

28.2 GENERAL CHARACTERISTICS AND CHEMICAL PROPERTIES OF TRANSITION ELEMENTS

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Ligands

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

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

monodentate ligand: H_2O , NH_3 , Cl^- and CN^-

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

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

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

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

4. Phosphine, $:\text{PH}_3$, and carbon monoxide, $:\text{CO}$, are monodentate ligands found in some transition element complexes.
Define monodentate ligand. [1]

bidentate ligand: 1,2-diaminoethane, *en*, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ and the ethanedioate ion, $\text{C}_2\text{O}_4^{2-}$

5. Explain what is meant by a bidentate ligand.

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

6. Bipyridine, bipy, is a bidentate ligand.

bipy

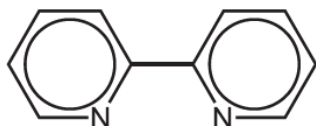


Fig. 4.1

Explain what is meant by a bidentate ligand. [2]

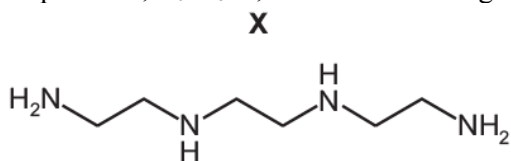
7. Cobalt forms the complex ion $[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{2+}$. The abbreviation *en* is used for the bidentate ligand 1,2-diaminoethane, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$. The complex ion shows both geometrical and optical isomerism.
Define the term *bidentate ligand*.

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

8. 1,2-diaminoethane, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, en, can act as a bidentate ligand.
Explain what is meant by a bidentate ligand.

[2]

9. Compound X, $\text{C}_6\text{H}_{18}\text{N}_4$, is a tetradentate ligand.



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

.....

 [1]

Polydentate ligand: EDTA⁴⁻

10. EDTA⁴⁻ 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 EDTA⁴⁻ is added to water containing $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$ to form a new complex, $[\text{CaEDTA}]^{2-}$, as shown.

equilibrium 1 $[\text{Ca}(\text{H}_2\text{O})_6]^{2+} + \text{EDTA}^{4-} \rightleftharpoons [\text{CaEDTA}]^{2-} + 6\text{H}_2\text{O}$

Circle on the structure of EDTA⁴⁻ in Fig. 1.2 the **six** atoms that form bonds with the metal ion. [1]

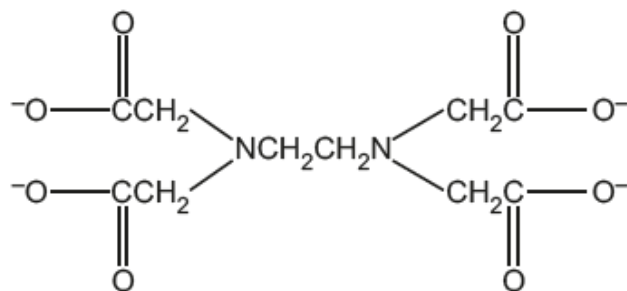
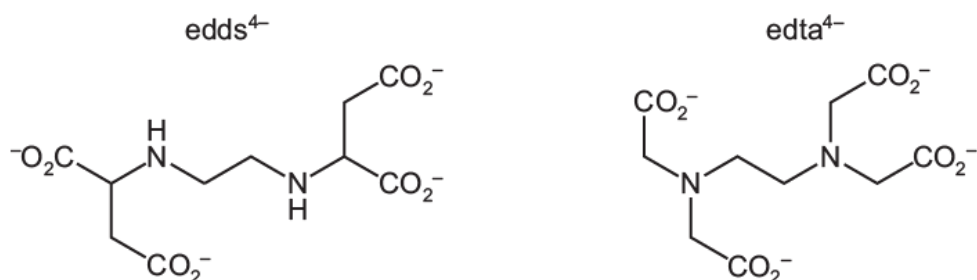


Fig. 1.2

11. Edds⁴⁻ and edta⁴⁻ are polydentate ligands that form octahedral complexes with $\text{Fe}^{3+}(\text{aq})$.



On the diagram of edds⁴⁻, circle each atom that forms a bond to the Fe^{3+} ion in $[\text{Fe}(\text{edds})]^-$. [1]

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

ligand	type of ligand
NH_3	
EDTA^{4-}	
CN^-	
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$	tridentate
$\text{C}_2\text{O}_4^{2-}$	

(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 $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ is a tridentate ligand. Suggest the meaning of a tridentate ligand.

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

(iii) Suggest how $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ acts as a tridentate ligand.

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

Complex

13. Fe^{2+} and Fe^{3+} ions can form a variety of complexes with different species. Define complex.

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

14. Aqueous solutions of cobalt(II) salts contain the complex ion $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. Define complex ion. [1]

15. Define a transition element complex.

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

16. 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	

17. An aqueous solution of $\text{Fe}(\text{NO}_3)_3$ contains the complex $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.
When solutions of $\text{KSCN}(\text{aq})$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ are mixed, a colour change is observed.
The red complex $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$ forms.
State the coordination number of Fe in $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.
..... [1]
18. The calcium ions in $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CaEDTA}]^{2-}$ have a coordination number of 6.
Explain what is meant by coordination number.
.....
..... [1]
19. The titanium ions in TiF_6^{2-} and $\text{Ti}(\text{acac})_2\text{Cl}_2$ have a coordination number of 6.
State what is meant by coordination number. [1]
20. E is a complex ion, $[\text{Fe}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{4-}$, containing Fe^{2+} with a coordination number of 6.
Define the term *coordination number*. [1]
21. 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		

