

FINAL PAPER

PART B

1995

AUSTRALIAN CHEMISTRY OLYMPIAD

Please note that this answer book will be photocopied when returned and then split so that answers are sent to the appropriate markers. For this reason it is extremely important that you observe instructions 5 to 7.

Instruction to candidates

- (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 a non programmable electronic calculator and molecular models.
- (3) You must attempt **all** questions.
- (4) Answers **must** provide **clearly laid out working** and **sufficient explanation** to show how you reached your conclusions.
- (5) Answers must be written in the blank space provided immediately below each question in the exam booklet. Rough working must be on the backs of pages. Only material presented in the answer boxes will be assessed.
- (6) Your name must be written in the appropriate place on **each page** of your answers.
- (7) Use **only black** or **blue ball point pen** for your written answers, pencil or other coloured pens are **not** acceptable.

Question 1

Buckminsterfullerene, C_{60} , is a new allotropic form of carbon. Its molecule resembles a soccer ball and has a spheroidal geometry. Sixty carbon atoms occupy the vertices of the polyhedron with an icosahedral symmetry. Each carbon atom is bonded to three other atoms using three of its four valence electrons to form σ bonds. The remaining electron is involved into the pi electronic system, which is delocalised over the whole carbon skeleton. The electronic states of C_{60} are commonly described by a model of free electrons moving on a sphere of radius r . In this model the energy levels are

$$E_L = \frac{h^2}{8\pi^2mr^2} L(L+1)$$

where h is the Planck constant ($h = 6.63 \times 10^{-34}$ J s), m is the mass of the electron ($m = 9.11 \times 10^{-31}$ kg), L is the angular momentum quantum number ($L = 0, 1, 2, \dots$). The level with quantum number L is $(2L+1)$ -fold degenerate. The optical transitions can occur between the levels with $\Delta L = \pm 1$.

- a) Determine the number of π electrons in the C_{60} molecule.
- b) What is the value of the quantum number L of the highest occupied level in the ground electronic state of the C_{60} molecule?
- c) How many unpaired electrons should the C_{60} molecule have according to the model of free electrons?

- d) The first absorption peak in the long-wave part of the C_{60} electronic spectrum is observed at the wavelength of 404 nm. Calculate the radius of the C_{60} molecule.
- e) It is known that C_{60} in its ground state has no unpaired electrons. To account for this fact, one must introduce an icosahedral symmetry in the model of free electrons. In the icosahedral environment, the degeneracy is lower than that in the spherical cage. All levels above $L = 2$ are split into groups containing 1, 3, 4, or 5 degenerate levels. Describe the splitting of levels with $L = 3, 4$ and 5 (no undegenerate levels are formed).
- f) Taking into account the above splitting, determine the number of unpaired electrons in the ground state of the following molecules: (a) K_3C_{60} ; (b) K_6C_{60} .

Question 2

- a) Ethylenediaminetetraacetic acid (EDTA) is a hexadentate ligand and is one of the most important and widely used reagents in titrimetry. The free acid of EDTA (H_4Y) and the dihydrate of the sodium salt, $Na_2[H_2Y] \cdot 2H_2O$ are available in highly pure form and are often used as primary standards.

The acid dissociation constants of H_4Y at 25°C are:

$$K_{a1} = 1.02 \times 10^{-2}$$

$$K_{a2} = 2.14 \times 10^{-3}$$

$$K_{a3} = 6.92 \times 10^{-7}$$

$$K_{a4} = 5.50 \times 10^{-11}$$

- (i) Calculate the concentration of Y^{4-} in a 0.0200 M EDTA solution that has been buffered to pH 10.00 at 25°C.
- (ii) A solution was prepared by dissolving 0.0150 mol of $Na_2[NiY]$ in 1000 mL of water. Calculate the concentration of Ni^{2+} in the solution if the pH is 10.00 at 25°C.



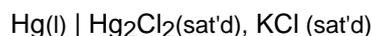
Show all your calculations and explain any approximations or assumptions you make.

