# ST ANDREW'S JUNIOR COLLEGE



## **JC2 Preliminary Examination**

H2 Chemistry (9729)

19 Sep 2019

### Paper 1 Multiple Choice

1 hour

Additional Materials: Multiple Choice Answer Sheet, Data Booklet

## **READ THESE INSTRUCTIONS:**

Write in soft pencil.

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

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer sheet.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

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

This document consists of **14** printed pages (including this page).

- 1 Which statement about one mole of sodium metal is always true?
  - **A** It has the same mass as one mole of  $^{12}$ C.
  - **B** It has the same number of atoms as 18 g of water.
  - **C** It has the same number of atoms as  $\frac{1}{12}$  mole of <sup>12</sup>C.
  - **D** It has the same number of atoms as 12 dm<sup>3</sup> of fluorine gas at r.t.p.
- 0.84 g of an oxide MO of a metal M was dissolved in excess sulfuric acid. 25.0 cm<sup>3</sup> of
   0.12 mol dm<sup>-3</sup> potassium manganate(VII) solution was required to oxidise M<sup>2+</sup> to M<sup>3+</sup>.

What is the relative atomic mass of M?

**A** 36.0 **B** 40.0 **C** 52.0 **D** 56.0

**3** X and Y are elements found in the first three periods of the Periodic Table. The outermost shell electronic configurations of two species are given as follows:



What can best be deduced from the above information?

- **A** X has a larger proton number than Y.
- **B** X has more unpaired electrons than Y at the ground state.
- **C** X exists as a gas while Y is a solid at standard condition.
- **D**  $X^{2-}$  and  $Y^{2+}$  are isoelectronic.

4 In an experiment, a sample of gaseous <sup>87</sup>Sr<sup>2+</sup> was passed through an electric field. The angle of deflection for <sup>87</sup>Sr<sup>2+</sup> was observed to be 2°.



The experiment was repeated with gaseous sample of particle **Q**. Which of following could be **Q**?

**A**  ${}^{74}As^{3-}$  **B**  ${}^{19}F^{-}$  **C**  ${}^{79}Se^{2-}$  **D**  ${}^{127}Te^{2-}$ 

**5** BeC $l_2$  reacts with CH<sub>3</sub>NH<sub>2</sub> to form compound **Z** ( $M_r$  = 142.0).

Which of the following statements are correct?

- 1 The hybridisation state of N in **Z** is sp<sup>3</sup>.
- 2 Hydrogen bonds exist between molecules of compound Z.
- 3 1 mol of compound **Z** is formed from 1 mol of BeC $l_2$  and 2 mol of CH<sub>3</sub>NH<sub>2</sub>.
- **A** 1, 2 and 3 **B** 1 and 2 only
- **C** 1 and 3 only **D** 3 only
- **6** Which of the following graphs correctly describes the variation of pV with temperature for a fixed amount of an ideal gas?



7 The conversion of graphite into diamond is an endothermic reaction.

 $C(graphite) \longrightarrow C(diamond)$ 

Which of the following statements are correct?

- 1 The carbon-carbon bonds in graphite are stronger than that in diamond.
- 2 The activation energy of the conversion of graphite to diamond is larger than that of the reverse reaction.
- 3 The enthalpy change of atomisation of diamond is less endothermic than that of graphite.
- 4 The enthalpy change of combustion of diamond is less exothermic than that of graphite.
- A 1 and 2 only B 1 and 3 only
- **C** 1, 2 and 3 only **D** 1, 2 and 4 only
- **8** Given the following enthalpy changes:

	$\Delta H$ / kJ mol <sup>-1</sup>
Enthalpy change of formation of $H_2S(g)$	-20.6
Enthalpy change of formation of $H_2O(l)$	-286.0
Enthalpy change of vaporisation of $H_2O(l)$	+40.7

What is the enthalpy change (in kJ mol<sup>-1</sup>) of reaction for the following reaction?

$$H_2S(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) + S(s)$$

**A** –224.7 **B** –265.4 **C** –306.6 **D** -347.3

- 9 Which equation corresponds to the enthalpy change stated?
  - $\begin{array}{ll} \textbf{A} & H_2 SO_4(aq) + 2 KOH(aq) \rightarrow K_2 SO_4(aq) + 2 H_2 O(l) & \Delta H^{\theta}_{\text{neutralisation}} \\ \textbf{B} & \text{Na}^+(s) + aq \rightarrow \text{Na}^+(aq) & \Delta H^{\theta}_{\text{hydration}}(\text{Na}^+) \\ \textbf{C} & A l_2 O_3(s) \rightarrow 2 A l^{3+}(g) + 3 O^{2-}(g) & \Delta H^{\theta}_{\text{lattice energy}}(A l_2 O_3) \\ \textbf{D} & O_2(g) \rightarrow 2 O(g) & 2 \Delta H^{\theta}_{\text{atomisation}}(O_2) \end{array}$

10 A chemical plant illegally dumped some radioactive waste in a landfill. This waste composed of two radioactive isotopes X and Y. The half-life of X is 4 days whereas that of Y is 2 days. The authorities found out about this illegal dumping only when the waste had been in the landfill for 8 days. They did an immediate analysis on a sample of the waste and found equal amounts of X and Y.

Considering that the decay of radioactive isotopes follows first-order kinetics, what is the initial molar ratio of **X** to **Y** if the waste had been in the landfill for 4 days?

- X
   :
   Y

   A
   1
   :
   2

   B
   1
   :
   4

   C
   2
   :
   1

   D
   4
   :
   1
- 11 Hydrogen reacts with nitrogen monoxide to form nitrogen and steam only. The rate equation for this reaction is rate =  $k[NO]^2[H_2]$ .

Which could be the mechanism for this reaction?

A slow NO + 2H<sub>2</sub>  $\rightarrow$  NH<sub>2</sub> + H<sub>2</sub>O NH<sub>2</sub> + NO  $\rightarrow$  N<sub>2</sub> + H<sub>2</sub>O

- **B**   $2NO \xrightarrow{slow} N_2 + O$  $2H_2 + O \rightarrow 2H_2O$
- $\begin{array}{c} \textbf{C} & \\ & \text{slow} \\ & 2\text{NO} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}_2 \end{array}$

 $N_2 + 2H_2 \rightarrow N_2H_4$ 

**D** slow  $2NO + H_2 \rightarrow N_2O + H_2O$  $N_2O + H_2 \rightarrow N_2 + H_2O$  **12** The table below shows the values of the ionic product of water,  $K_w$ , at two different temperatures.

Temperature / °C	$K_{\rm w}$ / mol <sup>2</sup> dm <sup>-6</sup>
25	$1.00 \times 10^{-14}$
60	$1.00 \times 10^{-13}$

Which of the following statements is correct for pure water?

- A The ionic dissociation of water is an exothermic process.
- **B** At 60 °C, the pH is less than 7.
- **C** At 60 °C, the pH is more than the pOH.
- **D** At 60 °C, the solution becomes more acidic.
- **13** The numerical value of the equilibrium constant,  $K_c$ , for the following reaction at 25°C is  $1.2 \times 10^5$ .

 $CO(g) + 2H_2(g) \implies CH_3OH(g) \qquad \Delta H^{\Theta} < 0$ 

Which statements about the reaction is correct?

- 1 The units for  $K_c$  is mol<sup>-1</sup>dm<sup>3</sup>.
- 2  $\Delta G^{\Theta}$  is less than zero.
- 3 The equilibrium position shifts when an inert gas is added at constant volume.
- A 1 and 3 only B 2 only
- **C** 2 and 3 only **D** 1, 2 and 3

14 The graph shows the change in pH when an alkali is gradually added to 25 cm<sup>3</sup> of an acid.



Which of the following statements about the titration is correct?

- **A** Acidic buffer is formed after the equivalence point.
- **B** Both phenolphthalein and methyl orange can be used as the indicator for this titration.
- **C** This is a titration between 0.10 mol dm<sup>-3</sup> of HC*l*(aq) and 0.10 mol dm<sup>-3</sup> of NH<sub>3</sub>(aq).
- **D** The maximum buffer capacity occurs when 12.5 cm<sup>3</sup> of alkali is added.
- 15 CaF<sub>2</sub> is a sparingly soluble salt and is added to a weakly acidic solution of HF. The pH of the solution is adjusted by adding NaOH. Which diagram shows how the solubility of CaF<sub>2</sub> will vary with the pH of the solution at constant temperature?



- 16 Why is ethanoic acid a stronger acid in liquid ammonia than in aqueous solution?
  - **A** Ammonium ethanoate is completely ionised in aqueous solution.
  - **B** Ammonium ethanoate is strongly acidic in aqueous solution.
  - **C** Ammonia is a stronger base than water.
  - **D** Liquid ammonia is more polar solvent than water.
- 17 Use of *Data Booklet* is relevant to this question.

The following circuit with a switch was set up as shown in the diagram:



Which electrode reactions will occur when the switch is closed?

	Anode reaction	Cathode reaction
Α	Silver dissolves preferentially	Hydrogen is evolved
В	Copper dissolves preferentially	Copper is precipitated
С	Silver dissolves preferentially	Copper is precipitated
D	Silver and copper both dissolve together	Hydrogen is evolved

**18** Some relevant redox half-equations are given below:

 $\begin{array}{ccc} \operatorname{Cr}_2\operatorname{O}_7^{2-} + 14\operatorname{H}^+ + 6\operatorname{e}^- \rightleftharpoons & 2\operatorname{Cr}^{3+} + 7\operatorname{H}_2\operatorname{O} & E^{\ominus} = +1.33 \ V \\ & & & & \\ \operatorname{S} + 2\operatorname{H}^+ + 2\operatorname{e}^- \rightleftharpoons & \operatorname{H}_2\operatorname{S} & & & \\ \end{array}$ 

Which of the following statements are true when hydrogen sulfide is bubbled into acidified aqueous sodium dichromate(VI)?

- 1 The solution turns orange to green.
- 2 White precipitate is observed.
- 3 The reaction has a positive entropy change.
- A 1 only B 1 and 2 only
- C 1, 2 and 3 D None of the statements are true

- **19** Elements **X**, **Y** and **Z** are in Period 3 of the Periodic Table.
  - The oxide of **X** gives an aqueous solution of pH less than pH 7.
  - The oxide of Y reacts with both strong acids and strong alkalis.
  - The oxide of **Z** gives an aqueous solution which is strongly alkaline.

What is the order of increasing atomic radius for these elements?

- **A** X < Y < Z
- **B** X < Z < Y
- $C \quad Y < Z < X$
- $D \quad Z < Y < X$
- **20** The graph below shows the variation in the boiling points for eight consecutive elements in the Periodic Table, all with atomic number between 10 and 20.



Which of the following statements is correct?

- A Element G does not conduct electricity.
- **B** Element **D** forms only one acidic oxide.
- C Element A and beryllium are in the same group
- D Element C forms a chloride which hydrolyses readily to give a strongly acidic solution.

21 A catalytic converter is part of the exhaust system in modern cars.



Which of the following statements are true concerning the reactions and processes in the catalytic converter?

- $1 \qquad CO_2 + NO \rightarrow CO + NO_2$
- $2 \qquad 2CO + 2NO \ \rightarrow 2CO_2 + N_2$

3 
$$C_xH_y + (2x + \frac{y}{2})NO \rightarrow xCO_2 + \frac{y}{2}H_2O + (x + \frac{y}{4})N_2$$

- 4 Platinum and rhodium catalyse the reactions
- A 1, 2, 3 and 4
   B 1 and 2 only
   C 2 and 3 only
   D 2, 3 and 4 only
- 22 Copper(II) sulfate solution reacted as shown in the scheme below.

$$\begin{array}{c|c} & \mathsf{NH}_3(\mathsf{aq}) & \mathsf{excess} \\ & \mathsf{NH}_3(\mathsf{aq}) & \mathsf{NH}_3(\mathsf{aq}) \\ & \mathsf{CuSO}_4_{(\mathsf{aq})} & \mathsf{J} & \mathsf{NH}_3(\mathsf{aq}) \\ & \mathsf{III} & \mathsf{III} \\ & \mathsf{SO}_2(\mathsf{g}) \\ & \mathsf{L} & \mathsf{SO}_2(\mathsf{g}) \\ & \mathsf{IV} & \mathsf{white solid} \end{array}$$

Which of the following statements are correct?

- 1 NH<sub>3</sub> functions as a ligand in reaction I.
- 2 The coordination number of complex L is 4.
- 3 The oxidation number of the Cu in **M** is +1.
- **A** 1, 2 and 3 **B** 1 and 2 only
- **C** 1 and 3 **D** 2 and 3 only

23 Limonene is an oil formed in the peel of citrus fruits.



When limonene reacts with excess bromine at room temperature in the dark, how many **more** chiral centers than limonene does the product molecule have?

A 2 B 3 C 4 D 5

24 The diagram below shows some laboratory apparatus.



heat

Which preparations could this apparatus be used for?

- A 1,2-dibromoethane from ethene and bromine
- B ethanal from ethanol, sodium dichromate(VI) and sulfuric acid
- **C** propanone from propan-1-ol, sodium manganate(VII) and sulfuric acid
- D butan-2-ol from butanone, lithium aluminum hydride in dry ether

**25** A prodrug is a molecule that can be converted into its active form in the body. An example is *Enalapril*, as shown below. The active form of *Enalapril* can be formed when enzymes in the body hydrolyse the esters found on the molecule.



Enalapril

Which of the following is not true about Enalapril?

- A Enalapril turns orange aqueous K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> green when heated in an acidic medium.
- **B** Enalapril does not react with 2,4–dinitrophenylhydrazine.
- **C** Enalapril reacts with two moles ethanoyl chloride.
- D The active form of *Enalapril* has the structure



**26** Compound V can be converted to compound W in three stages.



Compound V

Compound W

Which sequence of reagents and conditions can be used to carry out this conversion?

	Stage 1	Stage 2	Stage 3
Α	hot acidified KMnO₄	H <sub>2</sub> with Pt catalyst	heat with dilute H <sub>2</sub> SO <sub>4</sub>
В	hot acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	NaBH₄ in ethanol	heat with dilute H <sub>2</sub> SO <sub>4</sub>
С	hot Fehling's reagent, followed by acidification	NaBH₄ in ethanol	heat with a few drops of conc. H <sub>2</sub> SO <sub>4</sub>
D	hot Tollens' reagent, followed by acidification	LiA/H₄ in dry ether	heat with a few drops of conc. H <sub>2</sub> SO <sub>4</sub>

**27** Phenol has a  $pK_a$  of 10.0.

Which one of the following has a higher  $pK_a$  value than phenol?



**28** An acid anhydride is a carboxylic acid derivative that undergoes hydrolysis in water similar to acyl chlorides and esters. A mixture of carboxylic acids is produced in the case of the anhydride.



Based on the information above, which of the following can be deduced when maleic anhydride undergoes hydrolysis in the presence of water labelled with the <sup>18</sup>O isotope?



maleic anhydride

- **A** The resulting product is non-planar.
- **B** The product is labelled with the <sup>18</sup>O isotope.
- **C** Two carboxylic acid molecules are produced for every molecule of maleic anhydride.
- **D** The reaction is faster than when maleic anhydride undergoes hydrolysis in the presence of water labelled with the <sup>16</sup>O isotope.

- 29 Which of the following reactions will not form a racemic mixture of products?
  - Α CH<sub>3</sub>COCH<sub>3</sub> with HCN in trace amounts of NaOH
  - В CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COCH<sub>3</sub> with HCN in trace amounts of NaCN



In which reaction will the oxidation number of carbon change by 4? 30



- **A** 1, 2 and 3 B 2 only
- C 1 and 3 only D 1 only

### **End of Paper**

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- 1 Which statement about one mole of sodium metal is always true?
  - **A** It has the same mass as one mole of  $^{12}$ C.
  - **B** It has the same number of atoms as 18 g of water.
  - **C** It has the same number of atoms as  $\frac{1}{12}$  mole of <sup>12</sup>C.
  - **D** It has the same number of atoms as 12 dm<sup>3</sup> of fluorine gas at r.t.p.

#### Ans: D

2

 $12/24 = 0.5 \text{ mol of } F_2 = 1.0 \text{ mol of } F \text{ atoms} = 6.02 \text{ x } 10^{23} \text{ H atoms}$ 

0.84 g of an oxide MO of a metal M was dissolved in excess sulfuric acid. 25.0 cm<sup>3</sup> of

0.12 mol dm<sup>-3</sup> potassium manganate(VII) solution was required to oxidise M<sup>2+</sup> to M<sup>3+</sup>.

What is the relative atomic mass of M?

A 36.0 B 40.0 C 52.0 D 56.0 Ans: B Amt of  $MnO_4^- = 25/1000 \times 0.12 = 0.003 \text{ mol}$ Amt of e gained by  $MnO_4^- = Amt$  of e lost by  $M^{2+} = 5 \times 0.003 = 0.015 \text{ mol}$  $M_r$  of MO = 0.84/0.015 = 56  $A_r$  of M = 56-16 = 40

3 X and Y are elements found in the first three periods of the Periodic Table. The outermost shell electronic configurations of two species are given as follows:



What can best be deduced from the above information?

- **A** X has a larger proton number than Y.
- **B** X has more unpaired electrons than Y at the ground state.
- **C** X exists as a gas while Y is a solid at standard condition.
- **D**  $X^{2-}$  and  $Y^{2+}$  are isoelectronic.

#### Ans: B

Since X and Y are elements in the first three periods and their valence electronic configurations consist of s and p subshells, there are likely to be in period 2 or period 3.

**X** has the valence shell electronic configuration  $ns^2 np^4$  so it is a Group 16 element and it can be in Period 2 or Period 3. **X** can be O or S.

**Y** has the valence shell electronic configuration of  $(n+1)s^2$  and it should be in Period 3. **Y** can be Mg.

Option A: Since **Y** is Mg, X can have a smaller or larger proton than **Y**, depending on whether X is O or S

Option B: X would have 2 unpaired electrons while Y has no unpaired electrons.

Option C:  $\mathbf{X}$  can be oxygen which is a gas but it may also be sulfur which is a solid at standard condition.

Option D: If X is S, S<sup>2-</sup> is not isoelectronic with Mg<sup>2+</sup>.

4 In an experiment, a sample of gaseous <sup>87</sup>Sr<sup>2+</sup> was passed through an electric field. The angle of deflection for <sup>87</sup>Sr<sup>2+</sup> was observed to be 2°.



The experiment was repeated with gaseous sample of particle **Q**. Which of following could be **Q**?

**A**  ${}^{74}AS^{3-}$  **B**  ${}^{19}F^{-}$  **C**  ${}^{79}Se^{2-}$  **D**  ${}^{127}Te^{2-}$ Ans: D Angle of deflection = k(charge/mass)  $k = 2 \times 87/2 = 87$ Angle of deflection of  ${}^{74}AS^{3-} = 87(3/74) = 3.5^{\circ}$ Angle of deflection of  ${}^{19}F^{-} = 87(1/19) = 4.6^{\circ}$ Angle of deflection of Se<sup>-</sup> =  $87(2/79) = 2.2^{\circ}$ Angle of deflection of Te<sup>2-</sup> =  $87(2/127) = 1.4^{\circ}$ 

**5** BeC $l_2$  reacts with CH<sub>3</sub>NH<sub>2</sub> to form compound **Z** ( $M_r$  = 142.0).

Which of the following statements are correct?

- 1 The hybridisation state of N in **Z** is sp<sup>3</sup>.
- 2 Hydrogen bonds exist between molecules of compound **Z**.
- 1 mol of compound **Z** is formed from 1 mol of  $BeCl_2$  and 2 mol of  $CH_3NH_2$ .

Α	1, 2 and 3	В	1 and 2 only

**C** 1 and 3 only **D** 3 only

Ans: C

$$\begin{array}{cccc} Cl & H & Cl & H \\ | & & \\ Be & + & 2 & CH_3 \overrightarrow{NH}_2 & \longrightarrow & CH_3 - \overrightarrow{N} \rightarrow Be & \longrightarrow N - CH_3 \\ | & & & & | & & | \\ Cl & & & H & Cl & H \end{array}$$

Option 1 is correct as N has a sp<sup>3</sup> hybridisation state and hence tetrahedral shape around N in compound Z.

Option 2 is wrong since there is no lone pair on the N after bonded to Be, hence between the molecules, H-bond no longer exist.

Option 3 is correct as Be in  $BeCl_2$  has only 4 electrons and it can accommodate another 4 electrons to react octet configuration.

6

Which of the following graphs correctly describes the variation of pV with temperature for a fixed amount of an ideal gas?



### Ans: A

pV = nRT. For an ideal gas, pV  $\alpha$  T, hence straight line. But since the scale is in °C, pV = 0 only when T = -273 °C.

7 The conversion of graphite into diamond is an endothermic reaction.

 $C(graphite) \longrightarrow C(diamond)$ 

Which of the following statements are correct?

- 1 The carbon-carbon bonds in graphite are stronger than that in diamond.
- 2 The activation energy of the conversion of graphite to diamond is larger than that of the reverse reaction.
- 3 The enthalpy change of atomisation of diamond is less endothermic than that of graphite.
- 4 The enthalpy change of combustion of diamond is less exothermic than that of graphite.

Α	1	and	2	only	
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**C** 1, 2 and 3 only

**D** 1, 2 and 4 only

1 and 3 only

#### Ans: C

Option 1 is correct. Since  $\Delta H > 0$ , C-C bond energy in graphite is higher than the C-C bond energy in diamond.

Option 2 is correct. Since  $\Delta H > 0$ , the E<sub>a</sub> of forward reaction is larger than that of backward reaction.



