

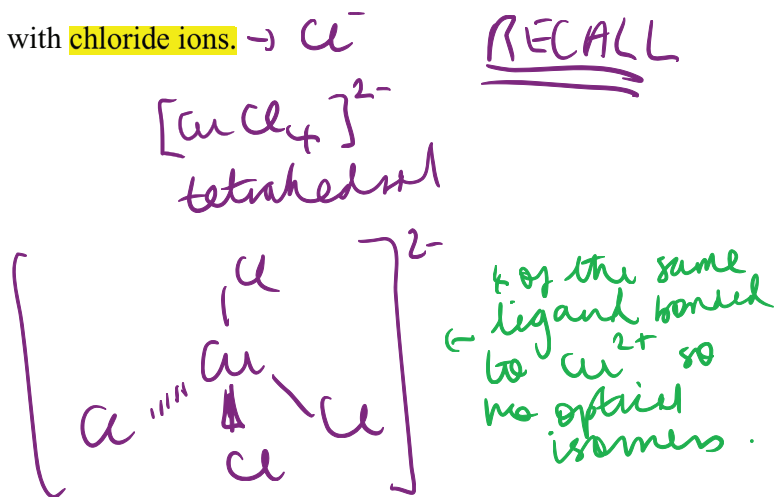
1. Copper(II) ions form an aqueous complex ion, X, with chloride ions. $\rightarrow \text{Cl}^-$

Which statement about X is true?

- A X has optical isomers
 B X has a square planar shape
 C X has the formula CuCl_4^{2+}
 D X has a yellow colour

Your answer

D



[1]

2. Two tests are carried out on an aqueous solution of copper(II) sulfate, $\text{CuSO}_4(\text{aq})$.

Test 1: Addition of potassium iodide solution

Test 2: Addition of barium chloride solution

Which of the following statements is/are true?

- ✓ 1: Test 1 produces an off-white precipitate and a brown solution.
 ✓ 2: Test 2 produces a white precipitate.
 ✗ 3: Test 1 and Test 2 are both redox reactions.

A 1, 2 and 3

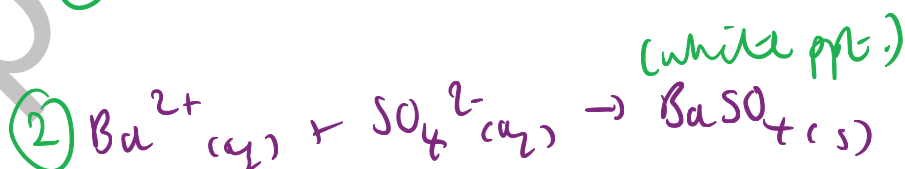
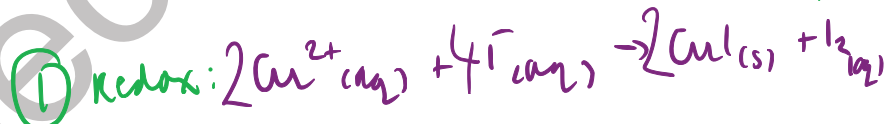
ⓑ Only 1 and 2

✗ c Only 2 and 3

✗ d Only 1

Your answer

ⓑ



↳ no change in ox. states ∴ not redox.

[1]

3. A student carries out a number of experiments on transition metal compounds.

4.800 g of a green hydrated crystalline solid A are heated in a crucible to remove the water of crystallisation. 1.944 g of water are removed to leave 0.0180 mol of solid residue B.

Solid B contains 32.8%, by mass, of the transition metal.

All of B is reacted with $\text{AgNO}_3(\text{aq})$ to form 7.695 g of a white precipitate, C.

The green crystalline solid A is dissolved in water to produce a green solution containing a complex ion, D.

When aqueous sodium hydroxide is added to solution of D, a grey-green precipitate, E, is observed, which dissolves in excess aqueous sodium hydroxide to form a green solution.

- (a) Determine the formulae of A, B, D and E.

Show all your working.



molar ratio

$$\frac{7.695}{108 + 35.5} = 0.05362 \text{ mol of AgCl}$$

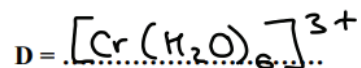
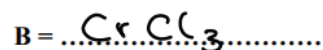
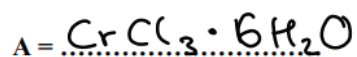
$$\frac{0.05362}{0.0180} = 3 \text{ Cl}^- \text{ ions}$$

$$\frac{4.800 - 1.944}{0.0180} = 158.7 \text{ g mol}^{-1} \text{ B}$$

$$158.7 - (35.5 \times 3) = 52.2 = \text{Cr}$$

$$\frac{1.944}{16 + 2} = 0.108 \text{ mol of H}_2\text{O}$$

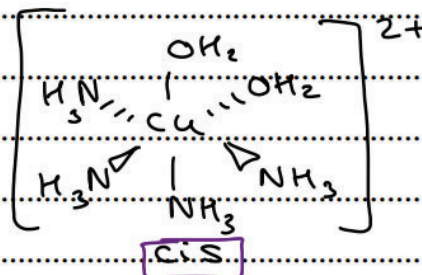
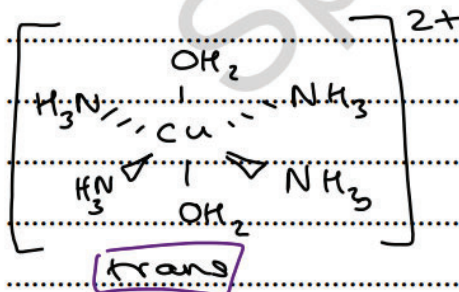
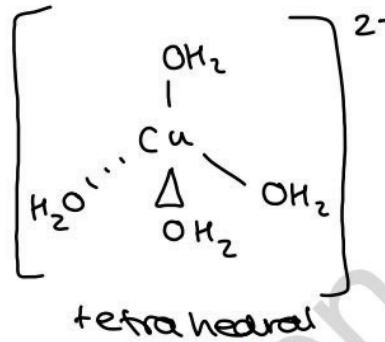
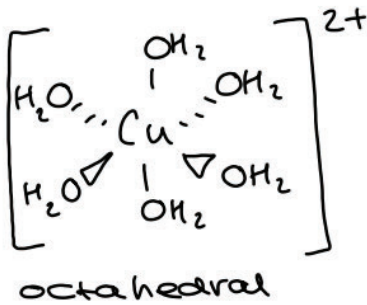
$$\frac{0.108}{0.0180} = 6 \text{ mol of H}_2\text{O}$$



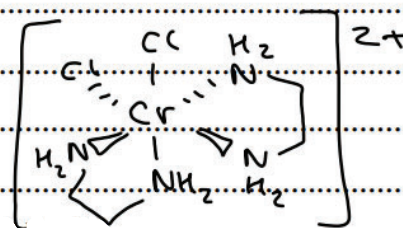
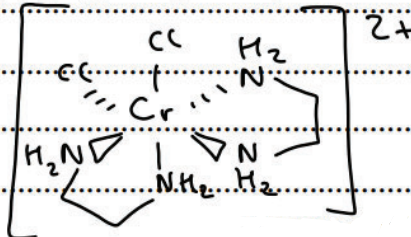
(b)* Transition metal complexes often have different shapes and may form a number of stereoisomers.

Describe the different shapes and the different types of stereoisomerism found in transition metal chemistry.

Use suitable examples and diagrams in your answer.



OPTICAL: bidentate ligands



4. This question looks at ions and complexes.

(a)* You are provided with two boiling tubes containing solutions of the same ionic compound. The compound contains one cation and one anion from the lists below.

- cations: Fe^{2+} , Mn^{2+} , NH_4^+
- anions: Cl^- , CO_3^{2-} , SO_4^{2-}

Solutions of common laboratory reagents are available.

Plan a series of tests that you could carry out on the samples to identify the ionic compound. Your tests should produce at least one positive result for each ion.

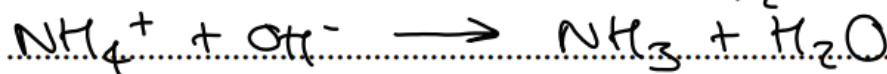
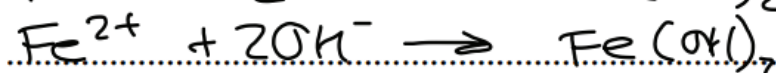
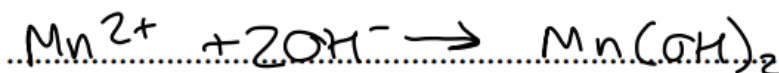
For each test,

- include details of reagents, relevant observations and equations
- explain how your observations allow the ions to be identified.

You may include flowcharts or tables in your answer.

all tests conducted in separate boiling tubes

Cation	test	result
Mn^{2+}	NaOH (aq)	pink ppt.
Fe^{2+}	NaOH (aq)	green ppt.
NH_4^+	NaOH (aq) and gentle heating	litmus paper turns blue



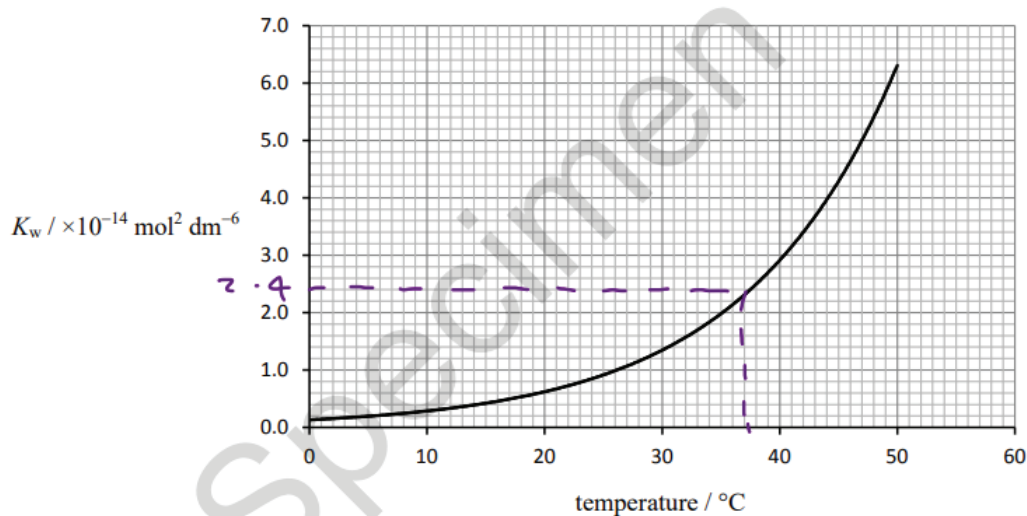
anion	test	result
CO_3^{2-}	HNO_3	effervescence
SO_4^{2-}	$\text{Ba}(\text{NO}_3)_2$	white ppt.
Cl^-	AgNO_3	white ppt.

