

## Suggested Answers for 2016 SH2 Chemistry Paper 2

(P) (a) **Preliminary Calculation**

For titration, 25cm<sup>3</sup> of sea water is used,

$$\text{Amt of Cl}^- \text{ in } 25.0 \text{ cm}^3 = 25/1000 \times 2.0 \times 10^{-3}$$

$$= 5.0 \times 10^{-5} \text{ mol}$$

$$= \text{Amt of Ag}^+$$

Assuming titre volume to be 25.00 cm<sup>3</sup>,

$$\text{Required [AgNO}_3] = (5.0 \times 10^{-5})/25 \times 1000$$

$$= 2.0 \times 10^{-3} \text{ mol dm}^{-3}$$

Hence, the 0.1 mol dm<sup>-3</sup> silver nitrate solution provided is unsuitable for use in the titration (i.e. too concentrated)

∴ Need to dilute the given 0.1 mol dm<sup>-3</sup> silver nitrate solution to 2.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>

∴ Need to dilute it 50 times.

**Preparation of a standard silver nitrate solution of 2.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>**

1. Using a burette, transfer 5.00 cm<sup>3</sup> of the given silver nitrate solution into a 250 cm<sup>3</sup> volumetric flask. Top up to the mark using deionised water.
2. Cap the flask, invert it and shake to obtain a homogeneous solution.

**Precipitation Titration**

1. Fill a burette with the newly-prepared 2.0 x 10<sup>-3</sup> mol dm<sup>-3</sup> silver nitrate solution.
2. Pipette 25.0 cm<sup>3</sup> of sea water into a 250 cm<sup>3</sup> conical flask.
3. Add 1 cm<sup>3</sup> of potassium chromate(VI) solution into the conical flask.
4. Titrate until brick-red precipitate first appears.
5. Repeat titration till results within ±0.10cm<sup>3</sup> are obtained.

**Sample calculation of concentration of chloride ions in sea water**

Let concentration of standard silver nitrate solution be **M** mol dm<sup>-3</sup>, titre volume be **y** cm<sup>3</sup>, volume of sea water used for titration be 25.0 cm<sup>3</sup>

$$\text{Amt of Ag}^+ = y/1000 \times \mathbf{M}$$

$$= \mathbf{yM}/1000 \text{ mol}$$

$$= \text{Amt of Cl}^-$$

$$[\text{Cl}^-] = \mathbf{yM}/1000 \div 25/1000$$

$$= \mathbf{yM}/25 \text{ mol dm}^{-3}$$

- (b) The student obtained a titre volume of 20.60 cm<sup>3</sup> from her experiment.

Determine the concentration of chloride ions remaining in the solution at the end point.

You may assume the following:

- 25.0 cm<sup>3</sup> of sea water was used in the titration
- 1 cm<sup>3</sup> of 1.00 mol dm<sup>-3</sup> potassium chromate(VI) solution, K<sub>2</sub>CrO<sub>4</sub> was used as the indicator
- K<sub>sp</sub> value of Ag<sub>2</sub>CrO<sub>4</sub> is 1.1 × 10<sup>-12</sup>



$$\text{Amt of CrO}_4^{2-} = 1/1000 \times 1.00$$

$$= 1.0 \times 10^{-3} \text{ mol}$$

$$\text{At endpoint, } [\text{CrO}_4^{2-}] = (1.0 \times 10^{-3}) / [(25.0+1+20.60)/1000]$$

$$= 0.02146 \text{ mol dm}^{-3}$$

$$\text{IP of Ag}_2\text{CrO}_4 = K_{\text{sp}}$$

$$[\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = 1.1 \times 10^{-12}$$

$$[\text{Ag}^+]^2 [0.02146] = 1.1 \times 10^{-12}$$

$$[\text{Ag}^+] = 7.16 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{IP of AgCl} = K_{\text{sp}}$$

$$[\text{Ag}^+] [\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$[7.16 \times 10^{-6}] [\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$[\text{Cl}^-] = 2.51 \times 10^{-5} \text{ mol dm}^{-3}$$

- (c) Subsequently, the student investigates the solubility of silver chloride in aqueous hydrochloric acid.

By considering the ions present in a solution of silver chloride in aqueous hydrochloric acid, predict and explain how the solubility of silver chloride will be affected by the concentration of the acid.

**Prediction:** Solubility of AgCl/ decreases when concentration of HCl/ increases.



In the presence of HCl, there is common ion effect. [Cl<sup>-</sup>] increases, position of equilibrium shifts right, solubility decreases.

