1 Cobalt is a transition element. Solid compounds of cobalt are often complexes and in solution, complex ions are formed.

(a) In its complexes, the common oxidation numbers of cobalt are +2 and +3.

Complete the electron configurations of cobalt as the element and in the +3 oxidation state:

cobalt as the element: $1s^2\ 2s^2\ 2p^6$ ....

cobalt in the +3 oxidation state: $1s^2\ 2s^2\ 2p^6$ .... **[2]**

(b) State **one** property of cobalt(II) and cobalt(III), other than their ability to form complex ions, which is typical of ions of a transition element.

....

.... **[1]**

(c) Complex ions contain ligands.

State the meaning of the term *ligand*.

....

....

.... **[1]**

(d) Aqueous cobalt(II) sulfate, $CoSO_4(aq)$, takes part in the following reactions.

For each reaction, state the formula of the transition element species formed and the type of reaction taking place.

(i) Aqueous cobalt(II) sulfate, $CoSO_4(aq)$, reacts with aqueous sodium hydroxide.

transition element species formed: ....

type of reaction: .... **[2]**

(ii) Aqueous cobalt(II) sulfate, $CoSO_4(aq)$, reacts with concentrated hydrochloric acid.

transition element species formed: ....

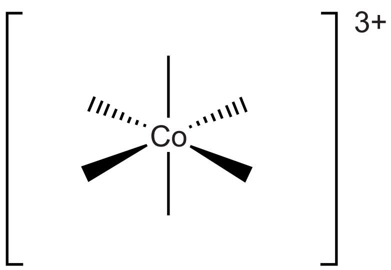
type of reaction: .... **[2]**

(e) Cobalt(III) chloride, $CoCl_3$, reacts with ammonia to form a range of complexes. These complexes contain different amounts of ammonia. Information about these complexes is summarised below.

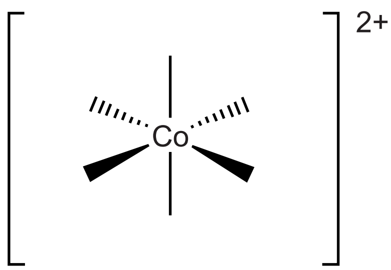
The complex ions **C** and **D** are stereoisomers.

complex	formula	formula of complex
A	$CoCl_3(NH_3)_6$	$[Co(NH_3)_6]^{3+}\ 3Cl^-$
B	$CoCl_3(NH_3)_5$	$[Co(NH_3)_5Cl]^{2+}\ 2Cl^-$
C	$CoCl_3(NH_3)_4$	$[Co(NH_3)_4Cl_2]^+\ Cl^-$
D	$CoCl_3(NH_3)_4$	$[Co(NH_3)_4Cl_2]^+\ Cl^-$

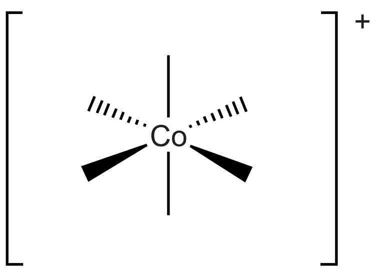
(i) Complete the diagrams below to suggest possible structures for the complex ion in complexes **A** to **D**.



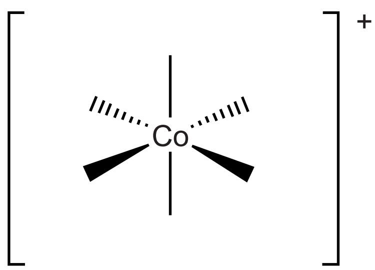
complex ion in A



complex ion in B



complex ion in C



complex ion in D

[4]

(ii) Chemists provided evidence for the formulae of these complexes from their reactions with aqueous silver nitrate. Aqueous silver nitrate reacts with aqueous halide ions in a precipitation reaction.

An excess of silver nitrate solution was reacted with 0.0100 mol of one of the complexes **A** to **D**. 2.868 g of a precipitate was formed.

Determine which complex was reacted.

In your answer you should explain how the result of the experiment would allow the formula of the complex to be identified.

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.... **[3]**

[Total: 15]

2 Iron and platinum are transition elements. They both form ions that combine with ligands to form complex ions. Some of these complexes are important in biological systems.

(a) Complete the electron structures of:

an atom of Fe: $1s^2 2s^2 2p^6$ ....

an ion of Fe^{2+}: $1s^2 2s^2 2p^6$ .... **[2]**

(b) State **one** property of Fe^{2+}, other than the ability to form complex ions, which is typical of an ion of a transition element.

....

.... **[1]**

(c) Aqueous iron(II) sulfate takes part in redox reactions.

Using oxidation numbers, show that both reduction and oxidation have taken place in the redox reaction of aqueous iron(II) sulfate shown below.

$$6FeSO_4 + 7H_2SO_4 + Na_2Cr_2O_7 \rightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O$$

....

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....

....

.... **[2]**

(d) Hexaaquairon(II) ions, $[Fe(H_2O)_6]^{2+}$, take part in a ligand substitution reaction with ammonia.

$$[Fe(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Fe(NH_3)_6]^{2+}(aq) + 6H_2O(l)$$

Write an expression for the stability constant, K_{stab}, for this equilibrium.

[2]

(e) Haemoglobin is a complex of iron(II).

(i) Explain how ligand substitutions allow haemoglobin to transport oxygen in the blood.

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.... **[2]**

(ii) In the presence of carbon monoxide, less oxygen is transported in the blood.

In terms of stability constants, suggest why.

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.... **[2]**

(f) Platin, $Pt(NH_3)_2Cl_2$, is a complex of platinum(II) that has two stereoisomers. One of these stereoisomers is used in medicine.

