VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME .....

CT GROUP .....

CHEMISTRY **9729/03**

Paper 3 Free Response **17 September 2018**

Candidates answer on separate paper. **2 hours**

Additional Materials: Cover Page
Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
You must start the answer to each question on a fresh piece of writing paper.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **11** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

1 (a) All the elements in the third period of the Periodic Table, sodium to sulfur, form chlorides by direct combination with chlorine. Aluminium chloride may be produced by passing a stream of chlorine over heated aluminium metal in a long hard–glass tube.

(i) With the aid of equations, explain the following observations when different amounts of water were added to solid aluminium chloride.

(I) When a limited amount of water was added, a white solid was formed together with steamy fumes.

(II) When excess water was added, a solution of pH 3 was obtained. [2]

For **(I)**: $AlCl_3$ reacts with a limited amount of water to give $Al(OH)_3(s)$ and $HCl(g)$:
$AlCl_3(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3HCl(g)$

For **(II)**:
$AlCl_3$ undergoes hydrolysis as Al^{3+} has high charge density / strong polarising power. Polarisation of H_2O molecules favours the loss of H^+, and hence, acidity of the solution increases (pH ≈ 3).
$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$
$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$

(ii) Both aluminium chloride and copper(I) complex solutions are colourless whereas a solution of copper(II) sulfate appears blue. Explain these observations. [3]

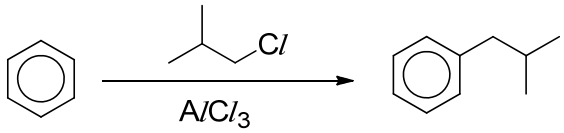
$AlCl_3$ solution is colourless because the energy gap between the n=2 and n=3 electronic shells is not within the visible light region. Hence, visible light is not absorbed.
Cu(I) complex is colourless because the 3d subshell is fully filled. Hence, no d-d /electronic transition can occur.
$CuSO_4$ solution appears blue because partially-filled 3d subshell is split into two different energy levels in the presence of ligands.
Electron from the lower energy level absorb a wavelength of light complementary to the observed colour and get promoted to the higher energy level. Thus, d-d transition can take place.

(iii) Briefly describe the process of anodisation of aluminium. Write ion-electron equations for the reactions occurring at the anode and the cathode. [2]

The aluminium is made the anode in the electrolysis of dilute sulfuric acid.
The oxygen released at the anode reacts with the aluminium surface to build up a thicker layer of aluminium oxide.

Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
Cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

(b) Compound **A** can be synthesised from benzene using aluminium chloride via a simple Friedel–Crafts alkylation as shown in **Reaction 1**. In addition, compound **B**, an isomer of compound **A** is also formed.

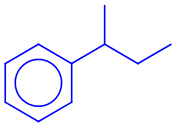
Reaction 1: 

+ compound **B**

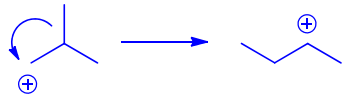
compound **A**

(i) Compound **B** rotates plane-polarised light. It is formed after the carbocation intermediate undergoes rearrangement through the movement of an alkyl group to an adjacent carbon atom bearing the positive charge.

Draw the structure of compound **B**. Explain why the rearrangement of the carbocation is favoured. [2]

B: 

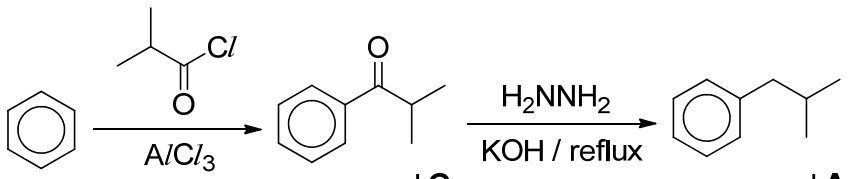
A primary carbocation rearranges into a secondary carbocation that is more stable because more electron-donating alkyl groups help dispersed the positive charge and stabilised the carbocation:



(ii) Explain why multi-substituted product is more favoured over mono-substituted product in **Reaction 1**. [1]

The alkyl group that is bonded to the benzene ring exerts electron–donating inductive effect.
This activates the benzene ring, making it even more susceptible towards electrophilic attack / reactive with respect to electrophilic substitution, thus forming multi-substituted product.

(c) Compound **A** can be formed via compound **C** as shown in **Reaction 2** below. **Step 1** involves Friedel–Crafts acylation, which have similar reaction conditions and mechanism as Friedel-Crafts alkylation.

