



**FINAL SELECTION
EXAMINATION
for the
2005 AUSTRALIAN CHEMISTRY
OLYMPIAD TEAM**

PART A

2004

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.

Instructions to Student

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.
3. All questions to be attempted. 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 **ALL** of the pages (even those you may have left blank) in this examination booklet.
8. Use only **black** or **blue pen** for your written answers, **pencil or other coloured pens are not acceptable**.

Supervisor Declaration

I certify that the final selection examination was carried out under strict examination conditions and that no improper actions occurred during the examination period.

Name of Exam Supervisor: *(please print)*

Signed: Date:

**Please use the enclosed pre-addressed Express Post Envelope to return the Examination.
(Mr R W Switzer, ASO Chemistry program, PO Box 589, Mudgeeraba QLD 4213).**

**EXAMINATIONS MUST BE RECEIVED BY
FRIDAY 11th MARCH 2005.**

Question 1 (20 minutes)

Data: Conjugated C-C bond length = 1.4×10^{-10} m
 Mass of electron $m_e = 9.109 \times 10^{-31}$ kg
 Planck's constant $h = 6.626 \times 10^{-34}$ J s
 Speed of light in a vacuum $c = 2.998 \times 10^8$ m s⁻¹

A flaw of the particle-in-a-box approximation, when it is applied to a pi-conjugated chain of carbon atoms, is that it assumes uniform zero potential energy inside the carbon chain pi system. A better approximation (Hückel, 1931) is to apply the linear combination of atomic orbitals (LCAO) method to the p atomic orbitals (with nodes in the plane of the carbon skeleton). In a pi-conjugated chain of n carbon atoms, the first n waveforms of the particle-in-a-box can be used qualitatively as a guide to the appropriate phase of each p orbital.

For example, in ethene ($n = 2$), the two waveforms and corresponding Hückel molecular orbitals are given in figure 1:

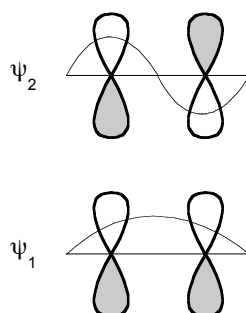


Figure 1

- (a) Draw the particle-in-a-box waveforms and corresponding Hückel molecular orbitals for the following:
- (i) 1,3-butadiene
 - (ii) 1,3,5-hexatriene

We will stick with the particle-in-a-box model when working with the energies of these waveforms.

- (b) Derive the formula that gives the allowed energy levels for a particle of mass m in a box of length L .

Woodward and Hoffmann (ca. 1965) found that, in single-step reactions, the symmetries of molecular orbitals (MO's) participating in the reaction are crucial in determining products. One such set of reactions is the electrocyclic reactions, which results in the formation of cyclobutene from butadiene, and cyclohexadiene from hexatriene:



Figure 2

In these electrocyclic reactions, the p orbitals of the two terminal carbons (of the pi-conjugated system) rotate 90° to form a sigma bond. The direction of rotation is such that the resulting p orbitals must give a positive overlap necessary for bonding. All other substituents of the terminal carbon rotate in the same direction as the p orbital rotation.

It should be noted that ideally the frontier orbitals (HOMO or LUMO) are involved in formation of the MO of the product. In electrocyclic reactions it is the HOMO that is involved.

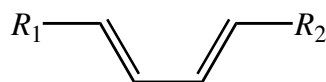


Figure 3

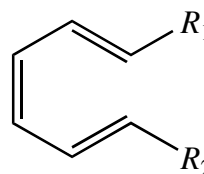


Figure 4

- (c) Predict whether the cis or the trans product will form when the following are reacted in normal thermal conditions, giving reasons for your choice:
- the butadiene derivative given in figure 3
 - the hexatriene derivative given in figure 4
- (d) Alternatively, these polyenes could be promoted to their first electronic excited state (by shining an appropriate light source on them) before the reaction.
- Explain whether or not the products in this *photochemical* reaction would be different from those you predicted for the thermal reaction in part (c).
 - What wavelength of light would be needed to promote the hexatriene derivative to its first excited state? Assume the box length to be six times the C-C bond distance. What region of the electromagnetic spectrum (e.g., microwave) is this?

