

- 3 (a)** A bottle labelled **FA 5** is thought to contain hydrated zinc sulfate. It would therefore contain zinc ions and sulfate ions as well as water of crystallisation.
- (i)** Devise and carry out tests to investigate whether zinc ions, sulfate ions and water of crystallisation are present.

Record the tests you carry out and the observations you see in the space provided.

[5] .

- (ii) Use your observations in (a)(i) to complete Table 3.1 to show whether each species is present in **FA 5**.

Use a tick (✓) if the species is present.

Use a cross (X) if the species is **not** present.

Table 3.1

Zn^{2+}	
SO_4^{2-}	
H_2O	

[1]

- (b) You are provided with solid **FA 6**.

- (i) Heat a few crystals of **FA 6** in a hard-glass test-tube until no further gas is evolved. Record all your observations.

Leave the test-tube until it is cool.

Keep the cooled residue for use in (b)(ii).

.....
.....
..... [2]

- (ii) To the cooled residue from (b)(i), add approximately 3 cm depth of distilled water and stir. Filter the solution formed into a test-tube.

The colour of the solution is

[1]

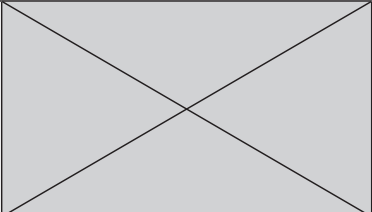
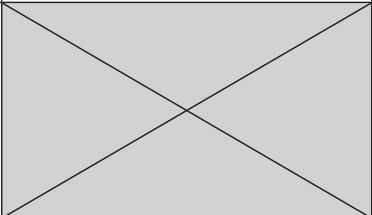
(c) You are provided with aqueous solutions **FA 7** and **FA 8** and with solid **FA 9**.

FA 7 is an aqueous solution of **FA 6**.

FA 7, **FA 8** and **FA 9** contain compounds which all have one metal that is the same but which may be in different oxidation states.

- (i) Carry out the following tests on **FA 7**, **FA 8** and **FA 9** and record your observations in Table 3.2. For each test use a 1 cm depth of a solution or a spatula measure of solid.

Table 3.2

test	observations		
	FA 7	FA 8	FA 9
Test 1 Add hydrogen peroxide.			
Test 2 Add aqueous sodium hydroxide, then			
leave to stand.			
Test 3 Add aqueous iron(II) sulfate.			

[4]

- (ii) Suggest the identity of the metal in **FA 6/FA 7**, **FA 8** and **FA 9**.

The metal is

[1]

- (iii) Complete Table 3.3 to suggest the oxidation state of the metal in **FA 6/FA 7** and **FA 8**.

Table 3.3

	FA 6/FA 7	FA 8
oxidation state		

[1]

[Total: 15]

Qualitative analysis notes

1 Reactions of cations

cation	reaction with	
	NaOH(aq)	NH ₃ (aq)
aluminium, Al ³⁺ (aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH ₄ ⁺ (aq)	no ppt. ammonia produced on warming	–
barium, Ba ²⁺ (aq)	faint white ppt. is observed unless [Ba ²⁺ (aq)] is very low	no ppt.
calcium, Ca ²⁺ (aq)	white ppt. unless [Ca ²⁺ (aq)] is very low	no ppt.
chromium(III), Cr ³⁺ (aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu ²⁺ (aq)	pale blue ppt. insoluble in excess	pale blue ppt. soluble in excess giving dark blue solution
iron(II), Fe ²⁺ (aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe ³⁺ (aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg ²⁺ (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn ²⁺ (aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn ²⁺ (aq)	white ppt. soluble in excess	white ppt. soluble in excess