$\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$ [add dilute NH_3 and ppt. dissolved]

$\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$ [6]

$\text{SO}_4^{2-} + \text{Ba}^{2+} \rightarrow \text{BaSO}_4$ Cl^- test

- (b) The dissociation of water is measured by the ionic product of water, K_w . The value of K_w varies with temperature as shown in the graph below.



Calculate the pH of water at body temperature, 37 $^\circ\text{C}$.

$$2.4 \times 10^{-14} = K_w$$

$$\sqrt{2.4 \times 10^{-14}} = [\text{H}^+] = 1.55 \times 10^{-7}$$

$$\text{pH} = -\log_{10} [\text{H}^+]$$

$$\text{pH} = -\log_{10} 1.55 \times 10^{-7} = 6.81$$

pH = 6.81 [3]

(c) A complex of cobalt has the following composition by mass:

Co, 21.98%; N, 31.35%; H, 6.72%; Cl, 39.75%

(i) Calculate the empirical formula of this complex.

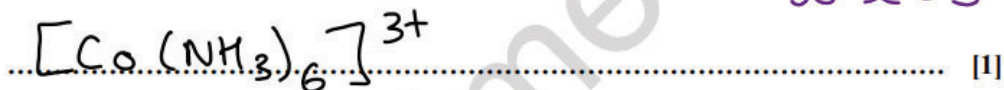
$$\begin{array}{cccc}
 \text{Co: } \frac{21.98}{58.9} & \text{N: } \frac{31.35}{14} & \text{H: } \frac{6.72}{1} & \text{Cl: } \frac{39.75}{35.5} \\
 = 0.373 & = 2.24 & = 6.72 & = 1.12 \\
 \frac{0.373}{0.373} & \frac{2.24}{0.373} & \frac{6.72}{0.373} & \frac{1.12}{0.373} = 3 \\
 = 1 & = 6 & = 18 & = 3
 \end{array}$$

empirical formula = $\text{CoN}_6\text{H}_{18}\text{Cl}_3$ [2]

(ii) The formula of this cobalt complex can be expressed in form $[\text{Co}(\text{L})_m]^{x+}(\text{Cl})_n$

Suggest the chemical formula of $[\text{Co}(\text{L})_m]^{x+}$.

$$\begin{array}{l}
 n = 3 \\
 \text{so } x = 3
 \end{array}$$



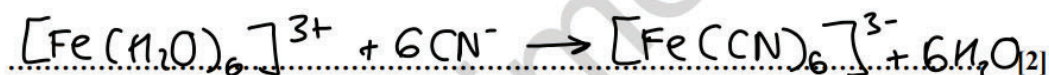
↑
 excluding Cl_3 and Co
 $\text{N}_6\text{H}_{18} = (\text{NH}_3)_6$

5. This question looks at properties of iron compounds and iron ions in different oxidation states.

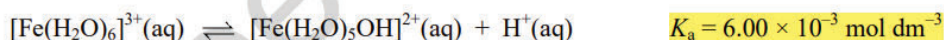
- (a) Fe^{2+} and Fe^{3+} are the most common ions of iron. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
- (i) Write the electron configuration, in terms of sub-shells, for the Fe^{2+} ion.
 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ [1]
 3d⁶: $\boxed{\uparrow\downarrow} \boxed{\uparrow} \boxed{\uparrow} \boxed{\uparrow} \boxed{\uparrow}$ *filled first and lost first*
- (ii) How many orbitals contain an unpaired electron in an ion of Fe^{2+} ?
 4 [1]

- (b) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ions take part in ligand substitution reactions. *forms* $[\text{Fe}(\text{CN})_6]^{3-}$
- An excess of aqueous potassium cyanide, $\text{KCN}(\text{aq})$, is added to an aqueous solution containing $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ions. A ligand substitution reaction takes place forming a complex ion that has a molar mass of 211.8 g mol^{-1} .

Write an equation for this ligand substitution reaction.



- (c) The complex ion, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, behaves as a weak Brønsted-Lowry acid in aqueous solution. The equation below represents the dissociation of aqueous $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ions, together with the K_a value.



- (i) Write the expression for the acid dissociation constant, K_a , for $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.

$$K_a = \frac{[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+} [\text{H}^+]}{[\text{Fe}(\text{H}_2\text{O})_6]^{3+}} \quad [1]$$

- (ii) Calculate the pH of a $0.100 \text{ mol dm}^{-3}$ solution of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ to two decimal places.

$$K_a = \frac{[\text{H}^+]^2}{[\text{Fe}(\text{H}_2\text{O})_6]^{3+}} \quad \leftarrow \text{assume } [\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+} = [\text{H}^+]$$

$$[\text{H}^+] = \sqrt{6 \times 10^{-3} \times 0.1} = 0.0245 \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10} [0.0245] = 1.61$$

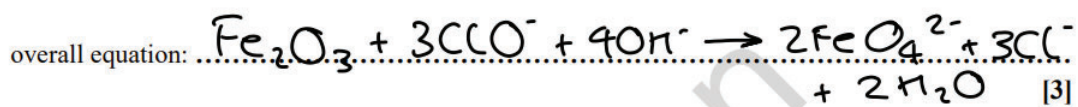
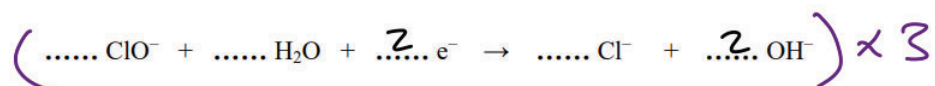
$$\text{pH} = \dots\dots\dots 1.61 \dots\dots\dots [2]$$

$-\log_{10} [\text{H}^+] = \text{pH}$

(d) Fe_2O_3 can be oxidised by ClO^- ions under alkaline conditions in a redox reaction.

Unbalanced half-equations for this reaction are shown below.

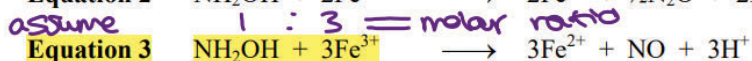
Balance the half-equations and construct an overall equation for the reaction.



6. Hydroxylamine, NH_2OH , is a strong reducing agent.

When heated in aqueous solution, NH_2OH reduces Fe^{3+} ions to Fe^{2+} ions.

A student suggests the three possible equations for the reaction, shown below.



The student plans to carry out an investigation to determine which equation is correct.

The method is outlined below.



Stage 1 Using a pipette, add 25.0 cm^3 of $4.32 \times 10^{-2} \text{ mol dm}^{-3}$ NH_2OH to a conical flask. Add 10 cm^3 of 1 mol dm^{-3} H_2SO_4 to the conical flask followed by an excess of a solution containing $0.0400 \text{ mol dm}^{-3}$ $\text{Fe}^{3+}(\text{aq})$.

Stage 2 Boil the mixture for 5 minutes and allow to cool.

Stage 3 Titrate the cooled mixture with $2.00 \times 10^{-2} \text{ mol dm}^{-3}$ $\text{KMnO}_4(\text{aq})$.

- (a) Determine the minimum volume of $0.0400 \text{ mol dm}^{-3}$ $\text{Fe}^{3+}(\text{aq})$ that the student should plan to use in Stage 1.

Explain your reasoning.

$$4.32 \times 10^{-2} \times 25 \times 10^{-3} = 1.08 \times 10^{-3} \text{ mol of } \text{NH}_2\text{OH}$$

$$1.08 \times 10^{-3} \times 3 = 3.24 \times 10^{-3} \text{ mol of } \text{Fe}^{3+}$$

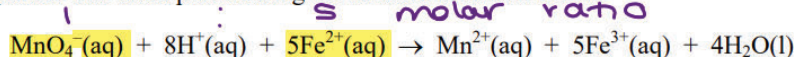
$$\frac{3.24 \times 10^{-3}}{0.04} \times 1000 = 81.0 \text{ cm}^3$$

volume = 81.0 cm^3

explanation: minimum amount of Fe^{3+}
required is maximum amount
theoretically required to react with all
 NH_2OH .

- (b) In the student's titration, 21.6 cm^3 of $\text{KMnO}_4(\text{aq})$ is required to reach the end point.

The equation that takes place during the titration is shown below.

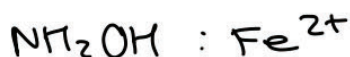


Analyse the student's results to determine which of the three equations is correct.

Show **all** your working.

$$21.6 \times 10^{-3} \times 2 \times 10^{-2} = 4.32 \times 10^{-4} \text{ mol of } \text{MnO}_4^-$$

$$4.32 \times 10^{-4} \times 5 = 2.16 \times 10^{-3} \text{ mol of } \text{Fe}^{2+}$$



↑

$$1.08 \times 10^{-3} \text{ mol}$$

$$1.08 \times 10^{-3} : 2.16 \times 10^{-3}$$

$$1 : 2$$

equation 2 only equation
with a 1:2 ratio of
 $\text{NH}_2\text{OH} : \text{Fe}^{2+}$

[3]

- (c) The student intends to repeat the procedure to check their results.

There is insufficient time for the student to repeat all three stages and the student decides to omit **Stage 2**, the boiling stage. Unfortunately the resulting titre is much less than the original titre.

The student rejects the results from the repeated procedure.

- (i) Suggest the purpose of the boiling in **Stage 2** and reasons for the second titre being much less than the original titre.

Boiling speeds up reaction so
there is less Fe^{2+}

↑

so second titre is
less than the original

[2]

- (ii) The main reason for insufficient time is the need to boil and cool the mixture for each titration.

Suggest how the procedure could be modified so that **Stage 2** does not need to be carried out repeatedly.

Give your reasoning.

