12 Aqueous ammonia is added in **excess** to an aqueous solution of Cu^{2+}.

What is the equation for the overall reaction?

☒ **A** $[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$

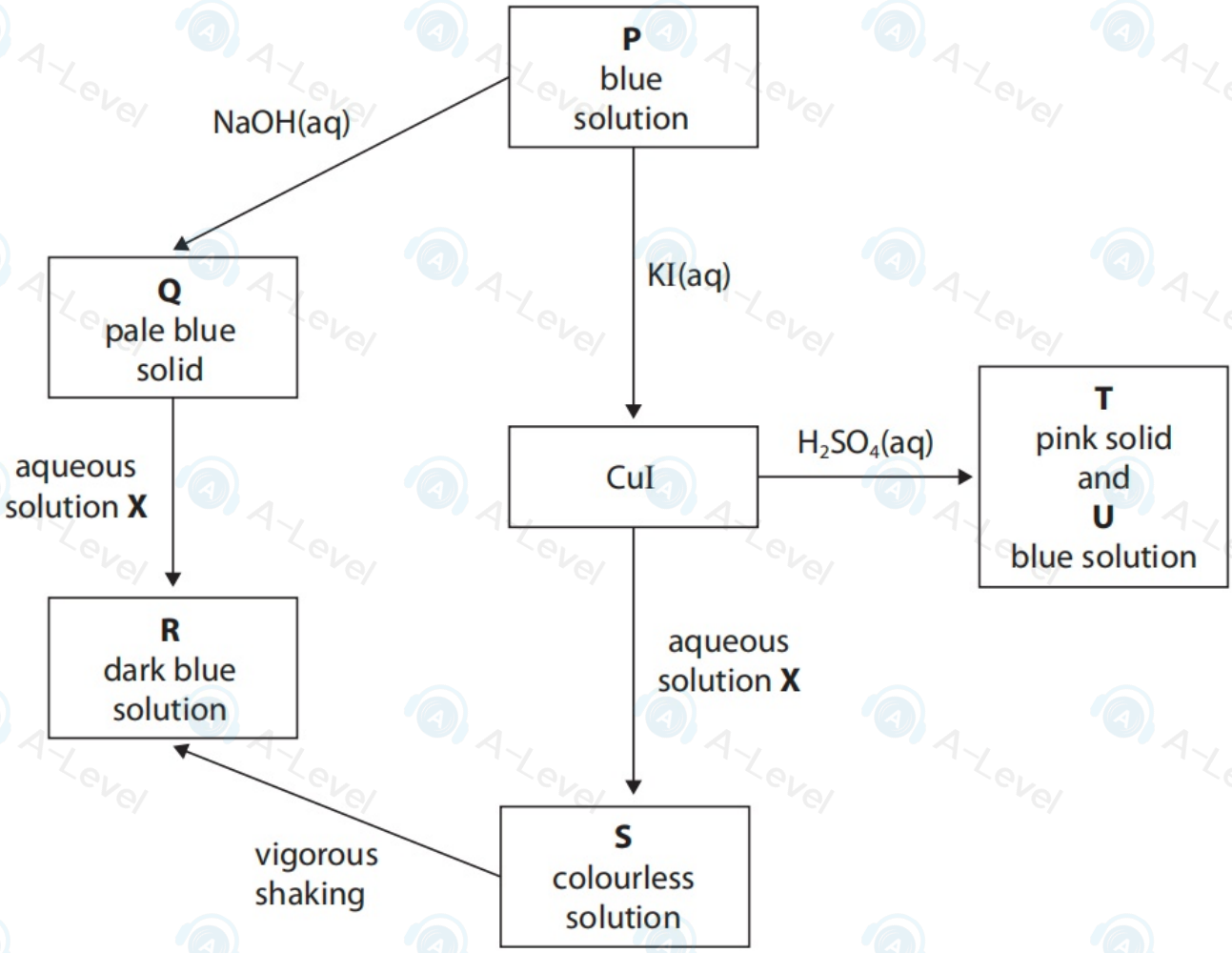
☒ **B** $[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Cu(NH_3)_2(H_2O)_4]^{2+} + 2H_2O$

☒ **C** $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$

☒ **D** $[Cu(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Cu(NH_3)_6]^{2+} + 6H_2O$

5 This question concerns the chemistry of copper.

In the reaction sequence, the substances P, Q, R, S, T and U contain copper in various oxidation states.



