



**Catholic Junior College**  
**JC2 Preliminary Examination**  
**Higher 2**

CANDIDATE  
NAME

CLASS

2T

INDEX  
NUMBER

**CHEMISTRY**

**Paper 2 Structured Questions**

**9729/02**

**29 August 2025**

**2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

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

A Data Booklet is provided.

The number of marks is given in brackets [ ] at the end of each question or part question.

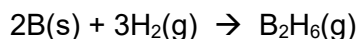
**WORKED  
SOLUTIONS**

For Examiner's Use	
Paper 1	<div>30</div>
Paper 2	Q1 /16
	Q2 / 7
	Q3 /10
	Q4 /18
	Q5 /13
	Q6 /11
	<div>75</div>
Paper 3	<div>80</div>
Paper 4	<div>55</div>
OVERALL (100%)	
GRADE	

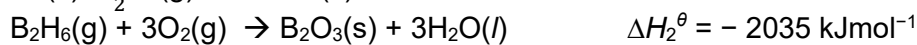
[Turn over

Answer **all** the questions in the space provided.

- 1 (a) Many chemical compounds used for rocket fuel and propellants are highly reactive and hazardous. One of these compounds, diborane,  $\text{B}_2\text{H}_6$ , can be formed from its elements according to the following equation:



Given the following data,



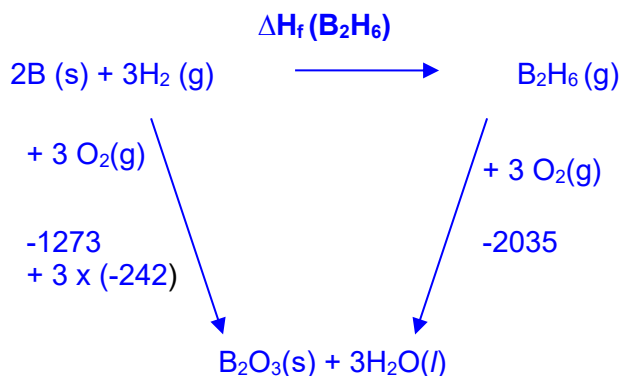
- (i) Name the enthalpy change represented by  $\Delta H_1^\theta$ .

Standard enthalpy change of formation of  $\text{B}_2\text{O}_3(\text{s})$

..... [1]

- (ii) By drawing an energy cycle diagram, calculate the enthalpy change of formation of diborane,  $\text{B}_2\text{H}_6(\text{g})$ .

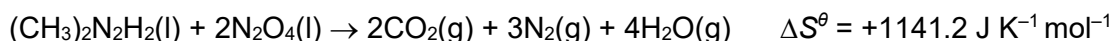
[3]



Using Hess's Law,

$$\begin{aligned} \Delta H_f(\text{B}_2\text{H}_6) &= -1273 + 3 \times (-242) - (-2035) \\ &= +36 \text{ kJ mol}^{-1} \end{aligned}$$

- (b) The reaction of 2,2-dimethylhydrazine,  $(\text{CH}_3)_2\text{N}_2\text{H}_2$ , with dinitrogen tetroxide,  $\text{N}_2\text{O}_4$ , is another energy source for rockets.



- (i) One of the reactants in the above reaction, dinitrogen tetroxide,  $\text{N}_2\text{O}_4$ , may be obtained from the more commonly available  $\text{NO}_2$ . State and explain the effect on the entropy,  $S$ , of the chemical system during the conversion of  $\text{NO}_2(\text{g})$  to  $\text{N}_2\text{O}_4(\text{g})$ .

$2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$ . When  $\text{NO}_2(\text{g})$  is converted to  $\text{N}_2\text{O}_4(\text{g})$ , entropy decreases

because there is a decrease in the number of gaseous molecules (from 2

molecules of  $\text{NO}_2$  to 1 molecule of  $\text{N}_2\text{O}_4$ ). Hence there are lesser ways of

arranging the particles resulting in a decrease in disorder of the system. .... [1]

- (ii) By using the standard enthalpy change of formation,  $\Delta H_f^\ominus$ , values given below, calculate the standard Gibbs free energy change,  $\Delta G^\ominus$ , in  $\text{kJ mol}^{-1}$  for the reaction of  $(\text{CH}_3)_2\text{N}_2\text{H}_2$  with  $\text{N}_2\text{O}_4$  at 298 K.

substance	$(\text{CH}_3)_2\text{N}_2\text{H}_2(\text{l})$	$\text{N}_2\text{O}_4(\text{l})$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{g})$
$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	+48.9	-19.6	-393.5	-241.8

$$\Delta H^\ominus = \Sigma \Delta H_f^\ominus(\text{products}) - \Sigma \Delta H_f^\ominus(\text{reactants})$$

$$= [2(-393.5) + 0 + 4(-241.8)] - [(+48.9 + 2(-19.6))]$$

$$= -1763.9 \text{ kJ mol}^{-1}$$

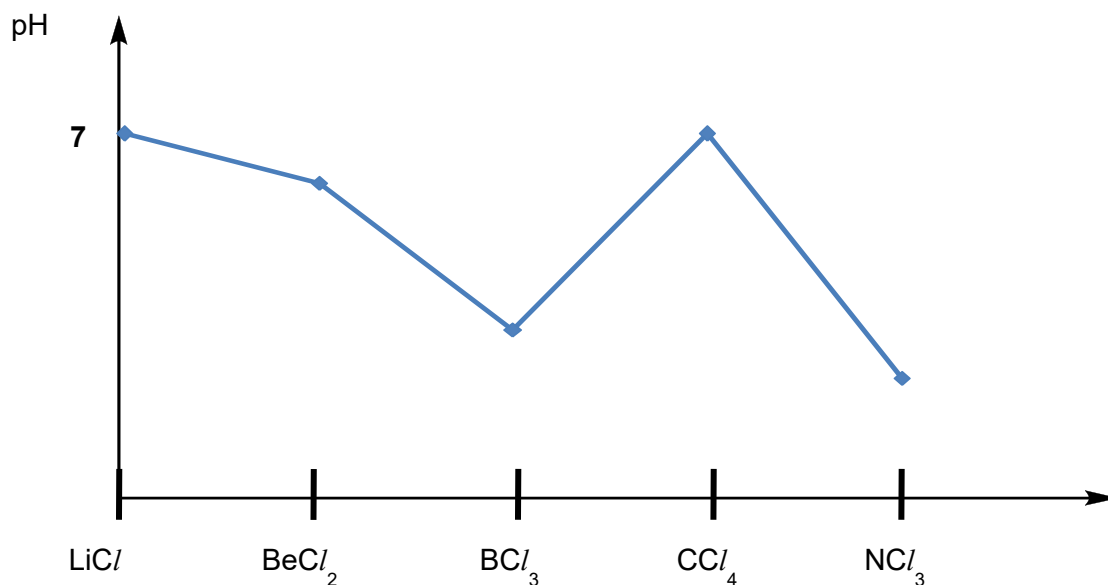
$$\text{Now, } \Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

$$= -1763.9 - [298(+1141.2 \times 10^{-3})]$$

$$= -2.10 \times 10^3 \text{ kJ mol}^{-1}$$

[3]

