AUSTRALIAN CHEMISTRY OLYMPIAD

FINAL PAPER

PART B

1994

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 5 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 nonprogrammable electronic calculator and molecular models.

(3) You must attempt **all** questions.

(4) Answers **must** provide **clearly laid out working** and **sufficient explanation** to show how you reached your conclusions.

(5) 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.

(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

On holidays in the Kosciusko National Park a biochemist from Darwin decides to cook some lunch having just walked to the summit of Mt. Kosciusko. Now that she is 2213 m higher than when she normally boils an egg, she notices her "10 minute" egg is undercooked. Coincidently, when at home her research involves determining activation energies required to denature certain proteins. She remembers that the E_a for egg albumin is around 85 kJ mol^{-1}. How long should she have cooked the egg at this altitude?

[Hint: The pressure between a higher point P_1 and a lower point P_2 within a column of gas separated by a height, h, is given by;

$$\ln(P_1/P_2) = -Mgh/RT$$

where, M is the molecular weight of gas in kgmol^{-1}, g = 9.81 ms^{-2}, R =8.31 J$K^{-1}mol^{-1}$, T is temperature in Kelvin. Assume the denaturation process to be 1st order kinetics.

[Enthalpy of vaporisation of water is 44 kJmol^{-1}]

Question 2

(a) An element X exists in 3 forms—allotropes, designated X(a), X(b), and X(c), all of which are solid.

A sample of X(a) is placed in an atmosphere of oxygen. The sample glows green and eventually bursts into flames forming a single oxide (α).

A sample of X(a) is placed in an atmosphere of chlorine. The sample bursts into flames forming a mixture of two chlorides (β) and (γ).

A sample of X(a) is dropped into liquid bromine. A violent explosion occurs and a mixture of two bromides (δ) and (ε) is formed.

When X(a) is heated at 260°C in an inert atmosphere it slowly turns to X(b). When X(a) is heated at 200°C under a pressure of 12000 atm it slowly turns to X(c). When either X(b) or X(c) are vaporised by heat in an inert atmosphere and allowed to condense the product is X(a).

(i) Draw or otherwise explain the structures of the 3 forms of X.

(ii) Give the formula and structural formula for α.

(iii) β is a liquid. Give its structural formula.

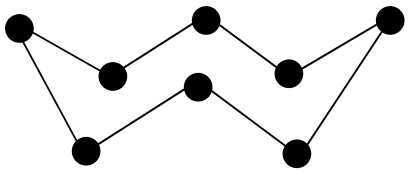
(iv) γ is an ionic solid made up of a pentaatomic cation and a heptaatomic anion. Draw structural formulas for each of the ions and give the shape and hybridisation of the central atom.

(v) γ in the vapour phase is an uncharged hexaatomic molecule. Draw its structural formula and give the shape and hybridisation of the central atom.

(vi) δ is a liquid. Give its structural formula.

(vii) ε is an ionic solid made up of a pentaatomic cation and a monoatomic anion. Draw the structural formula of the cation and give the shape and hybridisation of the central atom.

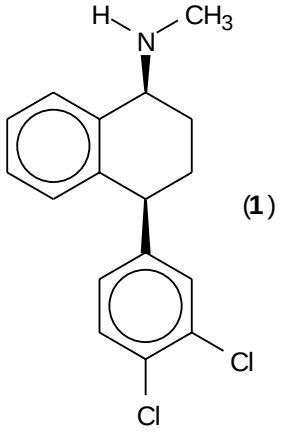
(b) When heated together under reduced pressure at about 500°C sulfur and selenium form a mixture of several binary compounds. Most abundant compounds in these mixtures are crown-shaped eight-membered ring molecules with a general formula Se_nS_{8-n} and the following shape.



Describe the structural isomers of Se_4S_4 . Which of these will exist as (not necessarily isolable) optical isomers?

Question 3

Sertraline (**1**) is a non-sedative antidepressant drug. Its synthesis is described below.