- (d) Identify the following variables in the investigation of solubility of silver chloride in hydrochloric acid.

Independent variable: concentration of HCl/ amount of HCl/ concentration of Cl<sup>-</sup>

Dependent variable: mass of AgCl/that dissolved / solubility of AgCl/ amount of AgCl/that dissolved

- (e) Calculate the solubility of silver chloride in a 2 mol dm<sup>-3</sup> hydrochloric acid solution.

$$[\text{Ag}^+] [\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$[x] [x+2.0] = 1.8 \times 10^{-10}$$

Assume  $x \ll 2.0$ ,

$$[x] [2.0] = 1.8 \times 10^{-10}$$

$$x = 9.00 \times 10^{-11} \text{ mol dm}^{-3}$$

[1]

[Total:12]

- 1 One means of measuring toxicity is using LD, which stands for "Lethal Dose". LD<sub>50</sub> is the amount of a material which causes the death of 50% of a group of test animals. LD<sub>50</sub> value is expressed as the weight of a chemical administered per kg body mass of a test animal.

Another means of measuring toxicity is using LC, which stands for "Lethal Concentration". The concentrations of the chemical in air that kills 50% of the test animals during the observation period is the LC<sub>50</sub> value.

The table below shows the values for the LD<sub>50</sub> and LC<sub>50</sub> along with the toxicity ratings.

Toxicity Rating	Commonly used term	LD <sub>50</sub> : Oral (mg kg <sup>-1</sup> )	LC <sub>50</sub> : Inhalation (ppm)
1	Extremely Toxic	1 or less	10 or less
2	Highly Toxic	1 – 50	10 – 100
3	Moderately Toxic	50 – 500	100 – 1000
4	Slightly Toxic	500 – 5000	1000 – 10,000
5	Practically Non-toxic	5000 – 15,000	10,000 – 100,000
6	Relatively Harmless	15,000 or more	100,000 >

- (a)  $9.90 \times 10^{-4}$  mol of a toxic compound, C<sub>4</sub>H<sub>5</sub>NO, was found to cause death in 50% of test animals weighing 1 kg.

Calculate the LD<sub>50</sub> of the compound and state its toxicity rating.

[2]

$$\begin{aligned} \text{Mass of compound} &= 9.90 \times 10^{-4} \times (48 + 5 + 14 + 16) \\ &= 0.08217 \text{ g} \end{aligned}$$

$$\text{Hence, LD}_{50} = \frac{0.19206 \times 10^3}{1 \text{ kg}} = 82.17 \text{ mg/kg}$$

$$\approx \underline{82.2 \text{ mg/kg}}$$

[1]

The compound is moderately toxic/3

[1]

- (b) Phosphine is a gas that is widely used in the semi-conductor industry as a dopant and as a precursor for the deposition of compound semiconductors.

For safety of operations, the permissible limits of phosphine must not exceed  $\frac{1}{10}$  of its  $LC_{50}$  value.

When expressing a small quantity of gas, parts per million (ppm) can be used to indicate it. Ppm is usually used for volume of gases and is expressed in the equation below:

$$\text{Concentration in ppm} = \frac{\text{volume of gas}}{\text{volume of air}} \times 10^6$$

- (i) Given that the  $LC_{50}$  for phosphine is  $55 \text{ mg m}^{-3}$  at room temperature, convert the  $LC_{50}$  to ppm and determine its toxicity rating. [3]

$$\begin{aligned} \text{Volume of PH}_3 &= \frac{55 \times 10^{-3}}{34.0} \times 24 \text{ dm}^3 \\ &= 1.6176 \times 10^{-3} \times 24 \text{ dm}^3 \\ &= \underline{0.03882 \text{ dm}^3} \end{aligned} \quad [1]$$

$$\begin{aligned} LC_{50} &= \frac{0.03882 \times 10^{-3}}{1} \times 10^6 \\ &= 38.82 \\ &\approx \underline{38.8 \text{ ppm}} \end{aligned} \quad [1]$$

The toxicity rating is highly toxic/2 [1]

- (ii) A semiconductor factory releases 36 g of phosphine in a day.