Option 3 is correct.  $\Delta H_{\text{atom}} of$  diamond is less endothermic than that of graphite

Option 4 is incorrect:  $\Delta H_c$  of diamond is more exothermic than that of graphite

8	Given the	following	enthalpy	changes:
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	$\Delta H / \text{kJ mol}^{-1}$
Enthalpy change of formation of H <sub>2</sub> S(g)	-20.6
Enthalpy change of formation of $H_2O(l)$	-286.0
Enthalpy change of vaporisation of $H_2O(l)$	+40.7

What is the enthalpy change (in kJ mol<sup>-1</sup>) of reaction for the following reaction?

$$H_2S(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) + S(s)$$

A -224.7 B -265.4 C -306.6 D -347.3 Ans: A  $H_2S(g) + \frac{\Delta H_r}{2O_2(g)} \rightarrow H_2O(g) + S(s)$  +40.7  $H_2O(l) + S(s)$  -20.6 $H_2(g) + S(s) + \frac{2}{2O_2(g)}$ 

 $\Delta H_r = -286 + 40.7 + 20.6 = -224.7$ 

В

9 Which equation corresponds to the enthalpy change stated?

Α	$H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$	$\Delta H^{\theta}_{neutralisation}$
В	$Na^{+}(s) + aq \rightarrow Na^{+}(aq)$	$\Delta H^{\theta}_{hydration}(Na^{+})$
С	$Al_2O_3(s) \rightarrow 2Al^{3+}(g) + 3O^{2-}(g)$	$\Delta H^{\theta}_{lattice\ energy}(Al_2O_3)$
D Ans	$O_2(g) \rightarrow 2O(g)$ s: D	$2 \Delta H^{\theta}_{atomisation}(O_2)$
Op	tion A: $H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$ 2 $\Delta H_2O(l)$	Η <sup>θ</sup> neutralisation
Op	tion B: Na <sup>+</sup> (g) + aq $\rightarrow$ Na <sup>+</sup> (aq) $\Delta H^{\theta}_{hydration}(Na^{+})$	
~		

Option C:  $2Al^{3+}(g) + 3O^{2-}(g) \rightarrow Al_2O_3(s) \Delta H^{\Theta}_{lattice energy}(Al_2O_3)$ 

10 A chemical plant illegally dumped some radioactive waste in a landfill. This waste composed of two radioactive isotopes X and Y. The half-life of X is 4 days whereas that of Y is 2 days. The authorities found out about this illegal dumping only when the waste had been in the landfill for 8 days. They did an immediate analysis on a sample of the waste and found equal amounts of X and Y.

Considering that the decay of radioactive isotopes follows first-order kinetics, what is the initial molar ratio of **X** to **Y** if the waste had been in the landfill for 4 days?

 X
 :
 Y

 A
 1
 :
 2

 B
 1
 :
 4

 C
 2
 :
 1

 D
 4
 :
 1

Ans: A

Day	0	1	2	3	4	5	6	7	8
Х	4x				<b>2x</b>				X
Υ	16x		8x		<b>4x</b>		2x		X

X:Y = 2x: 4x = 1x: 2x = 1:2

11 Hydrogen reacts with nitrogen monoxide to form nitrogen and steam only. The rate equation for this reaction is rate =  $k[NO]^2[H_2]$ .

Which could be the mechanism for this reaction?

A slow NO + 2H<sub>2</sub>  $\rightarrow$  NH<sub>2</sub> + H<sub>2</sub>O NH<sub>2</sub> + NO  $\rightarrow$  N<sub>2</sub> + H<sub>2</sub>O  $\begin{array}{ccc} \textbf{B} & & & \\ & 2\text{NO} & \xrightarrow{\text{slow}} & \text{N}_2 + \text{O} \\ & & 2\text{H}_2 + \text{O} & \xrightarrow{} & 2\text{H}_2\text{O} \end{array}$ 

 $\label{eq:slow} \begin{array}{c} \text{slow} \\ 2\text{NO} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}_2 \end{array}$ 

 $N_2 \textbf{+} 2H_2 \rightarrow N_2H_4$ 

 $\begin{array}{c} \textbf{D} & \\ & \text{slow} \\ & 2\text{NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \end{array}$ 

 $\begin{array}{c} N_2O + H_2 \rightarrow N_2 + H_2O \\ \mbox{Ans: } D \end{array}$ 

 $2NO + H_2 \rightarrow N_2O + H_2O$ 

 $\begin{array}{c} N_2O + H_2 \rightarrow N_2 + H_2O \\ Overall: \ 2NO + 2H_2 \rightarrow N_2 + 2H_2O \\ Rate: \ k \ [NO]^2[H_2] \end{array}$ 

Option A is wrong since Rate =  $k [NO][H_2]^2$ Option B is wrong since rate=  $k[NO]^2$ Option C is wrong since the products formed are N<sub>2</sub>H<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> instead.

**12** The table below shows the values of the ionic product of water,  $K_w$ , at two different temperatures.

Temperature / °C	<i>K</i> <sub>w</sub> / mol <sup>2</sup> dm <sup>-6</sup>
25	$1.00 \times 10^{-14}$
60	$1.00 \times 10^{-13}$

Which of the following statements is correct for pure water?

- **A** The ionic dissociation of water is an exothermic process.
- **B** At 60  $^{\circ}$ C, the pH is less than 7.
- C At 60 °C, the pH is more than the pOH.
- **D** At 60 °C, the solution becomes more acidic.

Ans: B

As  $K_w$  increases with increasing temperature, the rate constant of forward reaction increases more than the rate constant of the backward reaction, hence the forward reaction is endothermic and not exothermic. Option A is wrong.

```
pK_w at 60°C = -log K_w = 13
Hence, pH + pOH = 13, hence pH = 6.5
Option B is correct.
```

**13** The numerical value of the equilibrium constant,  $K_c$ , for the following reaction at 25°C is  $1.2 \times 10^5$ .

 $CO(g) + 2H_2(g) \iff CH_3OH(g) \qquad \Delta H^{\Theta} < 0$ 

Which statements about the reaction is correct?

- 1 The units for  $K_c$  is mol<sup>-1</sup>dm<sup>3</sup>.
- 2  $\Delta G^{\Theta}$  is less than zero.
- 3 The equilibrium position shifts when an inert gas is added at constant volume.
- A 1 and 3 only B 2 only

**C** 2 and 3 only

**D** 1, 2 and 3

Ans: B

Option 1 is wrong since the units is mol<sup>-2</sup>dm<sup>6</sup>. Option 2 is correct.  $K_c >>1$ , hence  $\Delta G^{\Theta} < 0$  (Correct)

Or  $\Delta G^{\Theta} = -RTlnK = -(8.31)(298)ln(1.2X10^5) = -29 kJ mol^{-1}$ .

Option 3 is wrong. At constant volume, the addition of an inert gas DOES NOT AFFECT the partial pressure of the reacting gases, even though the total pressure increases. Hence there is NO shift of the equilibrium position.

14 The graph shows the change in pH when an alkali is gradually added to 25 cm<sup>3</sup> of an acid.



Which of the following statements about the titration is correct?

- **A** Acidic buffer is formed after the equivalence point.
- **B** Both phenolphthalein and methyl orange can be used as the indicator for this titration.
- **C** This is a titration between 0.10 mol dm<sup>-3</sup> of HC*l*(aq) and 0.10 mol dm<sup>-3</sup> of NH<sub>3</sub>(aq).
- **D** The maximum buffer capacity occurs when 12.5 cm<sup>3</sup> of alkali is added.

Ans: C

Option A: Basic buffer occurs after the equivalence point.

Option B: Only methyl orange is suitable for a strong acid- weak base titration.

Option C: Strong acid-weak base titration leads to an acidic salt. pH of equivalence point is less than 7. (Correct)

Option D: Since this is a SA-WB titration, MBC occurs at 2V<sub>equilvalence</sub> instead of ½V<sub>equivalence</sub>.

15 CaF<sub>2</sub> is a sparingly soluble salt and is added to a weakly acidic solution of HF. The pH of the solution is adjusted by adding NaOH. Which diagram shows how the solubility of CaF<sub>2</sub> will vary with the pH of the solution at constant temperature?



Ans: D

 $CaF_2 (s) \rightleftharpoons Ca^{2+} (aq) + 2F^{-}(aq) ----Eqm 1$ HF (aq)  $\rightleftharpoons$  H<sup>+</sup> (aq) + F<sup>-</sup>(aq) ---- Eqm 2 When pH is very high, the H<sup>+</sup> is neutralised by the OH<sup>-</sup>, hence eqm 2 is shifted to RHS to produced more F<sup>-</sup>. This will cause the POE of Eqm 1 to shift to LHS, reducing the solubility of CaF<sub>2</sub> (s).

- 16 Why is ethanoic acid a stronger acid in liquid ammonia than in aqueous solution?
  - A Ammonium ethanoate is completely ionised in aqueous solution.
  - **B** Ammonium ethanoate is strongly acidic in aqueous solution.
  - **C** Ammonia is a stronger base than water.
  - **D** Liquid ammonia is more polar solvent than water.

#### Ans: C

A more basic solvent is able to extract the H<sup>+</sup> more readily and therefore increase the strength of the acid.

17 Use of *Data Booklet* is relevant to this question.

The following circuit with a switch was set up as shown in the diagram:



Which electrode reactions will occur when the switch is closed?

	Anode reaction	Cathode reaction
Α	Silver dissolves preferentially	Hydrogen is evolved
В	Copper dissolves preferentially	Copper is precipitated

- C Silver dissolves preferentially Copper is precipitated
- D Silver and copper both dissolve together Hydrogen is evolved

Ans : B

Cu has a more negative  $E^{\circ}$  value than Ag would oxidise preferentially to form  $Cu^{2+}$ ; Cu<sup>2+</sup> has a more positive  $E^{\circ}$  value than H<sub>2</sub>O, would be preferentially reduced to form Cu.

**18** Some relevant redox half-equations are given below:

 $\begin{array}{cccc} Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons & 2Cr^{3+} + 7H_2O & E^{\ominus} = +1.33 \ V \\ S + 2H^+ + 2e^- \rightleftharpoons & H_2S & E^{\ominus} = +0.14 \ V \end{array}$ 

Which of the following statements are true when hydrogen sulfide is bubbled into acidified aqueous sodium dichromate(VI)?

1 The solution turns orange to green.

- 2 White precipitate is observed.
- 3 The reaction has a positive entropy change.
- A 1 only B 1 and 2 only
- C 1, 2 and 3 D None of the statements are true

Ans: A

 $E^{\ominus}_{\text{cell}} = +1.33 - (+0.14) = +1.19 \text{ V}$ 

Since  $E^{\Theta}_{cell} > 0$  V, the reaction between acidified aqueous sodium dichromate(VI) and hydrogen sulfide is thermodynamically feasible. Option 1 is correct

Option 2 is wrong since S appears as yellow solid.

Option 3 is wrong since there is a decrease in number of gas molecules and hence entropy change should be negative.

- **19** Elements **X**, **Y** and **Z** are in Period 3 of the Periodic Table.
  - The oxide of **X** gives an aqueous solution of pH less than pH 7.
  - The oxide of **Y** reacts with both strong acids and strong alkalis.
  - The oxide of **Z** gives an aqueous solution which is strongly alkaline.

What is the order of increasing atomic radius for these elements?

```
A X < Y < Z
```

Ans: A

X could be phosphorus(0.110)/sulfur(0.104)

Y is aluminum (0.143nm)

Z is sodium (0.186 nm)

**20** The graph below shows the variation in the boiling points for eight consecutive elements in the Periodic Table, all with atomic number between 10 and 20.



Which of the following statements is correct?

- A Element G does not conduct electricity.
- **B** Element **D** forms only one acidic oxide.
- C Element A and beryllium are in the same group
- $\label{eq:D} \textbf{D} \quad \text{Element } \textbf{C} \text{ forms a chloride which hydrolyse readily to give a strongly acidic solution.}$

#### Ans : D

Option A: Element G is potassium, it can conduct electricity.

Option B: Element D is sulfur, it forms more than one acidic oxide (SO<sub>2</sub>, SO<sub>3</sub>).

Option C: Element A is aluminium, it is in Group 13.

Option D: Element C is phosphorus, its chloride hydrolyse completely to give HCl and  $H_3PO_4$ .

21 A catalytic converter is part of the exhaust system in modern cars.



Which of the following statements are true concerning the reactions and processes in the catalytic converter?

- $1 \qquad CO_2 + NO \rightarrow CO + NO_2$
- $2 \qquad 2CO + 2NO \ \rightarrow 2CO_2 + N_2$
- 3  $C_xH_y + (2x + \frac{y}{2})NO \rightarrow xCO_2 + \frac{y}{2}H_2O + (x + \frac{y}{4})N_2$
- 4 Platinum and rhodium catalyse the reactions
- **A** 1, 2, 3 and 4

- **B** 1 and 2 only
- **C** 2 and 3 only **D** 2, 3 and 4 only

Ans: D

Option 1 is wrong as CO and  $NO_2$  are pollutants.

22 Copper(II) sulfate solution reacted as shown in the scheme below.

$$\begin{array}{c} \mathsf{NH}_{3}(\mathsf{aq}) & \overset{\mathsf{excess}}{\underset{I}{\overset{\mathsf{NH}_{3}}(\mathsf{aq})}{\overset{\mathsf{NH}_{3}}(\mathsf{aq})} \\ \mathsf{CuSO}_{4}_{(\mathsf{aq})} & \overset{\mathsf{III}}{\overset{\mathsf{III}}{\overset{\mathsf{NH}_{3}}} & \mathsf{J} & \overset{\mathsf{MH}_{3}(\mathsf{aq})}{\overset{\mathsf{III}}{\overset{\mathsf{NH}_{3}}} & \mathsf{K} \\ \mathsf{conc.} & \mathsf{HC}/ & \overset{\mathsf{III}}{\overset{\mathsf{III}}{\overset{\mathsf{NH}_{3}}} & \overset{\mathsf{SO}_{2}(\mathsf{g})}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}} & \overset{\mathsf{H}_{3}(\mathsf{aq})}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}} \\ \mathsf{L} & \overset{\mathsf{SO}_{2}(\mathsf{g})}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}}} & \overset{\mathsf{R}_{3}(\mathsf{aq})}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}}} \\ \mathsf{L} & \overset{\mathsf{SO}_{2}(\mathsf{g})}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}}{\overset{\mathsf{NH}_{3}}}}}}}}}}}}}$$

Which of the following statements are correct?

- 1  $NH_3$  functions as a ligand in reaction I.
- 2 The coordination number of complex L is 4.
- 3 The oxidation number of Cu in **M** is +1.
- **A** 1, 2 and 3 **B** 1 and 2 only
- **C** 1 and 3 **D** 2 and 3 only

Ans: D

Option 1 is incorrect as NH<sub>3</sub> acts as a base.

Option 2 is correct as metal complex in **L**  $[CuCl_4]^{2-}$ , coordination number 4.

Option 3 is correct.

 $2[CuCl_4]^{2-} + SO_2 + H_2O \rightarrow CuCl(s) + 6Cl + SO_4^{2-} + 4H^+$ 

White solid is CuCl.

23 Limonene is an oil formed in the peel of citrus fruits.



Limonene

When limonene reacts with excess bromine at room temperature in the dark, how many **more** chiral centers than limonene does the product molecule have?





24 The diagram below shows some laboratory apparatus.



Which preparations could this apparatus be used for?

- A 1,2-dibromoethane from ethene and bromine
- B ethanal from ethanol, sodium dichromate(VI) and sulfuric acid
- C propanone from propan-1-ol, sodium manganate(VII) and sulfuric acid
- D butan-2-ol from butanone, lithium aluminum hydride in dry ether

#### Ans : B

Option A is wrong since ethene is a gas, could not be prepared by heating under reflux. Option B is correct ethanal could be prepared by heating under reflux with ethanol followed by distillation of ethanal which has a lower boiling point than ethanol. Option C is wrong since propanone should be prepared from propan-2-ol instead of propan-1-ol,

Option D is wrong since butan-2-ol has a higher boiling point than butanone and would not be distill out first.

**25** A prodrug is a molecule that can be converted into its active form in the body. An example is *Enalapril*, as shown below. The active form of *Enalapril* can be formed when enzymes in the body hydrolyse the esters found on the molecule.



Which of the following is **not** true about *Enalapril*?

- A Enalapril turns orange aqueous  $K_2Cr_2O_7$  green when heated in an acidic medium.
- **B** Enalapril does not react with 2,4–dinitrophenylhydrazine.
- **C** Enalapril reacts with two moles ethanoyl chloride.
- **D** The active form of *Enalapril* has the structure



#### Ans: C

Option A: The ester in Enalapril can be hydrolysed when heated with acid and ethanol formed will be oxidised to ethanoic acid by  $K_2Cr_2O_7$ 

Option B: No carbonyl group present.

Option C: There is only one amine group present hence it requires only 1 mol of ethanoyl chloride to react with to form amide.

Option D: The active form of *Enalapril* can be formed when enzymes in the body hydrolyse esters to form the above structure.

26 Compound V can be converted to compound W in three stages.



Compound V

Compound W

Which sequence of reagents and conditions can be used to carry out this conversion?

	Stage 1	Stage 2	Stage 3
Α	hot acidified KMnO <sub>4</sub>	H <sub>2</sub> with Pt catalyst	heat with dilute
			H <sub>2</sub> SO <sub>4</sub>
В	hot acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	NaBH₄ in ethanol	heat with dilute
			$H_2SO_4$

С	hot Fehling's reagent, followed	NaBH₄ in ethanol	heat with a few drops
	by acidification		of conc. $H_2SO_4$
D	hot Tollens' reagent, followed by	LiA/H₄ in dry ether	heat with a few drops
	acidification		of conc. H <sub>2</sub> SO <sub>4</sub>

Ans: C



Note that KMnO<sub>4</sub> cannot be used in stage as it will oxidise alkene. LiAIH<sub>4</sub> will reduce carboxylic acid as well hence it cannot be used in stage 2. H<sub>2</sub>SO<sub>4</sub> must be in conc form for the ester to form.

**27** Phenol has a  $pK_a$  of 10.0.

Which one of the following has a higher  $pK_a$  value than phenol?



Ans: C

Higher  $pK_a$  implies less acidic than phenol and C is has an electron-donating  $-CH_3$  group and hence the negative charge on O of the phenoxide conjugate base would be dispersed to a lesser extent.

The conjugate base is less stable, hence compound C is less acidic than phenol.

**28** An acid anhydride is a carboxylic acid derivative that undergoes hydrolysis in water similar to acyl chlorides and esters. A mixture of carboxylic acids is produced in the case of the anhydride.



Based on the information above, which of the following can be deduced when maleic anhydride undergoes hydrolysis in the presence of water labelled with the <sup>18</sup>O isotope?



maleic anhydride

- A The resulting product is non-planar.
- **B** The product is labelled with the <sup>18</sup>O isotope.
- **C** Two carboxylic acid molecules are produced for every molecule of maleic anhydride.

**D** The reaction is faster than when maleic anhydride undergoes hydrolysis in the presence of water labelled with the <sup>16</sup>O isotope.

#### Ans: B

Option B: One <sup>18</sup>O atom from heavy water is inserted into every product molecule of maleic anhydride hydrolysis.



Option C is wrong since a single dicarboxylic acid molecule is produced for every molecule of maleic anhydride hydrolysed.

Option A is wrong as the resulting product is planar since the C are all sp<sup>2</sup> hybridised.

Option D: not enough information is given to deduce that.

- 29 Which of the following reactions will **not** form a racemic mixture of products?
  - A CH<sub>3</sub>COCH<sub>3</sub> with HCN in trace amounts of NaOH
  - B CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COCH<sub>3</sub> with HCN in trace amounts of NaCN

C  $CH_3$   $CH_3CH_2CH_2$   $CH_2$  Cl with KOH(aq), heat under reflux  $CH_3CH_2CH_2$ 

 $\begin{array}{c} \mathsf{C}\mathsf{H}_3 \ \mathsf{H} \\ | \ | \\ \mathsf{C}\mathsf{H}_3\mathsf{C}\mathsf{H}_2\mathsf{C}\mathsf{H}_2 \\ -\mathsf{C} \\ -\mathsf{C} \\ -\mathsf{C} \\ -\mathsf{C} \\ -\mathsf{C}\mathsf{H}_3 \end{array} \text{ with } \mathsf{H}\mathsf{Br}(\mathsf{g}) \\ \end{array}$ 

Ans: A

Option A: Product formed does not have chiral carbon.

Option B: Nucleophile can attack the trigonal planar carbonyl carbon from either side.

Option C: S<sub>N</sub>1 reaction so a trigonal planar intermediate formed as it is a 3° alkyl halide

Option D: Carbocation intermediate is trigonal planar so Br-can attack from the top or front

30 In which reaction will the oxidation number of carbon change by 4?



- **A** 1, 2 and 3 **B** 2 only
- **C** 1 and 3 only **D** 1 only

Ans: A



**End of Paper** 

NAME

Class

# **ST ANDREW'S JUNIOR COLLEGE**



# **JC2 PRELIMINARY EXAMINATIONS**

Chemistry (9729)

30 August 2019

### **Paper 2 Structured Questions**

2 hours

Additional Materials: Data Booklet

## **READ THESE INSTRUCTIONS:**

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.

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.

### For Examiner's use:

Question	1	2	3	4	5	Total
Marks	9	8	20	25	13	75

This document consists of **20** printed pages (including this page).

1. (a) P, Q, R and S are consecutive elements in Period 4.