(**1**)

1,2-Dichlorobenzene is reacted with benzoyl chloride(PhCOCl) in the presence of anhydrous $AlCl_3$ to afford (**2**) ($C_{13}H_8OCl_2$). (**2**) Reacts with diethyl butan-1,4-dioate in the presence of a strong base, potassium *tert*-butoxide to afford the ester (**3**). ($C_{21}H_{20}O_4Cl_2$). (**3**) Can be converted to (**4**) ($C_{16}H_{12}O_2Cl_2$) by treatment with strong acid. Compound (4) is soluble in sodium bicarbonate. Catalytic hydrogenation of (**4**) yields (**5**) ($C_{16}H_{14}O_2Cl_2$). Reaction of (**5**) with $SOCl_2$ followed by anhydrous $AlCl_3$ yields (**6**). ($C_{16}H_{12}OCl_2$). The latter compound gives a positive 2,4-dinitrophenylhydrazine test but does not react with either Fehlings of Tollens reagents. (**6**) Reacts with methylamine to afford (**7**) which being unstable is immediately reduced with $NaBH_4$ in methanol to afford (**1**).

(a) Deduce structures of compounds (**2**) - (**7**)

(b) Write suitable mechanisms to account for the transformation of (**5**)-(**6**) and (**6**)-(**7**).

Question 4

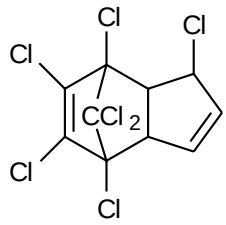
Silver nitrate is one of the most important and widely used titrimetric reagents. It is available in very high purity and is used for the determination of anions that form insoluble silver salts. Titrimetric methods based on silver nitrate are called *argentometric* methods.

(a) In this question, you will construct a titration curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.01000 M $AgNO_3$. $K_{sp}(AgBr) = 5.2 \times 10^{-13}$

The titration curve should have pAg as the y-axis and volume $AgNO_3$ added (mL) as the x-axis. Calculate pAg for the following volumes of added $AgNO_3$ and use these points to carefully draw your curve. Graph paper is available.

volume $AgNO_3$ /mL	pAg
0.00	
5.00	
10.00	
20.00	
23.00	
24.90	
25.00	
25.10	
27.00	
30.00	

(b) The Association of Official Analytical Chemists (AOAC) recommends a Volhard argentometric titration for the analysis of the insecticide heptachlor ($C_{10}H_5Cl_7$).



In the Volhard method, the following procedure is followed:

- The sample would be dissolved in some way and the chloride is precipitated by addition of excess standard silver nitrate solution.
- The excess silver ions are determined by titration with a standard solution of potassium thiocyanate:

$$Ag^+ + SCN^- \longrightarrow AgSCN(s)$$

- A small amount of iron(III) is added as an indicator to detect the equivalence point. The solution turns red with the first slight excess of thiocyanate ion:

$$Fe^{3+} + SCN^- \longrightarrow FeSCN^{2+}\ (red) \qquad K = 1.4 \times 10^2$$

- The titration must be carried out in slightly acidic solution to prevent the formation of iron(III) hydroxide.

According to the AOAC, the percentage of heptachlor is given by:

$$\%\ \text{heptachlor} = \frac{(\text{mL Ag} \times C_{Ag} - \text{mL SCN} \times C_{SCN}) \times 37.33}{\text{wt sample}}$$

where mL Ag and mL SCN and C_{Ag} and C_{SCN} are the volumes and analytical concentrations of silver nitrate and potassium thiocyanate respectively.

Qn. What does this calculation reveal about the stoichiometry of the heptachlor Volhard titration?

c) For the Volhard titration to be accurate, the observed *endpoint* should correspond exactly to the equivalence point ie when the amount of added thiocyanate is exactly equal to the amount of silver ions to be analysed. Any difference between the endpoint and equivalence point represents a "titration error".

It has been found from experiment that the average observer can just detect the red colour of $Fe(SCN)^{2+}$ when its concentration is 6.4×10^{-6} M.

In a titration of 50.0 mL of 0.050 M $AgNO_3$ with 0.100 M KSCN, what concentration of Fe^{3+} should be used to reduce the titration error to zero?