(a) What are the electronic structures of the three copper species?

(1)

		Cu	Cu^+	Cu^{2+}
☒	**A**	[Ar] $3d^9\ 4s^2$	[Ar] $3d^9\ 4s^1$	[Ar] $3d^9$
☒	**B**	[Ar] $3d^9\ 4s^2$	[Ar] $3d^8\ 4s^2$	[Ar] $3d^7\ 4s^2$
☒	**C**	[Ar] $3d^{10}\ 4s^1$	[Ar] $3d^9\ 4s^1$	[Ar] $3d^8\ 4s^1$
☒	**D**	[Ar] $3d^{10}\ 4s^1$	[Ar] $3d^{10}$	[Ar] $3d^9$

(b) Which rows show the substances with their correct oxidation states?

(1)

		Cu(0)	Cu(I)	Cu(II)
☒	**A**	S	U	P
☒	**B**	S	R	Q
☒	**C**	T	S	P

5: What is the colour of an aqueous solution of V^{2+} ions?

- ☒ **A** blue
- ☒ **B** green
- ☒ **C** purple
- ☒ **D** yellow

(Total for Question 5 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit

5 Chromium(III) hydroxide, $Cr(OH)_3(H_2O)_3$, is amphoteric.

This means that chromium(III) hydroxide dissolves in

- ☒ **A** water
- ☒ **B** strong acid only
- ☒ **C** strong alkali only
- ☒ **D** strong acid and strong alkali

13 Which equation shows the formation of a precipitate?

- ☒ **A** $[Zn(OH)_4]^{2-} + 2H_3O^+ \rightarrow [Zn(H_2O)_4(OH)_2]$
- ☒ **B** $[Zn(H_2O)_6]^{2+} + 4OH^- \rightarrow [Zn(OH)_4]^{2-} + 6H_2O$
- ☒ **C** $[Cr(H_2O)_3(OH)_3] + 3H_3O^+ \rightarrow [Cr(H_2O)_6]^{3+} + 3H_2O$
- ☒ **D** $[Cr(H_2O)_3(OH)_3] + 3OH^- \rightarrow [Cr(OH)_6]^{3-} + 3H_2O$

4 Aqueous sodium hydroxide and aqueous ammonia are added, until they are in excess, to separate portions of a pale green aqueous solution **E**.

Test	Observations
Aqueous sodium hydroxide is added to **E**	Green precipitate forms No further change in excess
Aqueous ammonia is added to **E**	Green precipitate forms Green precipitate dissolves in excess to form a pale blue solution

Which ion is present in **E**?

- ☒ **A** Cu^{2+}
- ☒ **B** Fe^{2+}
- ☒ **C** Ni^{2+}
- ☒ **D** V^{2+}

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7 What are the shapes of the complexes $[CuCl_4]^{2-}$ and $Pt(NH_3)_2Cl_2$?

	$[CuCl_4]^{2-}$	$Pt(NH_3)_2Cl_2$
☒ **A**	square planar	square planar
☒ **B**	square planar	tetrahedral
☒ **C**	tetrahedral	square planar
☒ **D**	tetrahedral	tetrahedral

(Total for Question 7 = 1 mark)

3 Which complex ion is colourless?

☒ **A** $[Al(H_2O)_6]^{3+}$

☒ **B** $[Cu(H_2O)_6]^{2+}$

☒ **C** $[Fe(H_2O)_6]^{3+}$

☒ **D** $[Ni(H_2O)_6]^{2+}$

3 The formula of a chromium compound is $[Cr(H_2O)_4Cl_2]^+Cl^-$.
The molar mass of the **compound** is 230.5 g mol^{-1}.

What is the percentage by mass of chlorine in the **complex ion**?

☒ **A** 18.2%

☒ **B** 30.8%

☒ **C** 36.4%

☒ **D** 46.2%

(Total for Question 3 = 1 mark)

2 An oxide of vanadium is the catalyst in one step of the contact process for the manufacture of sulfuric acid.

Which reaction involves the vanadium oxide catalyst and how does the oxidation number of vanadium change during the process?

	Reaction	Oxidation number changes for vanadium
☒ **A**	$S + O_2 \rightarrow SO_2$	$+5 \rightarrow +4 \rightarrow +5$
☒ **B**	$SO_2 \rightarrow SO_3$	$+4 \rightarrow +5 \rightarrow +4$
☒ **C**	$SO_2 \rightarrow SO_3$	$+5 \rightarrow +4 \rightarrow +5$
☒ **D**	$SO_3 + H_2O \rightarrow H_2SO_4$	$+4 \rightarrow +5 \rightarrow +4$

5 A **small** amount of aqueous ammonia is added to an aqueous solution containing zinc ions. A white precipitate forms.

Which is the equation for this reaction?

