FINAL PAPER

PART A

1997

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 7.

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 programmable electronic calculator and molecular models, molecular models are not considered essential.

(3) Questions 1 to 5 are compulsory. You may choose **any two** from questions 6, 7 or 8.

(4) Appropriate data can be found at the end of questions 3 and 4.

(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 (20 minutes)

a) Theoreticians often try to predict the structure of molecules before they can be observed spectroscopically. Much work has been performed on carbenes, molecules containing divalent carbon atoms. The simplest of these is methylene, CH_2, and the next simplest is fluoromethylene, HCF.

Describe the bonding in terms of a hybridised carbon atom.

b) Draw a diagram illustrating the relative energies of the MOs of the CF molecule. What is the bond order? Is it paramagnetic or diamagnetic?

c) Draw the occupied orbitals being careful to indicate where the wavefunction changes sign.

d) One way that intergalactic HCF might form is by attack of CF by a lone hydrogen atom, forming a C—H σ-bond.

In terms of orbitals, how might this bond be formed? Illustrate your answer. Is the molecule bent or straight?

Question 2 (25 minutes)

a) Sketch and name all the possible linkage and stereoisomers of the following coordination compounds.

(i) $[Pt(NH_3)_2(SCN)_2]$ (ii) $[Co(H_2NCH_2CO_2)_3]$

b) The fluorides CoF_2, FeF_2, MnF_2 and NiF_2 all have the rutile (TiO_2) structure in which the transition metal ion has an octahedral stereochemistry.

(i) Draw a clearly labelled d-orbital splitting diagram for each of the metal ions in these fluorides and determine the crystal field stabilisation energy (CFSE) in terms of Δ_o.

(ii) Arrange the fluorides in order of increasing stability and explain the trend.

(iii) The fluoride PdF_2 similarly has a regular rutile structure. Is this stereochemistry to be expected for the d^8 palladium(II) ion? Explain.

Question 3 (45 minutes)

a) For a certain reaction the following mechanism has been proposed:

$$HBr + O_2 \longrightarrow HOOBr$$
$$HOOBr + HBr \longrightarrow 2HOBr$$
$$HOBr + HBr \longrightarrow H_2O + Br_2$$

No HOBr is observed among the final products of the reaction which is found experimentally to be of first order with respect to HBr and O_2.

(i) What is the overall stoichiometric equation for the reaction?

(ii) Why is the above mechanism to be preferred to that which is perhaps suggested by the overall equation for the reaction?

(iii) Which of the steps in the above mechanism would appear to be the rate determining step?

(b) Glucose is the most utilised biochemical on this planet, its oxidation driving every living body. From our blood circulatory system glucose infuses into the interstitial fluid, in which all of our cells bathe. Cells can actively transport nutrients and wastes across their membranes expending chemical work as they do so. Typically these compounds are transported from areas of high concentration to low where they are utilised or alternatively excreted. Ultimately glucose is concentrated within the cell and converted to carbon dioxide and water, releasing energy. Although there are many intermediate reactions, all contribute to the total free energy of this oxidation. Estimate the total free energy gained by a cell from the oxidation of one mole of glucose at the concentration found in the interstitial fluid, to the eventual release of carbon dioxide into venous blood. Neglect the effect of water formed on solution concentrations and consider the interstitial fluid as if it were an infinite reservoir. [Hint: Consider the energetics to occur in three discrete parts.]

[Data:	Interstitial fluid:	Glucose ($C_6H_{12}O_6$)	5.0×10^{-3} mol L^{-1}
		Oxygen	4.2×10^{-5} mol L^{-1}
	Cell:	Glucose	1.0×10^{-4} mol L^{-1}
		Oxygen	1.4×10^{-5} mol L^{-1}
		Carbon dioxide	1.0×10^{-4} mol L^{-1}
	Venous blood:	Carbon dioxide	1.5×10^{-4} mol L^{-1}

$\Delta G°_f$ kJ mol^{-1} (@ 38°C and 1 atm.):	Glucose	– 917
	Carbon dioxide	– 394
	Water	– 237

$R = 8.314$ J K^{-1} mol^{-1} = 8.205×10^{-2} L atm K^{-1} mol^{-1}]

Question 4 (45 minutes)

In unpolluted areas, the percentage composition by volume of **dry** air is approximately:

N_2 (78%), O_2 (21%), CO_2 (0.03%) and other inert gases (balance).

The vapour pressure of water at 25°C is 3.17 kPa, and on an average day the actual partial pressure of water vapour is 60% of this value.

The air that an average human exhales, when dried, is approximately:

N_2 (80%), O_2 (19%), CO_2 (0.3%) and other inert gases (balance).

The vapour pressure of water at 37°C is 6.30 kPa and air exhaled is approximately 100% saturated with water vapour.

a) Calculate the partial pressure of CO_2 in
  (i) "normal" air (1 atm, 25°C)
  (ii) exhaled air (1 atm, 37°C)

b) Explain the following with reference to the principles of chemical equilibria:
  (i) How do we know that a person is not in equilibrium with the air?
  (ii) What would happen if they were?
  (iii) Why do people not reach equilibrium with the air over the course of day-to-day living?

