

**NATIONAL JUNIOR COLLEGE**  
**SH2 PRELIMINARY EXAMINATION**  
Higher 2

CANDIDATE  
NAME

SUBJECT  
CLASS

REGISTRATION  
NUMBER

**CHEMISTRY**

Paper 3 Free Response

**9729/03**

**23 September 2025**

**2 hours**

Candidates answer on Question Paper.  
Additional Materials: Data Booklet

**READ THE INSTRUCTIONS FIRST**

Write your subject class, registration number and name on all the work you hand in.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams or graphs.

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

**Section A**

Answer **all** questions.

**Section B**

Answer **one** question.

A Data Booklet is provided.

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

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

For Examiner's Use	
Section A	
1	/19
2	/20
3	/21
Section B (*circle the question you attempted)	
4	/20
5	/20
Paper 3 Total	/80

## Section A

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

- 1 (a) A student investigated the thermal decomposition of Group 2 compounds. He heated a mixture of 2.50 g of magnesium nitrate and magnesium carbonate using the setup shown in Fig. 1.1, till no further change was observed. A colourless gas of a volume of 80.8 cm<sup>3</sup> was collected at 30 °C and atmospheric pressure.

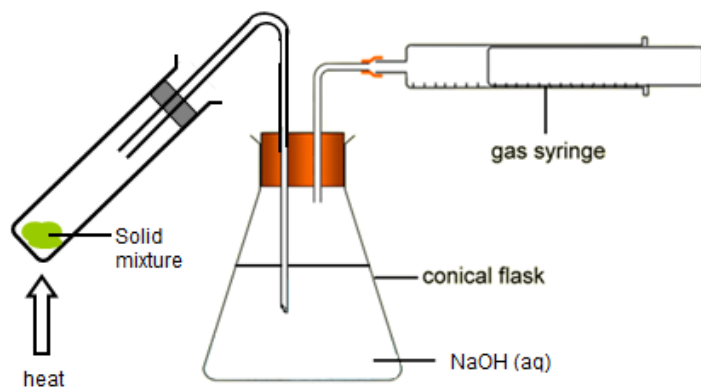
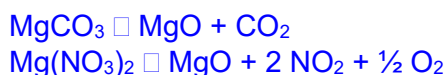


Fig 1.1

- (i) Write balanced equations for the thermal decomposition of  $\text{MgCO}_3$  and  $\text{Mg}(\text{NO}_3)_2$ . [1]



- (ii) Explain the purpose of sodium hydroxide in the above setup and hence identify the gas collected in the gas syringe. [2]

$\text{NaOH(aq)}$  reacts with the acidic gases ( $\text{CO}_2$  and  $\text{NO}_2$ ).

The gas collected in the gas syringe is  $\text{O}_2$ .

- (iii) Calculate the percentage by mass of magnesium nitrate present in the mixture. [3]



$$pV = nRT$$

$$\text{Amount of O}_2 \text{ gas collected} = \frac{101325 \times 80.8 \times 10^{-6}}{8.31 \times (30 + 273)} = 0.003252 \text{ mol}$$

$$\text{Amount of Mg}(\text{NO}_3)_2 = 2 \cdot 0.003252 = 0.006504 \text{ mol}$$

$$\text{Mass of Mg}(\text{NO}_3)_2 = 0.006504 \cdot (24.3 + 14 \cdot 2 + 16 \cdot 6) = 0.9644 \text{ g}$$

$$\% \text{ by mass of Mg}(\text{NO}_3)_2 \text{ in mixture} = \frac{0.9644}{2.50} \cdot 100\% = 38.6\%$$

- (b) The student carried out another experiment by heating equal amounts of carbonates of magnesium, calcium and barium for two minutes using a Bunsen burner. Table 1.1 shows the volume of gas collected.

**Table 1.1**

Group 2 carbonate	MgCO <sub>3</sub>	CaCO <sub>3</sub>	BaCO <sub>3</sub>
Volume of gas collected / cm <sup>3</sup>	80	25	5

Using relevant data from the *Data Booklet*, explain the results obtained by the student. [3]  
 The ionic radius of Mg<sup>2+</sup>, Ca<sup>2+</sup> and Ba<sup>2+</sup> are 0.065 nm, 0.099 nm and 0.135 nm respectively. Down Group 2, the ionic charge remains the same while the ionic radius increases, hence charge/size ratio decreases down the group.

Mg<sup>2+</sup> has the greatest polarising power, thus it can distort the electron cloud of CO<sub>3</sub><sup>2-</sup> to a larger extent. The C–O covalent bond in MgCO<sub>3</sub> is weakened more significantly and less amount of energy is required to decompose MgCO<sub>3</sub>.

As a result, MgCO<sub>3</sub> decomposes more readily than CaCO<sub>3</sub> and BaCO<sub>3</sub> as it produces the largest amount of CO<sub>2</sub> in the same time period.

- (c) Table 1.2 shows the bond length of various nitrogen-oxygen bonds.

**Table 1.2**

Bond	N–O	N=O	nitrogen-oxygen bond in NO <sub>3</sub>
Bond Length (nm)	0.136	0.115	0.128

Suggest an explanation for the observed NO bond length in nitrate ion. [2]  
 In NO<sub>3</sub><sup>-</sup>, the presence of continuous overlap of p orbitals across the 3 oxygen atoms and the nitrogen atom allows the  $\pi$  electrons and the lone pair of electrons on oxygen to be delocalised.  
 As a result, all the three NO bonds in NO<sub>3</sub><sup>-</sup> are an intermediate bond between an N–O bond and N=O bond (partial double bond) or bond order is between 1 and 2

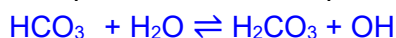
- (d) Sodium carbonate, a Group 1 carbonate, can be used to maintain the pH of swimming pool water to the ideal range of 7.0–7.6. If the concentration of sodium carbonate is too high, it will cause skin irritation to swimmers.

The management committee of a public swimming pool hired a chemist to advise them on the need to adjust the pH of pool water. The chemist titrated a 10.0 cm<sup>3</sup> sample of pool water (assume it contains only Na<sub>2</sub>CO<sub>3</sub>) against 0.05 mol dm<sup>-3</sup> HCl.

20.00 cm<sup>3</sup> of the HCl solution was required to turn the phenolphthalein indicator from pink to colourless. When the titration is repeated using methyl orange indicator, 40.00 cm<sup>3</sup> of HCl was required to reach the end point.

[The  $K_{b1}$  and  $K_{b2}$  values of Na<sub>2</sub>CO<sub>3</sub> at 25 °C are  $2.13 \times 10^{-4}$  and  $2.25 \times 10^{-8}$  respectively.]

- (i) The pH at the first equivalence point is found to be greater than 7. Write an equation to explain this observed pH. [1]



Note: must be reversible arrow for partial dissociation of weak base.

