Q1.

Iodine reacts slowly with propanone in the presence of an acid catalyst according to the equation
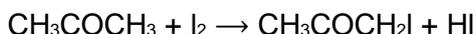
$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$$

The rate of this reaction can be followed by preparing mixtures in which only the initial concentration of propanone is varied. At suitable time intervals, a small sample of the mixture is removed and titrated with sodium thiosulfate solution. This allows determination of the concentration of iodine remaining at that time.The rate of this reaction can be followed by preparing mixtures in which only the initial concentration of propanone is varied. At suitable time intervals, a small sample of the mixture is removed and titrated with sodium thiosulfate solution. This allows determination of the concentration of iodine remaining at that time.

Five mixtures, **A**, **B**, **C**, **D** and **E**, are prepared as shown in **Table 1**.

Table 1

Mixture	A	B	C	D	E
Volume of 0.0200 mol dm^{-3} I$_2$(aq)/cm^3	40.0	40.0	40.0	40.0	40.0
Volume of 0.100 mol dm^{-3} H$_2$SO$_4$(aq)/cm^3	25.0	25.0	25.0	25.0	25.0
Volume of 1.00 mol dm^{-3} CH$_3$COCH$_3$(aq)/cm^3	25.0	20.0	15.0	10.0	6.5
Volume of distilled water/cm^3	0.0	5.0	10.0	15.0	18.5

(a)   Calculate the initial concentration, in mol dm^{-3}, of the propanone in mixture **A**.

Concentration = _____ mol dm^{-3}

(2)

(b)   State and explain why different volumes of water are added to mixtures **B**, **C**, **D** and **E**.

_____

_____

_____

_____

(2)

(c)   Calculate the volume of 0.0100 mol dm^{-3} sodium thiosulfate solution required to react with all of the iodine in a 10.0 cm^3 sample of mixture **E**, before the iodine reacts with propanone.

The equation for the reaction in the titration is

$$2Na_2S_2O_3(aq) + I_2(aq) \longrightarrow Na_2S_4O_6(aq) + 2NaI(aq)$$
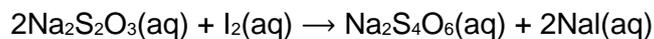
Volume = _____ cm^3

(4)

(d)   The results for mixture **E** are shown in **Table 2**.
V is the volume of 0.0100 mol dm^{-3} sodium thiosulfate solution needed, at different times, **t**, to react with the iodine in a 10.0 cm^3 sample of **E**.

