AUSTRALIAN CHEMISTRY OLYMPIAD

FINAL PAPER

PART B

1988

<u>Instruction to candidates</u>

(1) You are allowed **10 minutes** to read this paper, and **3 hours** to complete the questions.

(2) You are **not** permitted to refer to books, notes or periodic tables but you may use an electronic calculator and molecular models.

(3) You must attempt **all** questions, so be sure to allocate your time appropriately.

(4) Answers must be written in the blank space provided immediately below each question in the exam booklet. Rough working must be on the back of pages.

(5) Answers **must** provide **clearly laid out working** and **sufficient explanation** to show how you reached your conclusions.

Question 1

(a) The periodic system of the elements in our three-dimensional world is based on the four electron quantum numbers n = 1,2,3, . . .; l = 0,1, . . . , n-1; m_l = 0, ±1, ±2, . . . , ±l; and m_s = ±1/2. Let us move to Flatlandia. It is a two-dimensional world where the periodic system of the elements is based on three electron quantum numbers: n = 1,2,3, . . . ; m = 0, ±1, ±2, . . ., ±(n-1); and m_s = ±1/2, m plays the combined role of l and m_l of the three dimensional world (example s,p,d, . . . levels are related to m). The following tasks and the basic principles relate to this two-dimensional Flatlandia where the chemical and physical experience obtained from our common three-dimensional world is applicable.

Draw the first four periods of the Flatlandian periodic table of the elements. Number the elements according to their nuclear charge. Use the atomic numbers (Z) as the symbols of the elements. Write the electron configuration of each element.

(b) Draw the hybrid-orbitals of the elements with n = 2. Which element is the basis for the organic chemistry in Flatlandia (use the atomic number as a symbol)? Find the Flatlandian analogs for ethane, ethene and cyclohexane. What kind of aromatic ring compounds are possible in Flatlandia?

(c) Which rules in Flatlandia correspond to the octet and 18-electron rules in the three-dimensional world?

(d) Predict graphically the trends in the first ionization energies of the Flatlandian elements with n = 2. Show graphically how the electronegativities of the elements increase in the Flatlandian periodic table.

(e) Draw the molecular orbital energy diagrams of the neutral homonuclear diatomic molecules of the elements with n = 2. Which of these molecules are stable in Flatlandia?

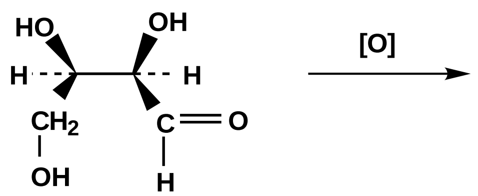
(f) Consider simple binary compounds of the elements (n = 2) with the lightest element (Z = 1). Draw their Lewis-structures, predict geometries and propose analogs for them in the three-dimensional world.

(g) Consider elements with $n \leq 3$. Propose an analog and write the chemical symbol from our three-dimensional world for each Flatlandian element. On the basis of this chemical and physical analogy predict which two-dimensional elements are solid, liquid or gas at the normal pressure and temperature.

Question 2

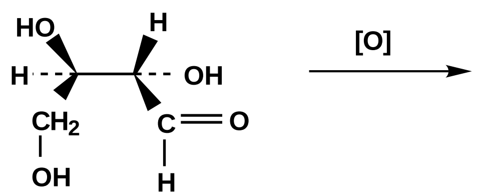
(a) D-erythrose (**A**) and D-threose (**B**) are easily oxidized to dicarboxylic acids **I** and **II**, respectively.

A



I

B



II

(i) Draw the structural formulae of **I** and **II**, using Newman projections of an eclipsed conformer.

(ii) How would you deduce by simple methods whether a sample of dicarboxylic acid is **I** or **II**?

(b) Lactic acid is produced industrially (by CCA-Biochem, the Netherlands) through the bacterial conversion of saccharose. In the process (S)-(+)-2-hydroxypropanoic acid (L-(+)-lactic acid) is formed, which is used in the food sector and also as a starting material for a number of chemical products.

(i) Give the spatial formula and the Fischer projection of L-(+)-lactic acid.

(ii) A fine-chemical produced from L-(+)-lactic acid is the so-called dilactide, a cyclic ester in which 2 molecules have been esterified with one another. This dilactide is polymerized to a polylactide, which among other things is being used in surgery as a "biodegrading" thread in the suturing of surgical wounds.

Note: In this question, for convenience, the ring may be considered planar.

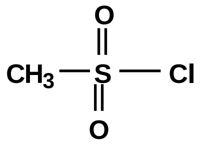
Draw the spatial structure of the dilactide prepared from (+)-lactic acid.