2 Reactions of anions

anion	reaction
carbonate, CO ₃ ²⁻	CO ₂ liberated by dilute acids
chloride, Cl ⁻ (aq)	gives white ppt. with Ag ⁺ (aq) (soluble in NH ₃ (aq))
bromide, Br ⁻ (aq)	gives cream/off-white ppt. with Ag ⁺ (aq) (partially soluble in NH ₃ (aq))
iodide, I ⁻ (aq)	gives pale yellow ppt. with Ag ⁺ (aq) (insoluble in NH ₃ (aq))
nitrate, NO ₃ ⁻ (aq)	NH ₃ liberated on heating with OH ⁻ (aq) and Al foil
nitrite, NO ₂ ⁻ (aq)	NH ₃ liberated on heating with OH ⁻ (aq) and Al foil; decolourises acidified aqueous KMnO ₄
sulfate, SO ₄ ²⁻ (aq)	gives white ppt. with Ba ²⁺ (aq) (insoluble in excess dilute strong acids); gives white ppt. with high [Ca ²⁺ (aq)]
sulfite, SO ₃ ²⁻ (aq)	gives white ppt. with Ba ²⁺ (aq) (soluble in excess dilute strong acids); decolourises acidified aqueous KMnO ₄
thiosulfate, S ₂ O ₃ ²⁻ (aq)	gives off-white/pale yellow ppt. slowly with H ⁺

3 Tests for gases

gas	test and test result
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater
hydrogen, H_2	'pops' with a lighted splint
oxygen, O_2	relights a glowing splint

2 (a) Iron can form stable ions in the +2 and +3 oxidation states.

Explain why transition elements have variable oxidation states.

.....
..... [1]

(b) Aqueous solutions of iron(II) salts contain the complex ion $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$.

Define complex ion.

.....
..... [1]

(c) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ can be converted into $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]$.

(i) Suggest a suitable reagent for this conversion. State the type of reaction.

reagent

type of reaction [1]

(ii) $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]$ is a green precipitate that turns brown on standing in air.

Table 2.1 shows electrode potentials for some electrode reactions.

Table 2.1

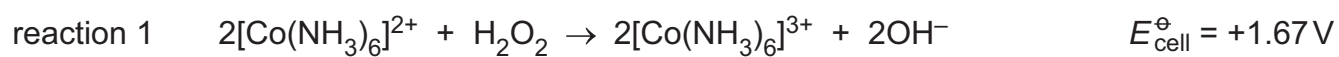
electrode reaction	$E^\ominus / \text{V}$
$\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3 + \text{H}_2\text{O} + \text{e}^- \rightleftharpoons \text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2 + \text{OH}^-$	-0.56
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^-$	+0.40

Use the information in Table 2.1 to explain why $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]$ turns brown on standing in air.

Include an equation for this reaction.

.....
.....
.....
.....
.....
..... [3]

(d) The complex $[\text{Co}(\text{NH}_3)_6]^{2+}$ reacts with hydrogen peroxide as shown.



Calculate $\Delta G^\ominus$, in kJ mol^{-1} , for reaction 1.

$\Delta G^\ominus = \dots\dots\dots \text{kJ mol}^{-1}$ [2]

[Total: 8]

- 5 (a) Copper shows typical properties of transition elements, including its behaviour as a catalyst.

Complete Table 5.1 to show the total number of **unpaired** electrons in the 3d and 4s orbitals of an isolated gaseous Cu atom and a Cu^{2+} ion.

