

**DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SWAZILAND**

C304

ANALYTICAL CHEMISTRY I

DECEMBER 2008 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 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 stationary phase is a critical component in chromatography.
- Explain the role of the stationary phase in gas chromatography. [1]
 - List and discuss any two (2) desirable properties of a stationary phase in gas chromatography. [2]
 - Explain how OV-17 as stationary phase is able to separate methanol from a mixture with its homolog ethanol in gas chromatography [3]
- b. State Beer's Law as applied to spectroscopy, and explain all terms appearing in it. [2]
- c.
- What is meant by "stray light" in spectroscopy? [1]
 - Use equations to explain why stray light leads to negative deviations from Beer's Law [3]
 - How is stray light eliminated in spectroscopy? [1]
- d. Draw a schematic diagram of a Ge(Li) detector, connect it to an electrical circuit, and show how the voltage measured is directly related to intensity of uv-visible radiation in a spectrometer. [4]
- e. Draw and label a vacuum phototube and explain how it works. [3]
- f. Draw and label the "PMT", explain how it works, and explain its advantage over other detectors used in uv-visible spectrometers. [5]

QUESTION 2 [25]

- a.
- State Snell's Law and explain all terms appearing in it. [2]
 - Draw and label the "Bunsen" arrangement of optical components in a spectrometer. [2]
 - Use equations to explain how the prism is able to act as a monochromator in spectroscopy. [2]
- b.
- Draw and label the Czerny-Turner arrangement of optical components in an infra-red spectrometer. [3]
 - Explain why a sample of Cl_2 does not show IR bands yet HCl does in infra-red spectroscopy [2]
 - Give two (2) reasons why sample placement relative to the monochromator in infra-red spectroscopy is different from UV-visible spectroscopy. [4]
 - Use the black body radiation theory to explain how slit width affects resolution in infra-red spectroscopy. [2]
- c.
- In gas chromatography, the injector temperature is always kept independent of column temperature. Explain why. [2]
 - Explain the role and importance of an internal standard in gas chromatography. [2]
 - Use diagrams to explain the concept of longitudinal diffusion in chromatography, and use equations to explain why it is so much pronounced in GC as opposed to LC. [4]

QUESTION 3 [25]

(a) Spectroscopy is based on the interaction of electromagnetic radiation with atoms and molecules, and spectroscopical techniques are classified according to the spectral range involved. In the table below:

Spectral Region	Energy (J)	Type of Transition	Wavelength (km)	Frequency (Hz)	Wavenumber (cm ⁻¹)	Energy (eV)
Acoustic	F	A	15			
Radio frequency		B	1	G		
uv-visible		C				
infra-red					4,000	H

i). State A, B, C [3]

ii. Calculate F, G, H [3]

b. For the molecule CO, carbon monoxide, its UV and UV-visible spectra are attributed to "outer electron" transitions its molecular orbitals. In regard to this,

i). Draw the molecular energy level diagram showing these orbitals [2]

ii). Show how a $\sigma \rightarrow \sigma^*$ transition takes place when the molecule absorbs radiation. [1]

iii). Show how an $n \rightarrow \pi^*$ transition takes place when the molecule absorbs radiation. [1]

iv). Of the transitions in iii and iv above, λ_{max} is observed at 350nm and 780nm. Assign these wavelengths to each of the two transitions. [2]

v). Use diagrams to explain how the $\sigma \rightarrow \sigma^*$ transition would result in an absorption band rather than a single line. [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. i). Use a diagram to explain the concept of eddy diffusion in chromatography. [3]

ii). State the HETP equation for eddy diffusion in chromatography. [2]

QUESTION 4 [25]

(a) The colour observed when samples absorb electromagnetic radiation in the uv-visible range depends on the colour observed. In the table below:

λ_{max} (nm)	Colour absorbed	Colour observed
380-420	Violet	K
500-520	L	Purple
580-620	Orange	M

state K, L, M [3]

c. The following calibration data was obtained in an experiment to measure trace iron in water using spectroscopy following complexation with bipyridine.

