TEMASEK JUNIOR COLLEGE

PRELIMINARY EXAMINATIONS

HIGHER 2

CHEMISTRY 9729/03

Paper 3 Free Response 16 September 2019

2 hours

Candidates answer on separate booklet.

Additional Materials: 12-Page Answer Booklet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, Centre number, index number and name on all the work you hand in.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
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.

Section A

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

1 The term *chelates*, originates from the Greek word *chele* for "claw". It refers to compounds containing ligands bonded to a central metal atom or ion at two or more points.

Ligand exchange occurs when ammonia and ethylenediamine (en), $H_2NCH_2CH_2NH_2$, are added separately to copper sulfate solution.

(a) (i) Explain all the changes observed when aqueous ammonia is added dropwise to $Cu^{2+}(aq)$ till in excess. Suggest the formulae of all relevant copper compounds formed and write equations for all reactions. [4]

When aqueous ammonia is added dropwise to blue $Cu^{2+}(aq)$ solution, a blue precipitate of $Cu(OH)_2$ is formed. Ammonia acts as a base.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Cu(OH)_2(H_2O)_4](s) + 2H_2O(l) \quad \text{— (1)}$$

Blue ppt

OR $Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$

In excess ammonia, blue precipitate $Cu(OH)_2(s)$ dissolves to give a dark blue solution due to the formation of the complex ion, $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$.

Ammonia acts as a ligand (or ligand exchange has taken place).

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l) \text{ — (2)}$$

Dark blue solution

Formation of the complex shifts the equilibrium in equation (1) to the left, thus, the blue precipitate dissolves.

(ii) Suggest why ethylenediamine can function as a *chelating ligand*. [1]

- **Ethylenediamine molecule has two lone pair of electrons on the nitrogen atoms to form two dative bonds with the Cu^{2+} ion.**

(iii) When ethylenediamine is added to $Cu^{2+}(aq)$, the following occurs.

$$[Cu(H_2O)_6]^{2+} + 2en \rightarrow [Cu(en)_2(H_2O)_2]^{2+} + 4H_2O$$

Predict whether ethylenediamine or ammonia gives a more positive entropy change when added to $Cu^{2+}(aq)$. [2]

$$Cu(H_2O)_6]^{2+} + 2en \rightarrow [Cu(en)_2(H_2O)_2]^{2+} + 4H_2O$$

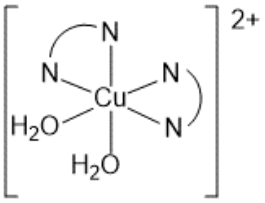
$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$$

- **Ethylenediamine (a bidentate ligand) gives a more positive change in entropy when added to $Cu^{2+}(aq)$ as**
- **there is an increase in number of particles (from 3 to 5) and thus more way of arranging the particles.**

(iv) Suggest the coordination number and shape of $[Cu(en)_2(H_2O)_2]^{2+}$. [1]

- **Coordination number = 6, Shape = Octahedral**

(v) The complex ion $[Cu(en)_2(H_2O)_2]^{2+}$ can exist as three stereoisomers, **A**, **B** and **C**. Isomers **A** and **B** rotate plane-polarised light but **C** does not. The structure of **A** is represented below.

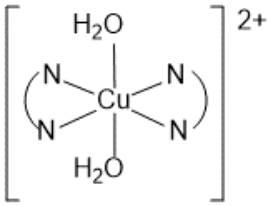


Isomer **A**

where  represents ethylenediamine (en)

Draw the structure of **C**. [1]

- **Isomer C**



(b) Photochromic glass used for sunglasses contains AgC*l* crystals which are added while the glass is in molten state. The glass darkens when exposed to bright light and the following reaction is involved.

$$Ag^+ + Cl^- \rightleftharpoons Ag + Cl$$

(i) Suggest why the glass darkens when exposed to bright light. [1]

- **In presence of UV light, colorless Ag^+ cations form elemental Ag and the glass appear darker.**

The glass darkens significantly within about a minute of exposure to bright light but takes a longer time to clear when there is less light. Small amount of CuC*l* crystals are often added to the glass to speed up the reverse process. No elemental copper is involved in the process.

$$Ag + Cl \rightarrow Ag^+ + Cl^-$$

(ii) Explain why the copper(I) ions can be described as a *homogeneous catalyst*. [2]

The copper(I) ions are in the •same phase as the reactants, and is •not consumed/used up by the reaction.

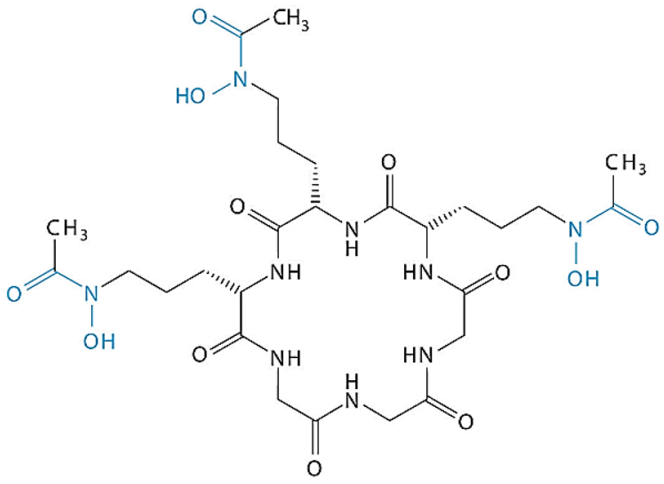
(iii) State the property, typical of transition metals, which allows copper(I) ions to behave as a homogenous catalyst in the reverse reaction. Include relevant chemical equations to support your answer. [3]

- **The catalytic activity of transition metals in homogenous catalysis depends on their ability to exist in variable oxidation states.**

The catalysed pathway for the reverse reaction.

- **$Cu^+ + Cl \rightarrow Cu^{2+} + Cl^-$**
- **$Cu^{2+} + Ag \rightarrow Cu^+ + Ag^+$**

(c) Microorganisms synthesise and secrete organic molecules called siderophores to increase the total concentration of available iron in the surrounding medium. Ferrichrome is a siderophore produced by fungi.



