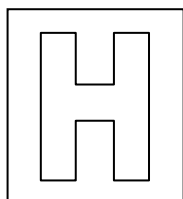


Candidate Name: _____



2023 Preliminary Examination Pre-University 3

H2 CHEMISTRY

9729/03

Paper 3 Free Response

18 September 2023

2 hours

Candidates answer on the Question Paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so.

Write your name, class and admission number in the spaces at the top of this page.

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. If additional space is required, you should use the page at the end of this booklet. The question number must be clearly shown.

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.

Question	A			B	Total
	1	2	3	4 / 5	
Marks	24	19	17	20	80

Section A

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

1 Aluminium is the most abundant metal in the Earth's crust. It has a great affinity towards oxygen, forming a protective layer of oxide on the surface when exposed to air.

(a) Aluminium is protected from corrosion by a protective oxide layer. The thickness of the aluminium oxide layer on the surface of aluminium can be increased by anodising the aluminium. H_2SO_4 is used as an electrolyte in the anodising of aluminium.

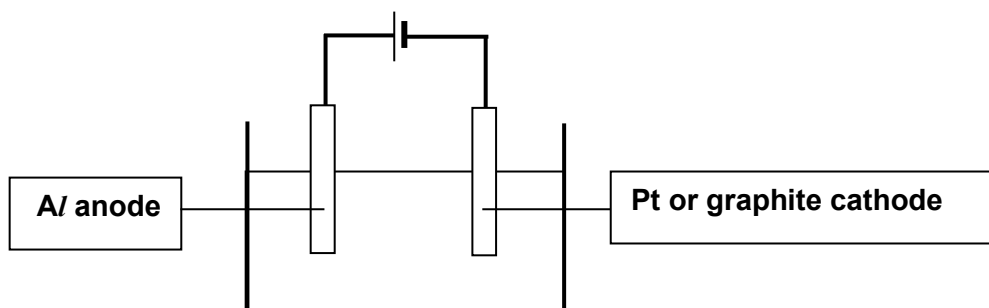
(i) Draw a well-labelled diagram to illustrate the electrolysis set-up for the anodisation of aluminium. [2]

(ii) Write chemical equations to show the reactions at the anode and cathode during anodising. Include the overall equation in your answer. [3]

(iii) The aluminium piece to be anodised has a surface area of 29.2 cm^2 . Determine the current required to pass through the set-up for 1.8 hours to form a 0.2 mm-thick protective layer of Al_2O_3 on the aluminium piece.

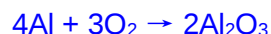
[Density of Al_2O_3 is 3.95 g cm^{-3}] [4]

(iv) Give one example of an anodised aluminium object, and explain the advantages of anodising it. [1]



- Correct orientation of the battery
- Correct labeling of both the electrodes with the material used
- Correct cell. i.e. An electrolytic cell and not a electrochemical cell

(ii) Anode: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$



Cathode: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

Overall: $2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2$

$$(iii) \text{ Volume of Al}_2\text{O}_3 = 29.2 \times 0.02 = 0.584 \text{ cm}^3$$

$$\text{Mass of Al}_2\text{O}_3 = 3.95 \times 0.584 = 2.3068 \text{ g}$$

$$\text{Amount of Al}_2\text{O}_3 = \frac{2.3068}{2(27.0) + 3(16.0)} = 0.02262 \text{ mol}$$

$$\text{Amount of O}_2 \text{ needed} = 0.02262 \times \frac{3}{2} = 0.033923 \text{ mol}$$

$$\text{Amount of e}^- = 4 \times 0.03392 = 0.13569 \text{ mol}$$

$$Q = 0.13569 \times 96500 = 13094 \text{ C}$$

$$\text{Current needed} = \frac{13094}{1.8 \times 60 \times 60} = 2.02 \text{ A}$$

(iv) Examples of anodized aluminium objects: drink cans, windows frames and grilles

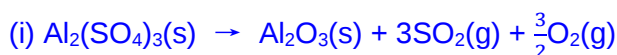
Anodised aluminium objects are more resistant to corrosion. Moreover, they can be decorative as well since the aluminium oxide layer is able to absorb dyes.

