



FINAL SELECTION
EXAMINATION
for the
2005 AUSTRALIAN CHEMISTRY
OLYMPIAD TEAM

PART B

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)

The theory of promotion-hybridization is quite successful at explaining why covalent molecules with a central atom from period 3 or higher (e.g. SF_6 , PF_5 , I_3) are stable even though they are hypervalent (i.e. they appear to “exceed the octet rule”). However, hybridization is inadequate in explaining the remarkable stability of molecules such as the so-called “hyperlithiated” carbon species such as CLi_6 . Molecular orbital theory can be applied to CLi_6 (Reed and Weinhold, 1985) for an alternate explanation to when and why hypervalent molecules with central atom of period 2 can be stable.

Of all the different types of atomic orbitals (e.g. s , p_x , d_{yz} , etc) of a general central atom, six of these will participate in the forming of sigma bonds with the molecular orbitals of six ligands *in an octahedral geometry*. The valence s orbital is one of them. Note that the ligands approach the central atom along the three coordinate axes.

- (a) Which other five atomic orbitals can also do this?

Now, we shall consider the molecular orbitals (MO) of the 6 Li 2s orbitals (in an octahedral geometry). The lowest energy MO is given below in figure 1:

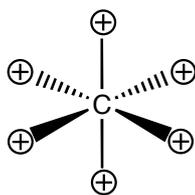


Figure 1

According to quantitative calculations, the MO in figure 1 is the **only** MO lower in energy than the uncombined lithium 2s orbital; all other MOs are slightly higher in energy than uncombined Li 2s and can thus be considered as antibonding. (Note that this is generally true for 2 to 8 Li atoms arranged symmetrically around the central atom).

The s orbital will overlap with the MO given in figure 1. Exactly one of the other five MOs will have the right symmetry to overlap (and form a sigma bond) with each of the other five atomic orbitals of the central atom.

- (b) Hence draw the other five MOs obtained by linear combinations of the 6 Li 2s orbitals. Indicate their relative energies on an energy diagram.
- When the central atom is carbon, three of the six MOs (of the 6 Li 2s orbitals) will not combine with the corresponding atomic orbital of carbon. One of these is the one drawn in figure 1. Because carbon is much more electronegative than lithium, the 2s orbital of carbon is too low in energy to mix with the MO in figure 1.
- (c) Which other two MOs will not combine when carbon is the central atom? Provide a rationale as to why this is so.
- (d) Hence, draw the molecular orbital energy diagram of CLi_6 . Keep in mind the relative energies of carbon AOs and the six Li MOs (as carbon is more electronegative than lithium).
- (e) Using the energy diagram in part (d), explain the stability of CLi_6 .
- (f) Propose an alternative to the “octet rule” when predicting stability of hyperlithiated species of period 2 atoms. Using this rule, identify possible neutral (i.e., not cations or anions) hyperlithiated species of nitrogen and oxygen that can exist due to the same stability reason as that of CLi_6 .
- (g) Can CH_6 exist? If so, why so? If not, why not?

Question 2 (20 minutes)

The transition metal elements are widely distributed in the Earth’s crust. Many of these elements find uses in everyday objects: iron pipes, copper wiring, chromium auto parts, etc.

- (a) Properties of Chromium

Chromium is a silvery-white, lustrous metal, whose name (from the Greek chroma, meaning colour) alludes to its many colourful compounds. The bright colours of chromium (VI) compounds lead to their use in pigments for artists’ paints and ceramic glazes.

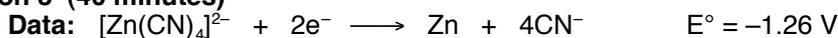
- (i) In an acidic solution, the yellow chromate ion (CrO_4^{2-}) changes into the orange dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$). Write the equation for the reaction.

- (ii) What is the oxidation state of each metal centre in the chromate ion and the dichromate ion?
- (iii) Is this a redox reaction? Explain.
- (iv) What is the main factor that controls the equilibrium position?
- (v) Draw the three-dimensional structures of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$.