☒ **A** $[Zn(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Zn(OH)_2(H_2O)_4]^{2+} + 2NH_4^+$

☒ **B** $[Zn(H_2O)_6]^{2+} + 2NH_3 \rightarrow Zn(OH)_2(H_2O)_4 + 2NH_4^+$

☒ **C** $[Zn(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Zn(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$

☒ **D** $[Zn(H_2O)_6]^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4(H_2O)_2 + 2H_2O + 2H_3O^+$

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4 What is the colour of the VO^{2+} ion in aqueous solution?

☒ **A** blue

☒ **B** green

☒ **C** violet

☒ **D** yellow

(Total for Question 4 = 1 mark)

6 Which electronic configuration is correct?

- ☒ **A** Ti^{2+} $[Ar]4s^2$
- ☒ **B** Cr $[Ar]3d^4 4s^2$
- ☒ **C** Fe^{3+} $[Ar]3d^3 4s^2$
- ☒ **D** Cu $[Ar]3d^{10} 4s^1$

2 Which ion shows the typical property of transition metals by forming coloured complexes?

- ☒ **A** Cu^+
- ☒ **B** Ni^{2+}
- ☒ **C** Sc^{3+}
- ☒ **D** Zn^{2+}

(Total for Question 2 = 1 mark)

1 What colour is vanadium(III) in aqueous solution?

- ☒ **A** blue
- ☒ **B** green
- ☒ **C** purple
- ☒ **D** yellow

17 Transition metal compounds can show a number of different types of isomerism. Hydration isomerism is where different numbers of water molecules act as ligands. The name chromium(III) chloride is given to several chemical compounds with the formula $CrCl_3 \cdot xH_2O$, including a number of hydration isomers.

(a) Anhydrous chromium(III) chloride, $CrCl_3$, is a violet solid which can react with water to produce three isomers.

$[Cr(H_2O)_6]^{3+}3Cl^-$ is violet.

$[Cr(H_2O)_5Cl]^{2+}2Cl^- \cdot H_2O$ is pale green.

$[Cr(H_2O)_4Cl_2]^{+}Cl^- \cdot 2H_2O$ is dark green.

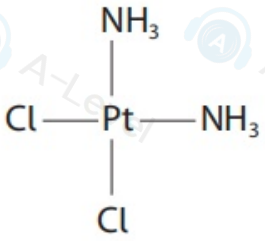
(i) Explain why the three isomers have different colours.

(3)

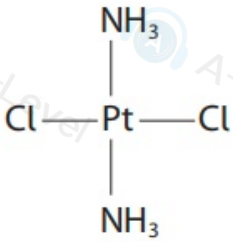
(ii) You are provided with three equimolar solutions of the three isomers. Suggest how you would quantitatively determine the relative numbers of free chloride ions in the three isomers using the standard test for a chloride ion.

(5)

(b) Complexes can exhibit both cis-trans and optical isomerism. The cis- and trans-isomers of diamminedichloroplatinum(II) are commonly known as *cis*-platin and *trans*-platin.

