

AUSTRALIAN CHEMISTRY OLYMPIAD

FINAL PAPER

PART A

1991

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-programable electronic calculator and molecular models.
- (3) You must attempt **all** questions.
- (4) 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.
- (5) Answers **must** provide **clearly laid out working** and **sufficient explanation** to show how you reached your conclusions.
- (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

- (a) In 1962, Neil Bartlett reported the synthesis of the first noble gas compounds, XeF_2 and XeF_4 . The two fluorides were prepared by the direct reaction of $\text{Xe}(\text{g})$, an element of the fifth row of the periodic table, and $\text{F}_2(\text{g})$.
 - (i) Write ground state valence electron configurations for Xe and F, and describe the valence orbitals of these two atomic species in terms of the quantum numbers n , l and m_l .
 - (ii) Draw the Lewis structure and predict the electron pair geometry and molecular structure of the two fluorides. What is the hybridisation of the central atom in each of these two compounds?

Would either of the two species be expected to have a dipole moment?
- (b) Draw **clearly labelled** molecular orbital energy level diagrams for He_2^+ , OF and O_2^+ . What is the bond order in each case and which species would be expected to be paramagnetic?

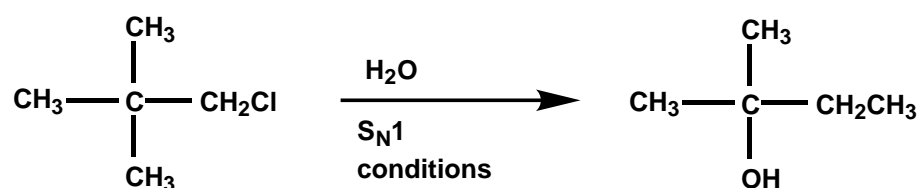
Question 2

- (a) Sketch and name all the possible stereoisomers of the following coordination compounds.
- $[\text{Pt}(\text{NH}_3)_2\text{ClBr}]$
 - $(\text{NH}_4)_2[\text{Fe}(\text{C}_2\text{O}_4)_2(\text{NH}_3)\text{Cl}]$
 - $[\text{Co}(\text{NH}_3)_3(\text{NCS})_3]$
- (b) Show how the crystal field theory may be used to account for the diamagnetism of tris(ethylenediamine)cobalt(III) chloride and the paramagnetism of the hexafluoroferrate(III) anion.

Question 3

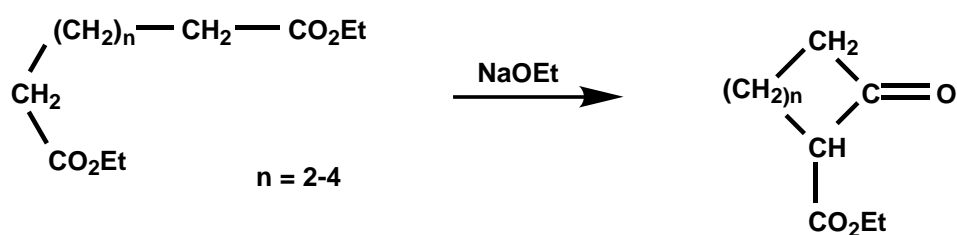
- (a) Carbonium ions have been postulated to be the reactive intermediate in the Friedel Crafts alkylation reaction. Frequently they are generated by reacting an alkyl halide with aluminum(III) chloride. However alternative strategies are also available. Thus for example when prop-2-enol is treated with hydrogen fluoride in the presence of benzene two products are formed: 3-phenyl-1-propene and 1,2-diphenylpropane. Give a clear explanation and mechanism of how these products are formed.
- (b) In addition to substitution reactions carbonium ions are also known to be key intermediates in certain addition and elimination reactions.

However another aspect of their chemistry is one in which the carbon skeleton rearranges. One such case is the so called "neopentyl" rearrangement shown below.