Reaction 2: 

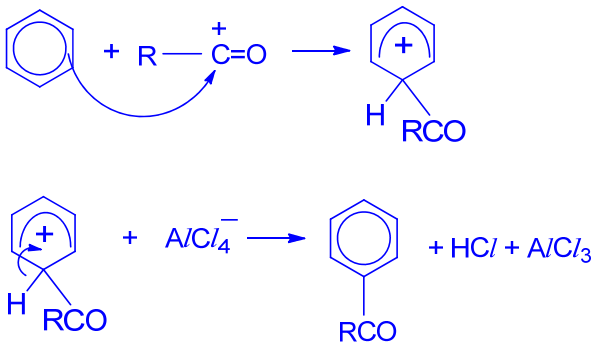
compound **C**

compound **A**

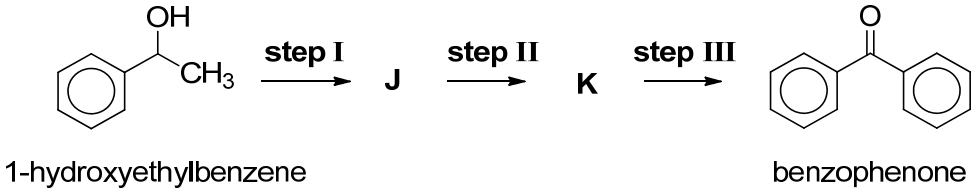
step 1 **step 2**

(i) Draw the mechanism for **step 1**. In your answer, show relevant charges, lone pairs of electrons and movement of electrons. [3]

Mechanism: Electrophilic substitution
Let R be $(CH_3)_2CH–$
$RCOCl + AlCl_3 \rightarrow RCO^+ + AlCl_4^-$

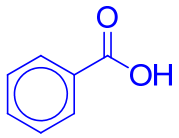


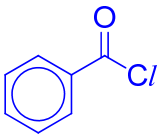
(ii) Hence, suggest reagents and conditions for **steps I** to **III** in the following synthesis of benzophenone from 1-hydroxyethylbenzene. Give the structural formulae of **J** and **K**.



1-hydroxyethylbenzene benzophenone

[4]

J: 

K: 

step I: $KMnO_4$, H_2SO_4, reflux
step II: PCl_5, room temperature OR PCl_3, reflux OR $SOCl_2$, reflux
step III: C_6H_6, anhydrous $AlCl_3$, room temperature

(d) A student wants to synthesise benzophenone using the reaction pathway illustrated in **(c)(ii)**. However, the solid sample of 1-hydroxyethylbenzene is contaminated with phenylamine. Briefly explain how you can separate 1-hydroxyethylbenzene from phenylamine via extraction. You are provided with

- ethanol, hexane, HCl(aq), NaOH(aq),
- separating funnel and
- apparatus commonly found in a college laboratory.

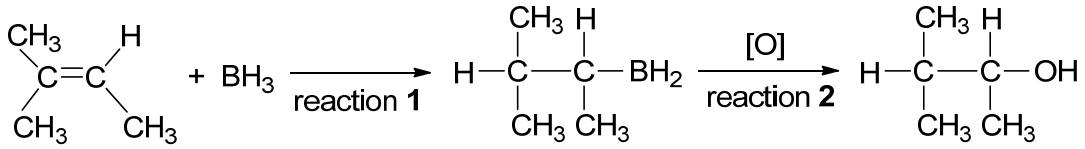
[3]

(i) Dissolve the solid sample in hexane.
(ii) Transfer the mixture to a separating funnel.
(iii) Add HCl(aq) to the mixture to convert phenylamine to the salt.
(iv) Shake the separating funnel and then drain off the bottom aqueous layer to get the organic layer.
(v) Evaporate the organic layer to obtain 1-hydroxyethylbenzene.

[Total: 20]

2 **(a)** Borane, BH_3, is used to synthesise alcohols from alkenes as shown in the reaction sequence below.

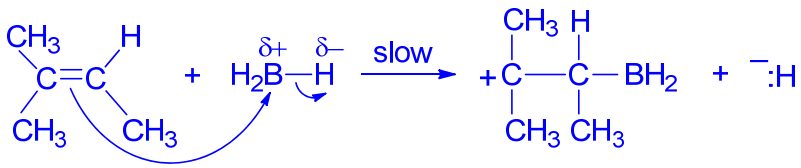
In reaction **1**, the BH_2 group from BH_3 is bonded to the **less** substituted carbon atom of the double bond. The remaining H atom from BH_3 is bonded to the other carbon atom.



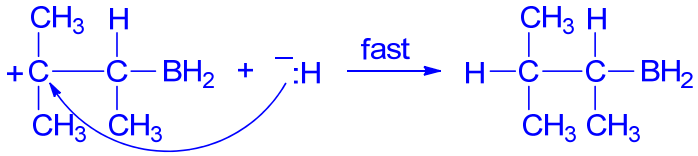
(i) Name and show the mechanism of reaction **1**. In your answer, show relevant charges, lone pairs of electrons and movement of electrons. [3]

Mechanism: Electrophilic addition

Step 1:



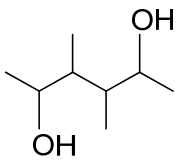
Step 2:



(ii) The product formed in reaction **1** contains a chiral centre. Explain whether the product formed rotates plane-polarised light. [2]

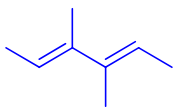
The product does not rotate plane-polarised light.
The alkene carbon atom is sp^2 hybridised (or trigonal planar).
Electrophile can attack from either the top or bottom plane of the C=C with equal probability. Hence, a racemic mixture is formed.