Using your value in (i), determine the minimum volume of the factory that will allow the volume of phosphine to be within permissible limits at room temperature. [2]

$$\begin{aligned} \text{Allowed amount of PH}_3 \text{ in ppm} &= 38.82 \div 10 \\ &= \underline{3.882 \text{ ppm}} \end{aligned} \quad [1]$$

Given amount of  $\text{PH}_3$  produced a day is 36g

$$3.882 = \frac{\text{vol of PH}_3}{\text{vol of factory}} \times 10^6$$

$$3.882 = \frac{\frac{36}{34} \times 24}{\text{vol of factory}} \times 10^6$$

$$\text{Minimum volume of factory} = \underline{6.546 \times 10^6 \text{ dm}^3} \quad [1]$$

[Total:7]

- 2 (a) Liquefaction of air is done industrially by surrounding pre-cooled high-pressure air in a coil surrounded by cold water. The air cools down by a large amount when it expands into a region of low pressure.

This behaviour is not exhibited by ideal gases.

- (i) State two assumptions of the kinetic theory of gases.

A gas is composed of tiny particles that have **negligible volumes** compared to the volume in which they move or the volume of the gas container.

There are **no attractive or repulsive forces** between the **gas particles**. [2]

- (ii) Suggest why air cools when it expands.

For expansion of air, energy is needed to **overcome the intermolecular forces of attraction** between the air molecules, which is absorbed from the surroundings. [1]

- (iii) Conversely, gases can be liquefied at room temperature by compressing them under high pressure. Explain why a gas liquefy when compressed.

When compressed, the gas particles are **close enough for the intermolecular forces of attraction to be significant** and liquification occurs. [1]

- (b) Critical temperature is the maximum temperature at which a gas can be converted into a liquid by an increase in pressure. When the temperature is above the critical temperature, the vapour cannot be liquefied no matter how much pressure is applied.

- (i) Draw the dot - and - cross diagram for the  $\text{N}_2\text{O}$ , where N is the central atom.



- (iii) Arrange the gases  $\text{N}_2\text{O}$ ,  $\text{F}_2$  and  $\text{H}_2\text{O}$ , in increasing order of their critical temperatures and explain your answer.

$\text{F}_2$  <  $\text{N}_2\text{O}$  <  $\text{H}_2\text{O}$

The hydrogen bonds between water molecules is the strongest, followed by the weaker permanent dipole-dipole interactions between  $\text{N}_2\text{O}$  molecules and the temporary dipole-induced dipole between the  $\text{F}_2$  molecules being the weakest.

Hence,  $\text{H}_2\text{O}$  can remain as a liquid even at high temperature due to strongest intermolecular forces and hence it has the highest critical temperature or the stronger the intermolecular forces, a higher temperature is needed to convert the liquid to gas and hence the higher the temperature.

[3]

[Total:8]

- 3 Hydrogen is a better source of fuel compared to fossil fuels as it is clean and renewable. The conventional method of obtaining pure hydrogen is to electrolyse water. However, many industries still prefer fossil fuel or coal as the main source of energy. One reason is the high cost of electrolysis.

(a) State another reason why the use of hydrogen as a fuel is not popular.

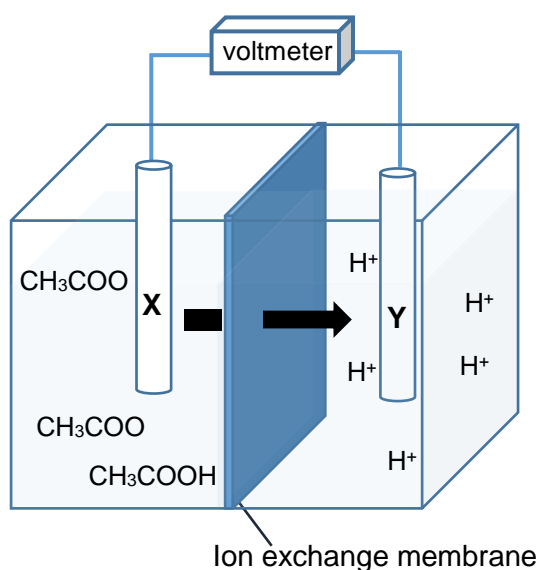
Hydrogen exists as a **gas** and it is **difficult/high cost to store or transport**.

Or

Hydrogen is dangerous as it is **explosive**.

[1]

- (b) The diagram below shows an alternative method of producing hydrogen from organic material where ethanoic acid is converted by bacteria to carbon dioxide.



- (i) Complete the table below.

Electrode	Type of reaction	Polarity
<b>X</b>	<b>Oxidation</b>	<b>Negative</b>
<b>Y</b>	<b>Reduction</b>	<b>Positive</b>

[1]

- (ii) Construct an equation for the reaction at each electrode.

