

Surname <i>StemUp Model Solution</i>	Centre Number	Candidate Number
First name(s)		2



GCE A LEVEL

1410U30-1



TUESDAY, 10 JUNE 2025 – MORNING

CHEMISTRY – A2 unit 3
Physical and Inorganic Chemistry

1 hour 45 minutes

For Examiner's use only		
Question	Maximum Mark	Mark Awarded
Section A 1. to 6.	10	
Section B 7.	16	
8.	13	
9.	19	
10.	22	
Total	80	

ADDITIONAL MATERIALS

- A calculator, pencil and ruler
- **Data Booklet** supplied by WJEC

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen. Do not use gel pen or correction fluid.

You may use a pencil for graphs and diagrams only.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions.

Section B Answer **all** questions.

Write your answers in the spaces provided in this booklet. If you run out of space, use the additional page(s) at the back of the booklet, taking care to number the question(s) correctly.

INFORMATION FOR CANDIDATES

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

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The assessment of the quality of extended response (QER) will take place in **Q9(b)(iii)**.



JUN251410U30101

SECTION A

Answer **all** questions.

1. Complete the Arrhenius equation below. [1]

$$k = Ae^{\frac{-E_a}{RT}}$$

2. Give a reason why SiCl_4 reacts vigorously with water whilst CCl_4 does not. [1]

Silicon has available d-orbitals in its outer shell but carbon does not, so water can bond to (attack) the silicon but not the carbon.

3. Many reactions use heterogeneous catalysts.

- (a) State what is meant by the term heterogeneous in this context. [1]

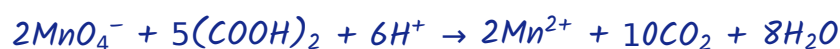
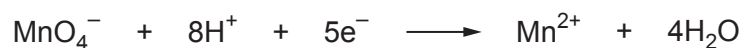
The catalyst is in a different physical state (phase) from the reactants.

- (b) Give an example of a heterogeneous catalyst and the reaction it catalyses. [1]

Iron (Fe) in the Haber process ($\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$).

4. Ethanedioic acid, $(\text{COOH})_2$, can be oxidised by acidified manganate(VII) ions.

Use the half-equations below to write the ionic equation for the reaction. [1]



5. A metal halide gives a lilac flame test and the addition of concentrated sulfuric acid causes it to release coloured fumes and a smell of rotten eggs.

Identify the metal halide, giving reasons for your answer.

[2]

Potassium iodide, KI. The lilac flame shows potassium (K^+) ions.

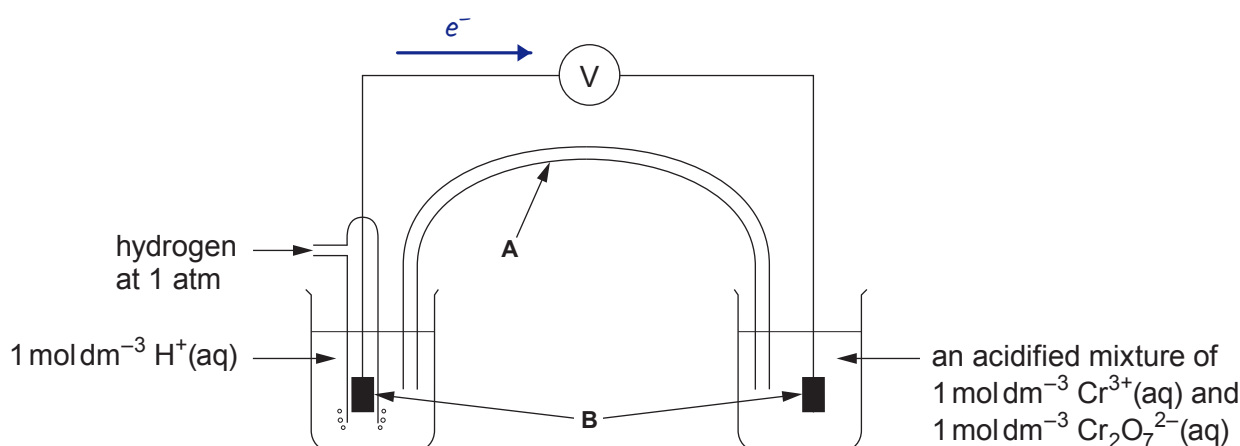
The smell of rotten eggs (H_2S) and coloured fumes (iodine) show iodide (I^-) ions.

