FINAL PAPER

PART A

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 candidate

(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) Questions 1, 2, 3 and 4 must be attempted. In the organic section you have a choice between questions 5 or 6, within question 6 there are further choices to be made. A guide for time allocation is supplied at the beginning of each question.

(4) Data is supplied, where necessary, 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 (25 minutes)

a) For each of the following species construct a clearly labelled d-orbital splitting diagram, calculate the 'spin only' magnetic moment and determine the crystal field stabilisation energy in terms of Δ_o:

(i) $[CoCl_4]^{2-}$ (ii) $[Co(CN)_6]^{4-}$ (iii) $[Co(NH_3)_6]^{3+}$ (iv) $[Co(NH_3)_6]^{2+}$ (v) $[CoF_6]^{3-}$

(b) Draw and name all of the possible stereoisomers for each of the following complexes:

(i) $K_3[Fe(C_2O_4)_3]$ (ii) $[Zn(H_2NCH_2CO_2)_2]$ (iii) $[Co(NO_2)(H_2O)(en)_2]SO_4$

What other types of isomerism could be exhibited by (iii)? Give an example of each type and name the isomer.

Question 2 (20 minutes)

Data: h = 6.626 x 10^{-34} Js, m = 9.104 x 10^{-31} kg, c = 2.998 x 10^{8} ms^{-1}, π = 3.142, C—C bond length in benzene = 140 pm.

a) The particle-in-a-box model has been beaten to death in recent years at the Australian Chemistry Olympiad.
The π-system of benzene can be modelled by approximating the six-fold symmetry of benzene to perfect circular symmetry and treating the electrons as particles confined to a ring. The energies of the allowed wave functions are described by a single quantum number n = 0,1,2, etc. The energies are given by

$$E = n^2 \frac{h^2}{8\pi^2 m r^2}$$ where r is the radius of the ring and m is the mass of the particle.

Applying the model to the benzene molecule, what is the quantum number of the filled orbital of highest energy?

b) Calculate the energies of the first five wave functions in the particle-in-a-ring model.

c) An absorption peak for gaseous benzene was observed around 80 nm. Assuming the particle-in-a-ring model predicts the electronic energy levels of benzene accurately, indicate which transition occurred during the absorption.

d) This model may not predict the electronic energy levels of the π-system of benzene accurately. What trend would be expected for the benzene π-system molecular orbital energies? What assumptions have been made in developing the model, such that it may not adequately predict the properties of the physical system?

e) Benzene (C_6H_6), the cyclopentadienyl anion ($C_5H_5^-$) and the tropylium cation ($C_7H_7^+$) all have delocalised cyclic π-systems containing 4n+2 electrons, and thus exhibit the familiar properties of aromaticity.
Which of the three species would be able to absorb light of the longest wavelength? Why? (Hint: the particle-in-a-ring model may be useful)

f) The following four species all absorb light in the UV part of the electromagnetic spectrum: phenol (C_6H_6O), benzonitrile (C_7H_5N), aniline (C_6H_7N) and benzene (C_6H_6).
Qualitatively predict the trend that is observed in the longest wavelength of light that is absorbed by these four species. Explain your predictions.

Question 3 (45 minutes)

a) The Citric Acid Cycle (also known as the Krebs Cycle) is the main biochemical pathway for the oxidation of carbohydrates in muscle tissue. One key step is the fumarate to malate conversion. Given that an enzyme catalysed equilibrium was setup and studied as a function of temperature, determine change in enthalpy, entropy and free energy of this system.

Temperature (°C)	Equilibrium Constant
14.3	4.78
20.2	4.46
25.0	3.98
30.0	3.55
34.6	3.27
40.0	3.09
44.4	2.75
49.6	2.43

Ideal Gas Constant = 8.314 J K^{-1} mol^{-1} = 8.205 x 10^{-2} L atm K^{-1} mol^{-1}

b) The gas-phase decomposition of acetic acid at 1189 K proceeds by way of two parallel reactions;

$CH_3COOH \longrightarrow CH_4 + CO_2$ $\quad k_1 = 3.74\ s^{-1}$

$CH_3COOH \longrightarrow H_2C{=}C{=}O + H_2O$ $\quad k_2 = 4.65\ s^{-1}$

What is the maximum percentage yield of the ketene obtainable at this temperature?