The hydrogen-iodine reaction has long been assumed to proceed by a mechanism of a parallel approach of the hydrogen and iodine molecules, resulting in a square intermediate, followed by breaking of H-H and I-I bonds and simultaneous formation of H-I bonds (see figure 5). According to Woodward-Hoffmann concepts, this mechanism would involve either electron flow from the hydrogen HOMO to the iodine LUMO or from the iodine HOMO to the hydrogen LUMO.

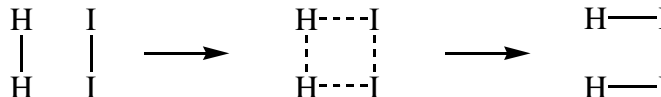


Figure 5

- (e) Use Woodward-Hoffmann's orbital symmetry concepts to show that this mechanism is **invalid**. (Hint: draw the HOMO and LUMO for both the hydrogen and iodine molecules)

Question 2 (20 minutes)

Consider the following coordination compounds: $[\text{Co}(\text{H}_2\text{O})_6]\text{SO}_4$, $\text{Cs}_2[\text{NiCl}_4]$ and $(\text{NBu}^n)_3[\text{Mn}(\text{CN})_6]$. [Note: $\text{Bu}^n = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$]

- Name each of the coordination compounds.
- Which of the compounds are expected to be paramagnetic? In each case clearly indicate the number of unpaired electrons associated with the transition metal ion in the complex and calculate the associated 'spin only' magnetic moment.
- For each of the transition metal ions in these complexes construct a clearly labelled d-orbital splitting diagram and calculate the crystal field stabilisation energy (CFSE) in terms of Δ_o .
- For each of the complex ions give an example of a related species containing the same transition metal ion with the same coordination number but a different ligand set and a different number of unpaired electrons. Why does each of these pairs of complexes have different numbers of unpaired electrons? In each case construct a clearly labelled d-orbital splitting diagram and calculate the crystal field stabilisation energy (CFSE) in terms of Δ_o .

Question 3 (20 minutes)

Data: $E^{\circ}_{(\text{Sn}^{4+}/\text{Sn}^{2+})} = 0.15 \text{ V}$ at 298K

$E^{\circ}_{(\text{Co}^{3+}/\text{Co}^{2+})} = 1.81 \text{ V}$ at 298K

$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$

$F = 96485 \text{ Cmol}^{-1}$

25.0 mL of a 0.0250M solution of Sn^{2+} is titrated with a 0.0500M Co^{3+} solution at 298K.

- (a) Write a balanced equation for the overall reaction.
- (b) Find E° , ΔG° and K for this reaction.

The titration was monitored by connecting the reaction vessel to a standard hydrogen electrode thus allowing the potential to be measured.

- (c) What is the potential (ie.the value of $E_{(\text{Sn}^{4+}/\text{Sn}^{2+})}$ or $E_{(\text{Co}^{3+}/\text{Co}^{2+})}$) after the addition of:
- (i) 5.00 mL of Co^{3+}
 - (ii) 10.00 mL of Co^{3+}
 - (iii) 15.00 mL of Co^{3+}
 - (iv) 20.00 mL of Co^{3+}
 - (v) 24.00 mL of Co^{3+}
 - (vi) 25.00 mL of Co^{3+}
 - (vii) 26.00 mL of Co^{3+}
 - (viii) 50.00 mL of Co^{3+}
- (d) When is the measured potential equal to $E^{\circ}_{(\text{Sn}^{4+}/\text{Sn}^{2+})}$? Explain.

Two indicators, A and B, are proposed for this titration. Use the information below to determine if the indicators are appropriate for this titration.

1.The electrochemical cell:

$\text{Pt (s)} \mid \text{A (aq)} 0.0100\text{M} \mid \text{A}^+ \text{ (aq)} 0.100\text{M} \parallel \text{Co}^{3+} \text{ (aq)} 0.0100\text{M} \mid \text{Co}^{2+} \text{ (aq)} 0.100\text{M} \mid \text{Pt (s)}$

Gives a voltage of 0.99 V.

