

AUSTRALIAN CHEMISTRY OLYMPIAD

FINAL PAPER

PART B

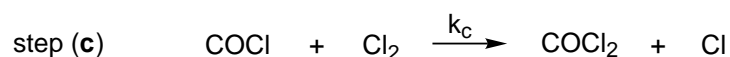
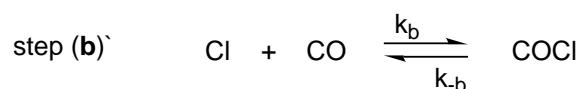
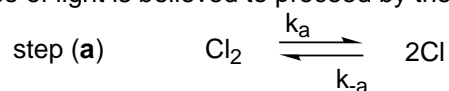
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Instruction to candidates

- (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.
- (3) You must attempt **all** questions.
- (4) 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.
- (5) Answers **must** provide **clearly laid out working** and **sufficient explanation** to show how you reached your conclusions.
- (6) Your name must be written in the appropriate place on **each page** of your answers.
- (7) Use **only black** or **blue ball point pen** for your written answers, pencil or other coloured pens are **not** acceptable.

Question 1

The formation of phosgene, COCl_2 by the reaction of carbon monoxide and chlorine in the presence of light is believed to proceed by the following mechanism;



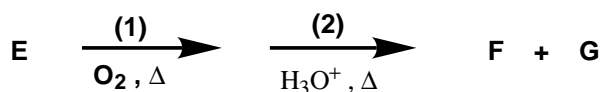
- (a) Deduce a differential rate law for the formation of phosgene;
 - (i) on the assumption that the equilibria in steps (a) and (b) are very fast compared with step (c).

- (ii) by making the steady state approximation for the reactive intermediates.
- (b) Using the rate law obtained in part (i) apply the isolation method to obtain the half life for the consumption of chlorine (Cl_2) as a function of chlorine (Cl_2) concentration.

Question 2

The reduction of a 4-substituted cyclic ketone **A** yields a mixture of liquid isomeric compounds **B** and **C** (with composition of 76.00% C and 12.75% H and density $d_4^{30} = 0.9092 \text{ gcm}^{-3}$) which during dehydration form one product **D**.

Dehydrogenation of compound **D** in the presence of palladium gives the product **E**. Product **E** forms the basis of an important two-stage industrial synthesis to form compounds **F** ($M = 94.114 \text{ gmol}^{-1}$) and **G**, the reaction conditions are shown in the following equation.



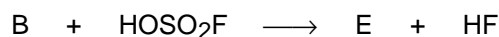
Product **G** undergoes the iodoform reaction and shows only one signal in ^1H NMR spectrum.

- (i) Give the formulas of products **A - G** and all possible constitutional isomers of the compound **G**.
- (ii) Determine the composition of the mixture of compounds **B** and **C**, assuming additivity, when the densities d_4^{30} , of the more stable isomer **B** and less thermodynamically stable isomer **C** are 0.9073 and 0.9120 gcm^{-3} respectively.
- (iii) Give the energetically favoured conformation of molecules of the compounds **A - C** taking into consideration spatial repulsive interaction.

Question 3

An element **A** is mixed with fluorine in a molar ratio 1:9 at room temperature and high pressure (ca. 1 MPa). Upon heating to 900°C three compounds **B**, **C**, and **D** are formed. All three products are crystalline solids with melting points below 150°C . The fluorine content of **C** is found to be 36.7% and that of **D** 46.5% (by weight).

When **B** is treated with anhydrous HOSO_2F at -75°C , a compound **E** is formed:



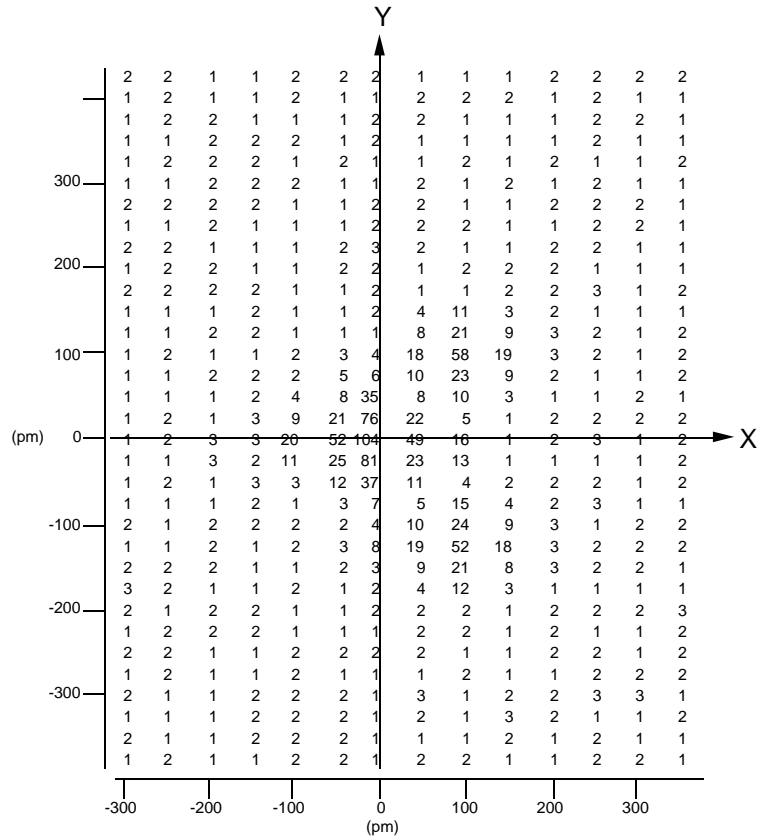
E is a crystalline solid which is stable for weeks at 0°C , but decomposes in days at room temperature.