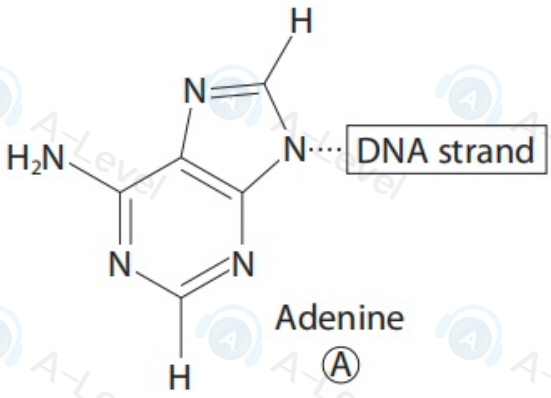


cis-platin

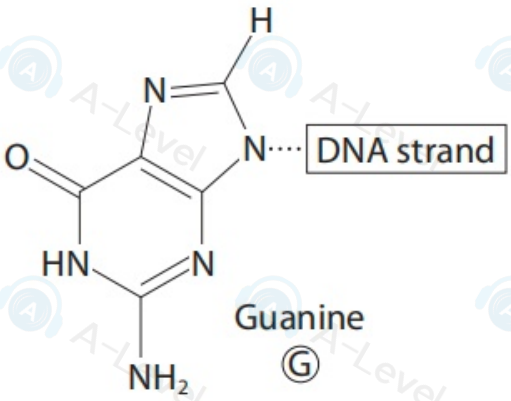


trans-platin

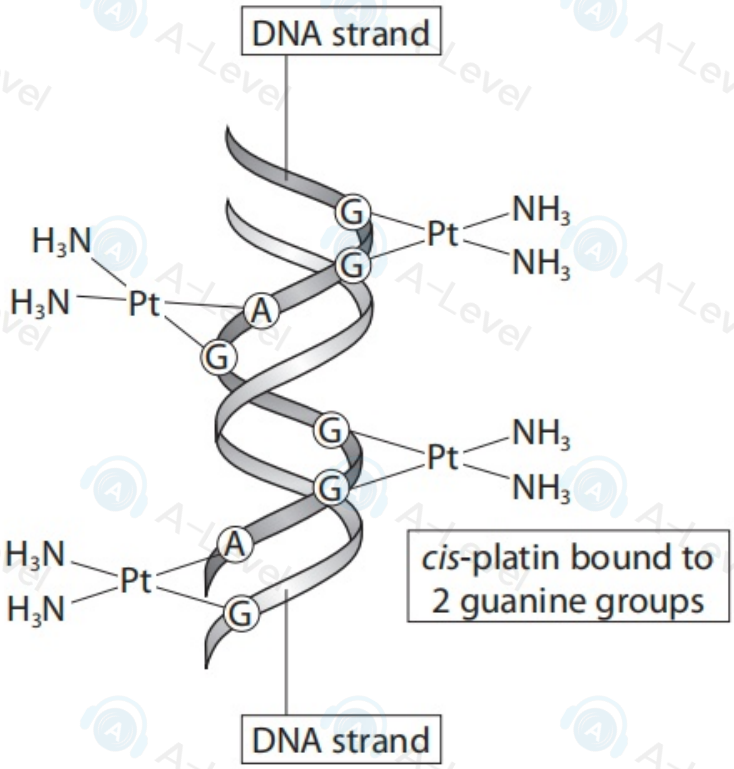
In chemotherapy medication, *cis*-platin is used to treat a number of cancers including testicular cancer and breast cancer, while *trans*-platin has no beneficial effect against cancer. The cis-isomer is effective because it binds with the deoxyribonucleic acid (DNA) molecules in a cancerous cell through adenine and guanine groups. This interferes with the replication of the cell and results in its destruction.



Adenine
Ⓐ



Guanine
Ⓖ



This works in three steps.

Step **1** Slow substitution of one chloride ligand by a water.

Step **2** This water ligand is easily displaced by guanine or adenine in the DNA strand.

Step **3** Finally the second chloride ligand is displaced by a different guanine or adenine from a different part of the strand.

(c) Reinecke's salt has the formula $NH_4[Cr(SCN)_x(NH_3)_y] \cdot zH_2O$. The anion exists as a trans-isomer.
It contains 14.67% chromium, 36.23% sulfur, 4.51% oxygen and 27.65% nitrogen by mass.

(i) Calculate the values x, y and z in Reinecke's salt.
You **must** show your working.

(3)

(ii) Draw a diagram of the **anion** of Reinecke's salt showing its three-dimensional shape.

(2)

(d) (i) Explain why the tetrahedral complex $[Co(NH_3)ClBrI]$ exists as two optical isomers.

(2)

(ii) Complete the diagram showing the **two** optical isomers of the tetrahedral complex.

(1)

18 This question is about coloured transition metal complex ions.

(a) The $[Fe(H_2O)_6]^{2+}$ complex ion is green and the $[Fe(H_2O)_6]^{3+}$ complex ion is yellow.

(i) Explain why the $[Fe(H_2O)_6]^{2+}$ complex ion is coloured.

(3)

(ii) Explain why the two iron complex ions are different colours.