In Stage 1, increase quantities
so that there is sufficient
solution for more than one
titration [1]

END OF QUESTION PAPER

Specimen

7. What is the bonding between the ligands and the metal ion in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$?

A Metallic

B Ionic

C Hydrogen

D Dative covalent

Your answer

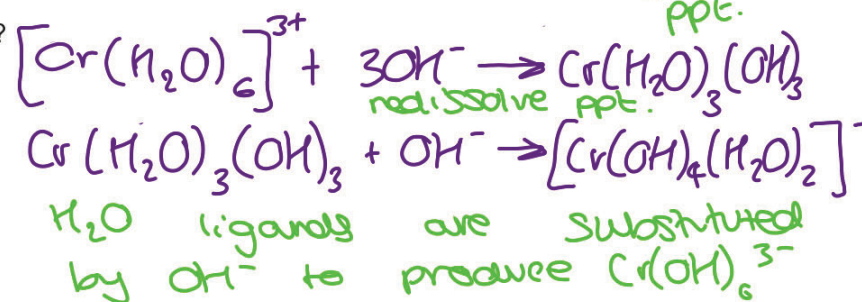
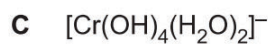
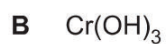
D

key piece of
recall that
you need to
know for your
exams

[1]

8. Aqueous Cr^{3+} ions are reacted with an excess of aqueous sodium hydroxide.

Which product is formed?



Your answer

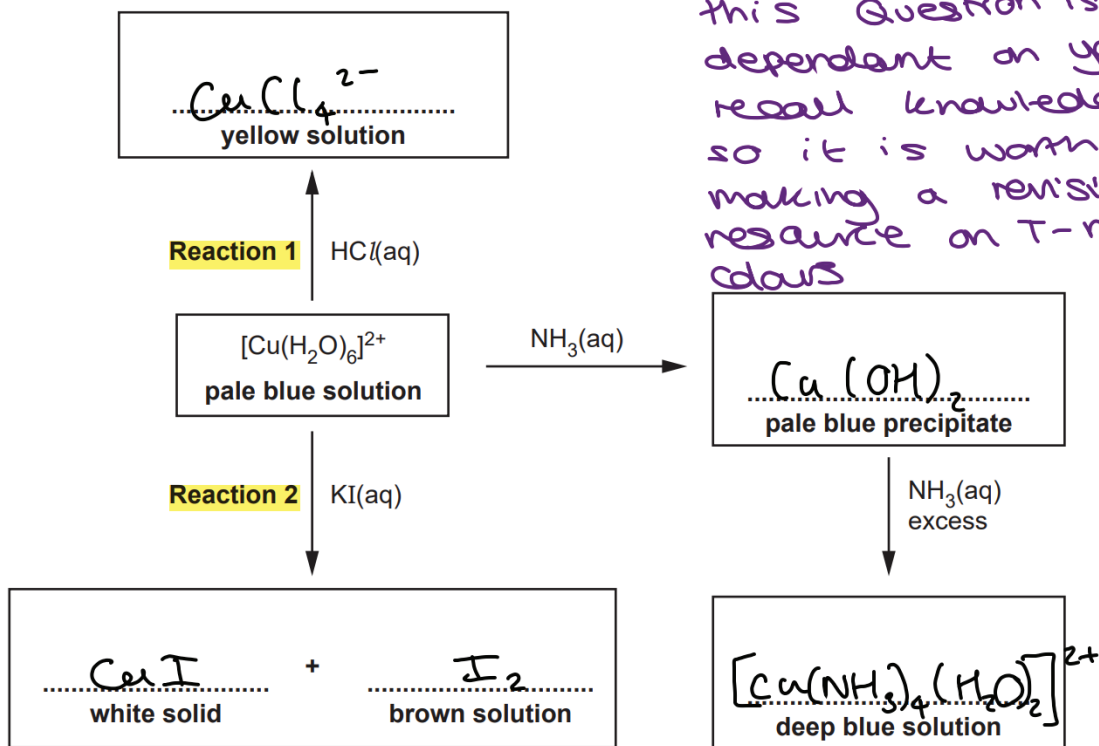
A

[1]

9. This question is about reactions of ions and compounds of transition elements.

(a) The flowchart shows reactions of the complex ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.

(i) In the boxes, write down the formulae of the species responsible for the observations.



[5]

(ii) Name the type of reaction for **Reaction 1** and **Reaction 2**.

Reaction 1 ... *ligand substitution*

Reaction 2 ... *redox*

[2]

(b)* A hydrated nickel(II) complex, **A**, is heated in a crucible to remove the water of crystallisation. The anhydrous complex **B** is formed. The results are shown below.

Mass of crucible + hydrated complex A	= 59.554 g	<i>mass of H₂O:</i>
Mass of crucible + anhydrous complex B	= 58.690 g	<i>59.554 - 58.690</i>
Mass of crucible	= 51.257 g	<i>= 0.864 g</i>
		<i>mass of B:</i>
		<i>58.69 - 51.257 = 7.433 g</i>

The anhydrous complex **B** is analysed and found to have a molar mass of 309.7 g mol⁻¹ and to contain the following percentage composition by mass:

Ni, 18.95%; C, 23.25%; N, 27.12%; H, 7.75%; Cl, 22.93%.

The anhydrous complex **B** contains a cation **C** comprising Ni, C, N and H only.

Cation **C** is six-coordinate, contains three molecules of the bidentate ligand **D**, and exists as optical isomers.

Determine the formula of **A**, **B**, **C** and **D** and show the 3D structures for the optical isomers of **C**.

Show all your working.

Ni: $\frac{18.95}{58.7} = 0.3228 = 1$ C: $\frac{23.25}{12} = 1.9375 = 6$ N: $\frac{27.12}{14} = 1.937 = 6$ H: $\frac{7.75}{1} = 7.75 = 24$
 $\frac{0.3228}{0.3228} = 1$ $\frac{1.9375}{0.3228} = 6$ $\frac{1.937}{0.3228} = 6$ $\frac{7.75}{0.3228} = 24$

Cl: $\frac{22.93}{35.5} = 0.64 = 2$ *Same empirical and molecular formula (same molar mass)*
 $\frac{0.64}{0.3228} = 2$ B: NiC₆N₆H₂₄Cl₂
 A: NiC₆N₆H₂₄Cl₂ · 2H₂O *molar ratio*

$\frac{0.864}{18} = 0.048 \text{ mol}$ $\frac{7.433}{309.7} = 0.024 \text{ mol}$
lose 2Cl with 1 each

C: [NiC₆N₆H₂₄]²⁺ D: H₂NCH₂CH₂NH₂
D × 3 *make sure Ni bonds to N NOT H*

[6]

10. Which statement(s) is/are correct for the complex $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$?

1 One of its stereoisomers is used as an anti-cancer drug. *recall*

~~2~~ It has bond angles of 109.5° . *lone pairs on N*

~~3~~ It has optical isomers.

4 bonded pairs + 0 lone pairs

A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

*4 different groups
2 groups and 2 of each
so not an optical isomer*

Your answer

D

[1]

11. This question is about some reactions of d block elements and their ions.

Table 21.1 shows standard electrode potentials which will be needed within this question.

<i>stage 2</i>	$Zn^{2+}(aq) + 2e^{-}$	\rightleftharpoons	$Zn(s)$	$E^{\ominus} = -0.76V$	<i>Cell with more negative E^{\ominus} undergoes oxidation</i>
	$Cr^{3+}(aq) + e^{-}$	\rightleftharpoons	$Cr^{2+}(aq)$	$E^{\ominus} = -0.42V$	
	$Ni^{2+}(aq) + 2e^{-}$	\rightleftharpoons	$Ni(s)$	$E^{\ominus} = -0.25V$	
<i>stage 1</i>	$I_2(aq) + 2e^{-}$	\rightleftharpoons	$2I^{-}(aq)$	$E^{\ominus} = +0.54V$	
	$Fe^{3+}(aq) + e^{-}$	\rightleftharpoons	$Fe^{2+}(aq)$	$E^{\ominus} = +0.77V$	
	$Cr_2O_7^{2-}(aq) + 14H^{+}(aq) + 6e^{-}$	\rightleftharpoons	$2Cr^{3+}(aq) + 7H_2O(l)$	$E^{\ominus} = +1.33V$	
	$H_2O_2(aq) + 2H^{+}(aq) + 2e^{-}$	\rightleftharpoons	$2H_2O(l)$	$E^{\ominus} = +1.78V$	

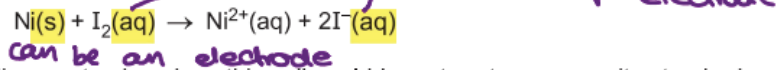
Table 21.1

(a) Complete the electron configuration of

a Ni atom: $1s^2 \dots 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$ *Filled first and last first*

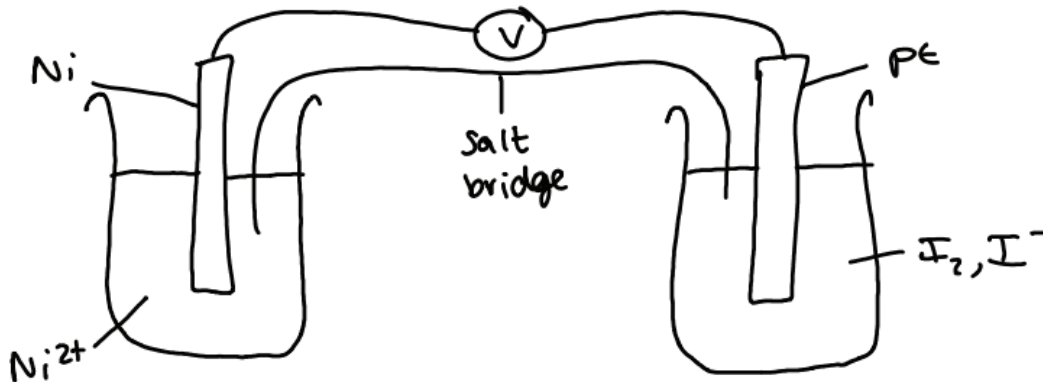
a Ni²⁺ ion: $1s^2 \dots 2s^2 2p^6 3s^2 3p^6 3d^8$ [2]

(b) A standard cell is set up in the laboratory with the cell reaction shown below.



(i) Draw a labelled diagram to show how this cell could be set up to measure its standard cell potential.

Include details of apparatus, solutions and the standard conditions required.



Standard conditions 1 mol dm^{-3} , 298 K

[4]

- (ii) Predict the standard cell potential of this cell.

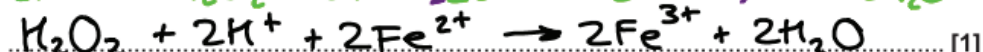
$$0.54 - (-0.25) = 0.79 \text{ V}$$

most positive - most negative

standard cell potential = 0.79 V [1]

- (c) Use the information in
- Table 21.1**
- to help you answer both parts of this question.