Ferrichrome

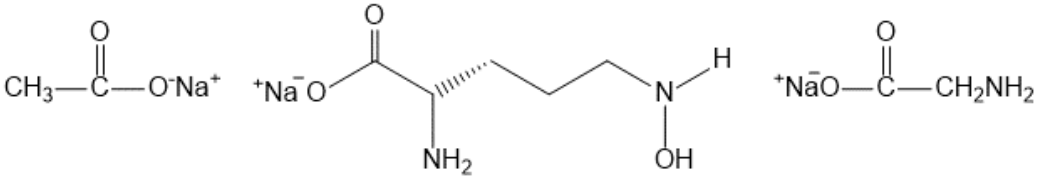
(i) Ferrichrome binds to iron(III) ions via its oxygen atoms. This process facilitates the transportation of iron(III) ions into the interior of a cell.

Suggest what bonds are formed during this process and why iron(III) does not bind to nitrogen atoms in ferrichrome. [2]

- **Ferrichrome binds to iron(III) ions through the formation of dative bonds between oxygen atoms and iron(III) ions.**
- **Lone pair of electrons on the nitrogen atoms are delocalised over the C=O group and are not available for dative bonding to iron(III) ions.**

(ii) Draw the structures of the products formed when ferrichrome is heated with aqueous sodium hydroxide. [3]

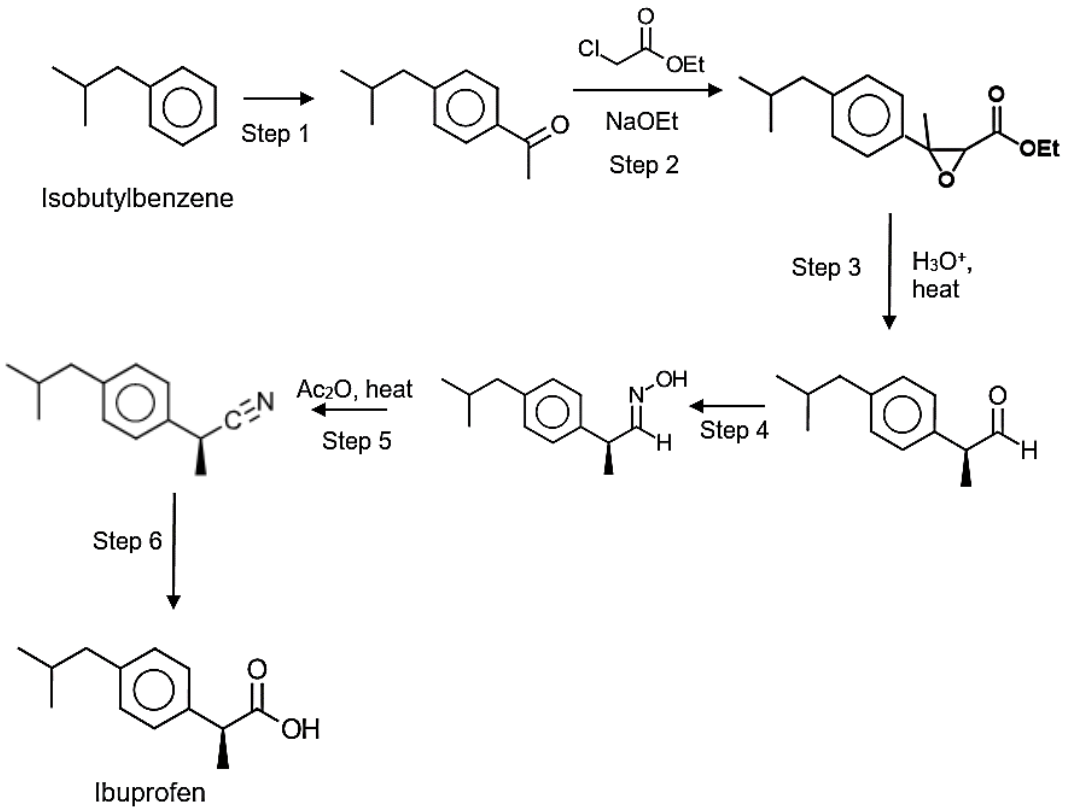
••• 1 mark for each structure



[Total: 20]

2 Ibuprofen is a nonsteroidal anti-inflammatory drug. It works by reducing hormones that cause inflammation and pain in the body. Ibuprofen is used to reduce fever and treat pain or inflammation.

The conventional synthesis of ibuprofen from isobutylbenzene is shown below. Step 4 of the synthesis resembles the reaction between a carbonyl compound and Brady's reagent.



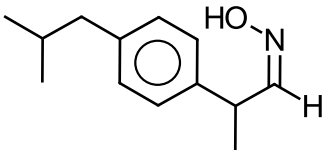
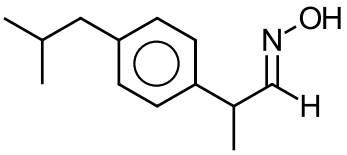
(a) Name the types of reaction that are occurring during steps 4 and 5. [2]

- **Step 4 : condensation reaction**
- **Step 5 : elimination**

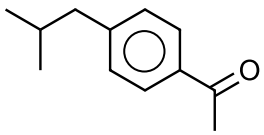
(b) Suggest the reagents and conditions for steps 1, 4 and 6. [3]

- **Step 1 : CH_3COCl , anhydrous $AlCl_3$, r.t.p**
- **Step 4 : NH_2OH, r.t.p**
- **Step 6 : dilute HCl, heat**

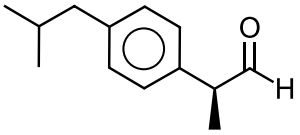
(c) Draw the structures of the stereoisomers of the product formed from step 4 and state the type of stereoisomerism exhibited. [2]

- **Type : cis-trans isomerism**
-  **and** 

(d) Describe a simple chemical test to distinguish between the two compounds, **X** and **Y** obtained from synthesis above. [2]



Compound **X**



Compound **Y**

●**Add Tollens reagent** (diammine silver(I) complex), **HEAT** to separate samples.

●**Silver mirror observed for compound Y. No silver mirror for compound X.**

Alternative tests :

*** Alkaline aq. Iodine and warm. Yellow ppt observed for compound X and no yellow ppt for compound Y.**

*** Fehling's reagent, heat. Brick-red observed for compound Y and no brick-red ppt for compound X**

*** Acidified $K_2Cr_2O_7$, heat. Orange dichromate turned green when added to compound Y. No colour change for compound X.**

(e) Potassium chloride and potassium iodide can be distinguished by treating the compounds separately with concentrated sulfuric acid.