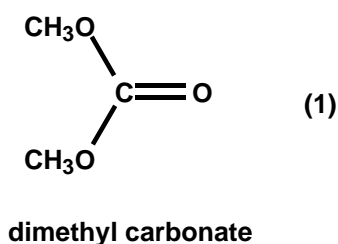
Give a clear mechanism for this reaction, and suggest why this reaction occurs.

- (c) Carbanions are associated frequently with methylene (CH_2) or methine (CH) groups adjacent to an electron withdrawing group such as a carbonyl group. Suggest a mechanism for the so called "Dieckmann Cyclisation", shown below



- (d) Grignard reagents are a well known source of nucleophilic carbon.

Predict the structure of the product of the reaction of excess phenyl magnesium bromide with dimethyl carbonate (1), assuming that the usual acid work up is employed.



- (e) A substance **A** ($C_5H_{10}O_2$) gives a positive test with 2,4-dinitrophenylhydrazine but will not reduce $[Ag(NH_3)_2]^{2+}$. Oxidation of **A** with CrO_3 in pyridine affords **B** which reacts with 2,4-dinitrophenylhydrazine and also reduces $[Ag(NH_3)_2]^{2+}$.

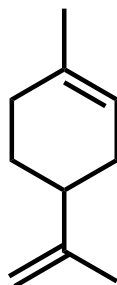
When 1 mole of **A** is treated with 3 moles of methyl magnesium iodide. One mole of methane is evolved. When the reaction mixture is acidified a second mole of gas is evolved and a product **C** ($C_6H_{14}O_2$) isolated.

Reaction of **C** with a trace of sulfuric acid affords **D** (C_6H_{10}), which upon reaction with ozone affords equimolar quantities of **E**, **F** and **G**.

E is identical to the product obtained from 2-propanol upon oxidation with an acidic aqueous solution of chromium oxide. Reaction of **F** with sodium borohydride affords methanol. Oxidation of **G** gives oxalic acid (ethanedioic acid).

Identify compounds **A** to **G**.

- (f) The structure of limonene, a terpene found in citrus oils is shown below. Predict the products formed when limonene reacts with the following reagents



limonene

- (i) excess HBr
- (ii) ozone followed by dimethyl sulfide
- (iii) warm concentrated $KMnO_4$
- (iv) diborane followed by basic H_2O_2

Question 4

A volume of a 0.2M potassium chlorosuccinate ($KO_2CCH_2CH(Cl)CO_2K$) was hydrolysed by an equal volume of 0.2 M potassium hydroxide. The hydroxide concentration was monitored with time at $25^\circ C$, the results are listed below.

time (seconds)	$[OH^-]$ ($mol\ L^{-1}$)
10	0.085
20	0.074
30	0.065
45	0.056
60	0.049
80	0.042
100	0.036

The experiment was repeated at $35^\circ C$ and it was found that the hydroxide concentration halved after 21 minutes.

- (a) What is the overall order of the reaction?
- (b) Calculate the activation energy for the reaction.

Question 5

- (a) The solubility product for mercuric sulfide, HgS , is 1.6×10^{-54} at 25°C . Calculate the solubility of mercuric sulfide in water at this temperature, and express your answer in terms of the number of Hg^{2+} and S^{2-} ions per litre. Does this seem reasonable? Discuss. Avogadro constant is 6.02×10^{23} .
- (b) A buffer solution is made by mixing 50 mL of 0.200 M acetic acid with 50 mL of 0.200 M sodium acetate. The pK_a for acetic acid is 4.8.
- (i) Calculate the pH of this buffer solution.
- (ii) How much does the pH change if 3 mL of 0.100 M HCl is added to the buffer solution?
- (c) (i) If 10.0 mL of 0.050 M AgNO_3 solution are added to 20.0 mL of 0.030 M NaCl solution, what are the final concentrations of all species in solution at equilibrium? Assume additive volumes.

K_{sp} for AgCl is 1.7×10^{-10}

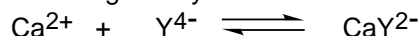
- (ii) In concentrated chloride solutions the reaction



occurs. What mass of solid NaCl must be added to the solution in part (i) in order to completely redissolve all the silver chloride? Assume no volume changes occur.