**Electrode X:**  $\text{CH}_3\text{COOH} + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 8\text{H}^+ + 8\text{e}^-$

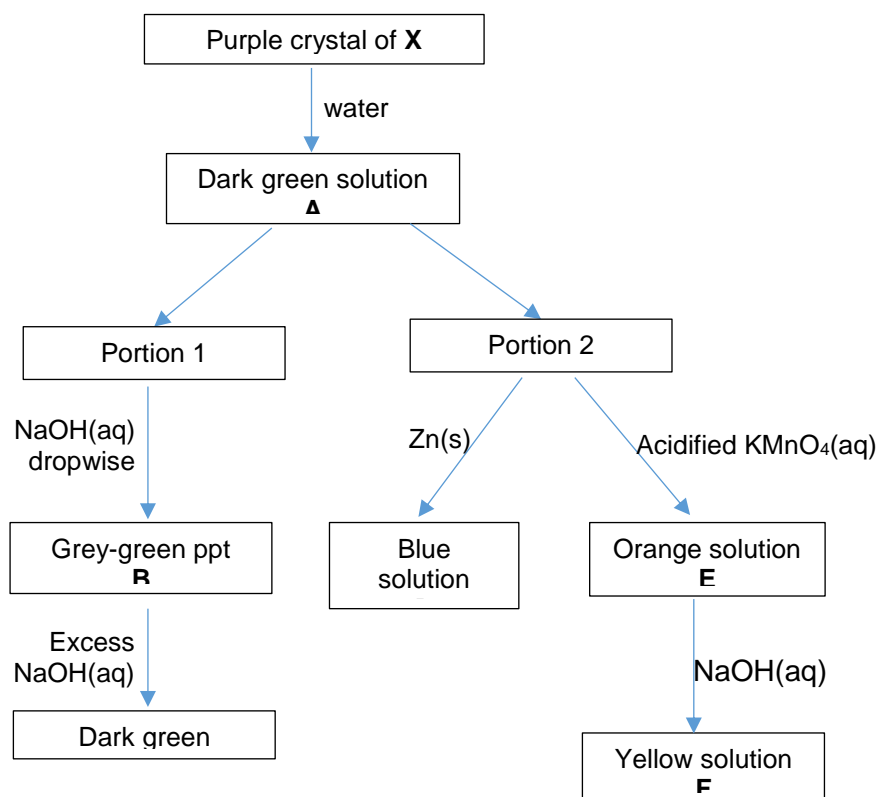
**Electrode Y:**  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

[2]

[Total: 4]

- 4 Chromium is a transition element which exhibits more than one oxidation state in its compounds, many of which are coloured.

The flow chart below shows the reaction of a purple chromium(III) compound, **X**, which has a crystalline structure.



- (a) (i) Write the electronic configuration of the chromium ion in **A**.



[1]

- (ii) Suggest an explanation for **A** being coloured.

When ligand approach  $\text{Cr}^{3+}$ , the 3d orbitals of  $\text{Cr}^{3+}$  splits into 2 different energy levels (d-d splitting).

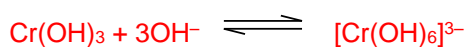
When an electron in the lower energy d orbital is excited to the higher energy d orbital, a photon with wavelength in the visible region is absorbed (d-d transition).

The colour of **A** observed is the complementary colour.

[3]

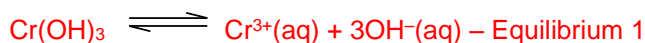
- (b) (i) Explain why **B** dissolves in excess  $\text{NaOH(aq)}$  to form **C**. You should use the ideas behind the Le Chatelier's principle and solubility product,  $K_{\text{sp}}$ , in your answer.

**B** is  $\text{Cr(OH)}_3$  and **C** is  $[\text{Cr(OH)}_6]^{3-}$ .



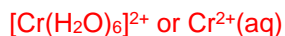
When excess  $\text{OH}^-$  is added, equilibrium shifts to the right to form  $[\text{Cr(OH)}_6]^{3-}$ . This decreases the concentration of  $\text{Cr}^{3+}$  and hence causing the ionic product of  $\text{Cr(OH)}_3$  to fall below its  $K_{\text{sp}}$ . Therefore,  $\text{Cr(OH)}_3$  dissolves.