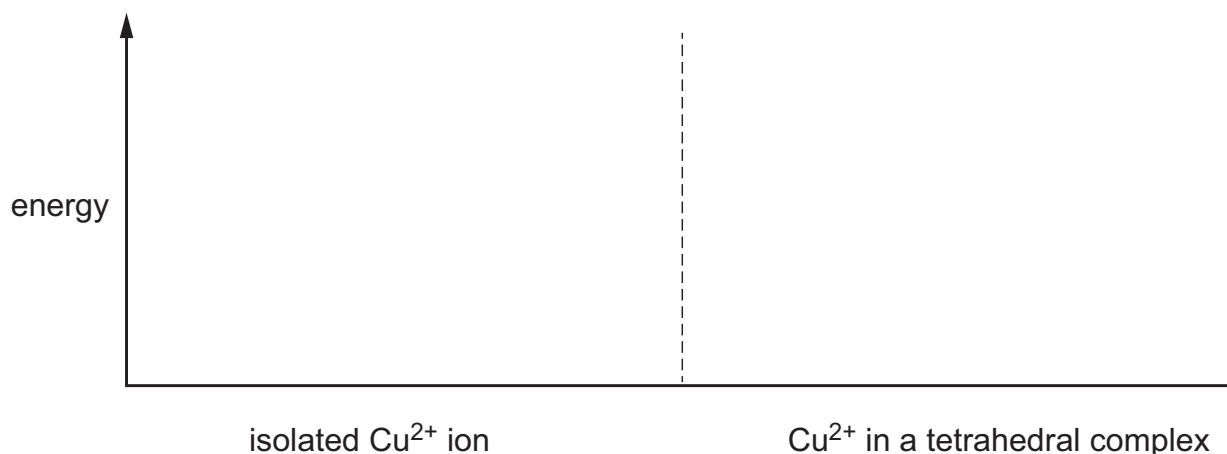
Table 5.1

species	number of unpaired electrons	
	3d	4s
Cu		
Cu^{2+}		

[1]

- (b) The 3d orbitals in an isolated Cu^{2+} ion are degenerate.

Complete the diagram to show the relative energies of the 3d orbitals in an isolated Cu^{2+} ion and in Cu^{2+} in a tetrahedral complex.



[2]

- (c) Explain why transition elements behave as catalysts.

.....
.....
..... [2]

(d) CN^- is a monodentate ligand.

Table 5.2 shows information about two complex ions that contain only CN^- ions as ligands.

Complete Table 5.2.

Table 5.2

metal ion	coordination number	formula of complex ion	charge of complex ion
Ag^+	2		
Fe^{2+}			4-

[2]

(e) The complex ion $[\text{Au}(\text{CN})_2\text{Br}_2]^-$ displays geometrical (cis/trans) isomerism.

Draw the structure of *trans*- $[\text{Au}(\text{CN})_2\text{Br}_2]^-$. State its shape and the Br-Au-Br bond angle.

shape

Br-Au-Br bond angle =

[2]

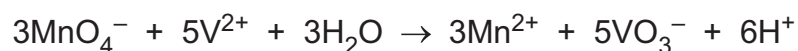
- (f) An impure sample of a vanadium(V) compound of mass 0.250 g is dissolved in aqueous acid. This solution contains VO_3^- ions.

An excess of zinc is added to this solution. All the VO_3^- ions are reduced to V^{2+} ions and Zn atoms are oxidised to Zn^{2+} ions.

The unreacted zinc is removed and the resulting solution is titrated with acidified MnO_4^- .

The end-point is reached when 22.5 cm^3 of $0.0750 \text{ mol dm}^{-3} \text{ MnO}_4^-$ is added.

A redox reaction takes place and all the V^{2+} reacts forming VO_3^- .



- (i) Calculate the percentage by mass of vanadium in the 0.250 g of impure sample.

Assume the impurities do not contain any vanadium ions.

Show your working.

percentage of vanadium = [3]

- (ii) Complete the equation for the reaction between acidified VO_3^- ions and Zn metal.



[2]

[Total: 14]

- 5** Cobalt is a transition element which forms compounds containing Co^{2+} and Co^{3+} ions. Cobalt(II) sulfate dissolves in water to form a solution containing the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complex ion.

(a) (i) Complete the electronic configurations of a Co^{2+} ion and a Co^{3+} ion.

$\text{Co}^{2+} = [\text{Ar}]$

$\text{Co}^{3+} = [\text{Ar}]$

[1]

(ii) Explain why transition elements can form complex ions.

.....

..... [1]

(iii) An excess of concentrated HCl is added to a solution containing $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.

Describe the colour change observed and the state of the cobalt-containing product.

The colour changes from to

The state of the cobalt-containing product is

[2]

(iv) Write an equation for the reaction occurring in **(a)(iii)**.

..... [1]

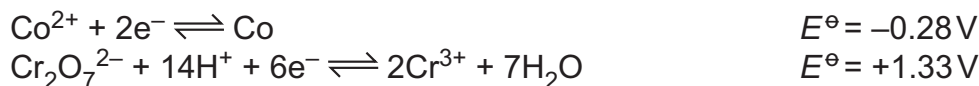
(v) Name the type of reaction occurring in **(a)(iii)**.

