

**DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF SWAZILAND**

C304

ANALYTICAL CHEMISTRY I I

JULY 2014 SUPPLEMENTARY 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) State Beer's Law as applied to spectroscopy, and explain all terms appearing in it. [2]
- b) i) What is meant by "stray light" in spectroscopy? [1]  
ii) Use equations to explain why stray light leads to negative deviations from Beer's Law [3]  
iii) How is stray light eliminated in spectroscopy? [1]
- c) Draw a schematic diagram of a Ge(Li) detector, and use diagrams to show how the voltage measured is directly related to intensity of uv-visible radiation in a spectrometer. [4]
- d) Draw and label a vacuum phototube and explain how it works. [3]
- e) A typical GC instrument has several standard components and accessories.  
(i) What is the role of the nitrogen gas cylinder normally associated with a gas chromatograph? [2]  
(ii) What is the role of the filter cartridge normally associated with a gas chromatograph? [3]  
(iii) Use a diagram to show how a soap bubble flow meter works. [3]  
(iv) Explain why columns are installed in an oven in GC but not in LC [3]

**QUESTION 2 [25]**

- a) Use diagrams to explain why atomic spectra appear as lines, whereas molecular spectra appear as bands [4]
- b) Draw and label the "PMT", explain how it works, and explain its advantage over other detectors used in uv-visible spectrometers. [4]
- c) The mobile phase is a critical component in chromatography.  
i) List and discuss any two (2) desirable properties of a mobile phase in gas chromatography. [2]  
ii) Use equations to explain how silanol groups are deactivated in chromatography [4]
- d) i) Use equations to explain what is meant by Reverse Phase Bonded Phase Chromatography [4]  
ii) Discuss the main advantage that bonded phase chromatography has over non-bonded phase chromatography [2]  
iii) Use diagrams to show how a flow through uv-detector works for HPLC [5]

**Question 3 [25]**

- a) Nebulization in atomic spectroscopy is considered inefficient.  
i) What is meant by nebulization? [1]  
ii) Use diagrams to explain how a cross flow nebulizer works. [3]  
iii) Why is nebulization using the nebulizer in a (ii) above inefficient? [2]
- b) A major breakthrough in atomic absorption spectrophotometry since the invention of the hollow cathode lamp was graphite furnace AA.  
(i) What is the major structural difference between flame AA and graphite furnace AA? Use diagrams to support your answer [3]

- (ii) Identify the physical stages involved in a furnace program and describe the processes that occur during each stage. At what stage is the signal sampled, and why? [4]
- (iii) Outline three (3) advantages of graphite furnace AA over flame AA [3]

c) The solid support is an important component of an HPLC instrument.

- i) What is the function of the solid support in HPLC? [2]
- ii) Describe the solid support Chromosorb P -AW in HPLC [3]
- iii) List and describe two desirable properties of a solid support in HPLC [4]

#### **Question 4 [25]**

a) Prisms are used as monochromators in spectroscopy.

- i) Draw the prism [1]
- ii) Use equations to explain how the prism works [3]
- iii) Draw and label the Bunsen arrangement of optical components in a spectrometer [3]

b) Gratings have a very good resolving power in spectroscopy.

- i) Physically how does a grating look like [2]
- ii) Use equations to explain how a grating works [3]
- iii) Calculate the second order resolving power of a grating which is 5cm long with 1180 lines per mm [3]

c) Chromatography is a very useful technique for the determination of alcohols in a sample.

- i) Explain how ethanol and methanol interact with OV-17 stationary phase in GC to effect to their separation [3]
- ii) Use equations to explain how benzoic acid can be detected in an electron capture detector (ECD) after derivatization [3]
- iii) Use diagrams to explain how an ECD works [4]

#### **Question 5 [25]**

a) Inductively Coupled Plasma (ICP) Optical Emission Spectroscopy is the most widely used atomic spectroscopy today.

- i) What is the operational definition of the inductively coupled plasma [2]
- ii) Draw the ICP torch and label its components [4]
- iii) Use a diagram to explain why it is possible to measure up to 35 elements simultaneously using ICP [3]

b) i) In liquid chromatography, two solvent reservoirs are usually used. Explain the reason for this. [2]

ii) In gas chromatography, dual columns are often used simultaneously. Explain the reason for this. [2]

c) One of the applications of GC is the separation of benzene from its mixture with cyclohexane, followed by quantification of the benzene.