- (ii) Calculate the concentration of Na<sub>2</sub>CO<sub>3</sub> in the pool water sample. [1]

Working range of phenolphthalein is pH 8–10. When phenolphthalein changes colour, it indicates the first reaction between CO<sub>3</sub><sup>2-</sup> and H<sup>+</sup> is completed.



$$\text{Amount of HCl used} = \frac{20}{1000} \cdot 0.05 = 0.001 \text{ mol}$$

$$\text{Amount of CO}_3^{2-} \text{ reacted} = 0.001 \text{ mol}$$

$$\text{Concentration of Na}_2\text{CO}_3 \text{ in } 10.0 \text{ cm}^3 \text{ sample} = 0.001 \div \frac{10}{1000} = 0.1 \text{ mol dm}^{-3}$$

OR

Working range of methyl orange is pH 3–5. When methyl orange changes colour, it indicates the complete reaction between CO<sub>3</sub><sup>2-</sup> and two H<sup>+</sup>.



$$\text{Amount of HCl used} = \frac{40}{1000} \cdot 0.05 = 0.002 \text{ mol}$$

$$\text{Amount of CO}_3^{2-} \text{ reacted} = 0.001 \text{ mol}$$

$$\text{Concentration of Na}_2\text{CO}_3 \text{ in } 10.0 \text{ cm}^3 \text{ sample} = 0.001 \div \frac{10}{1000} = 0.1 \text{ mol dm}^{-3}$$

- (iii) Using your answer to (ii), calculate the initial pH of the pool water sample. [2]



$$[\text{OH}^-] = \sqrt{K_b \times [\text{CO}_3^{2-}]}$$

$$[\text{OH}^-] = \sqrt{2.13 \times 10^{-4} \times 0.1}$$

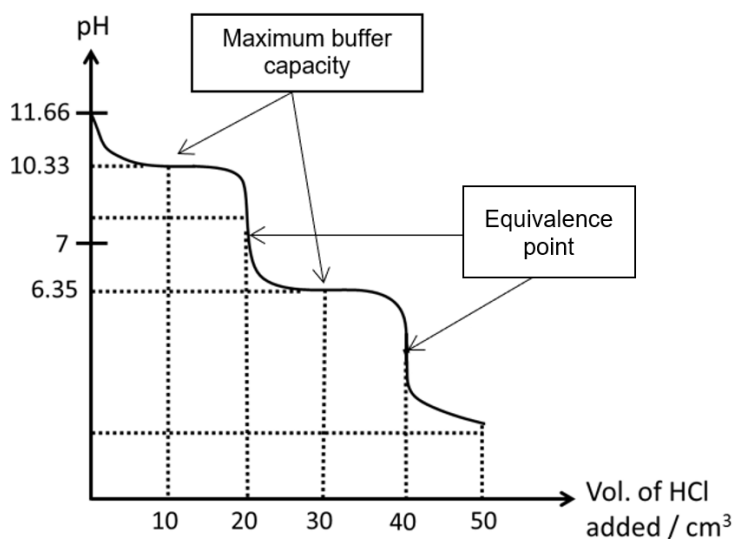
$$[\text{OH}^-] = 0.004615 \text{ mol dm}^{-3}$$

$$\text{pOH} = 2.336$$

$$\text{pH} = 14 - \text{pOH} = 11.66 \text{ (2 d.p.)}$$

allow ecf from (ii)

- (iv) Sketch the pH volume added curve you would expect to obtain when 50.00 cm<sup>3</sup> of the HCl solution is added to 10.0 cm<sup>3</sup> of the pool water sample. Label the various key points on the curve. [2]



First maximum buffering capacity occurs when there is 1:1 of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>

$$pOH = pK_{b1}$$

$$pH = 14 - pOH = 14 - [-\lg(2.13 \times 10^{-4})] = 10.33 \text{ (2 d.p.)}$$

Second maximum buffering capacity occurs when there is 1:1 of HCO<sub>3</sub><sup>-</sup> and H<sub>2</sub>CO<sub>3</sub>

$$pOH = pK_{b2}$$

$$pH = 14 - pOH = 14 - [-\lg(2.25 \times 10^{-8})] = 6.35 \text{ (2 d.p.)}$$

Shape of pH curve

- Correct shape with 2 equivalence points
- sharp change in pH at the equivalence points
- pH is approximately constant near the point of maximum buffering capacity
- Final pH would approach low pH

Label

- Axis with units
- initial pH
- pH and volume for maximum buffer regions
- pH > 7 at the first equivalence point

- (e) Lithium carbonate is a sparingly soluble salt with a  $K_{sp}$  value of  $8.15 \times 10^{-4}$ .

Calculate the solubility of lithium carbonate.

[2]

Let the solubility of Li<sub>2</sub>CO<sub>3</sub> be  $s$

	Li <sub>2</sub> CO <sub>3</sub> (s)	$\rightleftharpoons$	2Li <sup>+</sup> (aq)	+	CO <sub>3</sub> <sup>2-</sup> (aq)
I /mol dm <sup>-3</sup>			0		0
C /mol dm <sup>-3</sup>	-s		+2s		+s
E /mol dm <sup>-3</sup>			2s		s

$$K_{sp} \text{ of } Li_2CO_3 = [Li^+]^2[CO_3^{2-}] = (2s)^2(s)$$

$$8.15 \times 10^{-4} = 4s^3$$

$$s = 5.88 \times 10^{-2} \text{ mol dm}^{-3}$$

[Total : 19]

2 Cobalt is a *transition element* that can form coloured ions of various oxidation states in aqueous solutions.

(a) (i) Explain what is meant by the term *transition element*. [1]  
 Transition elements are d-block elements which form one or more stable ions with a partially filled d subshell.

(ii) Explain why aqueous solution of  $Co^{3+}$  ions is coloured. [3]  
 In the presence of ligands, electronic repulsion between lone pair electrons of ligands and the electrons in the 3d orbitals causes the degenerate 3d-orbitals of the  $Co^{3+}$  ions to split into two different energy levels with a (small) energy gap,  $\Delta E$ . This process is called d-splitting.

As the 3d subshell is partially filled, electrons in the lower energy d orbitals can absorb light of a certain wavelength in the visible light spectrum with energy corresponding to the energy gap,  $\Delta E$ , and be promoted to the higher energy 3d orbital. This process is called d-d transition.

The colour observed is the complement of the colour absorbed.

(iii) Explain why cobalt ions can exhibit variable oxidation states while calcium ion can only have oxidation state of +2. [2]  
 Due to the close similarity in energy of the 3d and 4s orbitals of cobalt, (different numbers of) 3d and 4s electrons can be removed to form stable ions of different oxidation states.

However, once the valence 4s electrons of calcium are removed, the subsequent electrons removed must come from the next inner quantum shell which required large additional amount of energy and hence, calcium ions does not have variable oxidation states.