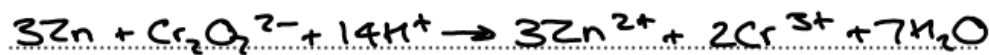
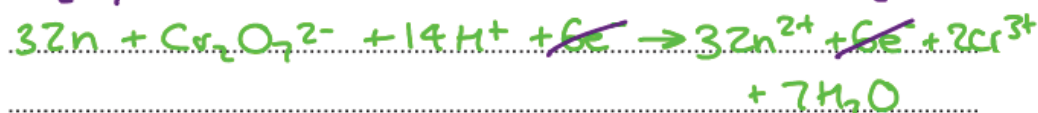
- (i) Write the overall equation for the oxidation of
- Fe^{2+}
- by acidified
- H_2O_2
- .



- (ii) Zinc reacts with acidified
- $\text{Cr}_2\text{O}_7^{2-}$
- ions to form
- Cr^{2+}
- ions in two stages.

Explain why this happens in terms of electrode potentials and equilibria.

Include overall equations for the reactions which occur.



E^\ominus of Zn is more negative than E^\ominus of $\text{Cr}_2\text{O}_7^{2-}$ so Zn system shifts left. [4]

(d)* Three different reactions of copper compounds are described below.

Reaction 1: Aqueous copper(II) sulfate reacts with excess aqueous ammonia in a ligand substitution reaction. A deep-blue solution is formed, containing an octahedral complex ion, C, which is a trans isomer.

Reaction 2: Copper(I) oxide reacts with hot dilute sulfuric acid in a disproportionation reaction. A blue solution, D, and a brown solid, E are formed.

Reaction 3: Copper(II) oxide reacts with warm dilute nitric acid in a neutralisation reaction, to form a blue solution. Unreacted copper(II) oxide is filtered off, and the solution is left overnight in an evaporating basin.

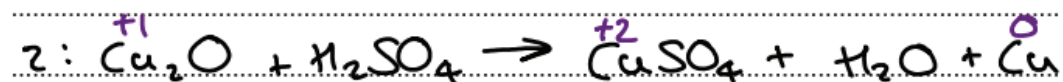
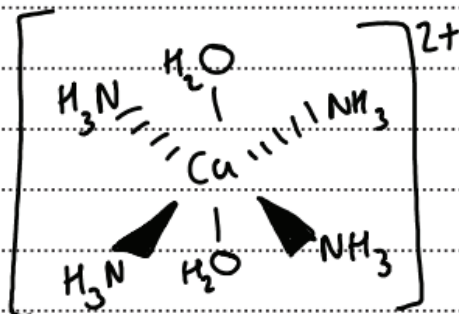
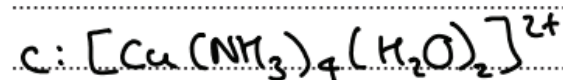
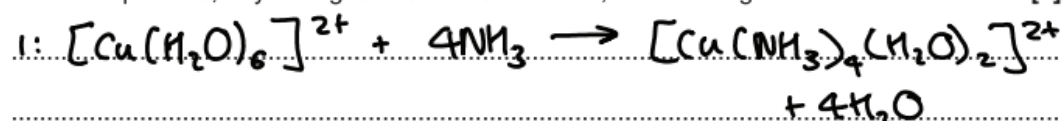
A hydrated salt, F, crystallises, with the percentage composition by mass:

Cu, 26.29%; H, 2.48%; N, 11.59%; O, 59.63%.

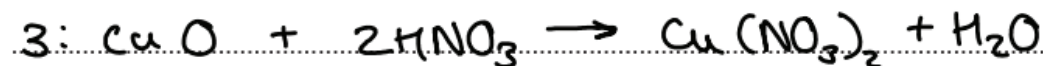
Identify C–F by formulae or structures, as appropriate.

Include equations, any changes in oxidation number, and working.

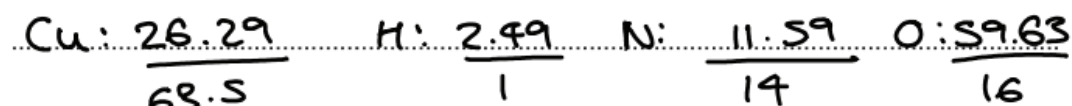
[6]



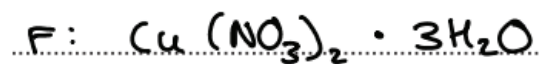
Cu oxidation states: $+1 \rightarrow +2 + 0$



Additional answer space if required.

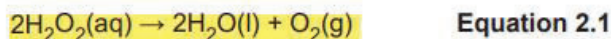


$$\begin{array}{cccc} = 0.41 & = 2.49 & = 0.82 & = 3.72 \\ \text{divide each of these numbers by the smallest (0.41)} & & & \\ \frac{0.41}{0.41} = 1 & \frac{2.49}{0.41} = 6 & \frac{0.82}{0.41} = 2 & \frac{3.72}{0.41} = 9 \end{array}$$



12. This question looks at reactions of hydrogen peroxide and of cobalt(II) ions.

(a) Aqueous hydrogen peroxide decomposes as shown in **equation 2.1**.



The reaction is catalysed by manganese(IV) oxide, MnO_2 .

A student investigates the decomposition of a hydrogen peroxide solution as outlined below.

- The student adds 50.00 cm^3 of $\text{H}_2\text{O}_2(\text{aq})$ to a conical flask.
- The student adds a small spatula measure of MnO_2 and quickly connects the flask to a gas syringe.
- The student measures the volume of oxygen every 200 seconds.

Results

Time/s	Volume of O_2/cm^3
0	0
200	15
400	28
600	36
800	41
1000	46
1200	48
1400	50

(i) Process the results as outlined below.

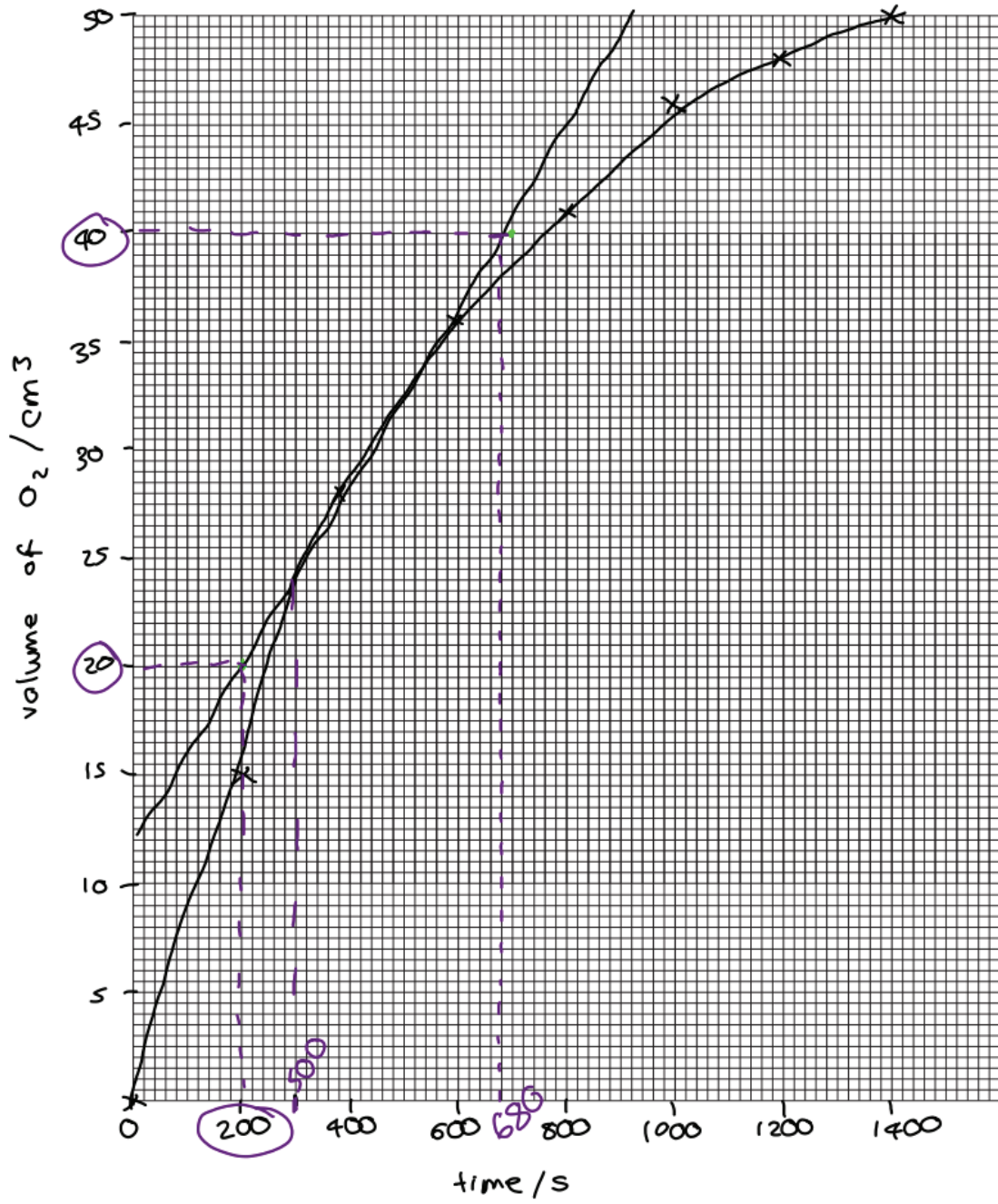
- On page 5, plot a graph of **volume of O_2** against **time**.
- Use your graph to find the **rate of the reaction**, in cm^3s^{-1} , at $t = 500 \text{ s}$.

Show your working on the graph and in the space below.

$$\frac{40 - 20}{680 - 200} = 0.042 \text{ cm}^3\text{s}^{-1}$$

tangent at 500 s

rate = 0.042 cm^3s^{-1} [5]



- (ii) The student allows the reaction in **equation 2.1** to proceed until no more gas is evolved. The volume of O_2 in the syringe is now 55 cm^3 , measured at RTP.

Calculate the initial concentration of the H_2O_2 .

