OCR A Chemistry A-Level

Module 5 - Physical Chemistry & Transition Elements

Redox

Notes and Example Calculations

Answers given at the end of the booklet

Electrode Potentials

Electrochemical cells can be made from two different metals immersed in salt solutions of their own ions and connected by a wire (external circuit). There are always two reactions within an electrochemical cell, oxidation and reduction, meaning it is a redox process.

The standard electrode potential of a half cell is the voltage measured against the standard hydrogen electrode under standard conditions. These are:
- 298 K
- 1 mol dm^{-3}
- 100 kPa

To work out the overall cell potential (when two half cells are connected):

$$Emf_{(cell)} = E^{o}_{(right)} - E^{o}_{(left)}$$

The half cell undergoing a reduction reaction has the more positive electrode potential. The oxidation half cell has the more negative electrode potential.

Example 1:
Work out the overall cell potential half cells 1 and 2 are connected.

	Half-reaction	E/V
1	$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$	-0.76
2	$Fe^{2+}(aq) + 2e \rightleftharpoons Fe(s)$	-0.44
3	$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq)$	+0.77
4	$Ag^{+}(aq) + e \rightleftharpoons Ag(s)$	+0.80
5	$Cl_2(g) + 2e \rightleftharpoons 2Cl^{-}(aq)$	+1.36

Step 1: Work out which half cell undergoes reduction or oxidation.

⇒ The more positive half cell is cell 2 therefore half cell 2 undergoes reduction and therefore half cell 1 undergoes oxidation.

Step 2: Calculate the overall cell potential using the formula: $E^{\circ}_{cell} = E^{\circ}_{reduction} - E^{\circ}_{oxidation}$

-0.44 - (-0.76) = **0.32 V**

Example 2:

Work out the overall cell potential half cells 4 and 5 are connected.

	Half-reaction	E/V
1	$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$	-0.76
2	$Fe^{2+}(aq) + 2e \rightleftharpoons Fe(s)$	-0.44
3	$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq)$	+0.77
4	$Ag^{+}(aq) + e \rightleftharpoons Ag(s)$	+0.80
5	$Cl_2(g) + 2e \rightleftharpoons 2Cl^{-}(aq)$	+1.36

Step 1: Work out which half cell undergoes reduction or oxidation.

⇒ The more positive half cell is cell 5 therefore half cell 5 undergoes reduction and therefore half cell 4 undergoes oxidation.

Step 2: Calculate the overall cell potential using the formula: $E^{\circ}_{cell} = E^{\circ}_{reduction} - E^{\circ}_{oxidation}$

⇒ 1.36 - 0.8 = **0.56 V**

Worked Exam Style Question

Question 1

Use the standard electrode potentials in the table below to answer the questions that follow.

I	$Fe^{2+}(aq) + 2e^{-} \rightleftharpoons Fe(s)$	$E^{\ominus} = -0.44$ V
II	$V^{3+}(aq) + e^{-} \rightleftharpoons V^{2+}(aq)$	$E^{\ominus} = -0.26$ V
III	$2H^{+}(aq) + 2e^{-} \rightleftharpoons H_2(g)$	$E^{\ominus} = 0.00$ V
IV	$O_2(g) + 4H^{+}(aq) + 4e^{-} \rightleftharpoons 2H_2O(l)$	$E^{\ominus} = +0.40$ V

An electrochemical cell was set up based on systems I and II

(ii)   Determine the cell potential of this cell.

Step 1: Work out which half cell undergoes reduction or oxidation.

⇒ The more positive half cell is II therefore half cell II undergoes reduction and therefore half cell I undergoes oxidation.
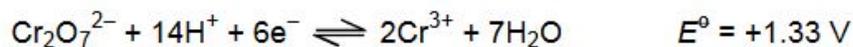
Step 2: Calculate the overall cell potential using the formula: $E^°_{cell} = E^°_{reduction} - E^°_{oxidation}$

⇒ -0.26 - (-0.44) = **0.18 V**

Try this question…

1.