Or



When excess  $\text{OH}^{-}$  is added, position of equilibrium 2 shifts right to form  $[\text{Cr(OH)}_6]^{3-}$ . The concentration of  $\text{Cr}^{3+}$  decreases and the ionic product of  $\text{Cr(OH)}_3$  falls below its  $K_{\text{sp}}$ .

- (ii) Identify the chromium-containing species in **D**.



[1]

- (iv) State the type of reaction and write an equation for the conversion of **E** to **F**.

Acid base reaction or Neutralisation reaction



[2]

- (c) Consider the two chromium complexes,  $[\text{CrCl}(\text{NH}_3)_5]\text{SO}_4$  and  $[\text{CrF}(\text{NH}_3)_5]\text{Cl}_2$ .

- (i) Describe a chemical test, which does **not** involve silver nitrate, that could distinguish between aqueous solutions of  $[\text{CrCl}(\text{NH}_3)_5]\text{SO}_4$  and  $[\text{CrF}(\text{NH}_3)_5]\text{Cl}_2$ .

Add  $\text{Ba}(\text{NO}_3)_2(\text{aq})$  or  $\text{BaCl}_2(\text{aq})$  or  $\text{Ba}(\text{OH})_2(\text{aq})$  or  $\text{Ca}(\text{NO}_3)_2(\text{aq})$ .  $[\text{CrCl}(\text{NH}_3)_5]\text{SO}_4$  will form a white precipitate and  $[\text{CrF}(\text{NH}_3)_5]\text{Cl}_2$  will not form any white precipitate or the solution will remain colourless.

[2]

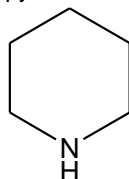
- (ii) Explain why the ionic radius of  $\text{Cr}^{2+}$  is much smaller than that of  $\text{Ca}^{2+}$ .

$\text{Cr}^{2+}$  has higher nuclear charge (more protons) than  $\text{Ca}^{2+}$  and the electrons in the d orbitals are poorly shielding. Therefore, the nuclear attraction on valence electron is higher in  $\text{Cr}^{2+}$  and electrons are attracted closer to the nucleus in  $\text{Cr}^{2+}$ .

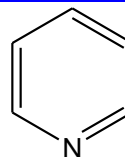
[1]

[Total: 12]

- 5 Piperidines are cyclic amines while pyridines are [heterocyclic organic compounds](#) structurally related to [benzene](#).



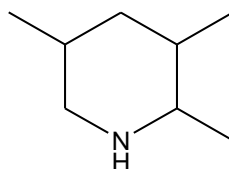
piperidine



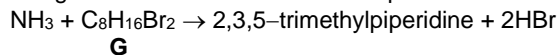
pyridine

- (a) The structure of 2,3,5-trimethylpiperidine is shown below.

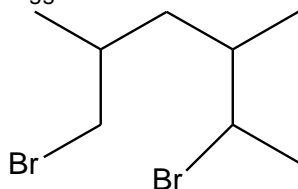




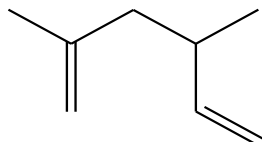
It can be synthesised by reacting ammonia with a dibromo compound **G**.



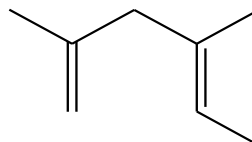
- (i) Suggest the structure of compound **G**.



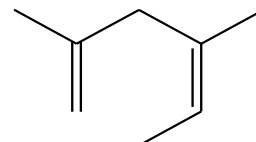
- (ii) When compound **G** is reacted with NaOH in ethanol, a mixture of isomeric alkenes with molecular formula  $\text{C}_8\text{H}_{14}$  is formed. Suggest the structures of all the isomers. You may use skeletal representations in your answers.



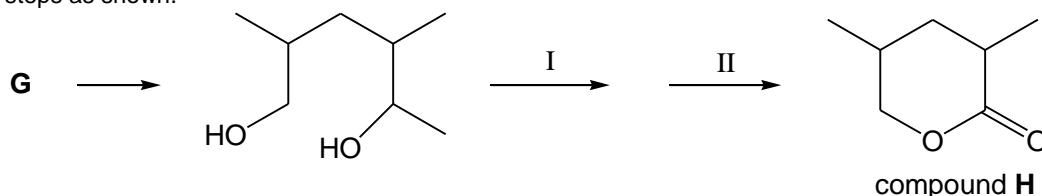
2,4-dimethylhexa-1,5-diene



geometirc isomers of 2,4-dimethylhexa-1,4-diene



- (iii) Compound **G** can be converted to compound **H** by first converting it to a diol, followed by two more steps as shown.