- (b) When an aqueous solution of cobalt(III) chloride,  $\text{CoCl}_3$ , is separately added to different amounts of aqueous ammonia under different conditions, two ionic compounds **A** and **B** are formed. Both **A** and **B** contained six-coordinated cobalt(III) complex ions containing both  $\text{NH}_3$  and  $\text{Cl}^-$  ligands.

When excess aqueous solution of silver nitrate,  $\text{AgNO}_3(\text{aq})$ , is added to one mole of **A** and one mole of **B** separately, same white precipitate is obtained. The amount of white precipitate formed is given in Table 2.1.

**Table 2.1**

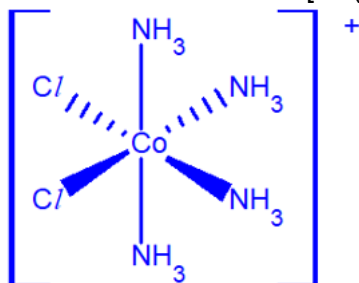
ionic compound	amount of white ppt formed with excess $\text{AgNO}_3(\text{aq})$
<b>A</b>	1 mol
<b>B</b>	2 mol

- (i) Identify the type of reaction for the reaction between  $\text{CoCl}_3$  and  $\text{NH}_3$ . [1]  
Ligand exchange reaction
- (ii) Identify the white precipitate. Explain why different amounts of white precipitate are formed from **A** and **B**. [2]  
The white precipitate is  $\text{AgCl}$ .

When different amounts of aqueous ammonia is added to  $\text{CoCl}_3$ , different number of  $\text{Cl}^-$  ligands formed coordinate bonds with  $\text{Co}^{3+}$  to form complex ions of different charges. Hence, different number of free  $\text{Cl}^-$  / counter  $\text{Cl}^-$  ions are present in **A** and **B**, resulting in different amount of  $\text{AgCl}$  being precipitated out.

- (iii) Deduce the formula for the **complex ions** in **A** and **B**. [2]  
**A**:  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  (1  $\text{Cl}^-$  ion that can react with  $\text{Ag}^+$ , 2  $\text{Cl}^-$  ligands + 4  $\text{NH}_3$  ligands)  
**B**:  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  (2  $\text{Cl}^-$  ion that can react with  $\text{Ag}^+$ , 1  $\text{Cl}^-$  ligands + 5  $\text{NH}_3$  ligands)
- (iv) The cobalt(III) complex ion in **A** exhibits *cis-trans* isomerism. Using your answer in (iii), draw the three-dimensional structure of the *cis* isomer of **A**.

If you are unable to deduce the formula for the complex ions found in **A** in (iii), you should use the formula  $[\text{Co}(\text{NH}_3)_2\text{Cl}_4]^-$ . This is **not** the correct answer. [1]



Note: show 2  $\text{Cl}^-$  ligands side by side in 3-D octahedral complex.

- (c) The reaction between iodide ions,  $\text{I}^-$ , and peroxodisulfate ions,  $\text{S}_2\text{O}_8^{2-}$ , in the absence of catalyst is slow.  $\text{Co}^{3+}$  ion can act as a homogeneous catalyst to speed up the reaction.

By considering suitable  $E^\ominus$  value from the *Data Booklet*, explain how  $\text{Co}^{3+}$  functions as a catalyst for the reaction between  $\text{I}^-$  and  $\text{S}_2\text{O}_8^{2-}$ , writing equations where appropriate. [3]

Step 1: Formation of intermediate



$$E^\ominus_{\text{cell}} = E^\ominus_{\text{red}} - E^\ominus_{\text{oxd}} = (+1.89 \text{ V}) - (+0.54) = +1.35 \text{ V (positive, spontaneous)}$$

Step 2: Regeneration of the catalyst



$$E^\ominus_{\text{cell}} = E^\ominus_{\text{red}} - E^\ominus_{\text{oxd}} = (+2.01 \text{ V}) - (+1.89) = +0.12 \text{ V (positive, spontaneous)}$$

There is high activation energy due to the collision of two negatively-charged ions (experiencing electrostatic repulsion). This two-step reaction provides a lower energy pathway because both steps involve collision between oppositely charged ions.



- (d) A series of experiments were carried out to investigate the kinetics of the uncatalysed reaction between  $\text{K}_2\text{S}_2\text{O}_8$ , and KI.



The initial concentrations of the  $\text{K}_2\text{S}_2\text{O}_8$  and KI solutions in the mixture, and the time taken for the mixture to darken for the various experimental runs are given in Table 2.2.

**Table 2.2**

Experiment	Initial concentration of $\text{K}_2\text{S}_2\text{O}_8$ / $\text{mol dm}^{-3}$	Initial concentration of KI / $\text{mol dm}^{-3}$	Time taken to darken/ s
1	0.10	0.20	35
2	0.05	0.20	70
3	0.20	0.067	50
4	0.02	0.75	?

- (i) Determine the rate equation for the uncatalysed reaction. [3]  
 Since we are monitoring time taken for a fixed amount of  $\text{I}_2$  to be formed,

$$\text{rate} \propto \frac{1}{\text{time taken}}$$

Comparing expt 1 & 2, [KI] remain constant and  
 $[\text{K}_2\text{S}_2\text{O}_8] \times 2$ , rate also  $\times 2$ .  
 Hence it is first order w.r.t  $\text{K}_2\text{S}_2\text{O}_8$ .

Comparing expt 1 & 3, let rate =  $k[\text{K}_2\text{S}_2\text{O}_8][\text{KI}]^x$   
 For expt 1 :  $\frac{1}{35} = k(0.10)(0.20)^x$   
 For expt 3 :  $\frac{1}{50} = k(0.20)(0.067)^x$

$$\begin{aligned} \text{Using } \frac{\text{expt 3}}{\text{expt 1}}, \\ \frac{1/50}{1/35} &= \frac{k(0.20)(0.067)^x}{k(0.10)(0.20)^x} \\ 0.35 &= \frac{(0.067)^x}{(0.20)^x} \end{aligned}$$

Taking lg on both sides,

$$0.4559 = 0.4750 x$$

$\times \text{H } 1$

Hence it is first order w.r.t KI.

$$\text{Rate} = k[\text{K}_2\text{S}_2\text{O}_8][\text{KI}]$$

- (ii) Calculate the time taken for the mixture in experiment 4 to darken. [1]

Using expt 1,

$$\text{Rate} = k[\text{K}_2\text{S}_2\text{O}_8][\text{KI}]$$

$$\frac{1}{35} = k(0.1)(0.2)$$

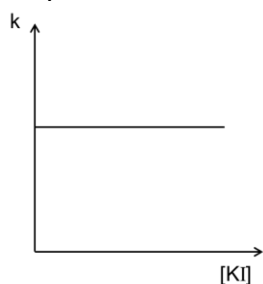
$$k = 1.429$$

Using the value of k for expt 4,

$$\frac{1}{\text{time taken}} = 1.429(0.02)(0.750),$$

$$\text{Time taken} = 46.7\text{s}$$

- (iii) Sketch the graph of rate constant, k, against concentration of KI at constant temperature. [1]



Note: rate constant k is only affected by temperature and catalyst.