Concentration (ppm)	0	2.05	3.99	6.01	7.98
Absorbance	0	0.125	0.250	0.374	0.499

- i) A 50ml of tap water diluted to 150ml gave an absorbance reading of 0.283. Calculate the concentration in $\mu\text{g/mL}$ of iron in the tap water. [4]
 - ii) Calculate the molar absorptivity of the complex given that the cell was 1.11 cm thick. [2]
- d. i) Draw the Van Deemter plot for gas chromatography, and on it indicate the optimum linear velocity [4]
- ii). Explain the difference between the Van Deemter plot for GC from that of LC [1]
- e. i) Use diagrams to explain how the thermal conductivity detector works in GC [4]
- ii). Use diagrams to explain how the flame ionization detector works in GC. [4]
- iii). The thermal conductivity detector is touted as a universal detector in GC as compared to the flame ionization detector. Use chemical equations to support this statement. [3]

QUESTION 5 [25]

- a. Explain the phenomenon of "atmospheric absorptions" in infra-red spectroscopy, how it causes spectral interference, and how it is eliminated. [3]
- b. Draw and label a "bolometer" used for detecting radiation intensity in infra-red spectroscopy. Explain how it works. [5]
- c. Infra-red spectroscopy is not normally used for quantitative analyses, yet it does detect organic compounds, which can be successfully measured by chromatographic techniques.
 - i). What is meant by gradient elution in chromatography, and under what circumstances is it preferred over isocratic elution? [3]
 - ii). State the HETP equation for resistance to mass transfer in the mobile phase in gas chromatography [3]
 - iii) Describe the experimental parameters that can be practically controlled to reduce bandbroadening due to resistance to mass transfer in the mobile phase in gas chromatography. [3]
- d. Use diagrams to describe the electron capture detector, and explain how it works in gas chromatography. [4]
- e. Use chemical equations to explain how benzoic acid, which can not be detected by the electron capture method, can be detected after derivatization in gas chromatography. [4]

QUESTION 6 [25]

- a. State the Maxwell Boltzman equation, and explain how it is used to determine whether atomic emission or atomic absorption can be used in a measurement during trace elemental analysis. [3]
- b. Use diagrams to explain why broadband sources cannot be used in atomic absorption instruments. [3]
- c. i). Draw a cross section of an air-acetylene flame. [3]
- ii). Explain how a tear drop-shaped plasma is formed in ICP-OES, and explain why it is not analytically useful. [3]
- d. With respect to the doughnut-shaped plasma in ICP-OES, given an estimate of the following operational parameters.
- | Temperature [1] | Frequency [1] | Power [1] |
|-----------------|---------------|-----------|
|-----------------|---------------|-----------|
- e. Explain how ICP reigns superior over flame or electrothermal atomization in atomic spectroscopy in terms of linear dynamic range. [2]
- f. No matter what GFAAS or ICP can offer to elemental analysis in terms of extraordinary detection limits, chromatography still remains the supreme technique for separation and subsequent detection of organic analytes in a mixture.
- i). State the equation describing efficiency of a separation column in chromatography as a function of retention time and bandbroadening as solutes elute through a column. [2]
- ii). State the equation describing resolution of two adjacent peaks as a function of retention time and bandbroadening as solutes elute through a column. [2]
- iii). Use diagrams to explain how the detection of para- and ortho- anilines in ink is possible in HPLC using a flow through cell [4].

Color	pH range	pK _{in}	Acid	Base
blue	1.2-2.8	1.6	red	yellow
yellow	2.9-4.0	3.3	red	yellow
Orange	3.1-4.4	4.2	red	yellow
Chromocresol green	3.8-5.4	4.7	yellow	blue
Methyl red	4.2-6.2	5.0	red	yellow
Chlorophenol red	4.8-6.4	6.0	yellow	red
Thymol blue	6.0-7.6	7.1	yellow	blue
Enol red	6.4-8.0	7.4	yellow	red
Resol purple	7.4-9.0	8.3	yellow	purple
Thymol blue	8.0-9.6	8.9	yellow	blue
Phenolphthalein	8.0-9.8	9.7	colorless	red
Thymolphthalein	9.3-10.5	9.9	colorless	blue

n	Q ₉₀	n	Q ₉₀	n	Q ₉₀
3	0.94	6	0.56	9	0.44
4	0.76	7	0.51	10	0.41
5	0.64	8	0.47		

15. Bond Enthalpies						
kJ mol ⁻¹ at 25°C (i.e. Bond Energies)						
Single	O	N	C	S	F	Cl
H	463	391	413	368	563	432
C	358	305	346	272	489	328
N	222	163	MISC.	275	192	
S-S	251	H-H	436	C=C	615	
S-F	327	N=N	946	C≡C	812	
S-Cl	271	N=O	607	C=O	749	