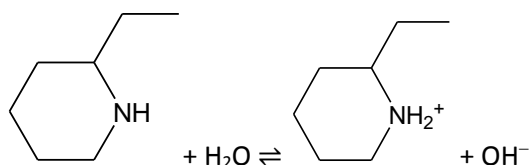
Complete the table below.

Step	Reagents and Conditions	Type of reaction
I	<b>aqueous alkaline iodine / <math>\text{I}_2</math>, NaOH(aq) / <math>\text{I}_2</math>(aq), NaOH(aq); warm (not heat)</b>	<b>Oxidation</b>
II	<b>concentrated sulfuric acid (trace amount); heat under reflux</b>	<b>Condensation</b>

- (b) The table below shows the  $\text{p}K_{\text{b}}$  values of three monoprotic bases, ammonia, 2-ethylpiperidine and 2,3-dimethylpyridine.

	$\text{NH}_3$ ammonia	 2-ethylpiperidine	 2,3-dimethylpyridine
$\text{p}K_{\text{b}}$	4.74	3.55	7.43

- (i) Give an equation which represents the reaction of 2-ethylpiperidine with water.



- (ii) Explain why 2-ethylpiperidine has a lower  $pK_b$  value than ammonia.

2-ethylpiperidine: 2° **aliphatic amine** with **2 electron-donating alkyl** groups, **lone ep of N is readily available** to be donated to  $\text{H}^+$   
 Ammonia does not have any electron-donating alkyl group.

A  $10.0 \text{ cm}^3$  sample of **J**, a solution containing 2-ethylpiperidine and 2,3-dimethylpyridine, was titrated against  $0.50 \text{ mol dm}^{-3} \text{ HCl(aq)}$  in the presence of two indicators, bromothymol blue and methyl orange. It was found that  $12.20 \text{ cm}^3$  of  $\text{HCl(aq)}$  were needed to change the colour of the first indicator and a **further  $7.80 \text{ cm}^3$**  were needed to change the colour of the second indicator.

- (iii) Use the data to calculate the concentration of each of the two bases in **J**.

In titrating a mixture of bases, the stronger or strongest base will be neutralised first.

$$\begin{aligned} \eta_{\text{2-ethylpiperidine in J}} &= \eta_{\text{HCl}} / \text{to reach 1st eq pt} \\ &= \frac{12.20}{1000} \times 0.50 = 6.10 \times 10^{-3} \text{ mol} \\ [\text{2-ethylpiperidine}] \text{ in J} &= \frac{\frac{12.20}{1000} \times 0.50}{\frac{10.0}{1000}} = 0.610 \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} \eta_{\text{2,3-dimethylpyridine in J}} &= \eta_{\text{HCl}} / \text{to reach 2nd eq pt} \\ &= \frac{7.80}{1000} \times 0.50 = 3.90 \times 10^{-3} \text{ mol} \\ [\text{2,3-dimethylpyridine}] \text{ in J} &= \frac{\frac{7.80}{1000} \times 0.50}{\frac{10.0}{1000}} = 0.390 \text{ mol dm}^{-3} \end{aligned}$$

- (iv) Calculate the initial pH of **J**.

$K_b(\text{2-ethylpiperidine})$  is  $10^{3.88}$  ( $\approx 7600$ )  $\times K_b(\text{2,3-dimethylpyridine})$ ,  $\therefore$  2-ethylpiperidine is a much stronger base)

