Q13.

This question is about compounds containing ethanedioate ions.

(a)　A white solid is a mixture of sodium ethanedioate ($Na_2C_2O_4$), ethanedioic acid dihydrate ($H_2C_2O_4.2H_2O$) and an inert solid. A volumetric flask contained 1.90 g of this solid mixture in 250 cm^3 of aqueous solution.

Two different titrations were carried out using this solution.

In the first titration 25.0 cm^3 of the solution were added to an excess of sulfuric acid in a conical flask. The flask and contents were heated to 60 °C and then titrated with a 0.0200 mol dm^{-3} solution of potassium manganate(VII). When 26.50 cm^3 of potassium manganate(VII) had been added the solution changed colour.

The equation for this reaction is

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$
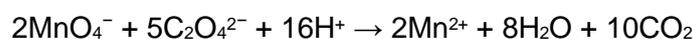
In the second titration 25.0 cm^3 of the solution were titrated with a 0.100 mol dm^{-3} solution of sodium hydroxide using phenolphthalein as an indicator. The indicator changed colour after the addition of 10.45 cm^3 of sodium hydroxide solution.

The equation for this reaction is

$$H_2C_2O_4 + 2OH^- \rightarrow C_2O_4^{2-} + 2H_2O$$
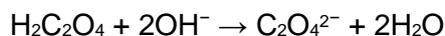
Calculate the percentage by mass of sodium ethanedioate in the white solid.

Give your answer to the appropriate number of significant figures.

Show your working.

Percentage by mass of sodium ethanedioate _____ %

(8)

(b)   Ethanedioate ions react with aqueous iron(III) ions in a ligand substitution reaction.

Write an equation for this reaction.

Suggest why the value of the enthalpy change for this reaction is close to zero.

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(2)

(c)   Draw the displayed formula of the iron complex produced in the reaction in part (b)

Indicate the value of the O—Fe—O bond angle.

State the type of isomerism shown by the iron complex.

Bond angle _____

Type of isomerism _____

(3)

(d)   Ethanedioate ions are poisonous because they react with iron ions in the body.
Ethanedioate ions are present in foods such as broccoli and spinach.

Suggest one reason why people who eat these foods do not suffer from poisoning.

_____

_____

(1)
(Total 14 marks)

Q14.

(a) Calcium phosphate reacts with aqueous nitric acid to produce phosphoric acid and calcium nitrate as shown in the equation.

$$Ca_3(PO_4)_2 \ + \ 6HNO_3 \ \longrightarrow \ 2H_3PO_4 \ + \ 3Ca(NO_3)_2$$

(i) A 7.26 g sample of calcium phosphate reacted completely when added to an excess of aqueous nitric acid to form 38.0 cm³ of solution.

Calculate the concentration, in mol dm⁻³, of phosphoric acid in this solution.
Give your answer to 3 significant figures.

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(5)

(ii) Calculate the percentage atom economy for the formation of calcium nitrate in this reaction.
Give your answer to 1 decimal place.

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(2)

(b) Write an equation to show the reaction between calcium hydroxide and phosphoric acid to produce calcium phosphate and water.

_____

(1)

(c)   Calcium dihydrogenphosphate can be represented by the formula $Ca(H_2PO_4)_x$ where x is an integer.
A 9.76 g sample of calcium dihydrogenphosphate contains 0.17 g of hydrogen, 2.59 g of phosphorus and 5.33 g of oxygen.

Calculate the empirical formula and hence the value of x.
Show your working.

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(4)
(Total 12 marks)

Q15.

A student carried out an experiment to find the mass of $FeSO_4.7H_2O$ in an impure sample, **X**.
The student recorded the mass of **X**. This sample was dissolved in water and made up to 250 cm³ of solution.
The student found that, after an excess of acid had been added, 25.0 cm³ of this solution reacted with 21.3 cm³ of a 0.0150 mol dm⁻³ solution of $K_2Cr_2O_7$

(a)   Use this information to calculate a value for the mass of $FeSO_4.7H_2O$ in the sample of **X**.

