**AUSTRALIAN CHEMISTRY OLYMPIAD**

<u>Instruction to candidates</u>

(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-programable 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 <u>black</u>** or **<u>blue</u> ball point pen** for your written answers, pencil or other coloured pens are **not** acceptable.

Question 1

According to VSEPR (valence-shell electron-pair repulsion) theory, the pairs of valence electrons adopt a configuration which minimises the repulsion between the bonding and non-bonding valence pairs. The optimal configuration for n pairs of electrons is given in the following diagram, where the atom is considered to be at the centre of the sphere and each point represents an electron pair.

(a)   (b)   (c)

(d)   (e)
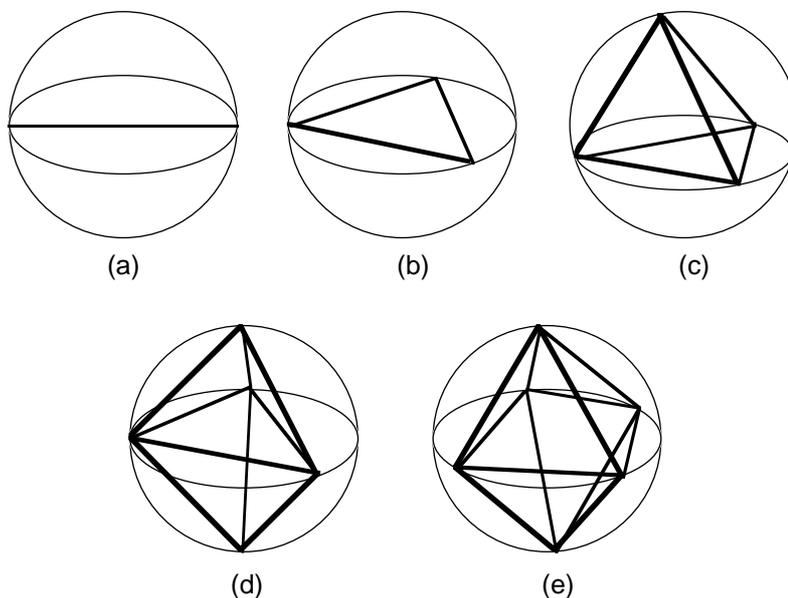
(a)   Comparison of the geometric structure of CCl_4, SCl_4 and XeF_4 molecules.
   (i)   Give the number of valence-electron pairs and their arrangement around each central atom.

   (ii)   Draw the possible structure (or structures) of each molecule.

   (iii)   If several forms are possible, choose one, taking into account the fact that the repulsion between pairs decreases as follows:

   free-pair / free-pair > bonded-pair / free-pair > bonded-pair / bonded-pair

(b)   Comparison of the geometric structure of $BeCl2$, $SnCl_2$, H_2S and XeF_2 molecules.
   (i)   Give the number of valence-electron pairs and their arrangement around each central atom.

   (ii)   Draw the possible structure (or structures) of each molecule.

   (iii)   If several forms are possible, choose one, taking into account the fact that the repulsion between pairs decreases as follows:

   free-pair / free-pair > bonded-pair / free-pair > bonded-pair / bonded-pair

(c)   Comparison of phosphorus halide compounds.
   (i)   Give the structure of the molecules having the formula PX_3 where X = F, Cl, Br and I, and justify your answer.

   (ii)   Give the maximum value of the X—P—X bond angle.

   (iii)   With reference to the volume occupied by the bonding pairs around the phosphorus, predict whether the X—P—X bond angles will be increased or decreased when X is F, Cl, Br and I.

   (iv)   The H—P—H bond angle in PH_3 is less than the X—P—X bond angles in phosphorus halides. Why?