[Total : 20]

- 3 (a) Adrenaline is both a hormone and neurotransmitter in the body. A chemistry undergraduate student has proposed to synthesise adrenaline from compound Y using a 3-step synthetic route as shown in Fig. 3.1.

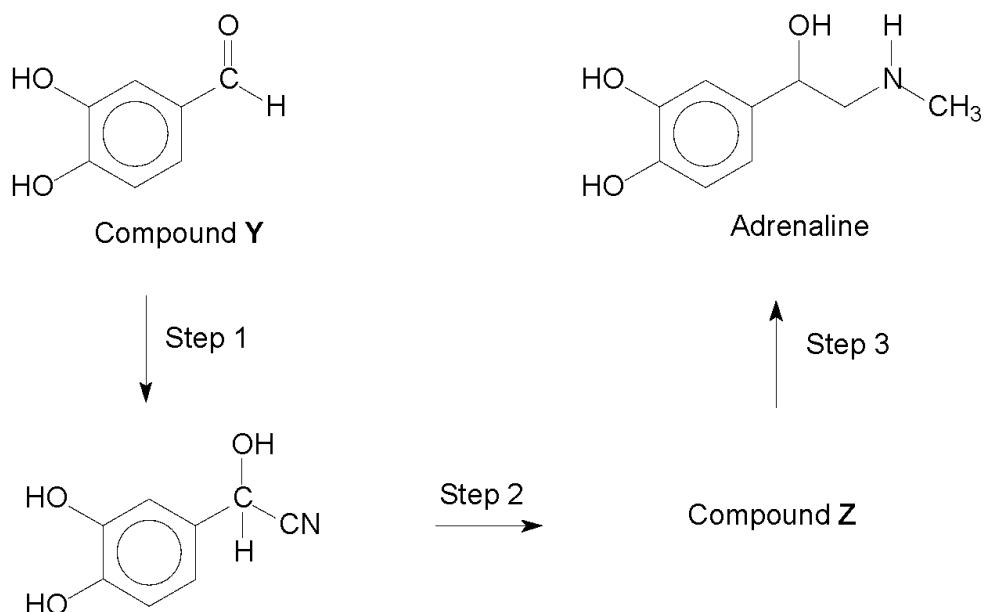


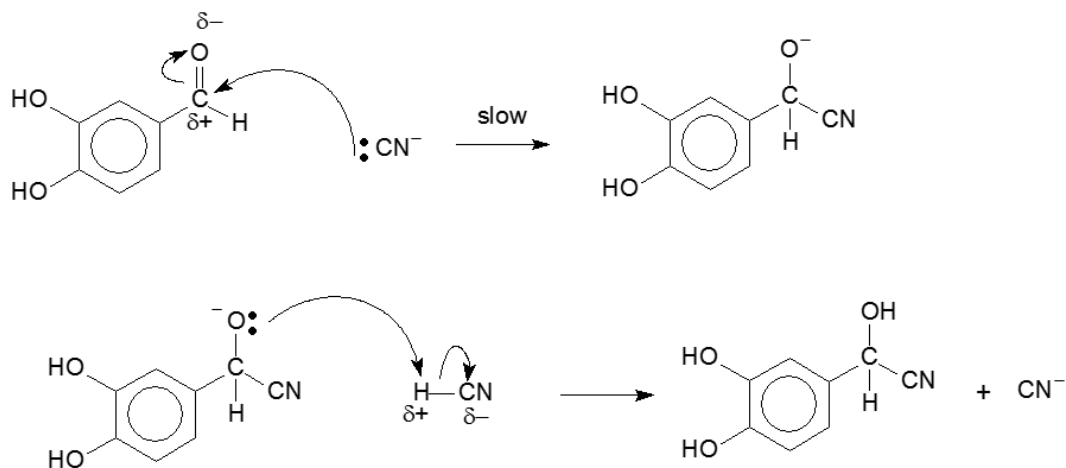
Fig 3.1

- (i) State the reagent and condition for Step 1 and describe the reaction mechanism. Include all relevant lone pairs, dipoles, charges, and curly arrows. Include the structure of the organic intermediate. [4]

HCN with trace amount of NaCN OR NaOH

Nucleophilic Addition

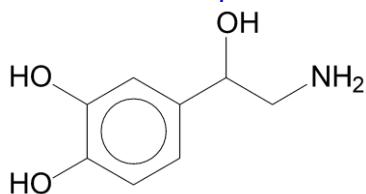
NaCN  $\rightleftharpoons$  Na<sup>+</sup> + CN<sup>-</sup>



- name of mechanism
- Label partial charges, negative charge on nucleophile
- Show lone pair electron on nucleophile
- Correct use of arrow to show movement of electrons
- Correct intermediate
- Reaction with HCN to regenerate CN<sup>-</sup>
- Label "slow" in step 1

- (ii) Identify the structure of compound **Z** and state the reagents and conditions needed for Step 2 and Step 3. [3]

Structure of compound **Z**:



Step 2:  $\text{LiAlH}_4$  in dry ether OR  $\text{H}_2(\text{g})$ ,  $\text{Pt}(\text{s})$  OR  $\text{H}_2(\text{g})$ ,  $\text{Ni}(\text{s})$  high temp & pressure

Step 3: limited  $\text{CH}_3\text{Br}$ , heat

Note: In step 3, compound **Z** acts as the nucleophile to react with  $\text{CH}_3\text{Br}$ .

With limited  $\text{CH}_3\text{Br}$ , N will be bonded to ONE  $\text{CH}_3$ .

With excess  $\text{CH}_3\text{Br}$ , N will be bonded to THREE  $\text{CH}_3$ .

- (iii) Suggest how the adrenaline synthesized through the above reaction scheme is different from the naturally occurring adrenaline secreted by the adrenal glands in the body. [2]

In this reaction, a racemic mixture of adrenaline (50%: 50% of both enantiomers) is produced as Step 1 involves an attack of the  $\text{CN}^-$  on a trigonal planar C atom.

Adrenaline produced in the body is stereospecific (only one of the enantiomers is formed)

Note: It is incorrect to state that the adrenaline synthesised is the enantiomer of naturally occurring adrenaline.

Analgesics are drugs that help to relieve pain. Paracetamol and morphine are the commonly used analgesics.

(b) Fig. 3.2 shows a two-steps reaction proposed by a student to synthesize paracetamol.