The electron density distribution of **E** (the electron density map of **E**), which is obtained through X-ray diffraction studies, is shown on two intersecting, mutually perpendicular planes (see enclosed). These planes are arbitrarily marked as X-Y and X-Z planes. The numbers indicated on these maps relate to the electron density in the neighbourhood of the atoms of **E** as a function of the spatial coordinates. The maxima of the electron density found in these maps coincide with the locations of the atoms. The values of the maxima are approximately proportional to the number of electrons in the atom in question. The cartesian coordinate axes are indicated on both planes. All significant electron density is shown on these maps.

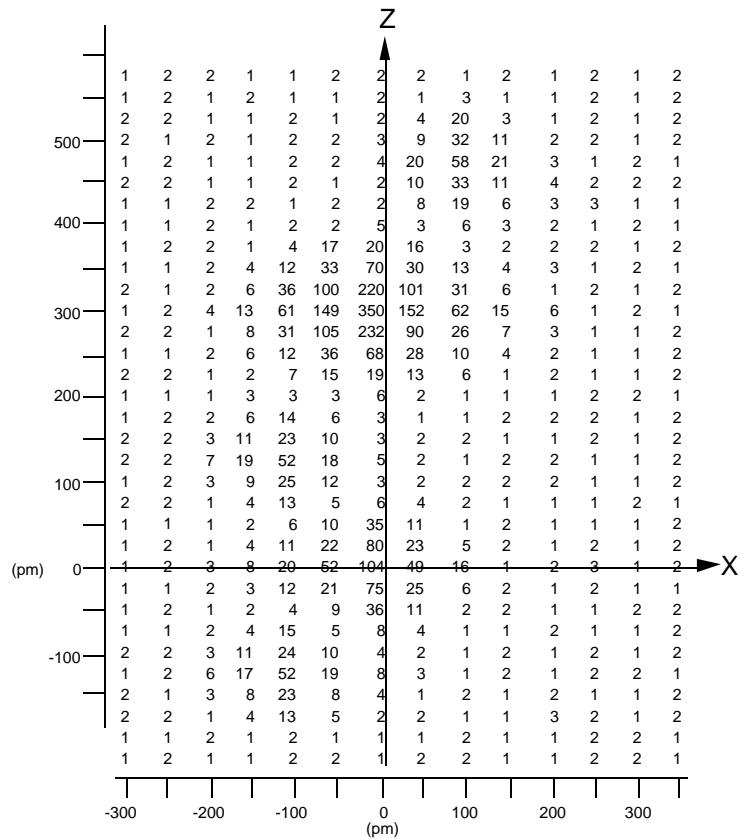
- (a) Show clearly where the maxima lie by drawing the contour curves around the maxima, that is connecting points of approximately equal electron densities. Label each maximum to show the identities of the atoms in **E**.

Answer on diagrams

The electron density distribution of **E** on the X-Y plane



The electron density distribution of **E** on the X-Z plane



- (b) For confirmation, the relative atomic mass of **A** was determined as follows: When 450.0 mg of **C** was treated with an excess of mercury, 53.25 cm³ of **A** was liberated at a pressure of 101.3 kPa at a temperature of 25°C. Calculate the relative atomic mass of **A**.
- (c) Identify **A**, **B**, **C**, **D** and **E**.
- (d) Use the valence shell electron-pair repulsion theory (VSEPR) to propose electron-pair geometries for **B** and **C**. Using the two electron density maps, sketch the molecular geometry of **E**.
- (e) The original mixture of **B**, **C** and **D** was hydrolysed in water. When **B** is hydrolysed, **A** and oxygen are liberated, and aqueous hydrogen fluoride is formed. When **C** is hydrolysed **A** and O₂ (in a molar ratio of 4:3) are liberated, and an aqueous solution of the oxide AO₃ and hydrogen fluoride are formed. The hydrolysis of **D** produces an aqueous solution of AO₃ and hydrogen fluoride.

Write the equations for the three hydrolysis reactions.