(i) Potassium chloride and concentrated sulfuric acid reacts in an equimolar ratio to produce white fumes of hydrogen chloride.

Write an equation for the reaction of potassium chloride with concentrated sulfuric acid. [1]

Reaction of KCl and H_2SO_4

●$KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl$

(ii) Potassium iodide reacts with concentrated sulfuric acid in a similar manner. However, the white fumes of hydrogen iodide would further react with concentrated sulfuric acid to produce violet fumes and hydrogen sulfide gas.

Suggest an explanation for the difference in reactions, and write equations for the above observations. [2]

Reaction of KI and H_2SO_4

$KI + H_2SO_4 \longrightarrow HI + KHSO_4$

Half equations:

$2I^- \rightarrow I_2 + 2e^-$ (x4)

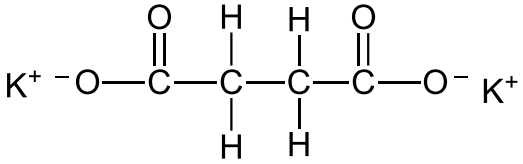
$H_2SO_4 + 8H^+ + 8e^- \rightarrow H_2S + 4H_2O$

● Overall: $8HI + H_2SO_4 \longrightarrow 4I_2 + H_2S + 4H_2O$

● I^- being a stronger reducing agent (than Cl^-) will reduce H_2SO_4 to H_2S and itself oxidised to I_2. OR ● $E^\ominus_{I_2/I^-}$ is more negative than $E^\ominus_{Cl_2/Cl^-}$, thus more easily oxidized, stronger reducing agent than Cl^-. $E^\ominus_{I_2/I^-} = +0.54V$; $E^\ominus_{Cl_2/Cl^-} = +1.36V$.

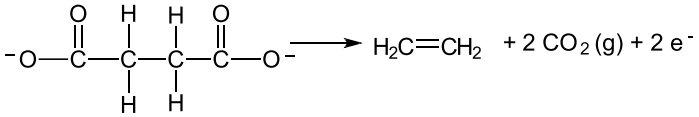
(f) When aqueous potassium salts of a dicarboxylic acid are electrolysed using inert platinum electrodes, alkenes are formed at the anode.

(i) The electrolysis of aqueous potassium succinate gives ethene at the anode.



Potassium Succinate

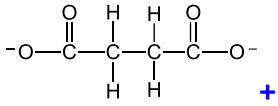
Write an ion-electron half equation for the oxidation of succinate at the anode. [1]



(ii) Write an equation for the reaction at the cathode and for the overall reaction. [2]

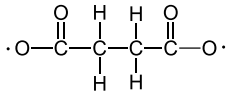
•At the cathode: $\mathbf{2H_2O + 2e^- \rightarrow H_2 + 2OH^-}$

[Explanation: Since $E^{\ominus}_{H_2O/H_2}$ is more positive than $E^{\ominus}_{K^+/K}$, H_2O is preferentially reduced at the cathode, liberating H_2.]

•Overall reaction:  **$+ 2H_2O \rightarrow H_2C{=}CH_2 + 2CO_2 + H_2 + 2OH^-$**

(iii) The mechanism of the reaction at the anode involves three steps:

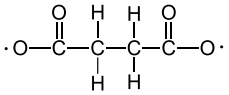
Step 1: There is an initial loss of 2 electrons on succinate ion to form



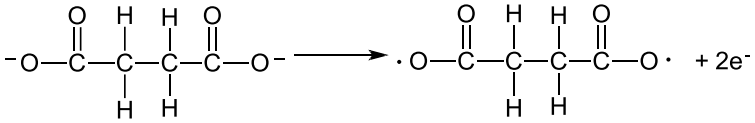
Step 2: This is followed by decarboxylation which involves the homolytic breaking of two C–C bonds, giving a radical intermediate $\bullet CH_2CH_2\bullet$

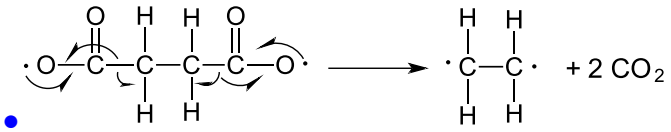
Step 3: The third step involves forming a covalent bond, producing ethene as the product.

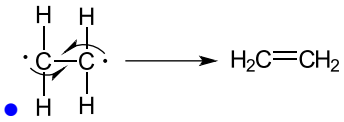
Use the information given above to draw the mechanism for Steps 2 and 3.

You are advised to use structural formulae for all species, such as  , so that it is clear which bonds are broken and which are formed.

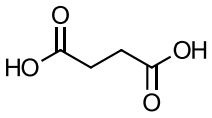
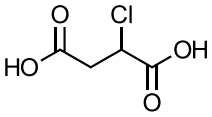
Represent with a half arrow ( ) for movement of a single unpaired electron and indicate any unpaired electrons by a dot (•). [2]







(g) The strength of a carboxylic acid depends on its structure. An example of this is the comparison of succinic acid and its derivatives.

Acid	pK_{a1}
	4.21
	-

Explain if pK_a of chlorosuccinic acid is lower or higher than the pK_a of succinic acid. [1]

●pK_a of chlorosuccinic acid is lower (a stronger acid)

Reason: presence of electron-withdrawing Cl-atom disperse the negative charge on anion more, better stabilising the anion more, so chlorosuccinic acid is a stronger acid (lower pK_a).

[Total: 18]

3 On 28 November 2018, an explosion erupted near the Hebei Shenghua Chemical Industrial plant, killing at least 23 people and injuring many more. It was reported that the explosion originated from a truck transporting ethyne gas, C_2H_2, which then set off a chain reaction that engulfed at least 50 other vehicles.

When mixed appropriately with air, C_2H_2 explodes upon ignition as follows.

$$C_2H_2\,(g) + \frac{5}{2}O_2\,(g) \longrightarrow 2CO_2\,(g) + H_2O\,(g)$$

This explosion may have generated an estimated 20.8 million kilojoules of energy.

(a) Describe the hybridisation of the orbitals in, and the bonds between, the carbon atoms within an ethyne molecule. [3]

- One of the 2s electrons in each C atom is promoted to the vacant 2p orbital, and **the s and one p orbital then hybridise/mix to give two sp hybrid orbitals** which contain one electron each.
- One **σ bond** between adjacent C atoms formed through / bonded by **head –on overlap of** one **sp hybrid orbital of each C atom**.