(iii) The diol **W** can be prepared by the same method as shown above.



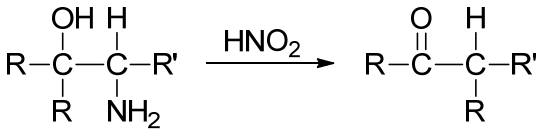
W

Draw the skeletal structure of the diene which could be used to prepare diol **W**. [1]



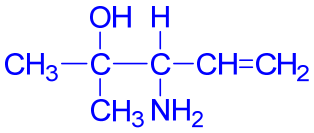
(b) A carbonyl compound, **Y**, $C_6H_{10}O$, can be synthesised from aminoalcohol, **X**, $C_6H_{13}ON$, in the presence of nitrous acid, HNO_2, via Tiffeneau-Demjanov Rearrangement.

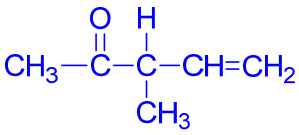
The simplified illustration of the rearrangement is shown below.

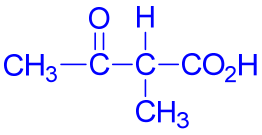


Y produces a yellow precipitate with iodine in alkaline solution. Treatment of **Y** with hot acidified solution of potassium manganate(VII) produces **Z,** $C_5H_8O_3$, along with a gas that forms a white precipitate in limewater. **Y** was also observed to decolourise bromine in tetrachloromethane readily.

(i) Explain the chemistry of the reactions described and deduce the structural formulae of **X**, **Y** and **Z**. [5]

X is 

Y is 

Z is 

Y undergoes oxidative cleavage with iodine in alkaline solution to give yellow ppt., CHI_3. Y has $CH_3CO–$ group.

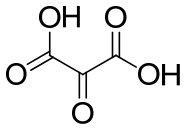
Y undergoes oxidative cleavage with hot acidified $KMnO_4(aq)$ to produce $CO_2(g)$ which forms white ppt. in limewater. Y is a terminal alkene (OR has $=CH_2$ group).

Y undergoes electrophilic addition with Br_2 in CCl_4. Y is an alkene.

(ii) With reference to the *Data Booklet*, identify an infra-red absorption range that will be shown by the functional group in **Y** but **not** in **X**. [1]

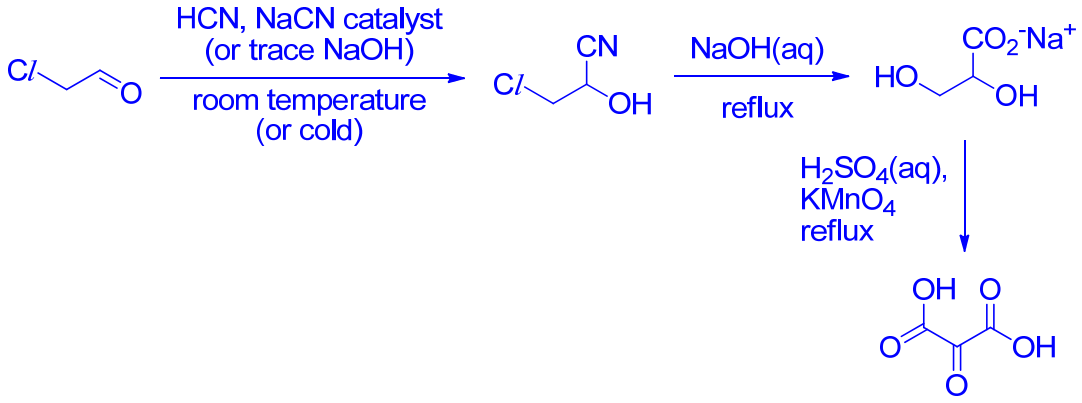
1670 – 1740 cm^{-1} due to ketone functional group.

(c) Devise a three–step synthesis to obtain compound **V** from the carbonyl compound, C*l*CH$_2$CHO.

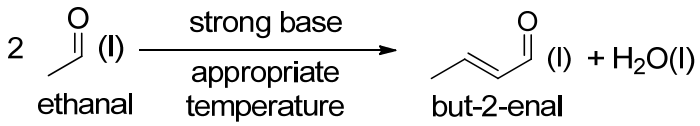


V

Give the reagents and conditions for each step. Draw the structural formulae of all the intermediates. [4]



(d) By either adjusting the reaction temperature or using a stronger base, ethanal can undergo Aldol Condensation reaction to form but-2-enal as shown below.