- b) A 24 hr urine specimen was diluted to 2.000 L. After the solution was buffered to pH 10, a 10.00 mL aliquot was titrated with 26.81 mL of 0.003474 M EDTA. The calcium in a second 10.00 mL aliquot was precipitated as calcium oxalate, $CaC_2O_4(s)$, redissolved in acid and titrated with 11.63 mL of the EDTA solution.

Assuming that 15 to 300 mg of magnesium, and 50 to 400 mg of calcium per day are normal, did this specimen fall within these ranges? Show all your calculations.



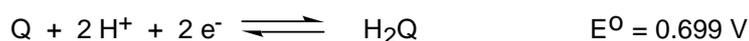
- c) (i) A saturated calomel electrode (SCE) can be represented schematically as:



The electrode potential of an SCE is 0.2444 V at 25°C.

Write an equation for the electrochemical reaction that occurs at the Hg electrode.

- (ii) Quinhydrone is an equimolar mixture of quinone (Q) and hydroquinone (H_2Q). These two compounds react reversibly at a platinum electrode:



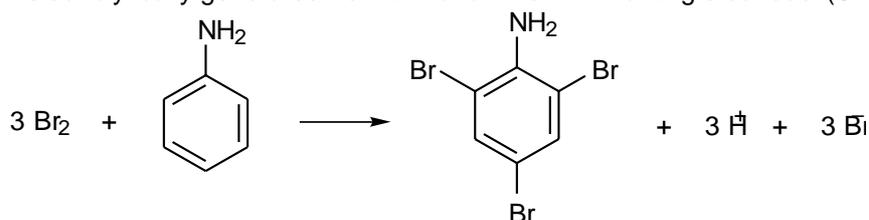
The pH of a solution can be determined by saturating it with quinhydrone and making it part of the cell:



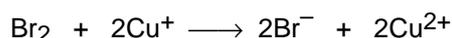
If such a cell has a potential of 0.313 V, what is the pH of the solution, assuming the liquid junction potential is zero?

- (iii) If the liquid junction potential was 5.9 mV, what effect would this have on the pH measurement?

- d) Traces of aniline ($C_6H_5NH_2$) can be determined by reaction with an excess of Br_2 that has been electrolytically generated from Br^- at an inert Pt 'working electrode' (STEP 1).



After this reaction is complete, the polarity of the working electrode is reversed (STEP 2) and the excess Br_2 is determined by completely reacting it with Cu^+ that is electrolytically generated from a known amount of Cu^{2+} :



Suitable amounts of KBr and $CuSO_4$ were added to a 25.00 mL sample containing aniline, and the following data obtained:

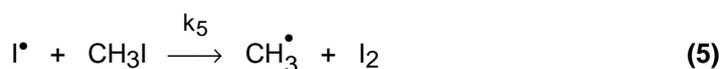
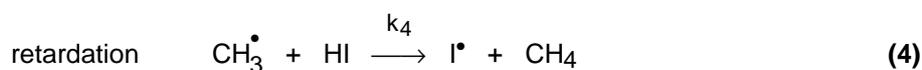
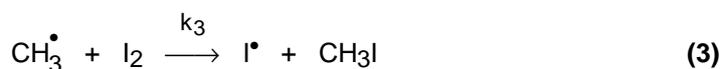
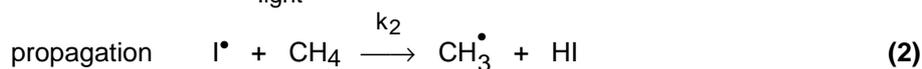
| | working electrode acting as: | generation time (min.) with a constant current of 1.51 mA |
|--------|------------------------------|--|
| STEP 1 | anode | 3.76 |
| STEP 2 | cathode | 0.270 |

Data: Relative atomic masses C 12.01 H 1.008 N 14.01
Faraday's constant $F = 96,485 \text{ C/mol}$

- Write equations for the electrochemical reactions at the working electrode in steps 1 and 2.
- Calculate the number of micrograms of aniline in the sample.

