

FINAL PAPER

PART B

1998

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 6 to 8.

Instruction to candidates

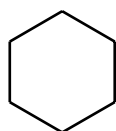
- (1) You are allowed **10 minutes** to read this paper, and **3 hours** to complete the questions.
- (2) You are **not** permitted to refer to books, notes or periodic tables but you may use a non programmable electronic calculator and molecular models, molecular models are not considered essential.
- (3) You must attempt **all** 5 questions. All questions are of equal value.
- (4) Appropriate data can be found with each question.
- (5) Answers **must** provide **clearly laid out working** and **sufficient explanation** to show how you reached your conclusions.
- (6) 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.
- (7) Ensure that your name is written in the appropriate place on **each page** of your examination booklet.
- (8) Use **only black** or **blue ball point pen** for your written answers, **pencil or other coloured pens are not acceptable**.

Question 1

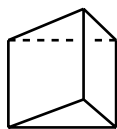
In the old days of Werner's time, the studies of complexes relied entirely on the classical methods like elemental analyses, measurement of conductivities when the complex dissociated in solution to form an electrolyte, magnetic susceptibility and magnetic moment of the complexes, identification of the existing geometrical isomers and optical isomers, etc.

- a) (i) In the case of coordination number 6, the central metal atom can adopt three possible geometries, ie., the flat hexagon (**A1**), the trigonal prism (**A2**), and the octahedron (**A3**). [Note The octahedron **A3** can also be regarded as the antitrighonal prism in relation to **A2**].

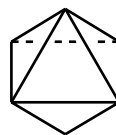
Werner was able to arrive at the right answer by counting the number of geometrical isomers that could exist for each of the three possible geometries (**A1**, **A2**, **A3**), by using complexes of the formula MA_4B_2 where A and B are all monodentate ligands. You are asked to count all the possible geometrical isomers and draw their structures for each of **A1**, **A2**, **A3** geometries.



A1



A2



A3

- (ii) To secure his conclusion Werner also recognised the possibility of existence of optical isomers. Let L-L be bidentate ligand and apply three (3) molecules of L-L to **A1**, **A2**, **A3** geometries. Draw all the possible complexes that would arise and identify the one(s) that would exist as optical isomers Also draw each pair of optical isomers.
- b) (i) When the coordination number is 4, the central metal atom can adopt either the tetrahedral or square planar geometries. Let A, B, C and D be the four monodentate ligands bonded to the central metal atom, M. Compare the outcomes of the two possible geometries, ie., tetrahedral and square planar, of MABCD with regard to geometrical and optical isomers.
- (ii) Replace ligands A, B, C, D in (i) with two of L-L, and make the comparisons as in (i).

Question 2

- a) Draw a diagram to illustrate the relative energies of the atomic and molecular orbitals in diatomic carbon molecules. Label the molecular orbitals and indicate the orbital occupancy, bond order and whether the species is paramagnetic, diamagnetic or ferromagnetic.
- b) What characteristics of the atomic orbitals and the way they are formed into molecular orbitals affect the energies of the molecular orbitals relative to those of atomic orbitals?
- c) Sketch the 90% inclusion surfaces for the bonding molecular orbitals that are formed primarily from carbon 2p orbitals. On the sketches, indicate axes as well as the positions of the carbon atoms and any other important characteristics.
- d) Consider the reaction of diatomic carbon in the gaseous phase to form ethyne by reacting with two atoms of hydrogen approaching axially.

With which carbon molecular orbitals might the hydrogen 1s orbital interact in order to form a bond? Why? What kind of bonds might form?

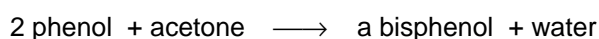
- e) Consider the following statement:

“When describing the molecular orbitals in ethyne, allowing the carbon 2s orbital and the axial carbon 2p orbital to mix in a linear combination before forming molecular orbitals with the hydrogen 1s orbital gives a better description of the bonding.”