D.F.	t ₅₀	t ₅₀	t ₅₅	t ₆₀
1	1.0	6.3	13	64
2	0.82	2.9	4.3	9.
3	0.76	2.35	3.2	5.
4	0.74	2.10	2.8	4.
5	0.73	2.02	2.57	4.
6	0.72	1.94	2.5	3.
7	0.71	1.90	2.36	3.
8	0.71	1.86	2.31	3.
9	0.70	1.83	2.26	3.
10	0.70	1.81	2.23	3.
20	0.69	1.72	2.09	2.
30	0.68	1.70	2.04	2.
∞	0.67	1.64	1.96	2.

12. ELECTRODE POTENTIALS, E°

Li ⁺ + e ⇌ Li	-2.713
Mg ²⁺ + 2e ⇌ Mg	-2.37
Al ³⁺ + 3e ⇌ Al	-1.66
Zn ²⁺ + 2e ⇌ Zn	-0.763
Fe ²⁺ + 2e ⇌ Fe	-0.44
Cd ²⁺ + 2e ⇌ Cd	-0.403
Cr ³⁺ + e ⇌ Cr ²⁺	-0.38
Tl ⁺ + e ⇌ Tl	-0.336
V ³⁺ + e ⇌ V ²⁺	-0.255
Sb ³⁺ + 2e ⇌ Sb	-0.14
Pb ²⁺ + 2e ⇌ Pb	-0.126
H ₂ + 2e ⇌ 2H ⁻	0.000
O ₂ + 2e ⇌ 2O ²⁻	0.09
O ²⁺ + 2H ⁺ + e ⇌ Ti ³⁺ + H ₂ O	0.10
2H ⁺ + 2e ⇌ H ₂ S	0.14
Sn ⁴⁺ + 2e ⇌ Sn ²⁺	0.14
Cu ²⁺ + e ⇌ Cu ⁺	0.17
O ₄ + 4H ⁺ + 2e ⇌ H ₂ O + H ₂ SO ₄	0.17
AgCl + e ⇌ Cl ⁻ + Ag	0.222
Saturated calomel	(0.244)
Hg ₂ Cl ₂ + 2e ⇌ 2Cl ⁻ + 2Hg	0.268
Bi ³⁺ + 3e ⇌ Bi	0.293
O ₂ + 4H ⁺ + 2e ⇌ U ⁴⁺ + 2H ₂ O	0.33
O ²⁺ + 2H ⁺ + e ⇌ V ³⁺ + H ₂ O	0.34
Cu ²⁺ + 2e ⇌ Cu	0.34
Fe(CN) ₆ ³⁻ + e ⇌ Fe(CN) ₆ ⁴⁻	0.355
Cu ⁺ + e ⇌ Cu	0.52
I ⁻ + 2e ⇌ 3I ⁻	0.545
AsO ₄ ³⁻ + 2H ⁺ + 2e ⇌ AsO ₃ ³⁻ + H ₂ O	0.56
I ₂ + 2e ⇌ 2I ⁻	0.621
HgCl ₂ + 2e ⇌ Hg ₂ Cl ₂ + 2Cl ⁻	0.63
O ₂ + 2H ⁺ + 2e ⇌ H ₂ O ₂	0.69
Quinone + 2H ⁺ + 2e ⇌ Hydroquinone	0.70
Fe ³⁺ + e ⇌ Fe ²⁺	0.771
Hg ₂ ²⁺ + 2e ⇌ 2Hg	0.792
Ag ⁺ + e ⇌ Ag	0.799
Hg ²⁺ + 2e ⇌ Hg	0.851
Hg ₂ ²⁺ + 2e ⇌ Hg ₂ ⁺	0.907
NO ₃ ⁻ + 3H ⁺ + 2e ⇌ HNO ₂ + H ₂ O	0.94
HNO ₂ + H ⁺ + e ⇌ NO + H ₂ O	0.98
VO ₂ ⁺ + 2H ⁺ + e ⇌ VO ²⁺ + H ₂ O	0.999
3Br ₂ + 2e ⇌ 2Br ⁻	1.08
IO ₃ ⁻ + 12H ⁺ + 10e ⇌ 6H ₂ O + I ₂	1.19
O ₂ + 4H ⁺ + 4e ⇌ 2H ₂ O	1.229
MnO ₂ + 4H ⁺ + 2e ⇌ Mn ²⁺ + 2H ₂ O	1.23
Cr ₂ O ₇ ²⁻ + 14H ⁺ + 6e ⇌ 7H ₂ O + 2Cr ³⁺	1.33
Cl ₂ + 2e ⇌ 2Cl ⁻	1.358
BrO ₃ ⁻ + 12H ⁺ + 10e ⇌ 6H ₂ O + Br ₂	1.50
MnO ₄ ⁻ + 8H ⁺ + 5e ⇌ 4H ₂ O + Mn ²⁺	1.51
Ce ⁴⁺ + e ⇌ Ce ³⁺	1.61