- Two **π bonds** are formed through **sideway overlap of the** two unhybridised **p orbitals of each C atom.**

(b) **(i)** Using the bond energies in the *Data Booklet*, calculate the enthalpy change of combustion of ethyne. [2]

$H–C\equiv C–H + \frac{5}{2} O=O \longrightarrow 2\ O=C=O + H–O–H$

- $\Delta H_c^{\ominus}$ = [2 BE(C–H) + BE (C≡C) + $\frac{5}{2}$ BE(O=O)] – [4 BE(C=O) + 2 BE(O–H)]

$\Delta H_c^{\ominus}$ = [2(410) + (840) + $\frac{5}{2}$ (496)] – [4(805) + 2(460)]

- = **–1240 kJ mol^{-1}**

(ii) Using your answer in **(b)(i)**, calculate the volume of ethyne gas transported by the truck at 28°C and 1 bar. [2]

- Amount of ethyne gas used for combustion = $\frac{20.8\times10^6}{1240}$ = 16774 mol

Using pV=nRT

- Vol. of ethyne gas produced = $\frac{16774\times8.31\times(273+28)}{1.00\times10^5}$ = 420 m^3

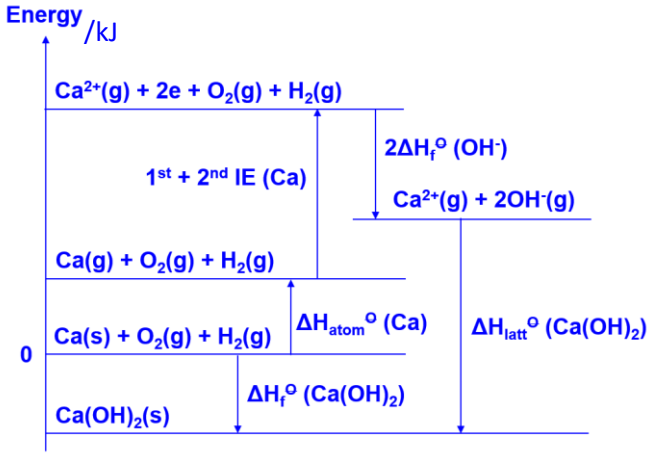
(c) One of the ways that ethyne gas can be produced is via the reaction of calcium carbide, CaC_2, with water, producing solid calcium hydroxide as a by-product.

(i) Using the following information and relevant data from the *Data Booklet*, construct an energy cycle to calculate the lattice energy of solid calcium hydroxide. [3]

$$Ca^{2+}(g) + 2OH^-(g) \longrightarrow Ca(OH)_2(s)$$

standard enthalpy change of atomisation of Ca (s)	= + 178 kJ mol^{-1}
standard enthalpy change of formation of OH^- (g)	= − 230 kJ mol^{-1}
standard enthalpy change of formation of $Ca(OH)_2$ (s)	= − 985 kJ mol^{-1}

Energy Level Diagram

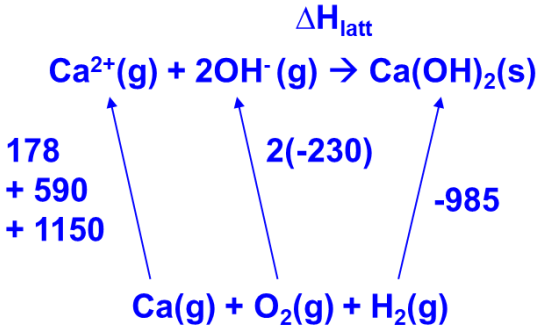


By Hess' Law,

$\Delta H_f^{\ominus}(Ca(OH)_2)$ $= \Delta H_{at}^{\ominus}(Ca) + 1^{st}$ IE (Ca) + 2^{nd} IE (Ca) + $2\Delta H_f^{\ominus}(OH^-)$ + $\Delta H_{latt}(Ca(OH)_2)$

$-985 = 178 + 590 + 1150 + 2(-230) + \Delta H_{latt}(Ca(OH)_2)$

$\Delta H_{latt}(Ca(OH)_2) = -2443\ kJ\ mol^{-1}$



(ii) Suggest, with reasoning, how the magnitude of the lattice energy of $Ca(OH)_2$ compares with that of calcium carbide, CaC_2, given the following data. [2]

Ion	Radius (pm)
OH^-	133
C_2^{2-}	118

$|\Delta H_{latt}| \propto \frac{q_+ q_-}{r_+ + r_-}$ for ionic compound

Ionic radius or r^-: $OH^- > C_2^{2-}$ q_+, r_+ constants

Ionic charge or r^-: $OH^- < C_2^{2-}$

Magnitude/value of the lattice energy CaC_2 is larger than that of $Ca(OH)_2$

(iii) The value of $\Delta G^{\ominus}$ for the reaction of calcium carbide with water is -148 kJ mol^{-1}.

$$CaC_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(s) + C_2H_2(g) \qquad \Delta H = -128 \text{ kJ mol}^{-1}$$

Calculate $\Delta S^{\ominus}$ in J mol^{-1} K^{-1} to one decimal place for the reaction. Explain the significance of its sign with reference to the equation. [2]

$\Delta G^{\ominus}$ = $\Delta H^{\ominus} - T\Delta S^{\ominus}$

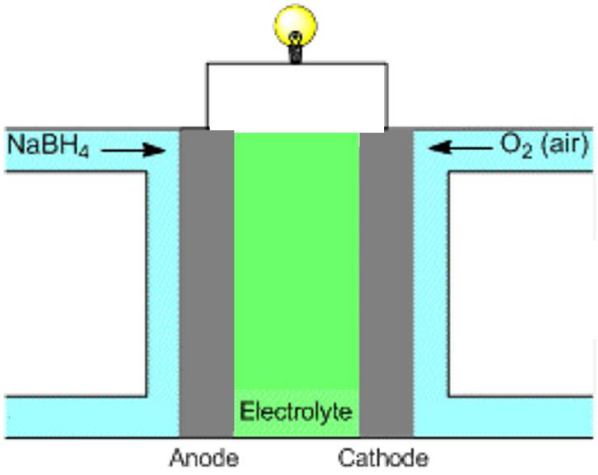
-148 = –128 – (298) $\Delta S^{\ominus}$

• $\Delta S^{\ominus}$ = +67.1 J mol^{-1} K^{-1} (to 1 dp)

• $\Delta S^{\ominus}$ is positive because there is **an increase in the number of moles of gaseous molecules** produced in the chemical reaction (from 0 in reactants to 1 in products) **and hence an increase in disorder** of the system.