- (i) In GC, what is meant by lateral diffusion? [3]

- (ii) State the equation that relates resistance to mass transfer in the mobile phase to linear velocity [3]  
iv) In GC, what is meant by resistance to mass transfer in the stationary phase? [3]  
(iv) State the equation that relates resistance to mass flow in the stationary phase to linear velocity [3]

**Question 6 [25]**

- a) Of the many applications of UV-visible spectroscopy, the determination of mixtures is of considerable interest. Use equations to explain how this is achieved [4]
- b) The Nernst Glower is a useful source of radiation in infrared spectroscopy.
- Describe the Nernst Glower as used in IR spectroscopy. [1]
  - Which of the molecules oxygen and hydrogen chloride is IR active and why? [2]
  - Why is it not possible to carry out quantitative analyses on dispersive IR? [2]
- c) Nebulization is a very wasteful approach to atomization.
- What does the term “nebulization” mean? [1]
  - Use diagrams to explain how nebulization is carried out in atomic spectroscopy. [3]
  - Use your answer in (a) ii above to explain why nebulization is considered inefficient. [2]
- d) Bandbroadening is important for peak resolution in HPLC.
- Use a drawing to explain the importance of linear velocity on HETP [3]
  - On this drawing, indicate the optimum linear velocity [2]
  - Use diagrams to explain the phenomenon of “race track effect”, how it affects bandbroadening, and how it is eliminated. [5]

11. ACID-BASE INDICATORS AT 25°C

Table with columns: Indicator, pH range, pKin, Acid, Base. Lists indicators like thymol blue, methyl yellow, methyl orange, etc.

14. DATA REJECTION—Q TABLE

Table with columns: n, Q90. Values for n=3, 4, 5 and corresponding Q90 values.

19. t TABLE

Table with columns: D.F., t50, t90, t95, t99. Values for D.F. from 1 to infinity.

15. Bond Enthalpies

Table showing bond energies in kJ mol⁻¹ at 25°C for single, double, and triple bonds of O, N, C, S, F, Cl.

12. ELECTRODE POTENTIALS, E°

Large table of electrode potentials for various half-reactions, including Na, Mg, Al, Zn, Fe, Cd, Cr, Tl, V, Sn, Pb, H2, O2, S, SO2, Ag, Bi, U, V, Cu, Fe, Hg, Br, Mn, Cr, Cl, Br, Mn, Ce.

16. HEATS OF FORMATION

Table of heats of formation in kJ mol⁻¹ at 25°C for various elements and compounds like H2, O2, Na+, H2O, CO2, NH3, HCl, HBr, AgCl, HCN, H2S, H2SO4, HClO4, HNO3, H3PO4, NaOH, NH3.

20. CONC. ACIDS AND BASES

Table listing molecular weight, density, weight percentage, and molarity for acids and bases like Acetic, H2SO4, HF, HCl, HBr, HNO3, HClO4, H3PO4, NaOH, NH3.

21. DENSITIES (g cm⁻³)

Table of densities for water and air at various temperatures, and for common salts like Na2CO3, NaCl, BaSO4, AgCl, Al, Fe, Brass, Hg, Pt.

22. MOBILITIES (m² v⁻¹ s⁻¹ x 10⁹)

Table of ionic mobilities for Li+, Na+, K+, Cl-, Br-, H3O+, NH4+, OH-, Ba2+, La3+, SO4=, PO4=3-, NO3-.

23. WATER V.P. (torr)

Table of vapor pressures of water at 0°C, 15°C, and 20°C.

24. MISCELLANEOUS

Mathematical formulas for standard deviation, confidence limits, E° calculation, log Li+/I- = abc = A = log 1/T, x = (-b ± √(b² - 4ac))/2a, nλ = 2d sin θ, 2.303 log10 a = loge a, h = 6.626 x 10⁻³⁴ J s, e = 1.602 x 10⁻¹⁹ C, NA = 6.022 x 10²³ mol⁻¹, F = 96487 C, g = 9.807 m s⁻², c = 2.998 x 10⁸ m s⁻¹, 1 amu = 1.661 x 10⁻²⁷ kg, R = 1.987 cal mol⁻¹ K⁻¹ = 0.08206 litre atm mol⁻¹ K⁻¹ = 8.314 J mol⁻¹ K⁻¹ = 8.314 kPa dm³ mol⁻¹ K⁻¹, 0°C = 273.15 K, 1 eV = 1.602 x 10⁻¹⁹ J, 1 cal = 4.1840 J, 760 torr = 101.3 kPa.

13. MEAN ACTIVITY COEFFICIENTS

Table of mean activity coefficients for M, KCl, Na2SO4, ZnSO4 at various concentrations (0.001, 0.01, 0.1, 1.0).