(b) Aluminium sulfate, $\text{Al}_2(\text{SO}_4)_3$, decomposes upon heating, forming aluminium oxide, sulfur dioxide gas and oxygen gas.

In an experiment, a 150 g sample of impure aluminium sulfate was heated until the sample reached a constant mass of 83.6 g.

(i) Write a balanced equation, with state symbols, for the decomposition of solid aluminium sulfate. [1]

(ii) Determine the percentage purity of the sample, assuming the impurities remained inert during the decomposition. [4]



$$(ii) \text{ Mass of gas lost} = 150 - 83.6 = 66.4 \text{ g}$$

Let the amount of O_2 be a , hence amount of $\text{SO}_2 = 2a$

$$\text{Mass of gas lost} = a(32.0) + 2a(32.1 + 32.0) = 66.4$$

$$32a + 128.2a = 66.4$$

$$a = 0.41448 \text{ mol}$$

$$\text{amount of Al}_2(\text{SO}_4)_3 = \frac{2}{3} \times 0.41448 = 0.2763 \text{ mol}$$

$$\text{mass of Al}_2(\text{SO}_4)_3 = 0.2763 \times [2(27.0) + 3(32.1) + 12(16.0)] = 94.58 \text{ g}$$

$$\% \text{ purity} = \frac{94.58}{150} = 63.1\%$$

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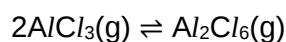
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- (c) Aluminium chloride is an active ingredient used in skin medication to control excessive sweating.

In the vapour phase, a dynamic equilibrium is established between aluminium chloride and its dimer as follows:

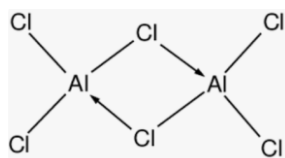


- (i) Aluminium chloride is often described as *electron deficient*. Explain what is meant by *electron deficient*. [1]
- (ii) With the aid of a diagram, explain how the dimer is formed. [2]
- (iii) Explain what is meant by *dynamic equilibrium*. [1]
- (iv) Write an expression for the equilibrium constant, K_p , for the dimerisation. [1]
- (v) In an experiment, 10 atm of $\text{AlCl}_3(\text{g})$ was allowed to reach equilibrium in a sealed vessel. At equilibrium it was found that the total pressure was 6.8 atm.
Calculate the value of K_p , stating its units. [3]
- (vi) Suggest a reason why the dimerisation would not take place readily if the AlCl_3 is placed in an aqueous system. [1]

[Total: 24]

(i) The aluminium atom in AlCl_3 has only 6 electrons surrounding it. Electron deficient implies that the central atom, Al has empty orbital in AlCl_3

(ii)



The lone pair on the Cl atom of one AlCl_3 molecule is donated to the empty orbital of the Al of another AlCl_3 molecule, forming a dative bond.

(iii) Dynamic equilibrium refers to a reversible reaction in which the rates of forward and reverse reactions have become equal and there is no change in the concentrations of the reactants and the products.

(iv) $K_p = \frac{P_{\text{Al}_2\text{Cl}_6}}{(P_{\text{AlCl}_3})^2}$

(v)

	$2\text{AlCl}_3(\text{g})$	$\rightleftharpoons$	$\text{Al}_2\text{Cl}_6(\text{g})$
initial partial pressure /atm	10		0
change	-2x		+x
eqm partial pressure /atm	$10 - 2x$		x

$$\text{Total pressure} = 10 - 2x + x = 6.8$$

$x = 3.2 = \text{eqm partial pressure of Al}_2\text{Cl}_6$

eqm partial pressure of $\text{AlCl}_3 = 10 - 2(3.2) = 3.6 \text{ atm}$

$$K_p = \frac{3.2}{3.6^2} = 0.247 \text{ atm}^{-1}$$

(vi) Under aqueous conditions, AlCl_3 will hydrolyse in water hence it will not have empty orbital to form dative bond.