13. MEAN ACTIVITY COEFFICIENTS

M	KCl	Na ₂ SO ₄	ZnSO ₄
0.001	0.965	0.89	0.70
0.01	0.901	0.72	0.39
0.1	0.769	0.45	0.15

16. HEATS OF FORMATION

ΔH° in kJ mol⁻¹ at 25°C
All ions in H₂O solution except as noted
All Elements = 0

H ₂	218	H ⁺	0.0	H ₂ O _g	-242
O ₂	249	Na ⁺	-240	H ₂ O _l	-286
C _g	717	Ag ⁺	106	CO _g	-111
N ₂	473	NH ₄ ⁺	-133	CO _{2g}	-394
F ₂	79	OH ⁻	-230	NH _{3g}	-46
Cl ₂	122	F ⁻	-333	NO _g	90
Br ₂	112	Cl ⁻	-167	NO _{2g}	33
I ₂	107	Br ⁻	-122	N ₂ O _{4g}	9
S ₈	279	I ⁻	-55	SO _{2g}	-297
P ₄	315	S=	33	SO _{3g}	-396
Na ₂	107	SO ₄ ²⁻	-909	H ₂ S _g	-21
K ₂	88	CO ₃ ²⁻	-677	NaF _s	-574
Na ⁺	609	HF _s	-271	NaCl _s	-411
K ⁺	514	HCl _s	-92	KF _s	-567
F ₂	-255	HBr _s	-36	KCl _s	-437
Cl ₂	-233	HI _s	26	AgCl _s	-127
CH _{4g}	-75	HCN _g	135	AgBr _s	-100
C ₂ H _{2g}	227	PH _{3g}	5	PCl _{3g}	-287
C ₂ H _{4g}	52	C ₆ H _{6l}	49	PCl _{5g}	-375
C ₂ H _{6g}	-85	CH ₃ OH _l	-238		
C ₃ H _{8g}	-105	C ₂ H ₅ OH _l	-235		
nC ₄ H _{10g}	-127	C ₂ H ₅ OH _g	-278		
nC ₈ H _{18g}	-209	COCl _{2g}	-219		
CCl _{4l}	-135	CH ₂ Cl _{2l}	-81		

17. ABS. ENTROPY S°

J mol⁻¹ K⁻¹ at 25°C

H _{2g}	131	P _{4wh}	164	SF _{6g}	292
N _{2g}	192	HF _g	174	NO _g	211
O _{2g}	205	HCl _g	187	NO _{2g}	240
Cl _{2g}	223	H ₂ O _g	189	N ₂ O _{4g}	304
F _{2g}	203	CO _g	198	NH _{3g}	192
Cgra	5.7	CO _{2g}	214	PCl _{3g}	312
S _{8r}	254	SO _{2g}	248	PCl _{5g}	365
CH _{4g}	186	SO _{3g}	256	BF _{3g}	254
C ₂ H _{6g}	229	CH ₃ OH _l	127		
C ₃ H _{8g}	270	C ₂ H ₅ OH _l	283		
C ₂ H _{2g}	201	C ₂ H ₅ OH _g	161		
C ₂ H _{4g}	219	(CH ₃) ₂ O _g	266		
C ₆ H _{6g}	269	CH ₃ COOH _l	282		