(i) With reference to the *Data Booklet*, calculate the enthalpy change for this Aldol Condensation reaction. [2]

bonds broken	
one C=O	+740
two C–H	2(+410)
Total	+1560

bonds formed	
one C=C	+610
two O–H	2(+460)
Total	+1530

ΔH = +1560 – (+1530) = +30 kJ mol^{-1}

(ii) Explain why the actual enthalpy change for the Aldol Condensation reaction is different from that calculated in **(d)(i)**. [1]

Bond energies quoted from *Data Booklet* are average values derived from a full range of molecules that contain the particular bonds.
OR
The bond energies quoted are for gaseous molecules but the reactants and products are in liquid state. Hence, the enthalpy changes of vapourisation are not accounted for.

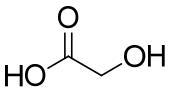
(iii) Suggest a simple chemical test to confirm the presence of but-2-enal in the product mixture. [1]

Test: Add $Br_2(aq)$ (at room temperature) to a small sample of the mixture.
Observation: If but-2-enal is formed, orange $Br_2(aq)$ decolourise.
OR
Test: Add Br_2 in CCl_4 (at room temperature) to a small sample of the mixture.
Observation: If but-2-enal is formed, orange-red Br_2 decolourise.

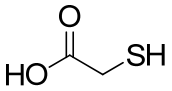
[Total: 20]

3 This question is about acids, bases and their derivatives.

(a) Glycolic acid and thioglycolic acid have very similar structures as shown below.



glycolic acid



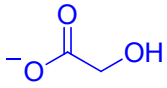
thioglycolic acid

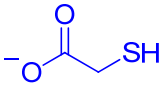
Glycolic acid has only one measurable pK_a value of 3.38. Thioglycolic acid has two measurable pK_a values of 3.67 and 10.31 respectively.

(i) Both oxygen and sulfur are Group 16 elements. Hence, suggest why the alcohol functional group of glycolic acid is a weaker acid than the –SH group of thioglycolic acid. [1]

The S–H bond is easier to break since S atom is bigger. Hence, less effective overlap of orbitals for the S–H bond.

(ii) Compare the first pK_a values of glycolic acid and thioglycolic acid. Explain its significance. [2]

Glycolic acid is the stronger acid since it has a lower pK_a value.
O atom is more electronegative than S,
hence the anion formed, 

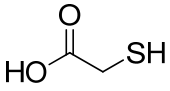
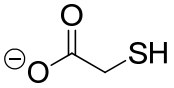
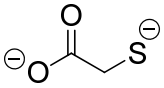
is more stable than that of thioglycolic acid, 

. This is due to the stronger electron withdrawing effect of O atom, dispersing the negative charge.

(iii) Suggest the major species present in solutions of thioglycolic acid with the following pH values.

- pH 0
- pH 7
- pH 14

[2]

pH 0	pH 7	pH 14
		

(iv) Assuming thioglycolic acid to be H_2A, calculate the percentage of each of the ionic species of thioglycolic acid present at pH 9.0. [3]
Let the thioglycolic acid be H_2A. As pH 9 is after the 1st end-point, we shall use

pK_a = 10.31 for calculation.

$pK_a = pH - \log_{10}\frac{[A^{2-}]}{[HA^-]}$

$10.31 = 9 - \log_{10}\frac{[A^{2-}]}{[HA^-]}$

$\log_{10}\frac{[A^{2-}]}{[HA^-]} = -1.31$

$\frac{[A^{2-}]}{[HA^-]} = 0.0490$

Or $K_a = \frac{[A^{2-}][H^+]}{[HA^-]}$

$\frac{[A^{2-}]}{[HA^-]} = \frac{K_a}{[H^+]} = \frac{10^{-10.31}}{10^{-9}} = 0.0490$

$[A^{2-}] + [HA^-] = 100\%$

$0.049[HA^-] + [HA^-] = 100\%$

$\Rightarrow [A^{2-}] = 4.67\%$; $[HA^-] = 95.3\%$

(v) Hence, calculate the volume of 0.100 mol dm^{-3} aqueous sodium hydroxide needed to form the solution in **(iv)** when added to 25.0 cm^3 of 0.100 mol dm^{-3} thioglycolic acid. [2]

$H_2A + NaOH \rightarrow HA^- + H_2O$

$HA^- + NaOH \rightarrow A^{2-} + H_2O$

Amount of H_2A used = $25/1000 \times 0.100 = 2.50 \times 10^{-3}$ mol

Amount of NaOH required

= amount of NaOH to form HA^- from H_2A + amount of NaOH to form 4.67% A^{2-}

= $2.50 \times 10^{-3} + (4.67\% \times 2.50 \times 10^{-3})$

= 2.62×10^{-3} mol

Volume of NaOH

= amount of NaOH / [NaOH]

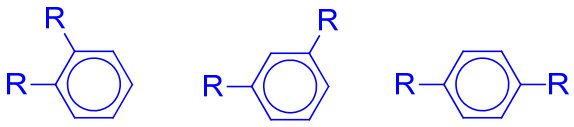
= $2.62 \times 10^{-3} \div 0.100$

= 0.0262 dm^3 = 26.2 cm^3

(b) The hydroxide ion is the strongest possible base in aqueous solution, but in organic solvents it is possible to have other stronger bases. In 2016, Australian researchers announced the formation of an organic gas-phase di-anion, DEB^{2-}. It is the strongest base known.