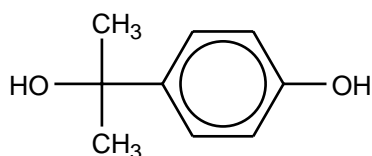
Do you agree with this statement? Give reasons supporting your view.

Question 3

- a) The condensation reaction of phenol with acetone in an acid medium to produce a bisphenol shows a first order dependence on phenol, acetone, and hydrogen ions.



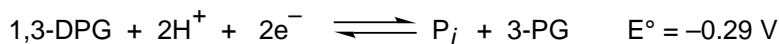
It was determined spectroscopically that;



exists as an intermediate, and that its formation represents the rate limiting step. Suggest a possible mechanism for this reaction and derive a rate equation.

- b) The small bio-molecule, ATP (adenosine tri-phosphate) is often called *the currency of energy* in biological systems for it stores and transports energy around cells. Nearly all biochemical pathways employ the hydrolysis of ATP to its di-phosphate (ADP) to drive reactions. The energetics of the formation of ATP is thus a crucial step in the maintenance of life. Three simple single step reactions (equilibria in fact) have been implicated in the production of ATP.

- (i) Look at the data collected for these reactions and decide if the formation of ATP is favourable.



NADH = nicotinamide adenosine dinucleotide, reduced form

DPG = diphosphoglyceraldehyde

$\text{P}_i = \text{PO}_4^{3-}$

Ideal Gas constant = $8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 8.205 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$

Faraday constant = $96\,540 \text{ C mol}^{-1}$

- (ii) Creatine phosphate (CP) also acts as a temporary store of energy for excitable tissue such as nerves. It functions to keep ATP concentrations high in cells that require rapid bursts of energy. Calculate the minimum ratio of ATP to ADP required to form creatine phosphate from creatine (C) at pH 7 at 30°C with $[\text{C}] = 2 \times 10^{-3} \text{ M}$ and $[\text{CP}] = 1 \times 10^{-4} \text{ M}$, given;



Question 4

Data: $\text{pK}_a(\text{HF}) = 3.17$ $\xi^0(\text{Cu}^{2+}/\text{Cu}^+) = 0.17 \text{ V}$
 $\text{K}_{\text{sp}}(\text{LaF}_3) < 1 \times 10^{-27}$ $\xi^0(\text{I}_3^-/\text{I}^-) = 0.54 \text{ V}$

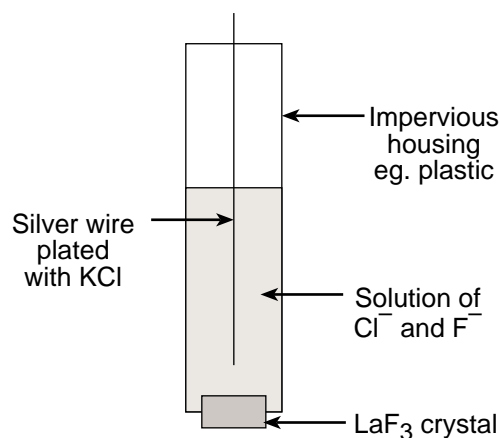
- a) A fairly common example of the important analytical technique of iodometry is the determination of Cu^{2+} . Indeed, you have already completed this determination as part of your practical examination. The first step of this determination is to reduce Cu^{2+} to Cu^+ with I^- . On mixing the reagents, the characteristic brown colour of iodine in aqueous solution (actually the I_3^- ion) rapidly forms.

- (i) Calculate the equilibrium constant for the reaction

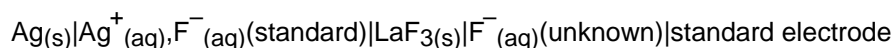


- (ii) Explain how this is inconsistent with the fact that the titration is known to be a good (quantitative) one.
- (iii) You may recall, however, that CuI is precipitated during this reaction. Explain, in terms of the relative thermodynamic stabilities of the various species, why this reaction proceeds despite the apparently unfavourable electrochemistry.
- (iv) Given that the reaction is indeed quantitative, estimate an upper bound (the maximum value consistent with reality) for the K_{sp} of CuI .