c) Devise the rate law for the decomposition of N_2O_5 based on the following mechanism;

$N_2O_5 \longrightarrow NO_2 + NO_3$	k_a
$NO_2 + NO_3 \longrightarrow N_2O_5$	k_{-a}
$NO_2 + NO_3 \longrightarrow NO_2 + O_2 + NO$	k_b
$NO + N_2O_5 \longrightarrow 3NO_2$	k_c

Question 4 (45 minutes)

Note: Data for this question can be found at the end of the question.

Indicators are a vital part of analytical chemistry. Understanding how they operate, and the errors involved in their use is, consequently, of utmost importance.

a) The most common indicators are of the acid/base type. Consider a generic acid-base indicator — let's call it **In**, so the acid form is **HIn**, and the basic form $\mathbf{In^-}$. If the colour of the acid form is of similar intensity to that of the basic form then the colour change will occur when the ratio [**HIn**]/[$\mathbf{In^-}$] is between about 0.1 and 10.

(i) What error in the concentration does this correspond to at the end-point of a strong-acid/strong base titration (ignore any buffering effect of the indicator itself, just think about the visible colour change)?

(ii) What would be the smallest concentration for the reagents that could be used in this titration if the error was to be kept below 1%?

(iii) An unknown solution of benzoic acid (20.00 mL, ~1×10^{-2} M) is titrated with NaOH (1.00×10^{-2} M).

(A) Calculate the pH of the equivalence point.

(B) Select a suitable indicator and calculate the experimental error of this determination as a percentage of the true value.

b) Another class of indicators are those which react with an excess of the titrant. As a practical example, in the determination of Ag^+ by titration with SCN^-, a small amount of Fe^{3+} indicates the addition of excess SCN^- by the formation of the highly coloured $FeSCN^{2+}$ complex. However, care must be taken to add an appropriate quantity of Fe^{3+}. Too much, and the colour may form before equivalence is reached, too little and the colour may not appear until significantly after the equivalence point. Assuming that $FeSCN^{2+}$ is visible at a concentration of about 1×10^{-7} M:

(i) Calculate what [Fe^{3+}] should be added for the most accurate end-point.

(ii) Calculate the upper and lower limits for [Fe^{3+}] that keep the accuracy of a titration of ~2×10^{-3} M Ag^+ with 2.00×10^{-3} M SCN^- to less than 1%.

c) A third type of indicator — one which you may not have encountered — is the redox indicator. These indicators have a reduced form and an oxidised form (which we can denote In_{red} and

In_{ox}, respectively) which differ in colour much like an acid/base indicator. Of course the determining factor here is not pH but the electrical potential of the titration mixture.

(i) Describe how the concentration of each of the indicator species will vary with the potential of the mixture (hint: the Nernst equation is very similar in form to the Henderson-Hasselbalch equation).

(ii) The Ce^{4+} ion is a good oxidant, and is far more stable than other common oxidants such as permanganate. However, its colour in not nearly so intense, and a redox indicator is often employed to aid in the detection of the end-point. Consider the titration of Fe^{2+} with Ce^{4+} in 1 M nitric acid.

(A) Calculate the concentration of all major species at the equivalence point.

(B) Hence, calculate the potential of the mixture with respect to the standard hydrogen electrode (hint: at all stages of the titration, the mixture in the flask is at equilibrium, so $\xi\,[Fe^{3+}/Fe^{2+}] = \xi\,[Ce^{4+}/Ce^{3+}]$).

(C) Describe, by sketching a graph, the change in the electrical potential of the titration mixture over the course of the titration.

(D) Which indicator(s) would be suitable for use in this titration?