- (d) Ethylenediaminetetraacetic acid, EDTA, is a chelating agent useful for the titration of calcium ion, and is used for determining water hardness by titration. It has four ionisable protons and can be represented by H_4Y .

The complex formed with calcium ion is given by:



with a formation constant of:

$$K_{\text{f}} = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}][\text{Y}^{4-}]}$$

At a given pH only a fraction, α , of the EDTA exists as Y^{4-} , and so the concentration of Y^{4-} in equilibrium is $\alpha C_{\text{H}_4\text{Y}}$, where $C_{\text{H}_4\text{Y}}$ is the **analytical** concentration of EDTA (the total of all forms existing at a given pH). Hence, $[\text{Y}^{4-}] = \alpha C_{\text{H}_4\text{Y}}$.

The formation constant for CaY^{2-} is 5.0×10^{10} . At pH 10, α is 0.35.

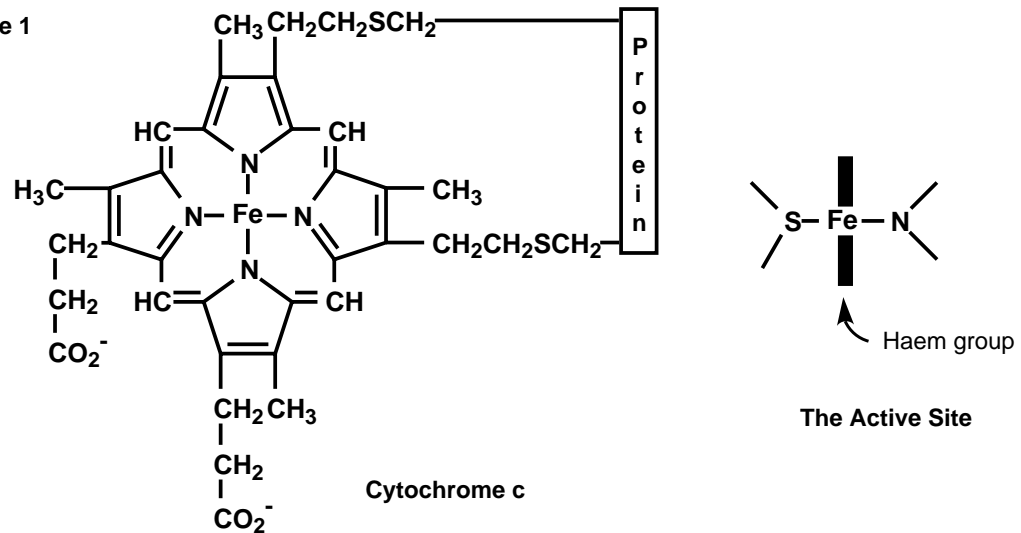
Calculate $[\text{Ca}^{2+}]$ and pCa ($-\log[\text{Ca}^{2+}]$) in 100 mL of a solution of 0.100 M Ca^{2+} at pH 10 after addition of

- (i) 0 mL
(ii) 50 mL
(iii) 150 mL
- of a 0.100 M EDTA solution.

Question 6

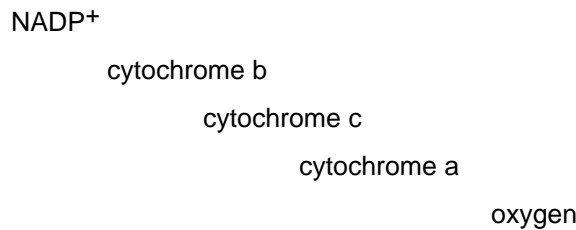
Plant and animal physiology involve a complicated and very interesting branch of biology and chemistry termed biochemistry characterised into what are termed "pathways". Each pathway involves the synthesis or consumption of one or more important chemical compounds for biochemical ends. One such pathway in the glycolytic pathway, in which glucose is consumed releasing energy for the organism to utilise. Another pathway, and the one of importance here is the electron transport pathway termed respiration. One series of steps in this pathway involves a group of enzymes (an enzyme is a biological catalyst) and complexes termed the cytochromes. The family of cytochromes are haem based units with an iron atom situated at the active site of the complex, as indicated in figure 1.

