28.2 General characteristic, chemical properties of Transition Elements

Learning outcomes

Candidates should be able to:

1. describe and explain the reactions of transition elements with ligands to form complexes, including the complexes of copper(II) and cobalt(II) ions with water and ammonia molecules and hydroxide and chloride ions
2. define the term ligand as a species that contains a lone pair of electrons that forms a dative covalent bond to a central metal atom / ion
3. understand and use the terms:

(a) monodentate ligand including as examples H_2O, NH_3, Cl^- and CN^-

(b) bidentate ligand including as examples 1,2-diaminoethane, *en*, $H_2NCH_2CH_2NH_2$ and the ethanedioate ion, $C_2O_4^{2-}$

(c) polydentate ligand including as an example $EDTA^{4-}$

4. define the term complex as a molecule or ion formed by a central metal atom / ion surrounded by one or more ligands

5. describe the geometry (shape and bond angles) of transition element complexes which are linear, square planar, tetrahedral or octahedral

6. (a) state what is meant by coordination number

(b) predict the formula and charge of a complex ion, given the metal ion, its charge or oxidation state, the ligand and its coordination number or geometry

7. explain qualitatively that ligand exchange can occur, including the complexes of copper(II) ions and cobalt(II) ions with water and ammonia molecules and hydroxide and chloride ions

8. predict, using $E^\ominus$ values, the feasibility of redox reactions involving transition elements and their ions

9. describe the reactions of, and perform calculations involving:

(a) $MnO_4^- / C_2O_4^{2-}$ in acid solution given suitable data

(b) MnO_4^- / Fe^{2+} in acid solution given suitable data

(c) Cu^{2+} / I^- given suitable data

10. perform calculations involving other redox systems given suitable data

Initial assessment

1. Draw a dot-and-cross diagram to show the bonding in an ammonium ion, NH_4^+. Only include the outer shell electrons.

Ligands

Ligand is a species that contains a lone pair of electrons that forms a dative covalent bond to a central metal atom/ion

Ligands are bases, and also nucleophiles

2. **(i)** Define the term *ligand*.

....

.... [1]

3. Methylamine, CH_3NH_2, is a monodentate ligand.
State what is meant by the term *monodentate* in this context.

....

.... [1]

4. Methylamine, CH_3NH_2, is another primary amine. CH_3NH_2 can act as a monodentate ligand.
Define monodentate ligand.

....

....

.... [2]

5. Phosphine, **:**PH_3, and carbon monoxide, **:**CO, are monodentate ligands found in some transition element complexes.
Define monodentate ligand. [1]

6. Explain what is meant by a bidentate ligand.

....

....

.... [2]

7. Bipyridine, bipy, is a bidentate ligand.

bipy

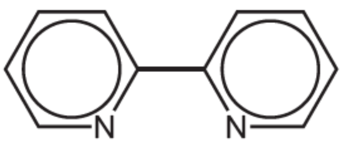


Fig. 4.1

Explain what is meant by bidentate ligand. [2]

8. Cobalt forms the complex ion $[Co(NH_3)_2(en)_2]^{2+}$. The abbreviation en is used for the bidentate ligand 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$. The complex ion shows both geometrical and optical isomerism.
Define the term *bidentate ligand*.

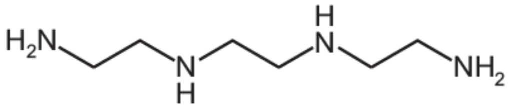
....

.... [2]

9. 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, en, can act as a bidentate ligand.
Explain what is meant by a bidentate ligand. [2]

10. Compound X, $C_6H_{18}N_4$, is a tetradentate ligand.

X



Suggest why one molecule of X can form four dative bonds.

....

....

.... [1]

11. $EDTA^{4-}$ is a polydentate ligand.
(i) Explain what is meant by a polydentate ligand.

…………………………..

…………………………..

…………………………... [2]

(ii) Group 2 metal ions can form complexes similar to those of transition elements.
A solution of $EDTA^{4-}$ is added to water containing $[Ca(H_2O)_6]^{2+}$ to form a new complex, $[CaEDTA]^{2-}$, as shown.
equilibrium 1 $[Ca(H_2O)_6]^{2+} + EDTA^{4-} \rightleftharpoons [CaEDTA]^{2-} + 6H_2O$
Circle on the structure of $EDTA^{4-}$ in Fig. 1.2 the **six** atoms that form bonds with the metal ion. [1]

EDTA^{4-}

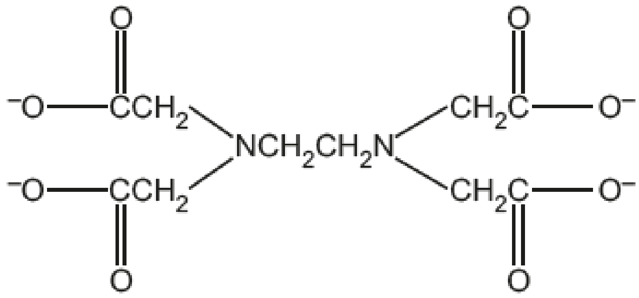
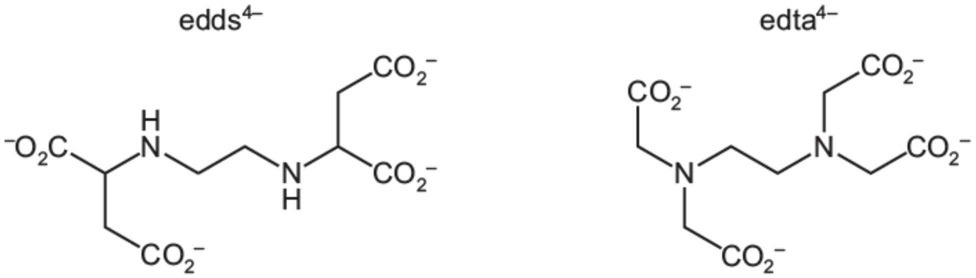


Fig. 1.2

12. $Edds^{4-}$ and $edta^{4-}$ are polydentate ligands that form octahedral complexes with $Fe^{3+}(aq)$.



On the diagram of $edds^{4-}$, circle each atom that forms a bond to the Fe^{3+} ion in $[Fe(edds)]^{-}$. [1]

13. Five ligands are listed in Table 6.1.
Table 6.1

ligand	type of ligand
NH_3	
$EDTA^{4-}$	
CN^-	
$H_2NCH_2CH_2NHCH_2CH_2NH_2$	tridentate
$C_2O_4^{2-}$	

(i) Complete Table 6.1 using the words monodentate, bidentate, and polydentate only.
Each of these three words may be used once, more than once, or not at all. [2]

(ii) The molecule $H_2NCH_2CH_2NHCH_2CH_2NH_2$ is a tridentate ligand.
Suggest the meaning of tridentate ligand.

....

.... [1]

(iii) Suggest how $H_2NCH_2CH_2NHCH_2CH_2NH_2$ acts as a tridentate ligand.

....