DEB^{2-} is produced from compound **A** which is a disubstituted benzene, $C_6H_4R_2$, where R− is the same substituent.

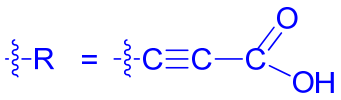
(i) Draw all the possible structures of $C_6H_4R_2$. [1]



(ii) Compound **A** has the molecular formula $C_{12}H_6O_4$ and effervesces on addition of sodium hydrogen carbonate.

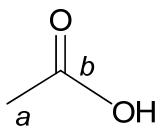
Suggest the functional group present in the substituent R− that is responsible for the effervescence. Hence, deduce a structure for R−. [1]

Carboxylic acid

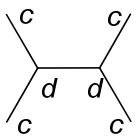


^{13}C nuclear magnetic resonance (NMR) spectroscopy is an analytical method. In simplistic use, it allows different types of carbon atoms to be deduced from the corresponding signals in the spectrum.

For example, the ^{13}C NMR spectra for the ethanoic acid and 2,3-dimethylbutane would both show two distinct signals since each molecule has only two different carbon environments. This is shown in the diagram below where equivalent carbon environments are labelled with the same letter.

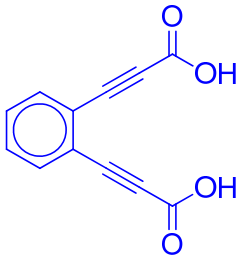


ethanoic acid



2,3-dimethylbutane

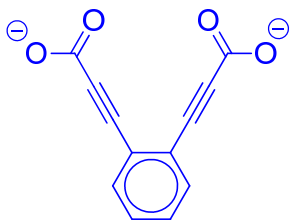
(iii) Compound **A** is found to have six signals in its ^{13}C NMR spectrum. Using your answers to **(b)(i)**, **(b)(ii)** and the information provided above, deduce the structure of compound **A**. [1]



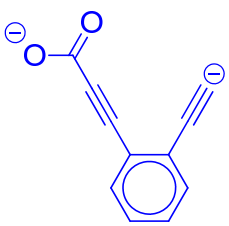
(iv) Compound **A** forms DEB^{2-} via intermediates $\mathbf{B}^{2-}$ and $\mathbf{C}^{2-}$ through the removal of positive ions or neutral molecule from the substituent R−.

Compound **A**		$\mathbf{B}^{2-}$		$\mathbf{C}^{2-}$		DEB^{2-}
$C_{12}H_6O_4$		$M_r = 212$		$M_r = 168$		$M_r = 124$

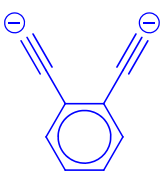
Determine the skeletal structures of $\mathbf{B}^{2-}$, $\mathbf{C}^{2-}$ and DEB^{2-}. [2]



$\mathbf{B}^{2-}$



$\mathbf{C}^{2-}$



DEB^{2-}

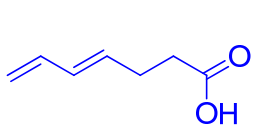
(c) An organic acid **D**, $C_7H_{10}O_2$, is refluxed with acidified $KMnO_4$ to produce only one organic compound **E**, $C_4H_6O_4$. Compound **D** decolourises bromine water. Gentle heating of the anhydrous crystals of compound **E** produces a neutral compound **F**, $C_4H_4O_3$, which does not react with sodium metal or give a precipitate with 2,4–dinitrophenylhydrazine.

Compound **F** reacts with ethanol in the presence of a catalyst to form compound **G**, $C_6H_{10}O_4$.

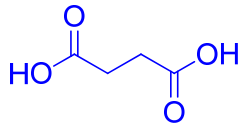
Compound **F** also reacts with methylamine, CH_3NH_2, to give a compound **H**, $C_5H_9NO_3$, which gives a salt on reaction with NaOH but not with HC*l*. Compound **H** does not display enantiomerism.

Both compounds, **G** and **H**, produce **E** on heating with dilute sulfuric acid.

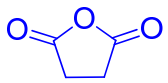
Suggest the structures of **D**, **E**, **F**, **G** and **H**. [5]



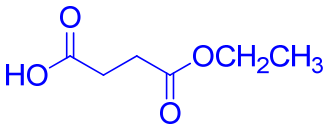
D



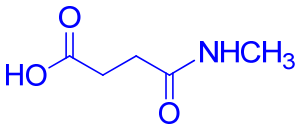
E



F



G



H

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** Chlorine dioxide, C*l*O_2, is a reddish-yellow gas that does not occur naturally in the environment. When added to aqueous hydroxide, chlorine dioxide undergoes the following reaction producing chlorate(III) and chlorate(V) ions.