Element	1 <sup>st</sup> I.E.	2 <sup>nd</sup> I.E.	3 <sup>rd</sup> I.E.	4 <sup>th</sup> I.E.	5 <sup>th</sup> I.E.
Р	908	1730	3828	5980	7970
Q	577	1980	2960	6190	8284
R	762	1540	3300	4390	9020
S	947	1798	2735	4837	6043

The table below shows the first four ionisation energies (in kJ mol<sup>-1</sup>) of the elements.

(i) Explain why the second ionisation energy of **Q** is higher than that of **R**. [2]



(ii) Explain why P is not considered to be a transition metal like most of the d-block metals.

.....

- (b) The idea of covalent bonding was first described in 1916 by an American physical chemist Gilbert Newton Lewis. HCOC*l* is an example of a polar covalent molecule.
  - (i) Explain what is *covalent bonding*.

[1]

.....

**1.** (b) (ii) State what is meant by the term *polar* when applied to a covalent bond.

.....

(iii) State and explain with reference to the Valence Shell Electron Pair Repulsion theory, the shape of HCOC*l* molecule.
 [2]

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- (iv) The molecule of HCOC*l* contains both  $\sigma$  (sigma) and  $\pi$  (pi) bonds. Draw labelled diagrams to show how orbitals overlap to form
  - a σ (sigma) bond

• a π (pi) bond

[2]

[1]

[Total:9]
2 Below is a labelled diagram of a hydrogen-oxygen fuel cell in an alkaline electrolyte.



(i) Write the half equations for both electrodes and hence the overall equation. [2]



(ii) Calculate  $\Delta G^{\circ}$  for the above reaction and state whether it is spontaneous. [3]

2. (a) (iii) The hydrogen-oxygen fuel cell produces 1.5 A of current. Hydrogen gas is contained in a 1 dm<sup>3</sup> tank at a pressure and temperature of 200 atm and 20 °C respectively. Determine the number of days the fuel cell can operate before the hydrogen gas runs out. Give your answer to the nearest whole number. You may assume there is an unlimited supply of O<sub>2</sub>.

## [Total:8]

 Spider silk is a protein fiber. Major amino acids in the silk proteins are alanine and glycine. Serine and glutamine are also present in significant quantities in some types of silk. The table below shows the typical amino acids present in spider silk.

Amino Acid	Formula of side chain	
	(R in RCH(NH <sub>2</sub> )CO <sub>2</sub> H)	
Glycine	_H	
Alanine	-CH <sub>3</sub>	
Serine	-CH <sub>2</sub> OH	
Glutamine	$-CH_2CH_2CONH_2$	

(a) (i) Glycine exists as crystalline solids. Draw the zwitterionic structure of glycine and account for the high melting point of glycine. [2]

------

**3. (a) (ii)** Write an equation to show the reaction between alanine and aqueous sodium carbonate.

[1]

(iii) Suggest a chemical test to distinguish between serine and glutamine. [2]

.....

(b) Natural spider silk has excellent mechanical properties. In a recent study, researchers discovered that graphene-based materials can be used to boost the properties of spider's silk up to three times the strength and ten times the toughness of the unmodified silks.

Graphene is the thinnest material known to exist, yet it is stronger than steel. It is made from only carbon and is a single layer of graphite just one atom thick as shown in Figure **3.1** below.



Figure 3.1

3. (b) (i) With reference to structure and bonding, explain why graphene is strong. [1]

------

(ii) Since its discovery in 2004, graphene has been widely studied and [1] manufactured as replacement materials for many touchscreen products. Suggest why graphene is a suitable touchscreen material in mobile phones.

.....

(c) Spider makes an excellent treat for a colony of marauding ants. To protect their homes, spiders coat their webs using a chemical called 2-pyrrolidone, which acts as a deterrent to many insects.

2-Pyrrolidone is a 5-membered cyclic amide (commonly known as lactam). It is a colourless liquid that is miscible with water and most common organic solvents.

ΝH

2-Pyrrolidone

**3.** (c) 2-pyrrolidone can be synthesised using 3-chloropropan-1-ol as the starting organic compound as shown in the reaction scheme below:



Α	В

3. (c) (iv) With the aid of an equation, explain why anhydrous condition is necessary [1] for the reaction in Step IV.



1,3-butandiol

[Total:20]

4 (a) Copper and iron are examples of native metals, which are found pure in its metallic form on its own or in alloys in nature.

Copper and iron form many complexes with a range of colours as shown in the table:

complex	colour	complex	colour
[Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>	dark blue	[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	yellow
[Cu(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	blue	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	red

(i) Explain why [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> is blue. [3]
(ii) The oxidation state of iron in both [Fe(CN)<sub>6</sub>]<sup>3-</sup> and [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> complexes is the same. However, they have different colours. Explain this observation. [1]

.....

- 4. (a) (iii) Draw fully labelled diagrams of the following:
  - One of the d-orbitals at the lower energy level in [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>. Label the diagram "lower".
  - One of the d-orbtials at the upper energy level in [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>. Label this diagram "upper". [2]

(b) Use of the Data Booklet is relevant to this question.

Fe<sup>2+</sup> is commonly used to catalyse the reaction between S<sub>2</sub>O<sub>8</sub><sup>2-</sup>and I<sup>-</sup>. In another similar reaction, peroxodisulfate(VI), S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, reacts with tartrate ion,  $[CH(OH)CO_2]_2^{2^2}$ , to give carbon dioxide and methanoate as shown in the following equation.

 $[CH(OH)CO_2]_2^{2^-} + 3S_2O_8^{2^-} + 2H_2O \rightarrow 2CO_2 + 2HCO_2^- + 6H^+ + 6SO_4^{2^-}$ The reaction is very slow, even when heated, hence a catalyst is used to speed up the reaction.

(i) Explain why the reaction is slow. [1]

4. (b) (ii) Given that the standard electrode potential for the following half-equation is

 $2CO_2 + 2HCO_2^- + 6H^+ + 6e^- = [CH(OH)CO_2]_2^{2-} + 2H_2O$   $E^{\theta} = + 0.56 \text{ V}$ Using suitable equations, explain why Mn<sup>2+</sup> is a suitable catalyst for this [2] reaction.

(iii) State the property of transition metal ions that enable them to function as a homogenous catalyst in the reaction. [1]

4. (c) Palladium is a transition element that is used as a catalyst in the Cassar reaction. The Cassar reaction is a type of substitution reaction between an alkyl chloride and a terminal alkene in the presence of a base and a palladium catalyst.



[R can be a substituted alkyl group containing –OH, –NH<sub>2</sub>, –NO<sub>2</sub>, –COOH]

The following scheme shows the synthesis of D using Cassar reaction in one of the steps.

$$\mathbf{A} + \mathbf{B} \xrightarrow{\text{Cassar reaction}} \mathbf{C} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7(\text{aq}), \text{ H}_2\text{SO}_4(\text{aq}), \text{ heat}} \mathbf{D}$$

The table below shows the observations when **A**, **B** and **D** react with various reagents.

reaction		observations
1	<b>A</b> + HC <i>l</i> (aq)	colourless solution
2	<b>B</b> + Br <sub>2</sub> (aq)	colourless solution
3	<b>D</b> + Na <sub>2</sub> CO <sub>3</sub> (aq)	Gas forms white ppt with
		Ca(OH) <sub>2</sub>

(i) Name the functional group that reaction 1 shows to be present in A

\_\_\_\_\_

[1]

[1]

(ii) State the type of reaction that takes place in reaction 2 and name the functional group present in B

.....

C is able to exhibit cis-trans isomerism. Draw the structures of A, B, C and (iii) D. [4] Α В

D

С

**4.** (c) (iv) Draw the structure of the product when  $CH_3CH(CH_2Cl)CH_2CH_2CH=CH_2$  undergoes the Cassar reaction.

(d) A solution containing  $Cu^{2+}$  and  $Zn^{2+}$  can be separated by selective precipitation.

The reagent used is hydrogen sulfide which behaves as a dibasic (diprotic) weak acid when in aqueous solution.

Aqueous hydrogen sulfide behaves as a dibasic acid.

 $H_2S$  (aq)  $\implies$   $H^+$  (aq) +  $HS^-$  (aq)  $K_{a1} = 8.9 \times 10^{-8} \text{ mol dm}^{-3}$ 

 $HS^{-}(aq) \longrightarrow H^{+}(aq) + S^{2-}(aq)$   $K_{a2} = 1.2 \times 10^{-13} \text{ mol dm}^{-3}$ 

Metal sulfides are precipitated by the following reaction.

 $M^{2+}(aq) + S^{2-}(aq) \iff MS(s)$ 

Relevant  $K_{sp}$  values are given in the table below.

Salt	$K_{ m sp}$ / mol <sup>2</sup> dm <sup>-6</sup>
CuS	6.3 × 10 <sup>−36</sup>
ZnS	1.6 × 10 <sup>-24</sup>

(i) Given that a solution contains 0.0010 mol dm<sup>-3</sup> Zn<sup>2+</sup> and 0.0010 mol dm<sup>-3</sup>
 Cu<sup>2+</sup>, determine the maximum sulfide concentration for each cation so that no precipitation occurs.

[1]

[1]

4. (d) (ii) Given that  $[H^+] = \sqrt{\frac{K_{a1}K_{a2}[H_2S]}{[S^{2^-}]}}$  and using your answer in (c)(i), calculate

the maximum pH that must be maintained to separate  $Zn^{2+}$  and  $Cu^{2+}$  ions, given that the concentration of  $H_2S$  in the solution is 0.0010 mol dm<sup>-3</sup>. [2]

(e) The Trinder spot test is a diagnostic test used in medicine to determine exposure to salicylates, in particular, salicylic acid. The test involved the Trinder reagent which is mixed with a patient's urine. A coloured complex is formed if salicylates are present.



Salicylic acid

(i) Suggest the compound that is present in the Trinder reagent added to salicylic acid and state the observation when if the test is positive.

.....[2]

**4.** (e) Another variation of the Trinder spot test has also been used to determine the presence of norfloxacin and oxytetracycline.



**5.** Sodium alginate is a natural polymer extracted from brown seaweed. Figure **5.1** shows the simplified representation of a sodium alginate polymer.



Figure 5.1 : simplified representation of sodium alginate polymer

In food chemistry, sodium alginate serves as a gel-forming agent as it can react with calcium salts to make "popping boba" in the bubble tea industry. This process is commonly known as spherification.

During spherification, a solution of sodium alginate is added to a solution of calcium salt. Na<sup>+</sup> ions are exchanged with  $Ca^{2+}$  ions and the cross linked calcium alginate polymers forms as shown in Figure **5.2**.



Figure 5.2: simplified representation of cross-linked calcium alginate polymer

(i) Cross-linking is the general term for the process of forming chemical bonds to join two polymer chains together. Explain, in terms of bonding, why Ca<sup>2+</sup> ions are able to cross-link the alginate polymers but Na<sup>+</sup> ions are unable to do so.

.....

[1]

5. (a) (ii) Explain why calcium alginate has a low solubility in water.

.....

.....

(b) During spherification, the pH of the flavoured liquid used is important. Below a pH of 3.6, sodium alginate tends to react and the resultant solution will thicken which makes it difficult to form spheres.

Although Ca<sup>2+</sup> is crucial in helping the alginate to gel, excess Ca<sup>2+</sup> present can also cause the liquid to gel prematurely which is undesirable.

Table 5.3 shows the pH of various flavoured liquid.

Flavoured Liquid	рН
cranberry juice	2.3
blueberry juice	3.4
tomato juice	4.6
watermelon juice	5.2
aloe vera juice	6.1

1 aple 5.3
------------

(i) Cranberry juice is not suitable for spherification to work.
 Suggest the type of reaction that takes place when sodium alginate is added to cranberry juice and hence explain why spherification will not occur in presence of cranberry juice.

[2]

[1]

.....

5. (b) (ii) A bubble tea shop wanted to make a "popping boba" by mixing 250 cm<sup>3</sup> of aloe vera juice with 300 cm<sup>3</sup> of blueberry juice. By determining the pH of the mixture, deduce if the spherification would happen. [3]

- (iii) Hard water is water that has a high mineral content. It is formed when water percolates through deposits of limestone which are made up of calcium and magnesium carbonates and bicarbonates.
  Suggest why spherification does not work well in hard water. [1]
- (iv) Draw the dot-cross diagram for calcium bicarbonate Ca(HCO<sub>3</sub>)<sub>2</sub>. [2]

**5.** (c) A student set up the following experiment to investigate the thermal stability of magnesium and calcium carbonates:



Each of the metal carbonate is heated strongly for 5 min and the time taken for a white precipitate to form in limewater is recorded in the following table:

Metal carbonate	Time taken (s)
X	70
Y	40

(i) What are the identities of X and Y?

[1]

[2]

X: ..... Y: ....

(ii) Explain the results.

[Total:13]

~END OF PAPER~

#### **Prelims Paper 2 Answers**

1. (a) P, Q, R and S are consecutive elements in Period 4.

The table below shows the first four ionisation energies (in kJ mol<sup>-1</sup>) of the elements.

Element	1 <sup>st</sup> I.E.	2 <sup>nd</sup> I.E.	3 <sup>rd</sup> I.E.	4 <sup>th</sup> I.E.	5 <sup>th</sup> I.E.
Р	908	1730	3828	5980	7970
Q	577	1980	2960	6190	8284
R	762	1540	3300	4390	9020
S	947	1798	2735	4837	6043

[1]

(i) Explain why the second ionisation energy of **Q** is higher than that of **R**.

Q is in group 13, there is a great jump in IE from 3<sup>rd</sup> IE to 4<sup>th</sup> IE

Q: 4s<sup>2</sup>4p<sup>1</sup> Q<sup>+</sup>: 4s<sup>2</sup>

R: 4s<sup>2</sup>4p<sup>2</sup> R<sup>+</sup>: 4s<sup>2</sup>4p<sup>1</sup>

Q: the second electron is removed from the <u>4s</u> orbital, whereas for R, the second electron is removed from the <u>4p</u> orbital. The <u>4p</u> orbital is <u>further</u> away from the nucleus than the 4s and <u>experiences additional shielding effect</u> by the two 4s electrons. These factors <u>outweigh the effect of increase in nuclear charge</u> from Q to R, resulting in a weaker attraction by nucleus. <u>Less energy</u> is required to <u>remove an electron</u> from 4p than the 4s orbital.

(ii) Explain why **P** is not considered to be a transition metal like most of the d-block metals.

They **do not** form stable ions with a partially filled d subshell. [1]

- (b) The idea of covalent bonding was first described in 1916 by an American physical chemist Gilbert Newton Lewis. HCOC*l* is an example of a polar covalent molecule.
  - (i) Explain what is *covalent bonding*. [1]
     Covalent bonding is the <u>electrostatic attraction</u> between a <u>shared pair of electrons</u> and the positively charged nuclei.
  - (ii) State what is meant by the term *polar* when applied to a covalent bond. [1]

A polar covalent bond is one in which the electron density is unequally shared due to the difference in electronegativity of atoms bonded, resulting in  $\partial$ + and  $\partial$ - across bond.

- (iii) State and explain with reference to the Valence Shell Electron Pair Repulsion theory, the shape of HCOC*l* molecule.
   <u>3 bond pair no lone pair so trigonal planar</u>. The 3 electrons bond pairs arrange themselves to maximise stability and minimise electronic repulsion.
- (iv) The molecule of HCOC*l* contains both  $\sigma$  (sigma) and  $\pi$  (pi) bonds. Draw labelled diagrams to show how orbitals overlap to form
  - a  $\sigma$  (sigma) bond
  - a π (pi) bond
  - $\sigma$  (sigma) bond is formed from  $\underline{\text{head-on overlap}}$  of

or

or





[2]

 $\pi$  (pi) bond is formed from **<u>side-on overlap</u>** of unhybridised p orbitals.



[Total:9]

2 Below is a labelled diagram of a hydrogen-oxygen fuel cell in an alkaline electrolyte.



- (i) Write the half equations for both electrodes and hence the overall equation. [2] Cathode:  $O_2(g) + 2H_2O(I) + 4e^- \rightarrow 4OH^-(aq)$ Anode:  $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(I) + 2e^-$ Overall equation :  $2H_2(g) + O_2(g) \rightarrow 2H_2O(I)$
- (ii) Calculate  $\Delta G^{e}$  for the above reaction and state whether it is spontaneous. [3]

 $E^{e_{cell}} = E^{e_{cathode^{-}}} E^{e_{anode}}$ = 0.40-(-0.83) = +1.23 V  $\Delta G^{e^{-}} = -nFE^{e_{cell}}$ = - 4x96500x1.23 = - 474780 Jmol<sup>-1</sup> = -475 kJmol<sup>-1</sup> It is spontaneous.

(iii) The hydrogen-oxygen fuel cell produces 1.5 A of current. Hydrogen gas is contained in a 1 dm<sup>3</sup> tank at a pressure and temperature of 200 atm and 20 °C respectively. Determine the number of days the fuel cell can operate before the hydrogen gas runs out. Give your answer to the nearest whole number. You may assume there is an unlimited supply of O<sub>2</sub>.

PV = nRT200 x 1.01325 x 10<sup>5</sup> x 1 x 10<sup>-3</sup> = n x 8.31 x 293 n (amt of H<sub>2</sub> gas) = 8.322 mol no. moles of electrons given out = 2n = 16.64 Q = 16.64 x 96500 = 1605760C Q = It [3]

12 days

[Total:8]

 Spider silk is a protein fiber. Major amino acids in the silk proteins are alanine and glycine. Serine and glutamine are also present in significant quantities in some types of silk. The table below shows the typical amino acids present in spider silk.

Amina Aaid	Formula of side chain	
Amino Aciu	(R in RCH(NH <sub>2</sub> )CO <sub>2</sub> H)	
Glycine	–H	
Alanine	–CH₃	
Serine	–CH₂OH	
Glutamine	$-CH_2CH_2CONH_2$	

(a) (i) Glycine exists as crystalline solids. Draw the zwitterionic structure of glycine and account for the high melting point of glycine. [2]

Crystalline solid of glycine has <u>giant ionic lattice structure</u> with <u>strong</u> <u>electrostatic forces of attraction exists between the zwitterions</u>. <u>A lot of</u> <u>energy</u> is required to overcome these strong ionic bonds between zwitterions.

(ii) Write an equation to show the reaction between alanine and aqueous [1] sodium carbonate.

(iii) Suggest a chemical test to distinguish between serine and glutamine. [2]

Test: K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>(aq),H<sub>2</sub>SO<sub>4</sub>(aq), heat Observation: For serine, orange dichromate turns green For glutamine, orange solution remains **OR** Test: NaOH(aq), **heat** Observation: For serine, no pungent gas observed and moist litmus paper remained red. For glutamine, pungent gas evolved turns <u>moist</u> red litmus blue

(b) Natural spider silk has excellent mechanical properties. In a recent study, researchers discovered that graphene-based materials can be used to boost the properties of spider's silk up to three times the strength and ten times the toughness of the unmodified silks.

Graphene is the thinnest material known to exist, yet it is stronger than steel. It is made from only carbon and is a single layer of graphite just one atom thick as shown in Figure **3.1** below.



Figure 3.1

(i) With reference to structure and bonding, explain why graphene is strong. [1]
 Graphene is an allotrope of C and just like graphite it has giant covalent structure. Each layer of graphene is made of hexagonal "ring" of carbon atoms strongly covalently bonded. A lot of energy is required to break these strong covalent C-C bonds.

(ii) Since its discovery in 2004, graphene has been widely studied and [1] manufactured as replacement materials for many touchscreen products.
 Suggest why graphene is a suitable touchscreen material in mobile phones.
 It is two-dimensional which makes it <u>thin/light/transparent</u>, suitable as touchscreen material.

Or it has high electrical conductivity due to presence of delocalized electrons that serve as mobile charge carriers.

(c) Spiders are excellent treats for colonies of marauding ants. To protect their homes, spiders coat their webs using a chemical called 2-pyrrolidone, which acts as a deterrent to many insects.

2-Pyrrolidone is a 5-membered cyclic amide (commonly known as lactam). It is a colourless liquid that is miscible with water and most common organic solvents.



2-Pyrrolidone

2-pyrrolidone can be synthesised using 3-chloropropan-1-ol as the starting organic compound as shown in the reaction scheme below:



(i)	State the type of reaction in Step V.	[1]
	(Intramolecular) condensation	
	(intramolecular) nucleophilic (acyl) substitution)	
(ii)	Suggest reagents and conditions for Step I, II and III.	[3]
	Step I :	
	Step II :	
	Step III :	
	Step I: KMnO <sub>4</sub> (aq), H <sub>2</sub> SO <sub>4</sub> (aq), heat OR K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , H <sub>2</sub> SO <sub>4</sub> (aq), heat	
	Step II: ethanolic KCN, heat	
	Step III: H <sub>2</sub> , Ni, heat	

(iii) Draw the structures of intermediate compounds A and B. [2]



(iv) With the aid of an equation, explain why anhydrous condition is necessary [1] for the reaction in Step IV.

 $PCl_5$  will hydrolyse readily in water as follows:  $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$ 

(v) 2-pyrrolidirol can be synthesised from 2-pyrrolidone.



[2]

# 2-pyrrolidirol

Deduce whether 2-pyrrolidone or 2-pyrrolidirol has a higher  $pK_b$ .

2-pyrrolidone is <u>less basic</u> hence a <u>higher  $pK_b$ </u> as it is an amide. The <u>lone</u> pair of electrons on N are delocalised over the O-C-N bond and <u>not available</u> for protonation.

(vi) Suggest a synthesis to form 3-chloropropan-1-ol from 1,3-butanediol.



[Total:20]

**4** (a) Copper and iron are examples of native metals, which are found pure in its metallic form on its own or in alloys in nature.