6. (a) Give the observation(s) expected when aqueous sodium hydroxide is added gradually to aqueous chromium(III) chloride until the sodium hydroxide is in excess.

[1]

A grey-green precipitate forms, which dissolves in excess sodium hydroxide to give a green solution.

- (b) The diagram shows the apparatus used to measure the standard electrode potential for the half-equation:



- (i) Name parts **A** and **B**.

[1]

A *salt bridge*

B *platinum (electrodes)*

- (ii) **Label the diagram** to show the direction of flow of electrons in the wire.

[1]



SECTION BAnswer **all** questions.

7. (a) Metal nitrates containing Group 2 metals decompose upon heating.



Metal nitrate	Standard enthalpy change of reaction / kJ mol^{-1}	Standard entropy change of reaction / $\text{J K}^{-1} \text{mol}^{-1}$
$\text{Mg}(\text{NO}_3)_2$	444	411
$\text{Ca}(\text{NO}_3)_2$		379
$\text{Ba}(\text{NO}_3)_2$	936	397

- (i) Give a reason why all the entropy changes are positive. [1]

Gases (NO_2 and O_2) are produced from a solid, and gases have a much higher entropy than solids.

- (ii) The minimum temperature for decomposition of calcium nitrate is
- 1500°C
- .

Find the standard enthalpy change for this reaction. [3]

$$T = 1500 + 273 = 1773 \text{ K}$$

at the minimum temperature $\Delta G = 0$, so $\Delta H = T\Delta S$

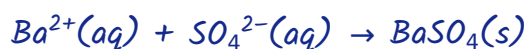
$$\Delta S = 379 \text{ J K}^{-1} \text{mol}^{-1} = 0.379 \text{ kJ K}^{-1} \text{mol}^{-1}$$

$$\Delta H = 1773 \times 0.379 = 672 \text{ kJ mol}^{-1}$$

Standard enthalpy change = 672 kJ mol^{-1} 

- (iii) Treatment of aqueous barium nitrate with sulfuric acid produces a white precipitate of barium sulfate, whilst addition of the same acid to aqueous magnesium nitrate does not give a precipitate.

- I. Write the ionic equation for the formation of the precipitate, including state symbols. [1]



- II. Use the data below to explain why barium sulfate is insoluble in water whilst magnesium sulfate is soluble. [3]

	Standard enthalpy change / kJ mol^{-1}
Lattice breaking enthalpy of MgSO_4	2833
Lattice breaking enthalpy of BaSO_4	2474
Hydration enthalpy of Mg^{2+} ion	-1920
Hydration enthalpy of Ba^{2+} ion	-1360
Hydration enthalpy of SO_4^{2-} ion	-1059

$$\Delta_{\text{sol}}H = \text{lattice breaking enthalpy} + \Delta_{\text{hyd}}H(\text{M}^{2+}) + \Delta_{\text{hyd}}H(\text{SO}_4^{2-})$$

$$\text{MgSO}_4: \Delta_{\text{sol}}H = 2833 + (-1920) + (-1059) = -146 \text{ kJ mol}^{-1}$$

$$\text{BaSO}_4: \Delta_{\text{sol}}H = 2474 + (-1360) + (-1059) = +55 \text{ kJ mol}^{-1}$$

$\Delta_{\text{sol}}H$ of MgSO_4 is negative (exothermic) so it is soluble; $\Delta_{\text{sol}}H$ of BaSO_4 is significantly positive (endothermic) so it is insoluble.



- (b) Ammonium nitrate is a soluble salt. Suggest the pH of an aqueous solution of ammonium nitrate, giving a reason for your answer. [2]

pH about 5 (weakly acidic).

NH_4^+ ions partially dissociate to release H^+ ions: $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$

- (c) Aqueous lead(II) nitrate forms precipitates when a variety of aqueous solutions are added.