- (c) (i) The chlorides of Period 2 elements behave similarly to chlorides of Period 3 elements. Based on your knowledge of chlorides of Period 3 elements, sketch a graph of pH against the chlorides of lithium to nitrogen. In your sketch, consider the chloride of carbon is immiscible with water. [3]



- (ii) Write an equation with state symbols to account for the pH of liquid  $\text{NCl}_3$  when dissolved in water. Aqueous  $\text{HNO}_2$  and steamy white fumes are formed in the reaction.



[2]

- (d) Describe and explain how the thermal stability of the hydrogen halides varies down Group 17. Include an equation for the thermal decomposition reaction in your answer.

**Describe:**

- Hydrogen halides decompose on heating to give hydrogen gas and halogens.



- The thermal stability decreases down from HCl, HBr and HI.

**Explain:**

- Down the group, as the size of the halogen atom increases.

- The **H–X** bond length increases and is weaker due to less effective orbital overlap.

- Hence, the bond energy of H–X decreases, and thermal stability decreases

down the group. [3]

[Total: 16]

- 2 Ammonia gas,  $\text{NH}_3$ , is used in industrial refrigeration systems. A refrigeration chamber contains 0.686 mol of ammonia gas at a temperature of 360K. The chamber volume is  $2.25 \text{ dm}^3$ .

(a) State two main assumptions of kinetic theory of gases.

The individual gas particles have negligible volume as compared to the

overall gas volume.

There are negligible forces of attraction between the gas particles.

[2]

(b) Calculate the pressure of ammonia, in kPa, in the chamber using the ideal gas equation.

$$pV = nRT$$

$$p (2.25 / 1000) = 0.686 (8.31)(360)$$

$$p = 912 \text{ kPa}$$

[1]

(c) To determine the pressure of ammonia in the chamber more precisely, the van der waals' equation shown below is used.

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \text{ (where } a \text{ and } b \text{ are constants)}$$

Given that the pressure obtained using van der waals' equation is lower than your answer in (b), explain the difference.

The pressure is lower due to the presence of hydrogen bonding between

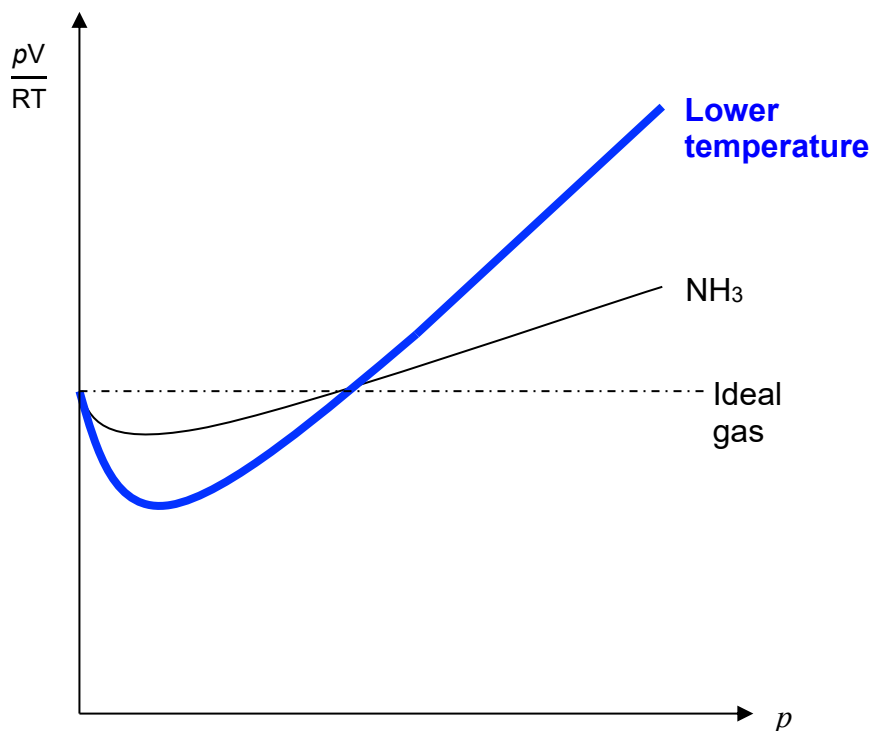
ammonia molecules.

[1]

(d) Under what conditions of temperature and pressure would you expect ammonia to be most like that of an ideal gas?

high temperature and low pressure. [1]

- (e) The graph below shows the compressibility curve of 1 mole of ammonia gas. On the same axes, draw the compressibility curve for 1 mole of ammonia at a lower temperature in the graph below and explain the shape of your graph. Your answer should include reference to intermolecular forces.



At lower temperature, the gas particles have lower kinetic energy, and hence do not have sufficient energy to overcome the intermolecular forces of attraction between one another. Thus, the intermolecular forces of attraction between the gas particles are more significant at lower temperature.

[2]

[Total: 8]

- 3 (a) A 2.67 g sample of a Period 3 chloride is heated to 227°C in a sealed flask. At this temperature, the chloride is a gas of volume 250 cm<sup>3</sup> and the pressure in the flask is 323 kPa. Using the general gas equation, calculate the  $M_r$  of the Period 3 chloride. Deduce its formula. [3]

$$pV = nRT$$

$$323 \times 10^3 \times 250 \times 10^{-6} = n \times 8.31 \times (227 + 273)$$

$$n = 0.01943 \text{ mol}$$

$$n = \text{mass} / M_r$$

$$0.01943 = 2.67 / M_r$$

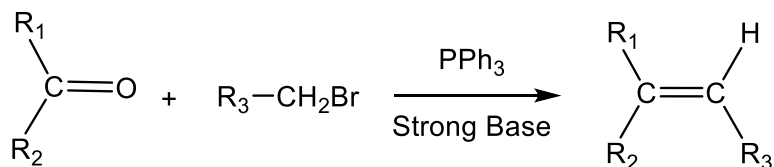
$$M_r = 137.4$$

Based on  $M_r$ , the period 3 chloride is likely to contain 3 Cl.