Data:

K_{sp} (AgSCN) $= 1\times10^{-12}$

K_{stab} ($[FeSCN]^{2+}$) $= 1\times10^{3}$

pKa (Benzoic acid) $= 4.20$

ξ^0 (Fe^{3+}/Fe^{2+}) $= 0.77$ V

ξ^0 (Ce^{4+}/Ce^{3+} in 1 M HNO_3) $= 1.61$ V

Acid/Base indicators :-

Name	**Colour (acid form)**	**Colour (basic form)**	**pK_a**
Thymol blue	red	yellow	1.7
Methyl orange	red	yellow	3.7
Bromocresol Purple	yellow	purple	6.3
Bromothymol blue	yellow	blue	7.0
Phenol red	yellow	red	7.9
Cresol red	yellow	red	8.3
Thymol blue	yellow	blue	8.9
Phenolphthalein	colourless	red	9.6

Redox Indicators :-

Name	**Colour (oxidised)**	**Colour (reduced)**	**ξ^0 at pH=0**
Nitroferroin	Pale blue	Red	1.25
Ferroin	Pale blue	Red	1.06
2,2'-Bipyridyl iron(II) sulfate	Faint Blue	Red	1.02
5,6-Dimethylferroin	Pale blue	Red	0.97
N-Phenylanthranilic acid	Purple red	Colourless	0.89

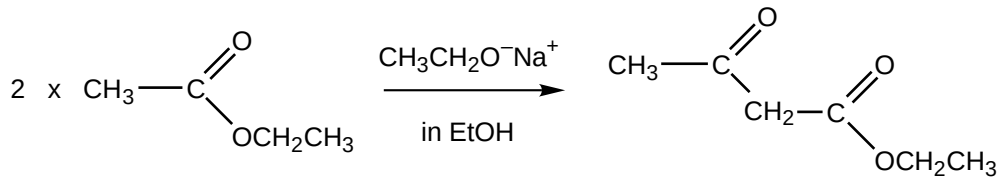
4,7-Dimethylferroin	Pale blue	Red	0.88
Diphenylaminesulfonic acid	Red-violet	Colourless	0.85
Diphenylbenzidine	Violet	Colourless	0.76
Diphenylamine	Violet	Colourless	0.76
3,3'-Dimethylnaphthidine	Purplish-red	Colourless	0.71
Starch-I_3^-,KI	Blue	Colourless	0.53
Methylene blue	Blue	Colourless	0.52

Organic Section (45 minutes)

Students must attempt **EITHER** Question 5 **OR** Question 6.

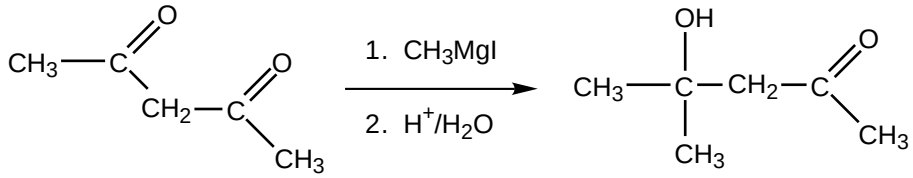
Question 5

a) The Claisen condensation is a reaction related to the aldol condensation, but which involves esters rather than ketones or aldehydes. An example is shown below:



The product is a β-keto ester, here called acetoacetic ester. From what you know of carbanion chemistry and the aldol condensation, suggest a mechanism for this particular reaction.

b) With the principles governing the aldol reaction in mind, why would the following reaction not be successful?

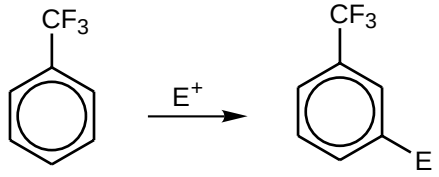


What alternative event occurs? Draw the stable charged species that is produced. Explain the reason for its stability.

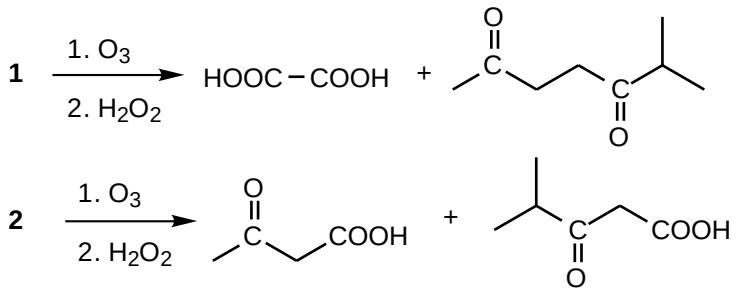
Question 6

In (a) do (i), (ii) and (iii)

a) (i) Explain why the trifluoromethyl group is meta directing in the reaction shown below.