Question 3

The photochemical reaction between gaseous molecular iodine and methane to produce iodomethane proceeds through the following steps



Data:

| Species | ΔH_f° (kJ mol^{-1}) |
|--------------------|--|
| I_2 (g) | 62 |
| I^\bullet (g) | 107 |
| CH_4 (g) | -75 |
| CH_3^\bullet (g) | 146 |
| CH_3I (g) | 27 |
| HI (g) | 26 |

$$R = 8.315 \text{ J/Kmol}; \quad h = 6.626 \times 10^{-34} \text{ Js}; \quad c = 3.0 \times 10^8 \text{ ms}^{-1}$$

Neglecting any further reactions, deduce the rate law for the production of CH_3I using the steady-state approximation.

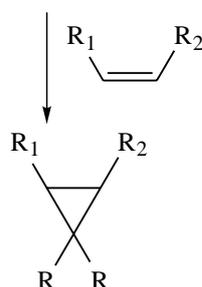
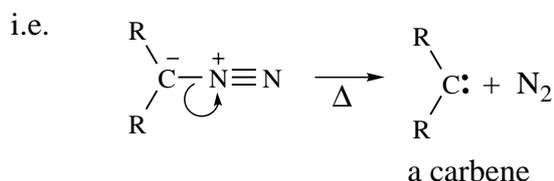
What is the maximum wavelength of light that can be used for the initiation step?

In a certain reaction, a sample of I_2 and CH_4 was irradiated and HI was removed as quickly as it was produced. If the quantum efficiency (ratio of product CH_3I molecules to absorbed photons) was 2.0×10^4 , calculate the ratio of the number of times reaction (3) occurred to the number of times that reaction (5) occurred. Assume that $1.0 \times 10^{-3}\%$ of the reactions are termination reactions, that each absorbed photon results in the breaking of one I_2 bond and that neither reactant is completely depleted.

Question 4

With the huge number of organic molecules known it is perhaps surprising that chemists should be fascinated by highly reactive short-lived species such as carbenes. These electronically neutral divalent species (see below) can be generated by the thermal decomposition of diazoalkyl derivatives.

Carbenes are especially useful in that they add to double bonds to form cyclopropanes.



Given this information you can now solve the following problem.

Hydrolysis of natural pyrethrins of Dalmatian origin produces *inter alia* (+)-chrysanthemic acid, a monoterpene of empirical formula $\text{C}_{10}\text{H}_{16}\text{O}_2$. Chrysanthemic acid decolourises solutions of bromine and can be reduced by hydrogen in the presence of palladium to **A** $\text{C}_{10}\text{H}_{18}\text{O}_2$. Ozonolysis of chrysanthemic acid gives acetone (propanone) and an optically active dibasic acid **B** $\text{C}_7\text{H}_{10}\text{O}_4$. **B** does not readily form an anhydride; but after prolonged treatment with acetic anhydride, **B** is converted into an anhydride which can be hydrolysed to an optically inactive dibasic acid **B'** $\text{C}_7\text{H}_{10}\text{O}_4$.

The synthesis of (\pm)-chrysanthemic acid is based upon the fact that the protons of acetylene (ethyne) are acidic and can be removed by a suitable base to yield a nucleophilic anion. Thus in the presence of a suitable base acetylene condenses with acetone to afford, after acidic workup, a diol **C** ($\text{C}_8\text{H}_{14}\text{O}_2$). Complete hydrogenation of **C** and subsequent dehydration of the resulting product affords a conjugated diene **D** (C_8H_{14}). Heating **D** with one equivalent of the ethyl diazoacetate ($\text{N}_2\text{CHCO}_2\text{C}_2\text{H}_5$) followed by base catalysed hydrolysis of the ester functionality in the product yields (\pm)-chrysanthemic acid.

- Deduce structures for chrysanthemic acid, and products **A** to **D**.
- Account for the optical activity of **B** and the optical inactivity of **B'**.