2. The electrochemical cell:

$\text{Pt (s)} \mid \text{B (aq)} 0.100\text{M} \mid \text{B}^+ \text{ (aq)} 0.0500\text{M} \parallel \text{A (aq)} 0.0500\text{M} \mid \text{A}^+ \text{ (aq)} 0.100\text{M} \mid \text{Pt (s)}$

Gives a voltage of 0.30 V.

- (e) Find the value of $E^{\circ}_{(\text{A}^+/\text{A})}$.
- (f) Is A an appropriate indicator for this titration?
- (g) Find the value of $E^{\circ}_{(\text{B}^+/\text{B})}$.
- (h) Is B an appropriate indicator for this titration?

Question 4 (20 minutes)

Data: $K_{\text{sp}}(\text{Cu}(\text{OH})_2) = 4.50 \times 10^{-21}$

$\text{MW}(\text{Cu}(\text{OH})_2) = 97.59 \text{ g mol}^{-1}$

$\text{p}K_{\text{b}}(\text{NH}_3) = 4.76$

- (a) For this part of the question you may assume all reactions occur at 298 K.

Complexation of metal ions can sometimes shift the equilibrium of a poorly soluble compound such that it can redissolve back into solution. One would already be familiar with the use of NH_3 to dissolve AgCl in the inorganic qualitative analysis practical.

Copper hydroxide has low solubility in water.

- (i) Calculate the solubility of $\text{Cu}(\text{OH})_2$ in water in g/100 mL.
 - (ii) What is the pH of the solution? Ignore the effects of water autodissociation.
- (b) Solubility of the metal hydroxide can be increased by complexing the metal ion to a ligand such as ammonia. 25.00 mL of NH_3 was added to a 5.00 mg sample of $\text{Cu}(\text{OH})_2$ such that all the metal hydroxide dissolved and the equilibrium concentration of NH_3 was 1.00×10^{-3} M.
- (i) What is the analytical concentration of Cu in solution?
 - (ii) Calculate the concentration of all Cu species at equilibrium.
 - (iii) Calculate the concentration of NH_3 and NH_4^+ at equilibrium.
 - (iv) What is the pH of the solution?
 - (v) What is the original concentration of the NH_3 solution?

Question 5 (40 minutes)

- (a) A white solid **X** was found by chemical tests to be an aromatic carboxylic acid of molecular formula $\text{C}_8\text{H}_8\text{O}_2$. To determine its structural formula, a 0.7311 g sample was ignited in excess oxygen in a “bomb” (constant-volume) calorimeter. The reaction compartment was surrounded by 611.8 g of water initially at 20.519 °C, and the heat capacity of the calorimeter itself (excluding the water) was 52.00 J K⁻¹. After the combustion was complete, the temperature of the water was measured to be 28.454 °C.

Data:

$$0^\circ\text{C} = 273.15 \text{ K}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$c_{\text{sp}}(\text{H}_2\text{O}(\text{l})) = 4.184 \text{ J K}^{-1} \text{ g}^{-1}$$

$$\Delta_f H^\circ(\text{H}_2\text{O}(\text{l})) = -285.83 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(\text{CO}_2(\text{g})) = -393.51 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(\textit{ortho}\text{-methylbenzoic acid}(\text{s})) = -417 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(\textit{meta}\text{-methylbenzoic acid}(\text{s})) = -426 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(\textit{para}\text{-methylbenzoic acid}(\text{s})) = -429 \text{ kJ mol}^{-1}$$