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

Unlike C*l*O_2, bromine dioxide is less stable and react with aqueous hydroxide to produce bromide and bromate(V) ions. Bromate(V) ion is formed more readily than chlorate(V) ion.

(i) Write a balanced equation for the reaction of bromine dioxide with sodium hydroxide. Hence, state the type of reaction. [2]

$6BrO_2 + 6NaOH \rightarrow NaBr + 5NaBrO_3 + 3H_2O$
Disproportionation.

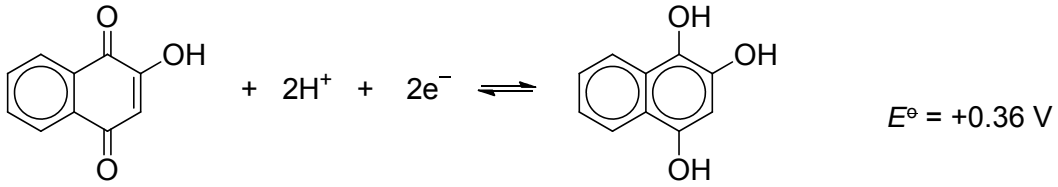
(ii) Explain why bromate(V) ion is formed more readily than the chlorate(V) ion in aqueous hydroxide. [1]

Bromine element is a stronger reducing agent than chlorine, hence, it is more likely to be oxidised to a higher oxidation state.
OR

Bromine atom is bigger / less electronegative, hence, easier to lose electrons to form the +5 oxidation state.

Lawsone is a dye that is extracted from the henna plant, *Lawsonia inermis*. Although its natural colour is yellow, lawsone reacts with the proteins in hair and skin to produce the characteristic brown henna colour.

Lawsone can be readily reduced to a colourless compound **A**, 1,2,4-trihydroxynaphthalene. However, the hair dye containing lawsone is relatively resistant to the decolourisation by chlorine water in swimming pools.



$E^{\ominus}$ = +0.36 V

lawsone

compound **A**,
1,2,4-trihydroxynaphthalene

(iii) With reference to the *Data Booklet*, explain why chlorine water cannot spontaneously decolourise lawsone. [2]

$2HOCl + 2H^+ + 2e^- \rightleftharpoons Cl_2 + 2H_2O$ $\quad E^{\ominus} = +1.64$ V
If lawsone undergoes decolourisation, it is reduced while chlorine water is oxidised.
$E^{\ominus}_{cell} = E^{\ominus}_{Red} - E^{\ominus}_{Ox}$ $\quad = +0.36 - (+1.64) = -1.28$ V
Since $E^{\ominus}_{cell} < 0$, the reaction is thermodynamically non-spontaneous.

(iv) The Gibb's free energy change, $\Delta G^{\ominus}$, is related to the equilibrium constant, K_c, through the following equation:

$$\Delta G^{\ominus} = -RT \ln K_c$$

where $\Delta G^{\ominus}$ is in J mol^{-1}.

Using the answer from **(a)(iii)** and the *Data Booklet*, calculate K_c. Hence, deduce whether the position of equilibrium lies more on the left or right hand side of the equilibrium under standard conditions. [2]

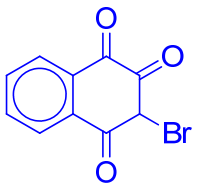
$\Delta G^{\ominus} = -nFE^{\ominus}_{cell} = -2 \times 96500 \times (-1.28) = 2.47 \times 10^5$ J mol^{-1}
$\Delta G^{\ominus} = -RT \ln K_c = -8.31 \times 298 \times \ln K_c = 2.47 \times 10^5$
$\Rightarrow K_c = 4.73 \times 10^{-44} << 1$ means position of equilibrium lies more to the left.

(v) Suggest a reagent that could be used to convert lawsone into compound **A** in the laboratory. [1]

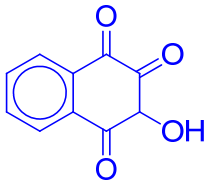
$NaBH_4$ (in ethanol) or $LiAlH_4$ (in dry ether)

(vi) When lawsone is reacted with Br_2(aq), compound **B** with molecular formula, $C_{10}H_5O_3Br$, is formed. **B** reacts with 3 mol of 2,4-DNPH. Reaction of **B** with NaOH(aq) gives **C**. Compound **C** reacts with HCl and $ZnCl_2$ to produce **D**. The reaction of **D** with methylamine gives **E** with molecular formula, $C_{11}H_9O_3N$, which further reacts with CH_3COCl to give a neutral compound **F**.