..... [1]

(vi) Write an equation for the reaction that occurs when an excess of $\text{NaOH}(\text{aq})$ is added to a solution containing $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.

..... [1]

- (b) Cobalt metal can be oxidised by acidified $\text{K}_2\text{Cr}_2\text{O}_7$. The relevant half-equations, and their $E^\ominus$ values, are shown.



- (i) A Co^{2+}/Co electrode is constructed in which $[\text{Co}^{2+}]$ is $0.020 \text{ mol dm}^{-3}$ at 298 K .

Use the Nernst equation to show that the E value for this Co^{2+}/Co electrode is -0.33 V .

[2]

- (ii) An electrochemical cell is constructed using the Co^{2+}/Co electrode described in (b)(i) and a $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ electrode in which all conditions are standard.

Calculate the value of E_{cell} .

$$E_{\text{cell}} = \dots\dots\dots [1]$$

- (iii) A current is drawn from the electrochemical cell described in (b)(ii).

Write an equation for the reaction taking place in the cell.

..... [1]

- (iv) Complete the sentences to identify the negative electrode and the direction of electron flow when a current is drawn from the cell described in (b)(ii).

The electrode is the negative electrode.

Electrons flow from the electrode to the electrode. [1]

- (c) A molten Co^{2+} salt is electrolysed using a current of 0.500 A .

0.547 g of cobalt metal forms at the cathode. Under the conditions used no other reduction reaction occurs at the cathode.

Calculate the time in minutes for which the current flows to produce this mass of cobalt.

Give your answer to **three** significant figures.

time = min [3]

6 (a) Nickel forms complexes.

- (i) Give the formula and charge of the tetrahedral complex formed by Ni atoms with carbon monoxide molecules. Carbon monoxide is a monodentate ligand. This is complex **E**.

E = [1]

- (ii) Give the formula and charge of the octahedral complex formed by Ni^{2+} ions with ethanedioate ions. This is complex **F**.

F = [2]

- (iii) Identify which complex, **E** or **F**, exists as a mixture of two stereoisomers and the type of stereoisomerism involved.

The complex which exists as a mixture of two stereoisomers is

The type of stereoisomerism involved is

[1]

- (b) Cadmium forms complexes with methylamine, CH_3NH_2 , and 1,2-diaminoethane, *en*. The values of the stability constants, K_{stab} , of these complex ions are given in Table 6.1.

Table 6.1

complex	K_{stab}
$[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$	3.5×10^6
$[\text{Cd}(\text{en})_2]^{2+}$	4.0×10^{10}

- (i) Explain, by reference to its structure, why CH_3NH_2 acts as a monodentate ligand.

..... [1]

- (ii) Some $\text{Cd}^{2+}(\text{aq})$ is added to a solution containing equal concentrations of CH_3NH_2 and *en*.

Predict which of the two complexes in Table 6.1 forms at the higher concentration.

Explain your answer.

complex that forms at the higher concentration

explanation

..... [1]

- (iii) Complete the expression for the K_{stab} of $[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$.

$K_{\text{stab}} =$

1 (a) Define a transition element.

.....

 [1]

(b) The 3d orbitals in an isolated gaseous Cu^{2+} ion are degenerate.

(i) Define the term degenerate.

.....
 [1]

(ii) Complete the electronic configuration of Cu^{2+} .

$1s^2$ [1]

(c) (i) State the colours of the aqueous solutions for the **two** copper(II) complex ions shown.

- $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq})$
- $[\text{CuCl}_4]^{2-}(\text{aq})$ [1]

(ii) Explain why aqueous complex ions of transition elements are usually coloured.

.....

 [3]

(d) (i) When an excess of $\text{NH}_3(\text{aq})$ is added to a solution of $[\text{CuCl}_4]^{2-}(\text{aq})$, $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq})$ is formed.

State the type of reaction.

Complete the equation for this reaction. State symbols are **not** required.

type of reaction

equation

$[\text{CuCl}_4]^{2-} + \dots\dots\dots \textcircled{14} [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + \dots\dots\dots$

- (ii) The $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ complex ion shows stereoisomerism.