Figure 1



As the Fe atom cycles between the 2+ and 3+ oxidation states, an electron is transported. Altering the ligation of the central Fe atom affects its standard reduction potential, and nature utilises this to allow a transfer of electrons between a series of complexes at different potentials, as indicated in figure 2.

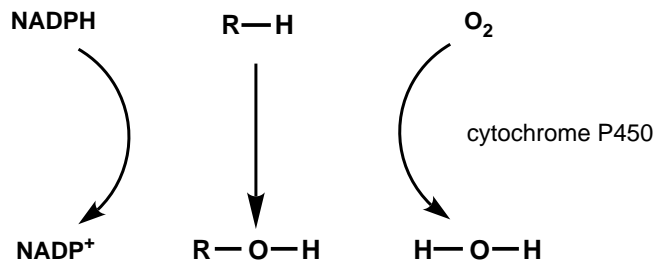
Figure 2



The role of the cytochrome is central to both the electron transport and biochemical processes such as biosynthesis and (barbiturate) detoxification. For example, cytochrome P450 acts as indicated in figure 3 to both reduce oxygen to water and allow incorporation of oxygen to a biological molecule, altering its biochemical activity.

In an effort to understand the processes involved, Professor Richard Holm modelled the cytochrome complexes, successfully contributing to our understanding of the factors affecting the reduction potentials of the Fe^{II/III}. He took Fe substituted haem and changed the ligands in the remaining two positions (recall Fe is 6 coordinate!!) and measured the resulting reduction potentials. This data is presented in the data table, with the cytochrome model, its measured Fe^{II/III} potential and ligation pattern. These complexes react in biological conditions, at a temperature of 36.9 °C, and normal pH buffered to 7.6. However a proton source is present as indicated in figure 3, and the local pH in the complexes locale can be considered to be 7. This proton source is NADPH (or nicotinamide adenine dinucleotide phosphate).

Figure 3



The following data and information is made available for you.

Data :

Equations:

$$\Delta G = \Delta H - T\Delta S$$

Nernst equation $E = E^\circ - \frac{RT}{nF} \ln Q$

Standard Entropies:

Substance	S° (JK ⁻¹ mol ⁻¹)
NaCl (s)	72
Na ⁺ (aq)	59
Cl ⁻ (aq)	57

Convention writes a redox reaction thus: anode half cell || cathode half cell

Reduction Potentials:

	Potential (volts)	Ligands (aside from haem)
standard Fe ^{II/III}	0.77	
NADP ⁺ / NADPH	-0.32	
cytochrome a	0.28	one N ligand
cytochrome c	0.25	one N, one S ligand
cytochrome P450	-0.34	one N, one S ligand
acidic reduction of oxygen	1.23	standard conditions

- (a) Why do the various cytochrome complexes have E° different from
 (i) each other, and
 (ii) the standard Fe^{II/III} values?
 Explain briefly and clearly giving the **fundamental** reason(s).
- (b) Of those listed in the data table, which Fe^{II/III} couple would be
 (i) easiest,
 (ii) most difficult, to reduce? Justify.
- (c) Give the E° value for the reduction of oxygen to water in the presence of NADPH under biological conditions.
- (d) Calculate ΔG° and ΔE° for the following couples:
 (i) cyt P450 || cyt a
 (ii) cyt a || cyt c
 (iii) cyt P450 || oxygen (biological conditions)
- Which is the most spontaneous reaction? Which is the fastest reaction?
- (e) Assuming that ΔH° is equal for the various cytochrome x || cytochrome y couples, give ΔH° and ΔS° for:
 cyt P450 || cyt a
 List and **justify** any assumptions required in your solution.