Copper and iron form many complexes with a range of colours as shown in the table:

complex	colour	complex	colour
[Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>	dark blue	[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	yellow
[Cu(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	blue	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	red

(i) Explain why  $[Cu(H_2O)_6]^{2+}$  is blue.

In the isolated gas phase, all partially filled 3d orbitals of the transition metal ions are degenerate. In the <u>presence of ligand</u> such as NH<sub>3</sub> or CN<sup>-</sup>, the <u>3d</u> <u>orbitals split into 2 energy level</u> with a small energy gap between them. An electron from the lower energy d orbital absorbs energy from the visible region (or visible spectrum) of the electromagnetic spectrum with wavelength corresponding to the energy gap is absorbed and <u>get</u> <u>promoted to a higher energy d orbital</u>. The orange light energy is absorbed and the <u>complementary blue colour is</u> <u>observed</u>.

(ii) The oxidation state of iron in both  $[Fe(CN)_6]^{3-}$  and  $[Fe(H_2O)_6]^{3+}$  complexes is the same. However, they have different colours. Explain this observation.

[1]

Different ligands ( $CN^-$  and  $H_2O$ ) split the energy gap between the d orbitals differently. Hence different wavelength of light is absorbed and colour reflected is different.

- (iii) Draw fully labelled diagrams of the following:
  - One of the d-orbitals at the lower energy level in [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>. Label the diagram "lower".
  - One of the d-orbitals at the upper energy level in [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>. Label this diagram "upper". [2]

Lower: any

[3]



(b) Use of the Data Booklet is relevant to this question.

Fe<sup>2+</sup> is commonly used to catalyse the reaction between S<sub>2</sub>O<sub>8</sub><sup>2-</sup>and I<sup>-</sup>. In another similar reaction, peroxodisulfate(VI), S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, reacts with tartrate ion,  $[CH(OH)CO_2]_2^{2-}$ , to give carbon dioxide and methanoate as shown in the following equation.

 $[CH(OH)CO_2]_2^{2^-} + 3S_2O_8^{2^-} + 2H_2O \rightarrow 2CO_2 + 2HCO_2^- + 6H^+ + 6SO_4^{2^-}$ The reaction is very slow, even when heated, hence a catalyst is used to speed up the reaction.

(i) Explain why the reaction is slow.

[1]

#### It involved two negative ions (S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and tartrate ion) which repel each other.

(ii) Given that the standard electrode potential for the following half-equation is

 $2CO_2 + 2HCO_2^- + 6H^+ + 6e^- \approx [CH(OH)CO_2]_2^{2^-} + 2H_2O$   $E^{\theta} = + 0.56 V$ Using suitable equations, explain why Mn<sup>2+</sup> is a suitable catalyst for this [2] reaction.

$$\begin{split} S_2 O_8^{2-} &+ 2e^- \rightleftharpoons 2SO_4^{2-} & E^\theta = +2.01 \ V \\ Mn^{3+} &+ e^- \rightleftharpoons Mn^{2+} & E^\theta = +1.54 \ V \end{split}$$

(Catalysed reaction using Mn<sup>2+</sup>)

$$2Mn^{2+} + S_2O_8^{2-} \rightarrow 2Mn^{3+} + 2SO_4^{2-}$$
$$E^{\theta}_{cell} = 2.01 - (1.54) = + 0.47 \text{ V}$$

6Mn<sup>3+</sup> + [CH(OH)CO<sub>2</sub>]<sub>2</sub><sup>2-</sup> + 2H<sub>2</sub>O → 6Mn<sup>2+</sup> + 2CO<sub>2</sub> + 2HCO<sub>2</sub><sup>-</sup> + 6H<sup>+</sup> E<sup>θ</sup><sub>cell</sub> = 1.54 - 0.56 = + 0.98 V

Alternative answer:

$$\begin{split} S_2O_8^{2^-} &+ 2e^- \rightleftharpoons 2SO_4^{2^-} & E^\theta = +2.01 \text{ V} \\ MnO_4^- &+ 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O & E^\theta = +1.52 \text{ V} \\ &5S_2O_8^{2^-} + 2Mn^{2+} + 8H_2O \Rightarrow 10SO_4^{2^-} + 2MnO_4^- + 16H^+ \\ &E^\theta_{cell} = 2.01 - (1.52) = + 0.49 \text{ V} \\ &6MnO_4^- + 18H^+ + 5[CH(OH)CO_2]_2^{2^-} \Rightarrow 6Mn^{2+} + 14H_2O + 10CO_2 \\ &+ 10HCO_2^- \\ &E^\theta_{cell} = 1.52 - 0.56 = + 0.96 \text{ V} \end{split}$$

(iii) State the property of transition metal ions that enable them to function as a [1] homogenous catalyst in the reaction.

Transition metal ions are able to <u>exhibit a variety of oxidation states</u> due to the similar energy of the 3d and 4s orbitals and hence both are able to be shared or lost.

(c) Palladium is a transition element that is used as a catalyst in the Cassar reaction. The Cassar reaction is a type of substitution reaction between an alkyl chloride and a terminal alkene in the presence of a base and a palladium catalyst.



[R can be a substituted alkyl group containing –OH, –NH<sub>2</sub>, –NO<sub>2</sub> –COOH]

The following scheme shows the synthesis of  ${\bf D}$  using Cassar reaction in one of the steps.

$$\mathbf{A} + \mathbf{B} \xrightarrow{\text{Cassar reaction}} \mathbf{C}_{5}\mathbf{H}_{11}\mathbf{NO} \xrightarrow{\text{K}_{2}Cr_{2}O_{7}(aq), H_{2}SO_{4}(aq), \text{ heat}} \mathbf{D}$$

The table below shows the observations when **A**, **B** and **D** reacts with various reagents.

reaction		observations
1	<b>A</b> + HC <i>l</i> (aq)	colourless solution
2	<b>B</b> + Br <sub>2</sub> (aq)	colourless solution
3	$D + Na_2CO_3(aq)$	Gas forms white ppt with
		Ca(OH) <sub>2</sub>

- (i) Name the functional group that reaction 1 shows to be present in A [1]
   (Primary) amine
- (ii) State the type of reaction that takes place in reaction 2 and name the functional group present in B [1]
   Electrophilic addition. Alkene
- (iii) C is able to exhibit cis-trans isomerism. Draw the structures of A, B, C andD. [4]

 $H_2N$  —  $CH_2Cl$ Compound A



Compound B





Trans isomer of compound C EITHER

Cis isomer of compound C



(iv) Draw the structure of the product when CH<sub>3</sub>CH(CH<sub>2</sub>C*l*)CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub> undergoes the Cassar reaction.



(d) A solution containing  $Cu^{2+}$  and  $Zn^{2+}$  can be separated by selective precipitation.

The reagent used is hydrogen sulfide which behaves as a dibasic (diprotic) weak acid when in aqueous solution.

Aqueous hydrogen sulfide behaves as a dibasic acid.

 $H_2S$  (aq)  $\implies$   $H^+$  (aq) +  $HS^-$  (aq)  $K_{a1} = 8.9 \times 10^{-8} \text{ mol } dm^{-3}$ 

 $HS^{-}(aq) \longrightarrow H^{+}(aq) + S^{2-}(aq)$   $K_{a2} = 1.2 \times 10^{-13} \text{ mol dm}^{-3}$ 

Metal sulfides are precipitated by the following reaction.

$$M^{2+}(aq) + S^{2-}(aq) \iff MS(s)$$

Relevant  $K_{sp}$  values are given in the table below.

Salt	K <sub>sp</sub> / mol² dm <sup>−6</sup>
CuS	6.3 × 10 <sup>−36</sup>
ZnS	1.6 × 10 <sup>-24</sup>

(i) Given that a solution contains 0.0010 mol dm<sup>-3</sup> Zn<sup>2+</sup> and 0.0010 mol dm<sup>-3</sup>
 Cu<sup>2+</sup>, determine the maximum sulfide concentration for each cation so that no precipitation occurs.

[1]

[1]

$$[S^{2-}]_{max}$$
 for ZnS=  $\frac{1.6 \times 10^{-24}}{0.0010}$  = 1.6 x 10<sup>-21</sup> mol dm<sup>-3</sup>

$$[S^{2-}]_{\text{max}}$$
 for CuS =  $\frac{6.3 \times 10^{-36}}{0.0010}$  = 6.3 x 10<sup>-33</sup> mol dm<sup>-3</sup>

(ii) Given that  $[H^+] = \sqrt{\frac{K_{a1}K_{a2}[H_2S]}{[S^{2-}]}}$  and using your answer in (d)(i), calculate

the maximum pH that must be maintained to separate  $Zn^{2+}$  and  $Cu^{2+}$  ions, given that the concentration of H<sub>2</sub>S in the solution is 0.0010 mol dm<sup>-3</sup>. [2]

 $K_{a1} K_{a2} = 1.068 \times 10^{-20} \text{ mol}^2 \text{ dm}^{-6}$ 

$$[H^+] = \sqrt{\frac{1.068 \times 10^{-20} \times 0.0010}{1.6 \times 10^{-21}}} = 0.08170 \text{ mol dm}^{-3}$$
$$pH = -\log 0.08170 = 1.09$$

(e) The Trinder spot test is a diagnostic test used in medicine to determine exposure to salicylates, in particular, salicylic acid. The test involved the Trinder reagent which is mixed with a patient's urine. A coloured complex is formed if salicylates are present.



Salicylic acid

(i) Suggest the compound that is present in the Trinder reagent added to salicylic acid and state the observation when if the test is positive. [2]

Neutral aq FeCl<sub>3.</sub>[1]

#### Violet [1] coloration is observed.

Another variation of the Trinder spot test has also been used to determine the presence of norfloxacin and oxytetracycline.



Na<sub>2</sub>CO<sub>3</sub>(aq). Effervescence observed and gas evolved formed white ppt in limewater for norfloxacin but no effervescence for oxytetracycline. Or

Neutral FeCl<sub>3</sub> (aq). Violet colouration for oxytetracycline but no violet colouration for norfloxacin.

### [Total:25]

**5** Sodium alginate is a natural polymer extracted from brown seaweed. Figure **5.1** shows the simplified representation of a sodium alginate polymer.



Figure 5.1 : simplified representation of sodium alginate polymer

In food chemistry, sodium alginate serves as a gel-forming agent as it can react with calcium salts to make "popping boba" in the bubble tea industry. This process is commonly known as spherification.

During spherification, a solution of sodium alginate is added to a solution of calcium salt. Na<sup>+</sup> ions are exchanged with  $Ca^{2+}$  ions and the cross linked calcium alginate polymers forms as shown in Figure **5.2**.



Figure 5.2: simplified representation of cross-linked calcium alginate polymer.

(i) Cross-linking is the general term for the process of forming chemical bonds [1] to join two polymer chains together. Explain, in terms of bonding, why Ca<sup>2+</sup> ions are able to cross-link the alginate polymers but Na<sup>+</sup> ions are unable to do so.

The divalent Ca<sup>2+</sup> ions are able to cross-link the alginate polymers because they can form <u>two ionic bonds</u>, while monovalent Na<sup>+</sup> ions can <u>only form one</u> <u>bond</u>. [1]

- (ii) Explain why calcium alginate has low solubility in water. [1]
   The energy released from the ion-dipole interactions between calcium alginate and the water molecules [1] is insufficient to overcome the strong ionic bonds between calcium ions and alginate ions and hydrogen bonds between the water molecules.[1]
- (b) During spherification, the pH of the flavoured liquid used is important. Below a pH of 3.6, sodium alginate tends to react and the resultant solution will thicken which makes it difficult to form spheres.

Although Ca<sup>2+</sup> is crucial in helping the alginate to gel, excess Ca<sup>2+</sup> present can also cause the liquid to gel prematurely which is undesirable.

Table **5.3** shows the pH of various flavoured liquids.

Table 5.3

Flavoured Liquid	рН
cranberry juice	2.3
blueberry juice	3.4
tomato juice	4.6
watermelon juice	5.2
aloe vera juice	6.1

(i) Cranberry juice is not suitable for spherification to work. [2]
 Suggest the type of reaction that takes place when sodium alginate is added to cranberry juice and hence explain why spherification will not occur in presence of cranberry juice.

Acid-base reaction.[1]

The sodium alginate will be protonated and <u>converted to the</u> covalent <u>conjugate acid molecule</u> (alginic acid). Without Na<sup>+</sup>, ion-exchange does not take place readily with Ca<sup>2+</sup> to make the cross-linked polymer. [1]

(ii) A bubble tea shop wanted to make a "popping boba" by mixing 250 [3]  $cm^3$  of aloe vera juice with 300 cm<sup>3</sup> of blueberry juice. By determining the pH of the mixture, deduce if the spherification would happen.  $[H^+]_{aloe vera} = 10^{-6.1} = 7.943 \times 10^{-7} \text{ mol dm}^{-3}$ Amt of H<sup>+</sup> in aloe vera = 7.943 x 10<sup>-7</sup> x 250/1000  $= 1.986 \times 10^{-7} \text{ mol}$ 

 $[H^+]_{blueberry} = 10^{-3.4} = 3.981 \times 10^{-4} \text{ mol dm}^{-3}$ Amt of H<sup>+</sup> in blueberry juice = 3.981 \times 10^{-4} \times 300/1000 = 1.194 \times 10^{-4} \text{ mol } [1 \text{ for both amount of H}^+]

 $[H^+]_{mixture} = (1.986 \times 10^{-7} + 1.194 \times 10^{-4})/0.55 = 2.175 \times 10^{-4} \text{ mol dm}^{-3}$ pH = 3.66 [1] > 3.6 Since pH > 3.6, spherification would happen. [1]

(iii) Hard water is water that has a high mineral content. It is formed when water [1] percolates through deposits of limestone which are made up of calcium and magnesium carbonates and bicarbonates. Suggest why spherification does not work well in hard water. The presence of <u>high concentration of calcium</u> in hard water will <u>solidify/gel</u> in the sodium alginate solution **immediately/prematurely** to form calcium alginate. [1]

(iv) Draw the dot-cross diagram for calcium bicarbonate Ca(HCO<sub>3</sub>)<sub>2</sub>.

;<u>ö</u> :<u>Ö</u>\*Č\*Ö; 21 2

[1] for ionic structure[1] for HCO<sub>3</sub><sup>2-</sup>

(c) A student set up the following experiment to investigate the thermal stability of magnesium and calcium carbonates:



Each of the metal carbonate is heated strongly for 5 min and the time taken for a white precipitate to form in limewater is recorded in the following table:

Metal carbonate	Time taken (s)
X	70
Y	40

- (i) What is the identity of **X** and **Y**?
  - X: Calcium carbonate
  - Y: Magnesium carbonate

[1]
### (ii) Explain the results.

Magnesium carbonate decomposes more easily and releases  $CO_2$  faster to form white ppt in limewater because <u>size of Mg<sup>2+</sup> is smaller than Ca<sup>2+</sup></u> <u>but charge remains. Hence charge density of Mg<sup>2+</sup> is larger than Ca<sup>2+</sup> [1].</u> <u>Electron cloud of carbonate in MgCO<sub>3</sub> will be distorted to a larger</u> <u>extent/polarising power of Mg<sup>2+</sup> is more, weakening the C-O bond more</u> [1].

[Total:13]

## **ST ANDREW'S JUNIOR COLLEGE**



# **JC2 Preliminary Examination**

H2 Chemistry (9729)

Paper 3 Free Response

Additional Materials: Data Booklet, Answer Booklet

### **READ THESE INSTRUCTIONS:**

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.

### Section A

Answer all questions. Marks [60]

## Section B

Answer one question. Marks [20]

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.

This document consists of 14 printed pages.

# 18 September 2019 2 hours

### Section A

Answer all the questions in this section.

1 (a) Use of the Data Booklet is relevant to this question.

The Hoffmann voltameter is used to electrolyse concentrated iron (III) chloride solution. The setup of the Hoffmann voltameter is shown below.



- (i) Describe the observations at the cathode and anode. Explain your answer with the aid of suitable ion-electron equations. [2]
- (ii) State the difference in the observations at the anode when dilute aqueous iron (III) chloride solution is used instead. Explain your answer using relevant E<sup>9</sup> data.
- (b) The electrolysis of a hot aqueous solution of NaX yielded a reddish brown gas, X<sub>2</sub>, at the anode and hydrogen gas at the cathode. The red litmus paper turned blue when dipped into the solution at the cathode.
  - (i) Suggest the identity of the reddish brown gas X<sub>2</sub>. [1]
  - (ii) Write an ion-electron equation for the reaction at the cathode. [1]
  - (iii) Some of the X<sub>2</sub> dissolved in the alkaline medium to form X<sup>-</sup> and XO<sub>3</sub><sup>-</sup> ions.
     Write a balanced equation to represent the reaction of X<sub>2</sub> in alkaline medium.

(iv) Describe a chemical test, which does **not** involve silver nitrate, that could distinguish between sodium chloride and sodium iodide. [2] Describe and explain how the thermal stability of the hydrogen halides varies (C) [2] down Group 17. When methylcyclopentane is treated with a small quantity of chlorine in the (d) presence of ultraviolet light, 4 mono-chlorinated constitutional isomers are produced. Draw the structures of the isomers and state the ratio in which they are formed. [3] (e) SiCl<sub>4</sub> reacts readily with water to form a solution of pH 2. However, SiO<sub>2</sub> does not react with water and only reacts with hot concentrated alkali such as NaOH. (i) Explain why SiCl<sub>4</sub> reacts readily with water, but SiO<sub>2</sub> only reacts with hot [3] concentrated NaOH. Use relevant equations to explain your answer. (ii) Using  $Cl_2(g)$  as an example, define the term bond energy. [1] (iii) Construct an energy level diagram to calculate the enthalpy change of formation of SiCl<sub>4</sub>. [3] Your diagram should include relevant data from the Data Booklet together with the following data: Enthalpy change of atomisation of Si = +338 kJmol<sup>-1</sup>

Enthalpy change of vapourisation of SiC $l_4$  = +29 kJmol<sup>-1</sup>

[Total: 21 marks]

2 (a) Phosphorus-containing compounds can react in various ways: as an acid, as a base, as an electrophile, as a nucleophile, as an oxidising agent and as a reducing agent.

Study the following reactions and decide in which way the phosphorus-containing compound is reacting in each case. Explain your answers fully.

(i) 
$$H_3PO_4 + H_2O \rightarrow H_2PO_4^- + H_3O^+$$
 [1]



(b) 2-chloropropanoyl chloride, W, can be obtained from propanoic acid by heating it with Cl<sub>2</sub> and PCl<sub>5</sub>.

Reaction 1 :  $CH_{3}CH_{2}CO_{2}H(l) + Cl_{2}(g) + PCl_{5}(s) \rightarrow CH_{3}CHClCOCl(l) + 2HCl(g) + POCl_{3}(l)$  W

 $\Delta H > 0$ 

[2]

- (i) Explain the different reactivities of the two chlorine atoms in **W** towards water.
- (ii) Explain fully why the pH of an aqueous solution of 2-chloropropanoyl chloride is 1.0 while that of an aqueous solution of propanoic acid of the same concentration is greater than 1.0.
   [2]

(iii) W can be used to produce sweet-smelling Z,  $C_6H_8O_4$ , via compounds X and Y, as shown in Fig. 2.1

$$W \xrightarrow{\text{NaOH}(\text{aq})}_{\text{heat}} X \xrightarrow{\text{H}_2\text{SO}_4(\text{aq})}_{Fig. 2.1} Y \xrightarrow{\text{conc H}_2\text{SO}_4}_{\text{heat}} Z$$

Suggest structures for compounds **X**, **Y** and **Z** in Fig. 2.1.

(iv) W can undergo the following reaction scheme.



State the reagents and conditions for Steps 1 and 2.

(v) V is an isomer of W.

**V** rotates the plane of polarised light. It gives a positive test with 2,4-dinitrophenylhydrazine.

Draw the displayed formula of **V**, identifying the chiral carbon. [1]

(vi) Use the table of characteristic values for infra-red absorption frequencies in the *Data Booklet* to answer this question.

Infra-red adsorption frequencies can be used to identify functional groups in organic compounds. For example, propanol shows absorptions at 970–1250cm<sup>-1</sup> and 3580–3620 cm<sup>-1</sup>.

Use the table to suggest how infra-red absorption frequencies can be used to distinguish 2-chloropropanoyl chloride from propanoic acid. [1]

(vii) Given that reaction 1 is endothermic, explain why the reaction will only take place with heating. [2]

[Total : 16 marks]

[3]

- **3** There are 2 isomers of 2-methylbutanoic acid, CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)COOH (M<sub>r</sub> 102.0) ; one of the isomers is sweet-smelling and the other has a stinky odour.
  - (a) (i) State the stereoisomerism exhibited by 2-methylbutanoic acid and how it arises.
     [2]
    - (ii) Hence, explain why the isomers have different smells. [1]
  - (b) Suggest a 2 stage synthesis of 2–methylbutanoic acid from 2–bromobutane. State reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds.
     [3]
  - (c) Safety regulations set by many countries state that a factory would be fined, if stinky smelling compounds reached unsafe levels. The factory would have to stop production and undergo cleansing.

When 2-methylbutanoic acid was synthesised using 2-bromobutane in a factory, both the sweet-smelling and the stinky isomers were obtained in equal proportions.

(i) The M<sub>r</sub> of 2–methylbutanoic acid in the liquid phase is 204.0.
 With the aid of a diagram, explain the above.

[2]

(ii) 2-methylbutanoic acid has a relatively low boiling point of 176 °C at 1 atm, and hence vaporises easily. This poses a problem when adhering to safety regulations.