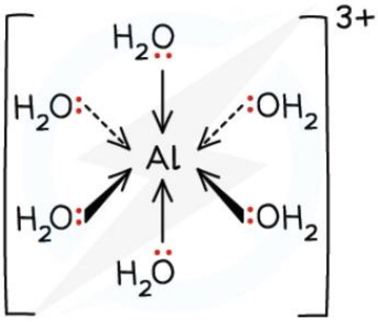
.... [1]

Complex

<u>Complex ion</u> is a species which consists of a central metal ion with a specific number of ions or molecules surrounding it, bound by coordinate bonds.

The molecules or ions surrounding the metal ion are called **<u>ligands</u>**, which always contain at least one lone pair of electrons.

e.g., $[Fe(H_2O)_6]^{2+}$



Coordination number = ?

Coordination number = the number of coordinate bonds formed by ligands with a transition element ion in a complex.

14. Fe^{2+} and Fe^{3+} ions are able to form a variety of complexes with different species.
Define complex.

....

....

.... [1]

15. Aqueous solutions of cobalt(II) salts contain the complex ion $[Co(H_2O)_6]^{2+}$.
Define complex ion. [1]

16. Define transition element complex.

....

.... [1]

17. The mineral ore cryolite, Na_3AlF_6, contains a single anion which is a complex ion.
Complete Table 1.1 to suggest the formula of the complex ion and to identify the ligand present in Na_3AlF_6. [1]
Table 1.1

complex ion in Na_3AlF_6	
ligand in Na_3AlF_6	

18. An aqueous solution of $Fe(NO_3)_3$ contains the complex $[Fe(H_2O)_6]^{3+}$.
When solutions of KSCN(aq) and $[Fe(H_2O)_6]^{3+}$(aq) are mixed, a colour change is observed.
The red complex $[Fe(H_2O)_5SCN]^{2+}$ forms.
State the coordination number of Fe in $[Fe(H_2O)_6]^{3+}$.

.... [1]

19. The calcium ions in $[Ca(H_2O)_6]^{2+}$ and $[CaEDTA]^{2-}$ have a coordination number of 6.
Explain what is meant by coordination number.

....

.... [1]

20. The titanium ions in TiF_6^{2-} and $Ti(acac)_2Cl_2$ have a coordination number of 6.
State what is meant by coordination number. [1]

21. **E** is a complex ion, $[Fe(C_2O_4)_2Cl_2]^{4-}$, containing Fe^{2+} with a coordination number of 6.
Define the term *coordination number*. [1]

22. Transition elements form complexes.
Molybdenum, Mo, forms an octahedral complex consisting of one Mo atom surrounded by carbon monoxide, CO, molecules. CO is a monodentate ligand. Iron forms an octahedral complex consisting of one Fe^{3+} and a number of cyanide, CN^-, ions. CN^- is a monodentate ligand.
Complete the table by stating the formulae and charges of the complexes described. [2]

	formula	charge
molybdenum complex		
iron(III) complex		

23. State the coordination number of copper in $[Cu(CH_3NH_2)_2(H_2O)_4]^{2+}$.

.... [1]

24. Iron forms complex ions with the monodentate ligand, CN–.
(i) Complex ion A contains one Fe^{3+} ion and six CN^- ligands.
Complex ion B contains one Fe^{2+} ion and six CN^- ligands.
State the formulae of these two complex ions. Include the overall charge of each complex ion.

complex ion A ....

complex ion B .... [1]

(ii) In complex ion A, the carbon atom of each CN^- ligand bonds to the Fe^{3+} ion.
State the type of bonding involved.

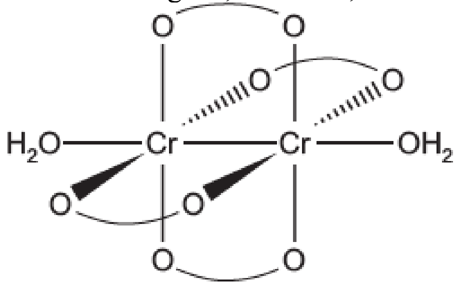
.... [1]

25. Transition elements behave as catalysts and can form complex ions.
Silver forms the linear complex ion $[Ag(CN)_2]^-$.
Copper forms the tetrahedral complex ion $[Cu(CN)_4]^{3-}$.
Titanium forms the complex $[TiCl_4(diars)_2]$, where *diars* is a neutral bidentate ligand.
State the oxidation state and the coordination number of titanium in $[TiCl_4(diars)_2]$.

oxidation state ....

coordination number .... [1]

26. The structure of $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ is shown. Ethanoate ions act as ligands in this complex.
The ethanoate ligand, $CH_3CO_2^-$, is shown as O O.



Water and ethanoate ions behave as different types of ligand in this complex.
Suggest an explanation for this statement.

....

.... [1]

(ii) Deduce the coordination number of Cr and the geometry around each Cr atom in this structure.

coordination number ....

geometry around Cr atom [1]

(iii) State the type of bond between the two atoms in the Cr–Cr bond.

.... [1]

27. Calculate the oxidation states of Cu in $[Cu(EDTA)]^{2-}$ and Cr in $[Cr(EDTA)]^{-}$.

Cu .... Cr .... [1]

Geometry

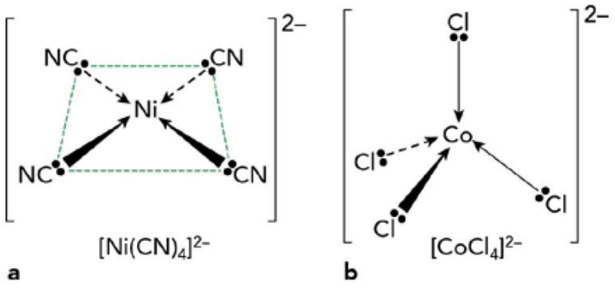
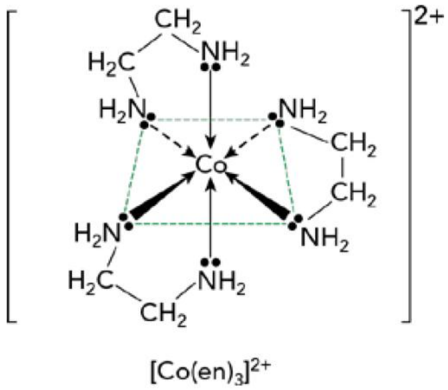


Figure: The complex ion formed between a transition metal ion and a larger ligand can only fit four, not six, ligands around the central ion. These are arranged in either a square planar shape (as in **a** $[Ni(CN)_4]^{2-}$) or a tetrahedral shape (as in **b** $[CoCl_4]^{2-}$).