The following equations relate to half-cells involving iron and chromium ions.

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad\qquad E^⊖ = +0.77\ V$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad E^⊖ = +1.33\ V$$

A cell was set up by combining these two half-cells.

Determine the emf of the cell under standard conditions.

[1 mark]

Redox Titrations

Method for balancing half equations:

1. Balance all atoms except for oxygen and hydrogen.
2. Add H_2O to balance oxygens (if needed).
3. Add H^+ ions to balance hydrogens (if needed).
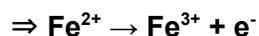4. Add e^- to balance out charges.

Example 1:
Write the full half equations for $Fe^{2+} \rightarrow Fe^{3+}$ and $Cr2O7^{2-} \rightarrow Cr^{3+}$ and then combine half equations.

Step 1: Write the full half equation for iron.
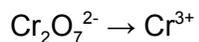
$Fe^{2+} \rightarrow Fe^{3+}$
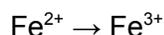
[The only thing that isn't balanced are the charges.]

$\Rightarrow$ **$Fe^{2+} \rightarrow Fe^{3+} + e^-$**

Step 2: Write the full half equation for the chromium ion using the method above.

$Cr_2O_7^{2-} \rightarrow Cr^{3+}$

[Balance oxygen.]

$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$

[Balance hydrogen.]

$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

[Balance changes]

$\Rightarrow$ **$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$**
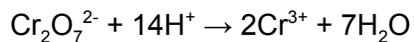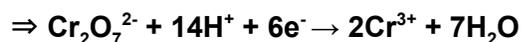
Step 3: Combine the two half equations.

$\Rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

[Balance electrons.]

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (x6)

$\Rightarrow$ $6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$

$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 6Fe^{3+} + 6e^- + 2Cr^{3+} + 7H_2O$

[Cancel the electrons]

$\Rightarrow \mathbf{6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O}$
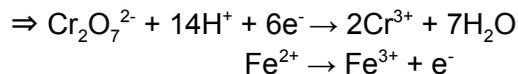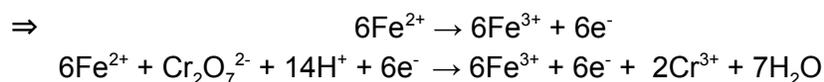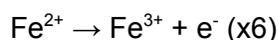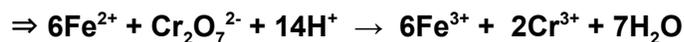
Worked Exam Style Questions

Question 1

Redox titrations using $KMnO_4$ in acidic conditions can be used to analyse reducing agents. Acidified $KMnO_4$ is a strong oxidising agent, readily removing electrons:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

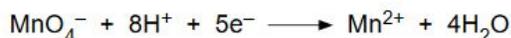A student analysed a solution of hydrogen peroxide, H_2O_2(aq), using a redox titration with $KMnO_4$ under acidic conditions. Under these conditions, H_2O_2 is a reducing agent.

The overall equation for the reaction is given below.

$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

(a) Deduce the simplest whole number half-equation for the oxidation of H_2O_2 under these conditions.

Step 1: Write the half equation for MnO_4^- from the overall equation.

$\Rightarrow 2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$
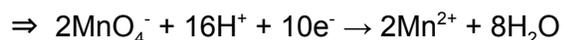
Step 2: Write in the missing components of the half equation for the oxidation of H_2O_2.
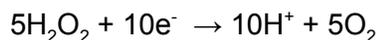
[There are 16 H^+ in the half equation for MnO_4^- therefore there must be 10H^+ ions on the other side of the half equation for the oxidation of H_2O_2.]

$5H_2O_2 \rightarrow 10H^+$
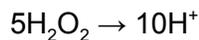
[5 oxygen molecules in the overall equation which are not present for the half equation of the reduction of MnO4-]

$5H_2O_2 \rightarrow 10H^+ + 5O_2$
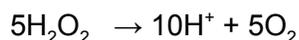
[Balance out the charges.]