$$\text{Atomic masses: C} = 12.01, \text{H} = 1.008, \text{O} = 16.00$$

- (i) Calculate q , w , ΔU and ΔH for this particular experiment (i.e., *not* molar quantities).
 - (ii) Hence calculate the standard molar enthalpies of combustion and formation, $\Delta_c H^\circ$ and $\Delta_f H^\circ$, for **X**. What is the structural formula of **X**?
- (b) One of the oldest “industrial” applications of chemistry (recorded by Julius Caesar in Britain in 55 BCE, although it was not new then) is the extraction of tin from its ore cassiterite by heating the ore with glowing coals:
- $$\text{SnO}_2 + \text{C} \rightarrow \text{Sn} + \text{CO}_2$$
- At 298 K, $\Delta H^\circ = 184.1 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = 210.3 \text{ J K}^{-1} \text{ mol}^{-1}$ for this reaction.
- (i) Calculate ΔS_{surr} and ΔS_{univ} for this reaction at 298 K. Is the reaction spontaneous at this temperature? Now consider performing this reaction at 1500 K. We *cannot* assume ΔH° and ΔS° to be the same as at 298 K, so we’ll have to calculate them, taking into account the heat capacities of the reactants and products as well as the fact that tin melts at 505 K.
 - (ii) Propose a suitable five-step pathway to calculate ΔH° and ΔS° at 1500 K.
 - (iii) Use the following data to calculate ΔH° and ΔS° at 1500 K for each step in your pathway from part (ii).

Heat capacities (assumed constant over the relevant temperature range)

	$c_p / \text{J K}^{-1} \text{mol}^{-1}$
Sn (s)	27.0
Sn (l)	29.0
SnO ₂ (s)	52.6
C (s)	8.53
CO ₂ (g)	37.1

$$\Delta_{\text{fus}}H^\circ (\text{Sn}) = 7.07 \text{ kJ mol}^{-1} \text{ at } 505 \text{ K.}$$

- (iv) Hence calculate ΔS_{surr} and ΔS_{univ} at 1500 K. Is this reaction spontaneous at this temperature?
- (c) The reaction between acetone and iodine in acidic aqueous solution was studied to determine its rate law. It was found that at pH = 1.30, the initial rate of reaction was independent of the initial iodine concentration. The concentration of acetone was monitored over time in a buffer at this pH, and the results are tabulated below:

t / h	0	24	48	72	96	120	144
[acetone] / mol L ⁻¹	0.200	0.163	0.133	0.109	0.089	0.080	0.080

- (i) What happened at about $t = 107 \text{ h}$?
- (ii) What is the order of this reaction with respect to acetone? What is the order of this reaction with respect to iodine? Explain your reasoning.

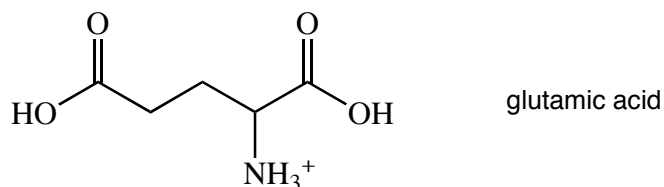
The initial rate of reaction was then determined in several different pH buffers, keeping the initial concentrations of acetone and iodine constant at 0.200 mol L⁻¹ and 0.015 mol L⁻¹ respectively, and the following data were obtained:

pH	$\left(\frac{d[\text{I}_2]}{dt}\right)_{\text{initial}} / 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$
1.30	0.468
1.00	0.936
0.82	1.40

- (iii) Write down the differential rate law for this reaction and determine its rate constant.

Question 6 (20 minutes)

Glutamic acid is an amino acid residue with an acidic sidechain; its structure is shown below:

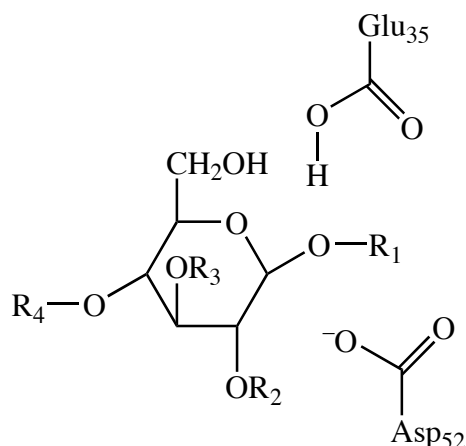


- (a) The pK_a values for each of the ionisable groups in glutamic acid are 2.2, 4.3 and 9.4. Which belongs to which group, and why?
- (b) The pI of an amino acid is defined as the pH at which the maximum mole fraction of amino acid having overall neutral charge is obtained. What is the pI of glutamic acid?