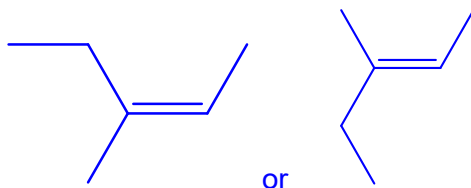
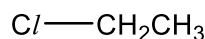
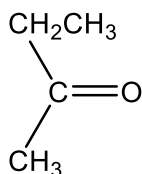
$$A_r \text{ of period 3 element} = 137.4 - 35.5 \times 3 = 30.9$$



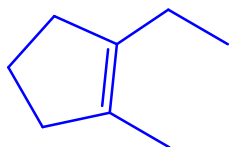
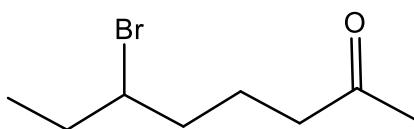
- (b) Triphenylphosphine (represented as  $\text{PPh}_3$ ) is used in a type of reaction known as a Wittig reaction. In the Wittig reaction, a carbonyl compound reacts with a halogenoalkane to form an alkene. The conversion is shown in the following unbalanced equation.



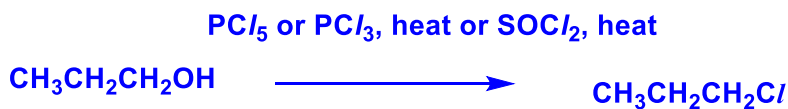
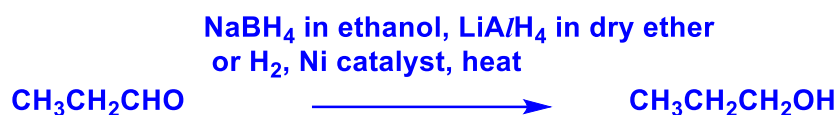
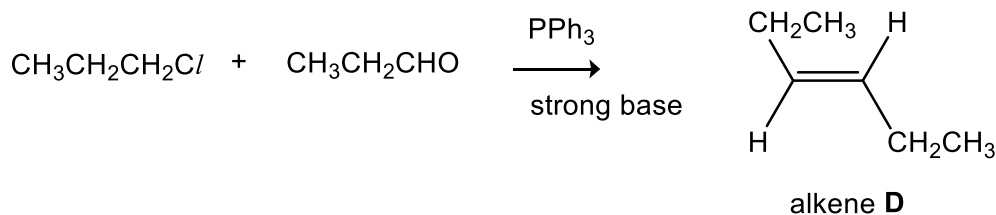
- (i) Draw the structure of the product formed from the Wittig reaction of the following compounds. [1]



- (ii) Predict the structural formula of the product formed when the following compound undergoes the Wittig reaction. [1]



- (iii) Alkene **D** can be formed from propanal,  $\text{CH}_3\text{CH}_2\text{CHO}$  via the Wittig reaction. Propose a 2-step synthesis to form 1-chloropropane, from propanal, for the Wittig reaction to take place. [2]





- (c) Many transition metals and their complexes are paramagnetic. Paramagnetism is a property of a substance which allows it to be weakly attracted to a magnet. This property is due to the presence of unpaired electrons in the substance.

Nickel forms many complexes with a co-ordination number of 4. Complexes with a co-ordination number of 4 can take on either the tetrahedral or the square planar geometry.

Table 3.1 shows the relative paramagnetism of two nickel complexes with **different** geometry, which contain  $\text{Ni}^{2+}$  ion with a co-ordination number of 4.

Table 3.1

formula of complex	relative paramagnetism
$[\text{NiCl}_4]^{2-}$	2
$[\text{Ni}(\text{CN})_4]^{2-}$	0

Fig. 3.2 shows how the d-orbitals of a transition metal ion such as nickel are split in complexes with these two different geometries.

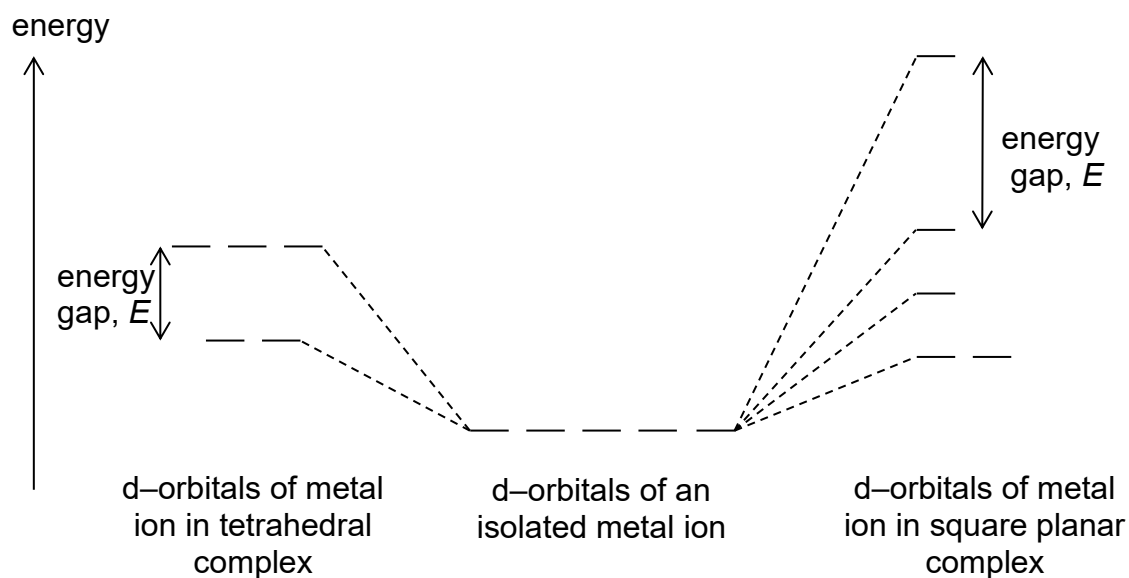
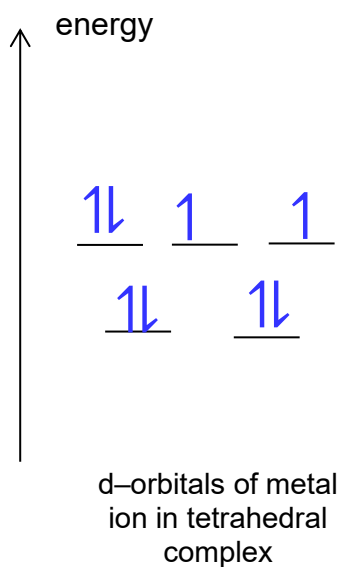