$5H_2O_2 + 10e^- \rightarrow 10H^+ + 5O_2$

[Cancel down the multiples.]

$\Rightarrow$ **$H_2O_2 + 2e^- \rightarrow 2H^+ + O_2$**

Question 2

The student diluted 25.0 cm³ of a solution of hydrogen peroxide with water and made the solution up to 250.0 cm³. The student titrated 25.0 cm³ of this solution with 0.0200 mol dm⁻³ $KMnO_4$ under acidic conditions. The volume of $KMnO_4$(aq) required to reach the end-point was 23.45 cm³.

- Calculate the concentration, in g dm⁻³, of the **undiluted** hydrogen peroxide solution.
- What volume of oxygen gas, measured at RTP, would be produced during this titration?

[6 marks]

$$H_2O_2 + 2e^- \rightarrow 2H^+ + O_2$$
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

Part 1
Step 1: Calculate the number of moles of $KMnO_4$/ MnO_4^- ions.

$\Rightarrow$ Moles = concentration x volume
= 0.02 x (23.45/1000)
= **4.69 x 10⁻⁴ moldm⁻³**

Step 2: Find the molar ratio.

Molar ratio: MnO_4^- : H_2O_2
              2 : 5
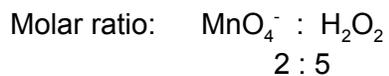
Step 3: Therefore work out the moles of H_2O_2.

$1.5 \times 4.69 \times 10^{-4} = 1.1725 \times 10^{-3}$ moles

Step 4: Work out the concentration of H_2O_2 in this sample.

⇒ Concentration = moles / volume
                = 1.1725×10^{-3} / 0.025
                = 0.0469 moldm^{-3}

Step 5: Work out the concentration of the undiluted of solution.

The dilution factor is 10.
(25 x 10 = 250)

⇒ 0.0469 x 10 = 0.469 moldm^{-3}

Step 5: Convert mol dm^{-3} to g dm^{-3}.

Mass = mr x mol

⇒ Mr of H_2O_2 = 2 + (16 x 2)
              = 34

⇒ 0.469 x 34 = **15.9 gdm^{-3}**

Part 2
Step 1: Using stoichiometry work out the number of moles of oxygen molecules.

Molar ratio: H_2O_2 : O_2
                1 : 1
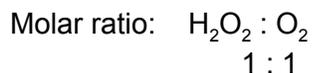
⇒ Moles of oxygen = 1.1725×10^{-3}

Step 2: Work out the volume of gas using: moles x 24 = volume

$\Rightarrow$ 1.1725 x 10^{-3} x 24 = **0.0281 dm³**

Question 3

Haematite is the main ore of iron. The percentage of iron in a sample of haematite can be determined using the method below.

Method

Stage 1. An excess of concentrated hydrochloric acid is added to a 3.25 g sample of haematite. The iron(III) oxide in the haematite reacts to form a solution containing Fe^{3+} ions.

Stage 2. An excess of aqueous tin(II) chloride is added. Sn^{2+} reduces the Fe^{3+} present to Fe^{2+}. Excess Sn^{2+} is removed.

Stage 3. The solution is diluted and made up to 250.0 cm³ in a volumetric flask.
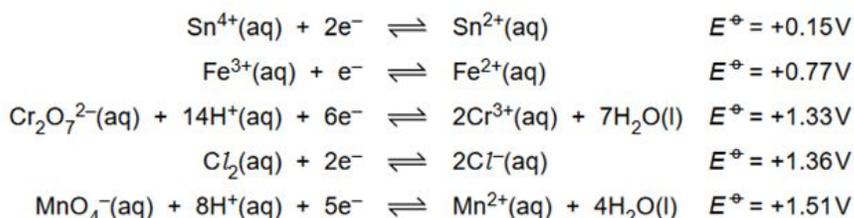
Stage 4. A 25.0 cm³ sample of this solution is pipetted into a conical flask.