Name of ligand	Formula	Example of complex	Co-ordination number	Shape of complex
water	H_2O	$[Fe(H_2O)_6]^{2+}$	6	octahedral (see Figure 24.4)
ammonia	NH_3	$[Co(NH_3)_6]^{3+}$	6	octahedral
chloride ion	Cl^-	$[CoCl_4]^{2-}$	4	tetrahedral (see Figure 24.5b)
cyanide ion	CN^-	$[Ni(CN)_4]^{2-}$	4	square planar (see Figure 24.5a)
hydroxide ion	OH^-	$[Cr(OH)_6]^{3-}$	6	octahedral
thiocyanate ion	SCN^-	$[FeSCN]^{2+}$ or $[Fe(SCN)(H_2O)_5]^{2+}$	6	octahedral
ethanedioate ion (abbreviated to 'ox' – oxalate – in the formulae of complexes)	$^-OOC–COO^-$	$[Mn(ox)_3]^{3-}$	6	octahedral
1,2-diaminoethane (abbreviated to 'en' in the formulae of complexes)	$NH_2CH_2CH_2NH_2$	$[Co(en)_3]^{3+}$	6	octahedral (see Figure 24.6)

Linear

Central metal atoms or ions with **two coordinate bonds** form **linear** complexes

The bond angles in these complexes are 180^0

The most common examples are a copper (I) ion, (Cu), or a silver (I) ion, (Ag), as the central metal ion with two coordinate bonds formed to two ammonia ligands

28. When 1.0 mol dm^{-3} $Na_2S_2O_3(aq)$ is added to a solution containing $Ag^+(aq)$ ions, a linear complex, P, is formed. $S_2O_3^{2-}$ ions are present in P as monodentate ligands.
Give the formula of P, including its charge.

.... [1]

Tetrahedral

When there are **four coordinate bonds** the complexes often have a **tetrahedral** shape
Complexes with four **chlorideions** most commonly adopt this geometry

Chloride ligands are large, so only four will fit around the central metal ion

The bond angles in tetrahedral complexes are 109.5

Square planar

Sometimes, complexes with **four coordinate bonds** may adopt a **square planar**geometry instead of a tetrahedral one
Cyanide ions (CN) are the most common ligands to adopt this geometry

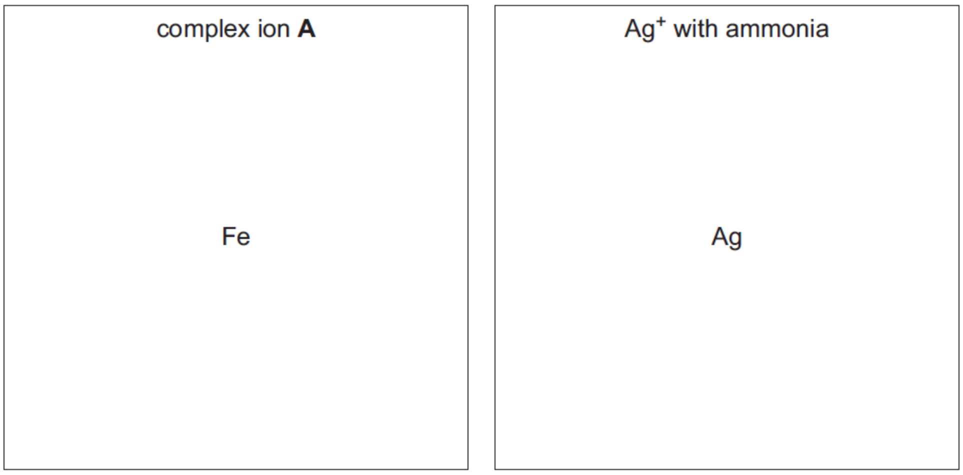
An example of a square planar complex is **cisplatin**

The bond angles in a square planar complex are 90

Octahedral

Octahedral complexes are formed when a central metal atom or ion forms **sixcoordinate bonds**

29. Complex ions have different geometries.
Complex ion A is octahedral.
Ag^{+} ions form a linear complex with ammonia.
Ni atoms form a tetrahedral complex with carbon monoxide molecules. The carbon atom in the monodentate carbon monoxide ligand bonds to the nickel atom.
Pd^{2+} ions form a square planar complex with chloride ions.
Complete Fig. 6.1 to show the geometry of each of these four ions, using three-dimensional bonds where necessary. Label one bond angle on each complex ion. [4]



Ni with carbon monoxide	Pd^{2+} with chloride
Ni	Pd

Fig. 6.1

30. Iron forms an octahedral complex consisting of one Fe^{3+} and a number of cyanide, CN^{-}, ions. CN^{-} is a monodentate ligand.
Draw a three-dimensional diagram to show the shape of this iron(III) complex.
Label one 180° bond angle on your diagram. [1]

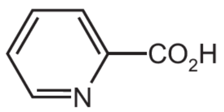
Fe

31. The $[MnCl_4]^{2-}$ complex does **not** contain any 180° bond angles.
Draw a three-dimensional diagram to show the shape of the $[MnCl_4]^{2-}$ complex.
State one bond angle on your diagram. [2]

Mn

32. The structure of picolinic acid is shown.

picolinic acid



The conjugate base of picolinic acid is a bidentate ligand, **Z**.
(i) Draw the structure of **Z**. [1]

(i) **Z** reacts with aqueous chromium(III) ions, $[Cr(H_2O)_6]^{3+}$, in a 3 : 1 ratio to form a new neutral complex. State the coordination number and the geometry of the chromium(III) centre in the complex.

coordination number .... geometry .... [1]

33. $Be(OH)_2$ is soluble in aqueous solutions containing an excess of hydroxide ions and forms the complex ion $[Be(OH)_4]^{2-}$. This complex ion has a similar shape to that of $[CuCl_4]^{2-}$.
Draw a three-dimensional diagram to show the structure of the complex ion $[Be(OH)_4]^{2-}$.
Name the shape of the $[Be(OH)_4]^{2-}$ complex ion.

shape ....[1]

34. Copper is a transition element. It forms a wide variety of compounds.
An aqueous solution of copper(II) sulfate, $CuSO_4$, contains $[Cu(H_2O)_6]^{2+}$ complex ions. If an excess of concentrated hydrochloric acid is added to this solution, a ligand exchange reaction occurs and $[CuCl_4]^{2-}$ complex ions are formed.
(i) Complete Table 5.1 to state the geometry, the coordination number of copper, and one bond angle in each of the two complex ions. [3]

Table 5.1

complex ion	geometry	coordination number	bond angle
$[Cu(H_2O)_6]^{2+}$			
$[CuCl_4]^{2-}$			

(ii) Draw a three-dimensional diagram to show the structure of the complex ion $[CoCl_4]^{2-}$.

35. Draw three-dimensional diagrams to show the shapes of $[Ag(CN)_2]^-$ and $[Cu(CN)_4]^{3-}$, in the boxes.
Label one bond angle on each diagram. [2]

Ag	Cu

36. Name the shape of the complex ion $[Ag(NH_3)_2]^+$.
State the bond angle for H-N-Ag and for N-Ag-N.

shape ....

bond angle for H-N-Ag = ... °

bond angle for N-Ag-N = ... ° [2]

37. The H—O—H bond angle in water is 104.5°.
Suggest the H—O—H bond angle in $[Fe(H_2O)_6]^{3+}$.
Explain your answer.

....

....

.... [1]

Ligand Exchange Reactions

The ligands in a complex can be exchanged, wholly or partially, for other ligands.

This is a type of substitution reaction.

It happens if the new complex formed is more stable than the original complex.

