



FINAL SELECTION EXAMINATION
for the
2004 AUSTRALIAN CHEMISTRY
OLYMPIAD TEAM

PART B

2003

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** 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:

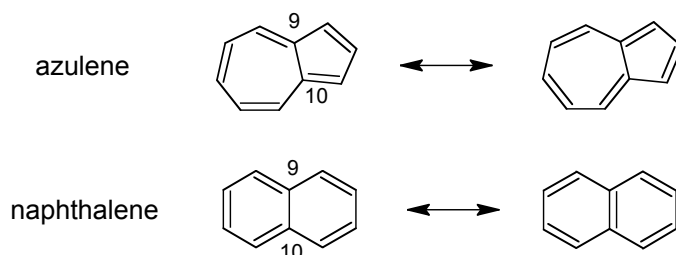
Please use the enclosed pre-addressed Express Post Envelope to return the Examination.
(Mr R W Switzer, RTASO Chemistry program, PO Box 589, Mudgeeraba QLD 4213).

EXAMINATIONS MUST BE RECEIVED BY
FRIDAY 19th MARCH 2004.

Question 1 (20 minutes)

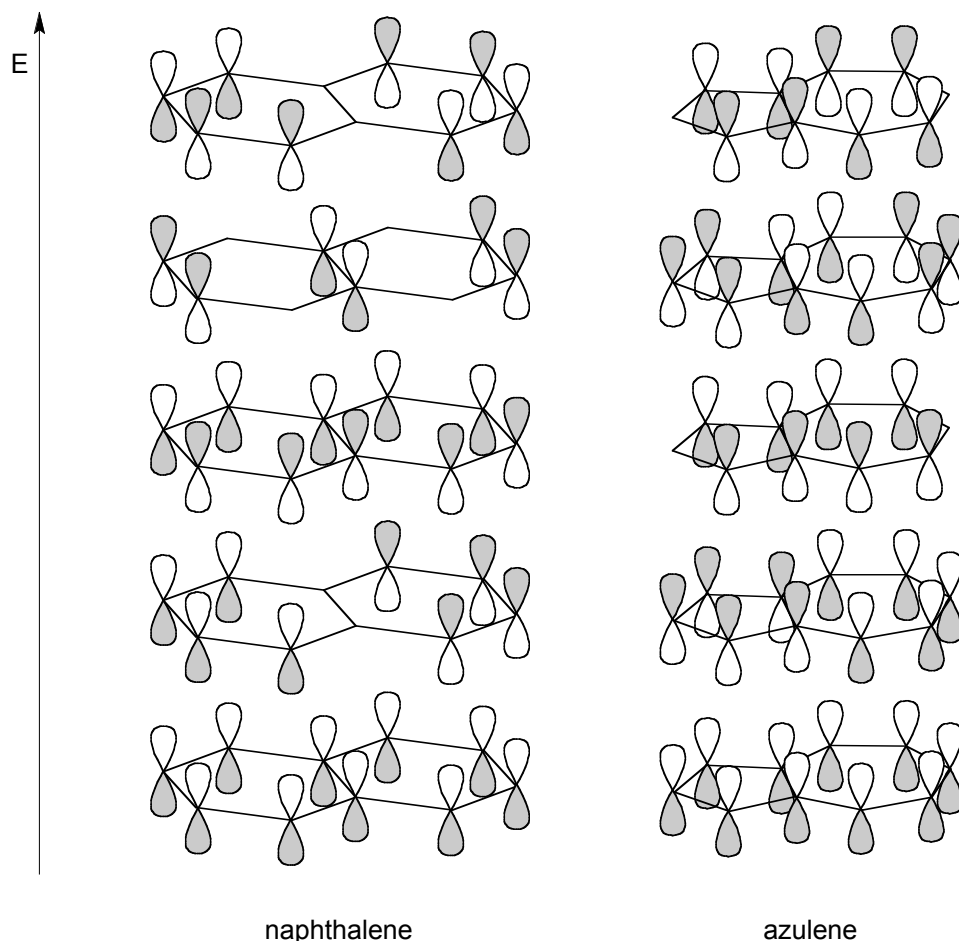
Data:	h	Planck's constant	$6.626 \times 10^{-34} \text{ J s}$
	c	Speed of light in vacuum	$2.998 \times 10^8 \text{ m s}^{-1}$
	m_e	Electron rest mass	$9.020 \times 10^{-31} \text{ kg}$
		Carbon-carbon bond length in azulene	1.4 \AA
	1 \AA	Ångström	10^{-10} m