Stage 5. The solution in the conical flask is titrated with 0.0200 mol dm^{-3} aqueous potassium dichromate(VI), $K_2Cr_2O_7$. The Fe^{2+} ions are oxidised to Fe^{3+} ions.

Stage 6. Stages 4 and **5** are repeated to obtain an average titre of 26.5 cm³.

You are provided with the following electrode potentials.

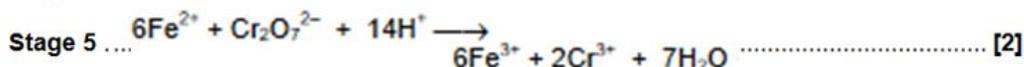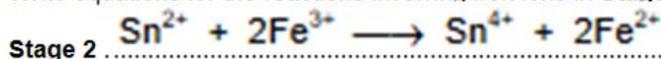You may need to use this information throughout this question.

$$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq) \qquad E^\ominus = +0.15V$$
$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^\ominus = +0.77V$$
$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l) \quad E^\ominus = +1.33V$$
$$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq) \qquad E^\ominus = +1.36V$$
$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \quad E^\ominus = +1.51V$$

(a) Write an equation for the reaction between iron(III) oxide and concentrated hydrochloric acid, occurring in **Stage 1**.

$$Fe_2O_3 + 6H^+ \longrightarrow 2Fe^{3+} + 3H_2O$$

.... [1]

(b) Write equations for the reactions involving iron ions in **Stages 2** and **5**.

Stage 2 $$Sn^{2+} + 2Fe^{3+} \longrightarrow Sn^{4+} + 2Fe^{2+}$$

Stage 5 $$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$ .... [2]

(c) Calculate the percentage by mass of iron in the haematite ore.

[5 marks]

Step 1: Work out the number of moles of potassium dichromate.

$\Rightarrow$ Moles = concentration x volume

$= 0.02 \times (26.5/1000)$

$= 5.3 \times 10^{-4}$

Step 2: Using stoichiometry work out the number of Fe^{3+} ions.

Molar ratio: $Cr_2O_7 : Fe^{3+}$

$1 : 6$
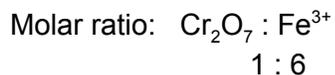
$\Rightarrow 5.3 \times 10^{-4} \times 6 = 3.18 \times 10^{-3}$

Step 3: Work out the number of moles in the original 250 cm^3.

The dilution factor is 10.

$\Rightarrow 3.18 \times 10^{-3} \times 10 = 3.18 \times 10^{-2}$

Step 4: Work out the mass of Fe^{3+} ions.

$\Rightarrow$ Mass = Mr x mole

$= 55.8 \times 3.18 \times 10^{-2}$

$= 1.77444$ g

Step 5: Calculate the percentage of mass of iron.

$(1.77444 / 3.25) \times 100 = $ **54.6 %**

Try these questions...

2.

The Dissolved Oxygen Concentration (DOC) in rivers and lakes is important for aquatic life. If the DOC falls below $5\,mg\,dm^{-3}$, most species of fish cannot survive.

Environmental chemists can determine the DOC in water using the procedure below.


- A sample of river water is shaken with aqueous Mn^{2+} and aqueous alkali.
  The dissolved oxygen oxidises the Mn^{2+} to Mn^{3+}, forming a pale brown precipitate of $Mn(OH)_3$.

  $$O_2(aq) + 4Mn^{2+}(aq) + 8OH^-(aq) + 2H_2O(l) \longrightarrow 4Mn(OH)_3(s)$$
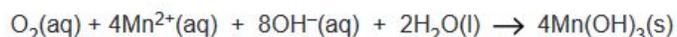
- The $Mn(OH)_3$ precipitate is then reacted with an excess of aqueous potassium iodide, which is oxidised to iodine, I_2.