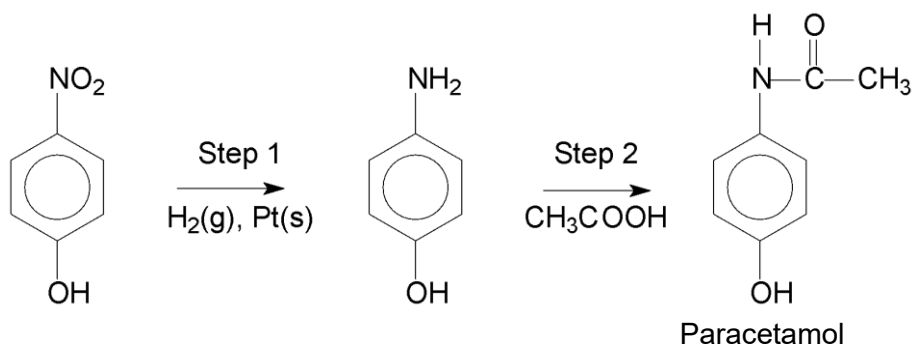


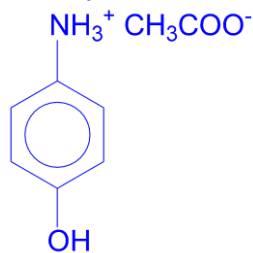
Fig. 3.2

His teacher pointed out there were mistakes in both Step 1 and 2.

(i) State the correct reagent and condition for Step 1. [1]  
*Sn, conc HCl, heat, followed by excess NaOH*

(ii) Using  $\text{CH}_3\text{COOH}$  in Step 2 would produce compound **G** instead of paracetamol.

Identify the structure of compound **G**. [1]



*amine undergoes acid-base reaction with  $\text{CH}_3\text{COOH}$  to give salt.*

*Note: No net charge for "compound". Must show both ions.*

(iii) Describe the observation when neutral  $\text{FeCl}_3(\text{aq})$  is reacted with paracetamol. [1]  
*Violet/purple colouration*

(c)

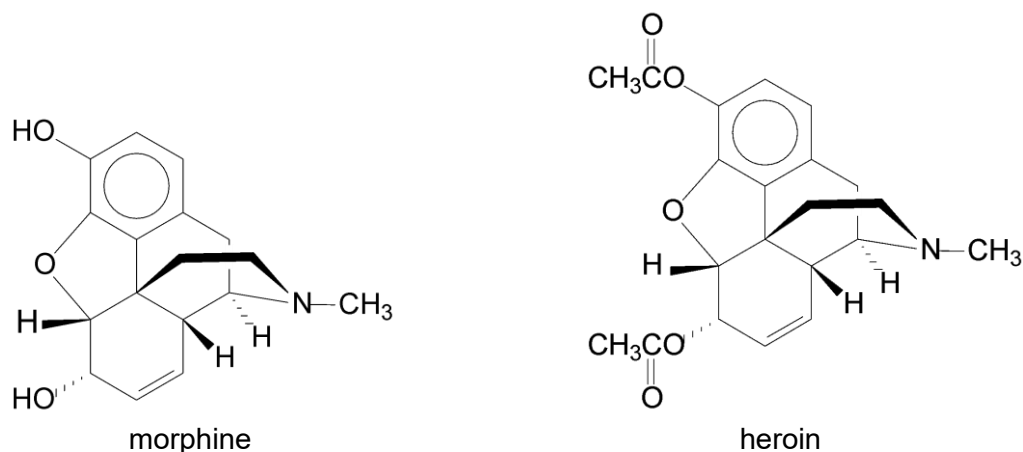


Fig. 3.3

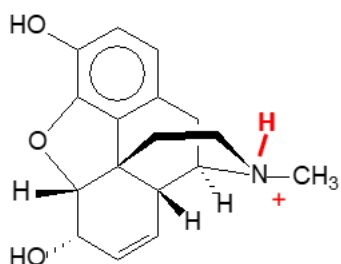
In contrast to paracetamol, narcotic analgesics such as morphine and heroin are used to relieve intense pain. Studies on the structural activity of morphine molecule has identified the three essential functional groups of morphine that bind strongly with the pain receptors and block the transmission of pain signals between brain cells are as follows:

1. Phenolic –OH group
2. Aromatic ring of phenol
3. Positively charged amine group

When injected into human body, these drug molecules need to cross the hydrophobic blood-brain barrier to reach the pain receptors. It is observed that polar molecules cross the blood-brain barrier less readily. In the brain, esterase enzymes catalyse the hydrolysis of the ester groups.



- (i) In the physiological pH of 7.4, the tertiary nitrogen atom of morphine and heroin is protonated. On Fig. 3.3, complete the structure to show the protonated form of morphine. [1]



- (ii) Suggest why heroin shows greater pain-relieving effect than morphine despite lacking the essential phenolic –OH group to bind with the pain receptors. [2]  
Heroin is a less polar molecule than morphine, and it is able to pass the predominantly non-polar blood-brain barrier more readily than morphine molecule.

In the brain, the heroin molecule undergoes hydrolysis by esterase enzymes to produce the morphine molecule which would have the essential phenolic –OH group to bind with the pain receptors.

- (d) Compound **P**,  $C_{10}H_{12}O_2$ , reacts with hot  $H_2SO_4(aq)$  to give compound **Q**,  $C_2H_4O_2$ , and compound **R**,  $C_8H_{10}O$ . Compound **R** reacts with  $Br_2(aq)$  to give compound **S**,  $C_8H_9OBr$ , a symmetrical molecule.

Suggest possible structures for **P**, **Q**, **R**, **S**. For each reaction, state the type of reaction described and make deductions about the functional groups present. [6]

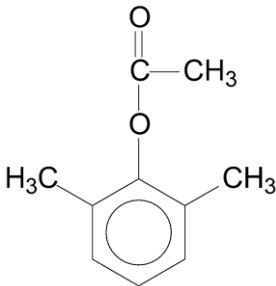
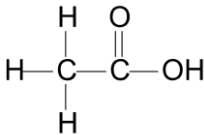
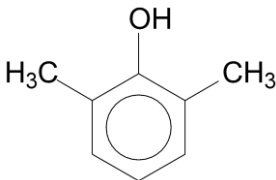
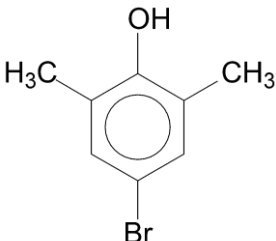
**P** undergoes acidic hydrolysis with hot  $H_2SO_4(aq)$ . Ester is present in **P**.

**Q** contains a carboxylic acid and **R** contains alcohol/phenol

**R** undergoes electrophilic substitution (1 H atom of **R** is replaced by 1 Br atom in **S**) with  $Br_2(aq)$ . **R** contains phenol.

Phenol with  $Br_2(aq)$  usually gives tri-substitution at position 2,4,6 of phenol. However since only 1 Br is substituted on the phenol, two of the 2,4,6 position must be occupied by side chain.

Since **S** is a symmetrical molecule, the two side chains must be at position 2 and 6 of phenol.