(2)

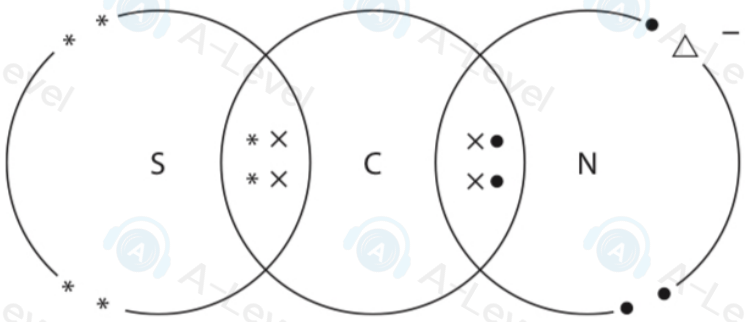
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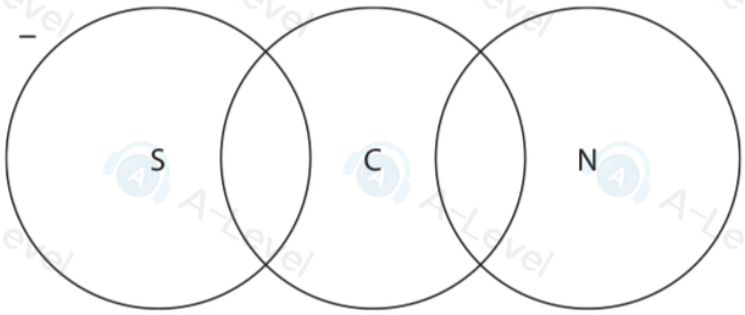
(b) The thiocyanate ion, SCN^-, forms a 'blood-red' coloured complex ion with iron(III) ions.

(i) The dot-and-cross diagram for the thiocyanate ion can be drawn in more than one way. For example, the negative charge can be on the nitrogen atom as shown.



Complete the alternative dot-and-cross diagram of the thiocyanate ion where the negative charge is on the sulfur atom.
Use (•) for the nitrogen electrons, (×) for the carbon electrons, (*) for the sulfur electrons and (△) for the extra electron.

(2)



(ii) 12.8 cm^3 of 0.05 mol dm^{-3} iron(III) chloride solution reacted with 8.0 cm^3 of 0.08 mol dm^{-3} ammonium thiocyanate to form a complex ion.
Deduce the formula of the **octahedral** complex ion that iron(III) ions form with thiocyanate ions in aqueous solution.
You **must** show your working.

(3)