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(5)

(b) The student found that the calculated mass of $FeSO_4.7H_2O$ was greater than the actual mass of the sample that had been weighed out. The student realised that this could be due to the nature of the impurity.

Suggest **one** property of an impurity that would cause the calculated mass of $FeSO_4.7H_2O$ in **X** to be greater than the actual mass of **X**.
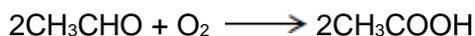Explain your answer.

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(2)
(Total 7 marks)

Q16.

This question explores some reactions and some uses of cobalt compounds.

(a) Ethanal is oxidised to ethanoic acid by oxygen. The equation for this reaction is

$$2CH_3CHO + O_2 \longrightarrow 2CH_3COOH$$

This redox reaction is slow at room temperature but speeds up in the presence of cobalt compounds.

Explain why a cobalt compound is able to act as a catalyst for this process.

Illustrate your explanation with **two** equations to suggest how, in the presence of water and hydrogen ions, Co^{3+} and then Co^{2+} ions could be involved in catalysing this reaction.

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(4)

(b)   In aqueous solution, the $[Co(H_2O)_6]^{2+}$ ion reacts with an excess of ethane-1,2-diamine to form the complex ion **Y**.

(i)   Write an equation for this reaction.

Explain, in terms of the chelate effect, why the complex ion **Y** is formed in preference to the $[Co(H_2O)_6]^{2+}$ complex ion.

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(3)

(ii)   Draw a diagram that shows the shape of the complex ion **Y** and shows the type of bond between the ethane-1,2-diamine molecules and the cobalt.
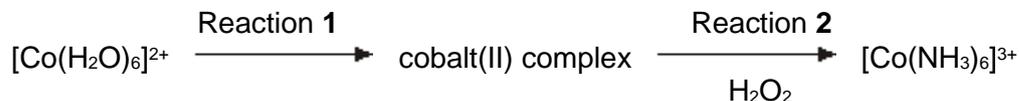
(3)

(c)   Compound **Z** is a complex that contains only cobalt, nitrogen, hydrogen and chlorine.

A solid sample of **Z** was prepared by reaction of 50 cm³ of 0.203 mol dm⁻³ aqueous cobalt(II) chloride with ammonia and an oxidising agent followed by hydrochloric acid.

When this sample of **Z** was reacted with an excess of silver nitrate, 4.22 g of silver chloride were obtained.

Use this information to calculate the mole ratio of chloride ions to cobalt ions in **Z**.

Give the formula of the complex cobalt compound **Z** that you would expect to be formed in the preparation described above.

Suggest **one** reason why the mole ratio of chloride ions to cobalt ions that you have calculated is different from the expected value.

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(5)
(Total 15 marks)

Q17.

Hydrogen peroxide is used as an oxidising agent in the preparation of transition metal complexes.

(a) Consider the following reaction scheme. All the complexes are in aqueous solution.

$$[Co(H_2O)_6]^{2+} \xrightarrow{\text{Reaction } 1} \text{cobalt(II) complex} \xrightarrow[H_2O_2]{\text{Reaction } 2} [Co(NH_3)_6]^{3+}$$

(i) Identify a reagent for Reaction **1** and describe the colour change that occurs.

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(3)

(ii) State the colour of the final solution formed in Reaction **2**.

_____

(1)

(b) Consider the following reaction scheme. All the complexes are in aqueous solution.

$$[Cr(H_2O)_6]^{3+} \xrightarrow[\text{Excess NaOH(aq)}]{\text{Reaction } 3} \text{chromium(III) complex} \xrightarrow[H_2O_2]{\text{Reaction } 4} CrO_4^{2-}$$
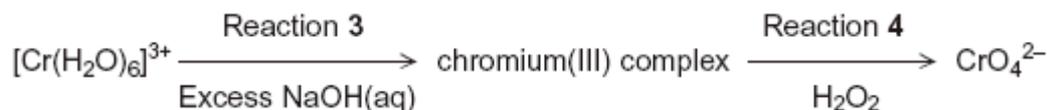
(i) For Reaction **3**, state the colour of the initial and of the final solution and write an equation for the reaction.