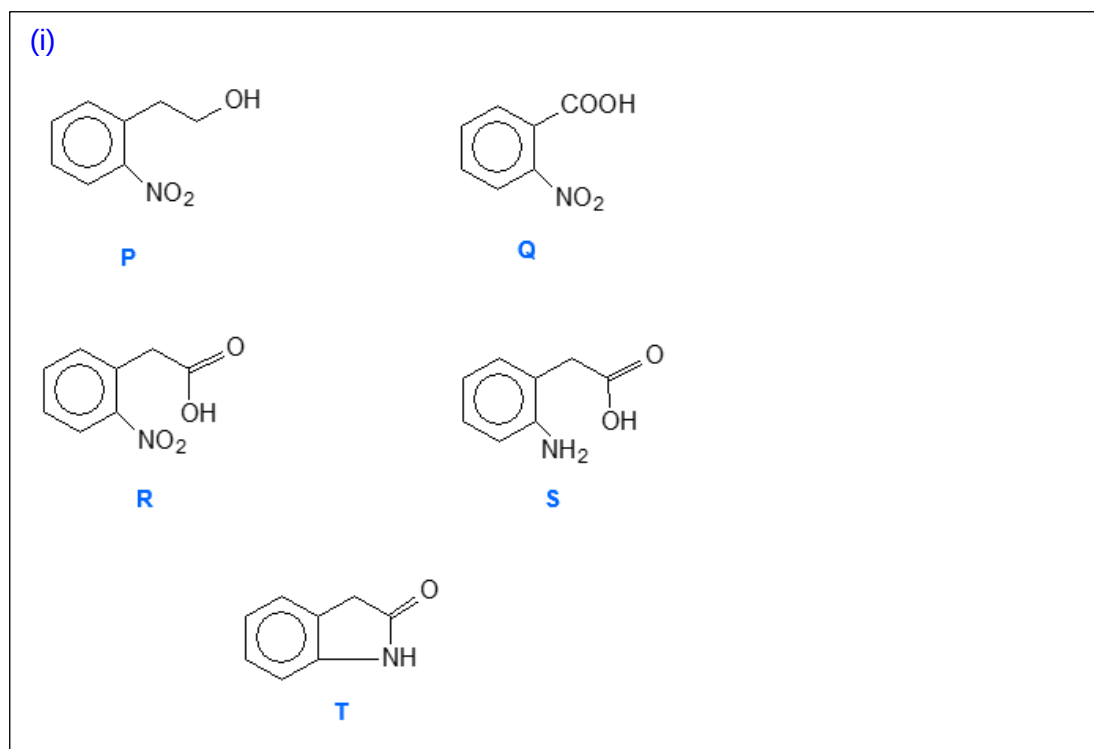
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- 2 (a) Compound **P** has a molecular formula $C_8H_9O_3N$. Treating **P** with hot acidified potassium manganate(VII) gives **Q**, $C_7H_5O_4N$, which produces effervescence with sodium hydrogencarbonate.

Heating **P** under reflux with acidified potassium dichromate(VI) gives **R**, $C_8H_7O_4N$. When **R** is treated with tin and concentrated hydrochloric acid, followed by careful neutralisation using an aqueous alkali, **S**, $C_8H_9O_2N$, is obtained.

1 mol of **S** reacts with 2 mol of aqueous bromine. Treatment of **S** with anhydrous phosphorus pentachloride produces **T**, C_8H_7ON .

- (i) Deduce the structures of compounds **P** – **T** and explain the chemistry of the reactions involved. [10]
- (ii) Compound **T** can be separated from any unreacted compound **S** that is left in the product mixture. This can be done by shaking the product mixture with cold dilute hydrochloric acid. The two layers (organic and aqueous layers) formed are then allowed to stand.
- State and explain which compound, **S** or **T**, will be present in the aqueous layer. [2]