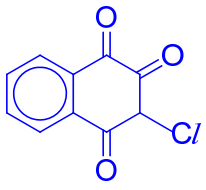
Suggest the skeletal formulae of compounds **B**, **C**, **D**, **E** and **F**. [5]



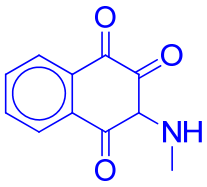
B



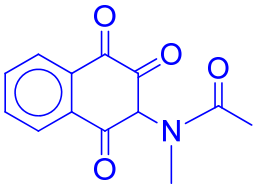
C



D

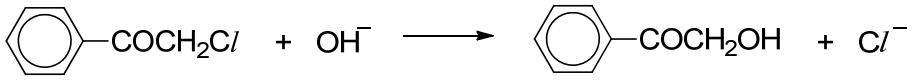


E



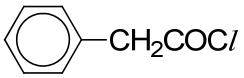
F

(b) Chloroacetophenone was formerly the most widely used tear gas, under the codename *CN*. It was used in warfare and in riot control. Residues of *CN* can be destroyed by the hydrolysis of alkali.

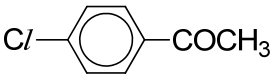


chloroacetophenone

G and **H** are isomers of chloroacetophenone.



G



H

(i) Arrange the isomers, chloroacetophenone, **G** and **H**, in increasing ease of hydrolysis. Explain your choice. [3]

Increasing ease of hydrolysis: H < chloroacetophenone < G
H: The partial double bond character due to the overlapping of the p-orbitals between the C*l* and C atoms of benzene makes the C−C*l* bond difficult to break.
G: The carbonyl carbon is highly electron-deficient due to the presence of electronegative O atom. Hence, more susceptible to nucleophilic attack by water molecule.

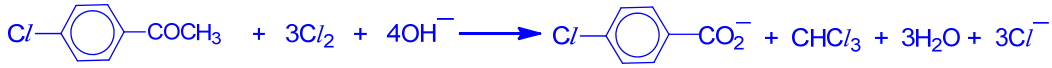
(ii) Iodoacetophenone is even more reactive than chloroacetophenone towards alkaline hydrolysis. Briefly explain why it is so. [1]

The C−I bond is weaker than the C−C*l* bond because less effective overlap of orbitals due to bigger I atom.

(iii) Suggest a suitable experimental technique for studying the rate of hydrolysis. [1]

Monitor the concentration of OH^- by titration with acid at regular time intervals.
OR Monitor the change in pH using a pH probe at regular time intervals.

(iv) Compound **H** reacts with alkaline aqueous iodine to give a yellow solid, CHI_3. Similar reaction occurs between compound **H** and alkaline aqueous chlorine. Write a balanced equation for the reaction of compound **H** with alkaline aqueous chlorine. State the observation. [2]



Pale greenish-yellow solution decolourised.

[Total: 20]

5 **(a)** Copper can be extracted from a double salt, $CuFeS_2$, by reacting it with oxygen and silicon dioxide. In this reaction, copper, iron(II) silicate, $FeSiO_3$, and an oxide of sulfur are produced. The oxide of sulfur does not decolourise acidified potassium manganate(VII).

(i) Draw a dot-and-cross diagram for $CuFeS_2$. [1]

$[Cu]^{2+}$ $[Fe]^{2+}$ 2 [xx S xx]$^{2-}$
oo
xx

(ii) Write a balanced equation for the overall reaction. Deduce the reducing agent in the reaction. [2]

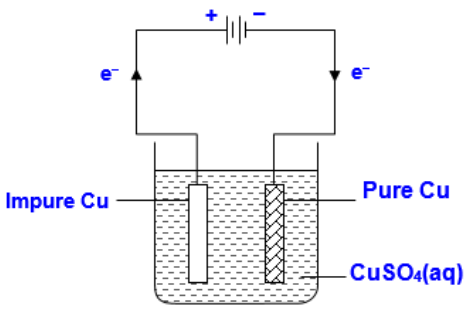
$CuFeS_2 + \frac{7}{2}O_2 + SiO_2 \rightarrow Cu + FeSiO_3 + 2SO_3$

S^{2-} or sulfide is the reducing agent as the oxidation number of S increases from –2 to +6

(iii) Copper(I) sulfide is one of the reaction intermediate. Write the full electronic configuration of copper(I). [1]

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

(iv) The crude copper obtained contains trace amount of silver and nickel. With relevant data from the *Data Booklet* and a labelled diagram, describe how the crude copper can be purified through electrolysis. [4]



Set up an electrolytic cell with pure Cu connected to the negative terminal of the power source whereas the crude Cu to the positive end. Aqueous copper(II) sulfate is the electrolyte used.
At the anode, both Ni and Cu are oxidised due to their more negative/less positive $E^{\ominus}$ value than Ag.
Cu is oxidized to form Cu^{2+}.

Ag will not be oxidised because of a more positive $E^{\ominus}$ value. It will fall off.
$Ni^{2+} + 2e^- \rightleftharpoons Ni \quad -0.25\ V$
$Cu^{2+} + 2e^- \rightleftharpoons Cu \quad +0.34\ V$
$Ag^+ + e^- \rightleftharpoons Ag \quad +0.80\ V$

At the cathode, Cu^{2+} is reduced to Cu because the $E^{\ominus}$ value is more positive than that of Ni^{2+}.