18. ΔG° FORMATION

kJ mol⁻¹ at 25°C

H ₂	203	HF _s	-273	H ₂ O _g	-229
F ₂	62	HCl _s	-95	H ₂ O _l	-237
Cl ₂	106	HBr _s	-54	SO _{2g}	-300
O ₂	232	HI _s	1.7	SO _{3g}	-371
NO _g	87	NH _{3g}	-16	PCl _{3g}	-268
NO _{2g}	51	CO _g	-137	PCl _{5g}	-305
N ₂ O _{4g}	98	CO _{2g}	-394	CH _{4g}	-51
C ₂ H _{4g}	68	C ₂ H _{2g}	209	C ₂ H _{6g}	-33
C ₆ H _{6l}	125	CH ₃ OH _l	-162		
CCl _{4l}	-65	C ₂ H ₅ OH _l	-175		
BF _{3g}	-1120	CHCl _{3g}	-70		
SF _{6g}	-1105	CH ₃ COOH _l	-374		

20. CONC. ACIDS AND BAS.

	M.W.	Density	Wt. %	Mol. ity
Acetic	60.05	1.05	99.5	1'
H ₂ SO ₄	98.07	1.83	94	1'
HF	20.01	1.14	45	2.
HCl	36.46	1.19	38	1'
HBr	80.91	1.52	48	
HNO ₃	63.01	1.41	69	1
HClO ₄	100.46	1.67	70	1
H ₃ PO ₄	98.00	1.69	85	1
NaOH	40.00	1.53	50	1
NH ₃	17.03	0.90	28	1

21. DENSITIES (g cm⁻³)

Water at	Air (70 cm)	0.00	
0°C	0.9168	Glass	2.7
10°	0.9997	Na ₂ CO ₃	2.5
20°	0.9982	NaCl	2.2
22°	0.9978	BaSO ₄	4.5
24°	0.9973	AgCl	5.6
26°	0.9968	Aluminum	2.7
28°	0.9963	Iron	7.9
30°	0.9956	Brass	8.4
90°	0.9653	Mercury	13.6
100°	0.0006	Platinum	21.4

22. MOBILITIES (m²V⁻¹s⁻¹ × 10⁴)

Li ⁺	39	H ₃ O ⁺	350	1/2 Ba ²⁺
Na ⁺	50	NH ₄ ⁺	73	1/3 La ³⁺
K ⁺	74	Ag ⁺	62	1/2 SO ₄ ²⁻
Cl ⁻	76	OH ⁻	198	1/2 PO ₄ ³⁻
Br ⁻	78	I ⁻	77	NO ₃ ⁻

23. WATER V.P. (torr)

0°C	4.5	25°	
15°	12.8	30°	
20°	17.5	50°	

24. MISCELLANEOUS

Std. dev. = $\sqrt{\sum(X_i - \bar{X})^2 / (n-1)}$
 Conf. limits = $\bar{X} \pm t_s \cdot \sqrt{n}$
 $E = E^\ominus - (0.0592/n) \log([Red]/[Ox])$
 $\log I_1 I_2 = abc = A = \log 1/T$
 $\log N_T = \log N_0 - 0.301T/T$
 $x = (-b \pm \sqrt{b^2 - 4ac})/2a$
 $n\lambda = 2d \sin \theta$
 $2.303 \log_{10} a = \log_e a$
 $h = 6.626 \times 10^{-34} \text{ J s}$
 $e = 1.602 \times 10^{-19} \text{ C}$
 $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
 $F = 96487 \text{ C}$
 $g = 9.807 \text{ m s}^{-2}$
 $c = 2.998 \times 10^8 \text{ m s}^{-1}$
 $1 \text{ amu} = 1.661 \times 10^{-27} \text{ kg}$
 $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$
 $= 0.08206 \text{ litre atm mol}^{-1} \text{ K}^{-1}$
 $= 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
 $= 8.314 \text{ kPa dm}^3 \text{ mol}^{-1} \text{ K}^{-1}$
 $0^\circ \text{C} = 273.15 \text{ K}$
 $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$
 $1 \text{ cal} = 4.1840 \text{ J}$