Complete the table to give the observations, if any, when the solutions below are added to aqueous lead(II) nitrate. [2]

Solution added	Observation(s)
sulfuric acid	<i>white precipitate</i>
potassium iodide	<i>bright yellow precipitate</i>



- (d) Metal nitrates are often found in rocks mixed with materials such as limestone. A student is provided with a rock which contains a mixture of sodium nitrate and calcium carbonate. Heating the rock causes both substances to decompose according to the following equations.



The boiling temperatures of the gases produced are as follows.

Substance	O ₂	CO ₂
Boiling temperature / K	90	195

A sample of 81.3 g of the rock was heated until both substances decomposed completely. The volume of gas produced was measured at 1 atm pressure at two different temperatures.

Temperature / K	Volume of gas produced / cm ³
200	1.193×10^4
100	1.028×10^3

Find the percentage by mass of calcium carbonate in the rock.

[4]

At 100 K only O₂ is a gas (CO₂ is solid as its b.p. is 195 K):

$$n(\text{O}_2) = pV \div RT = (1.01 \times 10^5 \times 1.028 \times 10^{-3}) \div (8.31 \times 100) \\ = 0.125 \text{ mol}$$

At 200 K both O₂ and CO₂ are gases:

$$n(\text{O}_2) + n(\text{CO}_2) = (1.01 \times 10^5 \times 1.193 \times 10^{-2}) \div (8.31 \times 200) \\ = 0.725 \text{ mol}$$

$$n(\text{CO}_2) = 0.725 - 0.125 = 0.600 \text{ mol, so } n(\text{CaCO}_3) = 0.600 \text{ mol}$$

$$\text{mass of CaCO}_3 = 0.600 \times 100.1 = 60.06 \text{ g}$$

$$\% \text{ CaCO}_3 = 60.06 \div 81.3 \times 100 = 73.9\%$$

Percentage calcium carbonate = ... 73.9 %



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8. (a) When chlorine gas reacts with concentrated aqueous sodium hydroxide solution, it produces sodium chloride, sodium chlorate(V) and water.

(i) Write an equation for this reaction.

[1]



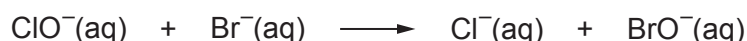
(ii) Use oxidation states to show why this reaction can be described as disproportionation.

[2]

The same element (chlorine) is both oxidised and reduced.

Chlorine is oxidised from 0 in Cl_2 to +5 in NaClO_3 , and reduced from 0 to -1 in NaCl .

- (b) Chlorate(I) ions can oxidise bromide ions according to the following equation.



(i) One method of studying the rate of this reaction is by sampling and quenching.

State how you would quench the samples.

[1]

Add each sample to a large volume of ice-cold water.

(ii) The reaction is first order with respect to each reactant therefore second order overall.

A student states that this means that successive half-life values for each reactant will be constant. Is the student correct?