The complexes of copper(II) ions can be used to show ligand substitution reactions, also called **ligand exchange reactions.**

Copper complexes

Whenever we write $Cu^{2+}(aq)$ we are really referring to the complex ion $[Cu(H_2O)_6]^{2+}$. This ion gives a solution of copper sulfate its blue colour.

On adding sodium hydroxide solution, we see a light blue precipitate forming.

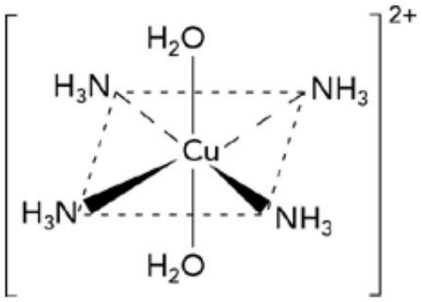
Two water ligands are replaced by two hydroxide ligands in the reaction:

$$\underset{\text{blue solution}}{[Cu(H_2O)_6]^{2+}}(aq) + 2OH^-(aq) \rightarrow \underset{\text{pale blue precipitate}}{Cu(OH)_2(H_2O)_4}(s) + 2H_2O(l)$$

If you now add concentrated ammonia solution, the pale blue precipitate dissolves and we get a deep blue solution:

$$\underset{\text{pale blue precipitate}}{Cu(OH)_2(H_2O)_4}(s) + 4NH_3(aq) \rightarrow \underset{\text{deep blue solution}}{[Cu(NH_3)_4(H_2O)_2]^{2+}}(aq) + 2H_2O(l) + 2OH^-(aq)$$

The first reaction can also be achieved by adding concentrated ammonia solution to copper sulfate solution drop by drop or by adding a dilute solution of ammonia. The pale blue precipitate formed will then dissolve and form the deep blue solution when excess ammonia is added. The structure of $Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ is shown in Figure



Water ligands in $[Cu(H_2O)_6]^{2+}$ can also be exchanged for chloride ligands if we add concentrated hydrochloric acid drop by drop. A yellow solution forms, containing the complex ion $[CuCl_4]^{2-}$:

$$\underset{\text{blue solution}}{[Cu(H_2O)_6]^{2+}}(aq) + 4Cl^-(aq) \rightarrow \underset{\text{yellow solution}}{[CuCl_4]^{2-}}(aq) + 6H_2O(l)$$

The mixture of blue and yellow solutions in the reaction mixture gives it a greenish colour

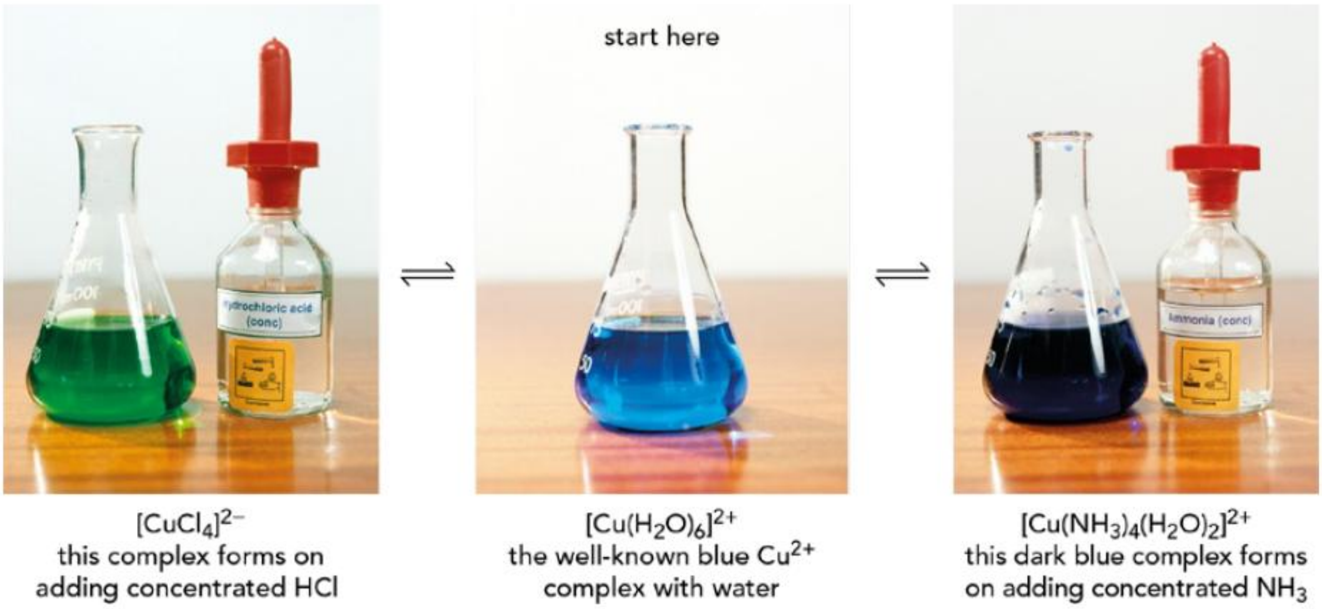


Figure 24.14: The equations for the changes are:
$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$
$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$

38. An excess of aqueous ammonia is added to dilute copper(II) sulfate solution. A dark blue complex, $[Cu(NH_3)_4(H_2O)_2]^{2+}$, is formed.

(i) Write an ionic equation for this reaction.

.... [1]

39. (a) Aqueous copper(II) sulfate, $CuSO_4$, contains the $[Cu(H_2O)_6]^{2+}$ complex ion.
(i) A few drops of $NH_3(aq)$ are added to $CuSO_4(aq)$.
Describe any observations made.

.... [1]

(ii) Write an equation for the reaction taking place.

.... [1]

(b) (i) An excess of $NH_3(aq)$ is added to $CuSO_4(aq)$.
Describe any further observations made.

.... [1]

(ii) Write an equation for the reaction taking place.

.... [1]

(iii) State the name for the type of reaction taking place.

.... [1]

40. Samples of $[Cu(H_2O)_6]^{2+}(aq)$ are reacted separately with an excess of solution **A** and with an excess of solution **B**.
The reaction of $[Cu(H_2O)_6]^{2+}(aq)$ with solution **A** is a precipitation reaction.
The reaction of $[Cu(H_2O)_6]^{2+}(aq)$ with solution **B** is a ligand substitution reaction.
Suggest a possible identity for solution **A** and for solution **B**. Give relevant observations and the formula of the copper-containing product for each reaction.

solution **A** ....

observations ....

formula of the copper-containing product ....

solution **B** ....

observations ....

formula of the copper-containing product .... [3]

41. An aqueous solution of copper(II) sulfate is a blue colour due to the presence of $[Cu(H_2O)6]^{2+}$ complex ions.
(i) Write an equation for the reaction between $[Cu(H_2O)6]^{2+}$ ions and NaOH(aq).

.... [1]

(ii) Write an equation for the reaction between $[Cu(H_2O)6]^{2+}$ ions and an excess of conc. HC*l*.

.... [1]

42. $Cu(NO_3)_2$ is added to water to form solution A.
Fig. 1.1 shows some reactions of solution A.