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(4)

(ii) Write a half-equation for the reduction of hydrogen peroxide to hydroxide ions.

Deduce an overall equation for Reaction **4** and state the colour of the final solution.

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(4)

(c)   The concentration of a hydrogen peroxide solution can be determined by titration with acidified potassium manganate(VII) solution. In this reaction the hydrogen peroxide is oxidised to oxygen gas.

A 5.00 cm^3 sample of the hydrogen peroxide solution was added to a volumetric flask and made up to 250 cm^3 of aqueous solution. A 25.0 cm^3 sample of this diluted solution was acidified and reacted completely with 24.35 cm^3 of 0.0187 mol dm^{-3} potassium manganate(VII) solution.

Write an equation for the reaction between acidified potassium manganate(VII) solution and hydrogen peroxide.
Use this equation and the results given to calculate a value for the concentration, in mol dm^{-3}, of the original hydrogen peroxide solution.
(If you have been unable to write an equation for this reaction you may assume that 3 mol of $KMnO_4$ react with 7mol of H_2O_2. This is **not** the correct reacting ratio.)

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(5)
(Total 17 marks)

Q18.

The electrons transferred in redox reactions can be used by electrochemical cells to provide energy.

Some electrode half-equations and their standard electrode potentials are shown in the table below.

Half-equation	E^o/V
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–0.44
$Li^+(aq) + e^- \rightarrow Li(s)$	–3.04

(a)   Describe a standard hydrogen electrode.

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(4)

(b)   A conventional representation of a lithium cell is given below.
This cell has an e.m.f. of +2.91 V

        $Li(s) \mid Li^+(aq) \parallel Li^+(aq) \mid MnO_2(s) , LiMnO_2(s) \mid Pt(s)$

Write a half-equation for the reaction that occurs at the positive electrode of this cell.

Calculate the standard electrode potential of this positive electrode.

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(2)

(c) Suggest what reactions occur, if any, when hydrogen gas is bubbled into a solution containing a mixture of iron(II) and iron(III) ions. Explain your answer.

_____

_____

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(2)

(d) A solution of iron(II) sulfate was prepared by dissolving 10.00 g of $FeSO_4.7H_2O$ (M_r = 277.9) in water and making up to 250 cm³ of solution. The solution was left to stand, exposed to air, and some of the iron(II) ions became oxidised to iron(III) ions. A 25.0 cm³ sample of the partially oxidised solution required 23.70 cm³ of 0.0100 mol dm⁻³ potassium dichromate(VI) solution for complete reaction in the presence of an excess of dilute sulfuric acid.

Calculate the percentage of iron(II) ions that had been oxidised by the air.

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(6)
(Total 14 marks)

Mark Scheme

Q13.

(a)   Moles MnO_4^- $\dfrac{26.50 \times 0.02}{1000}$ $= 5.30 \times 10^{-4}$

1

Moles in 25cm³ sample / pipette $C_2O_4^{2-}$ (from acid and salt)
$= 5.30 \times 10^{-4}$ **× 5/2 = (1.325 × 10⁻³)**

1

Moles NaOH = $\dfrac{10.45 \times 0.1}{1000}$ ($= 1.045 \times 10^{-3}$)

1

So moles $C_2O_4^{2-}$ from acid in 25cm³ sample / pipette
$= 1.045 \times 10^{-3}$ **÷ 2** $= 5.225 \times 10^{-4}$

1

Hence moles $C_2O_4^{2-}$ in sodium ethanedioate in 25 cm³

$= 1.325 \times 10^{-3} - 5.225 \times 10^{-4}$ ($= 8.025 \times 10^{-4}$)

1

So moles $C_2O_4^{2-}$ in sodium ethanedioate in original sample
$= 8.025 \times 10^{-4}$ **× 10   (= 8.025 × 10⁻³)**

1

Mass $Na_2C_2O_4 = 8.025 \times 10^{-3}$ **× 134(.0) = 1.075(35) g**
So % sodium ethanedioate in original sample