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

↑
volume = mol
molar volume
(24000 cm^3)

$$\frac{55}{24000} = 2.29 \times 10^{-3} \text{ mol}$$

$$2.29 \times 10^{-3} \times 2 = 4.58 \times 10^{-3} \text{ mol of } H_2O_2$$

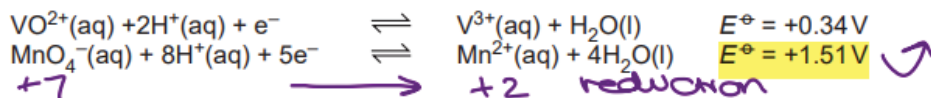
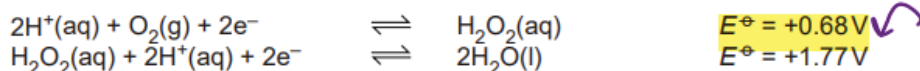
$$4.58 \times 10^{-3} \div 50 \times 10^{-3} = 0.092 \text{ mol dm}^{-3}$$

initial concentration of H_2O_2 = **0.092** mol dm^{-3} [3]

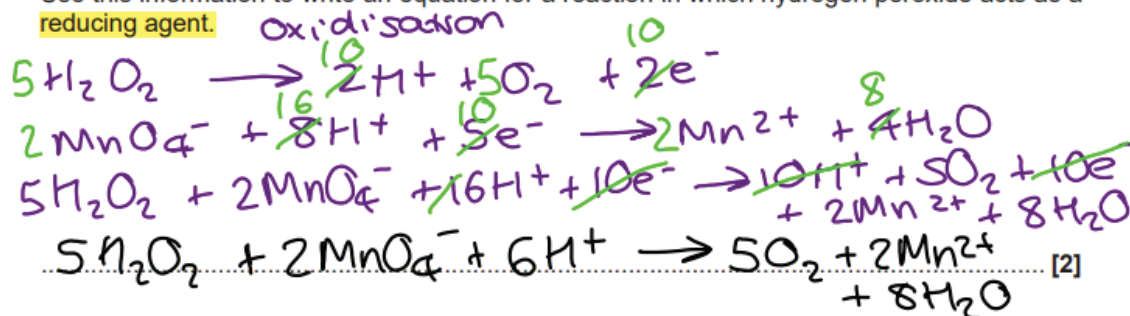


- (b) Hydrogen peroxide can act as an oxidising agent or as a reducing agent.

Some standard electrode potentials are shown below.



Use this information to write an equation for a reaction in which hydrogen peroxide acts as a **reducing agent**.



(c) Cobalt(II) forms complex ions with water ligands and with chloride ligands.

- With water ligands, cobalt(II) forms a pink octahedral complex ion, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.
- With chloride ligands, cobalt(II) forms a blue tetrahedral complex ion.

A student dissolves cobalt(II) sulfate in water in a boiling tube. A pink solution forms.

Experiment 1

The student places the boiling tube in a water bath at 100°C .

Concentrated hydrochloric acid is added dropwise.

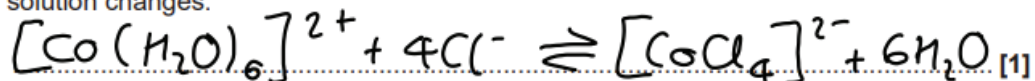
The colour of the solution changes from pink to blue.

Experiment 2

The student places the boiling tube from **experiment 1** in an ice/water bath at 0°C .

The colour of the solution changes from blue to pink.

- (i) Write the **equilibrium equation** for the reaction that takes place when the colour of the solution changes.



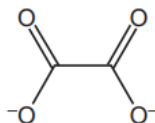
- (ii) Explain the observations and predict whether the formation of the blue colour is exothermic or endothermic.

equilibrium shifts right at 100°C
and shifts left at 0°C so
endothermic.

[2]

13. This question is about ethanedioic acid, $(\text{COOH})_2$, and ethanedioate ions $(\text{COO}^-)_2^{2-}$

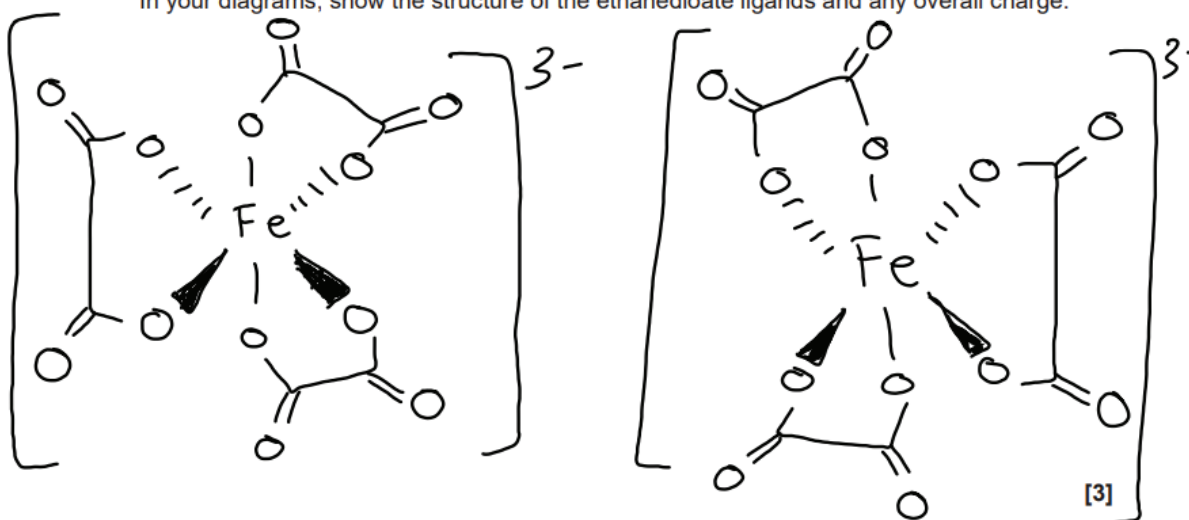
(a) The ethanedioate ion, shown below, can act as a bidentate ligand.



Fe^{3+} forms a complex ion with three ethanedioate ions. The complex ion has two optical isomers.

Draw the 3D shapes of the optical isomers. *mirror image*

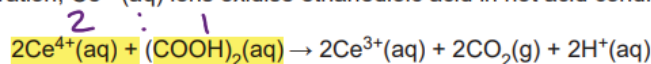
In your diagrams, show the structure of the ethanedioate ligands and any overall charge.



(b) Ethanedioic acid, $(\text{COOH})_2$, is present in rhubarb leaves.

A student carries out a redox titration using aqueous cerium(IV) sulfate, $\text{Ce}(\text{SO}_4)_2(\text{aq})$, to determine the percentage, by mass, of ethanedioic acid in rhubarb leaves.

In the titration, $\text{Ce}^{4+}(\text{aq})$ ions oxidise ethanedioic acid in hot acid conditions:



$\text{Ce}^{4+}(\text{aq})$ ions have a yellow colour. $\text{Ce}^{3+}(\text{aq})$ ions are colourless.

The student weighs 82.68 g of rhubarb leaves and extracts ethanedioic acid from the leaves.

The ethanedioic acid is added to dilute sulfuric acid to form a colourless solution which is made up to 250.0 cm^3 with distilled water.

The student heats 25.00 cm^3 of this solution to 70°C and titrates this volume with $0.0500\text{ mol dm}^{-3}$ $\text{Ce}(\text{SO}_4)_2$ from the burette.

The student repeats the titration to obtain concordant (consistent) titres.

$\pm 0.10\text{ cm}^3$

Titration results

The trial titre has been omitted.

	1	2	3
Final reading/cm ³	24.30	47.80	23.65
Initial reading/cm ³	1.05	24.30	0.50

titre / cm³ 23.25 23.50 23.15

- (i) This titration is self-indicating and the student does not need to add an indicator.

What colour change would the student observe at the end point?

Colour change from colourless to yellow [1]

- (ii) Calculate the percentage, by mass, of ethanedioic acid in the rhubarb leaves.

Give your answer to an **appropriate** number of significant figures.

$$\text{mean titre: } \frac{23.25 + 23.15}{2} = 23.20 \text{ cm}^3$$



$$23.20 \times 10^{-3} \times 0.05 = 1.16 \times 10^{-3} \text{ mol of Ce}^{4+}$$

$$\frac{1.16 \times 10^{-3}}{2} = 5.80 \times 10^{-4} \text{ mol of } (\text{COOH})_2 \text{ in } 25 \text{ cm}^3$$

$$5.80 \times 10^{-4} \times 10 = 5.80 \times 10^{-3} \text{ mol of } (\text{COOH})_2 \text{ in } 250 \text{ cm}^3$$



$$5.80 \times 10^{-3} \times ((12 + (16 \times 2) + 1) \times 2) = 0.522 \text{ g}$$

$$\frac{0.522}{82.68} \times 100 = 0.631 \% \text{ (3 SF.)}$$

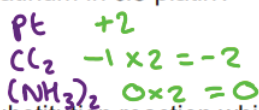
percentage of ethanedioic acid = 0.631 % [6]

14. This question is about two compounds used in medicine.

(a) *Cis-platin*, $\text{PtCl}_2(\text{NH}_3)_2$, is a complex of platinum which is used in cancer treatment.

(i) What is the oxidation number of platinum in *cis-platin*?

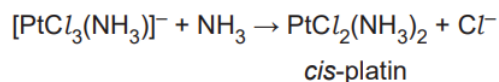
.....+2.....



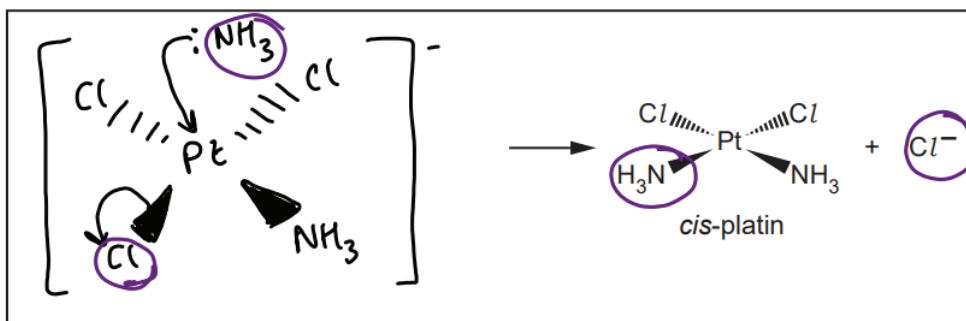
All compounds must have an oxidation number of 0 [1]

(ii) *Cis-platin* is prepared in a ligand substitution reaction which takes place in multiple steps.