Lysozyme is an enzyme that protects us against bacterial infection. It catalyses the hydrolysis of polysaccharide chains present in bacterial cell walls (it is these chains that are cross-linked in the reaction that penicillin inhibits). When the structural integrity of the cell wall is compromised, the bacteria burst open and die. Interestingly Sir Alexander Fleming (of

penicillin fame) also discovered the action of lysozyme: once when he had a cold a drop of his mucus fell into a bacterial culture and, much to his surprise, killed all the bacteria!

The active site of lysozyme with its substrate bound is shown below (R_1 and R_4 are the rest of the polysaccharide chain; the R_1 -OH moiety is cleaved in this reaction):



- (c) The pK_a values for the sidechains of aspartate and glutamate when free in solution are very similar, however in the active site of lysozyme, one is fully deprotonated and the other is fully protonated. Explain why this may occur.
- (d) Give a mechanism for the action of lysozyme. Explain the contributions of Glu_{35} and Asp_{52} to the mechanism.

Organic Section (45 minutes)

Question 7 (12 minutes)

(2*S*, 3*R*)-2-chloro-3-deutero-1,1-dimethylcyclohexane **A** was treated with sodium hydroxide in acetone to give **B**. **B** was subsequently treated with bromine in carbon tetrachloride to give the product **C**. (deutero refers 2H).

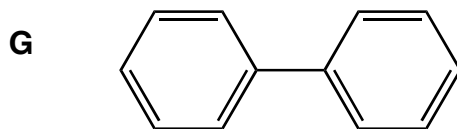
- (a) Draw the structure of **A**, and draw and name **B** and **C**, indicating any stereochemistry involved.

(*R*)-3-hydroxy-2,2,3-trimethylhexane **D** was treated with acid to produce alkene **E**. **E** was then treated with diborane followed by alkaline hydrogen peroxide, to give **F**.

- (b) Draw the structure of **D**, and draw and name **E** and **F**, indicating any stereochemistry involved.

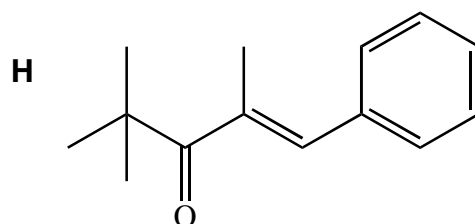
Question 8 (9 minutes)

What are the major product(s) when biphenyl (**G**) is treated with concentrated sulfuric and nitric acids? Draw the reaction mechanism to justify your answer. Consider only mononitrated products. There is no need to name the product(s).



Question 9 (10 minutes)

A chemistry researcher wants to synthesise 2,4,4-trimethyl-1-phenylpent-1-en-3-one (**H**).



- For this synthesis, he plans to use benzaldehyde and a ketone (**I**).
- (a) Draw and name the ketone **I** which he could use.
 - (b) Provide a mechanism for the formation of **H** from benzaldehyde and **I**. Include any other reagents/conditions which are required.
 - (c) Will **H** be the major product of this process? Why/why not?

Question 10 (9 minutes)

A sample of 2-methylcyclohexanone is divided into two flasks, which are treated as follows:

To flask 1 is added sodium hydroxide in acetone. The flask is stirred at 25 °C for 20 minutes, then the product **J** is isolated.

To flask 2 is added an aqueous solution of sodium ethoxide. The flask is stirred at 60 °C for 5 hours, after which time the product **K** is isolated.

J and **K** are analysed and found to be sodium salts which are structural isomers of one another.

- (a) Of products **J** and **K**, which is the kinetic product, and which the thermodynamic? Explain.
- (b) Show mechanisms for the formation of **J** and **K**, justifying the outcomes of the reactions, and clearly showing the structures of **J** and **K**.