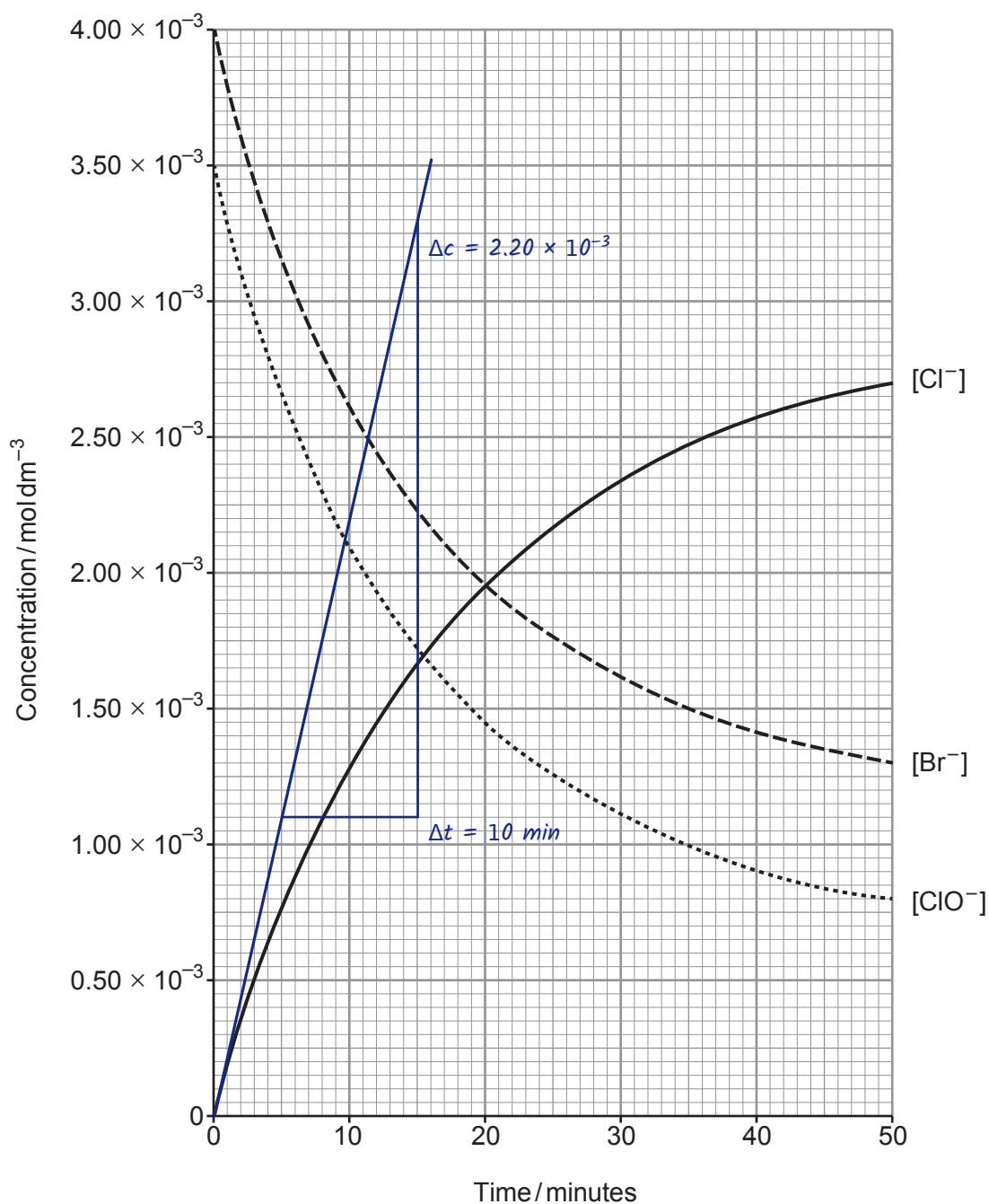
Give a reason for your answer.

[1]

No. The reaction is second order overall, and when one reactant's concentration halves the other also changes, which affects the rate, so the half-lives are not constant.



- (iii) A student follows the progress of the reaction at a temperature of 298 K. She obtains the results shown in the graph.



- I. Use the concentration of chloride ions to find the initial rate of the reaction.

[2]

Tangent drawn at $t = 0$ on the $[Cl^-]$ curve.

$$\text{gradient} = 2.20 \times 10^{-3} \div 10 = 2.20 \times 10^{-4}$$

$$\text{Rate} = 2.20 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$$

- II. Find the value of the rate constant for the reaction, giving its unit.

[4]

$$\text{rate} = k[ClO^-][Br^-]$$

$$\text{initial } [ClO^-] = 3.50 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{initial } [Br^-] = 4.00 \times 10^{-3} \text{ mol dm}^{-3}$$

$$k = \text{initial rate} \div ([ClO^-][Br^-])$$

$$k = 2.20 \times 10^{-4} \div (3.50 \times 10^{-3} \times 4.00 \times 10^{-3})$$

$$k = 15.7$$

$$k = 15.7$$

$$\text{Unit } \text{mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$$

- III. Another student chooses to plot the concentration of bromate(I) ions formed instead of the concentration of chloride ions formed.

State the differences in their graphs, if any, giving a reason for your answer.

[2]

No difference: the graphs would be identical.

Each time one chloride ion is produced, one bromate(I) ion is produced, so $[BrO^-]$ is always equal to $[Cl^-]$.