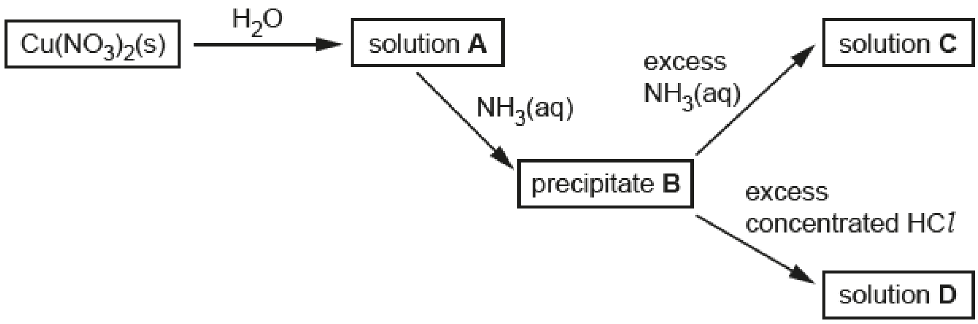


Fig. 1.1

(c) Complete Table 1.1 to show the formula and colour of each of the copper-containing species present in A, B, C and D. [4]

Table 1.1

	formula of copper-containing species formed	colour of copper-containing species formed
A		
B		
C		
D		

43. **a)** Samples of $[Cu(H_2O)_6]^{2+}$ are reacted separately with an excess of aqueous sodium hydroxide or with an excess of aqueous ammonia.

Give the following information about these reactions.

(i) reaction 1: $[Cu(H_2O)_6]^{2+}$ with an excess of aqueous of sodium hydroxide

colour and state of the copper-containing species ....

ionic equation ....

type of reaction .... [3]

(ii) reaction 2: $[Cu(H_2O)_6]^{2+}$ with an excess of aqueous ammonia

colour and state of the copper-containing species ....

ionic equation ....

type of reaction .... [3]

(b) Copper(I) oxide is added to hot dilute sulfuric acid. A blue solution, **X**, and a red-brown solid, **Y**, form. Suggest the identities of **X** and **Y**. Name the type of reaction.

X ....

Y ....

type of reaction ....[2]

44. Aqueous solutions of copper(II) salts contain $[Cu(H_2O)_6]^{2+}$ ions.

Equilibrium 3 and equilibrium 4 show two reactions of these ions.

equilibrium 3 $[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s) + 6H_2O(l)$

equilibrium 4 $[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$

(i) State the colour of $Cu(OH)_2(s)$ and $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$.

colour of $Cu(OH)_2(s)$ ....

colour of $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ .... [1]

(ii) Use Le Chatelier's principle to explain why a precipitate is formed when NaOH(aq) is added dropwise to $[Cu(H_2O)_6]^{2+}$(aq).

………

………

……… [1]

45. Aqueous manganese(II) ions show similar chemical properties to aqueous copper(II) ions when reacted separately with NaOH(aq) and with concentrated HCl.
(i) Write the ionic equation, and state the type of reaction, for the reaction of $[Mn(H_2O)_6]^{2+}$ with NaOH(aq).

ionic equation ……………………………………………………………………………………………

type of reaction …………………………………………………………………………………………… [2]

(ii) Write the ionic equation, and state the type of reaction, for the reaction of $[Mn(H_2O)_6]^{2+}$ with concentrated HCl.

ionic equation ……………………………………………………………………………………………

type of reaction …………………………………………………………………………………………… [2]

46. State the colour of the solution of $[Cu(NH3)_4]^{2+}$.

…………………………………………………………………………………… [1]

47. The solution of $[Cu(NH3)_4]^{2+}$ is heated gently in a fume cupboard so that NH3 is released. Some NH3 remains in solution and some forms NH3 gas. The colour of the solution changes; a precipitate of $Cu(OH)_2$ forms and is collected.
A sample of $Cu(OH)_2$ is added to concentrated hydrochloric acid. A reaction takes place forming a coloured copper complex, Y.
A sample of $Cu(OH)_2$ is added to dilute sulfuric acid. A reaction takes place forming a coloured copper complex, Z.
$[Cu(NH3)_4]^{2+}$, Y and Z are different colours.
(b) Suggest an equation for the reaction of $[Cu(NH3)_4]^{2+}$ to form $Cu(OH)_2$ as the aqueous solution of $[Cu(NH3)_4]^{2+}$ is heated.

…………………………………………………………………………………… [1]

(c) Suggest an equation for the reaction of $Cu(OH)_2$ with concentrated hydrochloric acid, forming Y.

…………………………………………………………………………………… [2]

(d) Complete the table with the colour and geometry of complex Y and the colour, geometry and formula of complex Z.

	Y	Z
colour of complex		
geometry of complex		
formula of complex		

[2]

Cobalt complexes

Aqueous cobalt(II) compounds also form complex ions. Whenever we write $Co^{2+}(aq)$, we are referring to the complex ion $[Co(H_2O)_6]^{2+}$. This ion gives an aqueous solution of cobalt(II) sulfate its pink colour. On adding sodium hydroxide solution, we see a blue precipitate of cobalt(II) hydroxide forming, which turns red when warmed if the alkali is in excess.

$$\underset{\text{pink solution}}{[Co(H_2O)_6]^{2+}(aq)} + 2OH^-(aq) \rightarrow \underset{\text{blue precipitate}}{Co(OH)^2(H_2O)_4(s)} + 2H_2O(l)$$

Water ligands in $[Co(H_2O)_6]^{2+}$ can also be exchanged for ammonia ligands if we add concentrated aqueous ammonia drop by drop.

$$\underset{\text{pink solution}}{[Co(H_2O)_6]^{2+}(aq)} + 6NH_3(aq) \rightarrow \underset{\text{brown solution}}{[Co(NH_3)_6]^{2+}(aq)} + 6H_2O(l)$$

The brown cobalt(II) complex ion is oxidised by oxygen in the air to $[Co(NH_3)_6]^{3+}(aq)$, a cobalt(III) complex ion.

Adding concentrated hydrochloric acid drop by drop to an aqueous solution of cobalt(II) ions results in the formation of a blue solution containing the tetrahedral complex $[CoCl_4]^{2-}(aq)$.

$$\underset{\text{pink solution}}{[Co(H_2O)_6]^{2+}(aq)} + 4Cl^-(aq) \rightarrow \underset{\text{blue solution}}{[CoCl_4]^{2-}\left(aq\right)} + 6H_2O(l)$$

Aqueous cobalt(II) ions usually form tetrahedral complexes with monodentate anionic ligands such as Cl^-, SCN^- and OH^-.

48. An aqueous solution of cobalt(II) chloride is a pink colour due to the presence of $[Co(H_2O)_6]^{2+}$ complex ions.
(i) Complete Table 6.1 to describe what is observed when the named reagent is added to an aqueous solution of cobalt(II) chloride. [2]

Table 6.1

reagent	colour of cobalt-containing product	state of cobalt-containing product
NaOH(aq)		
an excess of conc. HCl		

(ii) Write an equation for the reaction between $[Co(H_2O)_6]^{2+}$ ions and NaOH(aq).