Azulene, C_{10}H_8 , is an aromatic hydrocarbon isomeric to naphthalene. Interestingly, unlike naphthalene, it has no resonance structure with a double bond between carbons 9 and 10.

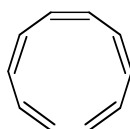


This suggests that its π -electrons are delocalised only around the edge of the ring, not across the C9-C10 bridge, and hence that it might be valid to predict these electrons' behaviour using the particle-in-a-ring model.

- (a) Suppose to begin with that this is indeed a valid model of the π -system.
- Sketch the wavefunctions of the lowest energy level and the two HOMOs.
 - Give a general expression for the possible wavelengths for a particle in a ring of circumference C .
 - Use the de Broglie wavelength relationship to derive a general expression for the energy levels accessible to a particle in this ring.
 - Choose an appropriate circumference for the azulene ring, and hence predict the main wavelength absorbed by azulene. In what region of the electromagnetic spectrum is this absorbance peak?
- (b) Don't forget, though, that all this work is based on nothing more substantial than a few VSEPR resonance structures. To confirm that our conjecture is correct, we turn to molecular orbital theory. Erich Hückel (1896-1980), a German physical chemist, developed a method of calculating the MOs of π -systems that predicts the orbitals depicted in the following diagram. (Note that the individual carbon p orbitals have been shown for clarity, although of course the real 90% inclusion surface would show these orbitals merging together. In addition, the diagram is not to scale, and only occupied MOs are shown.)



- (i) Use the rules of qualitative molecular orbital theory to predict the effect on the total energy of the π -system of breaking the C9-C10 bond in both naphthalene and azulene. Is our conjecture that the π -electrons are not delocalised across this bond in azulene correct? What about in naphthalene?
- (ii) This should explain why the result in (a) above applies to azulene – and why it doesn't to naphthalene. One question, however, remains. Based on the above analysis, we might expect the properties of azulene to be very similar to those of cyclodecapentaene.



cyclodecapentaene

In fact, though, their properties are radically different: azulene is a stable molecule while cyclodecapentaene is so unstable that it can't be isolated. Can you suggest – in terms of MO theory, of course – a reason why we can't apply the above result to cyclodecapentaene?

Question 2 (25 minutes)

Calcium cyanamide (CaCN_2) is a very versatile and powerful fertilizer. It can be produced easily from cheap and common chemicals such as CaCO_3 . The thermal decomposition of CaCO_3 leads to a white solid **A** and a colorless gas **B** which does not sustain combustion. A greyish solid **C** and a gas **D** form by the reduction of **A** with carbon. Both **C** and **D** can be further oxidized. The reaction of **C** with nitrogen finally leads to CaCN_2 .

- (a) Identify species **A** \rightarrow **D** and write balanced equations for each of the reactions leading to the synthesis of calcium cyanamide from calcium carbonate?
- (b) Both CaCN_2 and **C** readily react with water to give a gaseous product **E** and **F**, respectively. Identify **E** and **F** and write a balanced equation for the two reactions. Sketch the molecular structures of **E**, **F** and the cyanamide ion.
- (c) In solid state chemistry the cyanamide ion shows constitutional isomerism. The free acids of both anions (at least in the gas phase) are known (referred to as cyanamide). Draw the