In a factory, during the synthesis of 2–methylbutanoic acid, the workers did not seal the chemical container properly.

Given that the enthalpy change of vaporisation of 2–methylbutanoic acid is +59.1 kJ mol<sup>-1</sup>, use the following equation (Clausius–Clapeyron Equation) to determine the vapour pressure of 2–methylbutanoic acid in the factory at night when the temperature was 30.2 °C.

$$\ln P = \frac{\Delta H_{vaporisation}}{R} \left( \frac{1}{T_{b.p.}} - \frac{1}{T} \right)$$

P = vapour pressure in atm at temperature T K  $\Delta H_{vaporisation}$  = enthalpy change of vaporisation of the substance in J mol<sup>-1</sup> R = universal gas constant T<sub>b.p.</sub> = boiling point of the substance in K at 1 atm

[2]

[2]

(iii) Safety protocols dictated that stinky smelling substances above 300 ppm (parts per million) is considered a safety hazard and likely to be fined.
 Based on your answers in (a)(i) and (c)(ii), and given that the pressure in the factory is 1 atm, determine whether the factory would be fined.

 $[1 \times 10^{-6} \text{ atm in } 1 \text{ atm } = 1 \text{ ppm}]$ 

(d) Ethyl 2–methylbutanoate is an ester which is commonly found in citrus fruits, such as pineapple and oranges. It is commonly used as the starting material to form the sweet–smelling 2–methylbutanoic acid via hydrolysis.



7

The rate equation for the hydrolysis of esters was determined by a series of experiments. The hydrolysis of the ester, ethyl 2–methylbutanoate, was carried out, using 0.75 mol dm<sup>-3</sup> hydrochloric acid. The experiment was repeated using 0.75 mol dm<sup>-3</sup> sulfuric acid. The following graphs were obtained.



- Using the graphs above, deduce the order of reaction with respect to [H<sup>+</sup>] and [ester]. Hence, write the rate equation of the hydrolysis of the ester, ethyl 2–methylbutananoate.
- (ii) Calculate the rate constant for the hydrolysis of ethyl 2-methylbutanoate, including its units. [2]

[3]

- (iii) In the absence of an acid, the hydrolysis of the ester is very slow.
   With the aid of a relevant diagram, explain how the rate constant would change if the acid was removed.
   [3]
- (e) Ethyl 2-methylbutanoate can also be formed using 2-methylbutanoyl chloride and ethanol.

The reaction takes place under anhydrous conditions as 2-methylbutanoyl chloride undergoes hydrolysis in water to form 2-methylbutanoic acid.

The hydrolysis of 2-methylbutanoyl chloride occurs via a two-stage mechanism:

• The first stage (the addition stage of the reaction) involves a nucleophilic attack on the partial positive carbon atom by one of the lone pairs of electrons on the oxygen atom of a water molecule, giving intermediate **E**.



intermediate E

The second stage (the elimination stage) happens in two steps.

- 1. The carbon-oxygen double bond reforms with a chloride ion as the side product.
- A hydrogen ion is removed by the chloride ion to give
   2-methylbutanoic acid and hydrogen chloride.

Outline the mechanism for this reaction, given that intermediate **E** is formed after the first stage. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows. [3]

[Total: 23 marks]

### **Section B**

Answer **one** question from this section.

4 Phenolphthalein, a type of triarylmethane dye, is a common indicator used in acid-base titrations.



#### Phenolphthalein

In its uncharged form, aqueous phenolphthalein is colourless. At pH of 8.2 and above, both phenol groups are deprotonated to form a pink solution.

- (a) The p $K_b$  for trimethylamine, (CH<sub>3</sub>)<sub>3</sub>N, at 25 °C is 4.19.
  - (i) Trimethylamine can behave as a Lewis base. Use the reaction of trimethylamine with aluminium chloride to illustrate this behaviour, writing the equation for the reaction that occurs. [1]
  - (ii) Calculate the pH of an aqueous solution of 0.20 mol dm<sup>-3</sup> trimethylamine solution.
  - (iii) Calculate the pH of the resulting solution when 10 cm<sup>3</sup> of 0.20 mol dm<sup>-3</sup>
     trimethylamine solution and 5 cm<sup>3</sup> of 0.10 mol dm<sup>-3</sup> HC*l* solution are mixed. [2]
  - (iv) Calculate the pH of the resultant solution when 20 cm<sup>3</sup> of 0.10 mol dm<sup>-3</sup>
     HC*l* solution is added to 10 cm<sup>3</sup> of 0.20 mol dm<sup>-3</sup> trimethylamine solution. [2]
  - (v) Explain why phenolphthalein would not be a suitable indicator for the titration of trimethylamine with HC*l*. [1]

- (vi) Methylamine has a pK<sub>b</sub> of 3.36. Suggest a reason for the difference in basicity between methylamine and trimethylamine. [1]
- (b) Draw the structural formula of the product formed when phenolphthalein reacts with each of the following reagents:
  - (i) excess  $Br_2$  in the presence of  $A/Br_3$ . [2]

[2]

- (ii) sodium hydroxide with heat.
- (c) Under extremely acidic conditions (pH < 0), phenolphthalein can be protonated to form an orange solution. This is an endothermic process.</p>



Use Le Chatelier's Principle to explain the following observations.

- (i) An aqueous solution of phenolphthalein changed from colourless to orange when concentrated sulfuric acid was added to it. [1]
- (ii) A solution of orange phenolphthalein solution was placed in an ice bath and turned colourless. [1]

(d) Part of the process in synthesising phenolphthalein involves the reaction of phthalic anhydride according to the reaction scheme below.





(e) Pararosaniline (PRA), another triarylmethane dye, reacts with water to form acidified pararosaniline (APRA).



0.0040 mol of PRA was dissolved in 25.0 cm<sup>3</sup> of water and the solution allowed to reach equilibrium. After equilibrium was reached, the concentration of APRA was found to be 0.10 mol dm<sup>-3</sup>.

Write an expression for  $K_c$  for the equilibrium above, and use the data given to calculate its value. You can assume that  $[H_2O] = 55.5 \text{ mol dm}^{-3}$  throughout. [3] [Total: 20 marks]

- 5 Manganese is a highly abundant transition metal in the Earth's crust.
  - (a) The atomic radii of transition elements is relatively invariant. Explain. [2]
  - (b) Manganese sulfate, MnSO<sub>4</sub>, is often added to soils to promote plant growth as manganese is an important trace element crucial to photosynthesis and chloroplast formation.

Data concerning MnSO<sub>4</sub> at 298 K, are given in the table below.

Enthalpy change of formation MnSO <sub>4</sub> / kJ mol <sup>-1</sup>	-1365
Enthalpy change of hydration of Mn <sup>2+</sup> / kJ mol <sup>-1</sup>	-1851
Enthalpy change of hydration of SO <sub>4</sub> <sup>2-</sup> / kJ mol <sup>-1</sup>	-1004
Lattice energy of MnSO <sub>4</sub> / kJ mol <sup>-1</sup>	-2747

- (i) Define the term standard enthalpy change of solution.
- (ii) Calculate the enthalpy change of solution of MnSO<sub>4</sub> at 298 K. [1]

[1]

- (iii) Using your answer in (b)(ii), calculate the amount of heat evolved when 0.005 mol of MnSO<sub>4</sub> is dissolved in 60.0 cm<sup>3</sup> of water at 298 K. Hence, determine the final temperature of the solution.
   (You may assume that the specific heat capacity of water is 4.18 J g<sup>-1</sup> K<sup>-1</sup>) [2]
- (c) To promote plant growth, 0.0530 mol dm<sup>-3</sup> MnSO<sub>4</sub> solution is added to the soil. In addition, the pH of the soil must be carefully controlled. The pH of the soil cannot exceed 6.5, because it would cause the precipitation of solid manganese (II) hydroxide, which would prevent the plants from absorbing the necessary amount of manganese.
  - (i) Using the above information, calculate the  $K_{sp}$  of manganese (II) hydroxide. [2]
  - (ii) While the pH of the soil cannot exceed 6.5 in order to promote manganese intake in plants, it cannot fall too low either. Suggest a reason. [1]

(d) Manganese can also form complexes. One such complex is  $[Mn(C_{10}H_8N_2)_3]^{2+}$ , where  $C_{10}H_8N_2$  is the bipyridine molecule. Bipyridine acts as a bidentate ligand and has the structure shown below.



Bipyridine

(i) Describe and explain the features of the bipyridine molecule that enable it to act as a *bidentate* ligand. Hence, state the type of bond formed between the ligand and the central manganese ion.

[2]

- (ii) State the shape of the  $[Mn(C_{10}H_8N_2)_3]^{2+}$  complex and draw its structure. [2]
- (e) Compound A has the molecular formula C<sub>10</sub>H<sub>13</sub>C*l*. It reacts with NaOH under aqueous conditions and heat to form B, C<sub>10</sub>H<sub>14</sub>O. A does not react with aqueous Br<sub>2</sub>.

**B** does not react with hot acidified potassium dichromate. **B** reacts with hot acidified potassium manganate to form **C**,  $C_{10}H_{12}O_3$ .

In the presence of concentrated sulfuric acid, **C** reacts to form a sweet smelling compound **D**,  $C_{10}H_8O_2$ .

Deduce the structures of A - D, and explain the chemistry of the reactions described. [7]

[Total: 20 marks]

### **END OF PAPER**

## **ST ANDREW'S JUNIOR COLLEGE**



# **JC2 Preliminary Examination**

H2 Chemistry (9729)

Paper 3 Free Response

Additional Materials: Data Booklet, Answer Booklet

### **READ THESE INSTRUCTIONS:**

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.

### Section A

Answer all questions. Marks [60]

## Section B

Answer one question. Marks [20]

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.

This document consists of 14 printed pages.

# 18 September 2019 2 hours

### **Section A**

Answer all the questions in this section.

1 (a) Use of the Data Booklet is relevant to this question.

The Hoffmann voltameter is used to electrolyse concentrated iron (III) chloride solution. The setup of the Hoffmann voltameter is shown below.



- (i) Describe the observations at the cathode and anode. Explain your answer with the aid of suitable ion-electron equations. [2] Anode (+):  $2Cl^- \longrightarrow Cl_2 + 2e$ Greenish-yellow gas was evolved at the anode. Cathode (-):  $Fe^{3+} + e \longrightarrow Fe^{2+}$ The yellow solution turned green
- (ii) State the difference in the observations at the anode when dilute aqueous iron (III) chloride solution is used instead. Explain your answer using relevant E<sup>0</sup> data. [2] Anode (+): 2H<sub>2</sub>O → O<sub>2</sub> + 4H<sup>+</sup> + 4e (equation not required)
   <u>Colourless</u> gas is evolved the <u>E°(O<sub>2</sub>/H<sub>2</sub>O) is +1.23V</u> which is <u>more negative</u> (less positive) / preferentially oxidised compared to E°(Cl<sub>2</sub>/ Cl<sup>-</sup>) = +1.36V.
- (b) The electrolysis of a hot aqueous solution of NaX yielded a reddish brown gas, X<sub>2</sub>, at the anode and hydrogen gas at the cathode. The red litmus paper turned blue when dipped into the solution at the cathode.
  - (i) Suggest the identity of the reddish brown gas X<sub>2</sub>. [1]

 $Br_2$ 

- (ii) Write an ion-electron equation for the reaction at the cathode. [1] Cathode:  $2H_2O + 2e \longrightarrow H_2 + 2OH^-$ Comments:
  - Many students chose the SHE equation. This is not correct as H+ was not mentioned to be present.
- (iii) Some of the X<sub>2</sub> dissolved in the alkaline medium to form X<sup>-</sup> and XO<sub>3</sub><sup>-</sup> ions.
   Write a balanced equation to represent the reaction of X<sub>2</sub> in alkaline medium.

 $3Br_2 + 6OH^- \longrightarrow 5Br^- + BrO_3^- + 3H_2O$ 

- (iv) Describe a chemical test, which does not involve silver nitrate, that could distinguish between sodium chloride and sodium iodide. [2] Add Br₂ (aq).
  For KC*I*, orange Br₂ is not decolourised.
  For KI, orange solution of Br₂ turns brown.
  2I<sup>-</sup> + Br₂ → I₂ + 2Br<sup>-</sup>
- (c) Describe and explain how the thermal stability of the hydrogen halides varies down Group 17. [2]
   Down the group, size of halogen increases, leading to less effective orbital overlap between H and X.
   Bond energy of H X decreases / H-X bond is longer and weaker and is easily broken. Thus, thermal stability of hydrogen halides decreases down the group.
- (d) When methylcyclopentane is treated with a small quantity of chlorine in the presence of ultraviolet light, 4 mono-chlorinated constitutional isomers are produced. Draw the structures of the isomers and state the ratio in which they are formed.



- (e) SiCl<sub>4</sub> reacts readily with water to form a solution of pH 2. However, SiO<sub>2</sub> does not react with water and only reacts with hot concentrated alkali such as NaOH.
  - (i) Explain why SiCl₄ reacts readily with water, but SiO₂ only reacts with hot concentrated NaOH. Use relevant equations to explain your answer. [3] SiCl₄ has energetically available vacant orbitals to accept lone pair of electrons from H₂O and undergo complete hydrolysis. SiCl₄(I) + 2H₂O(I) →SiO₂(s) + 4HCl(aq)

SiO<sub>2</sub> is an acidic oxide and reacts with basic/ionic NaOH. SiO<sub>2</sub>(s)+ 2NaOH (conc.)  $\rightarrow$  Na<sub>2</sub>SiO<sub>3</sub>(aq) + H<sub>2</sub>O(*I*)

SiO<sub>2</sub> is a <u>giant covalent structure with strong covalent bonds</u>, requiring a <u>lot of energy to overcome/break</u>, and hence does not reacts with / not soluble in water.

(ii) Using Cl<sub>2</sub>(g) as an example, define the term *bond energy*. [1]
 Bond energy is the enthalpy change to break <u>one mole of CI-CI bonds</u> in <u>gaseous state</u>.

OR Cl<sub>2</sub>(g)  $\rightarrow$  2Cl(g)

(iii) Construct an energy level diagram to calculate the enthalpy change of formation of SiCl<sub>4</sub>.

Your diagram should include relevant data from the *Data Booklet* together [3] with the following data:

Enthalpy change of atomisation of Si = +338 kJmol<sup>-1</sup> Enthalpy change of vapourisation of SiC $l_4$  = +29 kJmol<sup>-1</sup>



[Total: 21 marks]

[1]

2 (a) Phosphorus-containing compounds can react in various ways: as an acid, as a base, as an electrophile, as a nucleophile, as an oxidising agent and as a reducing agent.

Study the following reactions and decide in which way the phosphorus-containing compound is reacting in each case. Explain your answers fully.

(i)  $H_3PO_4 + H_2O \rightarrow H_2PO_4^- + H_3O^+$ Acid . <u>donate proton (or H<sup>+</sup>)</u> to the water molecule.



It was oxidised due to the <u>addition of O</u> or Oxidation state of P decreased from +3 to +5 OR

 $(CH_3)_3NO$  was reduced since there was a loss of O or Oxidation state of N decreased from -1 to -3



Nucleophile.

The <u>lone pair of electrons</u> on the P attacks the electron deficient C of  $CH_3Br$  via nucleophilic substitution.

(b) 2-chloropropanoyl chloride, W, can be obtained from propanoic acid by heating it with Cl<sub>2</sub> and PCl<sub>5</sub>.

Reaction 1:

 $CH_{3}CH_{2}CO_{2}H(l) + Cl_{2}(g) + PCl_{5}(s) \rightarrow CH_{3}CHClCOCl(l) + 2HCl(g) + POCl_{3}(l)$  W

 $\Delta H > 0$ 

- (i) Explain the different reactivities of the two chlorine atoms in W towards water.
   [2] The carbonyl carbon of acyl chloride is bonded to 2 electronegative O and Cl making it highly electron deficient, while the carbon of the alkyl chloride is only bonded to Cl. Hence, acyl chloride is more susceptible to the attack of nucleophiles (water).
- (ii) Explain fully why the pH of an aqueous solution of 2-chloropropanoyl chloride is 1.0 while that of an aqueous solution of propanoic acid of the same concentration is greater than 1.0. [2]
   Aqueous 2-chloropropanoyl chloride is more acidic than aqueous propanoic acid. 2-chloropropanoyl chloride <u>hydrolyses fully in water</u> to form a carboxylic acid and <u>HC*I* which is a strong acid</u> which dissociates fully in water. <u>Propanoic acid dissociates partially</u> in water. OR

 $CH_{3}CHC/COCl + H_{2}O \longrightarrow CH_{3}CHC/COOH + H^{+} + Cl^{-}$   $CH_{3}CH_{2}COOH + H_{2}O \longleftarrow CH_{3}CH_{2}COO^{-} + H_{3}O^{+}$ 

(iii) W can be used to produce sweet-smelling Z,  $C_6H_8O_4$ , via compounds X and Y, as shown in Fig. 2.1

$$\mathbf{W} \xrightarrow{\text{NaOH}(\text{aq})} \mathbf{X} \xrightarrow{\text{H}_2\text{SO}_4(\text{aq})} \mathbf{Y} \xrightarrow{\text{conc H}_2\text{SO}_4} \mathbf{Z}$$

Suggest structures for compounds **X**, **Y** and **Z** in Fig. 2.1. [3]

- X: CH<sub>3</sub>CH(OH)CO<sub>2</sub><sup>-</sup>Na<sup>+</sup>
- **Y**: CH<sub>3</sub>CH(OH)CO<sub>2</sub>H





(iv) W can undergo the following reaction scheme.



[2]

State the reagents and conditions for Steps 1 and 2. Step 1: (excess) CH<sub>3</sub>NH<sub>2</sub>, heat Step 2: LiA/H<sub>4</sub>, dry ether

(v) V is an isomer of W.

**V** rotates the plane of polarised light. It gives a positive test with 2,4-dinitrophenylhydrazine.

Draw the displayed formula of **V**, identifying the chiral carbon. [1]



(vi) Use the table of characteristic values for infra-red absorption frequencies in the *Data Booklet* to answer this question.

Infra-red adsorption frequencies can be used to identify functional groups in organic compounds. For example, propanol shows absorptions at 970–1250cm<sup>-1</sup> and 3580–3620 cm<sup>-1</sup>.

Use the table to suggest how infra-red absorption range can be used to distinguish 2-chloropropanoyl chloride from propanoic acid. [1] 2-chloropropanoyl chloride will have an absorption at 700–800cm<sup>-1</sup> but propanoic acid would not have. OR Propanoic acid will have an absorption at 1210–1440cm<sup>-1</sup> but 2chloropropanoyl chloride would not have. OR Propanoic acid will have an absorption at 3580–3650cm<sup>-1</sup> but 2chloropropanoyl chloride would not have.

(vii) Given that reaction 1 is endothermic, explain why the reaction will only take place with heating. [2]  $\Delta G = \Delta H - T\Delta S$  $\Delta H$  is positive and  $\Delta S$  will be positive as more gaseous molecules formed [1]. Hence, a high temperature is required such that  $|T\Delta S| > |\Delta H|$  so  $\Delta G < 0$ [1]

#### [Total : 16 marks]

- **3** There are 2 isomers of 2-methylbutanoic acid, CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)COOH (M<sub>r</sub> 102.0) ; one of the isomers is sweet-smelling and the other has a stinky odour.
  - (a) (i) State the stereoisomerism exhibited by 2-methylbutanoic acid and how it arises.
     [2]

Enantiomerism

Any of the following 2 explanations

- the mentioning of two non-superimposable mirror images
- explanation in terms of diagram illustrating non-superimposable enantiomer

- (ii) Hence, explain why the isomers have different smells. [1]
   Either
   Different enantiomers interact differently with the chiral molecules in the human body
   OR
   Different enantiomers have different biological properties
- (b) Suggest a 2 stage synthesis of 2–methylbutanoic acid from 2–bromobutane. State reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds.
   [3]

Step 1: alcoholic KCN, heat

Step 2: aqueous H<sub>2</sub>SO<sub>4</sub>, heat

Intermediate: CH<sub>3</sub>CH(CN)CH<sub>2</sub>CH<sub>3</sub>



Allow for any strong acid solutions (e.g. dil HCl)

(c) Safety regulations set by many countries state that a factory would be fined, if stinky smelling compounds reached unsafe levels. The factory would have to stop production and undergo cleansing.

When 2-methylbutanoic acid was synthesised using 2-bromobutane in a factory, both the sweet-smelling and the stinky isomers were obtained in equal proportions.

(i) The M<sub>r</sub> of 2–methylbutanoic acid in the liquid phase is 204.0.
 With the aid of a diagram, explain the above. [2]
 2–methylbutanoic acid is a polar covalent molecule with hydrogen bonding between its molecules.



(ii) 2-methylbutanoic acid has a relatively low boiling point of 176 °C at 1 atm, and hence vaporises easily. This poses a problem when adhering to safety regulations.

In a factory, during the synthesis of 2–methylbutanoic acid, the workers did not seal the chemical container properly.