Table 2

t/min	5	10	20	30
V/cm³	17.5	17.2	16.6	16.0

Use these data and your answer to part **(c)** to plot a graph of **V** (y-axis) against **t** (x-axis) for mixture **E**.
Draw a best-fit straight line through your points and calculate the gradient of this line.
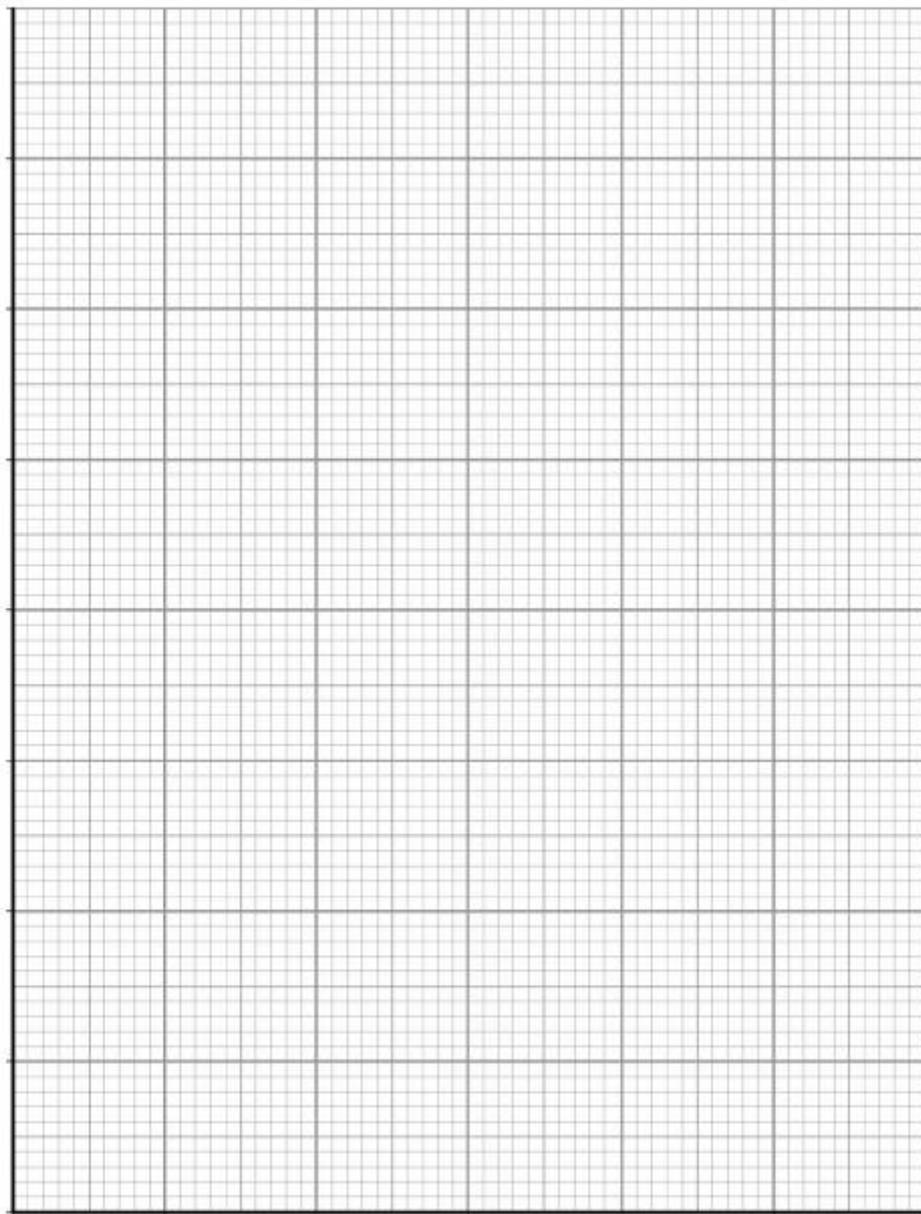
gradient = _____ cm^3 min^{-1}

(5)

(e)   The gradients for similar graphs produced by mixtures **A**, **B**, **C** and **D** are shown
       in **Table 3**.
       Each gradient is a measure of the rate of the reaction between iodine and propanone.

Table 3

Mixture	A	B	C	D
Gradient / cm^3 min^{-1}	−0.24	−0.20	−0.15	−0.10

Use information from **Table 1** and **Table 3** to deduce the order with respect to propanone.
Explain your answer.

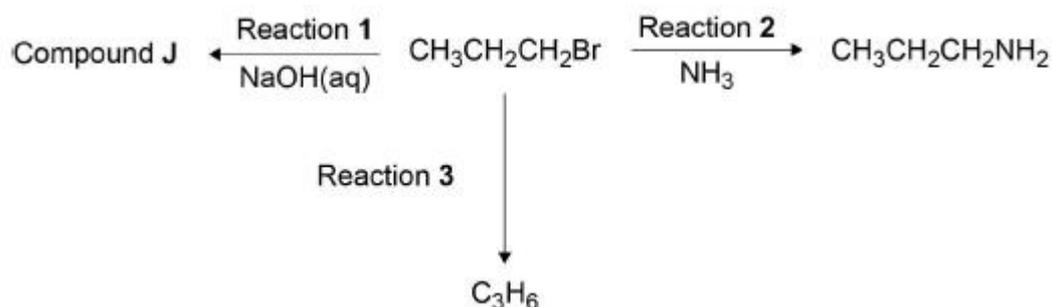_____

_____

_____

_____

_____

_____

(2)

(f)   Each sample taken from the reaction mixtures is immediately added to an excess of
       sodium hydrogencarbonate solution before being titrated with sodium thiosulfate solution.

       Suggest the purpose of this addition.
       Explain your answer.

_____

_____

_____

_____

_____

_____

(2)
(Total 17 marks)

Q2.

The diagram shows some compounds made from a halogenoalkane.

Compound **J** $\xleftarrow[\text{NaOH(aq)}]{\text{Reaction 1}}$ $CH_3CH_2CH_2Br$ $\xrightarrow[\text{NH}_3]{\text{Reaction 2}}$ $CH_3CH_2CH_2NH_2$

Reaction 3 ↓

C_3H_6

(a) Draw the displayed formula of compound **J**.

(1)

(b) Name the mechanism for Reaction **2** and give an essential condition used to ensure that $CH_3CH_2CH_2NH_2$ is the major product.