(b) Uses of Chromium

An antique automobile bumper is to be chrome plated. The bumper is dipped into an acidic $\text{Cr}_2\text{O}_7^{2-}$ solution where it serves as the cathode of an electrolytic cell. (The atomic mass of Cr is 51.996; 1 F = 96,485 C.)

- (i) Given that oxidation of H_2O occurs at the anode, write equations for the two half-reactions and the overall cell reaction.
 - (ii) How many moles of oxygen gas will be evolved for every 52.0 g of chromium deposited?
 - (iii) If the current is 10.0 amperes, how long will it take to deposit 52.0 g of chromium onto the bumper?
 - (iv) What is the chemical reason that chromium is so useful for decorative plating on metals?
- (c) A qualitative test for chromium involves the treatment of an acidic dichromate solution with H_2O_2 to give the unstable blue compound CrO_5 , which can be stabilized by extraction into ether or the addition of a unidentate ligand such as pyridine (py) to give the isolatable pentagonal pyramidal complex $\text{CrO}_5(\text{py})$.
- (i) Write a balanced equation for the formation of CrO_5 .
 - (ii) What is the oxidation state of chromium in CrO_5 and $\text{CrO}_5(\text{py})$? Sketch the structure of $\text{CrO}_5(\text{py})$.

Question 3 (40 minutes)

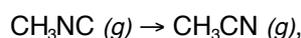
$K_f([\text{Au}(\text{CN})_2]^-) = 4.00 \times 10^{28}$

- (a) Metallic gold frequently is found in aluminosilicate rocks and it is finely dispersed among other minerals. It may be extracted by treating the crushed rock with aerated NaCN solution. During this process metallic gold is slowly converted to $[\text{Au}(\text{CN})_2]^-$, which is soluble in water (reaction 1).
- After equilibrium had been reached, the aqueous phase is pumped off and the metallic gold is recovered from it by reacting the gold complex with zinc, which is converted to $[\text{Zn}(\text{CN})_4]^{2-}$ (reaction 2).
- (i) Write balanced ionic equations for reactions 1 and 2.
- Gold in nature is frequently alloyed with silver which is also oxidised by aerated NaCN solution. 500.0 L of a solution 0.0100 M in $[\text{Au}(\text{CN})_2]^-$ and 0.00300 M in $[\text{Ag}(\text{CN})_2]^-$ was evaporated to one third of the original volume and was treated with 40.0 g of zinc.
- (ii) Assuming that deviation from standard conditions is unimportant and that all these redox reactions go essentially to completion, calculate the concentrations of $[\text{Au}(\text{CN})_2]^-$ and $[\text{Ag}(\text{CN})_2]^-$ after the reaction has ceased.
 - (iii) $[\text{Au}(\text{CN})_2]^-$ is a very stable complex under certain conditions. What concentration of cyanide ion is required to keep 99.0 mole % of the gold in solution in the form of the cyanide complex? You may assume that the formation of intermediate complexes is negligible.
- (b) A metal oxide **A** is dissolved in water and electrolysed. No gas was evolved in the reaction. A compound **B** was formed over the anode whilst a metal **C** was deposited on the cathode, with the mass of **C** being 1.79 times that of **B**. The combined weight of **B** and **C** was equal to **A**. Compound **B** was dissolved in slightly acidified water and electrolysed again. This time oxygen evolved at the anode whilst **C** is again formed at the cathode, this time the mass of **C** is half that of the amount of **C** obtained in the first electrolysis.

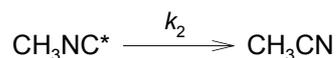
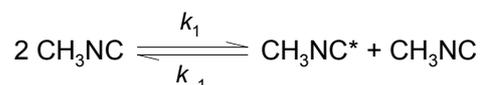
- (i) What is the percentage weight of oxygen in the metal oxide **A**?
- (ii) What is the percentage weight of oxygen in compound **B**?
- (iii) What is the ratio of the amount of metal reduced to metal oxidised in the first electrolytic step?
- (iv) Hence deduce the possible changes in oxidation state of the metal in the first electrolytic step (hint: there are two)
- (v) Hence deduce what **C** is (hint: oxygen has an oxidation number of -2 throughout the reactions).