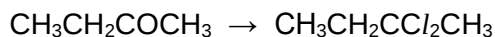
Reaction	Type of reaction	Deduction
Treating compound P , $C_8H_9NO_3$, with hot acidified potassium manganate(VII) gives compound Q , $C_7H_5NO_4$.	oxidation	loss of 1 C $\Rightarrow$ side-chain oxidation occurred.
Q produces effervescence with sodium hydrogen carbonate.	acid-base reaction (or acid-carbonate)	Q contains carboxylic acid group, $-COOH$.
Heating compound P under reflux with acidified potassium dichromate(VI) gives compound R , $C_8H_7NO_4$.	oxidation	gain in 1 O, loss of 2 H $\Rightarrow$ 1° alcohol in P is oxidised to $-COOH$ in R .
Compound R is treated with tin and concentrated hydrochloric acid, followed by careful neutralisation, compound S , $C_8H_9NO_2$ is obtained.	reduction	$-NO_2$ group in R is reduced to $-NH_2$ group in S .
1 mole of compound S reacts with 2 moles of aqueous bromine.	electrophilic substitution	S is a phenylamine. $-Br$ is substituted at positions 2, 4 or 2, 6 w.r.t the $-NH_2$ group
Treatment of compound S with anhydrous phosphorus pentachloride produces compound T , C_8H_7NO .	S is first converted to acyl chloride, by PCl_5 via nucleophilic substitution. The acyl chloride formed then undergoes intra-molecular condensation with the $-NH_2$ group to form a cyclic amide T .	The $-CH_2COOH$ group must be adjacent to the $-NH_2$ group in S to enable ring formation/formation of a cyclic amide

(ii) Compound **S** will be in the aqueous layer.

The basic $-NH_2$ group in compound **S** will react with cold dilute HCl to give an ionic product which can form strong ion-dipole interactions with water molecules.

- (b) PCl_5 reacts with ketones in a 1 : 1 molar ratio to give gem-dichlorides. A gem-dichloride contains two chlorine atoms bonded to the same carbon atom.

For example, when butanone is treated with PCl_5 , a gem-dichloride, 2,2-dichlorobutane, is obtained.



- (i) Suggest the phosphorus-containing by-product of this reaction. [1]
 (ii) Heating 2,2-dichlorobutane with alcoholic NaOH produces compounds **U** and **V**. **U** and **V** are constitutional isomers with the formula C_4H_6 . Treating **U** and **V** with hydrogen over a suitable catalyst procures butane.

Suggest the displayed formula of **U** and **V** and clearly indicate on your structures, the type of hybridisation for each C atom in the two structures. [4]

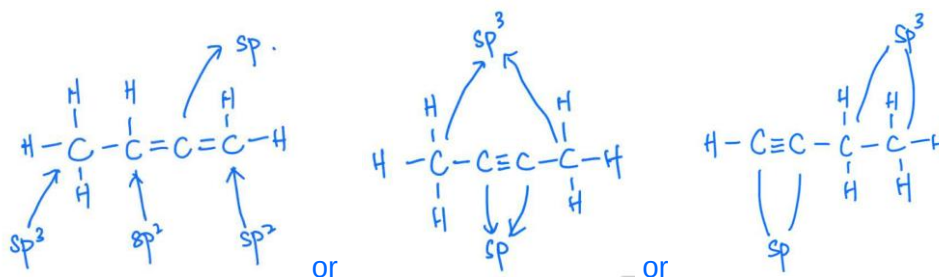
- (iii) If 1,1-dichlorocyclobutane is similarly heated with an excess of alcoholic NaOH , a product **W**, $\text{C}_4\text{H}_5\text{Cl}$, is obtained and no further loss of chlorine atoms occurs. **W** decolourises aqueous bromine.

Suggest the structure of **W**, and suggest why the expected loss of both chlorine atoms do not occur. [2]

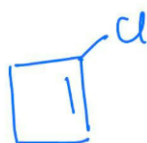
[Total: 19]

(i) POCl_3

(ii)



(iii)



ring strain. C with 2 double bonds is sp hybridised which should have a linear shape (180°). However to maintain the shape of the ring structure, it needs to be in 90°

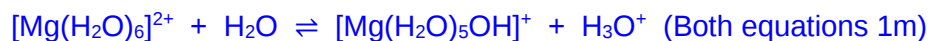
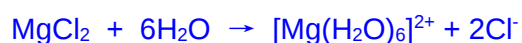
3 Chlorine is a yellowish-green gas with a choking smell. It has many uses, including in the treatment of drinking water.

