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 5 to 7.

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

Question 1

(a)   Write ground state valence electron configurations for Al, P^{3-}, V, Fe^{2+} and Sb^{3+}, and describe the valence orbitals of these five species in terms of the quantum numbers n, l and m_l. How many unpaired electrons does each species have in the ground state configuration?

(b)   Draw the Lewis structure and predict the electron pair geometry and molecular shape of BH_4^-, XeF_2, HCN and O_3. For each of the species draw a **clearly labelled** diagram showing the hybrid orbitals used in bonding. Which of these species would be expected to have a dipole moment?

(c)   Name and draw all the possible linkage, geometric and optical isomers of $[Co(NO_2)(NH_3)_5]Cl_2$, $[PtBrCl(en)]$ and $K_3[Al(C_2O_4)_3]$.

(d)   Draw a **clearly labelled** crystal field d-orbital splitting diagram for each of the following species: $MnCl_4^{2-}$, $Co(NH_3)_6^{3+}$, $Mn(H_2O)_6^{2+}$ and $Co(H_2O)_6^{2+}$. Which of the species would be expected to be paramagnetic and which one would have the highest number of unpaired electrons?

Question 2

Graph paper is attached at the end of the question should you require it for this question.

An experiment was conducted into the kinetics of a reaction using a spectrometer to follow the concentration of a light absorbing species as a function of time. During the experiment, the student in charge of proceedings notices a strange change in the value of absorbance at approximately T=10 minutes, ten minutes after the experiment was initiated.

The spectrometer was set to measure A_{550}, absorbance at 550 nm.

(a) From the following data, determine the order of the reaction with respect to the chromophoric species. Make any appropriate comments on the "strange" effect the student believed she saw. You may assume Beer's law is valid under the experimental conditions used. (A chromophore is a light absorbing species).

T (minutes)	A (arbitrary units)
0	148.413
2	44.701
4	13.464
6	4.055
8	1.221
10	0.3679
11	0.0343
12	0.0317
13	0.0295
14	0.0275
15	0.0258

(b) Given that $\varepsilon = 9876$ mol^{-1}m^{-1} for the units A is given in the table below, and the path length of the cuvette used is 1.2 cm, determine A°, the initial concentration of the chromophoric species.

(c) Given that the reaction under investigation was a complex organic reaction suspected of involving a substitution rate determining step, make any appropriate comments from your answer to the first part of this question.

Question 3

If you require graph paper for this question a sheet is attached at the end of the question.

For the gas phase dissociation reaction 2A $\longrightarrow$ 2B + C, the following data were recorded.

T (K)	$\Delta G°$ (kJ)	K_{eq}
298	140.0	2.82×10^{-25}
400	120.7	1.78×10^{-16}
500	101.5	2.51×10^{-11}
600	82.1	1.94×10^{-8}
700	63.6	1.82×10^{-5}
800	44.4	1.29×10^{-3}
900	27.7	0.0248
1000	11.1	0.264
1100	-5.9	1.89
1200	-23.0	10.0
1300	-40.2	40.8
1400	-57.0	132

Data: $\Delta G = \Delta G° - T\Delta S$
$\Delta G = \Delta G° + RT\ln Q$
R universal gas constant = 0.0821 L atm K^{-1} mol^{-1}
= 8.314 J K^{-1} mol^{-1}

(a)   From the table of data, determine the enthalpy (ΔH_{diss}) of dissociation and comment on its variation with temperature.

(b)   Determine ΔS for this system.

(c)   Calculate the percent composition of the gases in equilibrium at 298K and 850K if the total pressure is kept constant at 0.500 atmospheres.

Question 4

(a)   A person with average eyesight can see the red colour that $Fe(SCN)^{2+}$ imparts to an aqueous solution when the concentration of the complex is 6.4×10^{-6}M or greater. What minimum concentration of KSCN is required in a test kit to detect 1 ppm (ie 1 mg/L) of iron(III) in tap water?
        The formation constant of the complex is 1.4×10^2.

(b)   The concentration solubility product of CuI is 1.1×10^{-12}. The formation constant K_2 for the reaction of CuI with I^- to form CuI_2^- is 7.9×10^{-4}.
        Calculate the solubility of CuI in a 1.0×10^{-4} M solution of KI.

(c)   EDTA, often abbreviated to H_4Y, forms very stable complexes with almost all metal ions. Calculate the fraction of EDTA in the fully deprotonated form, Y^{4-} in a solution that is buffered to pH 10.20.
   The acid dissociation constants of H_4Y are:
        K_1 1.02×10^{-2}
        K_2 2.14×10^{-3}
        K_3 6.92×10^{-7}
        K_4 5.50×10^{-11}

(d)   Calculate the potential of a platinum electrode in a solution that has been produced by mixing 30.0mL of 0.0100 M potassium dichromate with 50.0 mL of 0.0500 M iron(II) chloride. The pH of the resulting solution is 1.00 and $E^0(Fe^{3+},Fe^{2+}) = 0.771$ V.

Question 5

(a)   Using suitable electron dot (Lewis diagrams) provide structures for the species arising from the following electron movements.