Question 4 (40 minutes)Data: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $0^\circ \text{ C} = 273.15 \text{ K}$

- (a) It has puzzled chemists for some time how unimolecular elementary steps can actually occur; it seems far likelier that a molecule should react when colliding with another molecule (as in a bimolecular elementary step) than that it should somehow shake itself apart. In 1921, Frederick Lindemann proposed that reactions such as the isomerisation of methyl isocyanate,



which is experimentally found to obey first-order kinetics (rate = $k[\text{CH}_3\text{NC}]$), actually occur by a mechanism where a molecule first gains sufficient energy to react from a collision with another molecule, then the energised molecule, written CH_3NC^* , isomerises to CH_3CN .



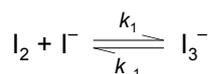
Use the steady-state approximation to determine the rate of formation of CH_3CN for this mechanism. Under what conditions does it agree with the experimental rate law? How could you test this mechanism?

- (b) Very fast reactions pose a different challenge to experimentalists bent on measuring their rate constants. With modern equipment we can mix solutions in about 10^{-3} s, but this isn't so brief on a molecular timescale: many reactions are already complete by the time the reaction mixture is homogenous.

To cope with this problem we need to be able to start reactions in even shorter times. One method is to change the temperature of a system at equilibrium; small temperature jumps can be achieved in about 10^{-8} s. If the change in temperature changes the equilibrium constant, then the system will no longer be at equilibrium, and we can measure the rate at which it adjusts to new equilibrium concentrations.

- (i) What thermodynamic condition must a reaction satisfy if a temperature jump is to change its equilibrium constant? Explain your reasoning.

One such reaction, which you have performed several times in the laboratory, is the formation of the triiodide ion in water:



Let's call the equilibrium concentrations at the new temperature $[\text{I}_2]_{\text{eq}}$, $[\text{I}^-]_{\text{eq}}$ and $[\text{I}_3^-]_{\text{eq}}$ respectively, and write the concentrations of each species as

$$[\text{I}_2] = [\text{I}_2]_{\text{eq}} - x$$

$$[\text{I}^-] = [\text{I}^-]_{\text{eq}} - x$$

$$[\text{I}_3^-] = [\text{I}_3^-]_{\text{eq}} + x$$

so that x is a parameter measuring the "distance" from the new equilibrium position, which eventually decreases to 0 as the reaction approaches equilibrium.

- (ii) From this definition of x , it follows that $\frac{dx}{dt}$ = (rate of forward reaction – rate of reverse reaction).
Express $\frac{dx}{dt}$ in terms of x , k_1 , k_{-1} , $[I_2]_{eq}$, $[I^-]_{eq}$ and $[I_3^-]_{eq}$.

We can simplify this expression in two ways. First, we can use the relationship between the rate and equilibrium constants for this reaction to relate k_1 , k_{-1} , $[I_2]_{eq}$, $[I^-]_{eq}$ and $[I_3^-]_{eq}$.

- (iii) Write down the relationship between these quantities.

Secondly, if the temperature jump is small then x will be small and x^2 so small that we can neglect it.

- (iv) Use this and your results from (ii) and (iii) to prove that $\frac{dx}{dt} = -rx$, where $r = k_1([I_2]_{eq} + [I^-]_{eq}) + k_{-1}$.

This is just the differential equation which we're used to solving for first-order reactions, and using the same techniques we can measure x over time and calculate r , the *relaxation constant*. In one experiment (Ruasse *et al.*, 1986), a solution initially containing 1.0 mmol L⁻¹ of I₂, 3.0 mmol L⁻¹ of I⁻, and no I₃⁻ was prepared and allowed to equilibrate at 18.0 °C. The temperature was then quickly increased to 25.0 °C. At 25.0 °C, $\Delta H^\circ = -18.8$ kJ mol⁻¹ and $\Delta S^\circ = -9.2$ J K⁻¹ mol⁻¹ for this reaction.