1

$\dfrac{1.075(35)}{1.90}$ × 100   = 56.6 %   to 3 sig fig

1

*The first CE is penalised by 2 marks; further errors are penalised
by one mark each*

M2 = M1 × 5/2

M4 = M3 ÷ 2
M5 = M2 − M4 (do not allow if negative and do not allow = M4-M2)
If no subtraction, max = 5 (M1, M2, M3, M4 and M6)
If incorrect subtraction, max = 6 (M1, M2, M3, M4, M6 and M7)

M6 = M5 × 10
*(M6 can be scored by multiplying M2 and M4 by 10 before
subtraction (giving $1.325 \times 10^{-2} - 5.225 \times 10^{-3} = 8.025 \times 10^{-3}$)*
M7 = M6 × 134
M8 = (M7/1.90) × 100   Allow 56.5 – 56.8%

(b) $[Fe(H_2O)_6]^{3+} + 3C_2O_4^{2-} \longrightarrow [Fe(C_2O_4)_3]^{3-} + 6H_2O$

1
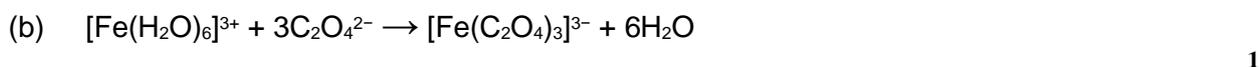
There are <u>6</u> Fe–O bonds broken and then made / <u>same</u> number and type of bond
being broken and made.

1
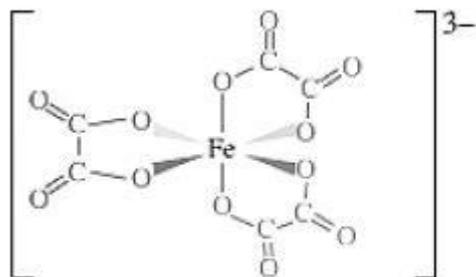
(c)

Ignore all charges even if wrong
Ignore absence of square brackets
Candidates do not need to show 3D shape

1

90° or 180°

1

optical

1

(d)   The ethanedioic acid is only present in small quantities/low

concentration in these foods.

1

[14]

Q14.
(a)   (i)   M1 - M_r calcium phosphate = 310(.3)
                     If M_r wrong, lose M1 and M5.

1

M2 - Moles calcium phosphate = $\dfrac{7.26}{M1}$ (= 0.0234)

0.0234 moles can score M1 and M2.
If M_r incorrect, can score M2 for $\dfrac{7.26}{M1}$.

Allow M2 and / or M3 to 2 significant figures here but will lose M5 if answer not 1.23.

1

M3 - Moles phosphoric acid = 2 × 0.0234 = 0.0468
Allow student's M2 × 2. If not multiplied by 2 then lose M3 and M5.

1

M4 - Vol phosphoric acid = 0.038(0) dm³
If not 0.038(0) dm³ then lose M4 and M5.

1

Conc phosphoric acid = $\dfrac{0.0468}{0.038(0)}$

M5 = <u>1.23</u> (mol dm⁻³)

This answer only – unless arithmetic or transcription error that has been penalised by 1 mark.
Allow no units but incorrect units loses M5.

1

(ii) $\dfrac{492.3}{688.3} \times 100$ **OR** $\dfrac{492}{688} \times 100$

1 mark for both M_r correctly placed.

= 71.5%

2
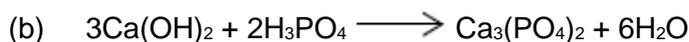
(b) $3Ca(OH)_2 + 2H_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6H_2O$
Allow multiples.

1

(c)

Ca	H	P	O
$\dfrac{1.67}{40.1}$	$\dfrac{0.17}{1}$	$\dfrac{2.59}{31}$	$\dfrac{5.33}{16}$
= 0.042	0.17	0.084	0.333
1	4	2	8

If $x = 2$ with no working, allow M4 only.
Ca = 1.67 g (M1).

1

Mark for dividing by correct A_r in Ca and P (M2).
If M1 incorrect can only score M2.

1

Correct ratio (M3).