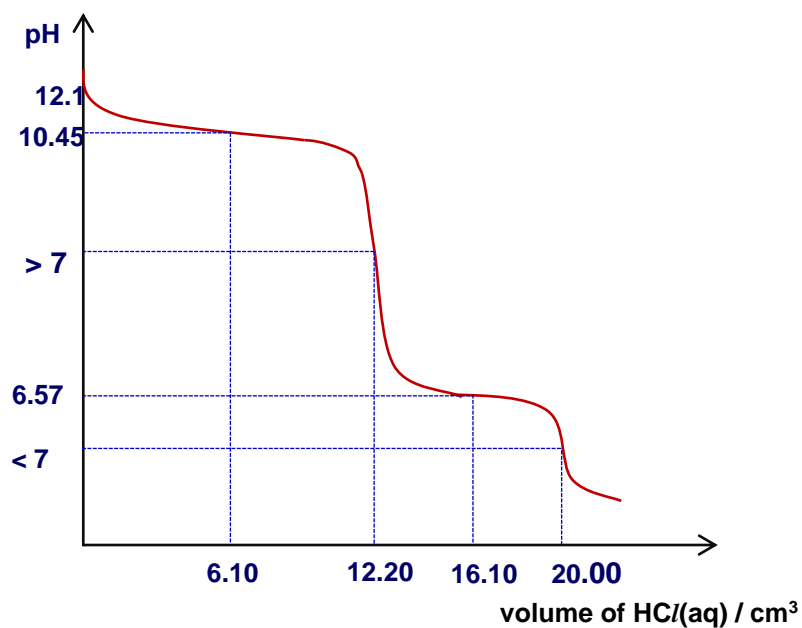
initial pH of solution **J** = pH of 2-ethylpiperidine in solution

$$\begin{aligned} [\text{OH}^-] &= \sqrt{[\text{base}] \times K_b} = \sqrt{(0.610 \times 10^{-3.55})} \\ &= 1.31 \times 10^{-2} \text{ mol dm}^{-3} \end{aligned}$$

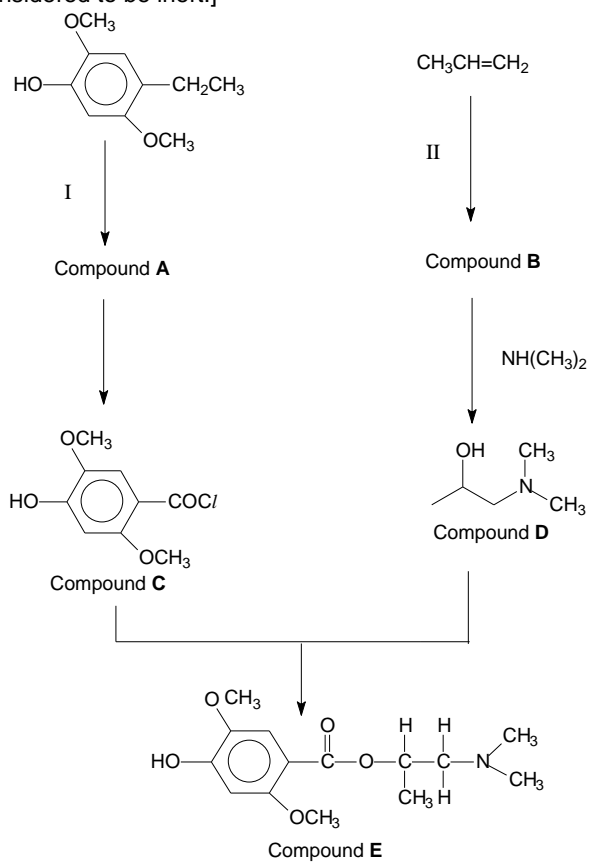
$$\therefore \text{pOH} = 1.88, \text{ pH} = 12.1$$

- (v) Hence, sketch the shape of the pH curve during this titration, showing the pH values and volumes of  $\text{HCl(aq)}$  at significant points.

- initial pH = **12.1**
- pH at 1<sup>st</sup> max buffer capacity = **10.45** ( $= 14 - 3.55$ ),  **$6.10 \text{ cm}^3 \text{ HCl(aq)}$**
- pH at 2<sup>nd</sup> max buffer capacity = **6.57** ( $= 14 - 7.43$ ),  **$16.10 \text{ cm}^3 \text{ HCl(aq)}$**
- 1<sup>st</sup> eq pt  **$12.20 \text{ cm}^3 \text{ HCl(aq)}$**
- 2<sup>nd</sup> eq pt  **$20.00 \text{ cm}^3 \text{ HCl(aq)}$**
- correct shape (2-steps)



- 6 The reaction scheme below shows the synthesis of compound **E** starting from an alkene and a phenol derivative.  
[The  $\text{CH}_3\text{O}-$  group can be considered to be inert.]

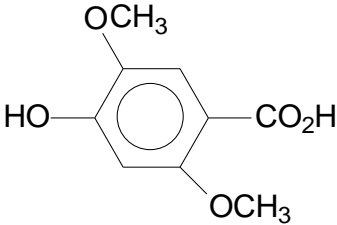
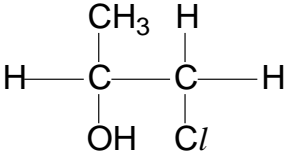


- (a) (i) State reagents and conditions for steps I and II.