Name of mechanism _____

Condition _____

(2)

(c) Calculate the mass, in grams, of $CH_3CH_2CH_2NH_2$ produced from 25.2 g of $CH_3CH_2CH_2Br$ in Reaction **2** assuming a 75.0% yield.

Give your answer to the appropriate number of significant figures.

Mass _____ g

(3)

(d)   When Reaction **2** is carried out under different conditions, a compound with molecular formula $C_9H_{21}N$ is produced.

Draw the skeletal formula of the compound.

Identify the functional group in the compound including its classification.

Skeletal formula

Functional group including classification _____

(2)

(e)   Identify the reagent and conditions used in Reaction **3**.

_____

(1)

(f)   Name and outline a mechanism for Reaction 3.
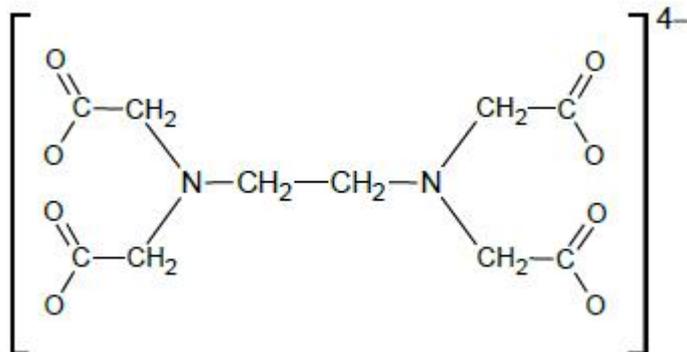
Name of mechanism _____

Mechanism

(4)
(Total 13 marks)

Q3.

EDTA is a useful laboratory chemical and is found in a wide variety of commercial products including detergents. It is very soluble in water and is often used in its ionic form $EDTA^{4-}$ as shown in the diagram below.

(a) $EDTA^{4-}$ can act as a multidentate ligand.

Explain the meanings of the terms **multidentate** and **ligand** with reference to the reaction of $EDTA^{4-}$ with $[Cu(H_2O)_6{}^{2+}](aq)$ ions to form a complex ion.

Draw on the diagram above a separate circle around each atom that bonds to the Cu^{2+} ion in this complex ion.

Multidentate _____

_____

Ligand _____

_____

(3)

(b)   Copper(II) compounds may be used as fungicides in vineyards. When used in this way, copper(II) ions can enter the water supply and cause problems because they are toxic in high concentrations.

The water supply near a vineyard can be tested for copper(II) ions by forming a blue aqueous complex with $EDTA^{4-}$ ions. The concentration of this complex can be determined using a colorimeter.

Outline the practical steps that you would follow, using colorimetry, to determine the concentration of this complex in a sample of water.

_____

_____

_____

_____

_____

(3)

(c)   The concentration of copper(II) ions, in the sample of water, determined by colorimetry was 7.56×10^{-5} mol dm^{-3}.

This result was checked by titrating a sample of the water with a solution containing $EDTA^{4-}(aq)$ ions.

The $EDTA^{4-}(aq)$ used in the titration had a concentration of 1.00×10^{-3} mol dm^{-3}.

Write an equation for the reaction between $[Cu(H_2O)_6]^{2+}$ and $EDTA^{4-}$ ions.

Calculate the volume of the $EDTA^{4-}$ solution needed to react with a 25.0 cm^3 sample of the water.

Justify whether this titration will give an accurate value for the concentration of copper(II) ions. If necessary, suggest a practical step that would improve the accuracy.
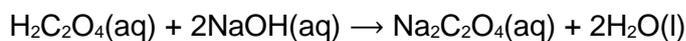
_____

_____

_____

_____

_____

_____

_____

(5)
(Total 11 marks)

Q4.

Ethanedioic acid ($H_2C_2O_4$) is a diprotic acid. Beekeepers use a solution of this acid as a pesticide.

A student carried out a titration with sodium hydroxide solution to determine the mass of the acid in the solution. The student repeated the titration until concordant titres were obtained.

$$H_2C_2O_4(aq) + 2NaOH(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$$

(a)   The student found that 25.0 cm³ of the ethanedioic acid solution reacted completely with 25.30 cm³ of 0.500 mol dm⁻³ sodium hydroxide solution.

Calculate the mass, in mg, of the acid in 25.0 cm³ of this solution.

Mass of acid = _____ mg

(4)

(b)   The student used a wash bottle containing deionised water when approaching the end-point to rinse the inside of the conical flask.

Explain why this improved the accuracy of the titration.