(a) (i) Write balanced chemical equations for the reactions that occur when separate samples of magnesium and phosphorus are heated in excess chlorine. [2]

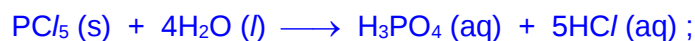
(ii) Describe the reaction of each of the resulting chloride with excess water, stating the approximate pH of the solution formed, and writing a balanced equation for any reaction that takes place. [3]



(ii) MgCl_2 dissolves in water and undergoes partial hydrolysis to give a slightly acidic solution of pH 6.5. ;



PCl_5 undergoes complete hydrolysis to form strongly acidic solution with pH 2.;



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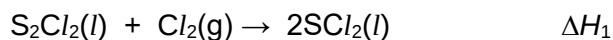
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- (b) Sulfur and chlorine can react together to form S_2Cl_2 .

S_2Cl_2 can further react with Cl_2 to form SCl_2 , as shown in the equation below.



- (i) Draw 'dot-and-cross' diagrams to illustrate the bonding in S_2Cl_2 and SCl_2 respectively.

State the bond angle about the S atom in SCl_2 . [3]

- (ii) Using relevant bond energy data from the *Data Booklet*, determine the enthalpy change for the reaction, ΔH_1 . [2]

- (iii) The actual value of ΔH_1 is less endothermic compared to your answer in (b)(ii).

Suggest two reasons for the discrepancy between the actual value and your answer in (b)(ii). [2]

- (iv) Define the term *entropy*. [1]

- (v) State the sign of the entropy change for the reaction between $S_2Cl_2(l)$ and $Cl_2(g)$. Explain your answer. [2]

- (vi) OCl_2 is a compound analogous to SCl_2 .

State and explain how the bond angle in OCl_2 would differ from that in SCl_2 . [2]

[Total: 17m]

(i)



Bond angle about S in $SCl_2 = 104.5^\circ$

(ii)

Bonds broken

Bonds formed

1 S-S: 264

2 S-Cl : $2 \times 250 = 500$

1 Cl-Cl : 244

$\Delta H_1 = 264 + 244 - 2(250) = +8.00 \text{ kJ mol}^{-1}$

(iii) The enthalpy change of vaporisation of S_2Cl_2 and SCl_2 were not taken into consideration in the calculation.

Bond energy values used are only average values.

(iv) Entropy is the measure of disorderliness.

(v) The sign of ΔS is negative. There is a decrease in number of gaseous particles resulting in less ways of arranging the particles hence disorderliness decreases.

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(vi) OCl_2 will have a larger bond angle. ;

O is more electronegative than S, causing the bonding electrons to be closer,
resulting in larger repulsion. ;

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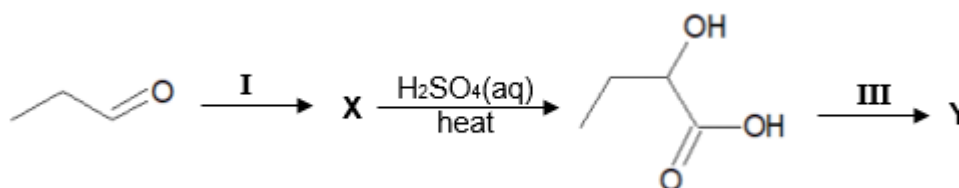
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Section B

Answer **one** question from this section.

- 4 (a) Propanal is an aldehyde which exists as a colourless liquid with a fruity smell. A cyclic diester, **Y**, can be formed from propanal as shown in the synthetic pathway below. **Y** has a molecular mass of 172 g mol^{-1} .



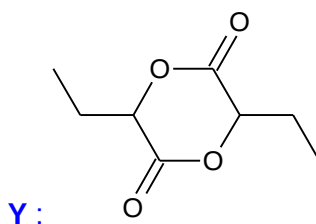
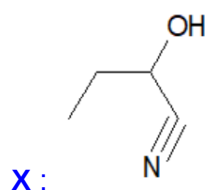
- (i) State the reagents and conditions for steps **I** and **III**. [2]
- (ii) Draw the structure of **X** and **Y**. [2]

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- (i)
 step **I** : HCN trace amount of NaOH or NaCN, cold
 step **III** : concentrated H_2SO_4 , heat under reflux

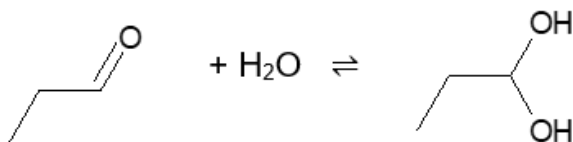
(ii)



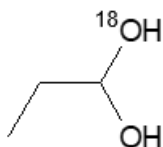
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- (b) Propanal undergoes reaction with water to yield a gem-diol. The reaction is reversible and a water molecule can be eliminated from the gem-diol to regenerate propanal.