(d) Similar to calcium carbide, sodium borohydride, $NaBH_4$, can be used in fuel cells.

Direct borohydride fuel cells (DBFCs), are fuel cells which are directly fed by $NaBH_4$ as the fuel and oxygen as the oxidant. The electrolyte used is potassium hydroxide. Sodium metaborate, $NaBO_2$, and water are formed as the only products during the discharging process.



(i) Deduce the ion-electron half–equations for the anode and cathode and hence write the overall cell reaction during discharging. [2]

- **Anode: $NaBH_4 + 8OH^- \rightarrow NaBO_2 + 6H_2O + 8e^-$**
  Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
- **Overall: $NaBH_4 + 2O_2 \rightarrow NaBO_2 + 2H_2O$**

(ii) A typical DBFC fuel cell generates about 1.64 V. Using the *Data Booklet*, calculate the E^{θ} involving the $NaBO_2/NaBH_4$ half-cell. [1]

$E^{\theta}_{cell} = E^{\theta}_{red} - E^{\theta}_{oxid}$

$1.64 = 0.40 - E^{\theta}_{oxid}$

• E^{θ} = -1.24 V

(iii) Use the half–equations you have written in **(d)(i)** to calculate the value of $\Delta G^{\ominus}$ and comment on the significance of $\Delta G^{\ominus}$. [1]

n = **8**

$\Delta G^{\ominus} = -n F E^{\ominus}_{cell}$

$\Delta G^{\ominus} = -(8 \times 1.64 \times 96500) =$ **-1266080 J mol^{-1}**

$\Delta G^{\ominus}$ is negative or G < 0 hence the **reaction is spontaneous** or energetically **feasible**

(iv) Explain qualitatively what happens to the cell potential, E_{cell} when a small amount of propanal contaminant is accidently added to the anode half-cell.

The contaminant does not take part in the cell reaction. [2]

$NaBO_2 + 6H_2O + 8e^- \rightleftharpoons NaBH_4 + 8OH^-$ -- (1) **E_{oxid}**

The **$NaBH_4$ is used to reduce the propanal** to propanol, causing the [$NaBH_4$] to decrease.

By *Le Chatelier's Principle*, the **equilibrium position (1) will shift right to increase $NaBH_4$, favouring the reduction reaction.**

E_{oxid} or **$E_{NaBO2/NaBH4}$ will become more positive/less -ve**

Hence, producing a less positive E_{cell} or **a value less than 1.64 V** .

(v) In a particular DBFC, a current of 1.35 x 10^{-2} A cm^{-3} was passed through the circuit for 95 minutes.

Calculate the mass of $NaBO_2$ that was produced per 25 cm^3 of solution. [2]

• Quantity of charge, Q = It = (1.35 x 10^{-2} A cm^{-3})(25) x (95 x 60) = **1923.8 C**

No of moles of electrons transferred = $\frac{1923.75}{96500}$ = 1.993 x 10^{-2} mol

No of moles of $NaBO_2$ = $\frac{0.01993}{8}$ = 2.49 x 10^{-3} mol

Mass of $NaBO_2$ = 2.49 x 10^{-3} x (23.0 + 10.8 + 32) = **0.164 g** • •

[Total: 22]

Section B

Answer **one** question from this section.

4 Chlorine-containing compounds have many useful applications. One such example is the use of chloric(I) acid, HC*l*O, to disinfect water in swimming pools.

HC*l*O dissociates in water as shown below.

$$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$$

(a) (i) Write an expression for K_a of HC*l*O. [1]

- $K_a = \dfrac{[H_3O^+][ClO^-]}{[HClO]}$

(ii) A disinfectant solution was prepared by dissolving 10 g of HC*l*O and x g of NaC*l*O in 100 cm^3 of water.

For effective disinfection, a pH of 7.35 was needed to reach the optimal $[ClO^-]$:[HC*l*O] ratio.

Given that the pK_a of HC*l*O is 7.55, determine the optimal $[ClO^-]$:[HC*l*O] ratio and hence the mass of NaC*l*O, x. [2]

$pH = pK_a + \lg \dfrac{[ClO^-]}{[HClO]}$ **or**

$7.35 = 7.55 + \lg \dfrac{[ClO^-]}{[HClO]}$

$\dfrac{[ClO^-]}{[HClO]}$ = • 0.631

$[ClO^-] = 0.631 \times \dfrac{\left(\frac{10}{1+35.5+16}\right)}{\frac{100}{1000}}$

= 1.20 mol dm^{-3}

$K_a = \dfrac{[H_3O^+][ClO^-]}{[HClO]}$

$10^{-7.35} = \dfrac{(10^{-7.35})[ClO^-]}{[HClO]}$

$\dfrac{[ClO^-]}{[HClO]} = 0.631$

Mass of ClO^- which needs to be added **$= \frac{100}{1000} \times 1.20 \times (23 + 35.5 + 16)$**

= • 8.95 g

(iii) A worker accidentally poured some alkaline solution into the disinfectant solution formed in **(a)(ii)** but found that the pH was still about 7.35.

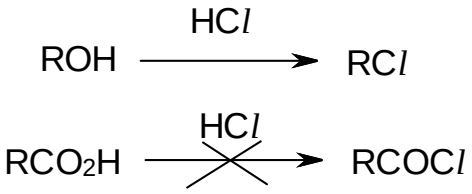
Write an equation to explain this. [1]

- **$HClO + OH^- \rightarrow ClO^- + H_2O$**

Since OH^- is neutralised by the weak acid, there is negligible change in pH.

(b) Hydrogen chloride is another chlorine-containing compound.

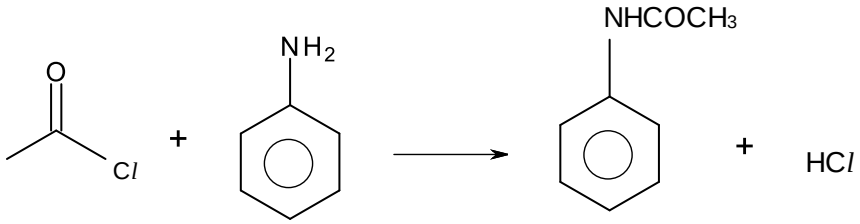
Alkyl chlorides can be synthesised from alcohols using hydrogen chloride. However, acyl chlorides **cannot** be prepared from carboxylic acids in the same way. One key factor is due to the stronger C-O bond present in carboxylic acids.