<p>Compound <b>P</b></p> 	<p>Compound <b>Q</b></p> 
<p>Compound <b>R</b></p> 	<p>Compound <b>S</b></p> 

**Common mistakes:**

Some students wrongly classify reaction of **P** with hot  $H_2SO_4(aq)$  as oxidation of alkene. Vigorous oxidation of alkene requires strong oxidizing agent,  $KMnO_4$ .

Some students wrongly classify reaction of **R** with  $Br_2(aq)$  as electrophilic substitution of benzene. Benzene requires anhydrous  $FeBr_3$  catalyst and  $Br_2$  for electrophilic substitution. Phenol, with strongly activating  $-OH$  attached to benzene, can undergo electrophilic substitution more readily with  $Br_2(aq)$ , without catalyst.

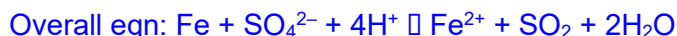
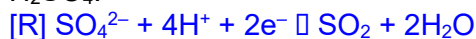
[Total : 21]

## Section B

Answer **one** question from this section.

- 4 A strip of iron metal was reacted until completion with an excess of hot concentrated sulfuric acid. A pale-green solution J that contained only  $\text{Fe}^{2+}(\text{aq})$  ions was obtained and effervescence of  $\text{SO}_2$  was also observed.

- (a) (i) Construct the balanced equation for the reaction between  $\text{Fe}(\text{s})$  and hot concentrated  $\text{H}_2\text{SO}_4$ . [1]



- (ii) The  $E^\circ_{\text{cell}}$  for this reaction is +0.61 V. Give two reasons why an equilibrium mixture is not produced when iron reacts with an excess of hot concentrated sulfuric acid. [3]

Any 2 points:

1. Positive  $E^\circ_{\text{cell}}$  shows that the reaction is spontaneous and the formation of product is favoured. Equilibrium is usually for redox reactions with  $E^\circ_{\text{cell}} = 0$ .
2. This is not a closed system.  $\text{SO}_2(\text{g})$  produced is allowed to escape from the reaction system. Equilibrium state cannot be achieved.
3.  $\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{SO}_2 + 2\text{H}_2\text{O}$   $E^\circ = +0.17 \text{ V}$

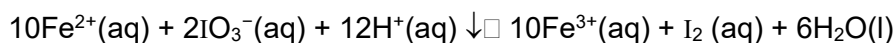
The  $E^\circ$  is given under standard conditions of 298 K and concentrations of all aqueous ions at  $1 \text{ mol dm}^{-3}$ .

When concentrated  $\text{H}_2\text{SO}_4$  is used, the concentration of  $\text{SO}_4^{2-}$  and  $\text{H}^+$  are greater than  $1 \text{ mol dm}^{-3}$ . This increase in concentration would shift the position of equilibrium to the right, (favouring reduction), increasing the E value for this half cell and hence causing  $E_{\text{cell}}$  to become more positive. The overall redox reaction would favour the formation of products when concentrated  $\text{H}_2\text{SO}_4$  is used, the reaction is unlikely to be an equilibrium mixture.



- (b) Solution **J** was cooled and an aliquot was mixed with an excess of acidified potassium iodate(V),  $\text{KIO}_3$ .

The overall stoichiometry of the reaction taking place in the conical flask is



All of the liberated iodine was titrated with standard aqueous sodium thiosulfate.



In one titration, a  $25.0 \text{ cm}^3$  aliquot of **J** requires  $18.60 \text{ cm}^3$  of  $0.150 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3(\text{aq})$  to reach the end-point.

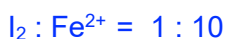
Calculate the molar concentration of  $\text{Fe}^{2+}$  in solution **J**.

[2]

$$\begin{aligned} \text{Amount of } \text{S}_2\text{O}_3^{2-} &= \frac{18.60}{1000} \times 0.150 \\ &= 0.00279 \text{ mol} \end{aligned}$$



$$\text{Amount of } \text{I}_2 = \frac{1}{2} \times 0.00279 = 0.001395$$



$$\begin{aligned} \text{No. of mol of } \text{Fe}^{2+} &= 10 \times 0.001395 \\ &= 0.01395 \text{ mol} \end{aligned}$$

$$[\text{Fe}^{2+}] \text{ in solution } \mathbf{J} = \frac{0.01395}{\frac{25.0}{1000}} = 0.558 \text{ mol dm}^{-3}$$

- (c) Liberated iodine is kept dissolved in solution by a large excess of iodide via the equilibrium:



Just before the end-point of the titration, the combined iodine concentration,  $[\text{I}_2] + [\text{I}_3^-]$ , is about  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ , while the iodide concentration remains at  $0.10 \text{ mol dm}^{-3}$ .

- (i) Write the  $K_c$  expression for the equilibrium. [1]

$$K_c = \frac{[\text{I}_3^-]}{[\text{I}_2][\text{I}^-]}$$

- (ii) Using these data and the  $K_c$  expression for the equilibrium, calculate the concentration of free iodine,  $[\text{I}_2]$ , present at this stage of the titration. [2]

$$\text{Given } [\text{I}_2] + [\text{I}_3^-] = 1.0 \times 10^{-4}$$

$$[\text{I}_3^-] = 1.0 \times 10^{-4} - [\text{I}_2] \quad \text{-- (1)}$$

$$K_c = \frac{[\text{I}_3^-]}{[\text{I}_2][\text{I}^-]} = 7.1 \times 10^2 \quad \text{-- (2)}$$

Substituting eqn 1 into eqn 2:

$$\frac{1.0 \times 10^{-4} - [\text{I}_2]}{[\text{I}_2][\text{I}^-]} = 7.1 \times 10^2$$

$$\frac{1.0 \times 10^{-4} - [\text{I}_2]}{[\text{I}_2](0.10)} = 7.1 \times 10^2$$

$$72 [\text{I}_2] = 1 \times 10^{-4}$$

$$[\text{I}_2] = 1.39 \times 10^{-6} \text{ mol dm}^{-3}$$

- (iii) Hence determine the percentage of the total iodine present as *free*  $\text{I}_2$ . [1]

$$\begin{aligned} \% \text{ of free } \text{I}_2 &= \frac{1.39 \times 10^{-6}}{1.0 \times 10^{-4}} \times 100 \\ &= 1.39\% \end{aligned}$$

**Note:** It is given that total iodine concentration,  $[\text{I}_2] + [\text{I}_3^-]$ , =  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$

- (d) Describe and explain the trend in the thermal stability of the hydrogen halides  $\text{HCl}$ ,  $\text{HBr}$  and  $\text{HI}$ . Include an equation for the thermal decomposition reaction in your answer. [3]



H-X bond is broken during the thermal decomposition of H-X. Down the Group, bond energy of H-X decreases from H-Cl ( $431 \text{ kJ mol}^{-1}$ ) to H-I ( $299 \text{ kJ mol}^{-1}$ ), and less energy is needed to overcome the H-X bond.