(iii) Sketch the spatial structure of the polylactide discussed above (at least three units). What is its tacticity? (isotactic, syndiotactic, atactic)

(iv) Draw the isomeric dilactides, which occur when one starts with racemic lactic acid and show the configuration of the chiral centres.

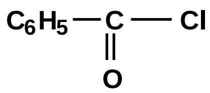
Note: In this question, for convenience, the ring may be considered planar.

(v) L-(+)-lactic acid is also one of the starting materials for the preparation of the herbicide Barnon (manufactured by Shell Chemicals, used against wild oats). In this case (+)-lactic acid is esterified with 2-propanol and then the hydroxyl group is treated with methane sulfonyl chloride



The product obtained is then submitted to a S_N2-reaction with 3-fluoro-4-chloro-aniline* in which reaction the methane sulfonate group leaves as $CH_3SO_3^-$.

Finally a benzoyl group is introduced with the aid of benzoyl chloride.



Draw the Fischer projection of the various consecutive reaction products.

* *Note 3-fluoro-4-chloroaniline is the same as 3-fluoro-4-chloro-aminobenzene.*

Question 3

(a) The concentration of the chloride ions in a solution can be determined by precipitating them by silver nitrate solution. The precipitate will, however, quickly decompose in the presence of light to elemental silver and chlorine. Assume that the latter will undergo disproportionation in the aqueous solution to form chlorate (V) and chloride ions. With excess of silver ions the chloride ions thus formed are precipitated. Chlorate (V) ions are not precipitated by the silver ions.

(i) Write the balanced equations of the above mentioned reactions.

(ii) The gravimetric determination of the chloride was carried out in excess of silver ions, 12% by mass of the precipitate formed was decomposed by light. Determine the size and direction of the error caused by the decomposition.

[Relative atomic masses: Ag =107.9, Cl =35.45, O = 16.00]

(b) Coloured compounds absorb visible light at selective wavelengths and may be characterized by their absorption spectra which plot absorbance (**A**) against wavelength (λ). For each wavelength (λ) the absorbance (**A**) is defined as

$$\mathbf{A} = \mathbf{a}.\mathbf{b}.\mathbf{c}$$

where **a** is a constant associated with absorbance at that particular wavelength, **b** is the path length of the sample cell and **c** is the concentration of the solution in g dm^{-3}. In dilute solutions containing more than one species the total absorbance at any one wavelength is the sum of the absorbances of the species present.

Copper and cobalt both form a complex [ML] with the ligand L when the pH is above 8. The absorption maximum for the copper complex lies at 450 nm while that of the cobalt complex lies at 300 nm. Calculate the copper and cobalt contents of the test solution (x and y, respectively) when the following data are known:

Solution **A**(450)	Cu-content (ppm)	Co-content (ppm)	**A**(300)	
1	2.0	0.0	0.125	0.730
2	0.0	2.0	0.640	0.681
test	x	y	0.681	1.026

Question 4

(a) Benzene diazonium chloride decomposes (completely) in aqueous solution to give chlorobenzene and nitrogen

$$C_6H_5N_2^+ (aq) + Cl^- (aq) \longrightarrow C_6H_5Cl(l) + N_2(g)$$

When 40.0 mL of an aqueous solution of $C_6H_5Na^+Cl^-$ is kept at 50°C and 1 atm pressure, the evolved gaseous nitrogen was measured as:

Time/sec	6	9	14	22	30	∞
N_2 vol/mL	19.3	26.0	36.0	45.0	50.4	58.3

(i) Derive the rate law expression for the reaction.

(ii) What is the value and units of the rate constant, k, for this reaction?

(iii) If the reaction is done in 0.1 M aqueous sodium bromide solution then the rate is not significantly altered but the product now contains both chlorobenzene and bromobenzene (~1:2). What does this information imply about the mechanism of the reaction?

(iv) Can you propose a simple mechanism for this reaction consistent with the above information?

(b) 1.00 g of pure calcium phosphide reacts with an excess of acid to give a gaseous product. This product is dried and afterwards heated to a temperature of 400°C where it decomposes into its elements in their gaseous state.

One of these elements is phosphorus. The decomposition products have a volume of 1060 cm^3 at a pressure of 1.013 bar.

Note: Relative atomic masses: Ca 40.08, P 30.97
Gas constant: $R = 8.314\ J.mol^{-1}.K^{-1}$; $1\ bar = 10^5\ kg.m^{-1}.s^{-2}$
$1J = 1kg.m^2.s^{-2}$

(i) What is the gaseous product from the reaction of calcium phosphide with acid?

(ii) How many moles of this gaseous product formed?

(iii) Determine the molecular formula of gaseous phosphorus from the given data under the conditions of the decomposition.