(i) Platin is a neutral complex.

Explain why platin is neutral.

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.... **[1]**

(ii) Draw diagrams of the two stereoisomers of platin and describe its bonding.

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....

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.... **[3]**

(iii) Describe the action of platin in the treatment of cancer patients.

....

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.... **[1]**

(g) The use of platin in medicine can cause unpleasant side effects for patients.

In the search for alternatives, chemists often start with the current drug and modify its properties by chemically changing some of the groups.

A recent discovery is a drug called carboplatin. The structure of carboplatin is similar to platin except that a single 1,1-cyclobutanedicarboxylate ion replaces the two chloride ligands in the structure of platin.

Draw the structures of,

- the 1,1-cyclobutanedicarboxylate ion
- carboplatin

1,1-cyclobutanedicarboxylate ion

carboplatin

[2]

[Total: 18]

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

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

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

$$O_2(aq) + 4Mn^{2+}(aq) + 8OH^-(aq) + 2H_2O(l) \rightarrow 4Mn(OH)_3(s)$$

- The $Mn(OH)_3$ precipitate is then reacted with an excess of aqueous potassium iodide, which is oxidised to iodine, I_2.

$$2Mn(OH)_3(s) + 2I^-(aq) \rightarrow I_2(aq) + 2Mn(OH)_2(s) + 2OH^-(aq)$$

- The iodine formed is then determined by titration with aqueous sodium thiosulfate, $Na_2S_2O_3$(aq).

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

A 25.0 cm^3 sample of river water was analysed using the procedure above.

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

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

DOC = ... mg dm^{-3} **[4]**

(ii) Comment on whether there is enough dissolved oxygen in the river water for fish to survive.

....

....

.... **[1]**

(b) The presence of nitrate(III) ions, NO_2^-, interferes with this method because NO_2^- ions can also oxidise iodide ions to iodine.

During the reaction, a colourless gas is produced with a molar mass of $30\,g\,mol^{-1}$.

(i) Predict the formula of the colourless gas.

.... **[1]**

(ii) Write an equation for the oxidation of aqueous iodide ions by aqueous nitrate(III) ions. Hydroxide ions are produced in this reaction.

.... **[2]**

[Total: 8]

4 Potassium manganate(VII) can be prepared in the laboratory by a two-step synthesis starting from manganese(IV) oxide.

Step 1

In this step, manganese(IV) oxide is heated strongly with potassium hydroxide and potassium chlorate(V), a powerful oxidising agent.

Manganese(IV) oxide, MnO_2, is oxidised to manganate(VI) ions.

Step 2

Potassium manganate(VI) is separated from the alkaline mixture from **step 1** as a green solid.

In this step, potassium manganate(VI) is heated in water. Manganate(VI) ions disproportionate forming manganate(VII) ions and a precipitate of manganese(IV) oxide.

(a) In **step 1**, a redox reaction takes place.

Add the correct number of electrons to the correct sides of the incomplete oxidation and reduction half-equations shown below.

$$MnO_2 + 4OH^- \rightarrow MnO_4^{2-} + 2H_2O$$

$$3H_2O + ClO_3^- \rightarrow 6OH^- + Cl^-$$

[2]

(b) In **step 2**, an equilibrium is set up.

$$3MnO_4^{2-}(aq) + 2H_2O(l) \rightleftharpoons 2MnO_4^-(aq) + MnO_2(s) + 4OH^-(aq)$$

The equilibrium position can be shifted by bubbling carbon dioxide gas through the mixture.

Suggest, with the aid of an equation, how the equilibrium position shifts.

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.... **[3]**

(c) Aqueous potassium manganate(VII), $KMnO_4$, in acidic conditions can be used in analysis.

A student analyses a sample of sodium sulfite, Na_2SO_3, using the following method.

- The student dissolves 0.720 g of impure sodium sulfite in water.
- The solution is made up to 100.0 cm^3.
- The student titrates 25.0 cm^3 of this solution with 0.0200 mol dm^{-3} $KMnO_4$ under acidic conditions. The volume of $KMnO_4$(aq) required to reach the end-point is 26.2 cm^3.

The equation for the reaction is shown below.

$$2MnO_4^- + 6H^+ + 5SO_3^{2-} \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

Determine the percentage purity of the sample of sodium sulfite.

percentage purity = ... % **[5]**

[Total: 10]

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

Method

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

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

Stage 3. The solution is diluted and made up to 250.0 cm^3 in a volumetric flask.

Stage 4. A 25.0 cm^3 sample of this solution is pipetted into a conical flask.

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

Stage 6. Stages 4 and **5** are repeated to obtain an average titre of 26.5 cm^3.

You are provided with the following electrode potentials.

You may need to use this information throughout this question.

$$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq) \qquad E^\ominus = +0.15\,V$$

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^\ominus = +0.77\,V$$

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^\ominus = +1.33\,V$$

$$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq) \qquad E^\ominus = +1.36\,V$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \qquad E^\ominus = +1.51\,V$$

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

.... **[1]**

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

Stage 2 ....

Stage 5 .... **[2]**

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

percentage iron = ... % **[5]**

(d) Aqueous potassium manganate(VII), $KMnO_4$(aq), is **not** suitable for titrating the solution in this method. Aqueous potassium dichromate(VI), $K_2Cr_2O_7$(aq), is used instead.

Suggest and explain why potassium dichromate(VI), $K_2Cr_2O_7$, is suitable for this titration whereas potassium manganate(VII), $KMnO_4$, is not suitable.

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....

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.... **[2]**

[Total: 10]