Thus, the thermal stability of the hydrogen halides decreases down the Group.

- (e) Three pure solid component labelled **D**, **E** and **F** are placed on the lab bench. It is known that the compounds are  $AlCl_3$ ,  $Na_2CO_3$  or  $MgSO_4$ .

A student performed several tests, and the results are summarised in Table 2.3.

**Table 2.3**

Compound	pH of the aqueous solution of the compound	results of adding NaOH(aq) to a solution of the compound	results of adding HCl(aq) to the solid compound
<b>D</b>	> 7	No observed reaction	Evolution of a gas
<b>E</b>	< 7	White ppt soluble in excess NaOH	No observed reaction
<b>F</b>	< 7	White ppt insoluble in excess NaOH	No observed reaction

- (i) Suggest the identity of Compound **D**, **E** and **F** based on the observations in Table 2.3. [2]

**Compound D :  $Na_2CO_3$**

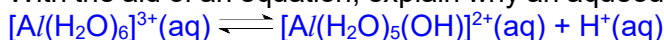
**Compound E :  $AlCl_3$**

**Compound F :  $MgSO_4$**

- (ii) Suggest the formula of the white compound observed when an excess of NaOH is added to a solution of the compound **F**. [1]

**$Mg(OH)_2$**

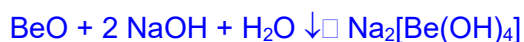
- (iii) With the aid of an equation, explain why an aqueous solution of **E** has a pH < 7. [2]



$Al^{3+}$  has a high  $\frac{\text{charge}}{\text{size}}$ , it polarise and weaken the O-H covalent bond in  $H_2O$  to a large extent and causes one of the six  $H_2O$  in  $[Al(H_2O)_6]^{3+}$  to dissociate into  $H^+$  and  $OH^-$ .  $[Al(H_2O)_5(OH)]^{2+}$  is produced and  $H^+(aq)$  is released into the solution during hydrolysis.

- (f) Beryllium oxide, BeO, has similar chemical properties as  $Al_2O_3$ .

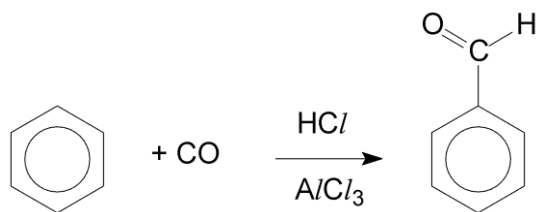
Write the chemical equations when separate samples of BeO are reacted with HCl(aq) and NaOH(aq). [2]



**Accept ionic equations**

[Total : 20]

- 5 (a) Benzaldehyde,  $\text{C}_6\text{H}_5\text{CHO}$ , served as a precursor in the production of various chemicals, including pharmaceuticals and dyes. Benzaldehyde can be synthesised from carbon monoxide and benzene by the Gatterman–Koch reaction in the presence of hydrogen chloride and aluminium chloride. This reaction is an electrophilic substitution reaction.



The following describes the mechanism for the reaction.

step 1: Carbon monoxide, hydrogen chloride and aluminium chloride reacts to form

the electrophile,  $\text{H}-\text{C}^+=\text{O}$ , and one other product.

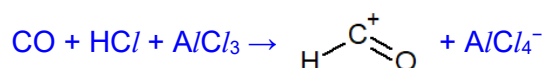
step 2: The electrophile reacts with benzene to form an intermediate in the rate-determining step.

step 3: The intermediate loses a  $\text{H}^+$  to regenerate hydrogen chloride and aluminium chloride.

- (i) Explain why benzene undergoes substitution reactions rather than addition reaction. [1]

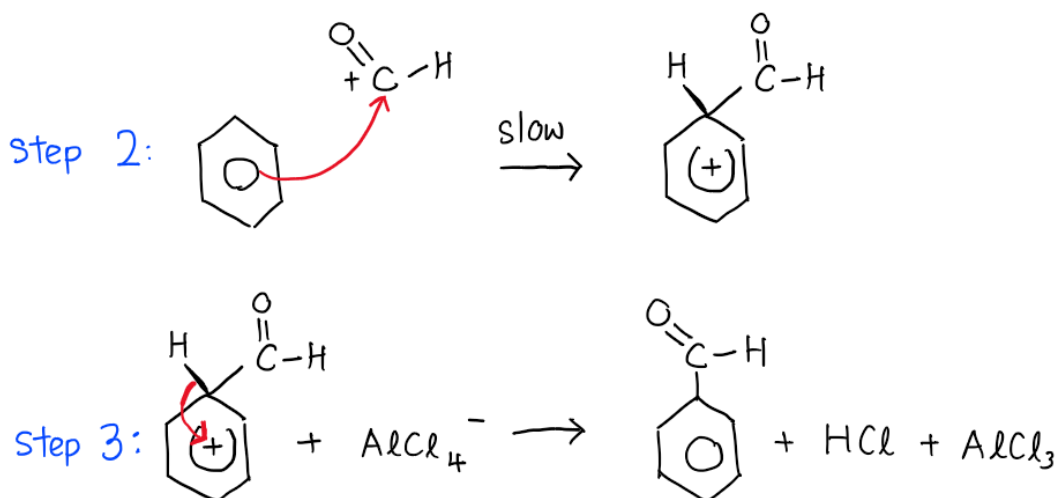
The ring of delocalised  $\pi$  electrons give benzene additional resonance stability. Addition reaction destroys this resonance stability and hence it is not favoured. Instead, benzene undergoes substitution reaction to maintain this resonance stability.

- (ii) Write the equation for the generation of the electrophile in step 1 of the Gatterman–Koch reaction. [1]



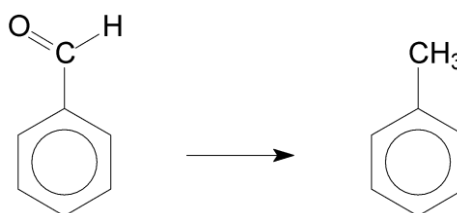
- (iii)  $\text{AlCl}_3$  acts as a *Lewis acid* in step 1 of the reaction. Describe how  $\text{AlCl}_3$  act as a *Lewis acid* in this step. [1]  
 $\text{AlCl}_3$  acts as a Lewis acid as it can accept the lone pair electrons from Cl in HCl.

- (iv) Draw a reaction mechanism for step 2 and step 3. Include all relevant charges and curly arrows. Include the structure of the organic intermediate. [2]



- Label positive charge on electrophile
- Label "slow" in step 2
- Correct use of arrow to show movement of electrons
- Correct intermediate with "opening" and positive charge.
- Break C H to regenerate aromatic ring
- Show balanced equation in regenerating  $\text{HCl}$  and  $\text{AlCl}_3$

- (v) Benzaldehyde formed can undergo further reaction to form methylbenzene.