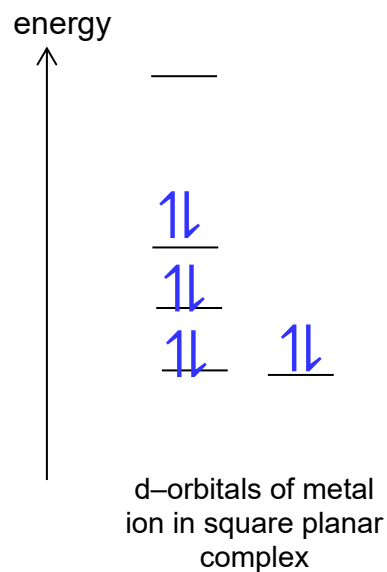
Fig. 3.2

- (i) Complete the diagram in Fig. 3.3 to show how the d electrons are arranged in the five non-degenerate d-orbitals

(I) in the tetrahedral  $[\text{NiCl}_4]^{2-}$  complex



(II) in the square planar  $[\text{Ni}(\text{CN})_4]^{2-}$  complex

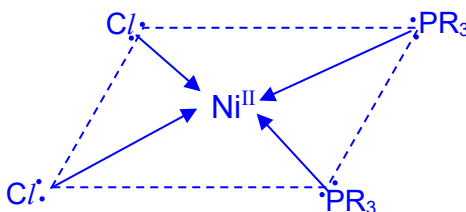


[2]

Fig. 3.3

- (ii) Nickel(II) chloride forms a square planar complex,  $\text{Ni}(\text{PR}_3)_2\text{Cl}_2$ , with the monodentate organic ligand, triethylphosphine which can be represented as  $\text{PR}_3$ .

The complex can occur in two forms, **G** and **H**, where **G** has an overall dipole and **H** has none. Suggest the structure of **G**. [1]

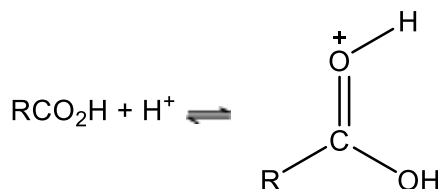


[Total: 10]

- 4 Esters are derivatives of carboxylic acids. Simple esters tend to have pleasant, fruity odours and are widely used as flavours and fragrances. Esterification generally refers to the formation of esters from alcohol and carboxylic acids, as shown in **Equation 1**. This Fischer esterification mechanism is thought to involve 5 steps.



**Step 1 :** The carboxyl oxygen on the carboxylic acid gains a proton.



**Step 2 :** Next, the electron-rich oxygen atom of the alcohol attacks the carbon atom of the carboxylic acid to form a positively-charged tetrahedral intermediate.

**Step 3 :** This is followed by transferring a proton to the hydroxyl oxygen of the carboxyl group.

**Step 4 :** Subsequently, water is removed to form the positively charged ester.

**Step 5 :** The ester is formed when a proton is transferred to the base.

- (a) (i) Suggest why protonation in **Step 1** is required before nucleophilic attack in **Step 2** can occur.

The protonation activates the carbonyl carbon toward nucleophilic attack. This is because O would withdraw electrons from C, making it even more partial positive.

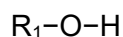
.....  
.....  
..... [1]

- (ii) State whether the acid catalyst acts as a homogeneous or heterogenous catalyst in this reaction. Explain your answer.

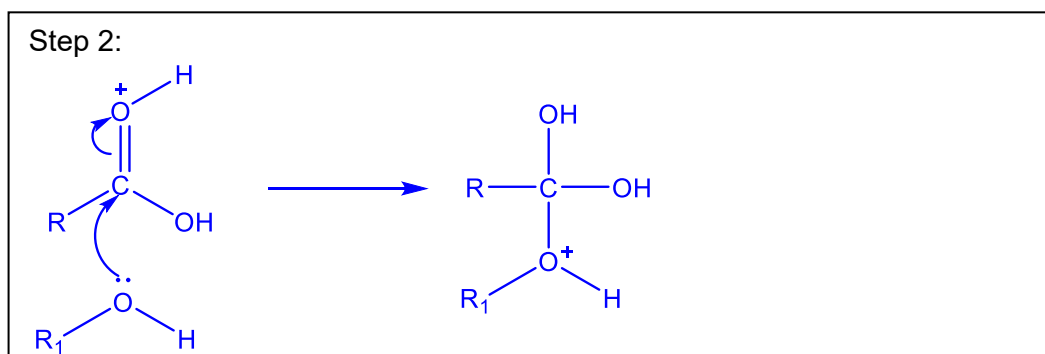
Homogeneous. Both the catalyst and the reactants are in the same phase. The acid catalyst is also regenerated at the end of the process.

.....  
.....  
.....[1]

- (iii) Using the information given, propose the mechanism for Step 2 in the given boxes below. The structure of the alcohol, R-OH is shown below.