9. Ethanoic acid can be produced in a reaction between iodomethane and carbon monoxide, followed by treatment with water.



- (a) Use data from one of the tables below to calculate the **more accurate** value of the standard enthalpy change for reaction 1. Give a reason for your choice of data. [3]

Bond	Bond energy / kJ mol^{-1}
C — H	413
C — C	346
C — I	240
C = O	745
C $\equiv$ O in carbon monoxide	1072

Substance	Standard enthalpy change of formation / kJ mol^{-1}
CH_3I	-14
CO	-111
CH_3COI	-162

Using the standard enthalpies of formation:

$$\Delta H = \Sigma \Delta_f H(\text{products}) - \Sigma \Delta_f H(\text{reactants})$$

$$\Delta H = -162 - (-14 + (-111))$$

$$\Delta H = -162 + 125 = -37 \text{ kJ mol}^{-1}$$

Enthalpy change for reaction 1 = ... **-37** kJ mol^{-1}

Enthalpies of formation give the more accurate value because bond energies are average values (from a range of compounds), not specific to these molecules.



(b) Reaction 2 produces a mixture of the weak acid CH_3COOH and the strong acid HI .

- (i) Suggest what effect the presence of HI will have on the dissociation of CH_3COOH in this mixture compared to an aqueous solution containing only CH_3COOH .
Give your reasoning. [2]

Less CH_3COOH will dissociate (its dissociation is suppressed).

HI dissociates fully, releasing H^+ ions, so the equilibrium $\text{CH}_3\text{COOH} \rightleftharpoons$

$\text{CH}_3\text{COO}^- + \text{H}^+$ shifts to the left (reactants): CH_3COO^- ions combine

with H^+ ions to form CH_3COOH .

- (ii) Calculate the pH of an aqueous solution of the strong acid HI of concentration $0.250 \text{ mol dm}^{-3}$. [2]

HI is a strong acid, fully dissociated: $[\text{H}^+] = 0.250 \text{ mol dm}^{-3}$

$$\text{pH} = -\log[\text{H}^+] = -\log 0.250$$

pH = 0.60



- (iii) A student is given 100 cm^3 of a solution of ethanoic acid of concentration 0.100 mol dm^{-3} and wishes to produce a buffer solution of pH 4.45. He has access to the full range of chemicals in a laboratory.

Describe how the buffer solution could be formed, calculating the amounts of any other substances required. Explain how the buffer solution works to keep the pH of the solution constant.

[6 QER]

$$K_a \text{ for } \text{CH}_3\text{COOH} = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{pH } 4.45: [\text{H}^+] = 10^{-4.45} = 3.548 \times 10^{-5} \text{ mol dm}^{-3}$$

$$K_a = [\text{H}^+][\text{CH}_3\text{COO}^-] \div [\text{CH}_3\text{COOH}]$$

$$[\text{CH}_3\text{COO}^-] = K_a[\text{CH}_3\text{COOH}] \div [\text{H}^+] = (1.74 \times 10^{-5} \times 0.100) \div 3.548 \times 10^{-5}$$

$$[\text{CH}_3\text{COONa}] = 0.0490 \text{ mol dm}^{-3}$$

$$\text{moles of } \text{CH}_3\text{COONa} = 0.0490 \times 100 \div 1000 = 4.90 \times 10^{-3} \text{ mol}$$

$$M_r(\text{CH}_3\text{COONa}) = 82.0, \text{ so mass} = 4.90 \times 10^{-3} \times 82.0 = 0.402 \text{ g}$$

A buffer is a mixture of a weak acid and a salt of that weak acid, so the buffer is made from the ethanoic acid and sodium ethanoate.

Dissolve 0.402 g of solid sodium ethanoate (calculated above) in the 100 cm^3 of 0.100 mol dm^{-3} ethanoic acid (the volume stays about 100 cm^3). (Alternatively add $4.90 \times 10^{-3}\text{ mol}$ of NaOH to the acid.)