State the type of reaction that benzaldehyde undergoes and explain your answer. [2]  
 Reduction reaction. This is because there is gain of hydrogen atoms/ loss of oxygen atoms by benzaldehyde.

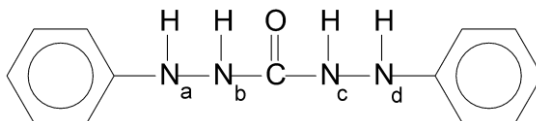
- (b) The concentration of chromium(VI) in aqueous solution may also be determined using a colorimeter.

On adding 1,5-diphenylcarbazide, DPC, to a solution of chromium(VI) ions, an intensely coloured octahedral complex is formed. The formula of the complex is  $[\text{Cr}(\text{DPC})_3]^{6+}$ .

- (i) The coordination number of the complex,  $[\text{Cr}(\text{DPC})_3]^{6+}$  is 6.

Explain what is meant by *coordination number* for the complex,  $[\text{Cr}(\text{DPC})_3]^{6+}$ . [1]  
 It is the number of co-ordinate bonds (dative bonds) that the central metal ion,  $\text{Cr}^{6+}$ , formed with DPC ligands.

- (ii) The structure of DPC is shown.



DPC is able to act as a bidentate ligand using lone pair electrons on  $N_a$  and  $N_d$ . Explain why the lone pair electrons on  $N_b$  and  $N_c$  are not available. [1]

Lone pair electrons on  $N_b$  and  $N_c$  are significantly delocalised to the adjacent  $C=O$  with highly electronegative O atom.

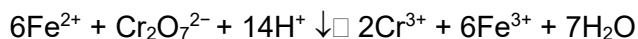
- (iii) Suggest why the intense colour of the complex,  $[Cr(DPC)_3]^{6+}$ , is not due to the movement of electrons between split d-orbitals in the chromium ion. [1]

$Cr^{6+}$  has an empty d subshell hence there is no d-splitting and d-d transition.

- (c) Potassium dichromate(VI),  $K_2Cr_2O_7$ , is present in very small amounts in cement, to help increase the time for the cement to set.

A 50.0 g sample of cement was washed with portions of deionised water to dissolve the potassium dichromate(VI). Any insoluble residues were removed by filtration and the filtrate was transferred to a volumetric flask. The volume was made up to 100.0 cm<sup>3</sup> using 2.0 mol dm<sup>-3</sup> sulfuric acid.

50.0 cm<sup>3</sup> of this solution was transferred to a conical flask and titrated with a solution of ammonium iron(II) sulfate,  $(NH_4)_2Fe(SO_4)_2$ , of concentration  $3.24 \times 10^{-4}$  mol dm<sup>-3</sup>. The following reaction occurs.



The indicator *N*-phenylanthranilic acid was used, which gave an intense red-violet colour at the end-point.

The mean titre of ammonium iron(II) sulfate was 10.90 cm<sup>3</sup>.

- (i) Suggest a reason why an indicator is necessary in this titration. [1]

The colour change from orange to green at the end-point is not distinctive / not sharp enough / not easy to detect (without an indicator).

- (ii) Calculate the percentage by mass of potassium dichromate(VI) in the cement sample. [3]

$$\begin{aligned} \text{Amt of } (NH_4)_2Fe(SO_4)_2 &= \frac{10.90}{1000} \times 3.24 \times 10^{-4} \\ &= 3.532 \times 10^{-6} \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Amt of } Cr_2O_7^{2-} \text{ (in 50.0 cm}^3\text{)} &= \frac{1}{6} \times 3.532 \times 10^{-6} \\ &= 5.886 \times 10^{-7} \text{ mol} \end{aligned}$$

$$\text{Amt of } Cr_2O_7^{2-} \text{ (in 100.0 cm}^3\text{)} = 2 \times 5.886 \times 10^{-7} = 1.177 \times 10^{-6} \text{ mol}$$

$$\begin{aligned} \text{Mass of } K_2Cr_2O_7 \text{ in sample} &= 1.177 \times 10^{-6} \times (2 \times 39.1 + 2 \times 52.0 + 7 \times 16.0) \\ &= 1.177 \times 10^{-6} \times 294.2 \\ &= 3.463 \times 10^{-4} \text{ g} \end{aligned}$$

$$\begin{aligned} \text{\% by mass of K}_2\text{Cr}_2\text{O}_7 \text{ in 50.0 g sample} &= \frac{3.463 \times 10^{-4}}{50.0} \times 100 \\ &= 6.925 \times 10^{-4} \% \end{aligned}$$

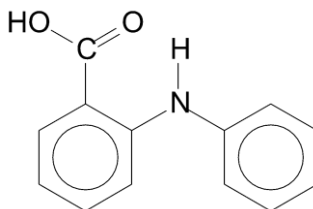
- (iii) Potassium dichromate(VI) can cause allergic contact dermatitis in some individuals. Regulations have been put in place in some countries to limit the content of potassium dichromate(VI) in cement to no more than 2mg per kg of cement.

Using your answer in (ii), determine if the 50.0 g sample of cement is safe for usage. [2]

$$\text{\% by mass of safe limit} = \frac{2 \times 10^{-3}}{1000} \times 100\% = 2 \times 10^{-4} \% \text{ by mass}$$

Since the sample contains  $6.93 \times 10^{-4} \%$  of  $\text{K}_2\text{Cr}_2\text{O}_7$  by mass, it exceeds the safe limit and is not safe for usage.

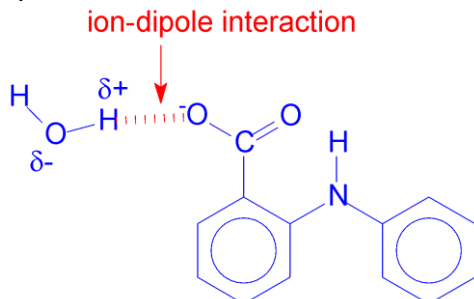
- (d) *N*-phenylanthranilic acid has the structure shown below.



- (i) Explain why *N*-phenylanthranilic acid has low solubility in water. [1]  
*N*-phenylanthranilic acid contains two benzene rings. Energy released in the formation of instantaneous dipole-induced dipole interactions between the benzene rings of *N*-phenylanthranilic acid molecules and water molecules is insufficient to overcome the hydrogen bonds between water molecules and the hydrogen bonds between *N*-phenylanthranilic acid molecules.

To use *N*-phenylanthranilic acid as an indicator for the reaction described in (c), it is first mixed with sodium hydroxide,  $\text{NaOH(aq)}$ .

- (ii) State the type of reaction between *N*-phenylanthranilic acid and  $\text{NaOH(aq)}$ . [1]  
 Acid-base reaction.
- (iii) Draw a labelled diagram to illustrate the interaction between the resultant organic species and a water molecule. [2]



Also accept hydrogen bond (then lone pair on  $\text{O}^-$  needs to be shown)

[Total : 20]