.... [1]

(iii) Write an equation for the reaction between $[Co(H_2O)_6]^{2+}$ ions and an excess of conc. HCl.

.... [1]

49. A solution of cobalt(II) sulfate contains the complex ion $[Co(H_2O)_6]^{2+}$.
A solution containing $[Co(H_2O)_6]^{2+}$ is reacted separately with an excess of each of NaOH(aq), NH_3(aq) and Na*Cl* (aq).
Write an equation for each of these reactions. State **one** observation that can be made immediately after the reaction, include the colour and state of the cobalt-containing product.
(i) $[Co(H_2O)_6]^{2+}$ and an excess of NaOH(aq)

equation ....

observation .... [2]

(ii) $[Co(H_2O)_6]^{2+}$ and an excess of NH3(aq)

equation ....

observation .... [2]

50. Aqueous solutions of cobalt(II) salts contain the complex ion $[Co(H_2O)_6]^{2+}$.
(i) Samples of $[Co(H_2O)_6]^{2+}$ are reacted separately with an excess of aqueous ammonia, with an excess of concentrated HCl and with an excess of aqueous sodium hydroxide, as shown in Fig. 2.1.

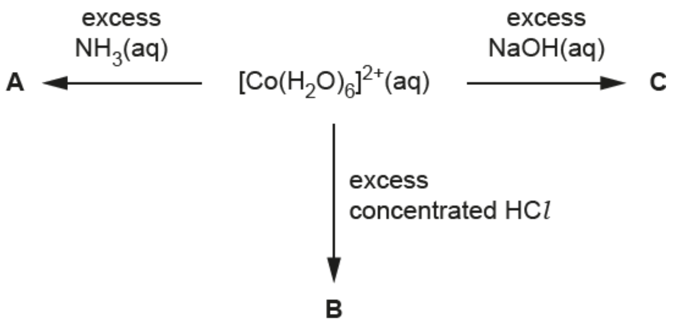


Fig. 2.1

Complete Table 2.1 about the reactions shown by $[Co(H_2O)_6]^{2+}$. [4]

reagent added to $[Co(H_2O)_6]^{2+}(aq)$	formula of cobalt species formed	colour and state of cobalt species formed	type of reaction
an excess of $NH_3(aq)$	**A** =		
an excess of concentrated HC*l*	**B** =		
an excess of NaOH(aq)	**C** =		

51. Cobalt(II) nitrate, $Co(NO_3)_2$, is a reddish-brown crystalline solid. It dissolves in water to form a solution containing $[Co(H_2O)_6]^{2+}$ complex ions.
(i) Complete Table 4.1 giving the formula of the cobalt-containing species that is formed in each of the three reactions described.
Table 4.1
reaction reagent added to $[Co(H_2O)_6]^{2+}(aq)$ cobalt-containing species formed
1 NaOH(aq)
2 an excess of $NH_3(aq)$
3 an excess of conc. HC*l* (aq) [2]

(ii) Describe the colour change seen in reaction 3.

original colour of $[Co(H_2O)_6]^{2+}(aq)$ ....

final colour after addition of an excess of conc. HC*l* (aq) .... [1]

52. Samples of $[Co(H_2O)_6]^{2+}$ are reacted separately with aqueous sodium hydroxide and with an excess of aqueous ammonia.
Give the following information about these reactions.
●● the reaction of $[Co(H_2O)_6]^{2+}$ with aqueous sodium hydroxide

colour and state of the cobalt-containing species ....

ionic equation ....

type of reaction ....

●● the reaction of $[Co(H_2O)_6]^{2+}$ with an excess of aqueous ammonia colour and state of the cobalt-containing species ....

ionic equation ....

type of reaction .... [6]

53. Transition metal atoms and transition metal ions form complexes by combining with species called ligands.
(a) When NaOH(aq) is added to an aqueous solution containing $[Co(H_2O)_6]^{2+}$ a precipitation reaction occurs accompanied by a colour change.
In this reaction two of the water ligands each lose one H^+ ion. The H^+ ions are gained by OH^- ions from the NaOH(aq).
(i) State the colour change seen in this precipitation reaction.

from .... to .... [1]

(ii) Complete the ionic equation for this precipitation reaction.

$[Co(H_2O)_6]^{2+}$ + ... + ... [1]

(iii) This precipitation reaction can also be described as a different type of reaction.
Name this type of reaction.

.... [1]

A solution of the bidentate ligand 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, is added to an aqueous solution of cobalt(II) sulfate. Oxygen is then bubbled into the mixture forming a complex ion with the formula $[Co(H_2NCH_2CH_2NH_2)_3]^{3+}$.
This complex ion exists as a mixture of two isomers. The geometry of both of these isomeric complexes is octahedral.
(i) In this reaction, cobalt undergoes **two** types of reaction. One type of reaction is the same as that described in **(c)(ii)**.
Name the **other** type of reaction that cobalt undergoes.

.... [1]

54. When cobalt(II) sulfate, $CoSO_4$, is dissolved in distilled water, solution A is formed.
The reaction scheme in Fig. 2.1 shows some reactions of solution A.

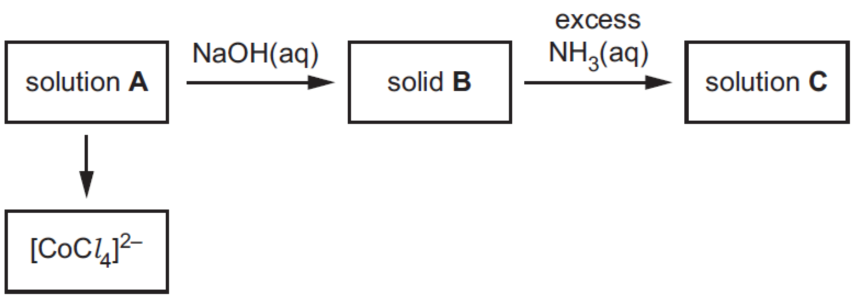


Fig. 2.1

Complete Table 2.1 to show the formula and colour of each of the cobalt-containing species present in A, B and C. Identify the type of reaction forming each of B and C.

	formula of cobalt-containing species	colour of cobalt-containing species	type of reaction
A			
B			
C			

(ii) Suggest a suitable reagent for the formation of $[CoCl_4]^{2-}$ from solution A.

.... [1]

55. (i) $[Co(H_2O)_6]^{2+}$ and an excess of Na*Cl* (aq)

equation ....

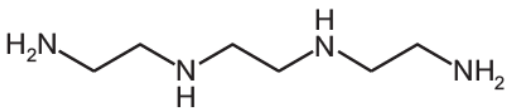
observation .... [2]

(ii) Name the type of reaction that occurs in **(i)**.

.... [1]

56. Compound X, $C_6H_{18}N_4$, is a tetradentate ligand.

X



$C_6H_{18}N_4$ reacts with aqueous cobalt(II) ions, $[Co(H_2O)_6]^{2+}$, in a 1 : 1 ratio to form a new complex ion.
Construct an equation for this reaction.