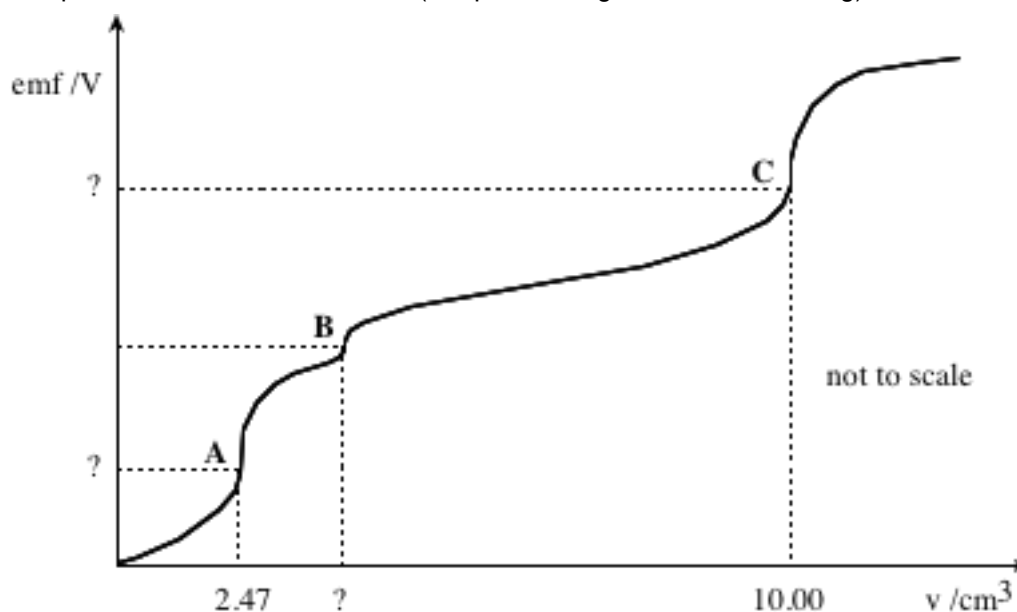
structural formulas of both isomeric free acids. Indicate on which side the equilibrium is favored. Draw a hybrid orbital diagram for each of the acids.

- (d) Cyanamide is known to dimerize at pH 7-9 to form dicyandiamide or on heating to *ca* 150 °C to trimerize to give melamine, a cyclic compound with a 'benzene-like' structure. Sketch the molecular structures of the dimer and trimer.

Question 3 (45 minutes)

Data:	$E_0(\text{Ag}^+/\text{Ag}) = 0.800 \text{ V}$	$\log K_{\text{stab}}([\text{Ag}(\text{CN})_2]^-) = 21.1$
	$E_0(\text{SCE}) = 0.285 \text{ V}$	$F = 96485 \text{ C mol}^{-1}$
	$\text{p}K_{\text{sp}}(\text{AgCN}) = 15.8$	$R = 8.315 \text{ J K}^{-1} \text{ mol}^{-1}$
	$\text{p}K_{\text{sp}}(\text{AgCl}) = 9.75$	$= 8.206 \times 10^{-2} \text{ L atm J K}^{-1} \text{ mol}^{-1}$

An electrochemical cell is prepared by placing a silver electrode in 25.00 mL of a neutral solution containing potassium chloride and potassium cyanide, then joining a standard calomel electrode with a potassium nitrate salt bridge. The KCl/KCN solution is then potentiometrically titrated with a standard 0.1000 M silver nitrate solution at 25 °C. The potentiometric curve obtained (cell potential against burette reading) is shown below.



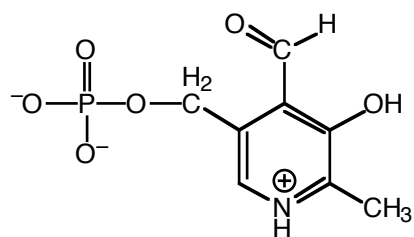
Throughout this problem, you may assume that protonation of the cyanide ion is negligible.

- The endpoints of the reactions taking place during the titration are marked with **A**, **B** and **C**. Write a balanced ionic equation for each reaction.
- What volume of the titrant is required to reach point **B**?
- Calculate the concentrations of KCl and of KCN in the sample solution.
- Calculate the emf readings at points **A** and **C** in volts.
- What is the molar ratio Cl^-/CN^- in the solution at point **C**?
- What is the molar ratio Cl^-/CN^- in the precipitate at point **C**?