Question 2
(a)   Not all types of mushrooms can be safely eaten. For instance, one type of mushroom, *Amanita muscaria*, contains the poisonous alkaloid muscarine pictured below, as a Harworth diagram.
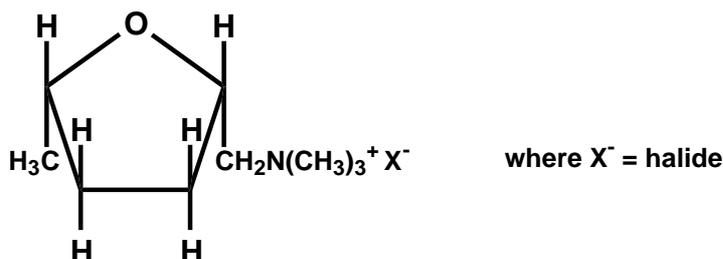

   (i)   Identify the chiral centres in the above molecule. (The numbering of positions begins at oxygen and proceeds clockwise).

   (ii)   How many stereo-isomeric forms of this compound are there? How many pairs of enantiomers? Is there a meso diastereomer?

   (iii)   Suppose you are a forensic chemist faced with the following problem. Someone has died after eating mushroom stew made with mushrooms picked from woods near the deceased's home. Could this person have picked some *Amanita muscaria* along with harmless *Amanita rubescens*? Or was this person poisoned by the addition of synthetic muscarine to their stew. Assume you have a solution of muscarine from the stew. How could you quickly determine whether the deceased was a victim of an unfortunate accident or the victim of foul play?

(b) (i)   Bisabolene $C_{15}H_{24}$ is found widely distributed in nature especially in myrrh and oil of bergamot. Hydrogenation over platinum in acetic acid gives compound **X** $C_{15}H_{30}$. Bisabolene also undergoes partial hydrogenation in cyclohexane to give compound **Y** $C_{15}H_{28}$. Ozonolysis of

Y gives 6-methyl-2-heptanone and 4-methylcyclohexanone. Ozonolysis of bisabolene gives amongst other products propan-2-one and 4-oxopentanoic acid.

On the basis of this data identify compound **Y** and suggest possible structures for bisabolene.

(ii) Bisabolene and an alcohol derived from bisabolene are amongst the products obtained from the acid catalysed cyclisation of the terpenoid alcohol nerolidol (shown below).
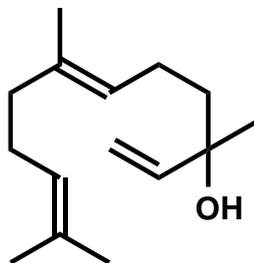
Propose a mechanism for the cyclisation of nerolidol to bisabolene and suggest a structure for the related alcohol bisabolol also produced in the acid catalysed reaction

(iii) What does this suggest about the structure of bisabolene?

(iv) Bisabolene reacts easily with hydrogen chloride to give compound **Z**. $C_{15}H_{27}Cl_3$ which is also formed when a mixture of bisabolene and bisabolol from nerolidol is treated with hydrogen chloride.

What is the structure of compound **Z**?

## Question 3

(a)   Three solutions of a weak organic monoprotic acid with the same concentration of 1×10^{-4} M were prepared in an aqueous buffer solution with pH = 9.20, in hydrochloric acid, and in aqueous sodium hydroxide, respectively.

Absorbances of the solutions were measured at two wavelengths. The results obtained are shown in the table below:

Solution in	Absorbance	
	$\lambda_1 = 285$ nm	$\lambda_2 = 346$ nm
buffer with pH = 9.20	0.373	0.0981
HCl(aq)	0.309	0
NaOH(aq)	0.501	0.295

Calculate the pKa value of the organic acid.

(b)   A sodium chloride solution concentration of 0.01 mol dm^{-3} may be titrated with AgNO$_3$ solution in a basic medium until a brown precipitate of Ag$_2$O is obtained according to the equation :

$$2\ AgOH \longrightarrow Ag_2O + H_2O$$
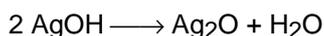
What must be the pH of the solution if the chloride concentration is to be determined with an accuracy of no greater than 0.1% below the correct value?

The solubility products of AgOH and AgCl are:

$$K_{spAgOH} = 5 \times 10^{-8} \qquad K_{spAgCl} = 10^{-9.7}$$

(c)   The **distribution coefficient** for the extraction of benzoic acid (HBz) from water into a water immiscible organic solvent is:

$$K_D = \frac{[HBz]_o}{[HBz]_w}$$

where $[HBz]_O$ is the molar concentration in the organic phase and $[HBz]_W$ the concentration in the aqueous phase.