17. ABS. ENTROPY S°

Table of absolute entropies in J mol⁻¹ K⁻¹ at 25°C for various gases and liquids like H2, N2, O2, Cl2, F2, Cgra, Sgr, CH4, C2H2, C2H4, C2H6, C3H8, C4H10, C4H8, C6H6, C6H12, P4, HF, HCl, H2O, CO, CO2, SO2, SO3, NH3, CH3OH, C2H5OH, C2H5OH, (CH3)2O, CH3COOH, SF6.

18. ΔG° FORMATION

Table of standard Gibbs free energies of formation in kJ mol⁻¹ at 25°C for various compounds like HF, HCl, HBr, HI, NH3, CO, CO2, C2H2, C2H4, C2H6, C3H8, C4H10, C4H8, C6H6, C6H12, CCl4, BF3, SF6, NH4Cl, H2O, H2O, SO2, SO3, CH3OH, C2H5OH, (CH3)2O, CH3COOH, (CH3)2O.

1. PERIODIC CHART OF THE ELEMENTS

Periodic table showing elements 1-118 with atomic symbols, numbers, and names. Includes Lanthanide and Actinide series at the bottom.

4. NET STABILITY CONSTANTS

Table of net stability constants for various complexes including Ag(CN)2-, Ag(NH3)2+, Ag(S2O3)2-3, Al(OH)4-, Ca(EDTA), Cd(CN)4, Cd(NH3)4+, Co(NH3)6+3, Cr(OH)4-, Cu(CN)4-8, Cu(NH3)4+, Fe(CN)6-3, Fe(CN)6-4, Fe(SCN)++, HgCl4, Hg(CN)4, Hg(SCN)4, HgI4, Mg(EDTA), Ni(NH3)4+, Pb(OH)3-, Zn(CN)4, Zn(NH3)4+, and Zn(OH)4.

2. IONIZATION CONSTANTS (K1) FOR WEAK ACIDS

Table of ionization constants for weak acids: Acetic, 2-Amino-pyridinium Ion, Ammonium Ion, Anilinium Ion, Arsenic, Benzoic, Boric, Carbonic, Chloroacetic, Chromic, Citric, Dichloroacetic, EDTA, Formic, alpha-D(+)-Glucose, Glycinium Ion, Hydrazinium Ion, Hydrocyanic, Hydrofluoric, Hydroxyl-ammonium Ion, Hypochlorous, H2S, Imidazolium Ion, Lactic, Methylammonium Ion, Monoethanol-ammonium Ion, Nicotinium Ion, Oxalic, Phenol, Phthalic, Phosphoric, Phosphorous, Pyridinium Ion, Succinic, Sulfuric, Sulfurous, Trimethyl-ammonium Ion, Uric, and Water, Kw, 24°C.

5. FIRST IONIZATION ENERGIES, e.v.

Table of first ionization energies in eV for elements 1-118.

6. ELECTRONEGATIVITIES, Pauling

Table of Pauling electronegativity values for elements 1-118.

7. ATOMIC RADII picometers

Table of atomic radii in picometers for elements 1-118.

3. SOLUBILITY PRODUCT CONSTANTS

Table of solubility product constants for various salts: AgBr, Ag2CO3, AgCl, Ag2CrO4, Ag[Ag(CN)2], AgI, Ag3PO4, Ag2S, AgCNS, Al(OH)3, BaCO3, BaCrO4, BaC2O4, BaSO4, CaCO3, CaF2, CaC2O4, CdS, Cu(OH)2, CuS, Fe(OH)3, Hg2Br2, Hg2Cl2, HgS, KClO4, MgCO3, MgC2O4, MgNH4PO4, Mg(OH)2, MnS, PbCrO4, PbS, PbSO4, SrCrO4, Zn(OH)2, ZnS.

8. IONIC RADII pm

Table of ionic radii in pm for various ions: Li+, Na+, K+, Rb+, Cs+, Sr+2, Ba+2, Al+3, N+3, P+3, O-2, S-2, Se-2, Te-2, F-, Cl-, Br-, I-, Fe+2, Mg+2, Ca+2.

9. LATTICE ENERGIES

Table of lattice energies in kJ/mol for various salts: LiF, NaCl, KBr, RbI, CsI, LiCl, NaBr, KCl, RbBr, CsBr, LiBr, NaI, KBr, RbI, CsI.

10. HALF LIVES

Table of half-lives for various isotopes: H3, F20, C14, Na24, P32, S35, Cl36, K40, Ca45, Fe59, Co60, Br82, Sr90, I129, I131, Cs137, Au198, Ra226, U235, U238, Pu239.