Suggest an explanation for the stronger C-O bond in carboxylic acids. [1]

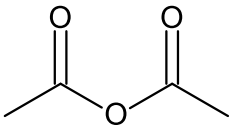
- **The strengthening of the C-O bond is due to the effective overlap/delocalisation of the lone pair of electrons on the O of the O-H into the C=O resulting in a partial double bond character.**

(c) Acetanilide is an analgesic and can be formed from ethanoyl chloride and phenylamine.



acetanilide

Instead of ethanoyl chloride, ethanoic anhydride is more commonly used in the laboratory to form acetanilide in a similar manner.



ethanoic anhydride

(i) Suggest the other organic product that is produced together with acetanilide. [1]

- **CH_3CO_2H**

The experimental procedure for the laboratory synthesis of acetanilide using ethanoic anhydride is given below.

1. Mix phenylamine and hydrochloric acid in a beaker.
2. Stir the mixture until a clear solution is obtained.
3. To the clear solution, add ethanoic anhydride and immediately add a solution of sodium ethanoate.
4. Stir the mixture vigorously.
5. Cool the solution in an ice water bath.
6. Filter the acetanilide formed. Wash with cold water and crystallise using a mixture of water and methanol.

(ii) In step 1, HC*l* was added to increase the solubility of phenylamine in water. Explain. [1]

- **$C_6H_5NH_3^+$ is formed which forms ion-dipole interactions with water and hence is more soluble than $C_6H_5NH_2$ which has a non-polar benzene ring.**

(iii) Sodium ethanoate is essential to ensure phenylamine is present in step 3 to react with ethanoic anhydride.

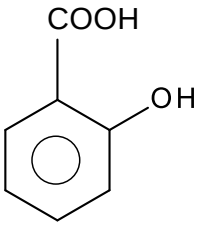
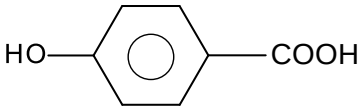
Suggest the role of sodium ethanoate. [1]

- **Sodium ethanoate acts as a base to react with $C_6H_5NH_3^+$ to regenerate the free amine so that it can act as a nucleophile.**

(iv) Suggest how you could check that the acetanilide obtained in step 6 is pure. [1]

- **Determine the melting point of the acetanilide obtained. If the melting point has a narrow range/fixed temperature, it is pure.**

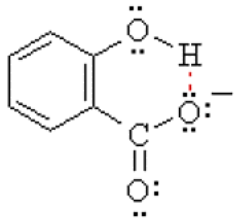
(d) Aspirin is another analgesic and it can be synthesised from salicylic acid. The pK_a values of salicylic acid and its isomer are given below:

Acid	pK_{a1}	pK_{a2}
 Salicylic acid	3.0	13.4
 4-hydroxybenzoic acid	4.1	9.7

Explain the following:

(i) pK_{a1} of salicylic acid is smaller than pK_{a1} of 4-hydroxybenzoic acid. [1]

- **This is because the 2-hydroxybenzoate ion is stabilised by intramolecular hydrogen bonding. In 4-hydroxybenzoate ion, the –OH group is too far away for hydrogen bonding to form.**



(ii) pK_{a2} is larger than pK_{a1} of 4-hydroxybenzoic acid. [1]

- **Electrostatically unfavourable / more difficult to remove H^+ from a negatively charged anion, conjugate base less likely to dissociate 2nd H^+.**

  OR

- **Removal of 2nd H^+ would destabilise the anion as stabilisation by intramolecular H-bonding is no longer present.**

(e) When compound **A**, $C_{10}H_{11}NO$, is oxidised with acidified manganate(VII) ions, $[C_7H_8NO_2]^+$ and compound **B**, $C_3H_4O_3$, are formed. Compound **B** produces effervescence when Na_2CO_3 is added to it and gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent.

Compound **A** reacts readily with 4 moles of $Br_2(aq)$ to give compound **C**, $C_{10}H_9NO_2Br_4$.

Compound **A** also gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent and reacts with hot alkaline aqueous iodine to give compound **D**, $C_9H_8NO_2Na$.

Suggest the structures of compounds **A**, **B**, **C** and **D**. Explain the reactions that occur. [9]

[✔] A has a high C:H ratio, hence a benzene ring is present.

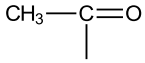
[✔] B undergoes acid-carbonate/acid-base/neutralisation reaction with Na_2CO_3, it has $-CO_2H$ group or it is a carboxylic acid.

[✔] B undergoes condensation reaction with 2,4-dinitrophenylhydrazine. B is a product of strong oxidation, it is a ketone not aldehyde.

[✔] A undergoes condensation reaction with 2,4-dinitrophenylhydrazine. It can be a ketone or aldehyde/ carbonyl compound.

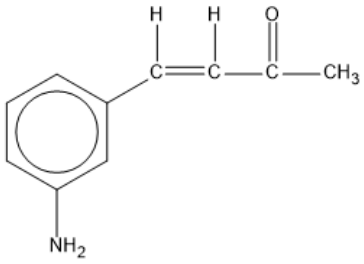
[✔]A undergoes electrophilic addition with aq Br_2, one Br atom and one OH atom are added at the carbon-carbon double bond of A (or confirm A has alkene group).

[✔] A undergoes electrophilic substitution with $Br_2(aq)$. Since C has 4 Br atoms, the remaining 3 Br atoms are at the benzene ring, implying that A is a phenylamine/ has activating group like NH_2 bonded to benzene and the [✔] 2-, 4- and 6- positions with respect to NH_2 group are unsubstituted.