However, part of the benzoic acid in the aqueous layer will exist as Bz^-, depending on the magnitude of K_a and the pH of the aqueous layer. The **distribution ratio**, which is the ratio of the concentrations of **all** the species of the solute in each phase, in such a case better describes the extraction efficiency:

$$D = \frac{[HBz]_O}{[HBz]_W + [Bz^-]_W}$$

Derive an expression for D that contains the constants K_D, K_a and the variable $[H^+]_W$ *i.e.* the molar concentration of H^+ in water.
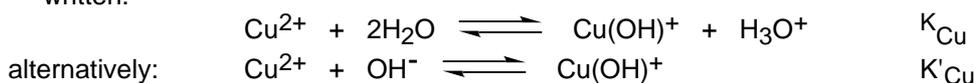
Question 4

Solutions containing the complex cation, $FeSCN^{2+}$, in concentrations equal to and above 10^{-5} mol L^{-1} are dark red in colour. The dissociation constant, K_D, for this complex is 10^{-2}.

(a)   If 500 mL of 2×10^{-3} M $FeCl_3$ is added to an equal volume of 2×10^{-2} M KSCN, what are the concentrations of all the ionic species present? Is the solution coloured?

(b)   The fluoride anion will also complex with iron(III) in solution to form FeF^{2+} with a dissociation constant of 10^{-5}. If potassium fluoride is added to the solution described in (a), how much would be required to change the colour of the solution?

(c)   HF is unusual in the series of hydrohalogenic acids in that it is considered to be a weak acid having a pK_a of 3.2. HSCN however is considered a strong acid. To one litre of water was added 10^{-3} mol of $FeCl_3$, 10^{-2} mol of KSCN and 10^{-1} mol of KF. If this solution is titrated slowly with HCl until the red colouration just appears what will be the final pH? (Ignore volume changes)

Question 5

(a) $CuSO_4$ $5H_2O$ is perhaps the best known copper salt. When 10g of the salt is dissolved in 250-mL of water the resultant pH of the solution is 5.0. The hydrolysis reaction can be written:

$$Cu^{2+} + 2H_2O \rightleftharpoons Cu(OH)^+ + H_3O^+ \qquad K_{Cu}$$

alternatively: $Cu^{2+} + OH^- \rightleftharpoons Cu(OH)^+ \qquad K'_{Cu}$

where $K'_{Cu} = \dfrac{K_{H_2O}}{K_{Cu}}$

Similar expressions may be written for the sulfate anion.

Calculate K_{Cu} and K_{SO_4}.

Data:
   Relative atomic masses: Cu 63.55   S 32.06   O 16.00   H 1.008   Cl 35.45

(b)   A solution of $Cu(ClO_4)_2$ at the same concentration as above has a pH 0.5 units lower. Account for this observation.

Question 6

Zinc blende is a sulfide ore used for the industrial production of zinc metal. The production of zinc from zinc sulfide proceeds in two stages:

• the roasting of zinc sulfide in air to form zinc oxide
• the reduction of the zinc oxide with carbon monoxide to form the metal.

We will only consider the first step in this preparation. The roasting involves burning the zinc sulfide in air at 1350 K, the air being considered as a mixture of only oxygen and nitrogen in a volume ratio of 1:4. The reaction proceeds according to the following equation

$$ZnS\ (s)\ +\ \tfrac{3}{2}O_2\ (g)\ \longrightarrow\ ZnO\ (s)\ +\ SO_2\ (g)$$
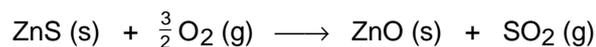
Industrially it is important to know whether the reaction can be self-sustaining, *ie* that the heat produced is sufficient to bring the reactants from ambient temperature to the reaction temperature.

All necessary data required for this problem can be found at the end of the question.

(a)   Suppose that the zinc blende is pure zinc sulfide. Starting with a stoichiometric mixture of one mole of zinc blende and the necessary quantity of air at 298 K, calculate the temperature to which the mixture would be raised by the heat evolved during the roasting of the mineral at 1350 K under standard pressure. Is the reaction self-sustaining?

