DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

C304 **ANALYTICAL CHEMISTRY I I**

DECEMBER 2012 FINAL EXAMINATION

Time Allowed: Three (3) Hours

Instructions:

1. **This examination has six (6) questions and one (1) data sheet. The total number of pages is four (4), 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) Of the many applications of UV-visible spectroscopy, the determination of stoichiometry has been of interest in complexation reactions.

i) Describe the "Molar Ratio Method", and explain how it is used to determine stoichiometry. [4]
ii) Describe the "Jobs Method", and how it is used to determine stoichiometry. [5]

b) The Globar is a useful source of radiation in infrared spectroscopy.

i) Draw a plot of a blackbody radiator as a source of infrared radiation for spectroscopy in terms of energy density vs wavelength at 6000 K, and at 10000 K. [2]
ii) Explain, using the blackbody radiation plot in (i) above, why dispersive IR instruments suffer from poor resolution. [3]

c) One of the applications of GC is the separation of benzene from its mixture with cyclohexane, followed by quantification of the benzene. A typical chromatogram of this mixture in a 2-m long column shows the appearance of peaks as follows:

Air peak (retention time - 0.5 minutes ; peak width - 5 seconds)
Cyclohexane peak (retention time - 1 minute ; peak width - 9 seconds)
Benzene peak (retention time – 1.5 minute ; peak width - 11 seconds)
Toluene peak (retention time – 1.8 minutes ; peak width - 13 seconds)

(i) In the experiment, explain the role of toluene (explain how it serves this role) [2]
(ii) Use the benzene peak in the chromatogram to calculate N; show how this value was obtained [3]
(iii) Are the cyclohexane and benzene peaks properly resolved [3]

d) Bandbroadening is important for peak resolution in HPLC. Use diagrams to explain the phenomenon of "race track effect", how it affects bandbroadening, and how it is eliminated. [3]

Question 2 [25]

a) Nebulization is a very wasteful approach to atomization in atomic spectroscopy.

i) What does the term "nebulization" mean? [1]
ii) Use diagrams to explain how nebulization is carried out in atomic spectroscopy. [3]
iii) Use your answer in (a) ii) above to explain why nebulization is considered inefficient. [2]

b) Atomic spectroscopy is a powerful tool available to the analyst today.

i) Two elements, X and Y are to be analyzed by flame AA and emission. The transition for X is designated $^2S_{1/2} \longrightarrow {}^2P_{3/2}$ and has a wavelength of 852.1 nm. For Y, it is $^1S_0 \longrightarrow {}^1S_1$ at 228 nm. What is the ratio of excited to ground state atoms for each element, if the flame is operated at 2250 ^{0}C [5]
ii) Which of the two elements would be best analyzed by absorption, and why? [2]

c) The stationary phase is a critical component in chromatography.

i) Use diagrams to explain the role of the stationary phase in gas chromatography. [3]
ii) List and discuss any two (2) desirable properties of a stationary phase in gas chromatography. [4]

d) Explain how OV-17 as stationary phase is able to separate methanol from a mixture with its homolog ethanol in gas chromatography [3]

Question 3 [25]

a) For a spectroscopic band occurring at 1685 cm^{-1},

i) convert to energy in joules [2]
ii) state in which region of the electromagnetic spectrum the band falls [1]
iii) state the kind of transition expected in this region [1]

b) (i) Sample cells used for infrared spectroscopy are not made of glass. Explain why, and list 2 typical materials used for this purpose. [3]
(ii) Use a diagram to explain how gas samples are handled in IR spectroscopy [3]
(iii) Use a diagram to explain how the "bolometer" works as a detector in IR spectroscopy. [4]

c) Longitudinal diffusion causes bandbroadening in chromatography.

i) Use a diagram to explain this phenomenon [3]
ii) State the equation that relates longitudinal diffusion to linear velocity in a packed column, an explain all terms appearing in it. [3]

d) A typical GC instrument has several standard components and accessories.

(i) What is the role of a nitrogen gas cylinder normally associated with a GC instrument? [2]
(ii) Draw a soap bubble flow meter and explain how it works in GC [3]

Question 4 [25]

a) In spectroscopy, what is meant by
i) a chromophore (1)
ii) a bathochromic shift (1)

b) In the determination of trace iron in water by spectrophotometry,
i) Explain the role of bipyridine. (1)
ii) Why is a pH=4.5 buffer added? (1)
iii) Why is hydroxylamine hydrochloride added? (1)
iv) Sketch the spectrum expected, and indicate λ_{max} given that the maximum absorption is at 520 nm. (3)

c) i) In liquid chromatography, two solvent reservoirs are usually found. Explain the reason for this. [2]
ii) In gas chromatography, dual columns are often used simultaneously. Explain the reason for this. [2]

d) With the aid of a diagram, briefly but informatively explain how the following detectors work in chromatography:
i) Thermal Conductivity Detector [4]
ii) Flame Ionization Detector [4]

e) Use chemical equations to explain how benzoic acid, which is difficult to be detected by the electron capture method, can be detected after derivatization in gas chromatography. [5]

Question 5 [25]

a) Explain using diagrams, why atomic spectra appear as lines, whereas molecular spectra appear as bands [3]

b) Using appropriate equations, explain why measurements in spectroscopy are best carried out at the "peak" rather than at the "shoulders" of molecular spectra. [4]

c) The cheapest (affordable) uv-visible instruments (typically the *Bosch and Laumb Spectronic 20* series) use the "Bunsen" arrangement of the optical components.

(i) By means of a diagram, explain what is meant by this arrangement. [3]

(ii) Explain how this arrangement enables light from the source to be split into individual wavelengths. [3]

d) Fully explain the meaning of the expression "chromatography is a semi-batch, differential migration, phase distribution technique". [3]

e) Discuss each of any two (2) desirable properties of a solid support for gas chromatography, and explain how each property relates to the Van Deempter equation. [4]

f) Describe each of the two ways of performing elution in Liquid Chromatography, and explain why one would prefer elution in each case. [5]

Question 6 [25]

a) Given the following uv-visible spectroscopy data:

	blank	2 ppm	4 ppm	6 ppm	Unknown
I	A	3276	2070	1305	3050
I_0	5200	5200	5200	5200	5200

(i) What is meant by a "blank", and why is it used in instrumental analysis? (2)
(ii) State the value of "A" (1)
(iii) Plot the calibration curve. (2)
(iv) What is the concentration of the unknown in ppm? (1)

b) i) Explain how a tear drop-shaped plasma is formed in ICP-OES, and explain why it is not analytically useful. [3]
ii) With respect to the doughnut-shaped plasma in ICP-OES, given an estimate of the following operational parameters.

Temperature [1] Frequency [1] Power [1]

iii) Explain how ICP reigns supreme over flame or graphite furnace atomization in atomic spectroscopy in terms of linear dynamic range. [2]

c) Write down the equation for Gaussian peaks in liquid chromatography, explain all terms appearing in it, and explain the analytical significance of its integral. [5]

d) Describe the solid support "Chromosorb W – AW - DMCS" that is widely used in gas chromatography. [6]

PERIODIC TABLE OF 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								

Atomic mass → 10.811; Symbol → B; Atomic No. → 5

TRANSITION ELEMENTS

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.

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	$1.380\,66 \times 10^{-23}\ \mathrm{J\ K^{-1}}$
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	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}\ \mathrm{J\ T^{-1}}$
Electron g value	g_e	$2.002\,32$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e$	$5.291\,77 \times 10^{-11}\ \mathrm{m}$
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}