Given that the enthalpy change of vaporisation of 2–methylbutanoic acid is +59.1 kJ mol<sup>-1</sup>, use the following equation (Clausius–Clapeyron Equation) to determine the vapour pressure of 2–methylbutanoic acid in the factory at night when the temperature was 30.2 °C.

$$\ln P = \frac{\Delta H_{\text{vaporisation}}}{R} \left(\frac{1}{T_{\text{b.p.}}} - \frac{1}{T}\right)$$

P = vapour pressure in atm at temperature T K  $\Delta H_{vaporisation} = \text{enthalpy change of vaporisation of the substance in J mol^{-1}}$ R = universal gas constant T<sub>b.p.</sub> = boiling point of the substance in K at 1 atm  $\ln P = \frac{59100}{8.31} \left( \frac{1}{273 + 176} - \frac{1}{273 + 30.2} \right)$ P = 4.92 × 10<sup>-4</sup> atm

[2]

[2]

(iii) Safety protocols dictated that stinky smelling substances above 300 ppm (parts per million) is considered a safety hazard and likely to be fined.
 Based on your answers in (a)(i) and (c)(ii), and given that the pressure in the factory is 1 atm, determine whether the factory would be fined.

 $[1 \times 10^{-6} \text{ atm in } 1 \text{ atm } = 1 \text{ ppm}]$ Mole fraction of the odorous 2–methylbutanoic acid



(d) Ethyl 2–methylbutanoate is an ester which is commonly found in citrus fruits, such as pineapple and oranges. It is commonly used as the starting material to form the sweet–smelling 2–methylbutanoic acid via hydrolysis.



ethyl 2-methylbutanoate

The rate equation for the hydrolysis of esters was determined by a series of experiments. The hydrolysis of the ester, ethyl 2–methylbutanoate, was carried out, using 0.75 mol dm<sup>-3</sup> hydrochloric acid. The experiment was repeated using 0.75 mol dm<sup>-3</sup> sulfuric acid. The following graphs were obtained.



Using the graphs above, deduce the order of reaction with respect to [H<sup>+</sup>] and [ester]. Hence, write the rate equation of the hydrolysis of the ester, ethyl 2–methylbutananoate.

[3]









12

#### Gradients of the lines



Change in concentration of ester =  $0.007 \text{ mol dm}^{-3}$ Time taken for HC*l* curve = 15 min Time taken for H<sub>2</sub>SO<sub>4</sub> curve = 7.5 min Rate for HC*l* curve =  $4.67 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$ Rate for H<sub>2</sub>SO<sub>4</sub> curve =  $9.33 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$ 

Half life of line using HC*l* is 27 minutes, and half life of line using  $H_2SO_4$  is 13.5 minutes. Order of reaction with respect to [ester] is 1. Half life of the 2 lines decrease to half when [H<sup>+</sup>] was doubled, order of reaction with respect to [H<sup>+</sup>] is 1. rate = k[H<sup>+</sup>][ester]

(ii) Calculate the rate constant for the hydrolysis of ethyl 2-methylbutanoate, including its units.

[2]

$$\mathbf{k} = \frac{\ln 2}{\mathbf{t}_{1/2}[\mathsf{H}^+]}$$

 $= \frac{\ln 2}{27(0.75)} \text{ (values used here must be correct, part (i) } t_{1/2})$  $= 0.0342 \text{ [1] mol}^{-1} \text{ dm}^3 \text{ min}^{-1} \text{ (may also use } t_{1/2} \text{ for } \text{H}_2\text{SO}_4\text{)}$ If student calculates k' = 0.0257 min}^1

Can use initial rates from one experiment – ecf from gradient in (i) Rate =  $k[H^+][Ester]$ 4.67 × 10<sup>-4</sup> = k(0.75)(0.015) – using HCI values k = 0.0415 mol<sup>-1</sup> dm<sup>3</sup> min<sup>-1</sup> OR 9.33 × 10<sup>-4</sup> = k(1.5)(0.015) – using H<sub>2</sub>SO<sub>4</sub> values k = 0.0415 mol<sup>-1</sup> dm<sup>3</sup> min<sup>-1</sup>

(iii) In the absence of an acid, the hydrolysis of the ester is very slow.
 With the aid of a relevant diagram, explain how the rate constant would change if the acid was removed.



With the absence of the catalyst, the <u>activation energy was larger</u> than the catalysed reaction pathway. The proportion of particles with <u>energy equal to or greater than the activation</u> <u>energy is smaller.[1]</u> The <u>frequency of effective collisions decreases</u> and hence the <u>rate</u> <u>constant decreases</u>[1].

(e) Ethyl 2-methylbutanoate can also be formed using 2-methylbutanoyl chloride and ethanol.

The reaction takes place under anhydrous conditions as 2-methylbutanoyl chloride undergoes hydrolysis in water to form 2-methylbutanoic acid.

The hydrolysis of 2-methylbutanoyl chloride occurs via a two-stage mechanism:

• The first stage (the addition stage of the reaction) involves a nucleophilic attack on the partial positive carbon atom by one of the lone pairs of electrons on the oxygen atom of a water molecule, giving intermediate **E**.



intermediate E

The second stage (the elimination stage) happens in two steps.

- 1. The carbon-oxygen double bond reforms with a chloride ion as the side product.
- A hydrogen ion is removed by the chloride ion to give
   2-methylbutanoic acid and hydrogen chloride.

Outline the mechanism for this reaction, given that intermediate **E** is formed after the first stage. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows. [3]

First stage



[Total: 23 marks]

### **Section B**

Answer **one** question from this section.

4 Phenolphthalein, a type of triarylmethane dye, is a common indicator used in acid-base titrations.



#### Phenolphthalein

In its uncharged form, aqueous phenolphthalein is colourless. At pH of 8.2 and above, both phenol groups are deprotonated to form a pink solution.

- (a) The p $K_b$  for trimethylamine, (CH<sub>3</sub>)<sub>3</sub>N, at 25 °C is 4.19.
  - (i) Trimethylamine can behave as a Lewis base. Use the reaction of trimethylamine with aluminium chloride to illustrate this behaviour, writing the equation for the reaction that occurs. [1]
     (CH<sub>3</sub>)<sub>3</sub>N + A/Cl<sub>3</sub> → (CH<sub>3</sub>)<sub>3</sub>N-A/Cl<sub>3</sub>
  - (ii) Calculate the pH of an aqueous solution of 0.20 mol dm<sup>-3</sup> trimethylamine solution. [1]  $K_b = 10^{-4.19} = 6.46 \times 10^{-5} \text{ mol dm}^{-3}$  $[OH^-] = \sqrt{6.46 \times 10^{-5} \times 0.2} = 3.59 \times 10^{-3} \text{ mol dm}^{-3}$ pOH = 2.44, pH = 11.56
  - (iii) Calculate the pH of the resulting solution when 10 cm<sup>3</sup> of 0.20 mol dm<sup>-3</sup> trimethylamine solution and 5 cm<sup>3</sup> of 0.10 mol dm<sup>-3</sup> HC*l* solution are mixed. [2] Amount of trimethylamine remaining = 2 x 10<sup>-3</sup> – 5 x 10<sup>-4</sup> = 1.5 x 10<sup>-3</sup> mol Amount of salt formed = 5 x 10<sup>-4</sup> mol pOH = pK<sub>b</sub> + lg [salt]/[base] = 4.19 + lg ( $\left[\frac{5 \times 10^{-4}}{\frac{15}{1000}}\right] / \left[\frac{1.5 \times 10^{-3}}{\frac{15}{1000}}\right]$ ) = 3.71 pH = 10.29

- (iv) Calculate the pH of the resultant solution when 20 cm<sup>3</sup> of 0.10 mol dm<sup>-3</sup> HC*l* solution is added to 10 cm<sup>3</sup> of 0.20 mol dm<sup>-3</sup> trimethylamine solution. [2] Amt of salt formed = 2 x 10<sup>-3</sup> mol [salt] = 2 x 10<sup>-3</sup> / (10+20) = 0.0667 mol dm<sup>-3</sup> [conj. Acid] = [salt] = 0.0667 mol dm<sup>-3</sup> K<sub>a</sub> of conj acid = K<sub>w</sub>/K<sub>b</sub> = 1.55 x 10<sup>-10</sup> mol dm<sup>-3</sup> [H<sup>+</sup>] =  $\sqrt{1.55 \ x \ 10^{-10} \ x \ 0.0667}$  = 3.21 x 10<sup>-6</sup> pH = 5.49
- (v) Explain why phenolphthalein would not be a suitable indicator for the titration of trimethylamine with HC*l*.
   The working range of phenolphthalein does not coincide with the equivalence point pH / region of rapid pH change in the titration curve / vertical section of the titration curve.
   OR
   Phenolphthalein will turn colourless at pH 8.2 before the equivalence point is reached.
- (vi) Methylamine has a pK<sub>b</sub> of 3.36. Suggest a reason for the difference in basicity between methylamine and trimethylamine. [1]
   Trimethylamine is less basic than methylamine due to the steric effects of the 3 bulky methyl groups, hence it cannot accept protons easily.
- (b) Draw the structural formula of the product formed when phenolphthalein reacts with each of the following reagents:
  - (i) excess  $Br_2$  in the presence of  $A/Br_3$ .

[2]



(ii) sodium hydroxide with heat.



(c) Under extremely acidic conditions (pH < 0), phenolphthalein can be protonated to form an orange solution. This is an endothermic process.</p>

+

[2]



Use Le Chatelier's Principle to explain the following observations.

- (i) An aqueous solution of phenolphthalein changed from colourless to orange when concentrated sulfuric acid was added to it. [1] The addition of concentrated sulfuric acid increases the concentration of H<sup>+</sup>. By LCP, the position of equilibrium will shift right to reduce the concentration of H<sup>+</sup> ions, thus forming more orange phenolphthalein.
- (ii) A solution of orange phenolphthalein solution was placed in an ice bath and turned colourless. [1]
   When a solution of phenolphthalein was cooled, the position of equilibrium will shift left to produce heat by favouring the exothermic backwards reaction. Hence more colourless phenolphthalein is formed and the solution turns colourless.
- (d) Part of the process in synthesising phenolphthalein involves the reaction of phthalic anhydride according to the reaction scheme below.



19

(i) Name and describe the type of mechanism in Step II.



(e) Pararosaniline (PRA), another triarylmethane dye, reacts with water to form acidified pararosaniline (APRA).



0.0040 mol of PRA was dissolved in 25.0 cm<sup>3</sup> of water and the solution allowed to reach equilibrium. After equilibrium was reached, the concentration of APRA was found to be 0.10 mol dm<sup>-3</sup>.

Write an expression for  $K_c$  for the equilibrium above, and use the data given to calculate its value. You can assume that  $[H_2O] = 55.5 \text{ mol dm}^{-3}$  throughout. [3]  $K_c = [APRA] / \{[PRA][H_2O]\}$ 

 $[PRA]_{initial} = 0.004 / 25 \times 1000 = 0.16 \text{ mol dm}^{-3}$ 

	PRA	+	H <sub>2</sub> O <->	APRA
Initial / mol dm <sup>-3</sup>	0.16		55.5	0
Change / mol dm <sup>-3</sup>	-0.10		0	+0.10
Final / mol dm <sup>-3</sup>	0.06		55.5	0.10

 $K_c = 0.10 / (0.06 \times 55.5) = 0.0300 \text{ mol}^{-1} \text{ dm}^3$ 

[Total: 20 marks]

[2]

[1]

- 5 Manganese is a highly abundant transition metal in the Earth's crust.
  - (a) The atomic radii of transition elements is relatively invariant. Explain.

Electrons are added to <u>inner</u> 3d subshell. The inner 3d electrons <u>effectively</u> <u>shield</u> the outer 4s electrons from the nucleus, <u>cancelling the effect</u> of the increasing nuclear charge due to increasing proton number across the period.

Thus, the *increase* in effective nuclear charge becomes *insignificant*.

Hence atomic radii remains relatively invariant.

(b) Manganese sulfate, MnSO<sub>4</sub>, is often added to soils to promote plant growth as manganese is an important trace element crucial to photosynthesis and chloroplast formation.

Data concerning MnSO<sub>4</sub> at 298 K, are given in the table below.

Enthalpy change of formation MnSO <sub>4</sub> / kJ mol <sup>-1</sup>	-1365
Enthalpy change of hydration of Mn <sup>2+</sup> / kJ mol <sup>-1</sup>	-1851
Enthalpy change of hydration of SO <sub>4</sub> <sup>2-</sup> / kJ mol <sup>-1</sup>	-1004
Lattice energy of MnSO <sub>4</sub> / kJ mol <sup>-1</sup>	-2747

- (i) Define the term standard enthalpy change of solution. The enthalpy change when <u>one mole of a substance is completely</u> <u>dissolved in a large excess of water</u> to form an infinitely dilute solution at <u>298 K and 1 bar</u>.
- (ii) Calculate the enthalpy change of solution of MnSO<sub>4</sub> at 298 K. [1]  $\Delta H_{soln}^{\Theta} = \Delta H_{hyd}^{\Theta} - L.E. = (-1851 - 1004) - (-2747) = -108 \text{ kJ mol}^{-1}$
- (iii) Using your answer in (b)(ii), calculate the amount of heat evolved when 0.005 mol of MnSO<sub>4</sub> is dissolved in 60.0 cm<sup>3</sup> of water at 298 K. Hence, determine the final temperature of the solution.
   (You may assume that the specific heat capacity of water is 4.18 J g<sup>-1</sup> K<sup>-1</sup>) [2]
Heat evolved = 0.005 x 108 = 0.54 kJ  $Q = mc\Delta T$   $\Delta T = Q/mc = (0.54x \ 10^3)/(60x4.18) = 2.15 \ ^{\circ}C / K$ T = 298 + 2.15 = 300 K (3s.f.)

- (c) To promote plant growth, 0.0530 mol dm<sup>-3</sup> MnSO<sub>4</sub> solution is added to the soil. In addition, the pH of the soil must be carefully controlled. The pH of the soil cannot exceed 6.5, because it would cause the precipitation of solid manganese (II) hydroxide, which would prevent the plants from absorbing the necessary amount of manganese.
  - (i) Using the above information, calculate the  $K_{sp}$  of manganese (II) hydroxide. [2]

pOH = 14 - 6.5 = 7.5 [OH<sup>-</sup>] = 3.16 x 10<sup>-8</sup> mol dm<sup>-3</sup> Mn(OH)<sub>2</sub>(s) → Mn<sup>2+</sup> (aq) + 2OH<sup>-</sup>(aq) K<sub>sp</sub> = [Mn<sup>2+</sup>][OH<sup>-</sup>]<sup>2</sup> = (0.0530) x (3.16 x 10<sup>-8</sup>)<sup>2</sup> = 5.29 x 10<sup>-17</sup> mol<sup>3</sup> dm<sup>-9</sup>

(ii) While the pH of the soil cannot exceed 6.5 in order to promote manganese intake in plants, it cannot fall too low either. Suggest a reason. [1] The soil would be too acidic and may damage the roots of plants. OR

Too much manganese would be absorbed and it is biologically toxic when in excess amounts.

(d) Manganese can also form complexes. One such complex is  $[Mn(C_{10}H_8N_2)_3]^{2+}$ , where  $C_{10}H_8N_2$  is the bipyridine molecule. Bipyridine acts as a bidentate ligand and has the structure shown below.



Bipyridine

(i) Describe and explain the features of the bipyridine molecule that enable it to act as a *bidentate* ligand. Hence, state the type of bond formed between the ligand and the central manganese ion.

[2]

There are <u>two nitrogen atoms, each with a lone pair of electrons</u>, which can be donated to vacant low-lying orbitals of the manganese ion to form <u>2 dative bonds</u>.

(ii) State the shape of the [Mn(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>3</sub>]<sup>2+</sup> complex and draw its structure. [2]
 Shape: Octahedral



(e) Compound A has the molecular formula C<sub>10</sub>H<sub>13</sub>C*l*. It reacts with NaOH under aqueous conditions and heat to form B, C<sub>10</sub>H<sub>14</sub>O. A does not react with aqueous Br<sub>2</sub>.

**B** does not react with hot acidified potassium dichromate. **B** reacts with hot acidified potassium manganate to form **C**,  $C_{10}H_{12}O_3$ .

In the presence of concentrated sulfuric acid,  $\bm{C}$  reacts to form a sweet smelling compound  $\bm{D},\,C_{10}H_8O_2.$ 

Deduce the structures of A - D, and explain the chemistry of the reactions described.

[7]

Observations	Deductions	
Reacts with NaOH under aqueous	CI is substituted by OH	
conditions to form B, $C_{10}H_{14}O$ .	Nucleophilic substitution.	
	Alcohol formed.	
	A is alky chloride	
A does not react with aqueous Br <sub>2</sub> .	No alkene present.	
B does not react with acidified	OH group cannot be oxidised, alcohol is	
potassium dichromate.	a <u>tertiary alcohol</u>	

B reacts with hot acidified potassium	Since –OH group is tertiary alcohol and
manganate to form $\mathbf{C}$ , $C_{10}H_{12}O_3$ .	cannot be oxidised, it does not react
	with KMnO <sub>4</sub> . Hence, must be some
	other form of oxidation.
	Cannot be alkene due to earlier test.
	Since 2 H was lost and 2 O was added,
	then most likely to be side chain
	$\underline{oxidation}$ of $CH_3$ on benzene to form
	- <u>COOH</u> .
	Benzene ring present.
In the presence of concentrated sulfuric	Condensation reaction.
acid, C reacts to form a sweet smelling	D is an ester. Internal condensation
compound <b>D</b> , $C_{10}H_8O_2$ .	occurred between the OH group and

occurred between the OH group and the COOH group.

This implies the <u>two groups must be</u> next to each other on the benzene ring.







В





[Total: 20 marks]

**END OF PAPER** 

**ST ANDREW'S JUNIOR COLLEGE** 

Class



Chemistry (9729)

# **Paper 4 Practical**

Candidates answer on the Question Paper

Additional Materials : As listed in the Confidential Instructions

: Insert

# READ THESE INSTRUCTIONS FIRST.

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

Give details of the practical shift and laboratory in the boxes provided above. 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** the questions in the spaces provided on the Question Paper.

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

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed on pages 21 and 22.

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

For Examiner's use:

Question	Practical	Planning	Total
Marks	44	11	55

This document consists of 22 printed pages.

27 Aug 2019

2.5 hours

Laboratory

Shift

TION



- 1 To standardise a 0.03 mol dm<sup>-3</sup> of iron(III) chloride solution and determine the concentration of sodium thiosulfate solution.
  - (a) Planning

**FA1** is a standard solution containing 0.03 mol dm<sup>-3</sup> of FeCl<sub>3</sub> solution.

You are to design an experiment to show how FA1 is prepared using solid  $FeCl_3$ .

You are provided with :

a solid sample of approximately 1.50 g of  $FeCl_3$  (M<sub>r</sub> = 162.3),

250 cm<sup>3</sup> volumetric flask and

the usual laboratory apparatus

In your plan, you should include details on:

- the mass of FeCl<sub>3</sub>(s) you use with justification,
- the apparatus you would use, and
- the procedures which you would follow.

Do not carry out this plan as FA1 is provided for you to continue with 1(b).

[3]

1 (b) In addition to FA1, you are also provided with the following:

**FA2** is 0.060 mol dm<sup>-3</sup> potassium iodide, KI.

**FA3** is aqueous sodium thiosulfate,  $Na_2S_2O_3$ .

When **FA1** is combined with **FA3**, a complex,  $[Fe(S_2O_3)_2]^-$ , is formed.

**Reaction 1:**  $Fe^{3+}(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Fe(S_2O_3)_2]^{-}(aq)$ 

To 1 cm<sup>3</sup> of **FA3** in a test–tube, add 2–3 drops of **FA1** and shake them thoroughly. State the colour of the complex formed.

Colour : .....

[1]

(c) A student aimed to determine the concentration of **FA3** using volumetric analysis involving the use of **FA1** and **FA2**.

**Reaction 2:**  $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$ 

**Reaction 3:**  $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$ 

Using the above reactions, the student planned and carried out the following procedure.

- 1. Fill a 50.00  $\text{cm}^3$  burette with **FA3** solution.
- Using a 10 cm<sup>3</sup> measuring cylinder, measure 5 cm<sup>3</sup> of FA1 and place it in a 100 cm<sup>3</sup> conical flask.
- Using another 10 cm<sup>3</sup> measuring cylinder, measure 5 cm<sup>3</sup> of FA2 into the conical flask.
- 4. Run **FA3** from the burette into the conical flask. Near the endpoint, when the brown solution becomes pale, add 2 drops of starch.
- 5. Continue adding **FA3** slowly, the endpoint is reached when the solution **first becomes colourless**.
- 6. Record the titration results, to an appropriate level of precision, in an appropriate table and repeat the experiment once more.

1 (c) (i) Carry out the student's procedure <u>twice only</u> to obtain two titration readings. <u>Your titre values need not be consistent</u>.

Note: After the end point is reached, you may observe the appearance of the coloured mixture again. There is no need to titrate any further.

Record your titration in an appropriate table in the space below.

# (ii) Planning

A teacher commented that it is appropriate for the student to use 5 cm<sup>3</sup> instead of 25 cm<sup>3</sup> of **FA1** for this titration. Justify the teacher's comment using suitable calculations.

Assume the concentration of **FA3** is 0.006 mol dm<sup>-3</sup>.

# 1 (c) (iii) Planning

Justify whether the amount of **FA2** that the student used in step **3** of the procedure in **1(c)** is sufficient to determine the concentration of **FA3**.

(iv) The student did the titration several times but could not get consistent titre values of FA3. Based on your observation during titration, suggest a reason why.

 •••
 [1]

(v) Suggest another reason why the results obtained are not reliable.

 [1]

(c) (vi) The student performed the titration and had a titration value of 18.50 cm<sup>3</sup>. Given the errors (uncertainties) associated with each reading using a measuring cylinder and burette are ±0.1 cm<sup>3</sup> and ±0.05 cm<sup>3</sup> respectively, calculate the maximum total percentage error (uncertainty) from the apparatus in the titration.