The equation for the final step forming *cis-platin* is shown below.

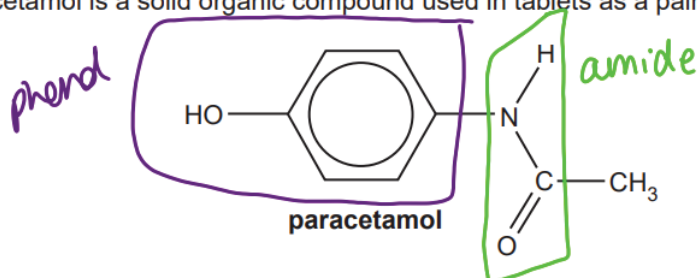


In the box, outline the mechanism for the formation of *cis-platin* from $[\text{PtCl}_3(\text{NH}_3)]^-$. Use curly arrows and lone pairs where appropriate.



[2]

(b) Paracetamol is a solid organic compound used in tablets as a painkiller.

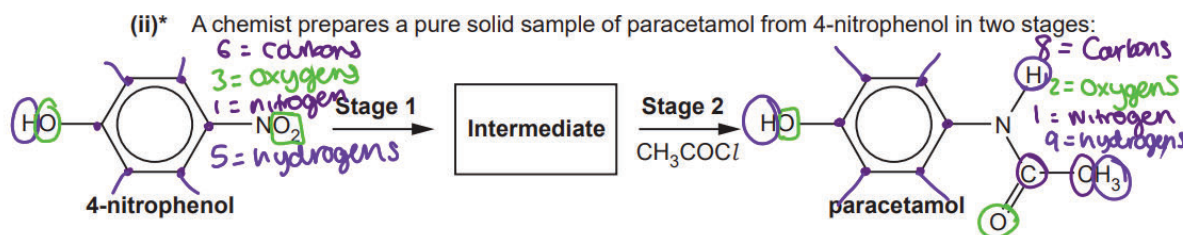


(i) Name the functional groups present in paracetamol.

phenol.....

amide.....

[2]



Describe a two-stage synthesis of 5.00 g of pure paracetamol from 4-nitrophenol. The overall percentage yield of paracetamol from 4-nitrophenol is 40.0%.

In your answer, include the mass of 4-nitrophenol required, the reagents and intermediate, and details of the purification of paracetamol. [6]

mass of 4-nitrophenol:

$$\frac{5}{(12 \times 8) + (16 \times 2) + 14 + 9} = 0.0331 \text{ mol of paracetamol}$$

mass
mol x RFM

$$0.0331 \times \frac{100}{40} = 0.0828 \text{ mol of 4-nitrophenol}$$

$$0.0828 \times ((12 \times 6) + (16 \times 3) + 14 + 5) = 11.50 \text{ g}$$

intermediate: 4-aminophenol



- dissolve impure solid in minimum volume of hot solvent
- cool solution and filter solid
- scratch with glass rod

Additional answer space if required.

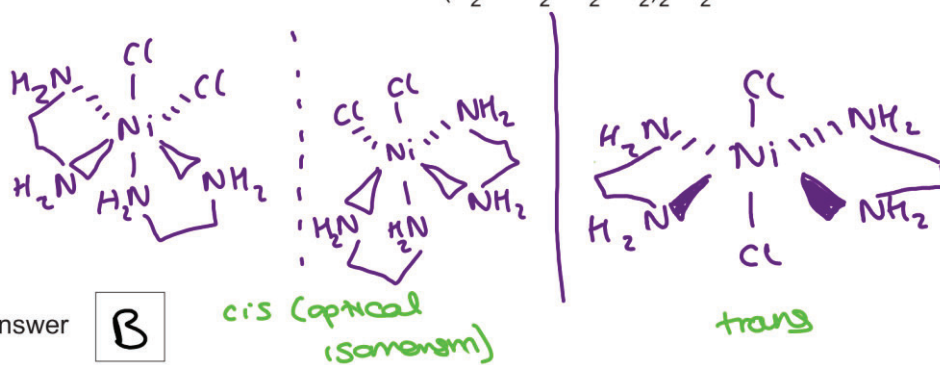
- wash with cold solvent and dry

15. What is the number of stereoisomers that $\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2$ can form?

- A 2
- B 3**
- C 4
- D 6

Your answer

B



[1]

16. Which property/properties is/are **correct** for a transition element?

- 1 The element has ^{ions}~~atoms~~ with a partially filled d sub-shell.
- 2 The existence of more than one oxidation state in its compounds. ✓
- 3 The formation of coloured ions. ✓

- A** 1, 2 and 3
B Only 1 and 2
C Only 2 and 3
D Only 1

Your answer

C

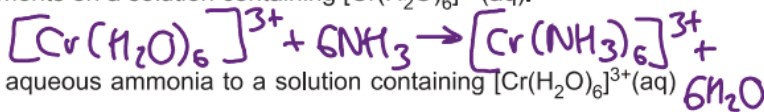
[1]

17. This question is about reactions of ions and compounds of transition elements.

- (a) A student carries out two experiments on a solution containing $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$.

Experiment 1

The student adds an excess of aqueous ammonia to a solution containing $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ until a purple solution is formed.

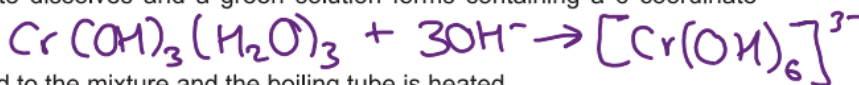


Experiment 2

The student carries out the following reaction sequence.

- Step 1** NaOH(aq) is added slowly to a solution containing $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ in a boiling tube.
A grey-green precipitate forms.

- Step 2** An excess of NaOH(aq) is added to the boiling tube.
The precipitate dissolves and a green solution forms containing a 6 coordinate complex ion.

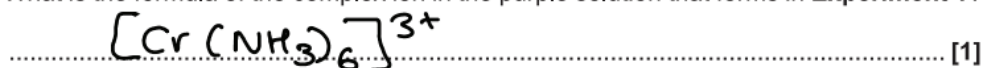


- Step 3** H_2O_2 is added to the mixture and the boiling tube is heated.
A yellow solution forms.

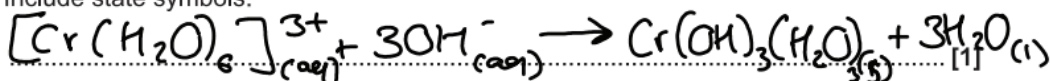


- Step 4** The solution in the boiling tube is acidified.
The solution now contains $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$.

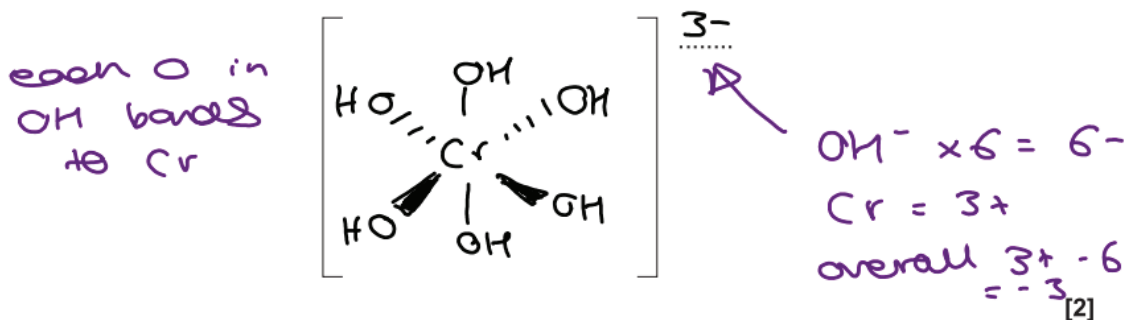
- (i) What is the formula of the complex ion in the purple solution that forms in **Experiment 1**?



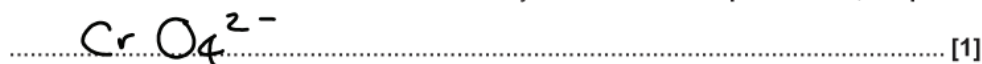
- (ii) Suggest an equation for the reaction in **Experiment 2, Step 1**.
Include state symbols.



- (iii) Draw a 3-D diagram for the shape of the complex ion that forms in **Experiment 2, Step 2**.
Include the charge of the ion.



- (iv) What is the formula of the ion that causes the yellow colour in **Experiment 2, Step 3**?



- (v) State the colour of the solution that forms in **Experiment 2, Step 4**.



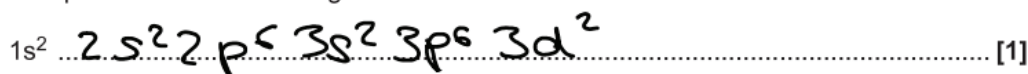
- (b) Vanadium ions have four common oxidation states. **Table 18.1** shows the colours of the ions in aqueous solution.

Oxidation state of vanadium	Vanadium ion	Colour
+5	$\text{VO}_2^+(\text{aq})$	yellow
+4	$\text{VO}^{2+}(\text{aq})$	blue
+3	$\text{V}^{3+}(\text{aq})$	green
+2	$\text{V}^{2+}(\text{aq})$	violet

filled first +
lost first
↓

Table 18.1 $\text{V}: 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

- (i) Complete the electron configuration of a V^{3+} ion.



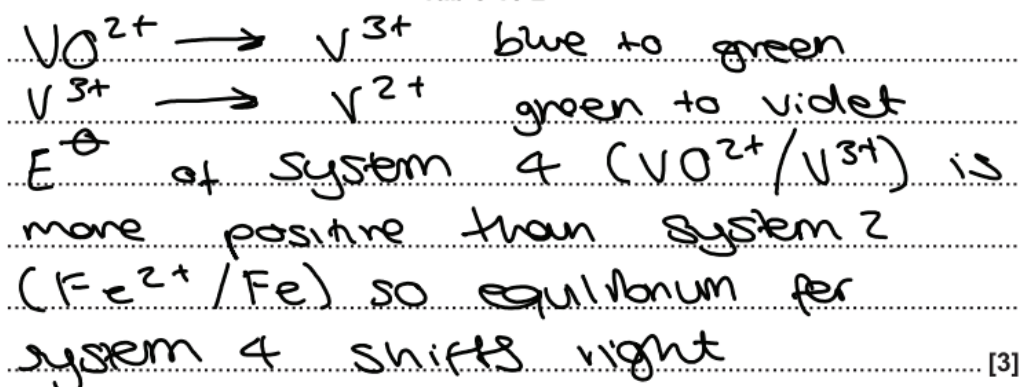
- (ii) The student adds excess iron to a solution containing $\text{VO}^{2+}(\text{aq})$ ions, and observes that the colour of the solution changes from blue to green and then to violet.