- f) The composition of the mixture of **B**, **C** and **D** was determined by carrying out the hydrolysis quantitatively. Upon treating a sample of the mixture with water, 60.2 cm³ of gas was liberated (measured at 290K and 100 kPa). It was found that oxygen content by volume of this gas was 40.0%. The amount of AO₃ which is dissolved in water was analysed by titration with aqueous FeSO₄ solution which has the concentration of 0.100 molL⁻¹. The titration required 36.0cm³ of the FeSO₄ solution. During the titration Fe²⁺ is oxidized to Fe³⁺ and AO₃ is reduced to **A**. Calculate the composition (% by moles) of the original mixture of **B**, **C** and **D**.

Question 4

In order to accurately measure the pH of a test solution, a potentiometric (ie zero current) electrochemical cell was employed which contained two electrodes:

- (i) a silver/ silver chloride reference electrode, filled with 3.5M KCl solution, and
 (ii) a glass-membrane pH electrode whose response to pH is given by

$$E = E_{\text{glass}}^{\circ} - \frac{RT}{F} \text{pH}$$

Where the potentials have units of volts.

- (a) Write down an expression which relates the measured cell potential to pH and to the concentration of KCl in the reference electrode.
- (b) Calculate E_{glass}° .
- (c) In practice, the KCl used to fill the reference electrode is never perfectly pure. If a commercial sample of KCl, containing 1% KBr, was used to prepare the 3.5M "KCl" solution, calculate the error that this impurity caused in measurement of the pH of the pH 7 buffer.
- (d) What error is introduced if the KCl contained 0.1% KBr?

Data: (at 25°C)

$$E_{\text{Ag}^+:\text{Ag}}^{\circ} = 0.2046\text{V}$$

$$K_{\text{sp}}(\text{AgCl}) = 1.78 \times 10^{-10}$$

$$K_{\text{sp}}(\text{AgBr}) = 5.25 \times 10^{-13}$$

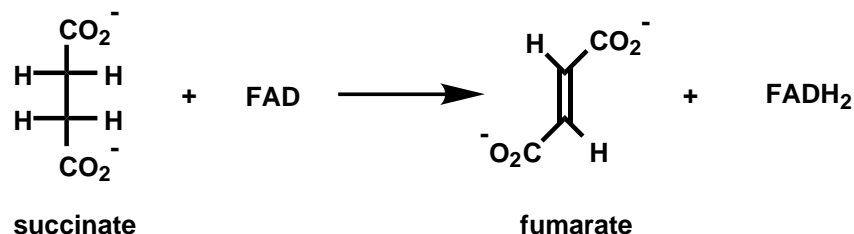
$$F = 96487 \text{ C/mol}$$

$$R = 8.314 \text{ J/Kmol}$$

Question 5

- (a) The dehydrogenation of succinate to fumarate is one step in the tricarboxylic acid or Krebs cycle. This reaction is catalysed by an enzyme called succinate dehydrogenase in the presence of a coenzyme Flavine-adenine-dinucleotide.

The reaction may be summarised as follows.



The stereochemistry of the dehydrogenation reaction has been studied by using deuterium labelled substrates, specifically 2,3-dideuteriosuccinates*, which were prepared by the catalytic deuteration (Deuterium gas / palladium on carbon catalyst) to fumaric (E-butenedioic acid) and maleic acid.(Z-butenedioic acid). [Note like normal hydrogenation this is a syn addition]

- (i) Draw Fischer projections for the stereoisomers which can be obtained by catalytic deuteration of maleic acid . Do the same for fumaric acid.
- (ii) Indicate which of the above isomers of 2,3-dideuteriosuccinic acid are optically active and designate the stereochemical relationships between all of the stereoisomers.
- (iii) Using Newman projections show the most favoured conformation of each of the above isomers.
- (iv) When the 2,3-dideuteriosuccinates are subjected to enzymatic dehydrogenation using the enzyme succinate dehydrogenase the results are as follows:

2,3-dideuteriosuccinates obtained from	percentage of dideuterated fumarate formed after enzymatic oxidation of 2,3-dideuterated succinates
fumaric acid	4%
maleic acid	48.5%

If you assume that within experimental error these figures are 0 and 50% respectively, deduce with the aid of your Newman structures, whether the enzymatic dehydrogenation reaction proceeds with syn or anti stereochemistry.

- (b) In the following step of the Krebs cycle, and in the presence of the enzyme fumarase, fumarate adds on a molecule of water to yield (S)-malate [(S)-2-hydroxybutanedioate]. If the 2,3-dideuterofumarate obtained above is reacted with the fumarase enzyme the product is exclusively (2S, 3S)-2,3-dideuteromalate.

Using clearly drawn saw horse diagrams determine the stereochemistry of hydration reaction

* Note at biological pH most carboxylic acids exist as salts and consequently they are frequently referred to as the anion eg succinate rather than the acid eg succinic acid.