The ethanoic acid only partially dissociates: $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

The sodium ethanoate fully dissociates: $\text{CH}_3\text{COONa} \rightarrow \text{CH}_3\text{COO}^- + \text{Na}^+$, so the buffer contains a large reservoir of both CH_3COO^- ions and undissociated CH_3COOH molecules.

When a small amount of acid is added, the added H^+ ions combine with CH_3COO^- ions, so the equilibrium shifts to the left hand side, removing the H^+ .

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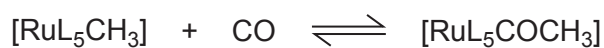


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- (c) The complex $[\text{Ru}(\text{CO})_2(\text{P}(\text{CH}_3)_3)_2\text{CH}_3\text{I}]$ catalyses the reaction of iodomethane with carbon monoxide. One stage in the process is the reversible reaction below, with five of the ligands shown as L.



The values of the equilibrium constant for this process at different temperatures in methylbenzene solvent are listed in the table.

Temperature / °C	$K_c / \text{mol}^{-1} \text{dm}^3$
34	1220
42	694
49	406
56	290
64	196
74	120



- (i) Suggest what information this table allows us to deduce about the energy changes during this reversible reaction. [2]

The forward reaction is exothermic.

K_c decreases as temperature increases, so the equilibrium shifts to the left at higher temperature (and to the right as temperature decreases).

- (ii) A solution containing a mixture of complex $[\text{RuL}_5\text{CH}_3]$ of concentration $1.25 \times 10^{-3} \text{ mol dm}^{-3}$ and carbon monoxide of concentration $7.55 \times 10^{-4} \text{ mol dm}^{-3}$ is placed in a sealed tube, heated to a set temperature and the mixture allowed to reach equilibrium. The equilibrium mixture contains $1.37 \times 10^{-4} \text{ mol dm}^{-3}$ of $[\text{RuL}_5\text{COCH}_3]$.

Find the value of K_c and hence suggest the temperature used for the experiment. [4]

$$[\text{CO}] = 7.55 \times 10^{-4} - 1.37 \times 10^{-4} = 6.18 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{RuL}_5\text{CH}_3] = 1.25 \times 10^{-3} - 1.37 \times 10^{-4} = 1.113 \times 10^{-3} \text{ mol dm}^{-3}$$

$$K_c = [\text{RuL}_5\text{COCH}_3] \div ([\text{RuL}_5\text{CH}_3][\text{CO}])$$

$$K_c = 1.37 \times 10^{-4} \div (1.113 \times 10^{-3} \times 6.18 \times 10^{-4}) = 199$$

199 is just above K_c at 64 °C (196), so the temperature is about 63 °C

$$K_c = \underline{199} \text{ mol}^{-1} \text{ dm}^3$$

$$\text{Temperature} = \underline{63} \text{ °C}$$



10. Copper is present in a range of alloys, including those listed below.

Alloy	Typical copper content (% by mass)	Other element(s) present
brass	65-95	zinc
cupronickel	60-90	nickel
bronze	85-90	tin
electrum	6-25	gold silver
leaded tin bronze	70-85	tin lead

One method of finding the copper content of an alloy is by treating the alloy with concentrated hydrochloric acid in the presence of air to form a solution containing metal ions and diluting this to a known volume. This solution can then be analysed by titration.

- (a) The class teacher notes that this method would not be suitable for analysing electrum or leaded tin bronze.

Suggest how the method could be changed to allow for the analysis of electrum and leaded tin bronze. Give your reasoning. [2]

Use (concentrated) nitric acid instead of hydrochloric acid.

Hydrochloric acid gives insoluble chloride precipitates with silver (AgCl) and lead (PbCl₂), but silver nitrate and lead nitrate are both soluble.

- (b) Several of the metals added to copper to form these alloys are amphoteric.

Identify **one** amphoteric metal from the table and state what is meant by the term amphoteric. [2]

Zinc (or tin).

Amphoteric metals react with both acids and bases (alkalis).



- (c) A 1.72 g sample of an alloy was used to make 250 cm³ of an aqueous solution containing copper and other metal ions. Samples of 25.0 cm³ of the solution were measured out and the copper ions reacted with excess iodide ions to form iodine.