- (v) Calculate the equilibrium constant K for this reaction at 25.0 °C.

- (vi) Hence calculate $([I_2]_{eq} + [I^-]_{eq})$ at 25.0 °C.

- (vii) The relaxation constant r was measured to be 2.4×10^7 s⁻¹. Use this and your results from (iv), (v) and (vi) to calculate the rate constants k_1 and k_{-1} for the formation and dissociation of the triiodide ion.

- (c) Kinetic data can even be used to compute *thermodynamic* parameters for short-lived intermediates. For instance, the isopropyl radical has been characterised (Seakins *et al.*, 1992) through the reaction



The reaction was found to have Arrhenius parameters $A = 9.5 \times 10^8$ L mol⁻¹ s⁻¹ and $E_a = -6.4$ kJ mol⁻¹ as written, and $A' = 5.1 \times 10^{10}$ L mol⁻¹ s⁻¹ and $E_a' = 36$ kJ mol⁻¹ in the reverse direction.

- (i) Calculate ΔH° and ΔS° for this reaction, assuming that these quantities are independent of temperature over the range considered.

- (ii) Hence calculate $\Delta_f H^\circ$, S° and $\Delta_f G^\circ$ for the isopropyl radical at 298 K.

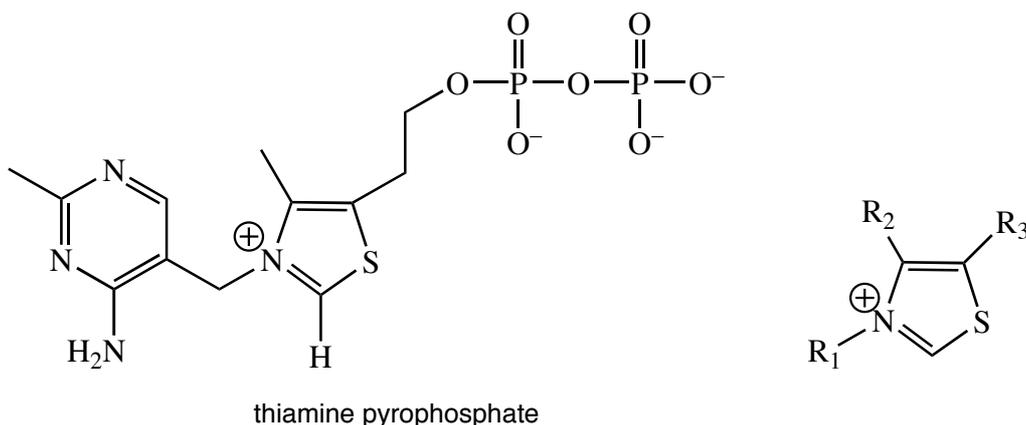
Data at 298 K:

	$\Delta_f H^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
C ₃ H ₈	-103.85	269.91
HBr	-36.40	198.70
Br [·]	111.88	175.02
H ₂		130.68
C		5.47

- (iii) Can you suggest why the reaction appears to have a negative activation energy?

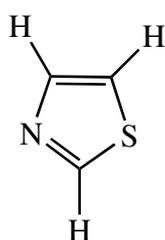
Question 5 (20 minutes)

Thiamine (vitamin B1) is a cofactor present in all living systems. Its active form, thiamine pyrophosphate, is shown below, with an abbreviated form on the right:

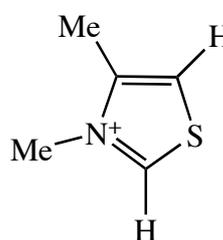


The first step in thiamine pyrophosphate reactions relies on the fact that it can be easily deprotonated.

- (a) Explain the difference in pKa values between the following two compounds (C2 and H2 are the carbon and hydrogen, respectively, between the N and S).