Suggest the mechanism for this reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

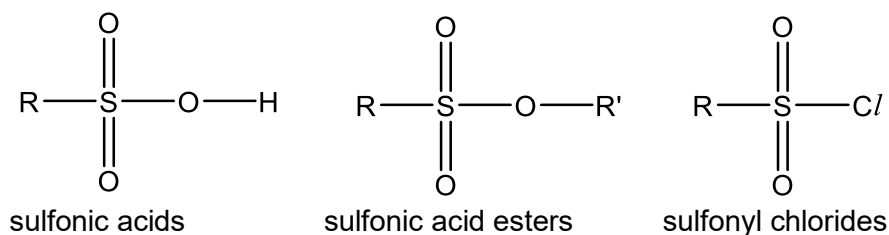


- (iv) Suggest the type of reaction taking place in Step 2

Nucleophilic addition

.....[1]

- (b) Organic sulfonic acids,  $RSO_2OH$ , sulfonic acid esters,  $RSO_2OR'$ , and sulfonyl chlorides,  $RSO_2Cl$ , show similar chemical properties to those of carboxylic acids, esters and acyl chlorides respectively. R and R' can represent alkyl groups or H atoms.



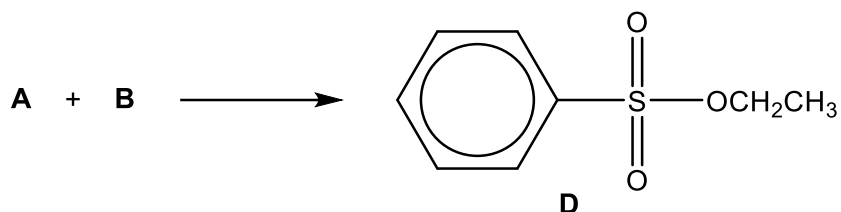
- (i) Based on your answer in (a)(i), explain why the rate of esterification will be faster when sulfonic acid is used instead of carboxylic acid.

Sulfur atom in sulfonic acid is more electrophilic/ electron deficient than the carbon in carboxylic acid as it is bonded to 1 more electronegative O atom and thus is more susceptible to nucleophilic attack by the alcohol.

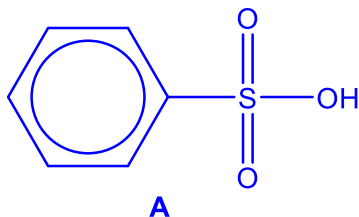
.....[1]

- (ii) The sulfonic acid ester **D** is synthesised from the corresponding sulfonic acid **A** and another organic molecule **B**.

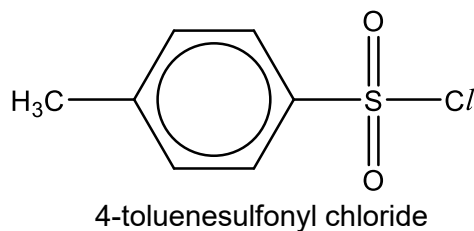
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Suggest the structures of **A** and **B**.

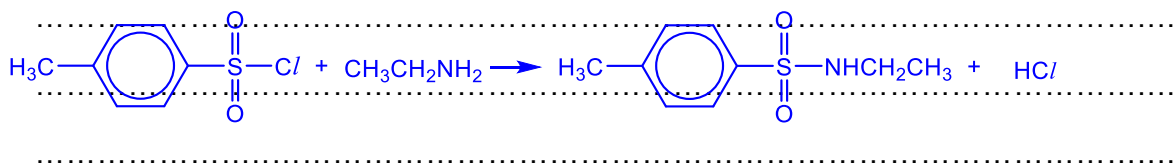
[2]

**B:**  $\text{CH}_3\text{CH}_2\text{OH}$ 

- (iii) Sulfonyl chlorides react with amines in a manner similar to acyl chlorides to form sulfonamide. 4-toluenesulfonyl chloride reacts readily with ethylamine,  $\text{CH}_3\text{CH}_2\text{NH}_2$ , at room temperature.



Suggest an equation for the reaction of 4-toluenesulfonyl chloride with ethylamine.

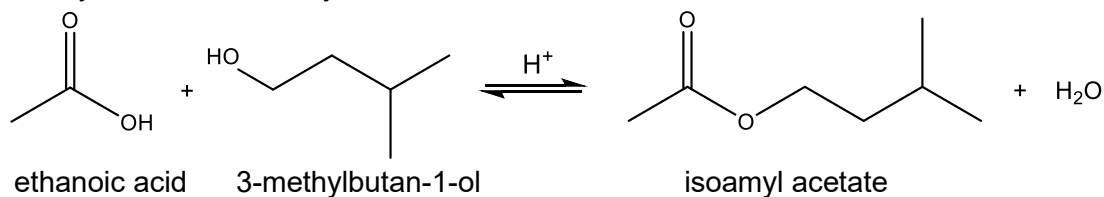


[1]

[1]

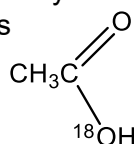
- (c) At the newly opened Minion Land in Universal Studios Singapore, many banana-flavoured treats can be found at the stalls for visitors to immerse themselves in the Minions experience. The ester, isoamyl acetate with molecular formula  $C_7H_{14}O_2$  is the compound responsible for the fruit's distinctive taste.

Isoamyl acetate can be synthesised via esterification as follows:

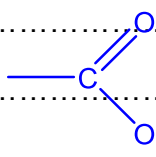


- (i) When isoamyl acetate undergoes acid hydrolysis in a solution containing  $H_2O^{18}$ , atoms of the  $^{18}O$  isotope appear in the product as  $CH_3C(=O)^{18}OH$  and not as  $(CH_3)_2CHCH_2CH_2^{18}OH$ .

Explain why this is the case.



The C-O single bond in the

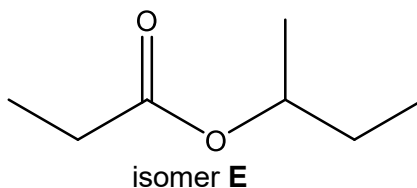


group of the ester is broken.

[2018P1Q28]

[1]

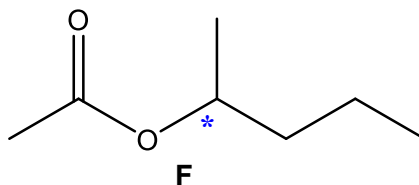
- (ii) An isomer of isoamyl acetate with molecular formula,  $C_7H_{14}O_2$ , **E** has the following structure. Describe a reaction by which you could distinguish between isoamyl acetate and isomer **E**.



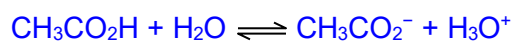
To two separate test tubes containing isoamyl acetate and isomer **E**, add aqueous iodine and aqueous sodium hydroxide, and heat in a hot water bath. Test tube containing isomer **E** will form a yellow ppt of  $CHI_3$ . No yellow ppt will be seen in the test tube containing isoamyl acetate.