.... [1]

57. When an excess of CN–(aq) ions is added to green $[Fe(H_2O)_6]^{2+}$(aq) ions, yellow $[Fe(CN)_6]^{4-}$ complex ions are formed.
Heating $[Fe(CN)_6]^{4-}$ with dilute nitric acid and then neutralising the product with Na_2CO_3(aq) produces red crystals, containing the $[Fe(CN)_5NO]^{2-}$ complex ion.
NO is a neutral, monodentate ligand.
(i) State the shape of the $[Fe(H_2O)_6]^{2+}$(aq) complex ion.

.... [1]

(ii) Write the equation for the reaction between $[Fe(H_2O)_6]^{2+}$(aq) ions and an excess of CN–(aq) ions.

.... [1]

Complete the diagram to show the three-dimensional structure of the $[Fe(CN)_5NO]^{2-}$ complex ion.

[1]

58. The anhydrous iron(III) compound $K_3[Fe(C_2O_4)_3]$ decomposes on heating to form a mixture of $K_2[Fe(C_2O_4)_2]$, $K_2C_2O_4$ and CO_2.
Complete the equation for the decomposition of $K_3[Fe(C_2O_4)_3]$.

.... $K_3[Fe(C_2O_4)_3]$ .... $\rightarrow$ $K_2[Fe(C_2O_4)_2]$ + ... $K_2C_2O_4$ + ... CO_2 [1]

59. When $edds^{4-}(aq)$ is added to $Fe^{3+}(aq)$, the following reaction occurs.
$[Fe(H_2O)_6]^{3+}(aq) + edds^{4-}(aq) \rightarrow [Fe(edds)]^{-}(aq) + 6H_2O(l)$
State the type of reaction that occurs.

.... [1]

60. Tollens' reagent can be used to distinguish between aldehydes and ketones. Tollens' reagent contains $[Ag(NH_3)_2]OH$, which can be prepared in a two-step process.
step 1 Aqueous NaOH is added dropwise to aqueous $AgNO_3$ to form Ag_2O as a brown precipitate.
step 2 Aqueous NH_3 is added dropwise to Ag_2O to form a colourless solution containing $[Ag(NH_3)_2]OH$.
Construct equations for each of the steps in the preparation of $[Ag(NH_3)_2]OH$.

step 1 ....

step 2 .... [2]

61. When 1.0 mol dm^{-3} NaCN(aq) is added to a solution of P, a mixture which includes a second linear complex, Q, is formed. In this mixture the concentration of Q is much greater than the concentration of P.
(i) Write an equation for the reaction that occurs when NaCN(aq) is added to a solution of P.

.... [1]

(ii) Suggest a reason why the concentration of Q is much greater than the concentration of P in the mixture.

....

....

.... [1]

(iii) Name the type of reaction in which P forms Q.

.... [1]

62. Write an ionic equation for the reduction of TiO2+ by zinc metal in acidic conditions.

.... [1]

63. $[Fe(C_2O_4)_2Cl_2]^{4-}$ contains ligands which are anions of ethanedioic acid, HO_2CCO_2H.
Complete the table to show any observations for the reactions of HO_2CCO_2H with the named reagents.
Where no change is observed, write 'none'. [2]

reagent	observations with HO_2CCO_2H
warm acidified manganate(VII)	
2,4-dinitrophenylhydrazine	
warm Tollens' reagent	

64. Some reactions of TiO_2 are shown in Fig. 3.1.
The anion, acac–, is a bidentate ligand.

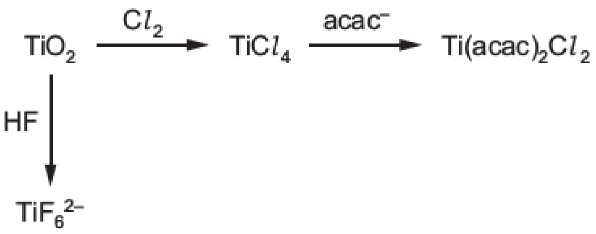


Fig. 3.1

(i) Write an equation for the formation of TiF_6^{2-} from TiO_2.

.... [1]

65. $(NH_4)_2Cr_2O_7$ decomposes readily on heating to form Cr_2O_3, steam and an inert colourless gas.
Construct an equation for the thermal decomposition of $(NH_4)_2Cr_2O_7$.

.... [1]

Calculations (Stoichiometry)

66. Most naturally occurring samples of iron(II) oxide are found as the mineral wüstite.
Wüstite has formula $Fe_{20}O_x$. It contains both Fe^{2+} and Fe^{3+} ions.
90% of the iron is present as Fe^{2+} and 10% is present as Fe^{3+}.
Deduce the value of x.

x = ... [1]

67. VO_2^+ can be reduced to V^{2+} by $C_2O_4^{2-}$ in acidic conditions.
equation 2 $2VO_2^+ + 3C_2O4^{2-} + 8H^+ \rightarrow 2V^{2+} + 6CO_2 + 4H_2O$
(i) In a titration, 25.00 cm^3 of 0.0300 mol dm^{-3} $VO_2^+(aq)$ is added to 10 cm^3 of dilute sulfuric acid.
A solution of 0.0400 mol dm^{-3} $C_2O_4^{2-}(aq)$ is then added from a burette until the end-point is reached.
The titration is repeated and concordant results obtained, as shown in Table 3.1.
Table 3.1

	1	2
volume of $C_2O_4^{2-}(aq)$ added / cm^3	28.15	28.10

Show that these results are consistent with the stoichiometry of equation 2. [2]

68. Ethanedioate ions, $C_2O_4^{2-}$, form complexes with transition element ions.

The concentration of $C_2O_4^{2-}$ ions can be found by reaction with acidified $Cr_2O_7^{2-}$ ions.
$C_2O_4^{2-}$ ions are protonated and form HOOCCOOH molecules which are oxidised by $Cr_2O_7^{2-}$.
The half-equations are shown.
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
$2CO_2 + 2H^+ + 2e^- \rightarrow$ HOOCCOOH
(i) Construct an equation for the reaction between acidified $Cr_2O_7^{2-}$ and HOOCCOOH.

.... [1]

(ii) A 25.0 cm^3 sample of a solution of $Na_2C_2O_4$ reacts with exactly 16.20 cm^3 of an acidified solution of 0.0500 mol dm^{-3} $K_2Cr_2O_7$.
Calculate the concentration of the solution of $Na_2C_2O_4$.