1
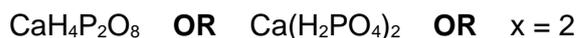
$CaH_4P_2O_8$ **OR** $Ca(H_2PO_4)_2$ **OR** $x = 2$
Value of x or correct formula (M4).

1

Alternative

Ca   H$_2$PO$_4$
Ca = 1.67 g (M1).
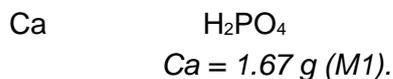
$\dfrac{1.67}{40.1}$ $\dfrac{8.09}{97.0}$

Mark for dividing by correct A_r / M_r in Ca and H_2PO_4 (M2).
If M1 incorrect can only score M2.

= 0.042   0.083
   1   2

Correct ratio (M3).
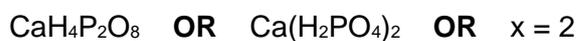
$CaH_4P_2O_8$ **OR** $Ca(H_2PO_4)_2$ **OR** $x = 2$
Value of x or correct formula (M4).

[12]

Q15.

(a) moles of $Cr_2O_7^{2-}$ per titration = 21.3 × 0.0150 / 1000 = <u>3.195 × 10^{-4}</u>

1

$(Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+})$ $Cr_2O_7^{2-}$:Fe^{2+} = 1:6

If 1:6 ratio incorrect cannot score M2 or M3

1

moles of Fe^{2+} = 6 × 3.195 × 10^{-4} = 1.917 × 10^{-3}

Process mark for M1 × 6 (also score M2)

1

original moles in 250 cm^3 = 1.917 × 10^{-3} × 10 = 1.917 × 10^{-2}

Process mark for M3 × 10

1

mass of $FeSO_4.7H_2O$ = 1.917 × 10^{-2} × 277.9 = 5.33 (g)

Mark for answer to M4 × 277.9

(allow 5.30 to 5.40)

*Answer **must** be to at least 3 sig figs*

Note that an answer of 0.888 scores M1, M4 and M5 (ratio 1:1 used)

1

(b) (Impurity is a) reducing agent / reacts with dichromate / impurity is a version of $FeSO_4$ with fewer than 7 waters (not fully hydrated)

Allow a reducing agent or compound that that converts Fe^{3+} into Fe^{2+}

1

Such that for a given mass, the impurity would react with more dichromate than a similar mass of $FeSO_4.7H_2O$

OR for equal masses of the impurity and $FeSO_4.7H_2O$, the impurity would react with more dichromate.

Must compare mass of impurity with mass of $FeSO_4.7H_2O$

1

[7]

Q16.

(a) Cobalt has variable oxidation states

Allow exists as Co(II) and Co(III)

1

(It can act as an intermediate that) lowers the activation energy

Allow (alternative route with) lower E_a

1

$CH_3CHO + 2Co^{3+} + H_2O \rightarrow CH_3COOH + 2Co^{2+} + 2H^+$

Allow multiples; allow molecular formulae

Allow equations with H_3O+

1

$\frac{1}{2}$O$_2$ + 2Co^{2+} + 2H$^+$ → 2Co^{3+} + H$_2$O

1

(b) (i)   [Co(H$_2$O)$_6$]$^{2+}$ + 3H$_2$NCH$_2$CH$_2$NH$_2$ → [Co(H$_2$NCH$_2$CH$_2$NH$_2$)$_3$]$^{2+}$ + 6H$_2$O
Do not allow en in equation, allow C$_2$H$_8$N$_2$

1

The number of particles increases / changes from 4 to 7
*Can score M2 and M3 even if equation incorrect or missing
provided number of particles increases*

1

So the entropy change is positive / disorder increases / entropy increases

1

(ii)   Minimum for **M1** is 3 bidentate ligands bonded to Co
*Ignore all charges for M1 and M3 but penalise charges on any
ligand in M2*

1

Ligands need not have any atoms shown but diagram must show 6 bonds
from ligands to Co, 2 from each ligand

Minimum for **M2** is one ligand identified as H$_2$N-----NH$_2$
Allow linkage as −C−C− or just a line.