(i)
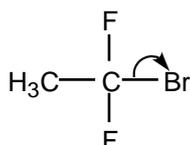
(ii)
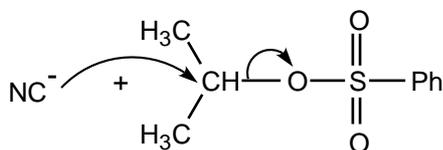
(iii)
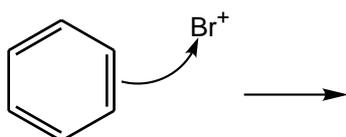
(iv)   Identify the electrophiles in the following list of reagents

BH_3, H_3O^+, $HCl_{(g)}$, NH_2^-, $CH_3C\!\!\begin{smallmatrix}O\\\\O^-\end{smallmatrix}$, NH_3, CS_2
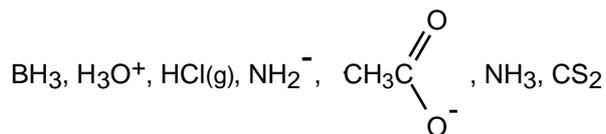
(v) Identify the nucleophiles in the following list of reagents

NH_2^+, OH^-, $AlCl_3$, H_2O, $H\!-\!C\!\!\begin{smallmatrix}O\\\\O^-\end{smallmatrix}$, $HC\!\equiv\!CH$, PH_3
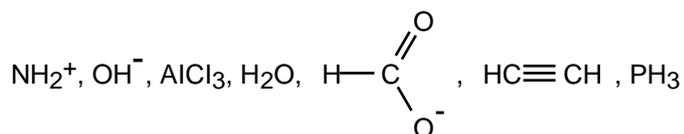
(b) (i) Assuming that the following electrophilic additions obey Markovnikov's rule give the final products of the following reactions

1. $CH_3CH\!=\!CH_2 \xrightarrow{\text{HBr}}$

2. $\xrightarrow{\text{ICl}}$
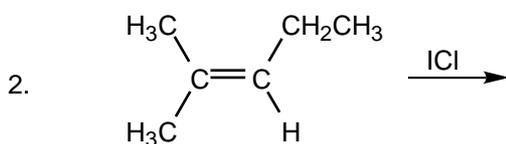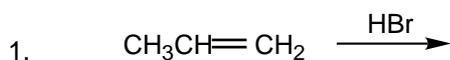
(ii) Offer a clear explanation to account for the following observations


cyclohexene   trans-1,2-dibromocyclohexane
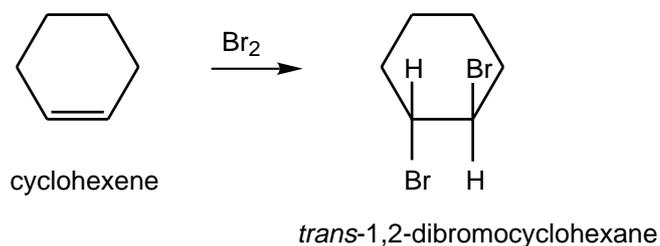
(iii) What would you expect the outcome to be if chlorine were to replace bromine as the reagent in the previous reaction?

(c) (i) Predict the outcome of the following electrophilic substitutions assuming that only one new group bonds to the aromatic ring (ie. monosubstitution occurs)

1. $\xrightarrow{CH_3\cdot CCl / AlCl_3}$

2. $\xrightarrow{HNO_3 / H_2SO_4}$

4

3.

$$Cl_2 / Fe$$
$$\Delta$$
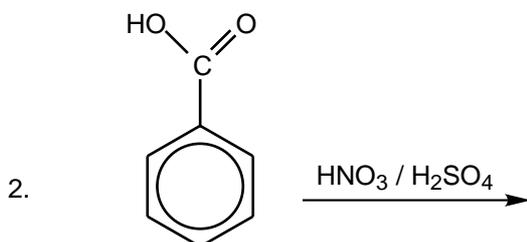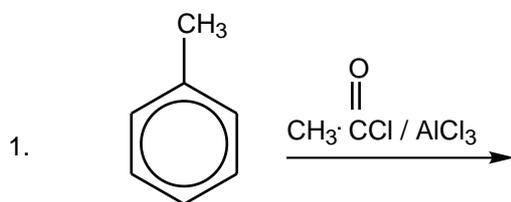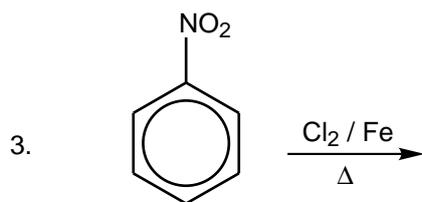
    (ii)   Write clear mechanisms to account for all these reactions.

(d) (i)   Give the structure for the product(s) obtained when 1-methylcyclopentene reacts with each of the following reagents

         1. OsO_4 followed by H_2S

         2.   *m*-chloroperbenzoic acid followed by H_3O^+

    (ii)   Which if any of the products would be capable of separating into a pair of enantiomers?