- (i) State the type of reaction for the above reaction. [1]
- (ii) The reaction is slow but the rate is increased by the addition of a small amount of NaOH as catalyst. Suggest why NaOH is needed to initiate the reaction in the mechanism. [1]
- (iii) The oxygen in water is primarily ^{16}O but water enriched with the heavy isotope, H_2^{18}O , is also available. When propanal is dissolved in H_2^{18}O , the ^{18}O becomes incorporated into the gem-diol which regenerates propanal.



- Using your answer to (a)(ii), suggest how ^{18}O is incorporated into the gem-diol. [1]
- (iv) Suggest a reason why the addition of water to aldehydes proceeds more rapidly than it does to ketones. [1]
- (v) With the aid of a labelled Boltzmann distribution diagram, explain how the addition of NaOH catalyst increases the rate of the reaction. [3]

(i) nucleophilic addition

(ii) NaOH provides the OH^- ions which is a stronger nucleophile for the nucleophilic attack on the carbonyl carbon.

(iii) $\text{OH}^- + \text{H}_2^{18}\text{O} \rightleftharpoons \text{H}_2\text{O} + ^{18}\text{OH}^-$

The OH^- will deprotonate H_2^{18}O to form the $^{18}\text{OH}^-$. $^{18}\text{OH}^-$ then attacks the propanal via nucleophilic addition reaction.

(iv) The carbonyl carbon in aldehyde is less sterically hindered than that in ketones, hence more easily attacked by the nucleophile.

OR

The carbonyl carbon in aldehyde is more electron deficient (δ^+) than that of ketones as ketones have an additional electron donating alkyl group.

[illegible]

(c) 2-hydroxybutanoic acid can also be formed from propanal in two steps.

(i) 2-hydroxybutanoic acid is a weak Brønsted acid.

Define the term *Brønsted acid*.

[1]

(ii) Draw the structure of the conjugate base of 2-hydroxybutanoic acid.

[1]

(iii) Explain whether 2-hydroxybutanoic acid has a larger or smaller K_a than butanoic acid.

[2]

2-hydroxybutanoic acid has a pK_a of 3.99.

A 20.0 cm³ sample of 2-hydroxybutanoic acid was titrated against a solution of 1 mol dm⁻³ of sodium hydroxide, using a suitable indicator. It was found that the colour change occurred when 17.20 cm³ of sodium hydroxide was added.

A sketch (not drawn to scale) of the pH titration curve is shown in Figure 4.1.

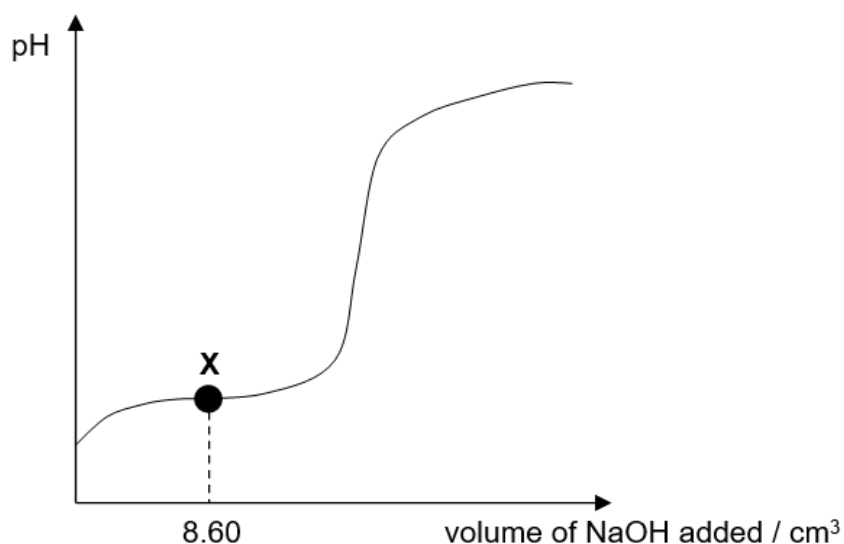


Figure 4.1

(iv) State the pH value at point X.