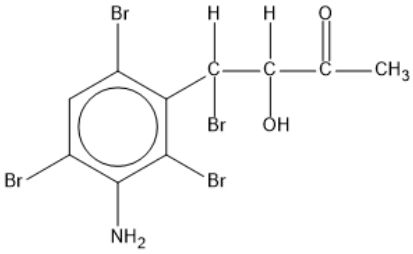
[✔] A is undergoes oxidation with by alkaline aq iodine, suggesting that it has  **group and it forms a salt of carboxylic acid E.**

Every [✔]: 1 mark [Max: 5m]

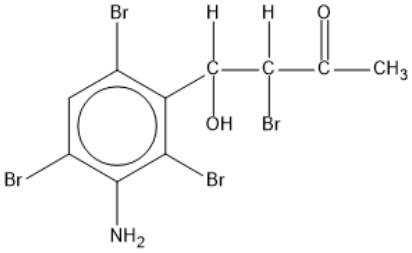
A: **B: CH_3COCO_2H**



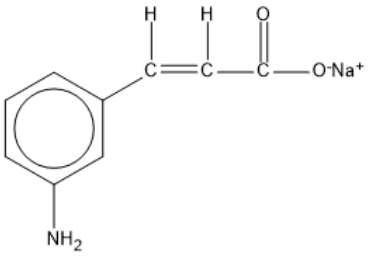
C:



or



D:



[Each structure 1m]

[Total: 20]

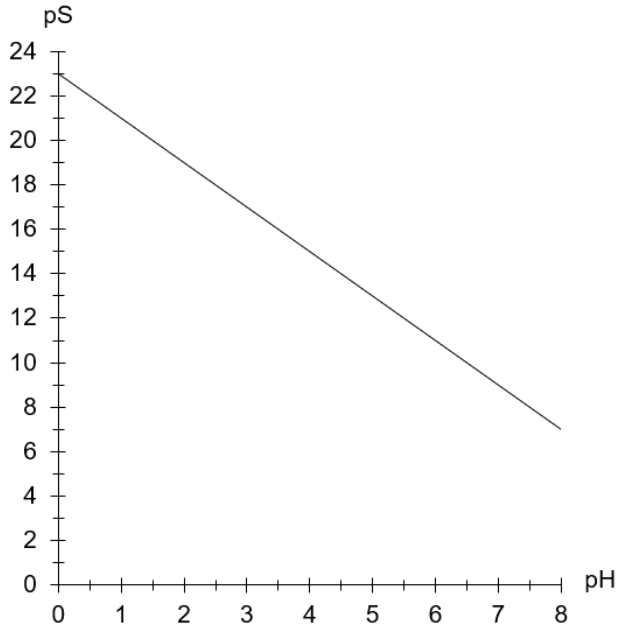
5 (a) Hydrogen sulfide gas, H_2S, is a reagent used in qualitative analysis. When H_2S is passed into a solution containing metal cations, metal sulfides are precipitated.

In aqueous medium, H_2S dissociates partially in a step-wise manner to give two equilibrium reactions:

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

The relationship between the H^+ ion concentration and S^{2-} ion concentration, as a result of H_2S dissociation, is shown in the graph below, where $pS = -\log_{10}[S^{2-}]$.



Solution **X** contains 0.1 mol dm^{-3} $CuSO_4$ and 0.05 mol dm^{-3} $MnSO_4$. Hydrogen sulfide gas is bubbled into **X** until saturation and the pH is maintained at 2.0.

The value of the solubility product of CuS and MnS are 1.0×10^{-44} and 1.4×10^{-15}, respectively.

(i) With reference to CuS, define the term *solubility product*. [1]

K_{sp} of CuS is the • product of the concentrations of Cu^{2+} ions and S^{2-} ions in a saturated solution at a given temperature.

(ii) Calculate the minimum concentration of sulfide ions needed to precipitate CuS. [1]

K_{sp} of CuS = $[Cu^{2+}][S^{2-}] = 1.0 \times 10^{-44}$ mol^2 dm^{-6}

• Min $[S^{2-}]$ for precipitation of CuS = $1.0 \times 10^{-44} / 0.1 = 1.0 \times 10^{-43}$ mol dm^{-3}

(iii) The minimum concentration of sulfide ions needed to precipitate MnS is 2.80×10^{-14} mol dm^{-3}.

Using the graph above and your answer in **(a)(ii)**, explain whether it is possible to separate copper and manganese ions in **X** at pH = 2. [2]

• From graph, when pH = 2, pS = 19 → $[S^{2-}] = 10^{-19}$ mol dm^{-3}

• Since [S^{2-}] at pH = 2 is greater than min [S^{2-}] for precipitation of CuS but smaller than min [S^{2-}] for precipitation of MnS, ionic product of CuS exceeds its K_{sp}. Hence, only CuS will be precipitated and separation of the 2 ions is possible at pH = 2.

OR

• At pH = 2, pS = 19 → [S^{2-}] = 10^{-19} mol dm^{-3}

- **Ionic product of CuS = 0.1×10^{-19} = $1.00 \times 10^{-20} > K_{sp}$**
- **Ionic product of MnS = 0.05×10^{-19} = $5.00 \times 10^{-21} < K_{sp}$**
- **Only CuS is precipitated, so separation is possible.**

(iv) Determine the maximum pH for solution **X** before separation of copper and manganese ions is no longer possible. [1]

Max [S^{2-}] before MnS is precipitated = 2.80×10^{-14} mol dm^{-3}

pS = -lg 2.80×10^{-14} ≈ 13.5 *[accept range 13 to 14]*

From graph, when pS = 13.5, • pH = 4.75 *[Accept 4.5 < pH < 5.0]*

(b) When water ligands in a hydrated metal ion are substituted by other ligands, the equilibrium constant for the reaction is referred to as the stability constant, K_{stab}, of the new complex. The higher the value of K_{stab}, the more likely the complex will be formed.

The stability constants for 3 reactions are given below.

Reaction	Colour of complex formed	Value of $\log_{10}(K_{stab})$
$Fe^{3+}(aq) + 6CN^-(aq) \rightleftharpoons [Fe(CN)_6]^{3-}(aq)$	Yellow	31.0
$Fe^{3+}(aq) + EDTA^{4-}(aq) \rightleftharpoons [Fe(EDTA)]^-(aq)$	Brown	25.1
$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$	Red	2.1

Describe the colour change(s) of the solution when excess NaSCN is added to $[Fe(EDTA)]^-$, followed by an excess of KCN(aq).