Solution:
$n(Cr_2O_7^{2-})$ = 16.20/1000 x 0.0500 = 8.1 x 10^{-4} moles

From the above chemical equation,
$n(Cr_2O_7^{2-})$ / n $(C_2O_4^{2-})$ = 1:3

or, n $(C_2O_4^{2-})$ = 3 x $n(Cr_2O_7^{2-})$ = 8.1 x 10^{-4} x 3 = 2.43 x 10^{-3} moles

$[Na_2C_2O_4]$ = n/V = 2.43 x 10^{-4} /25 x 1000= 0.097 mol dm^{-3}

$[Na_2C_2O_4]$ = ...(ans = 0.097 mol $dm^{-3)}$...... mol dm^{-3} [2]

69. The number of moles of water of crystallisation in a hydrated ionic salt can be determined by titration using aqueous $EDTA^{4-}$ ions with a suitable indicator.
• 0.255 g of hydrated chromium(III) sulfate, $Cr_2(SO_4)_3$•nH_2O, is dissolved in water and made up to 100 cm^3 in a volumetric flask.
• 25.0 cm^3 of this solution requires 26.2 cm^3 of 0.00800 mol dm^{-3} aqueous $EDTA^{4-}$ ions to reach the end-point.
The reaction occurs as shown.
$[Cr(H_2O)_6]^{3+} + EDTA^{4-} \rightarrow [CrEDTA]^- + 6H_2O$
Use the data to calculate the value of n in the formula of $Cr_2(SO_4)_3$•nH_2O.
Show your working.

n = ... [3]

70. A piece of a copper-containing alloy has a mass of 0.567 g. It is dissolved in an acid giving 100.0 cm^3 of a blue solution in which all the copper is present as Cu^{2+} ions.
An excess of KI(aq) is added to a 25.0 cm^3 sample of this solution.
All of the copper is precipitated as white CuI(s).
Cu2+ ions are the only component in the solution that react with KI(aq). This is reaction 1.
reaction 1 $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$
The liberated I_2 is then titrated with 0.0200 mol dm^{-3} $S_2O_3^{2-}$. This is reaction 2.
reaction 2 $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$
The titration requires 20.10 cm^3 of 0.0200 mol dm^{-3} $S_2O_3^{2-}$ to reach the end-point.
(i) Calculate the number of moles of I_2 that are reduced in this titration.

number of moles of I_2 = ... mol [1]

(ii) Calculate the number of moles of copper in the original piece of alloy.

number of moles of copper = ... mol [1]

(iii) Calculate the percentage of copper in the alloy.

percentage of copper = ... % [1]

71. A solution contains 3.70 g of $Na_2[Cu(C_2O_4)_2(H_2O)_2]$ dissolved in 100 cm^3 of solution. A 25.0 cm^3 sample of this solution is warmed and then oxidised by 0.0100 mol dm^{-3} acidified potassium manganate(VII).
The equation for the redox reaction is shown.
$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$
Calculate the minimum volume of 0.0100 mol dm^{-3} acidified potassium manganate(VII) needed to oxidise all of the ethanedioate ions, $C_2O_4^{2-}$, in the 25.0 cm^3 sample. Show all your working.
[Mr: $Na_2[Cu(C_2O_4)_2(H_2O)_2]$, 321.5]

minimum volume = ...(ans = 230).......... cm^3 [3]

Calculations (electrode potentials)

72. $V^{2+}(aq)$ can be oxidised by $H_2O_2(aq)$.
Table 3.2 gives some relevant data.

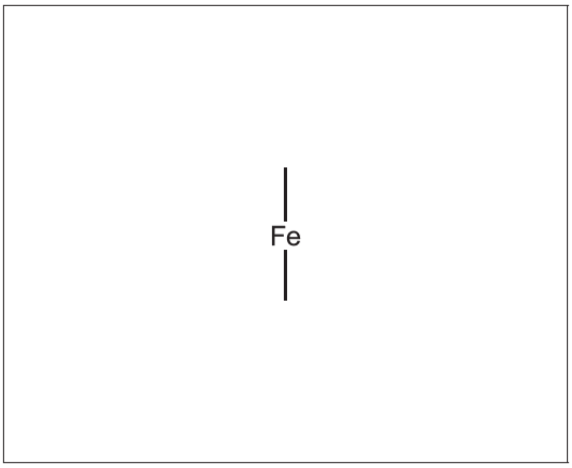
	half-equation	E o / V
1	$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77
2	$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00
3	$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34
4	$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	–0.26

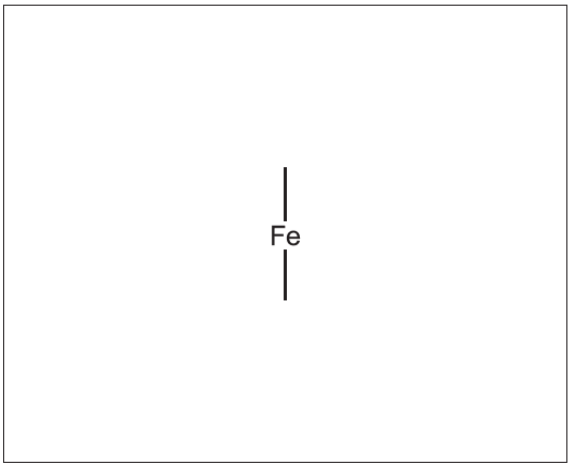
(i) Identify the vanadium species that forms when an excess of $H_2O_2(aq)$ reacts with $V^{2+}(aq)$ under standard conditions.
Explain your answer with reference to the data in Table 3.2.

....

....

.... [1]





73. $[Cr(H_2O)_6]^{3+}(aq)$ shows some similar chemical properties to $[Co(H_2O)_6]^{2+}(aq)$.
Samples of $[Cr(H_2O)_6]^{3+}$ are reacted separately with either NaOH(aq), $H_2O_2(aq)$, or excess $NH_3(aq)$.
Use this information and the ***Data Booklet*** to suggest the formula of the chromium species formed. State the type of reaction taking place in each case. [5]

reagent added to
$[Cr(H_2O)_6]^{3+}(aq)$
formula of chromium
species formed type of reaction
NaOH(aq)
$H_2O_2(aq)$
an excess of $NH_3(aq)$

74. (a) When concentrated hydrochloric acid is added to a solution containing $[Co(H_2O)_6]^{2+}$, a blue solution of $[CoCl_4]^{2-}$ is formed and the following equilibrium is established.
$[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$
Use Le Chatelier's principle to suggest the expected observations when silver nitrate solution is added dropwise to the blue solution of $[CoCl_4]^{2-}$. Explain your answer.

....

....

.... [2]

(b)A solution of $Cl^-(aq)$ is added to $Cd^{2+}(aq)$ and allowed to reach equilibrium. The equilibrium concentrations are given.

$[Cd^{2+}(aq)] = 0.043\ mol\ dm^{-3}$
$[Cl^{-}(aq)] = 0.072\ mol\ dm^{-3}$
Use your expression in **(f)(ii)** to calculate the concentration of $CdCl_4^{2-}(aq)$ in the equilibrium mixture.

$[CdCl_4^{2-}(aq)]$ = ... $mol\ dm^{-3}$ [1]

75. When a sample of hydrated lithium ethanedioate, $Li_2C_2O_4 \bullet H_2O$, is gently heated, two gaseous products are formed and a white solid residue remains.
The residue is added to $HNO_3(aq)$. A gas is produced that turns limewater milky.
Complete the equation for the decomposition of $Li_2C_2O_4 \bullet H_2O$.

$Li_2C_2O_4 \bullet H_2O$ .... + ... + ... [1]

*****This is not a complete note. It is just to guide you. It is recommended to study the prescribed textbooks along with this material. *****