Question 4 (45 minutes)

Data:	Atomic weights: C 12.0107g mol ⁻¹ N 14.0067 g mol ⁻¹ O 15.9994 g mol ⁻¹	
	$C_p(\text{O}_2(\text{g})) = 27.4 \text{ J K}^{-1} \text{ mol}^{-1}$	$C_p(\text{CO}_2(\text{g})) = 31.0 \text{ J K}^{-1} \text{ mol}^{-1}$
	$C_p(\text{N}_2(\text{g})) = 29.1 \text{ J K}^{-1} \text{ mol}^{-1}$	
	At 298 K: $\Delta_f H^\circ(\text{CO}_2(\text{g})) = -393.3 \text{ kJ mol}^{-1}$	$\Delta_f H^\circ(\text{CO}(\text{g})) = -110.4 \text{ kJ mol}^{-1}$

- Consider the combustion reaction of carbon monoxide.
 - What is the value for $\Delta_{\text{comb}} H^\circ(\text{CO}(\text{g}))$ at 298K?
 - Air from a bus garage was sucked first through a desiccant (to remove water vapour) and then through a vessel containing hopcalite, a catalyst that can bring about complete combustion of carbon monoxide at room temperature. The temperature difference between the air entering

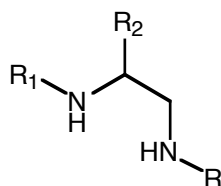


Pyridoxal phosphate (PLP)

- (a) Draw the structure of this imine intermediate.
- x The second step is a typical PLP reaction; a resonance-stabilised one-carbon reactive intermediate is produced, along with another resonance-stabilised intermediate.
- (b) Give the mechanism for this reaction; and draw resonance structures for both the one-carbon reactive intermediate and the other intermediate.

The one-carbon reactive intermediate then reacts in a series of steps with tetrahydrofolate to form methylenetetrahydrofolate and water (and a proton).

- (c) Draw the mechanism for this reaction. For clarity you may abbreviate the structure of tetrahydrofolate to the following:



The last step is addition of a proton to form a glycine-PLP imine, which is then hydrolysed to glycine and PLP.

- (d) Draw a mechanism for the hydrolysis of the glycine-PLP imine.

Question 6 (30 minutes)

A mixed aldol condensation with benzaldehyde and *p*-methylacetophenone (*p*-methylphenyl methyl ketone) in the presence of sodium ethoxide, gives **A** and **B** as the major products ($C_{16}H_{16}O_2$ and $C_{18}H_{20}O_2$ respectively). **A** reacts with acidified sodium dichromate to form **C**, but **B** gives no reaction. When **C** is treated with sodium ethoxide in ethanol, followed by 2-(iodomethyl)-1,3-dichloropropane, **D** is formed, which when treated with zinc amalgam in concentrated hydrochloric acid forms **E**. Heating **E** with aluminium chloride gives **F**.

When **B** is treated with hydrogen and a palladium on carbon catalyst **G** is formed, which when heated in concentrated sulfuric acid gives **H**, which decolourises bromine water. **H** subsequently reacts with ethanoyl chloride and $AlCl_3$ to produce a mixture of products, of which **I** is the major product. Upon treatment with iodine in sodium hydroxide, **I** gives **J** ($C_{19}H_{20}O_2$) and a yellow precipitate. Treatment of **J** with OsO_4 followed by basic hydrolysis affords **K**, which does not react with bromine water. When **K** is heated with concentrated sulfuric acid **L** is formed. **L** is resistant to oxidation by acidified potassium dichromate solution.

- (a) Draw the structures of all compounds **A-K**. If different stereoisomers of a compound are possible, draw only one, but indicate which others are possible.
- (b) Draw the structure of **L**. How many stereoisomers of **L** are possible? How many will be produced from this synthetic route?