(b)   Zinc blende however is never pure: it is mixed with a gangue which can be assumed to be entirely silica, SiO_2. Assuming that the gangue does not react during the roasting, calculate the minimum zinc sulfide content of the mineral for which the reaction would be self-sustaining g at 1350 K, despite the presence of silica. Give the answer in grams of ZnS per hundred grams of mineral.

Data:

Standard enthalpy of reaction for the roasting zinc sulfide : $\Delta H°_f(1350K) = -448.98\ kJ\ mol^{-1}$

Standard molar heat capacities, averaged over the temperature range considered:

	Heat capacity $(J\ K^{-1}\ mol^{-1})$
ZnS (s)	58.05
SO_2 (g)	51.10
N_2 (g)	30.65
ZnO (s)	51.64
O_2 (g)	34.24
SiO_2 (s)	72.50

Relative atomic masses: Zn 65.38   S 32.06   Si 28.09   O 16.00

Question 7

An element **X** occurs naturally in small quantities both in its elemental state and in minerals comprised mainly of X_2O_3 or X_2S_3. **X** is a relatively weak conductor of electricity and its conductivity decreases with an increase in temperature, but increases rapidly at its melting point (545K). When **X** melts it does so with a reduction in volume. At its boiling point (1833K, 101.4kPa) the density of the vapour of **X** is 3.111 gL^{-1}. The vapour density varies with temperature being 1.122 gL^{-1} at 2280K and 0.919 gL^{-1} at 2770K.

X does not react with dilute non-oxidising acids, but is oxidised by concentrated sulfuric acid or aqua regia to form the sulfate or chloride of **X**(III) respectively.

X(III) salts form complex compounds with alkali metal halides or sulfates:

eg XCl_4^- , XCl_5^{2-} , XCl_6^{3-} , $X(SO_4)_2^-$, $X(SO_4)_3^{3-}$

X also forms compounds at the oxidation state of -3, eg **X**N or XH_3, and at the +4 oxidation state, eg X_2O_4.

X(III) halides are formed by direct reaction of **X** with appropriate halogens, but only in the case of fluorine is it possible to form XF_5. This reflects the strong oxidising ability of **X**(V) which is the oxidation state also found in the XO_3^- anion. These latter anions are as expected strong oxidants and will oxidise Mn^{2+} to MnO_4^- in acidic media.

The behaviour of many **X**(III) salts in water is unusual and XCl_3 converts slowly to **X**OCl which is relatively water insoluble. Many **X**(III) salts dissolve in ether or acetone.

Compounds of **X** with tellurium are non-stoichiometric, ie X_2Te_{3-y}, and depending upon y these can be either "n" or "p" semiconductors.

Compounds of **X** are toxic but have been used in small quantities as gastric drugs or disinfecting agents.

Identification of **X** in the qualitative analysis scheme depends upon its extremely insoluble sulfide (K_{sp} **X$_2$S$_3$** $\approx 1.6 \times 10^{-72}$), and the fact that compounds of **X** yield the free element upon reduction in basic media with sodium stannite ($Na_2[SnO_2]$). The stannite anion being oxidised to stannate (SnO_3^{2-}).

Data: Molar volume is 22.414 L at 273°C, 1Atm.

(a)   Identify the element **X** and write down its valence electron configuration.

(b)   How would you determine if **X**OCl contained **X**O$^+$ and Cl$^-$ or **X**$^+$ and OCl$^-$ in aqueous solution?

(c)   Write an equation for the reaction of **X**$^{3+}$ in aqueous solution to yield **X**O$^+$.

(d)   Would a solution of **X**(NO$_3$)$_3$ in water be acidic or basic?

(e)   Write a balanced ionic equation for **X**O$_3^-$ reacting with Mn^{2+} in acidic media.

(f)   Write a balanced equation for the reduction of **X**$^{3+}$ with SnO$_2$.

(g)   Name two elements other than **X** which form ions of the type YO^{n+}.

(h)   Name two elements other than **X** which form covalent compounds of the type YOCl$_n$.