_____

_____

_____

(1)

(c)   Give the meaning of the term concordant titres.
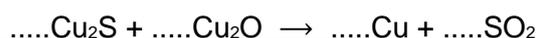
_____

_____

_____

(1)
(Total 6 marks)

Q5.

Copper can be produced from rock that contains $CuFeS_2$

(a)   Balance the equations for the two stages in this process.

.....$CuFeS_2$ + ...O_2 + ...SiO_2 $\rightarrow$ .....Cu_2S + ...Cu_2O + ...SO_2 + ...$FeSiO_3$

.....Cu_2S + ...Cu_2O $\rightarrow$ .....Cu + ...SO_2

(2)

(b)   Suggest two reasons why the sulfur dioxide by-product of this process is removed from the exhaust gases.

Reason 1 _____

_____

_____

Reason 2 _____

_____

_____

(2)

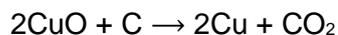(c)   A passenger jet contains 4050 kg of copper wiring.

A rock sample contains 1.25% $CuFeS_2$ by mass.

Calculate the mass, in tonnes, of rock needed to produce enough copper wire for a passenger jet.   (1 tonne = 1000 kg)

Mass of rock _____ tonnes

(4)

(d)   Copper can also be produced by the reaction of carbon with copper(II) oxide according to the equation

$$2CuO + C \longrightarrow 2Cu + CO_2$$

Calculate the percentage atom economy for the production of copper by this process.

Give your answer to the appropriate number of significant figures.

Percentage atom economy _____

(2)

(Total 10 marks)

Q6.

When an acidified solution of sodium nitrite ($NaNO_2$) is added to aqueous potassium iodide, iodine and nitrogen monoxide (NO) are formed.

(a)   Give the oxidation state of nitrogen in the following species.

NO_2^-_____

NO_____

(2)

(b)   Write a half-equation for the conversion of NO_2^- in an acidic solution into NO

_____

(1)

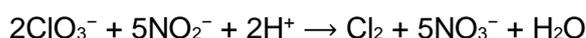(c)   Write a half-equation for the conversion of I^- into I_2

_____

(1)

(d)   Write an overall ionic equation for the reaction of NO_2^- in an acidic solution with I^-

_____

(1)

(e)   State the role of NO_2^- in the reaction with I^-

_____

(1)

(f)   In aqueous solution, nitrite ions react with acidified chlorate(V) ions according to the equation

$$2ClO_3^- + 5NO_2^- + 2H^+ \rightarrow Cl_2 + 5NO_3^- + H_2O$$

25.0 cm³ sample of an aqueous solution of sodium nitrite required 27.40 cm³ of a 0.0200 mol dm⁻³ solution of potassium chlorate(V) for complete reaction.

Calculate the concentration, in g dm⁻³, of sodium nitrite in the sample.

Concentration of sodium nitrite _____ g dm⁻³

(4)
(Total 10 marks)

Mark schemes

Q1.

(a)   Amount of propanone = (25.0 × 1) / 1000 = 0.025 mol

   1

   Concentration in mixture **A** = 0.025 / (90.0/1000) = 0.278 mol dm^{-3}

   1

(b)   To make volumes constant for all mixtures.

   1

   So that volume of propanone is proportional to concentration.

   1

(c)   Amount of iodine in mixture **E** = (40.0 × 0.02) / 1000 = 8.0 × 10^{-4} mol

   1

   Amount of iodine in sample = 8.0 × 10^{-4} × (10 / 90) = 8.89 × 10^{-5} mol
         As 10 cm^3 sample taken from total volume of 90 cm^3

   1

   Amount of thio required = 2 × 8.89 × 10^{-5} = 1.78 × 10^{-4} mol

   1

   Volume of thio = (1.78 × 10^{-4} / 0.01) × 1000 = 17.8 cm^3

   1

(d)   Scale
         Graph must cover at least half the grid and axes must be plotted in correct orientation but ignore labeling.

   1

   Points
         Must be correctly plotted to within ± half a small square.

   1

   Best-fit straight line
         Must be the best-fit line possible if point(s) are plotted incorrectly.
         Penalise doubled or kinked lines.

   1

   Gradient = y / x

   1

   = −0.060
         Allow −0.059 to −0.061
         Ignore any units given.

   1

(e)   Gradients / rates are proportional to volumes / concentrations of propanone **or** B to D show that gradient / rate halves when vol / concentration halves.

   1

   So first order with regard to propanone.