[2]

- (iii) Another isomer with molecular formula  $C_7H_{14}O_2$ , **F** contains a chiral centre. Use an asterisk (\*) to mark the chiral centre present on the molecule of **F**. [1]



- (d) Ethanoyl chloride instead of ethanoic acid may be used to synthesise isoamyl acetate.
- (i) Write an equation for the reaction of ethanoyl chloride with water and hence explain why the solution has a lower pH as compared to ethanoic acid.



Ethanoyl chloride undergoes hydrolysis readily with water to form a strongly acidic solution of **HCl**. Ethanoic acid only partially dissociate in water to give  $H_3O^+$ .

[2]

- (ii) Chloroethanoyl chloride,  $CH_2ClCOCl$ , **H**, can be obtained from ethanoic acid by heating it with  $Cl_2$  and  $PCl_5$ .

**H** can then be used to produce **J**,  $C_4H_{10}NCl$ , via compound **I**, as shown in Figure 4.1.

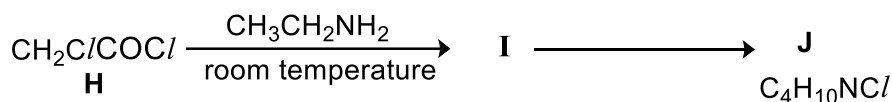
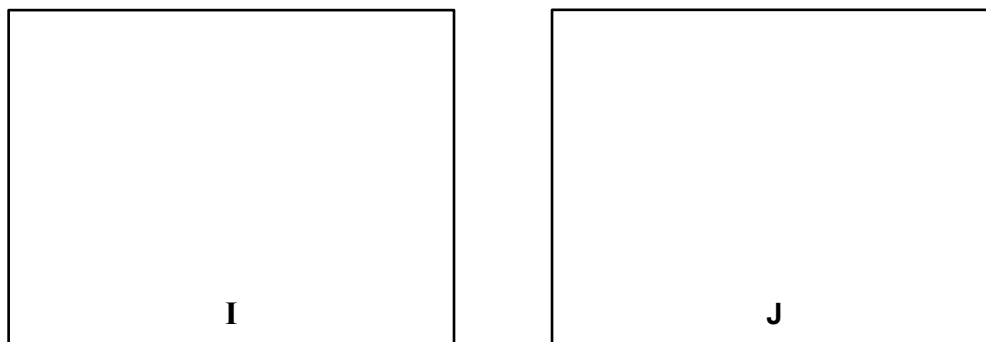


Figure 4.1

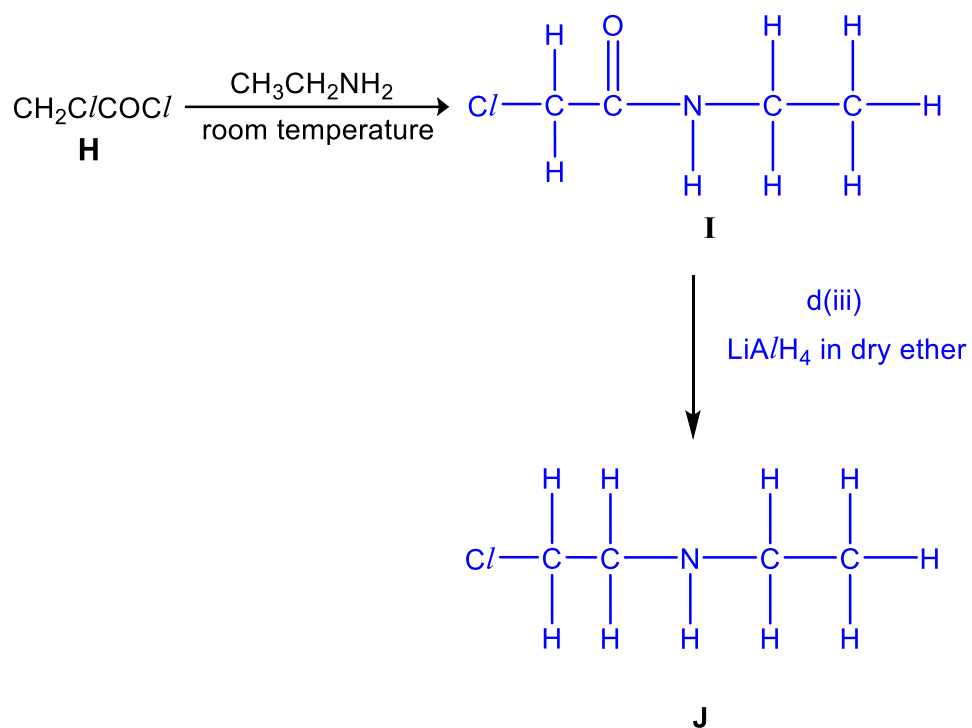
Suggest structures for compounds **I** and **J** in Figure 4.1.

[2]



- (iii) State the reagents and conditions to convert **I** to **J**.

.....[1]



[Total: 18]



- 5 (a) Ammonia in aqueous solution is a weak base, its dissociation constant,  $K_b$ , being  $1 \times 10^{-5} \text{ mol dm}^{-3}$ .

What is the pH of a  $0.100 \text{ mol dm}^{-3}$  aqueous solution of ammonia? [2]



$$\begin{aligned} [\text{OH}^-] &= \sqrt{K_b \times [\text{base}]} \\ &= \sqrt{(1 \times 10^{-5}) \times 0.100} \\ &= 1 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} \text{pOH} &= -\lg(1 \times 10^{-3}) = 3.00 \\ \text{pH} &= (14 - 3.00) = 11.0 \end{aligned}$$

- (b)  $45.4 \text{ cm}^3$  of ammonia gas is passed into  $25.00 \text{ cm}^3$  of  $0.0400 \text{ mol dm}^{-3}$  of sulfuric acid at standard temperature and pressure (s.t.p). All the ammonia is neutralised by the acid to form ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ .

- (i) Write a balanced equation, with state symbols, for the reaction between ammonia and sulfuric acid. [1]



- (ii) Calculate the amount of ammonia gas passed into the acid. [1]

$$\text{Amount of NH}_3 = \left( \frac{45.4}{22700} \right) = 0.00200 \text{ mol}$$

- (iii) Calculate the concentration of  $\text{NH}_4^+$  ions formed in the solution. [1]

$$\text{Amount of H}_2\text{SO}_4 = \left( \frac{25.00}{1000} \times 0.0400 \right) = 0.00100 \text{ mol}$$

$$\text{Amount of } (\text{NH}_4)_2\text{SO}_4 = \frac{0.00200}{2} = 0.00100 \text{ mol}$$

$$[\text{NH}_4^+] = \left( 2 \times 0.00100 \times \frac{1000}{25.00} \right) = \underline{0.0800 \text{ mol dm}^{-3}}$$

- (iv) Calculate the pH of the aqueous solution of the salt formed, assuming  $K_w$  is  $1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ . [2]

The salt,  $(\text{NH}_4)_2\text{SO}_4$  undergoes hydrolysis in water.



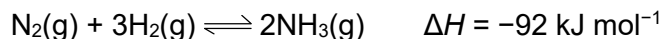
$$\begin{array}{ccc} 0.0800 \text{ mol dm}^{-3} & & ? \end{array}$$

$$K_a = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{1 \times 10^{-5}} = 1.00 \times 10^{-9}$$

$$\begin{aligned} [\text{H}^+] &= \sqrt{K_a \times [\text{NH}_4^+]} \\ &= \sqrt{(1.00 \times 10^{-9}) \times (0.0800)} \\ &= \underline{8.94 \times 10^{-6} \text{ mol dm}^{-3}} \end{aligned}$$

$$\begin{aligned} \text{pH} &= -\lg [\text{H}^+] \\ &= -\lg(8.94 \times 10^{-6}) = \underline{5.05} \end{aligned}$$

- (c) The Haber process is the principal commercial method used to manufacture ammonia gas from nitrogen and hydrogen, as shown in the following equation:



The table below shows the percentage of ammonia gas by volume in the equilibrium mixtures at various temperatures and pressures. In all cases, the molar ratio of  $\text{N}_2$  and  $\text{H}_2$  in the mixtures is 1:3.

Temperature/ °C	% of ammonia gas		
	at 1 atm	at 10 atm	at 100 atm
200	1.10	7.42	25.8
300	0.22	1.94	12.6
400	0.07	0.61	5.2

- (i) State Le Chatelier's principle.

Le Chatelier's principle states that if a change (e.g., change in concentration, pressure or temperature) is made to a system in dynamic equilibrium, the system reacts in such a way to oppose the change, and a new equilibrium is formed......[1]

- (ii) From the data provided above, state how the percentage of ammonia gas varies with changes in temperature, at a fixed pressure and how the percentage of ammonia gas varies with changes in pressure, at a fixed temperature, in the equilibrium mixture.

The percentage of ammonia gas decreases with increasing temperature, at a fixed pressure......

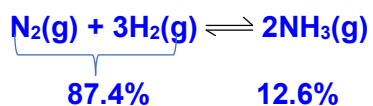
The percentage of ammonia gas increases with increasing pressure, at a fixed temperature......[1]

- (iii) Hence, explain how changes in temperature and pressure affect the percentage of ammonia, in the equilibrium mixture, with reference to Le Chatelier's principle.

By Le Chatelier's principle, since the forward reaction is exothermic, so when temperature is increased, the position of equilibrium shifts to the left as heat energy is absorbed by the reverse endothermic reaction, resulting in decrease in percentage of ammonia gas......

By Le Chatelier's principle, when pressure is increased, the position of equilibrium shifts to the right to decrease the number of gaseous molecules so as to reduce the pressure, resulting in increase in percentage of ammonia gas......[2]

- (iv) Calculate the partial pressure of each gas in the equilibrium mixture at a pressure of 100 atm and a temperature of 300 °C. Hence, determine  $K_p$  at 300 °C, stating the units. [2]



$$P_{\text{NH}_3} = \left( \frac{12.6}{100} \times 100 \right) \text{ atm} = 12.6 \text{ atm}$$

$$P_{\text{N}_2} = \left( \frac{1}{4} \times \frac{87.4}{100} \times 100 \right) \text{ atm} = 21.9 \text{ atm}$$

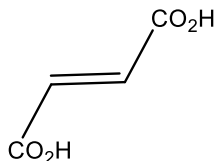
$$P_{\text{H}_2} = \left( \frac{3}{4} \times \frac{87.4}{100} \times 100 \right) \text{ atm} = 65.6 \text{ atm}$$

$$\begin{aligned} K_p &= \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} \\ &= \frac{12.6^2}{21.9 \times (65.6)^3} \\ &= 2.57 \times 10^{-5} \text{ atm}^{-2} \end{aligned}$$

[Total: 13]

- 6 Double indicator acid-base titrations can be used to determine the composition of a mixture of acids in addition to the pH of buffer solutions formed from polyprotic acids.

Maleic acid is a diprotic weak acid,  $\text{H}_2\text{A}$  and its structure is as shown below:



- (a) The table below gives the  $\text{p}K_{\text{a}}$  values of maleic acid at 298 K.

Equation	$\text{p}K_{\text{a}}$
$\text{H}_2\text{A} \rightleftharpoons \text{HA}^- + \text{H}^+$	1.90 ( $\text{p}K_{\text{a}1}$ )
$\text{HA}^- \rightleftharpoons \text{A}^{2-} + \text{H}^+$	6.20 ( $\text{p}K_{\text{a}2}$ )

Explain why the value of  $\text{p}K_{\text{a}2}$  is higher than that of  $\text{p}K_{\text{a}1}$ .

A higher  $\text{p}K_{\text{a}2}$  implies it is more difficult to lose (the second) proton due to the

stronger electrostatic force of attraction between the increasing negatively

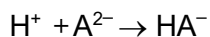
charged anion and the proton......[1]

- (b) A double indicator titration was performed to determine the pH of the buffer solution that was prepared by mixing unknown volumes of  $\text{Na}_2\text{A}$  and  $\text{NaHA}$ .

25.0  $\text{cm}^3$  of the buffer solution was titrated against 0.200  $\text{mol dm}^{-3}$   $\text{HCl}$  using bromocresol green as an indicator for the first end-point. 16.90  $\text{cm}^3$  of the titrant was required for this titration.

An additional titre volume of 19.20  $\text{cm}^3$  was required to reach the second end point using thymol blue as an indicator.