(e)   The following transformation was observed. Propose a mechanism for it.
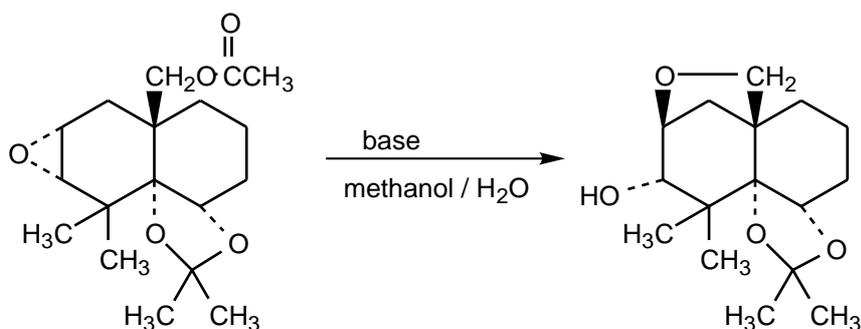
(f)   The following experimental observations were made. Even though the two reactions proceeded at very different rates, the relative amounts of the products obtained were practically identical.


	substitution products	elimination product
	63.7%	36.3%

               64.3%   +   35.7%
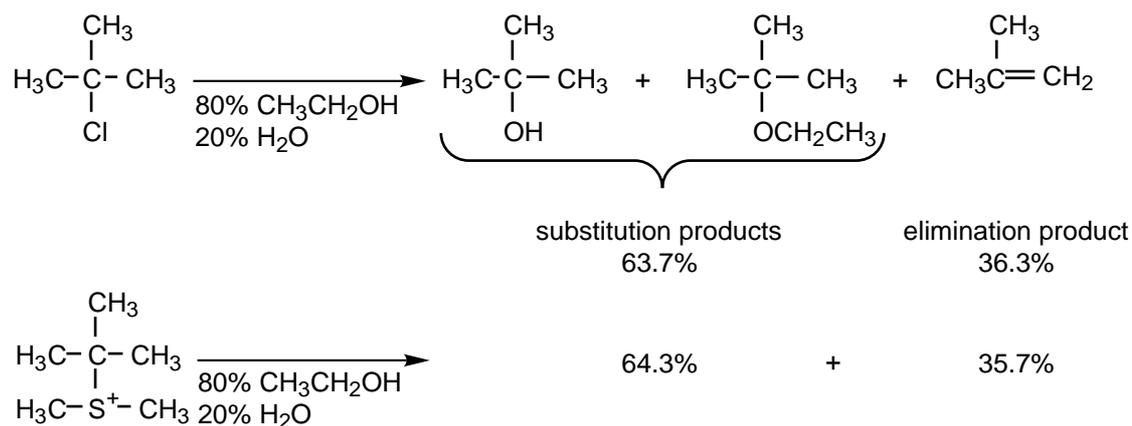
The first reaction is 7.5 times faster than the second reaction.

    (i)   What do these data suggest about the mechanism of the reaction?

    (ii)   Why are the rates of the two reactions different?

5

The naturally occurring sesquiterpene, β-curcumene, has been found to be a mixture of two isomers. The following sequence of reactions has been used to determine the structure of one of them.

$$A \xrightarrow[\text{workup}]{\text{oxidative}} 2CH_3COCH_3 \ + \ B \ (C_7H_{12}O_3)$$

$$B \xrightarrow[\text{2) } H_3O^+]{\text{1) } I_2/NaOH} C \ + \ CHI_3$$
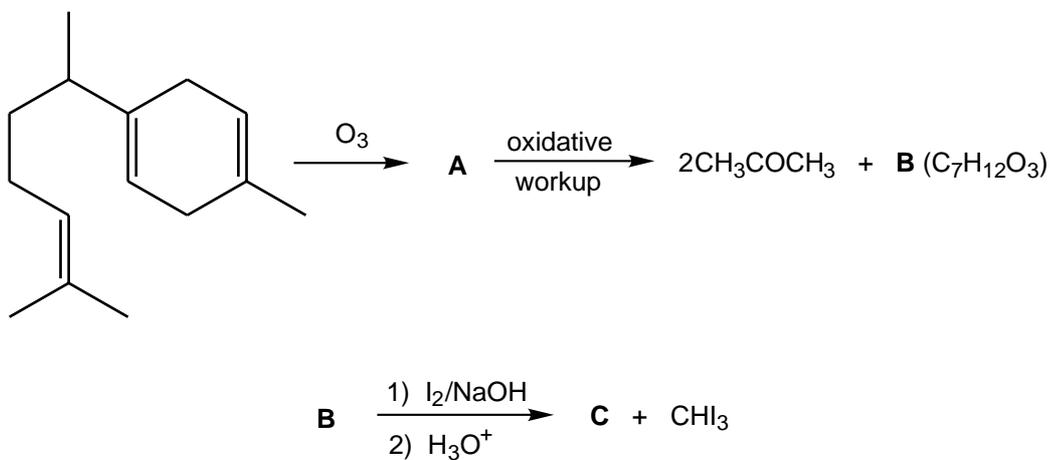
Draw the formulas representing the letters in the series of reactions.
Write a mechanism to show the conversion of **B** to **C**.