1

Minimum for **M3** is one bidentate ligand showing two arrows from separate
nitrogens to cobalt

1

(c)   Moles of cobalt = (50 × 0.203) / 1000 = <u>0.01015</u> mol
Allow 0.0101 to 0.0102

1

Moles of AgCl = 4.22/143.4 = 0.0294
Allow 0.029
*If not AgCl (eg AgCl$_2$ or AgNO$_3$), lose this mark and can only score
M1, M4 and **M5***

1

Ratio = Cl$^-$ to Co = 2.9 : 1
*Do not allow 3 : 1 if this is the only answer but if 2.9:1 seen
somewhere in answer credit this as **M3***

1

[Co(NH$_3$)$_6$]Cl$_3$ (square brackets not essential)

1

Difference due to incomplete oxidation in the preparation
Allow incomplete reaction.
Allow formation [Co(NH$_3$)$_5$Cl]Cl$_2$ etc.
Some chloride ions act as ligands / replace NH$_3$ in complex.
Do not allow 'impure sample' or reference to practical deficiencies

1

[15]

Q17.

(a) (i) Ammonia
If reagent is missing or incorrect cannot score M3

1

Starts as a pink (solution)

1

Changes to a yellow/straw (solution)
Allow pale brown
Do not allow reference to a precipitate

1

(ii) (dark) brown
Do not allow pale/straw/yellow-brown (i.e. these and other shades except for dark brown)

1

(b) (i) Ruby/red-blue/purple/violet/green
Do not allow red or blue
If ppt mentioned contradiction/CE =0

1

Green
If ppt mentioned contradiction/CE =0

1

$[Cr(H_2O)_6]^{3+} + 6OH^- \rightarrow [Cr(OH)_6]^{3-} + 6H_2O$

1

Formula of product
Can score this mark in (b) (ii)

1

(ii) $H_2O_2 + 2e^- \rightarrow 2OH^-$

1

$2[Cr(OH)_6]^{3-} + 3H_2O_2 \rightarrow 2CrO_4^{2-} + 8H_2O + 2OH^-$
Allow 1 mark out of 2 for a balanced half-equation such as Cr(III) → Cr(VI) + 3e⁻
or $Cr^{3+} + 4H_2O \rightarrow CrO_4^{2-} + 8H^+ + 3e^-$ etc
also for $2Cr(III) + 3H_2O_2 \rightarrow 2CrO_4^{2-}$ (unbalanced)

2

Yellow
Do not allow orange

1

(c) $2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$
if no equation and uses given ratio can score M2, M3, M4 & M5

1

Moles $MnO_4^- = (24.35/1000) \times 0.0187 = \underline{4.55 \times 10^{-4}}$

Note value must be quoted to at least 3 sig. figs.

M2 is for 4.55 × 10⁻⁴

1

Moles $H_2O_2 = (4.55 \times 10^{-4}) \underline{\times 5/2} = 1.138 \times 10^{-3}$

M3 is for × 5/2 (or 7/3)

Mark consequential on molar ratio from candidate's equation

1

Moles H_2O_2 in 5 cm³ original

M4 is for × 10

1

$= (1.138 \times 10^{-3}) \underline{\times 10} = 0.01138$

Original $[H_2O_2] = 0.01138 \underline{\times (1000/5)} = 2.28$ mol dm⁻³

(allow 2.25-2.30)

M5 is for consequentially correct answer from (answer to mark 4) × (1000/5)

Note an answer of between 2.25 and 2.30 is worth 4 marks)

If candidate uses given ratio 3/7 max 4 marks:

__M1__: Moles of MnO₄⁻ = __4.55 × 10⁻⁴__

__M2__: Moles H₂O₂ = (4.55 × 10⁻⁴) __× 7/3__ = 1.0617 × 10⁻³

__M3__: Moles H₂O₂ in 5 cm³ original

= (1.0617 × 10⁻³) × 10 = 0.01062

M4: Original [H₂O₂] = 0.01062 × (1000/5) = 2.12 mol dm⁻³

(allow 2.10 to 2.15)

1

[17]