[1]

(v) State whether the value of the pH at equivalence point would be 7, smaller than 7 or larger than 7.

Write an equation to support your answer.

[2]

(vi) Calculate the concentration of 2-hydroxybutanoic acid in the sample.

[2]

[Total: 20]

(i) proton donor

(ii) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{COO}^-$

(iii) 2-hydroxyethanoic acid has a larger K_a as it is a stronger acid.



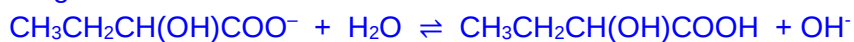
The electron-withdrawing $-\text{OH}$ group disperses the negative charge on the conjugate base of 2-hydroxybutanoic acid / 2-hydroxybutanoate ion hence stabilising the conjugate base/ 2-hydroxybutanoate ion. The equilibrium position of reaction (1) lies more to the right, producing more H^+ ions, resulting in 2-hydroxybutanoic acid being a stronger acid.

OR

Intramolecular hydrogen bond can be formed in the 2-hydroxybutanoate ion between the carboxylate ion and the H of the alcohol group hence stabilising the conjugate base/ 2-hydroxybutanoate ion. The equilibrium position of reaction (1) lies more to the right, producing more H^+ ions resulting in 2-hydroxybutanoic acid being a stronger acid.

(iv) 3.99

(v) Larger than 7



(vi) amount of $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{COOH}$ = amount of NaOH = 0.0172 mol

$$[\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{COOH}] = 0.0172 / 0.020 = 0.860 \text{ mol dm}^{-3}$$

- 5 Transition metal ions are often brightly coloured and can exist in a wide range of oxidation states. Vanadium was named after the Scandinavian goddess of beauty and fertility, Vanadis because of the wide range of colours found in vanadium compounds. The colours of the various vanadium ions are given in Table 5.1.

Vanadium Species	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
Colour	Yellow	Blue	Green	Violet

Table 5.1

- (a) V^{2+} ions are used in a redox titration to determine the concentration of Fe^{3+} ions in an unknown solution. Fe^{3+} can be reduced to Fe^{2+} and the solution is acidic throughout the entire process. The indicator used in the titration is potassium thiocyanate, KSCN. The thiocyanate ions, SCN^- , form an intense blood red complex ion with Fe^{3+} in solution while it appears colourless when complexed with Fe^{2+} . It was found that V^{2+} reacts in a 1 : 1 ratio with Fe^{3+} .
- (i) State the electronic configuration of V^{3+} ion and hence explain why a solution containing V^{3+} ions is coloured. [4]
- (ii) Write the oxidation and reduction half equations for the redox reaction.
Hence write the overall balanced equation. [2]
- (iii) State the colour change observed at the end point of the titration. [1]

(i) V^{3+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$

In the presence of water ligands, the 3d subshells of V are split into 2 groups of different energy levels.

d electrons in the lower energy level absorb a certain wavelength of light from the visible region of the electromagnetic spectrum and are promoted to the higher energy level.

The wavelengths that are not absorbed are then transmitted and hence the colour observed is the complement to the colour absorbed.

(ii) $\text{V}^{2+} \rightarrow \text{V}^{3+} + \text{e}^-$ and $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$;

Overall: $\text{V}^{2+} + \text{Fe}^{3+} \rightarrow \text{V}^{3+} + \text{Fe}^{2+}$;

(iii) Blood red (Fe^{3+} -SCN complex) to green (V^{3+} and Fe^{2+})

- In a particular experimental set-up, $^{51}\text{V}^{2+}$ ions are deflected through an angle of $+4.3^\circ$.