Complete the three-dimensional diagrams in Fig. 1.1 to show the **two** different stereoisomers of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$.

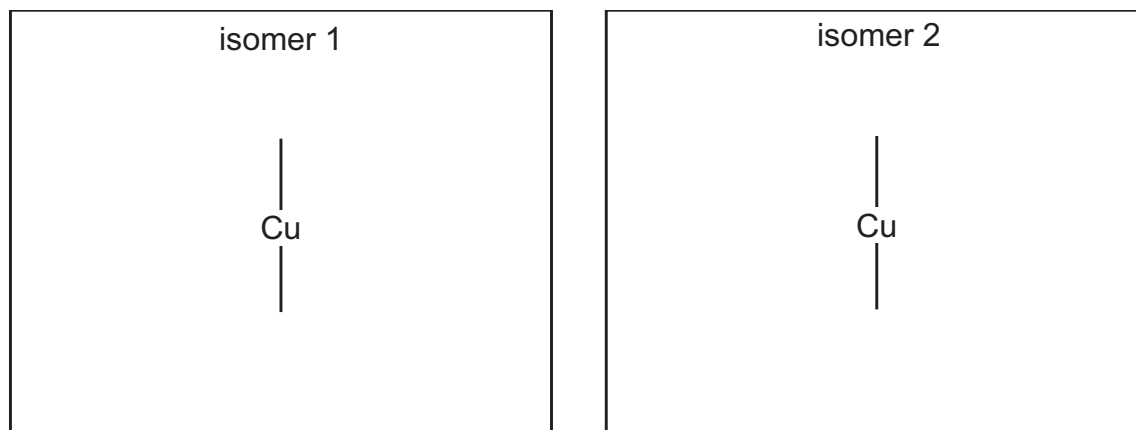


Fig. 1.1

[2]

- (iii) Deduce which stereoisomer in (d)(ii) is polar.

Explain your answer.

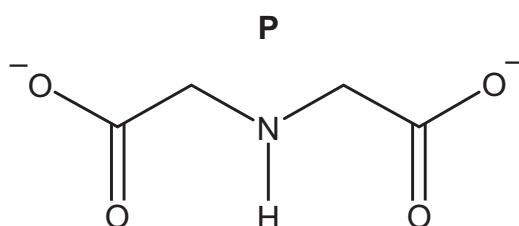
polar isomer

explanation

.....

[1]

- (e) The dianion **P** can act as a tridentate ligand.



- (i) Suggest how **P** can form **three** dative covalent bonds.

.....

.....

..... [1]

- (ii) 2 moles of dianion **P**, $\text{C}_4\text{H}_5\text{NO}_4^{2-}$, react with 1 mole of aqueous cobalt(III) ions, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ to form 1 mole of complex ion **Q**.

Deduce the formula and charge of **Q**.

..... [1]

- (f) Table 1.1 shows values for the stability constants, K_{stab} , of some silver(I) complexes.

Table 1.1

complex	value of K_{stab}
$[\text{Ag}(\text{CN})_2]^{-}(\text{aq})$	1.1×10^{18}
$[\text{Ag}(\text{NH}_3)_2]^{+}(\text{aq})$	1.2×10^7
$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}(\text{aq})$	2.9×10^{13}

- (i) Define the stability constant of a complex.

.....
.....
..... [1]

- (ii) Use the information in Table 1.1 to identify the most stable silver(I) complex.

Explain your answer.

most stable

explanation

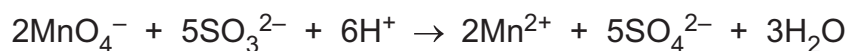
..... [1]

(g) Sodium sulfite, Na_2SO_3 , is used as a food preservative.

A 3.75 g sample of impure Na_2SO_3 is dissolved in distilled water and made up to 250 cm^3 in a volumetric flask.

10.0 cm^3 of this solution requires 18.70 cm^3 of acidified $0.0150\text{ mol dm}^{-3}$ MnO_4^- (aq) to reach the end-point.

The equation for the reaction is shown.



Calculate the percentage by mass of Na_2SO_3 in the sample.

percentage by mass of Na_2SO_3 = [3]

[Total: 19]