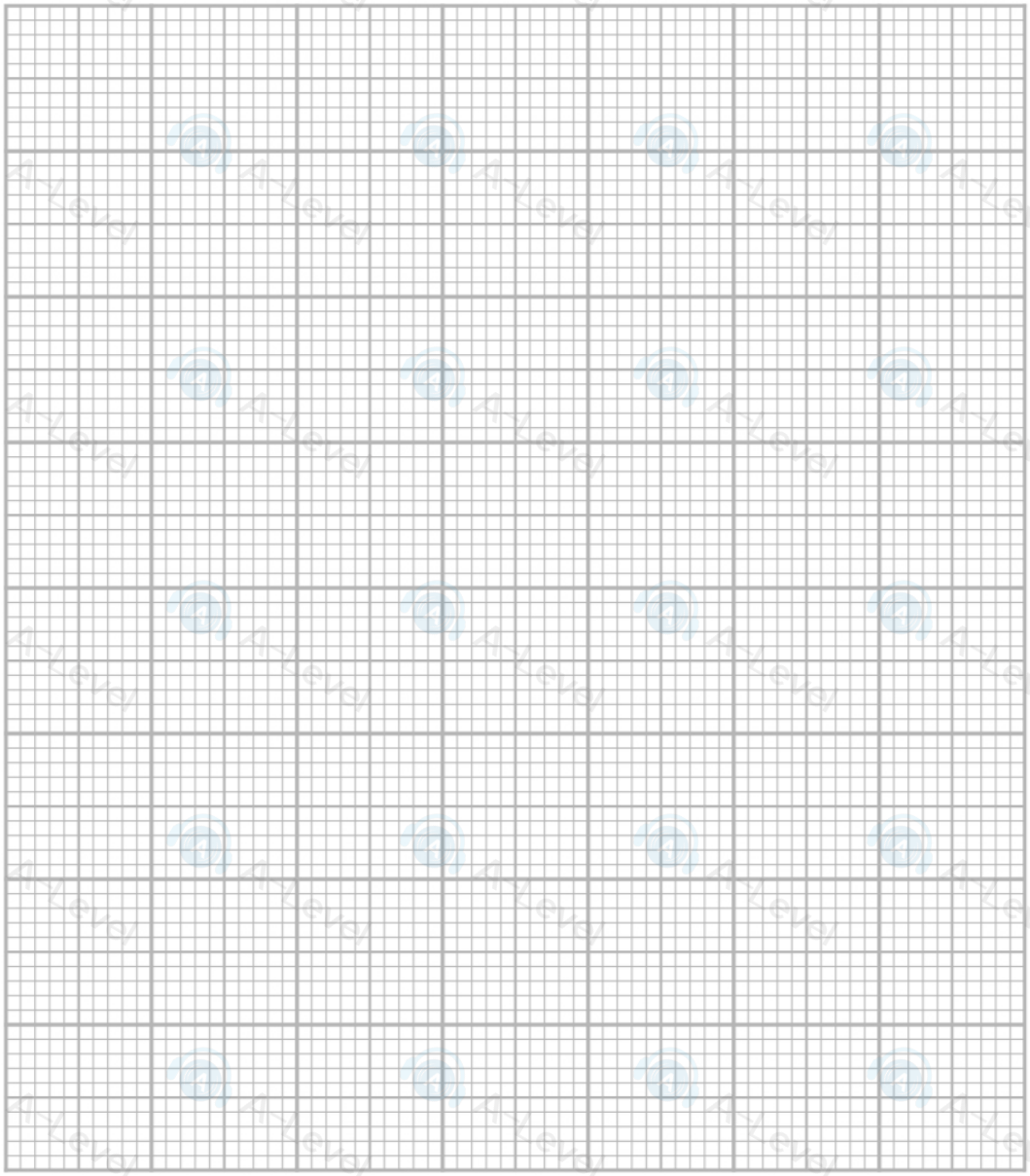
Formula

(c) Colorimetry was used to determine the concentration of a solution of copper(II) sulfate.
Six solutions of copper(II) sulfate of known concentration were prepared and their absorbance at a wavelength of 635 nm measured. The results are shown.

Concentration of $CuSO_4(aq)$ / mol dm^{-3}	0.00	0.10	0.20	0.30	0.40	0.50
Absorbance at 635 nm	0.00	0.28	0.55	0.83	1.10	1.38

(i) Plot a graph of absorbance against concentration using the data in the table.

(3)



(ii) 50.0 cm^3 of a solution of copper(II) sulfate of unknown concentration was pipetted into a 250.0 cm^3 volumetric flask and the volume made up to the mark with deionised water.
The absorbance at a wavelength of 635 nm for this diluted copper(II) sulfate solution was 0.72.

Determine the concentration of the **original** copper(II) sulfate solution.
You **must** show your working on the graph.

(2)

(iii) Give **one** possible reason why any concentrations of copper(II) sulfate determined from the graph of values over 0.50 mol dm^{-3} are uncertain.

(1)

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(d) The complex ion formed from cobalt(III) ions and ethane-1,2-diamine is a yellow-orange colour.
The equation for the formation of this complex ion is shown.

$$[Co(H_2O)_6]^{3+} + 3H_2NCH_2CH_2NH_2 \rightarrow [Co(H_2NCH_2CH_2NH_2)_3]^{3+} + 6H_2O$$

(i) Give a reason, by referring to the equation, why the formation of the diamine complex from the aqueous complex ion is thermodynamically favoured.

(1)

(ii) Explain, by reference to the structure of ethane-1,2-diamine, why it is a bidentate ligand.

(2)

(iii) Explain how the H—N—H bond angles would be expected to change in ethane-1,2-diamine when the complex ion is formed.

(3)

(Total for Question 18 = 22 marks)

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16 Iron is generally prescribed when a person is suffering from anaemia. Many people find it easier to take medicine in liquid form rather than solid tablets.

An iron solution, advertised for this purpose, contains iron as Fe^{2+}.
An adult is advised to take 90.0 mg of iron daily.

A 25.0 cm^3 sample of the solution was made up to 100.0 cm^3 using sulfuric acid and deionised water.
25.0 cm^3 samples of the diluted iron(II) solution were titrated with a 0.0125 mol dm^{-3} potassium manganate(VII) solution.
The mean titre was 16.20 cm^3.

The reaction is shown.

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Calculate the volume of iron solution required to obtain a 90.0 mg dose of iron.
Give your answer to an appropriate number of significant figures.

Volume required by an adult to obtain a 90.0 mg dose ..... cm^3

(Total for Question 16 = 6 marks)

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