- of $^{56}\text{Fe}^{3+}$. [1]

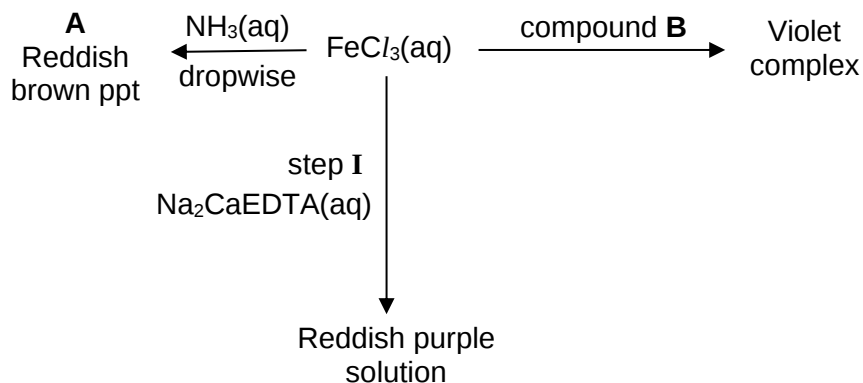
- -3.1° .

[1]

mass = 70.7 ;

[illegible]

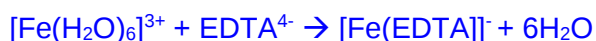
(c) The following scheme shows the reactions of iron and its compounds.



- (i) Identify compounds **A** and **B**. [2]
- (ii) State the type of reaction undergone in step **I** and write an ionic equation for the reaction taking place in step **I**. [2]
- (iii) Another iron-containing compound, FeCO_3 , undergoes thermal decomposition the same way as CaCO_3 .
Using relevant data from the *Data Booklet*, state and explain which compound, FeCO_3 or CaCO_3 , has higher thermal stability. [3]

(i) **A** – $\text{Fe}(\text{OH})_3$; **B** – phenol

(ii) ligand exchange



(iii) ionic radius of $\text{Fe}^{2+} = 0.061 \text{ nm}$

ionic radius of $\text{Ca}^{2+} = 0.099 \text{ nm}$;

Since Fe^{2+} has a smaller ionic radius, it will have higher charge density and able to distort the electron cloud of the carbonate ion to a larger extent, weakening the C-O bond. Hence FeCO_3 decomposes more easily. Therefore CaCO_3 has higher thermal stability.

.....

 (d) Calcium hydroxide is sparingly soluble in water and has a solubility product with a numerical value of 5.50×10^{-6} .

(i) Write an expression for the solubility product, K_{sp} , of calcium hydroxide and calculate the solubility of calcium hydroxide in water. [2]

(ii) A lab technician tried to precipitate Ca(OH)_2 by mixing $0.20 \text{ mol dm}^{-3} \text{ Ca}^{2+}(\text{aq})$ with equal volume of $0.20 \text{ mol dm}^{-3} \text{ NH}_3(\text{aq})$.

Show through calculation why precipitation of Ca(OH)_2 will not occur.

$[K_b \text{ of } \text{NH}_3 = 1.80 \times 10^{-5} \text{ mol dm}^{-3}]$

[2]

[Total: 20]

(i) $K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2$

Let the solubility be x

$$(x)(2x)^2 = 5.50 \times 10^{-6}$$

$$x = 0.0111 \text{ mol dm}^{-3}$$

(ii) new $[\text{Ca}^{2+}] = 0.20 \div 2 = 0.100 \text{ mol dm}^{-3}$

$$\text{new } [\text{NH}_3] = 0.20 \div 2 = 0.100 \text{ mol dm}^{-3}$$

$$[\text{OH}^-] \text{ after mixing} = (1.80 \times 10^{-5} \times 0.10)^{0.5} = 0.00134 \text{ mol dm}^{-3}$$

$$Q_{sp} = (0.100)(0.00134)^2 = 1.80 \times 10^{-7} \text{ mol}^3 \text{ dm}^{-9}$$

Since $Q_{sp} < K_{sp}$, no precipitation will take place.

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END OF PAPER
Additional answer space

If you use this page to complete the answer to any question, the question number must be clearly shown.

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