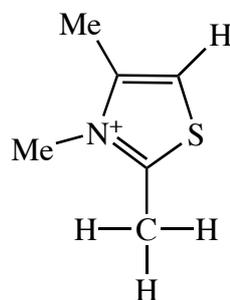


$$\text{pK}_a(\text{H}_2) = 29.4$$



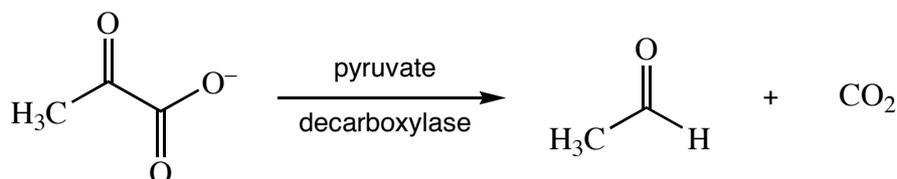
$$\text{pK}_a(\text{H}_2) = 16.5$$

- (b) Draw structures to explain the acidity of the C2-methyl protons in the following compound:



$$\text{pK}_a(\text{C2-methyl}) = 13.9$$

Thiamine pyrophosphate is used as a cofactor in pyruvate decarboxylase, used by yeast to convert pyruvate into acetaldehyde, as shown below:



- (c) From (a) and (b), or otherwise, propose a mechanism for this reaction (you may use the abbreviated structure of thiamine pyrophosphate in the first diagram to save time).
- (d) On December 3, 1984 in Bhopal, India, approximately 40 tonnes of methyl isocyanate ($\text{Me}-\text{N}=\text{C}=\text{O}$) was released from a Union Carbide insecticide plant, resulting in the deaths of tens of thousands of people, with hundreds of thousands also affected. In terms of what you know

about reaction mechanisms and the macromolecules present in the body, why do you think methyl isocyanate is toxic?

Organic Section (40 minutes)

Question 6 (30 minutes)

The linear (*i.e.* non-cyclic) compound **A** ($C_8H_{16}O_2$) was treated with concentrated sulfuric acid to give **B** ($C_8H_{14}O$). In the presence of palladium on carbon, **B** took up one equivalent of hydrogen to give compound **C**. Upon treatment of **B** with hot, concentrated potassium permanganate, 2 fragments, **D** ($C_2H_4O_2$) and **E** ($C_6H_{10}O_3$) were obtained. Both **D** and **E** were found to be soluble in sodium hydroxide and sodium bicarbonate solutions. Compound **E** was a 4-oxocarboxylic acid. Both compounds **A** and **E** gave negative iodoform and silver mirror tests.

- (a) Give two possible structures of **A** consistent with this information, and draw out the reaction schemes, clearly labelling products **A** to **E**.

Compound **B** is treated with ozone in a reducing environment, yielding compounds **F** and **G**. When treated with $I_2/NaOH$, only **F** gave a pale yellow precipitate. **G** was treated with base, followed by an acidic work-up, and the 5-membered homocycle **H** (C_6H_8O) was obtained. (Homocyclic means that all the ring atoms are identical; heterocyclic means that there can be more than one type of ring atom).

On the other hand, when **B** was subjected to ozonolysis under oxidising conditions, the compounds **D** and **E** were formed. **E** was treated with ethanol and a catalytic amount of sulfuric acid, to give compound **I** ($C_8H_{14}O_3$). Upon treatment of **I** with $NaBH_4$, the 5-membered heterocycle **J** ($C_6H_{10}O_2$) was formed.

- (b) Draw out the reaction scheme and clearly label products **F** to **J**.
- (c) Suggest mechanisms for the conversion of **G** to **H** and **I** to **J**.
- (d) State whether products **H** and **J** formed from this reaction scheme will be optically active or inactive. Why/why not?

Question 7 (10 minutes)

Propose a sequence of reactions which might be used to synthesise compound **K** from toluene and phenol. Include the structures of all intermediates, and state the reagents and conditions necessary for each step.