[3]

[Total: 14 marks]

**2** To investigate the kinetics of the reaction between iron(III) ions and iodide ions In this experiment, you are investigating the rate of reaction between iron(III) ions and iodide ions.

You are provided with: **FA1** is 0.03 mol dm<sup>-3</sup> of FeC $l_3$  solution **FA2** is 0.060 mol dm<sup>-3</sup> potassium iodide, KI **FA3** is sodium thiosulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

The reaction is started by mixing a solution of iron(III) chloride with sodium thiosulfate, potassium iodide, and starch. The iodine,  $I_2$ , produced in **reaction 2** reacts immediately with thiosulfate ions,  $S_2O_3^{2-}$  in **reaction 3**.

**Reaction 1:** Fe<sup>3+</sup>(aq) + 2S<sub>2</sub>O<sub>3</sub><sup>2−</sup>(aq)  $\rightleftharpoons$  [Fe(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>]<sup>−</sup>(aq) **Reaction 2:** 2Fe<sup>3+</sup>(aq) + 2I<sup>−</sup>(aq) → 2Fe<sup>2+</sup>(aq) + I<sub>2</sub>(aq)

Reaction 3:  $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$ 

When all the thiosulfate have been used, the iodine produced will turn starch indicator blue–black. The rate of the reaction can therefore be determined by finding the time for the blue–black colour to appear.

You are advised to read the instructions before starting any practical work and draw a table, in an appropriate format, for your results in the space on page 10.

For each of the five experiments, you will need to include the

- volume of FA2, V<sub>FA2</sub>,
- volume of water, V<sub>water</sub>,
- calculated squared volume of FA2, (V<sub>FA2</sub>)<sup>2</sup>,
- reaction time, *t* to nearest second, and
- calculated rate in mol dm<sup>-3</sup> s<sup>-1</sup>

Record all calculated values to 3 significant figures.

# 2 (a) Method

#### **Experiment 1**

- 1. Use the measuring cylinders to measure the following:
  - 20 cm<sup>3</sup> of **FA1**
  - 20 cm<sup>3</sup> of **FA3**
  - 1 cm<sup>3</sup> of starch indicator
- 2. Using another measuring cylinder, measure 10 cm<sup>3</sup> of FA2.
- 3. Pour the measured **FA1** and starch into a dry 100 cm<sup>3</sup> beaker.
- 4. Pour in the **FA3**, followed by **FA2** <u>immediately</u> into the same beaker. Start the stopwatch on adding **FA2**.
- 5. Stir the mixture and place the beaker on the printed page on page 2 of the insert.
- 6. The mixture turns brown and then yellow before turning a blue–black colour. Stop the stopwatch when this blue–black colour appears and obscures the wordings.
- 7. Record the time to the nearest second in the space on page 10.
- 8. Wash the beaker thoroughly with water and carefully dry the beaker with paper towel.

# **Experiment 2**

- 9. Repeat step 1 in Experiment 1.
- 10. Using a measuring cylinder, add 2 cm<sup>3</sup> of **FA2.** Make up the volume to 10 cm<sup>3</sup> using deionised water using another measuring cylinder.
- 11. Pour the measured **FA1**, starch and deionised water into a dry 100 cm<sup>3</sup> beaker.
- 12. Pour in the **FA3**, followed by **FA2** <u>immediately</u> into the same beaker. Start the stopwatch on adding **FA2**.
- 13. Stir the mixture and place the beaker on the printed page on page 2 of the insert.

- 14. Stop the stopwatch when this blue–black colour appears and obscures the wordings.
- 15. Record the time to the nearest second in the space on page 10. The timing should not exceed 6 minutes.
- 16. Wash the beaker thoroughly with water and carefully dry the beaker with paper towel.

# Experiments 3-5

Carry out three further experiments to investigate the effect of changing the concentration of **FA2** by altering the volume of aqueous potassium iodide, **FA2**, used.

You should use a volume of **FA2** that is at least 2 cm<sup>3</sup> and the total volume of the reaction mixture must always be 51 cm<sup>3</sup>.

2 (a) With reference to 1(b), consider the colour change observed when FA2 was added to the solution prepared in step 6 of Experiment 1 before the blue-black colour appeared. Suggest an explanation for the sequence of colour change in terms of the chemistry involved.

[2]

2 (b) Show, by means of calculation, that the change in the concentration of I<sup>-</sup>,  $\Delta$ [I<sup>-</sup>], which occurred when the blue-black colour appeared was  $2.35 \times 10^{-3} \text{ mol dm}^{-3}$ .

Assume the concentration of  $Na_2S_2O_3$  to be 0.006 mol dm<sup>-3</sup>.

# (c) Results

The rate of the reaction can be calculated as shown.

rate = 
$$\frac{\Delta[1]}{\text{reaction time}}$$

Calculate the rate of reaction for each experiment and complete your table.

2 (d) (i) Plot a graph of rate on the y-axis against  $(V_{FA2})^2$  on the x-axis on the grid in Figure 2.1. Draw the best fit line taking account of all the plotted data points.





[4]

2 (d) (ii) Explain why the volume of FA2 in each experiment can be used as the [I<sup>-</sup>].

(iii) Deduce the order of reaction with respect to [I<sup>-</sup>]. Use evidence from your graph to support your deduction.

Order of reaction with respect to  $[I^-]$ : ...... [1]

(e) (i) Use your graph and the formula in 2(c) to calculate the time that the reaction would have taken if 5.0 cm<sup>3</sup> of FA2 had been used. Show your working clearly.

time = ..... [2]

2 (e) (ii) Calculate the initial concentration of iron(III) ions and the initial concentration of iodide ions in the reaction mixture if 5.0 cm<sup>3</sup> of FA2 had been used.

initial [Fe<sup>3+</sup>] = .....[1] initial [I<sup>-</sup>] = .....

(iii) Given that the reaction is first order with respect to [Fe<sup>3+</sup>], calculate the rate constant.

rate constant = .....[2]

(f) At the end of Experiment 1, a student washed the beaker and used it immediately for Experiment 2. State and explain how the student's action would affect the time *t* for Experiment 2.

[Turn Over

2 (g) List 1 possible source of experimental errors and suggest the corresponding improvement to reduce the experimental error.

[2]

[Total: 22 marks]

# 3 Qualitative Analysis

You are provided the following reagents and the *Qualitative Analysis Notes* on page 21 and 22.

**FA1** is 0.03 mol dm<sup>-3</sup> of FeC $l_3$  solution

**FA4** is 6% volume  $H_2O_2$ 

**FA5** is 0.00215 mol dm<sup>-3</sup> of **X<sup>-</sup>** solution

(a) You are to perform the tests described in **Table 3.1** and record your observations in the same table.

Your answers should include

- details of colour changes throughout the tests and precipitates formed,
- the identity of any gases evolved, and details of the test used to identify each one.

You should indicate clearly at what stage in a test a change occurs.

Marks are not given for chemical equations.

No additional or confirmatory tests for ions present should be attempted.

	Test	Observations
i.	To 5 cm <sup>3</sup> of <b>FA1</b> , add	
	aqueous silver nitrate in	
	excess. Filter the mixture.	
	Separate the filtrate into	
	three test tubes for (ii), (iii)	
	and <b>(iv)</b> .	
	Place the filter funnel	
	containing the residue on a	
	new test tube, add aqueous	
	ammonia over the residue.	
	Add HNO3 dropwise to the	
	filtrate until no more	
	change.	

Table 3.1

	Test	Observations
ii.	To a new test tube	
	containing 1 cm <sup>3</sup> of <b>FA4</b> ,	
	add a few drops of filtrate	
	from the first test tube from	
	(i). Wait and observe the	
	effervescence. Test for the	
	identity of the gas.	
iii.	To the second test tube	
	containing 1 cm <sup>3</sup> of filtrate	
	from (i), add aqueous	
	sodium hydroxide till	
	excess.	
	Add 1 cm <sup>3</sup> of <b>FA4</b> .	
iv.	To the last test tube	
	containing 1 cm <sup>3</sup> of filtrate	
	from (i), add 1 cm <sup>3</sup> of <b>FA5</b> .	
	<del></del>	
ν.	I o a new test tube	
	containing a fresh sample	
	of FA1, test the pH of the	
	solution with a Universal	
	indicator paper.	
	Add aqueous ammonia	
	dropwise. Add <b>FA1</b>	
	dropwise to dissolve the	
	precipitate formed. Stop	
	adding <b>FA1</b> once the	
	precipitate disappears.	

3 (b) With reference to the observation made in test (i), identify the ppt and explain its solubility in aqueous ammonia.

.....[2]

(c) In the presence of strong base,

 $H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$ 

Electrode Reaction	E <sub>0</sub> /V
Fe <sup>3+</sup> + e ≓ Fe <sup>2+</sup>	+0.77
Fe(OH) <sub>3</sub> + e ≓ Fe(OH) <sub>2</sub>	-0.56
$O_2 + 2H_2O + 2e \rightleftharpoons H_2O_2$	+0.68
$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O$	+1.23
$O_2 + H_2O + 2e \rightleftharpoons HO_2^- + OH^-$	-0.08

With reference to the electrode potential given, explain the difference in the observation for effervescence made when **FA4** is added in test (ii) and (iii).

(d) Write an equation to explain the colour of the Universal Indicator paper on addition of FA1 before adding aqueous ammonia.

.....[1]

[Turn Over

3 (e) The pH of the resultant solution in test (v) is 7. Explain the chemistry behind the changes of pH in test (v) when aqueous ammonia is added dropwise followed by FA1.

[2]

(f) Predict what happen when the resultant solution in test (v) is added to phenol.

	[1]
--	-----

# 3 (g) Planning

Thermometry is sometimes used to determine the number of ligands attached to the central metal atom or ion. One of such monodentate ligand is  $X^-$  present in **FA5**.

A student performed an experiment to determine the structural formula of the hexa-coordinated complex.

$$[Fe(H_2O)_6]^{3+} + nX^- \rightarrow [Fe(H_2O)_{6-n}X_n]^{3-n} + nH_2O \qquad \Delta H < 0$$

He used varying volumes of **FA1** and **FA5** only, while keeping the total volume of the mixture at 80 cm<sup>3</sup>. He recorded the change in temperature.

- (i) Outline how you would:
  - determine the effect of changing the volumes of FA1 and FA5 on the temperature change of the experiment and hence,
  - vary the volumes of FA1 and FA5 to form the needed hexacoordinated complex, [Fe(H<sub>2</sub>O)<sub>6-n</sub>X<sub>n</sub>]<sup>3-n</sup>.

You are provided with the same solutions, which were used in **3(a)** described. There is no need to perform the experiment.

No details regarding the use of specific apparatus are required.


(ii) The student plotted a graph and concluded that n=1 in the structural formula of [Fe(H<sub>2</sub>O)<sub>6-n</sub>X<sub>n</sub>]<sup>3-n</sup>. On the axes of Figure 3.1, sketch a graph that the student would obtain from your experiment in 3(g)(i) to draw this conclusion. Indicate the volume of FA1 that the student would use to reach this conclusion on the x-axis of the graph.



Temperature Change / °C

Volume of **FA1** used / cm<sup>3</sup>

[2]

[Total: 19 marks]

# Qualitative Analysis Notes [ppt. = precipitate]

# (a) Reactions of aqueous cations

a a tí a n	reaction with		
cation	NaOH(aq)	NH <sub>3</sub> (aq)	
aluminium, A <i>l</i> <sup>3+</sup> (aq)	white ppt. soluble in excess	white ppt. insoluble in excess	
ammonium, NH <sub>4</sub> <sup>+</sup> (aq)	ammonia produced on heating		
barium, Ba <sup>2+</sup> (aq)	no ppt. (if reagents are pure)	no ppt.	
calcium, Ca <sup>2+</sup> (aq)	white ppt. with high [Ca <sup>2+</sup> (aq)]	no ppt.	
chromium(III), Cr <sup>3+</sup> (aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess	
copper(II), Cu <sup>2+</sup> (aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution	
iron(II), Fe <sup>2+</sup> (aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess	
iron(III), Fe <sup>3+</sup> (aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess	
magnesium, Mg <sup>2+</sup> (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess	
manganese(II), Mn <sup>2+</sup> (aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess	
zinc, Zn <sup>2+</sup> (aq)	white ppt. soluble in excess	white ppt. soluble in excess	

#### (b) Reactions of anions

anion	reaction				
carbonate, CO <sub>3</sub> <sup>2–</sup>	CO <sub>2</sub> liberated by dilute acids				
chloride, C <i>l</i> <sup>–</sup> (aq)	gives white ppt. with Ag <sup>+</sup> (aq) (soluble in NH <sub>3</sub> (aq))				
bromide, Br <sup>–</sup> (aq)	gives pale cream ppt. with Ag <sup>+</sup> (aq) (partially soluble in NH <sub>3</sub> (aq))				
iodide, I <sup>-</sup> (aq)	gives yellow ppt. with Ag <sup>+</sup> (aq) (insoluble in NH <sub>3</sub> (aq))				
nitrate, NO <sub>3</sub> <sup>–</sup> (aq)	NH <sub>3</sub> liberated on heating with OH <sup>-</sup> (aq) and A <i>l</i> foil				
nitrite, NO <sub>2</sub> ⁻(aq)	$NH_3$ liberated on heating with OH <sup>-</sup> (aq) and A <i>l</i> foil; NO liberated by dilute acids (colourless NO $\rightarrow$ (pale) brown NO <sub>2</sub> in air)				
sulfate, SO <sub>4</sub> <sup>2–</sup> (aq)	gives white ppt. with Ba <sup>2+</sup> (aq) (insoluble in excess dilute strong acids)				
sulfite, SO <sub>3</sub> <sup>2–</sup> (aq)	SO <sub>2</sub> liberated with dilute acids; gives white ppt. with Ba <sup>2+</sup> (aq) (soluble in dilute strong acids)				

# (c) Tests for gases

gas	test and test result
ammonia, NH <sub>3</sub>	turns damp red litmus paper blue
carbon dioxide, CO <sub>2</sub>	gives a white ppt. with limewater (ppt. dissolves with excess CO <sub>2</sub> )
chlorine, $Cl_2$	bleaches damp litmus paper
hydrogen, H <sub>2</sub>	"pops" with a lighted splint
oxygen, O <sub>2</sub>	relights a glowing splint
sulfur dioxide, SO <sub>2</sub>	turns aqueous acidified potassium manganate(VII) from purple to colourless

# (d) Colour of halogens

halogen	colour of element	colour in aqueous solution	colour in hexane	
chlorine, Cl <sub>2</sub>	greenish yellow gas	pale yellow	pale yellow	
bromine, Br <sub>2</sub>	reddish brown gas/liquid	orange	orange-red	
iodine, I <sub>2</sub>	black solid/purple gas	brown	purple	

# 1 To standardise a 0.03 mol dm<sup>-3</sup> of iron(III) chloride solution and determine the concentration of sodium thiosulfate solution.

#### (a) Planning

**FA1** is a standard solution containing 0.03 mol dm<sup>-3</sup> of FeCl<sub>3</sub> solution.

You are to design an experiment to show how FA1 is prepared using solid  $FeCl_3$ .

You are provided with :

a solid sample of approximately 1.50 g of FeC $l_3$  (M<sub>r</sub> = 162.3),

250 cm<sup>3</sup> volumetric flask and

the usual laboratory apparatus

In your plan, you should include details on:

- the mass of FeCl<sub>3</sub>(s) you use with justification,
- the apparatus you would use, and
- the procedures which you would follow.

# Do not carry out this plan as FA1 is provided for you to continue with 1(b).

To make standard solution, a 250 cm<sup>3</sup> volumetric flask is used.

Amount of FeCl<sub>3</sub> in 250 cm<sup>3</sup> =  $0.03 \times 250 / 1000 = 7.50 \times 10^{-3}$  mol

Mass of FeC $l_3$  = 7.50 × 10<sup>-3</sup> x 162.3 = <u>1.22 g</u>

Procedure:

- 1. Weigh accurately about <u>1.22 g</u> (2 d.p) of  $FeCl_3$  into a <u>dry clean weighing bottle</u>.
- 2. <u>Dissolve the solid</u> using distilled water (~ 50 cm<sup>3</sup>) in a <u>100 cm<sup>3</sup> beaker</u>.
- Transfer the solution after ensuring all the solid has dissolved. Rinse the weighing bottle and beaker with water and transfer all washings into a 250 cm<sup>3</sup> volumetric flask to ensure quantitative transfer
- 4. <u>Top up the solution with distilled water to the 250 cm<sup>3</sup> mark.</u>

5. <u>Stopper and shake well</u> to obtain a homogenous solution. Label this solution **FA 1.** procedures 1-5.

(b) In addition to FA1, you are also provided with the following:

FA2 is 0.060 mol dm<sup>-3</sup> potassium iodide, KI.

**FA3** is aqueous sodium thiosulfate,  $Na_2S_2O_3$ .

When **FA1** is combined with **FA3**, a complex,  $[Fe(S_2O_3)_2]^-$ , is formed.

**Reaction 1:**  $Fe^{3+}(aq) + 2S_2O_3^{2-}(aq) \Rightarrow [Fe(S_2O_3)_2]^{-}(aq)$ 

To 1 cm<sup>3</sup> of **FA3** in a test–tube, add 2–3 drops of **FA1** and shake them thoroughly. State the colour of the complex formed.

(Pale) purple/ lilac /Pink/ violet.

- [1]
- (c) A student aimed to determine the concentration of FA3 using volumetric analysis involving the use of FA1 and FA2.

**Reaction 2:**  $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$ 

**Reaction 3:**  $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$ 

Using the above reactions, the student planned and carried out the following procedure.

- 1. Fill a 50.00 cm<sup>3</sup> burette with **FA3** solution.
- Using a 10 cm<sup>3</sup> measuring cylinder, measure 5 cm<sup>3</sup> of FA1 and place it in a 100 cm<sup>3</sup> conical flask.
- 3. Using another 10 cm<sup>3</sup> measuring cylinder, measure 5 cm<sup>3</sup> of **FA2** into the conical flask.
- 4. Run **FA3** from the burette into the conical flask. Near the endpoint, when the brown solution becomes pale, add 2 drops of starch.
- 5. Continue adding **FA3** slowly, the endpoint is reached when the solution **first becomes colourless**.
- 6. Record the titration results, to an appropriate level of precision, in an appropriate table and repeat the experiment once more.
  - (i) Carry out the student's procedure <u>twice only</u> to obtain two titration readings.
     <u>Your titre values need not be consistent</u>.

Note: After the end point is reached, you may observe the appearance of the coloured mixture again. There is no need to titrate any further.

	1	2
Final burette reading/ cm <sup>3</sup>	14.50	28.60
Initial burette reading/ cm <sup>3</sup>	0.00	14.50
Volume of <b>FA3</b> / cm <sup>3</sup>	14.50	14.10

Record your titration in an appropriate table in the space below.

# (ii) Planning

A teacher commented that it is appropriate for the student to use 5 cm<sup>3</sup> instead of 25 cm<sup>3</sup> of **FA1** for this titration. Justify the teacher's comment using suitable calculations.

Assume the concentration of **FA3** is 0.006 mol dm<sup>-3</sup>.

**Reaction 2:**  $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$ 

**Reaction 3:**  $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$ 

No. of moles of 5 cm<sup>3</sup> of **FA1** = 5 / 1000 x 0.03 =  $1.5 \times 10^{-4}$  mol No. of moles of  $I_2 = 1.5 \times 10^{-4} / 2 = 7.5 \times 10^{-5}$  mol No. of moles of  $S_2O_3^{2-} = 7.5 \times 10^{-5} x 2 = 1.5 \times 10^{-4}$  mol

If the concentration of **FA3** is 0.006 mol dm<sup>-3</sup>,

Approximate titre volume =  $1.5 \times 10^{-4} / 0.006 \times 1000 = 25 \text{ cm}^3$ 

OR

If 25 cm<sup>3</sup> of **FA1** = 25/1000 x  $0.03 = 7.5 \times 10^{-4}$  mol

No. of moles of  $S_2O_3^{2-}$  = 7.5 × 10<sup>-4</sup> mol Approximate titre volume = 7.5 × 10<sup>-4</sup> / 0.006 x 1000 = 125 cm<sup>3</sup>

If 25 cm<sup>3</sup> of **FA1** is used, the titre value will be 5 times (125 cm<sup>3</sup>) and <u>exceeds</u> the capacity of the burette. It results in high inaccuracy as refilling of burette is required.

[2]

#### (iii) Planning

Justify whether the amount of **FA2** that the student used in step **3** of the procedure in **1(c)** is sufficient to determine the concentration of **FA3**.

No. of moles of KI required =  $1.5 \times 10^{-4}$  mol Minimum volume of **FA2** =  $1.5 \times 10^{-4}$  / 0.06 x 1000 = 2.5 cm<sup>3</sup> To ensure excess **FA2** (KI), add 5 cm<sup>3</sup> of KI (accept 3 – 5 cm<sup>3</sup>).

(iv) The student did the titration several times but could not get consistent titre values of FA3. Based on your observation during titration, suggest a reason why.

**Reaction 1:**  $Fe^{3+}(aq) + 2S_2O_3^{2-}(aq) \Rightarrow [Fe(S_2O_3)_2]^{-}(aq)$ 

**Reaction 2:**  $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$ 

**Reaction 3:**  $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$ 

After the dark blue colouration disappear to get the colourless solution, <u>the purple</u> <u>colour reappeared</u> because the position of equilibrium of reaction 1 shift left due to the decrease in  $[S_2O_3^{2-}]$  during the titration. This result in the increase in the  $[Fe^{3+}]$  which reacts with excess KI to <u>produce more l\_2</u>. The <u>presence of l\_2 in starch</u> <u>is revealed as the reappearance of blue black colouration</u>. Hence, it is difficult to judge the correct end point and titration results is consistent.