The iodine was titrated using sodium thiosulfate solution of concentration 0.0500 mol dm⁻³. The mean volume of sodium thiosulfate needed for complete reaction was 33.05 cm³.

- (i) Write the equations for the following reactions:

- Cu²⁺(aq) with I⁻(aq)
- I₂(aq) with S₂O₃²⁻(aq)

Hence show that 1 mol of S₂O₃²⁻(aq) is equivalent to 1 mol of Cu²⁺(aq) in the titration.

[3]



2Cu²⁺ produce 1 I₂, which reacts with 2S₂O₃²⁻, so 2Cu²⁺ ≡ 2S₂O₃²⁻, i.e.

1 mol Cu²⁺ ≡ 1 mol S₂O₃²⁻.

- (ii) Find the percentage by mass of copper in the alloy and hence identify which alloy(s) could be present in the sample.

[4]

$$n(\text{S}_2\text{O}_3^{2-}) = 0.0500 \times 33.05 \div 1000 = 1.6525 \times 10^{-3} \text{ mol}$$

$$= n(\text{Cu}^{2+}) \text{ in } 25.0 \text{ cm}^3$$

$$n(\text{Cu}) \text{ in } 250 \text{ cm}^3 = 1.6525 \times 10^{-3} \times 10 = 1.6525 \times 10^{-2} \text{ mol}$$

$$\text{mass of Cu} = 1.6525 \times 10^{-2} \times 63.5 = 1.05 \text{ g}$$

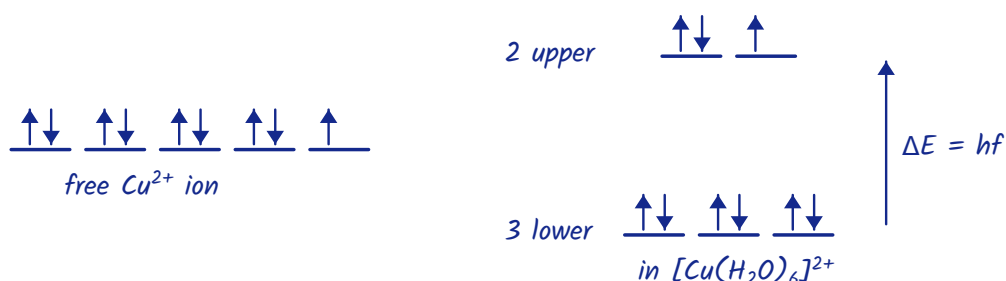
$$\% \text{ Cu} = 1.05 \div 1.72 \times 100 = 61.0\%$$

Percentage copper = 61.0 %

The alloy must be cupronickel (60 to 90% copper); brass needs at least 65% copper.



- (d) (i) Aqueous solutions formed from copper(II) compounds contain $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions. Explain why these solutions are pale blue. [3]



The H_2O ligands split the d-orbitals into 2 upper and 3 lower levels. Electrons absorb specific frequencies of visible light (red/orange) to promote electrons from a lower to a higher energy level, $\Delta E = hf$.

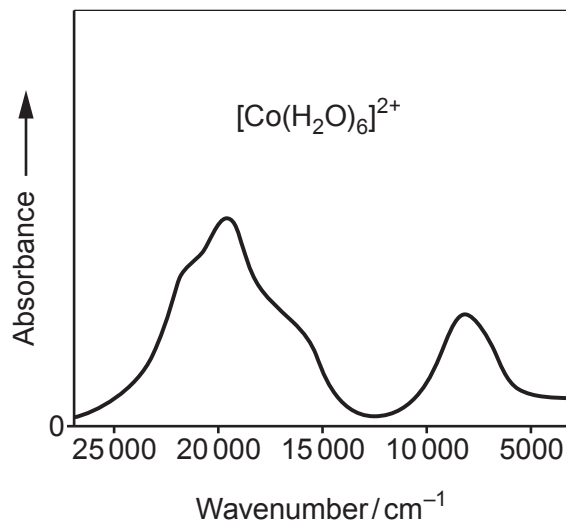
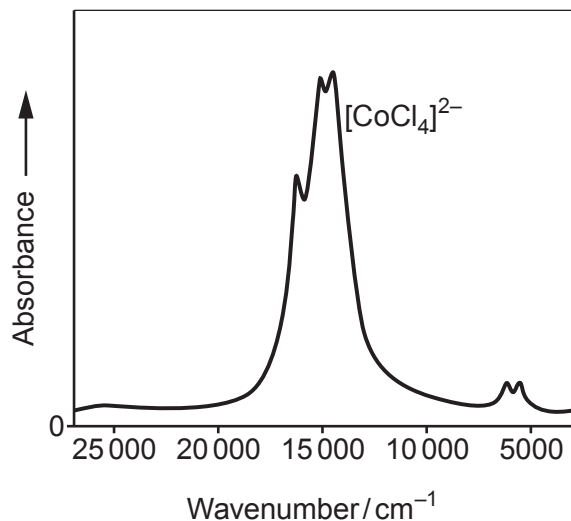
The colour seen is the frequencies not absorbed: red is absorbed so blue is transmitted.