The following questions concern the equilibrium that is established when CO_2 interacts with water. The relevant equations are:

$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq) \qquad K = 0.034\ molL^{-1}atm^{-1}$$
$$H_2CO_3(aq) \longrightarrow HCO_3^-{}_{(aq)} + H^+(aq) \qquad Ka_1 = 1\times10^{-6.35}\ molL^{-1}$$
$$HCO_3^-(aq) \longrightarrow CO_3^{2-}(aq) + H^+(aq) \qquad Ka_2 = 1\times10^{-10.33}\ molL^{-1}$$

c) Using the partial pressure of CO_2 in exhaled air, calculate the approximate concentration of H_2CO_3 in the blood. Explain why your answer is a lower bound.

d) Calculate the pH, and $[CO_3^{2-}]$ for a water solution in equilibrium with:
  (i) air at 1 atm, 25°C
  (ii) exhaled air at 1 atm, 25°C

e) Blood is naturally buffered at pH = 7.41. Assuming that your answer to part (c) is the true value for the H_2CO_3 concentration in blood, calculate the concentrations of:
  (i) H^+
  (ii) CO_3^{2-} and
  (iii) HCO_3^- in blood.

g) Hydrofluoric acid is very dangerous to use because F^- ions are small enough to penetrate the skin. What concentration of F^- would be required in the blood to cause serious problems with Ca^{2+} if CaF_2 has $K_{sp} = 3 \times 10^{-11}$?

[Data: 1 atm = 101.3 kPa]

Organic Section (45 minutes)

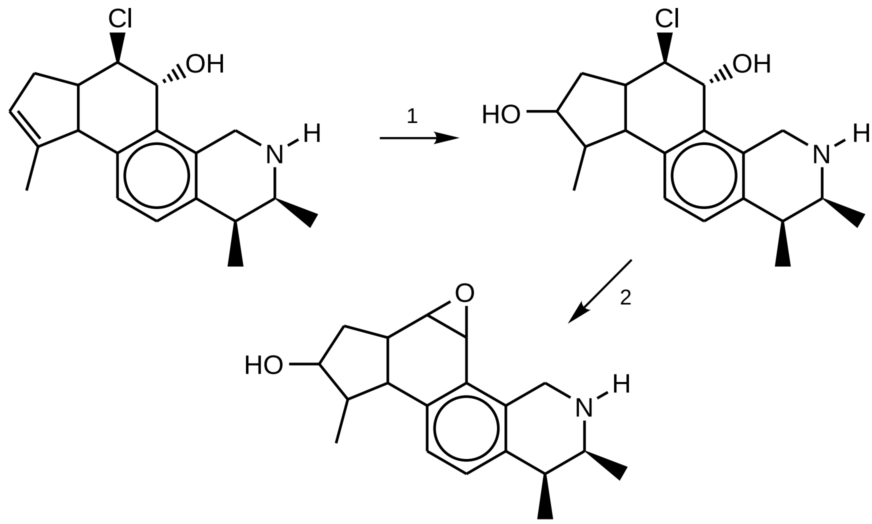
Students must attempt Question 5 and any 2 other questions of their choice in this section.

Question 5

a) Draw Fischer projections of all the stereoisomers of 2,3-dimethylbutanedicarboxylic acid and label the chiral centres in each.

c) When (R)-2-chlorobutane is reacted with water, a substitution reaction occurs, and 2-butanol is found to be produced as a racemic mixture. What must the transition state between reactant and product look like for this to occur? Draw out the mechanism using wedge diagrams.

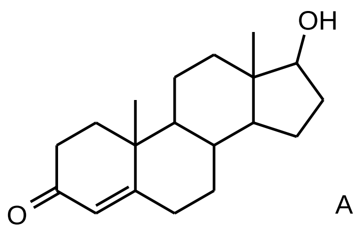
Question 6



a) What reagents should be used in each step of the above sequence?

Give a mechanism for the second step.

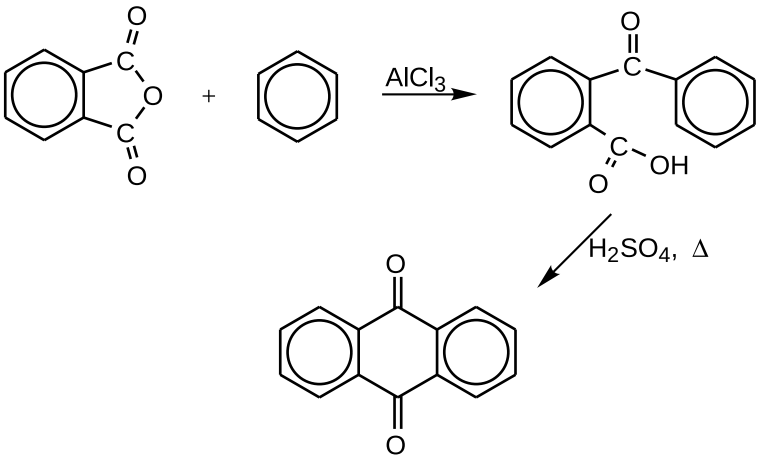
b) Testosterone (A), is a well-known human hormone and, like molecules such as estrogen and cholesterol, has the general four ring steroid structure. A researcher wants to react A with ethylmagnesium bromide. What are the two possible products (assume he works the solution up afterwards), and which one will actually form? Why?



A

Question 7

The anthraquinones are widely used in the dye industry, since the degree of conjugation gives them intense colours. They are prepared by an adaptation of the Friedel-Crafts acylation:



Give a full mechanism (including any charged intermediates) for this conversion.

Question 8

Acetylene is reacted firstly with lithium amide ($LiNH_2$), giving **A**, which is then combined with 1-bromo-2-methylpropane to give **B**. **B** is reduced with hydrogen over a $Pd/BaSO_4$ catalyst, giving **C**. **C** is treated with dilute acid, giving **D**, followed by reaction with acidified dichromate, to give **E**. **E** is then treated with a strong base and undergoes a condensation reaction, giving a mixture of products.

a) Draw the structures **A**-**E**.

b) Name every product that could form in the final step.