- b) The phenomenon observed here — namely the difference in the stability of the same ion between a crystalline and an aqueous environment — is of great importance to analytical chemistry. Not only can it be employed to aid in a traditional titration, such as the one mentioned above, but it can also be made use of directly in certain situations. The most important of these is the ion-selective electrode. Perhaps the most famous ion-selective electrode is the fluoride electrode. The active part is a crystal of LaF_3 , which can conduct electricity by the movement of F^- ions through defects in the lattice. The electrode is constructed as shown below.



The wire and the Cl^- in solution form a standard silver/silver chloride half-cell[†]. An unknown, but constant, junction potential is formed by the exchange of F^- between the solution inside the electrode and that portion of the crystal closer to the inner surface. When immersed in a solution of unknown F^- , another potential is formed at the outer surface of the crystal. The overall electrode looks (schematically) like:



[†]The standard silver/silver chloride half-cell consists of a silver wire, plated at the end with AgCl , and immersed in a solution saturated with respect to AgCl , and at known concentration (usually saturated) of KCl . It is not necessary for you to know the value of the e.m.f. produced by this cell in order to answer the question properly.

- (i) Write an expression for the overall e.m.f. that you would expect to measure from this cell.
- (ii) In practice, the electrode used to complete the cell is usually another standard silver/silver chloride electrode. Suggest a reason for this.
- (iii) Predict how the measured potential of the system would depend on the concentration of F^- in the test solution. Describe the mathematical relationship, not just the sign of the dependency. Explain your reasoning.
- (iv) Like most "real" systems, the observed potential of this electrode deviates significantly from the ideal value at extreme F^- ion concentration. Predict the direction of the deviation at both very low and very high $[\text{F}^-]$. Again, explain your reasoning.

Question 5

The anti-inflammatory drug "Opren" was introduced earlier this decade owing to its ability to repair damage as well as to reduce inflammations. One of the possible routes to this product starts from the readily available ethylbenzene. From this starting material, both intermediates **A** and **B** can be prepared. These are then joined together in the last step of the reaction.

Preparation of A

Ethylbenzene is allowed to react with chlorine in the presence of iron(III)chloride as catalyst, followed by oxidation with potassium permanganate to give **C** ($\text{C}_7\text{H}_5\text{ClO}_2$). **A** ($\text{C}_7\text{H}_4\text{Cl}_2\text{O}$) results from the reaction of **C** with thionyl chloride.

Preparation of B

Ethylbenzene is photolysed in the presence of bromine. The obtained product **D** is allowed to react with NaCN and a derivative **E** is isolated. **E** is treated with a mixture of nitric and sulfuric acids, and then hydrogenated in the presence of the catalyst palladium, to give **F** ($\text{C}_9\text{H}_{10}\text{N}_2$). The product **F** is allowed to react with nitrous acid. The reaction mixture, poured in water and heated, leads to **G**, which gives a highly coloured solution when dissolved in an

alcoholic iron(III)chloride solution. **B** ($C_9H_{10}N_2O$) is obtained from **G**, repeating the sequence **E-F**.

Finally, in adding **A** and **B** together, **H** ($C_{16}H_{11}ClN_2O$) is produced. **H** is tricyclic (one ring is five-membered), and the mechanism proceeds via two nucleophilic attacks. **H** is then hydrolysed in concentrated hydrochloric acid to give "Opren" ($C_{16}H_{12}ClNO_3$).

- a) Draw species **A-H** and Opren. Point out possible isomers along the way, but assume that where isomers are possible, the major one (according to steric hindrance effects) is used.
- b) Suggest a mechanism for the formation of **H**.
- c) What would be the effect of adding aluminium trichloride to the reaction whose product is **H**?