(v) 5.0 g of crude copper containing 0.1 g of silver and 0.1 g of nickel is purified through electrolysis as in **(a)(iv)**. During electrolysis, 80% of the current is used to oxidise the metals. With reference to the *Data* Booklet, determine the time needed to purify the copper completely using a current of 2 A. [2]

Amount of Cu = 4.8/63.5 = 0.0756 mol
Amount of Ni = 0.1/58.7 = 0.00170 mol
Total amount of electrons needed = (0.0756 + 0.00170) x 2 = 0.1546 mol
Charge needed = 0.1546 x 96500 = 14918.9 C
Time = Q/I
$= \frac{14918.9}{2} \times \frac{100}{80}$ s
$= \frac{7459.45}{60} \times \frac{100}{80}$ min
= 155.3 min or 155 min

(vi) A student accidentally added some iron(III) nitrate into a solution of copper(II) nitrate. You are provided with

- $NH_3(aq)$, $NaOH(aq)$, $HNO_3(aq)$ and
- apparatus commonly found in a college laboratory.

Describe how the student could separate these two metal ions in the mixture. Give relevant equations and state the types of reactions that have occurred. [3]

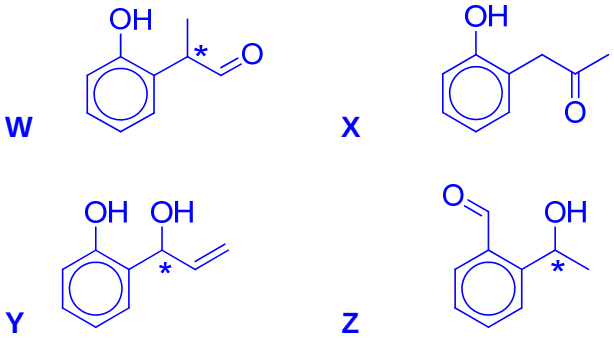
Add aqueous NH_3 to the mixture. Cu^{2+} undergoes precipitation to form $Cu(OH)_2$ when ionic product > K_{sp}. Then in excess $NH_3(aq)$, ligand exchange reaction takes place with NH_3.
$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
$Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$
$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(H_2O)_2(NH_3)_4]^{2+} + 4H_2O$
Fe^{3+} will form insoluble $Fe(OH)_3$ through precipitation when ionic product > K_{sp}.
$Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$
Filter the mixture.

(b) Compounds **W**, **X**, **Y** and **Z** are constitutional isomers with molecular formula $C_9H_{10}O_2$ and none of them shows *cis-trans* isomerism. All four isomers can form intra-molecular hydrogen bonding. The results of seven tests carried out on the four isomers are shown below.

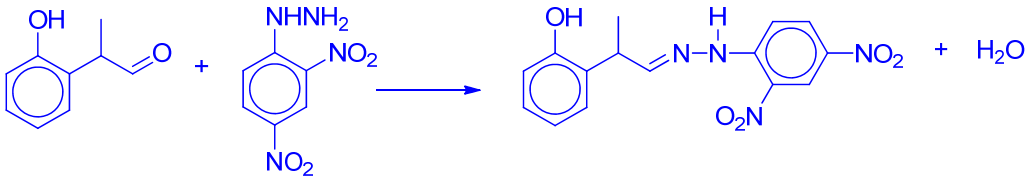
	Test	W	X	Y	Z
1	Rotate plane-polarised light	Yes	No	Yes	Yes
2	Add dilute NaOH at room temperature	Soluble	Soluble	Soluble	Insoluble

3	Heat with acidified $K_2Cr_2O_7$	Orange solution turned green	Orange solution did not turn green	Orange solution turned green	Orange solution turned green
4	Add 2,4-DNPH	Orange precipitate	Orange precipitate	No orange precipitate	Orange precipitate
5	Warm with Fehling's solution	Brick-red precipitate	No brick-red precipitate	No brick-red precipitate	No brick-red precipitate
6	Warm with Tollens' reagent	Grey ppt	No grey ppt	No grey ppt	Grey ppt
7	Warm with I_2(aq) and NaOH(aq)	No pale yellow precipitate	Pale yellow precipitate	No pale yellow precipitate	Pale yellow precipitate

(i) Use the information in the table above to suggest a skeletal formula for each of these four isomers. [4]



(ii) Write a balanced equation for the reaction between **W** and 2,4-DNPH. [1]



(iii) Explain why **W** is soluble in NaOH(aq) at room temperature. [2]

W contains phenol which undergo neutralization with NaOH to form ionic sodium phenoxide.

The ion-dipole interactions formed between the ions and water release sufficient energy to overcome the hydrogen bondings between water molecules and ionic bonds in sodium phenoxide.

[Total: 20]

End of Paper