Use the relevant standard electrode potentials shown in **Table 18.2** to explain these observations.

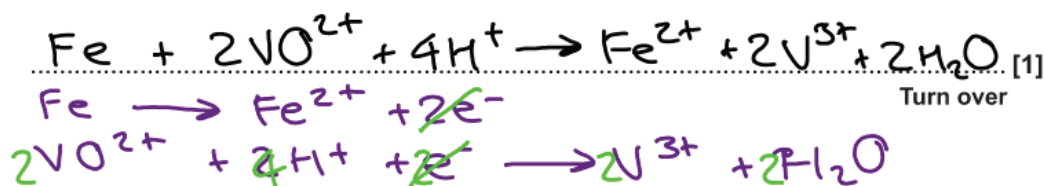
Redox system			E^\ominus/V
1	$\text{V}^{2+}(\text{aq}) + 2e^-$	$\rightleftharpoons \text{V}(\text{s})$	-1.18
2	$\text{Fe}^{2+}(\text{aq}) + 2e^-$	$\rightleftharpoons \text{Fe}(\text{s})$	-0.44
3	$\text{V}^{3+}(\text{aq}) + e^-$	$\rightleftharpoons \text{V}^{2+}(\text{aq})$	-0.26
4	$\text{VO}^{2+}(\text{aq}) + 2\text{H}^+ + e^-$	$\rightleftharpoons \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+0.34
5	$\text{Fe}^{3+}(\text{aq}) + e^-$	$\rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
6	$\text{VO}_2^+(\text{aq}) + 2\text{H}^+ + e^-$	$\rightleftharpoons \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+1.00

want to start with Fe and VO^{2+}

Table 18.2



- (iii) Construct an equation for the first colour change from blue to green.



Turn over

- (c) Iron(II) gluconate, $C_{12}H_{22}FeO_{14}$, is the active ingredient in some brands of iron supplements.

A student carries out an experiment to determine the mass of iron(II) gluconate in one tablet of an iron supplement, using the method below.

Stage 1 The student crushes two tablets and dissolves the powdered tablets in dilute sulfuric acid.

Stage 2 The student makes up the solution from Stage 1 to 250.0 cm^3 in a volumetric flask.

Stage 3 The student then titrates 25.0 cm^3 portions of the solution obtained in Stage 2 with $0.00200\text{ mol dm}^{-3}$ potassium manganate(VII).

The student obtains a mean titre of 13.50 cm^3 .

In this titration, 1 mol of manganate(VII) ions reacts with 5 mol of iron(II) ions.

- (i) Explain why the student used $0.00200\text{ mol dm}^{-3}$ potassium manganate(VII) solution for this titration, rather than the more usual concentration of $0.0200\text{ mol dm}^{-3}$ used in manganate(VII) titrations.

$0.00200\text{ mol dm}^{-3}$ gives a larger titre so a smaller percentage error [1]

- (ii) Use the student's results to determine the mass, in mg, of iron(II) gluconate in one tablet.

Give your answer to 3 significant figures.

$$13.5 \times 10^{-3} \times 0.002 = 2.7 \times 10^{-5} \text{ mol of MnO}_4^-$$

$$2.7 \times 10^{-5} \times 5 = 1.35 \times 10^{-4} \text{ mol of Fe}^{2+}$$

$$1.35 \times 10^{-4} \times 10 = 1.35 \times 10^{-3} \text{ mol of Fe}^{2+} \text{ in } 25\text{ cm}^3 \text{ in } 250\text{ cm}^3$$

$$1.35 \times 10^{-3} \times ((12 \times 12) + (22 \times 1) + 55.8 + (14 \times 16)) = 0.6018 \text{ g 2 tablets}$$

$$= 0.301 \text{ g (3sf.) } \downarrow \text{ tablet}$$

$$= 301 \text{ mg}$$

mass of iron(II) gluconate in one tablet = 301 mg [5]

(iii) Some iron supplements contain iron(II) sulfate or iron(II) fumarate.

The information in **Table 18.3** is taken from the labels of two iron supplements, **A** and **B**.

Iron supplement	Iron compound	Mass of iron compound in one tablet / mg
A	iron(II) sulfate, FeSO_4	180
B	iron(II) fumarate, $\text{C}_4\text{H}_2\text{FeO}_4$	210

Table 18.3

Choose which iron supplement, **A** or **B**, would provide the greater mass of iron per tablet.

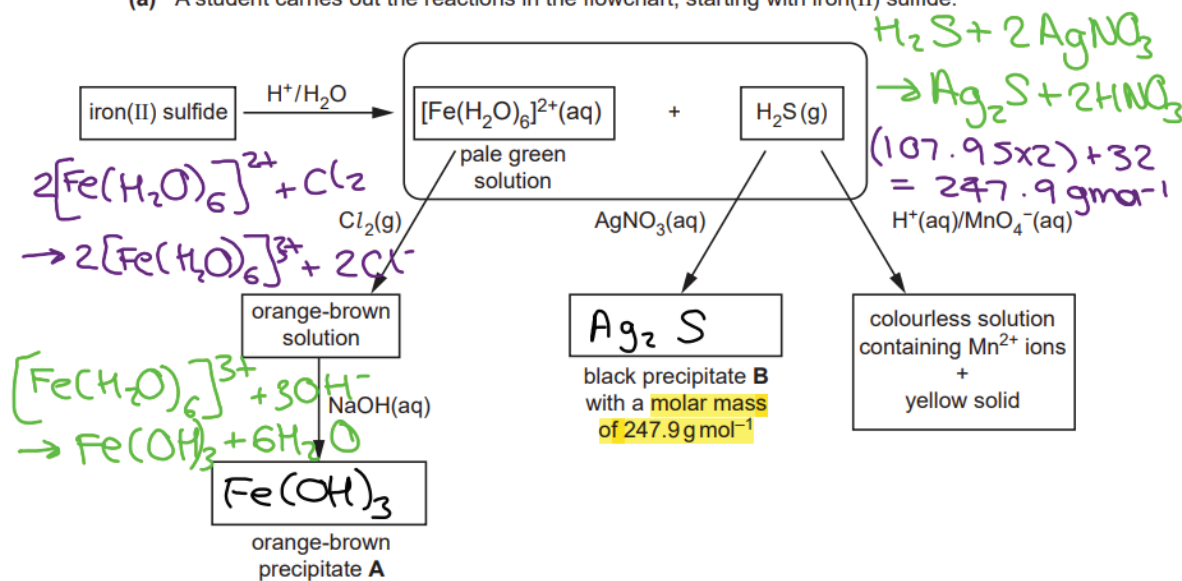
$$\frac{55.8}{(55.8 + 32 + (16 \times 4))} \times 180 = 66 \text{ mg}$$

$$\frac{55.8}{((4 \times 12) + 2 + 55.8 + (4 \times 16))} \times 210 = 69 \text{ mg}$$

iron supplement: **B** [1]

18. This question is about reactions of iron compounds.

(a) A student carries out the reactions in the flowchart, starting with iron(II) sulfide.



(i) In the boxes, write the formulae of **A** and **B**. [2]

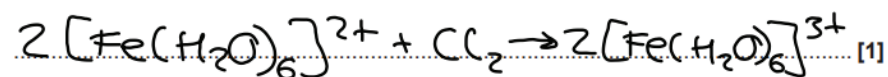
(ii) The student thinks that the reaction of iron(II) sulfide with H^+/H_2O is a redox reaction.

Explain, with reasons, whether the student is correct.

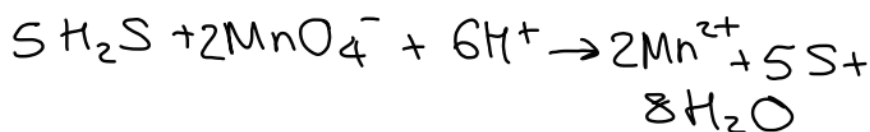
student is incorrect as no oxidation numbers change
e.g. Fe stays +2

[1]

(iii) Write the equation for the reaction of $[Fe(H_2O)_6]^{2+}(aq)$ with $Cl_2(g)$.



(iv) Construct an equation for the reaction of $H_2S(g)$ with $H^+(aq)/MnO_4^-(aq)$.



(b)* Compound C is a hydrated ionic compound with the empirical formula: $\text{FeH}_{18}\text{N}_3\text{O}_{18}$.

A student investigates the thermal decomposition of compound C as outlined below.

Stage 1

The student gently heats 0.00300 mol of compound C to remove the water of crystallisation. 0.486 g of water is collected, leaving 0.00300 mol of the anhydrous compound D.

Stage 2

The student strongly heats 0.00300 mol of compound D, which decomposes to form a solid oxide E (molar mass of 159.6 g mol^{-1}) and 270 cm^3 of a gas mixture, measured at RTP, containing gases F and G.

Stage 3

The student cools the 270 cm^3 gas mixture of F and G.

- Gas F is a compound that condenses to form 0.414 g of a liquid.
- Gas G remains and has a volume of 54 cm^3 , measured at RTP. Gas G is tested and it relights a glowing splint.

Determine the formulae of C, D, E, F and G.

Show all your working and equations for the reactions.



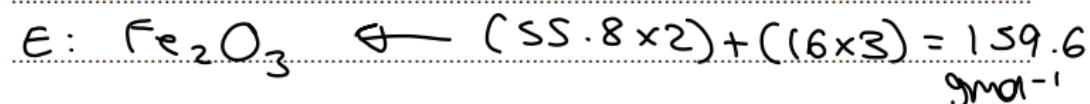
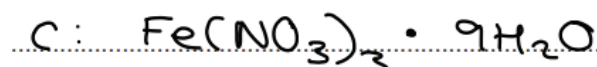
$$\frac{\text{Vol}}{\text{molar vol}} = \text{mol}$$

(24000 cm^3) [6]

$$\frac{0.486}{18} = 0.027 \text{ mol of H}_2\text{O}$$

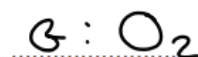
$$0.027 : 0.003 \quad 1:9$$

9 H₂O



$$\frac{270 - 54}{24000} = 0.009 \text{ mol of F}$$

$$\frac{0.414}{0.009} = 46 \text{ g mol}^{-1} = \text{NO}_2 = \text{F}$$



19. Which statement about elements in the d block of Period 4 of the periodic table is correct?

A ✓ Cr atoms have the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$. Hund's Rule

B ✓ Cu⁺ ions contain an incomplete 3d sub-shell. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

C ✓ Fe²⁺ ions contain 3 unpaired electrons. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

D ✓ Sc forms ions with different oxidation states.



