	Sr <sup>90</sup>	28 years	U <sup>238</sup>	4.51 × 10 <sup>9</sup> y
Cl <sup>36</sup>	3.1 × 10 <sup>5</sup> y	I <sup>129</sup>	1.7 × 10 <sup>7</sup> y	Pu <sup>239</sup>	24.4 y

Electrode Potentials, E<sup>0</sup>

H<sup>+</sup> + e<sup>-</sup> ⇌ 1/2 H<sub>2</sub> E<sup>0</sup> = 0.000V

Ca<sup>2+</sup> + 2e<sup>-</sup> ⇌ Ca(s) E<sup>0</sup> = -0.246V

AgCl + e<sup>-</sup> ⇌ Ag(s) + Cl<sup>-</sup> E<sup>0</sup> = -0.023V

Cu<sup>2+</sup> + 2e<sup>-</sup> ⇌ Cu(s) E<sup>0</sup> = 0.34V