   1

(f)   To stop / quench the reaction at that time.
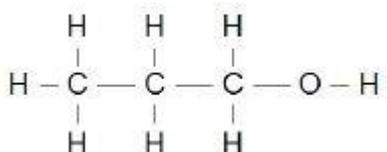
Ignore NaHCO₃ reacts with the HI produced.

1

By removing the acid catalyst for the reaction (by neutralisation).

1

[17]

Q2.

(a)

Must be displayed

1

(b)   <u>Nucleophilic substitution</u>

1

<u>Excess NH₃</u>

Ignore aqueous, alcoholic, conc, dil, temp, heat, pressure

1

(c)   Amount of CH₃CH₂CH₂Br   25.2/122.9 (=0.205) (mol)

M1

Amount of CH₃CH₂CH₂NH₂   M1 × 0.75 (= 0.154) (mol)

M2

Mass CH₃CH₂CH₂NH₂   M2 × 59.0 = 9.07g   Must be 3sf

M3

If either Mr incorrect or used incorrectly then only award 1 mark for 75% yield calculation
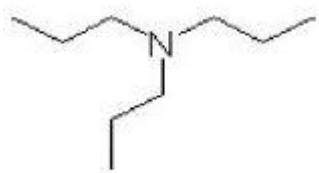*(ignore rounding to 123 for CH₃CH₂CH₂Br)*

OR
Max mass amine = M1 × 59.0 (= 12.1) (g)
Actual mass = M2 × 0.75 = 9.07g Must be 3sf

Allow 9.09 but if 9.08 check for AE
18.9 scores 1 for 75%

(d)

Must be skeletal
Ignore lone pair

<div style="text-align: right">1</div>

<u>tertiary amine or 3° amine (only award if a tertiary amine shown)</u>

<div style="text-align: right">1</div>
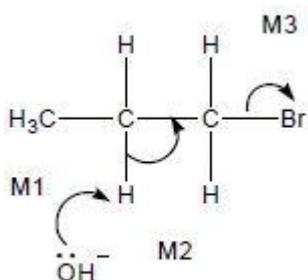
(e)   NaOH/ ethanol   or KOH / ethanol (both required)
> ***NOT*** *aqueous*
> *Ignore heat, temp, conc., dil,*
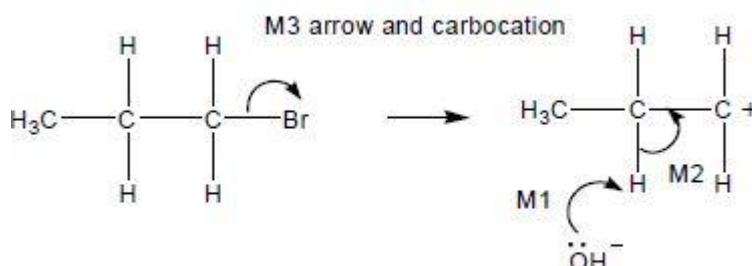> *Accept alcoholic for ethanol*

<div style="text-align: right">1</div>

(f)   (Basic) Elimination

Also credit E1 mechanism

<div style="text-align: right">1</div>

M1 arrow from <u>lone pair on O</u> of hydroxide to correct H (or to space mid way between hydroxide O and H)

M2 arrow from C-H bond to C-C bond following attack by OH⁻ on the correct H

M3 arrow from C-Br bond to Br

If nucleophilic substitution shown then allow M3 only in mechanism

If wrong haloalkane used then Max 2 for mechanism
> *M3 curly arrow for loss of Br⁻ & structure of carbocation*
> *M1 arrow from* <u>lone pair on O</u> *of hydroxide to H (or to space mid way between hydroxide O and H) (same as E2)*
> *M2 arrow from C-H bond to C-C bond (same as E2)*

<div style="text-align: right">3</div>

<div style="text-align: right">[13]</div>

Q3.

(a)   Multidentate − EDTA can form many / six dative bonds with central cation.

<div style="text-align: right">1</div>

Ligand − lone pair (on N or O of EDTA) can form dative bond with copper(II) ions.

1

6 circles drawn on $EDTA^{4-}$ structure − 2 × N and 4 × −O

1

(b)   Calibrate a colorimeter / produce a calibration curve.

1

By testing the colorimeter with solutions of copper-EDTA complex of known concentration.

1

Add excess EDTA salt to the sample.

1

(c) $[Cu(H_2O)_6]^{2+} + EDTA^{4-} \longrightarrow [Cu(EDTA)]^{2-} + 6H_2O$

1

Amount of copper(II) = $(25.0 \times 7.56 \times 10^{-5}) /1000 = 1.89 \times 10^{-6}$ mol

1

Volume of $EDTA^{4-}$ = $(1.89 \times 10^{-6} / 0.001) \times 1000 = 1.89$ cm³

1

This is too small to be accurate.