  $$2Mn(OH)_3(s) + 2I^-(aq) \longrightarrow I_2(aq) + 2Mn(OH)_2(s) + 2OH^-(aq)$$
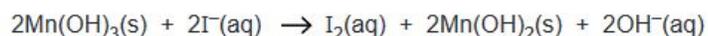
- The iodine formed is then determined by titration with aqueous sodium thiosulfate, $Na_2S_2O_3(aq)$.

  $$2S_2O_3{}^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6{}^{2-}(aq) + 2I^-(aq)$$
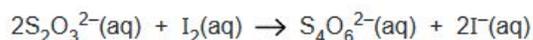
A $25.0\,cm^3$ sample of river water was analysed using the procedure above.

The titration required $24.6\,cm^3$ of $0.00100\,mol\,dm^{-3}$ $Na_2S_2O_3(aq)$.

(a) (i) Calculate the DOC of the sample of river water, in $mg\,dm^{-3}$.

[4 marks]
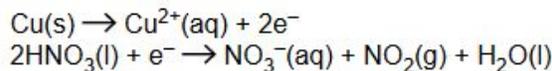
3.

Brass is an alloy which contains copper.
The percentage of copper in brass can be determined using the steps below.

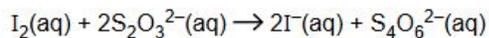|	
Step 1	2.80 g of brass is reacted with an excess of concentrated nitric acid, HNO_3. The half-equations taking place are shown below. $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $2HNO_3(l) + e^- \rightarrow NO_3^-(aq) + NO_2(g) + H_2O(l)$
Step 2	Excess aqueous sodium carbonate is added to neutralise any acid. The mixture effervesces and a precipitate forms.
Step 3	The precipitate is reacted with ethanoic acid to form a solution which is made up to 250 cm^3 with water.

Step 4	A 25.0 cm^3 sample of the solution is pipetted into a conical flask and an excess of aqueous potassium iodide is added. A precipitate of copper(I) iodide and a solution of iodine, I_2(aq), forms.
Step 5	The resulting mixture is titrated with 0.100 mol dm^{-3} sodium thiosulfate to estimate the iodine present: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$
Step 6	**Steps 4** and **5** are repeated to obtain an average titre of 29.8 cm^3.

- For **steps 1**, **2** and **4**, write ionic equations, including state symbols, for the reactions taking place.

- Determine the percentage, by mass, of copper in the brass.
  Give your answer to **one** decimal place.

[9 marks]

Answers

Q1.

$$\text{Emf} = (+)\, 0.56 \text{ V} \qquad\qquad\qquad\qquad\qquad\qquad 1$$

Q2.

Answer	Mark	Guidance
amount $S_2O_3^{2-}$ used $= 0.00100 \times \dfrac{24.6}{1000} = 2.46 \times 10^{-5}$ mol ✓ **amount O_2 in 25 cm^3 sample** $= \dfrac{2.46 \times 10^{-5}}{4} = 6.15 \times 10^{-6}$ mol ✓ **Concentration of O_2 in sample** $= 6.15 \times 10^{-6} \times \dfrac{1000}{25} = 2.46 \times 10^{-4}$ (mol dm^{-3}) ✓ **mass concentration of O_2 in mg dm^{-3}** $= 2.46 \times 10^{-4} \times 32$ g $= 7.872 \times 10^{-3}$ (g dm^{-3}) $= 7.872$ (mg dm^{-3}) ✓	4	ANNOTATE WITH TICKS AND CROSSES, etc **ALLOW** 0.0000246 (mol) $\text{ECF} = \dfrac{\text{answer above}}{4}$ **ALLOW** 0.00000615 g **ECF** answer above $\times \dfrac{1000}{25}$ **ALLOW** 0.000246 g **ECF** = answer above $\times$ 32 x 1000 **ALLOW** 7.9 **OR** 7.87 **ALLOW** 2 SF up to calculator value **Must be in mg for mark** **Note:** Candidate may work out steps 3 and 4 in the opposite order, *ie* **mass of O_2 in sample** $= 6.15 \times 10^{-6} \times 32 \times 1000 = 1.968 \times 10^{-1}$ mg **mass concentration of O_2 in mg dm^{-3}** $= 1.968 \times 10^{-1} \times \dfrac{1000}{25} = 7.872$ (mg dm^{-3})

Q3.