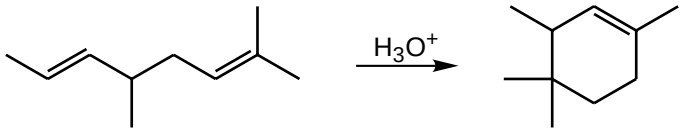
(ii) α-Terpinene (**1**) and γ-terpinene (**2**) are isomeric compounds ($C_{10}H_{16}$) that are constituents of many plants. Upon catalytic hydrogenation, they both afford 1-isopropyl-4-methylcyclohexane. However, on ozonolysis followed by oxidative workup, each compound yields different products. Provide structures for **1** and **2** and explain your reasoning.



(iii) The common practice of washing laboratory glassware with propanone (acetone) can lead to unintended consequences. For example, a student plans to carry out the preparation of methylmagnesium iodide, CH_3MgI, which he will add to benzaldehyde, C_6H_5CHO. What compound is he intending to synthesise after aqueous workup? Using his freshly washed glassware, he carries out the procedure and finds that he has produced an unexpected tertiary alcohol as a product. What substance did he make? How did it form?

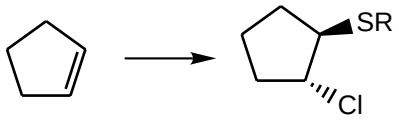
In (b) do (i) and EITHER (ii) OR (iii)

b) (i) Many additions to double bonds are initiated by electrophiles, and one common electrophile is H^+, which can initiate carbocation formation. Using this knowledge , coupled with what you know of the reactivity of carbocations, provide a mechanism for the following reaction.



Either

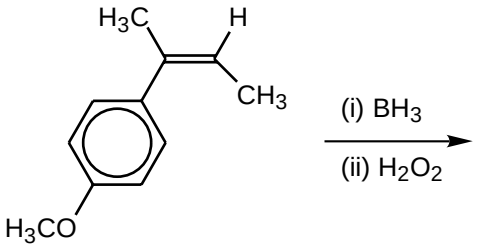
(ii) Sulfenyl chloride (RSCl) will undergo electrophilic addition to double bonds, as shown below.



Propose a suitable mechanism for this reaction being sure to explain why only one stereoisomer is formed in the reaction.

Or

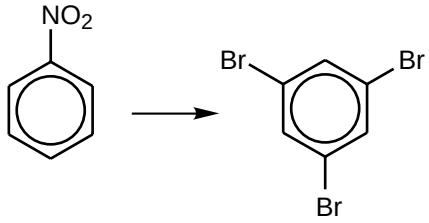
(iii) Deduce the structure, and stereochemistry of the product obtained in the following reaction.



Illustrate your answer with an appropriate saw-horse diagram or flying wedge diagram.

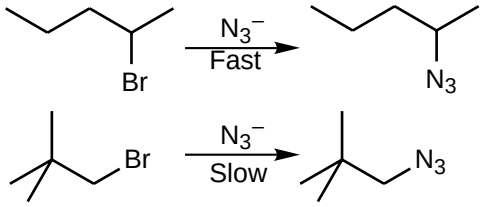
In (c) do (i) OR (ii) AND (iii)

c) (i) Devise a synthetic sequence to achieve the following transformation.



Or

(ii) Azide anion is known to react by an S_N2 pathway thousands of times more rapidly with 2-bromopentane than with its isomer neopentyl bromide (1-bromo-2,2-dimethylpropane) despite the fact that the leaving group is at a secondary site in the former and at a primary site in the latter.



Explain this difference in reactivity.

And

(iii) To reach the conclusion that the reaction with 2-bromopentane cited in the previous question did ideed occur through an S_N2 reaction, the chemists studying the reaction did several additional experiments in which they:

1. used optically active (*R*)-2-bromopentane.
2. doubled the concentration of alkyl bromide.
3. doubled the concentration of azide ion.

Predict what they would have seen in each experiment if the reaction really took place through an S_N2 pathway.