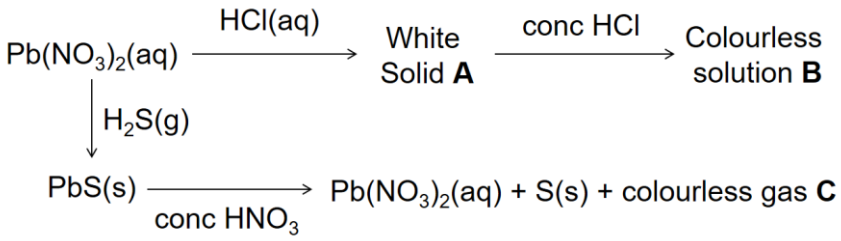
Explain the observation, with reference to the table above. [2]

Brown to yellow.

SCN^- cannot substitute $EDTA^{4-}$ as $[Fe(SCN)]^{2+}$ is less stable than $[Fe(EDTA)]^-$ from a lower K_{stab} value, so colour remains brown.

CN^- can substitute $EDTA^{4-}$ ligands as $[Fe(CN)_6]^{3-}$ is more stable than $[Fe(EDTA)]^-$ from a larger K_{stab} value, so colour changes from brown to yellow.

(c) A solution of $Pb(NO_3)_2$ is subjected to the following reactions.



(i) Suggest the identity of white solid **A** and complex anion present in colourless solution **B**. [2]

A is • $PbCl_2$

B is • $[PbCl_4]^{2-}$

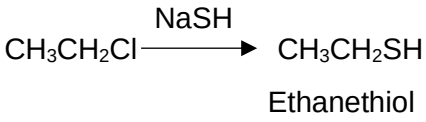
(ii) Colourless gas **C** is obtained from the reaction of solid PbS and concentrated HNO_3, which is readily oxidised in air to form a brown acidic gas.

Suggest the identity of **C**. [1]

• NO

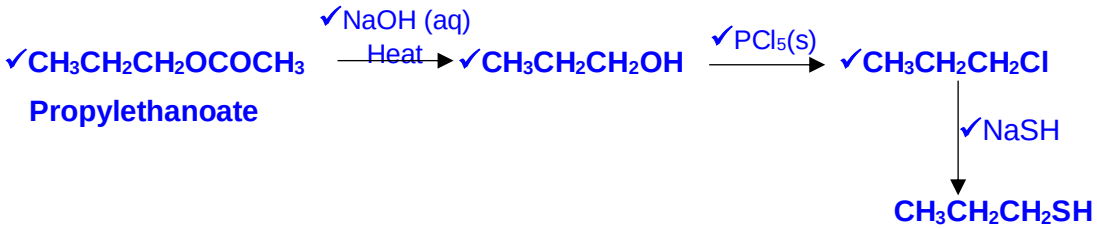
(d) Thiols are sulfur-containing compounds that can be prepared from alkyl halides and the hydrosulfide nucleophile, ^{-}SH.

Ethanethiol is prepared from chloroethane using NaSH as shown below.



(i) Suggest a synthesis of propanethiol starting from propylethanoate.

You should state the reagents and conditions for each step, and show clearly the structure of any intermediate compounds. [3]



6 ✓ 3m **3-5 ✓ 2m** **2✓ 1m**

CH_3CH_2SH can react with a base, NaH, to give $CH_3CH_2S^-$.

$CH_3CH_2SH + NaH \rightarrow CH_3CH_2S^-Na^+ + H_2$ ----- Reaction 1

$CH_3CH_2S^-$ further reacts with chloroethane, to yield diethyl sulfide

$CH_3CH_2S^-Na^+ + CH_3CH_2Cl \rightarrow CH_3CH_2SCH_2CH_3 + NaCl$ ----- Reaction 2

Diethyl sulphide

(ii) Suggest why $CH_3CH_2S^-$, is a better nucleophile than $CH_3CH_2O^-$. [1]

• The valence electron (3p) on S are further away and less tightly held, hence they are stronger nucleophiles.

[Alternative answers: Oxygen is more electronegative than Sulfur and hence less likely to donate the lone pair of electrons. Hence, $CH_3CH_2O^-$ is a weaker nucleophile.

or Oxygen is smaller than sulfur and the electrons are closer and more strongly held than that in sulfur. Hence, $CH_3CH_2O^-$ is a weaker nucleophile.]

(iii) Diethyl sulfide is a good nucleophile.

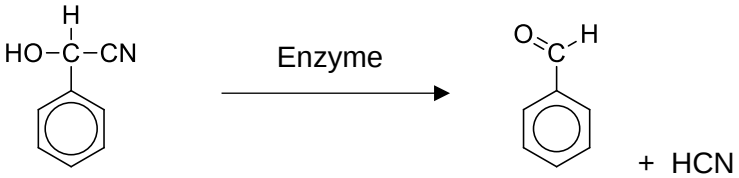
In Reaction 2, a side product, $C_6H_{15}SCl$, is formed when chloroethane is used in excess. $C_6H_{15}SCl$ gives a white precipitate with aqueous silver nitrate.

Suggest the structural formula of the side product $C_6H_{15}SCl$. [1]

Free Cl^- anion is present and the white ppt formed is AgCl

• $(CH_3CH_2)_3S^+ Cl^-$ (Similar to RX reaction with ammonia)

(e) The millipede *Apheeloria corrugate* protects itself by secreting the cyanohydrin mandelonitrile and an enzyme that decompose mandelonitrile into benzaldehyde and HCN.



Mandelonitrile

(i) State the type of reaction for the formation of Mandelonitrile from benzaldehyde. [1]

• Nucleophilic addition

(ii) Suggest a chemical test that will give a positive test for Mandelonitrile but not for benzaldehyde. [2]

1. **Na(s),**

   Observation: $H_2(g)$ evolved with Mandelonitrile but not benzaldehyde

2. **$PCl_5(s)$**

   Observation: White fumes of HCl(g) evolved with Mandelonitrile but not benzaldehyde

3. **NaOH(aq), heat**

   Observation: $NH_3(g)$ evolved with Mandelonitrile but not benzaldehyde

(iii) A student made the following statement, "benzaldehyde can be directly synthesized from phenylmethanol, $C_6H_5CH_2OH$, but not from benzoic acid."

Based on your knowledge of the reagents and conditions for each reaction, deduce if the statement is true. [2]

The statement made by the student is true.

- **Benzaldehyde can be formed from phenylmethanol via oxidation using acidified $K_2Cr_2O_7$ warm with immediate distillation. Upon distillation, the aldehyde can be separated and not be further oxidized to propanoic acid.**
- **Benzoic acid can only be reduced by $LiAlH_4$ and it reduces directly back to phenylmethanol and benzaldehyde cannot be isolated.**

[Total: 20]