Answer	Mark	Guidance
step 1 $Cu + 4HNO_3 \longrightarrow Cu^{2+} + 2NO_3^- + 2NO_2 + 2H_2O$ **OR** $Cu + 2H^+ + 2HNO_3 \longrightarrow Cu^{2+} + 2NO_2 + 2H_2O$ **OR** $Cu + 4H^+ + 2NO_3^- \longrightarrow Cu^{2+} + 2NO_2 + 2H_2O$ ✓ **step 2** **2 equations with 1 mark for each** $Cu^{2+} + CO_3^{2-} \longrightarrow CuCO_3$ ✓ $2H^+ + CO_3^{2-} \longrightarrow H_2O + CO_2$ ✓ **step 4** $2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$ ✓	4	**ANNOTATE ALL Q8 WITH TICKS AND CROSSES, etc** **ALLOW** multiples throughout **IGNORE** state symbols throughout **ALLOW** $Cu(NO_3)_2$ for $Cu^{2+} + 2NO_3^-$ **AWARD 2 MARKS for a combined equation:** $Cu^{2+} + 2H^+ + 2CO_3^{2-} \longrightarrow CuCO_3 + H_2O + CO_2$ ✓✓ **DO NOT ALLOW** $2H^+ + CO_3^{2-} \longrightarrow H_2CO_3$ **ALLOW** $2Cu^{2+} + 4KI \longrightarrow 2CuI + I_2 + 4K^+$ **ALLOW** $Cu^{2+} + I^- \longrightarrow Cu^+ + \frac{1}{2}I_2$
FIRST, CHECK THE ANSWER ON ANSWER LINE **IF** answer = 67.6%, award **5 marks.** **Ignore any attempted equation in step 4** **IF** answer = 33.8% **AND IF** Cu^{2+}/I_2 in **step 4** equation shown with 1:1 molar ratio, award 5 marks for **ECF** -- amount $S_2O_3^{2-}$ used = $0.100 \times \frac{29.8}{1000} = 2.98 \times 10^{-3}$ mol ✓ amount $I_2 = 1.49 \times 10^{-3}$ mol **OR** amount $Cu^{2+} = 2.98 \times 10^{-3}$ mol ✓ amount Cu^{2+} in original 250 cm³ = **10 x** 2.98×10^{-3} = 2.98×10^{-2} mol ✓ Mass of Cu/Cu^{2+} in brass = $63.5 \times 2.98 \times 10^{-2}$ g = 1.8923 g ✓ percentage Cu in brass = $\frac{1.8923}{2.80} \times 100$ = 67.6% ✓ **MUST** be to **one** decimal place (in the question)	5	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below -- **Working must be to 3 SF throughout until final % mark** BUT ignore trailing zeroes, ie for 0.490 allow 0.49 **ECF** answer above **ECF** 10 x answer above **ECF** 63.5 x answer above **ALLOW** 1.88 g **ECF** $\frac{\text{answer above}}{2.80} \times 100$ Answer **must** be to one decimal place **ALLOW** % Cu = 67.5 % **IF** mass of Cu has been rounded to 1.89 g in previous step **Common ECFs:** **6.76%** x10 missing 3/5 marks for calculation 2 d.p. MS states 1 d.p. **33.8%** IF Cu^{2+}/I_2 in **step 4** equation with 2:1 ratio **OR** not attempted, response, 4/5 marks for calculation (moles Cu^{2+} incorrect)