Your answer

A

Sc doesn't lose e⁻s to form an ion with incomplete d-subshell most stable Sc ion is Sc³⁺ [1]

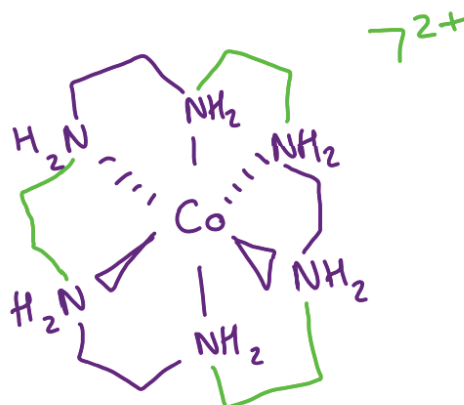
20. Which statement(s) for the complex ion $[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{2+}$ is/are correct?

- all same bidentate ligands so no cis and trans
- 1 It has *cis* and *trans* isomers. X
- 2 It has optical isomers. ✓
- 3 It is six-fold coordination. ✓

- A 1, 2 and 3
- B Only 1 and 2
- C Only 2 and 3
- D Only 1

Your answer

C



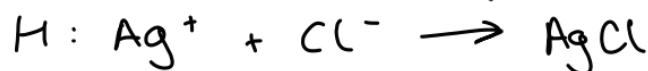
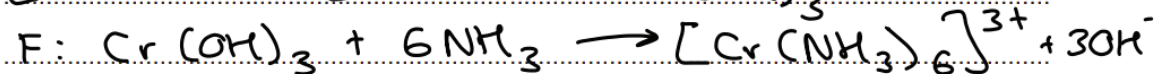
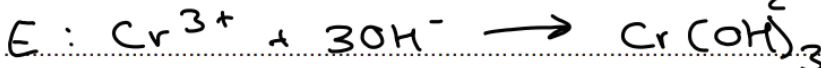
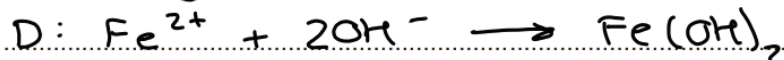
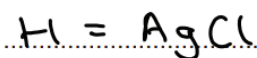
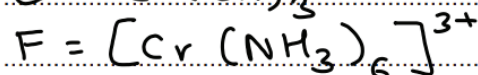
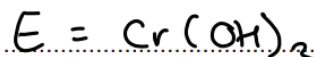
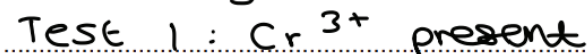
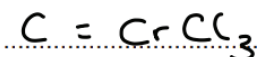
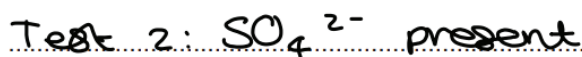
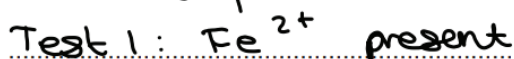
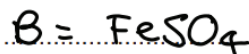
[1]

21. (a)* **B** and **C** are compounds of two different transition elements.

A student carries out test tube reactions on aqueous solutions of **B** and **C**.
The observations of the student's tests are shown below.

	Test	B(aq)	C(aq)
1	NH ₃ (aq) added dropwise	green precipitate D	grey-green precipitate E
	excess NH ₃ (aq) added	no further change	purple solution F
2	HNO ₃ (aq)	no change	no change
	followed by Ba(NO ₃) ₂ (aq)	white precipitate G	no change
3	HNO ₃ (aq)	no change	no change
	followed by AgNO ₃ (aq)	no change	white precipitate H

Analyse the results to identify **B** to **H**, and construct ionic equations for the formation of products **D** to **H**. [6]



Additional answer space if required

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- (b) A compound of nickel, J, has the formula $(\text{NH}_4)_2[\text{Ni}(\text{SCN})_x(\text{NH}_3)_y]$ and contains SCN^- and NH_3 ligands.

The percentage by mass of three of the elements in compound J is shown below:
 Ni, 16.26%; S, 35.56%; N, 31.00%.

- (i) Calculate the values of x and y in the formula of compound J.

empirical formula calculation

Ni : S : N	$\frac{16.26}{58.7}$:	$\frac{35.56}{32.1}$:	$\frac{31.0}{14}$	
1 : 4 : 8	= 0.277		= 1.11		= 2.21	
	$\frac{0.277}{0.277}$		$\frac{1.11}{0.277}$		$\frac{2.21}{0.277}$	
	= 1		= 4		= 8	

$x = 4$

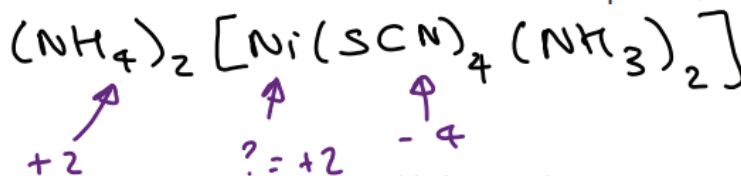
$2 + x + y = 8$

x = 4

y = 2

[3]

- (ii) Determine the oxidation number of nickel in compound J.



oxidation number: +2

[1]

- (c) Sodium sulfite(IV), Na_2SO_3 , is used as a preservative in some foods. Food safety legislation allows a maximum of **850 mg** Na_2SO_3 **per kg** of burger meat.

A chemist determines the amount of Na_2SO_3 in a sample of burger meat using a manganate(VII) titration.

Step 1 The Na_2SO_3 from **525 g** of burger meat is extracted to form a solution containing $\text{SO}_3^{2-}(\text{aq})$ ions.

Step 2 The solution from **step 1** is made up to **250.0 cm³** in a volumetric flask with water. **25.0 cm³** of this diluted solution is pipetted into a conical flask.

Step 3 The pipetted solution from **step 2** is acidified with dilute sulfuric acid and then titrated with **0.0100 mol dm⁻³** potassium manganate(VII), KMnO_4 .



12.60 cm³ of $\text{KMnO}_4(\text{aq})$ is required to reach the endpoint.

Analyse the results to determine whether the burger meat complies with food safety legislation.



$$0.01 \times 12.6 \times 10^{-3} = 1.26 \times 10^{-4} \text{ mol}$$

$$\frac{1.26 \times 10^{-4}}{2} \times 5 = 3.15 \times 10^{-4} \text{ mol } \text{SO}_3^{2-} \text{ in } 25 \text{ cm}^3$$

$$3.15 \times 10^{-4} \times 10 = 3.15 \times 10^{-3} \text{ mol } \text{SO}_3^{2-} \text{ in } 250 \text{ cm}^3$$

$$3.15 \times 10^{-3} \times ((23 \times 2) + 32.1 + (16 \times 3)) = 0.397 \text{ g of } \text{Na}_2\text{SO}_3 \text{ in } 525 \text{ g meat}$$



$$0.397 \times \frac{1000}{525} = 0.7566 \text{ g} = 756.6 \text{ mg}$$

$$756.6 \text{ mg} < 850 \text{ mg}$$

less than maximum permitted level

22. Transition metal ions can bond to ligands to form complex ions with different shapes.

Explain what is meant by the terms **ligand**, **coordination number** and **ligand substitution**, using suitable examples of **complex ions with different shapes**, limited to **monodentate ligands**.

Your answer should include diagrams and equations where appropriate.

ligand: Donates a lone pair to a metal ion forming dative covalent (coordinate) bond with metal ion

each ligand [6] forms one coordinate bond

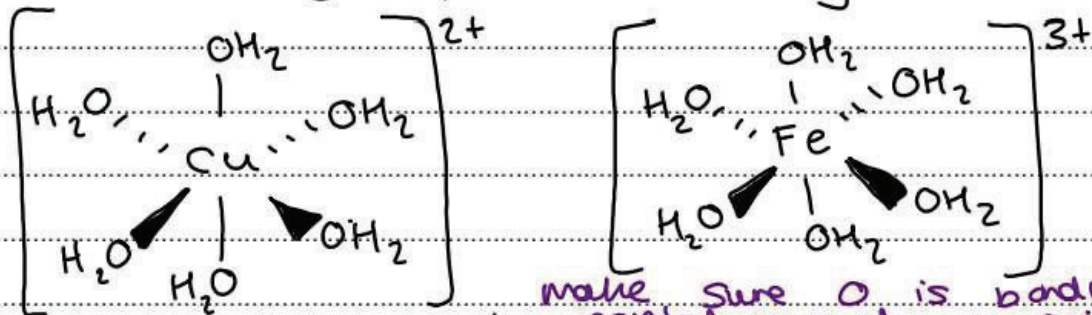
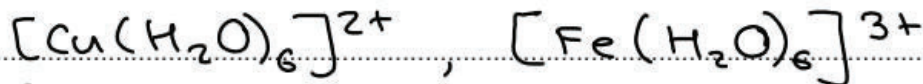
Coordination number: number of coordinate bonds to metal ion

ligand substitution: one ligand replacing another

Cl⁻ is such a big ligand you can't fit more than 4 around central 2⁺ metal ion



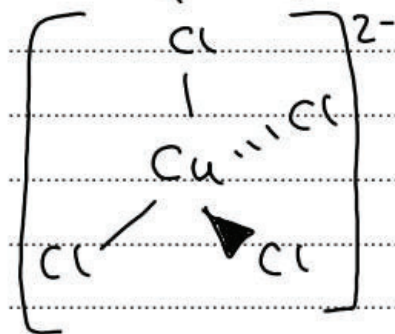
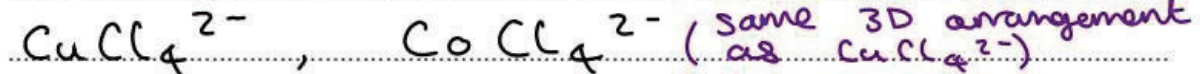
Coordination number: 6 octahedral



Additional answer space if required

to make sure O is bonding central metal as O is donating its lone pair of electrons not H

Coordination number: 4 tetrahedral



square planar: $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$



N bonding to Pt not H

cis-platin

trans-platin