Step I:  $\text{KMnO}_4$ , dil  $\text{H}_2\text{SO}_4$ , heat

Step II:  $\text{Cl}_2(\text{aq})$  or  $\text{Br}_2(\text{aq})$

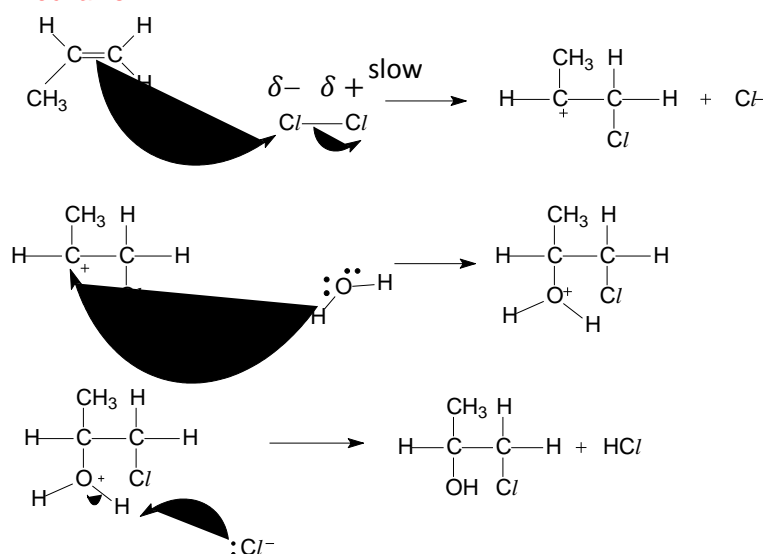
(ii) Suggest the identities of compounds **A** and **B**.

A	Compound B
	

(iii) Describe a mechanism for the reaction taking place in step II. In your answers, include all necessary curly arrows, lone pairs and relevant dipoles.

Electrophilic Addition

Detailed mechanism:

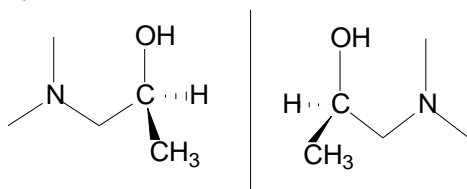


Penalty:

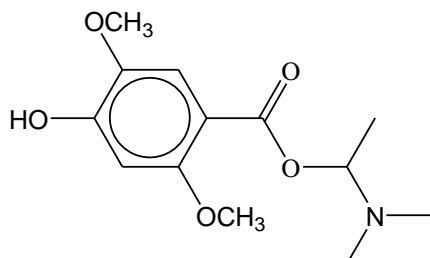
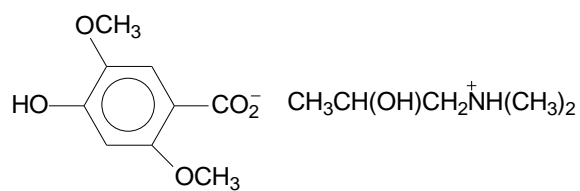
- any missing arrow/ wrong direction of arrow/arrow pointing to wrong atoms (for 1st and 2nd step)
- missing partial charge
- OH- instead of H2O attack in 2nd step
- missing slow step in 1st step
- missing lone pair on nucleophile

(iv) State the type of stereoisomerism exhibited by **D**. Draw appropriate structures to illustrate your answer.

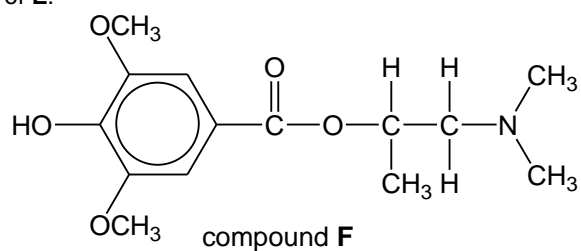
Optical Isomerism



(v) Draw the organic product formed when compound **A** reacts with compound **D**.



(b) Compound **F** is an isomer of **E**.



Describe a simple chemical test to distinguish between compounds **E** and **F**.

Add aqueous bromine:

**E**: yellow brown / orange bromine decolourises

**F**: yellow brown / orange colour remains

Or

Add liquid bromine:

**E**: reddish brown bromine decolourises

**F**: reddish brown colour remains