[1]

[1]

[1]

(v) Suggest another reason why the results obtained are not reliable.

The limiting reagent  $\text{FeC}l_3$  was measured using a <u>10 cm<sup>3</sup> measuring cylinder</u> which has a **low precision**. Hence, the amount measured in each titration may vary slightly.

OR

The volume of **FA1** and **FA2** used are small, this would results in high percentage error.

(vi) The student performed the titration and had a titration value of 18.50 cm<sup>3</sup>. Given the errors (uncertainties) associated with each reading using a measuring cylinder and burette are  $\pm 0.1$  cm<sup>3</sup> and  $\pm 0.05$  cm<sup>3</sup> respectively, calculate the maximum total percentage error (uncertainty) from the apparatus in the titration. Percentage uncertainty (error) in using the **measuring cylinder** =  $(\pm 0.1 / 5.0) \times 100 \% = \pm 2.00 \%$ 

Each measuring cylinder reading has an uncertainty (error) of  $\pm 2.00$  %. Since two readings using measuring cylinder are made, total percentage error from measuring cylinder is **2.00 x 2 = \pm 4.00 %** 

Percentage uncertainty (error) in using the **burette** =  $\frac{(\pm 0.05 \times 2)}{18.50} \times 100 \% = \pm 0.541 \%$ 

Hence **maximum percentage error (uncertainty)** from the apparatus in the experiment

 $= (\pm 4.00) + (\pm 0.541) = \pm 4.54$  % (3 significant figures)

#### [Total: 14 marks]

**2** To investigate the kinetics of the reaction between iron(III) ions and iodide ions In this experiment, you are investigating the rate of reaction between iron(III) ions and iodide ions.

You are provided with: **FA1** is 0.03 mol dm<sup>-3</sup> of FeC $l_3$  solution **FA2** is 0.060 mol dm<sup>-3</sup> potassium iodide, KI **FA3** is sodium thiosulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

The reaction is started by mixing a solution of iron(III) chloride with sodium thiosulfate, potassium iodide, and starch. The iodine,  $I_2$ , produced in **reaction 2** reacts immediately with thiosulfate ions,  $S_2O_3^{2-}$  in **reaction 3**.

**Reaction 1:** Fe<sup>3+</sup>(aq) + 2S<sub>2</sub>O<sub>3</sub><sup>2-</sup>(aq)  $\Rightarrow$  [Fe(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>]<sup>-</sup>(aq) **Reaction 2:** 2Fe<sup>3+</sup>(aq) + 2I<sup>-</sup>(aq) → 2Fe<sup>2+</sup>(aq) + I<sub>2</sub>(aq) **Reaction 3:** I<sub>2</sub>(aq) + 2S<sub>2</sub>O<sub>3</sub><sup>2-</sup>(aq) → 2I<sup>-</sup>(aq) + S<sub>4</sub>O<sub>6</sub><sup>2-</sup>(aq)

When all the thiosulfate have been used, the iodine produced will turn starch indicator blue–black. The rate of the reaction can therefore be determined by finding the time for the blue–black colour to appear.

[3]

You are advised to read the instructions before starting any practical work and draw a table, in an appropriate format, for your results in the space on page 10.

For each of the five experiments, you will need to include the

- volume of FA2, V<sub>FA2</sub>,
- volume of water, V<sub>water</sub>,
- calculated squared volume of FA2, (V<sub>FA2</sub>)<sup>2</sup>,
- reaction time, t to nearest second, and
- calculated rate in mol dm<sup>-3</sup> s<sup>-1</sup>

Record all calculated values to 3 significant figures.

# (a) Method

# **Experiment 1**

- 1. Use the measuring cylinders to measure the following:
  - 20 cm<sup>3</sup> of **FA1**
  - 20 cm<sup>3</sup> of **FA3**
  - 1 cm<sup>3</sup> of starch indicator
- 2. Using another measuring cylinder, measure 10 cm<sup>3</sup> of **FA2**.
- 3. Pour the measured **FA1** and starch into a dry 100 cm<sup>3</sup> beaker.
- 4. Pour in the **FA3**, followed by **FA2** <u>immediately</u> into the same beaker. Start the stopwatch on adding **FA2**.
- 5. Stir the mixture and place the beaker on the printed page on page 2 of the insert.
- 6. The mixture turns brown and then yellow before turning a blue–black colour. Stop the stopwatch when this blue–black colour appears and obscures the wordings.
- 7. Record the time to the nearest second in the space on page 10.
- 8. Wash the beaker thoroughly with water and carefully dry the beaker with paper towel.

#### **Experiment 2**

- 9. Repeat step 1 in Experiment 1.
- 10. Using a measuring cylinder, add 2 cm<sup>3</sup> of **FA2.** Make up the volume to 10 cm<sup>3</sup> using deionised water using another measuring cylinder.
- 11. Pour the measured **FA1**, starch and deionised water into a dry 100 cm<sup>3</sup> beaker.
- 12. Pour in the **FA3**, followed by **FA2** <u>immediately</u> into the same beaker. Start the stopwatch on adding **FA2**.
- 13. Stir the mixture and place the beaker on the printed page on page 2 of the insert.
- 14. Stop the stopwatch when this blue–black colour appears and obscures the wordings.
- 15. Record the time to the nearest second in the space on page 10. The timing should not exceed 6 minutes.
- 16. Wash the beaker thoroughly with water and carefully dry the beaker with paper towel.

# Experiments 3–5

Carry out three further experiments to investigate the effect of changing the concentration of **FA2** by altering the volume of aqueous potassium iodide, **FA2**, used.

You should use a volume of **FA2** that is at least 2 cm<sup>3</sup> and the total volume of the reaction mixture must always be 51 cm<sup>3</sup>.

2 (a) With reference to 1(b), consider the colour change observed when FA2 was added to the solution prepared in step 6 of Experiment 1 before the blue-black colour appeared. Suggest an explanation for the sequence of colour change in terms of the chemistry involved.

**Reaction 1:**  $Fe^{3+}(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Fe(S_2O_3)_2]^{-}(aq)$ yellow purple

**Reaction 2:**  $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$ 

**Reaction 3:**  $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$ 

The brown solution is due to a <u>mixture</u> of purple complex  $[Fe(S_2O_3)_2]^-$  and yellow  $Fe^{3+}(aq)$ .

Since the I<sub>2</sub> formed reacted immediately with thiosulfate,  $[S_2O_3^{2-}(aq)]$  decreased, and the position of equilibrium in Reaction 1 shifts left.

Thus, <u>concentration of  $[Fe(S_2O_3)_2]^-$  decreased</u>. Hence, the <u>colour of the solution</u> <u>gradually fades</u> until the <u>solution became pale yellow due to  $Fe^{3+}$ .</u>

<sup>2</sup> (b) Show, by means of calculation, that the change in the concentration of I<sup>-</sup>,  $\Delta$ [I<sup>-</sup>], which occurred when the blue-black colour appeared was 2.35 × 10<sup>-3</sup> mol dm<sup>-3</sup>.

Assume the concentration of  $Na_2S_2O_3$  to be 0.006 mol  $dm^{-3}.$ 

Reaction 2: 2Fe<sup>3+</sup>(aq) + 2I<sup>-</sup>(aq) → 2Fe<sup>2+</sup>(aq) + I<sub>2</sub>(aq)  
Reaction 3: I<sub>2</sub>(aq) + 2S<sub>2</sub>O<sub>3</sub><sup>2-</sup>(aq) → 2I<sup>-</sup>(aq) + S<sub>4</sub>O<sub>6</sub><sup>2-</sup>(aq)  
Amount of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> = 
$$\frac{20}{1000} \times 0.006 = 1.20 \times 10^{-4}$$
 mol  
 $\Delta$ [I<sup>-</sup>] =  $\frac{1.20 \times 10^{-4}}{\frac{51}{1000}} = 2.35 \times 10^{-3}$  mol dm<sup>-3</sup>

(c) Results

The rate of the reaction can be calculated as shown.

rate = 
$$\frac{\Delta[I^-]}{\text{reaction time}}$$

Calculate the rate of reaction for each experiment and complete your table.

Expt	V <sub>FA2</sub> / cm <sup>3</sup>	V <sub>water</sub> / cm <sup>3</sup>	t/s	(V <sub>FA2</sub> ) <sup>2</sup> / cm <sup>6</sup>	Rate / 10 <sup>-5</sup> mol dm <sup>-3</sup> s <sup>-1</sup>
1	10.0	0.0	26	100	9.04
2	2.0	8.0	304	4.00	0.773
3	4.0	6.0	128	16.0	1.84
4	6.0	4.0	69	36.0	3.41
5	8.0	2.0	34	64.0	6.91

[1]

2 (d) (i) Plot a graph of rate on the y-axis against  $(V_{FA2})^2$  on the x-axis on the grid in **Figure 2.1**. Draw the best fit line taking account of all the plotted data points.





Since total volume of the mixture is kept constant by adding deionised water, volume of **FA2** used is proportional to [I<sup>-</sup>]. [1]

2 (d) (iii) Deduce the order of reaction with respect to [I<sup>-</sup>]. Use evidence from your graph to support your deduction.

Observe from the graph, any one of the following:

 the graph is <u>linear/gradient</u> and pass through origin is a constant, showing that <u>rate ∞ squared volume/ concentration of FA2/ state that it is a graph of</u> <u>rate against [I<sup>-</sup>]<sup>2</sup>.</u>

<u>OR</u>

- the rate increase by xxx for every additional xxx cm<sup>3</sup> of FA2 used
- when squared volume of FA2 double, rate double (or other multiples)
- ✓ Therefore, the reaction is second order with respect to [I<sup>-</sup>]

[1]

(e) (i) Use your graph and the formula in 2(c) to calculate the time that the reaction would have taken if 5.0 cm<sup>3</sup> of FA2 had been used. Show your working clearly.

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If 5.0 cm<sup>3</sup> of FA2 is used, V_{FA2}^2 = 25 \text{ cm}^6, rate = 2.6 x 10<sup>-5</sup> mol dm<sup>-3</sup> s<sup>-1</sup> (read from graph) [1]
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Time =  $\Delta[I^-]$ / rate =  $\frac{2.35x \ 10^{-3}}{2.6 \ x \ 10^{-5}}$  = 90.4 s (to 3 sf or nearest seconds).

(d) (ii) Calculate the initial concentration of iron(III) ions and the initial concentration of iodide ions in the reaction mixture if 5.0 cm<sup>3</sup> of FA2 had been used.

 $[Fe^{3+}] = \frac{0.030 \times 20.0}{51.0} = 0.0118 \text{ mol } dm^{-3}$  $[I^{-}] = \frac{0.060 \times 5.0}{51.0} = 5.88 \text{ x } 10^{-3} \text{ mol } dm^{-3}$
rate = k[Fe<sup>3+</sup>][I<sup>-</sup>]<sup>2</sup>  
Ecf order of reaction from d(iii)  

$$k = \frac{rate}{[Fe^{3+}][I^{-}]^{2}}$$

$$= \frac{2.6 \times 10^{-5}}{(0.00118) \times (5.88 \times 10^{-3})^{2}}$$

$$= 637 [1] \text{ mol}^{-2} \text{ dm}^{6} \text{ s}^{-1}$$

(f) At the end of Experiment 1, a student washed the beaker and used it immediately for Experiment 2. State and explain how the student's action would affect the time *t* for Experiment 2.

<u>Dilution</u> of the reacting mixture will occur due to <u>residual water</u> left after washing.- Time, t, for experiment 2 will be <u>longer/increase</u>.

(g) List 1 possible source of experimental errors and suggest the corresponding improvement to reduce the experimental error.

	experimental errors	improvements
1	The temperature of the set-up	Performed the experiment in a
	may not be constant throughout	water bath with controlled
	the experiment. A change of	temperature
	temperature can affect the rate	
	and the time recorded.	
2	It was difficult to start the	Allow the stopwatch to run and
	stopwatch while reagents was	add reagents at a convenient
	added. The time for the cross to	time.
	be obscured would thus be	
	inaccurately determined.	

[Total: 22 marks]

[2]

[2]

## 3 Qualitative Analysis

You are provided the following reagents and the *Qualitative Analysis Notes* on page 21 and 22.

**FA1** is 0.03 mol dm<sup>-3</sup> of FeC $l_3$  solution

**FA4** is 6% volume  $H_2O_2$ 

**FA5** is 0.00215 mol dm<sup>-3</sup> of X<sup>-</sup> solution

(a) You are to perform the tests described in **Table 3.1** and record your observations in the same table.

Your answers should include

- details of colour changes throughout the tests and precipitates formed,
- the identity of any gases evolved, and details of the test used to identify each one.

You should indicate clearly at what stage in a test a change occurs.

Marks are not given for chemical equations.

No additional or confirmatory tests for ions present should be attempted.

Test		Observations	Explanation (teacher's notes)
i.	To 5 cm <sup>3</sup> of <b>FA1</b> , add aqueous silver nitrate in excess. Filter the mixture.	White ppt formed.The solution remained pale yellow/ colourless.	C <i>l</i> <sup>−</sup> is present.
	Separate the filtrate into three test tubes for (ii), (iii) and (iv).	The <u>filtrate</u> was a <u>pale</u> <u>yellow/ colourless</u> solution. The <u>residue</u> was a <u>white</u> ppt.	The filtrate contains Fe <sup>3+</sup> ions. The white ppt is AgC <i>I</i> .
	Place the filter funnel containing the residue on a new test tube, add aqueous ammonia over the residue.	The white ppt was <u>soluble</u> aqueous ammonia to form a <u>pale yellow/colourless</u> <u>solution</u> . With HNO <sub>3</sub> , <u>white ppt</u> formed and	$Cl^-$ is present. $[Ag(NH_3)_2]^+$ is formed. It should be a colourless solution but the ppt is covered with traces of Fe <sup>3+</sup> , hence the solution appears pale vellow.

Table 3.1

	Add HNO3 dropwise to the	white ppt insoluble in	Reversal of
	filtrate until no more	excess nitric acid in a colourless solution.	equilibrium. HNO <sub>3</sub> neutralise the NH <sub>3</sub>
	change.		and hence AgCI is
			formed again.
ii.	To a new test tube	The pale yellow solution	FA4 acts an
	containing 1 cm <sup>3</sup> of <b>FA4</b> ,	turned light brown/orange.	reducing agent as
	add a few drops of filtrate	Effervescence of	Hence, hydrogen
	from the first test tube from	colourless, odourless gas	peroxide FA4 undergoes oxidation.
	(i). Wait and observe the	Gas <u>relighted a glowing</u>	
	effervescence. Test for the	splinter. Oxygen evolved.	
	identity of the gas.		
	To the second test tube	Brown/ orange ppt	Fo <sup>3+</sup> is present
	containing 1 cm <sup>3</sup> of filtrate	<u>insoluble</u> in <u>excess</u> aqueous	r e is present.
	from (i) add aqueous	NaOH.	$E_0(OH)_1$ cannot be
	sodium hydroxido till		reduced by FA4.
		The brown ppt insoluble in	However, more $O_2$
	Add 1 cm <sup>3</sup> of <b>EA</b> /	Vigorous <u>effervescence</u> of	exists as $HO_2^-$ and
		colourless, odourless gas is	have a greater
		The gas <u>relighted a glowing</u>	(gets oxidised more
		splinter. Oxygen evolved.	easily by remaining
iv.	To the last test tube	(Blood) red solution formed.	Fe <sup>3+</sup> (aq) undergoes
	containing 1 cm <sup>3</sup> of filtrate		a ligand exchange.
	from (i), add 1 cm <sup>3</sup> of FA5.		
	To a new test tube	The III paper turned	Eo <sup>3+</sup> colution in
v.	a new lest lube	red/brown or. The pH was 1	acidic because of
	of <b>EA1</b> toot the nH of the	<u>or 2</u> .	appreciable
	or FAT, lest the prior the		nyururysis.
	indicator paper.		
	Add aqueous ammonia	Brown/ orange ppt formed	Ammonia is
	dropwise Add <b>FA1</b>		acidic Fe <sup>3+</sup> . There
	dropwise to dissolve the	A vollow/ orango/ light	are no excess Fe <sup>3+</sup> .
	precipitate formed. Stop	brown solution was formed	drops to 7. This is
	adding <b>EA1</b> once the	on adding FA1.	how neutral FeCl <sub>3</sub>
			is made.
	precipitate uisappears.		

3 (b) With reference to the observation made in test (i), identify the ppt and explain its solubility in aqueous ammonia.

The white ppt is <u>AgC*l*.[1]</u> The ppt is soluble in aqueous ammonia because of the <u>formation of complex[1]</u>,  $[Ag(NH_3)_2]^+$ .

(c) In the presence of strong base,

 $H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$ 

Electrode Reaction	E <sup>e</sup> /V
Fe <sup>3+</sup> + e ≓ Fe <sup>2+</sup>	+0.77
$Fe(OH)_3 + e \rightleftharpoons Fe(OH)_2$	-0.56
$O_2 + 2H_2O + 2e \rightleftharpoons H_2O_2$	+0.68
$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O$	+1.23
$O_2 + H_2O + 2e \rightleftharpoons HO_2^- + OH^-$	-0.08

With reference to the electrode potential given, explain the difference in the observation for effervescence made when **FA4** is added in test (ii) and (iii).

The effervescence is more vigorous for step (iii) as the  $H_2O_2$  is in alkaline medium and exists as  $HO_2^-$ .  $HO_2^-$  is a stronger reducing agent as the  $E^{\Theta}(O_2/HO_2^-)$  is more negative than that of  $H_2O_2$ . Hence the  $E^{\Theta}$ (cell) is more positive when hydrogen peroxide reacts with Fe<sup>3+</sup> in alkaline medium.

(d) Write an equation to explain the colour of the Universal Indicator paper on addition of FA1 before adding aqueous ammonia.

 $[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+$  $[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$ The presence of H<sup>+</sup> result in a pH of 1 or 2.

15

[1]

[2]

[2]

3 (e) The pH of the resultant solution in test (v) is 7. Explain the chemistry behind the changes of pH in test (v) when aqueous ammonia is added dropwise followed by FA1.

When ammonia is added, the reddish brown ppt of  $Fe(OH)_3$  was formed, and the pH was >7.

When more FA1 was added, the H<sup>+</sup> from FA1 neutralised the ammonia, hence the pH dropped to 7 and the ppt disappeared.

(neutralised by the H<sup>+</sup> from the FA1.

OR

<u>The ppt disappeared</u> as the <u>OH<sup>-</sup> in Fe(OH)<sub>3</sub> is removed by H<sup>+</sup></u>.

There are no excess Fe<sup>3+</sup> to make the solution acidic . Hence, the pH drops to 7. ) [2]

(f) Predict what happen when the resultant solution in test (v) is added to phenol.

A purple/violet complex is formed.

[1]

## (g) Planning

Thermometry is sometimes used to determine the number of ligands attached to the central metal atom or ion. One of such monodentate ligand is X<sup>-</sup> present in **FA5**.

A student performed an experiment to determine the structural formula of the hexacoordinated complex.

$$[Fe(H_2O)_6]^{3+} + nX^- \rightarrow [Fe(H_2O)_{6-n}X_n]^{3-n} + nH_2O \qquad \Delta H < 0$$

He used varying volumes of **FA1** and **FA5** only, while keeping the total volume of the mixture at 80 cm<sup>3</sup>. He recorded the change in temperature.

- (i) Outline how you would:
  - determine the effect of changing the volumes of FA1 and FA5 on the temperature change of the experiment and hence,
  - vary the volumes of FA1 and FA5 to form the needed hexacoordinated complex, [Fe(H<sub>2</sub>O)<sub>6-n</sub>X<sub>n</sub>]<sup>3-n</sup>.

You are provided with the same solutions, which were used in the test (iv) described. There is no need to perform the experiment.

No details regarding the use of specific apparatus are required.

## For experiment 1

<u>A 10 cm<sup>3</sup> portion of **FA1** was added to 70 cm<sup>3</sup> of **FA5**. The mixture was mixed thoroughly and the <u>highest temperature</u> reached was noted down.</u>

The procedure was <u>repeated for experiments 2 to 7 (minimum 5)</u>, with the following changes in the volume of **FA1** and **FA5** as stated in the table below.

Experiment	Volume of <b>FA1</b> / cm <sup>3</sup>	Volume of <b>FA5</b> / cm <sup>3</sup>	ΔT / °C
1	10	70	
2	20	60	
3	30	50	
4	40	40	
5	50	30	
6	60	20	
7	70	10	

(ii) The student plotted a graph and concluded that n=1 in the structural formula of [Fe(H<sub>2</sub>O)<sub>6-n</sub>X<sub>n</sub>]<sup>3-n</sup>. On the axes of Figure 3.1, sketch a graph that the student would obtain from your experiment in 3(g)(i) to draw this conclusion. Indicate the volume of FA1 that the student would use to reach this conclusion on the x-axis of the graph.

[3]



Amount of X<sup>-</sup> used =  $\frac{80 - y}{1000} \times 0.00215 = (1.72 \times 10^{-4} - 2.15 \times 10^{-6} \text{ y}) \text{ mol}$ 

Since ratio of Fe<sup>3+</sup> : X<sup>-</sup> is 1 : 1; 3 x 10<sup>-5</sup> y = 1.72 x 10<sup>-4</sup> - 2.15 x 10<sup>-6</sup> y Intersection occurred at 5.35 cm<sup>3</sup> of FA1

[Total: 19 marks]

[2]