The reaction between  $\text{A}^{2-}$  and  $\text{H}^+$  from  $\text{HCl}$  occurs in two steps:



- (i) Calculate the concentration of  $\text{A}^{2-}$  present in the buffer solution initially.

$$\text{Amount of } \text{A}^{2-} = \left( \frac{16.90}{1000} \times 0.200 \right) = \text{Amount of HCl} = 3.38 \times 10^{-3} \text{ mol}$$

$$[\text{A}^{2-}] = \left( 3.38 \times 10^{-3} \times \frac{1000}{25.0} \right) = 0.135 \text{ mol dm}^{-3}$$

[1]

- (ii) Calculate the volume of hydrochloric acid used to fully react with the  $\text{HA}^-$  present in the buffer solution **initially** and hence calculate the initial concentration of  $\text{HA}^-$ .

$$\begin{aligned}\text{Amount of HC/ required to react with HA}^- \text{ from A}^{2-} \text{ at the second end-} \\ \text{point} &= \left( \frac{25.00}{1000} \times 0.1352 \right) \\ &= 3.38 \times 10^{-3} \text{ mol} \\ &= \text{Amount of A}^{2-}\end{aligned}$$

$$\begin{aligned}\text{Vol. of HC/ required to react with HA}^- \text{ from A}^{2-} &= \left( \frac{3.38 \times 10^{-3}}{0.200} \times 1000 \right) \\ &= 16.90 \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{Vol. of HC/ required to react with HA}^- \text{ present initially} &= 19.20 - 16.90 \\ &= 2.30 \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{Amount of HA}^- &= \left( \frac{2.30}{1000} \times 0.200 \right) = \text{Amount of HC/} = 4.60 \times 10^{-4} \text{ mol} \\ [\text{HA}^-] &= (4.60 \times 10^{-4} \times \frac{1000}{25.0}) = 0.0184 \text{ mol dm}^{-3}\end{aligned}$$

[2]

- (iii) Using your answers to (b)(i) and (ii), calculate the initial pH of the buffer solution.

$$\begin{aligned}\text{pH} &= \text{p}K_{a2} + \lg \frac{[\text{A}^{2-}]}{[\text{HA}^-]} \\ &= 6.20 + \lg \frac{[0.1352]}{[0.0184]} \\ &= 7.07\end{aligned}$$

[1]

- (iv) Hence using your calculations from (b)(i) and (ii), calculate the concentration of  $\text{H}_2\text{A}$  at the second equivalence point.

$$\begin{aligned}\text{Amount of H}_2\text{A at 2}^{\text{nd}} \text{ EP} &= \text{Amt of A}^{2-} \text{ ions} + \text{Amt of HA}^- \text{ ions in original mixture} \\ &= 3.38 \times 10^{-3} + 4.60 \times 10^{-4} \text{ mol} \\ &= 3.84 \times 10^{-3} \text{ mol} \\ [\text{H}_2\text{A}] &= (3.84 \times 10^{-3} \times \frac{1000}{25.0+36.10}) = 0.06284 \text{ mol dm}^{-3}\end{aligned}$$

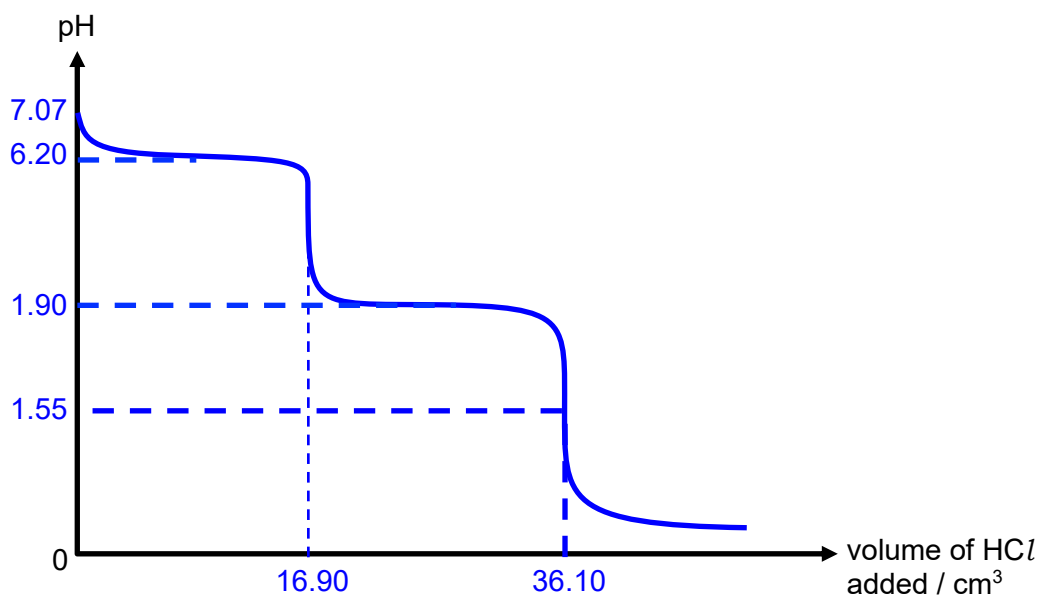
[1]

- (v) Hence, calculate the pH of  $\text{H}_2\text{A}$  at the second equivalence point.

$$\begin{aligned}[\text{H}^+] &= (K_a \times [\text{H}_2\text{A}])^{0.5} \\ &= (10^{-1.90} \times 0.06284)^{0.5} \\ &= 0.0281 \text{ mol dm}^{-3} \\ \text{pH} &= -\lg (0.0281) \\ &= 1.55\end{aligned}$$

[1]

- (c) Using the information provided in the question in addition to your answers from (b)(iii) – (b)(v), sketch a graph to show the pH changes that occur when 50.00 cm<sup>3</sup> of 0.200 mol dm<sup>-3</sup> HCl is added to 25.0 cm<sup>3</sup> of the initial buffer solution. Indicate clearly in your sketch, all relevant pH and volumes of HCl used.



[3]

- (d) Explain why a weak acid cannot be used in place of hydrochloric acid as a titrant for this titration.

There will be no sharp decrease of pH that is typically found along with the end-point, hence there is no indicator that can be used to produce a distinct colour change to identify the end-point. [1]

[Total: 11]