- (ii) Copper(I) compounds are often white solids. Give a reason why these compounds are not coloured. [1]

The d-orbitals are full ($3d^{10}$), so electrons cannot be promoted between the split d levels.



- (iii) Many metal complexes change colour when a new ligand is added. The absorption spectra of two cobalt(II) complexes are given below.



Suggest which wavenumber, in cm⁻¹, should be used to study the conversion of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ into $[\text{CoCl}_4]^{2-}$. Give a reason for your selection. [2]

14 000 cm⁻¹. At this wavenumber the chloro complex, $[\text{CoCl}_4]^{2-}$, absorbs strongly but the aqua complex, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, absorbs (almost) nothing, so the absorbance rises as $[\text{CoCl}_4]^{2-}$ forms.



- (e) The standard electrode potentials for some reactions of copper and thallium ions are given below.

Half-equation	Standard electrode potential, E^θ / V
$\text{Tl}^{3+} + 2\text{e}^- \rightleftharpoons \text{Tl}^+$	+1.25
$\text{Cu}^+ + \text{e}^- \rightleftharpoons \text{Cu}$	+0.52
$\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+$	+0.16
$\text{Tl}^+ + \text{e}^- \rightleftharpoons \text{Tl}$	-0.34

- (i) When copper(I) ions are formed in solution, the reaction below occurs.



Use the standard electrode potential values to explain why this reaction occurs. [2]

$\text{Cu}^{2+}/\text{Cu}^+$ (+0.16 V) is less positive than Cu^+/Cu (+0.52 V), so one Cu^+ reduces another to Cu. EMF = +0.36 V: positive so feasible.

- (ii) I. Copper(I) ions can act as a reducing agent. Identify the final thallium containing species formed when copper(I) ions reduce thallium(III) ions.

Use the standard electrode potential values to explain your answer. [2]

Tl^+ , thallium(I) ions.

$\text{Tl}^{3+}/\text{Tl}^+$ (+1.25 V) is more positive than $\text{Cu}^{2+}/\text{Cu}^+$ (+0.16 V), EMF = +1.09 V, so Cu^+ reduces Tl^{3+} to Tl^+ ; but Tl^+/Tl (-0.34 V) is less positive, EMF = -0.50 V, so Tl^+ is not reduced to Tl.

- II. A student suggests that the more stable oxidation state of thallium can be predicted from its position in the Periodic Table.

Suggest, giving a reason, which oxidation state of thallium will be more stable. [1]

Thallium(I), +1, as the inert pair effect increases down the group.

END OF PAPER



Question number	Additional page, if required. Write the question number(s) in the left-hand margin.
9(b)(iii)	When a small amount of base is added, the OH^- ions remove H^+ ($\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$), so the equilibrium shifts to the right as more CH_3COOH dissociates to replace the H^+. The OH^- ions also react with undissociated acid molecules forming ethanoate ions and water. Because $[\text{CH}_3\text{COOH}]$ and $[\text{CH}_3\text{COO}^-]$ are both large, their ratio hardly changes, so $[\text{H}^+] = K_a[\text{CH}_3\text{COOH}] \div [\text{CH}_3\text{COO}^-]$ and the pH stay almost constant.

Examiner
only

[illegible]