1

Dilute the $EDTA^{4-}$ solution / use larger volume of river water.

1

[11]

Q4.

(a)   **M1**   Amount NaOH = 0.02530 × 0.500 = 0.01265 mol
        567-590 = 4 marks
        0.567-0.590 = 3 marks

1

M2   Amount acid = 0.006325 mol (i.e. **M1** ÷ 2)
        Allow ECF at each stage

1

M3 M_r = 90(.0)
        ***M3** can be scored from use of value of 90(.0) within working*

1

M4   mass acid = 569 (mg) (allow 567 to 576) (i.e. **M2 × M3** in mg)
        ***M4** should be to at least 2sf. Any individual marks for **M1/2/3** should be to at least 2sf (or 90 for **M3**)*

1

        1134-1180 = 3 marks (due to not dividing moles of NaOH by 2)
        1.134-1.180 = 2 marks (due to not dividing moles of NaOH by 2 and not converting to mg)

(b)   Idea that it ensures all ethanedioic acid / acid / sodium hydroxide / alkali / reactants are in the mixture / solution / reaction or the idea that some of the ethanedioic acid / acid / sodium hydroxide / alkali / reactants would be on the sides of the flask
        the idea that it is the transfer of all the acid/alkali alone is not

enough

1

(c)   Titres that are within 0.1 cm³ of each other

Units are needed

Allow 0.05-0.15 cm³

Do not allow idea of identical results

Allow answers that refer to titres that are within the uncertainty of the burette/apparatus of each other

1

[6]

Q5.

(a) $4CuFeS_2 + 9\frac{1}{2}O_2 + 4SiO_2 \rightarrow Cu_2S + Cu_2O + 7SO_2 + 4FeSiO_3$

Allow multiples

1

$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$

1

(b)   ANY TWO
  •   Prevents acid rain (which damages buidlings / ecology)
  •   Toxic OR causes breathing problems
  •   Reduces waste product OR makes use of the waste OR improves atom economy OR Reduces need for sulfur mining OR used to produce sulfuric acid OR any named products

2

(c)   M1, M2, M3 are process marks

M1   Mol Cu = $\frac{450 \times 1000}{63.5}$ (= 63780)

1

M2   Mass CuFeS₂ = (63780) × 183.5 (= 1.17 × 10⁷g)

1

M3   Mass ore = (1.17 × 107) × $\frac{100}{1.25}$

1

M4   Mass ore = 936 tonnes (Allow 936 –937)

1

Alternative method
M1 % of Cu in CuFeS₂ = (63.5/183.5) × 100 = 34.6%
M2 % of Cu in the rock = (34.6/100) × 1.25 = 0.4325%
M3 mass of rock = 4050 × 100/0.4325 = 936416kg
M4 mass of rock in tonnes = 936 tonnes

Notes
M1 A_r Cu must be used
M2 M_r CuFeS₂ to have been used
M3 Grossing up for the mass of rock
M4 Final answer correct in tonnes

(d)   % atom economy = $\frac{(2 \times 63.5)}{171}$ × 100

1

= 74.3% must be 3sf

1

[10]

Q6.

(a) NO_2^- +3 or III or 3 or 3+

1

NO +2 or II or 2 or 2+

1

(b) $NO_2^- + e^- + 2H^+ \rightarrow NO + H_2O$ (OR double)

1

(c) $2I^- \rightarrow I_2 + 2e^-$ (OR half)

1

(d) $2NO_{2-} + 2I^- + 4H^+ \rightarrow I_2 + 2NO + 2H_2O$

1

(e) Oxidising agent

Allow to accept / gain electrons
Allow Oxidant
Do not allow accept / gain pairs of electrons
Do not allow Oxidise

1

(f) Mol ClO_3^- = 0.02 × $\frac{27.4}{1000}$ = 5.48 × 10^{-4}

1

Mol NO_2^- = $\frac{5}{2}$ (0.02 × $\frac{27.4}{1000}$) = 1.37 × 10^{-3})

1

[NO_2^-] = mol NO_2^- /($\frac{25}{1000}$)
[$NaNO_2$] = 0.0548 moldm^{-3}

1

Conc $NaNO_2$ = (0.0548) × 69.0 = 3.78 gdm^{-3}

1

Minimum 2 sf

[10]