22. State the coordination number of copper in $[\text{Cu}(\text{CH}_3\text{NH}_2)_2(\text{H}_2\text{O})_4]^{2+}$.
..... [1]
23. 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

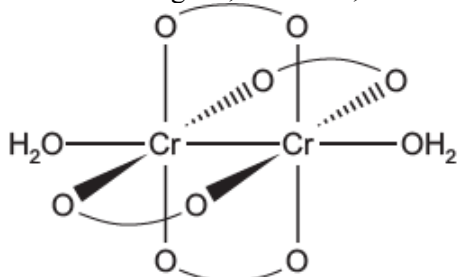
complex ion B [1]

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

oxidation state

coordination number [1]

25. The structure of $[\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ 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]

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

Cu Cr [1]

27. Phenanthroline, $\text{C}_{12}\text{H}_8\text{N}_2$, and ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, are bidentate ligands. Ruthenium(III) ions, Ru^{3+} , form an octahedral complex with phenanthroline and chloride ions. The complex ion contains two phenanthroline molecules. Iron(III) ions, Fe^{3+} , form an octahedral complex with ethanedioate ions only. Deduce the formula and charge of each of these complex ions.

Ru^{3+} complex

Fe^{3+} complex [2]

Geometry

28. When $1.0 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3(\text{aq})$ is added to a solution containing $\text{Ag}^+(\text{aq})$ ions, a linear complex, P, is formed. $\text{S}_2\text{O}_3^{2-}$ ions are present in P as monodentate ligands. Give the formula of P, including its charge.

..... [1]

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]

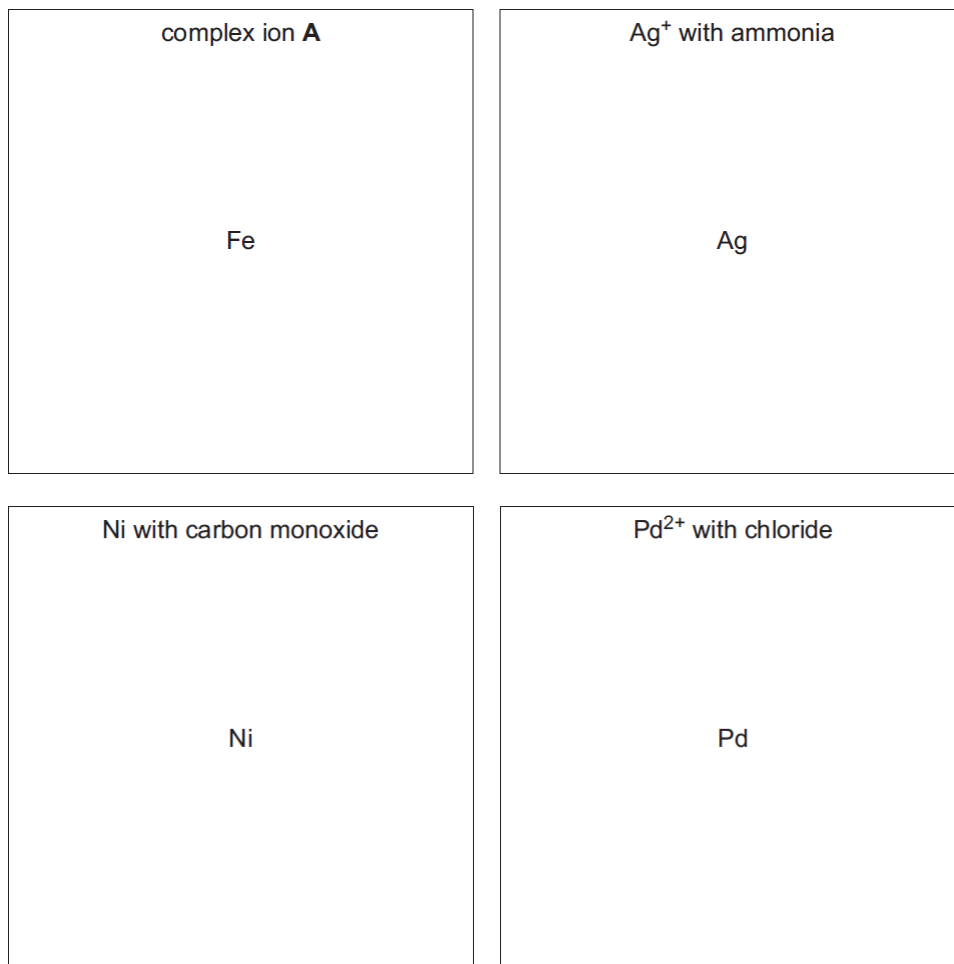


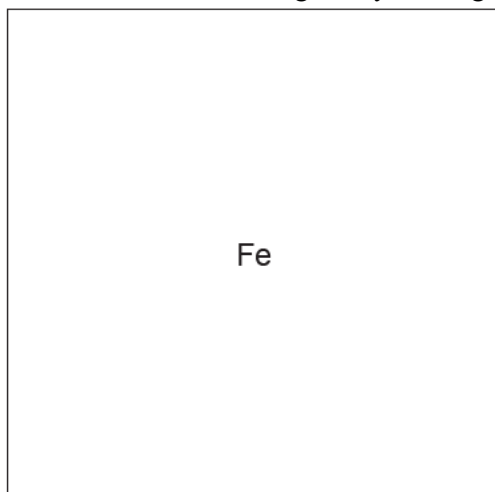
Fig. 6.1

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.

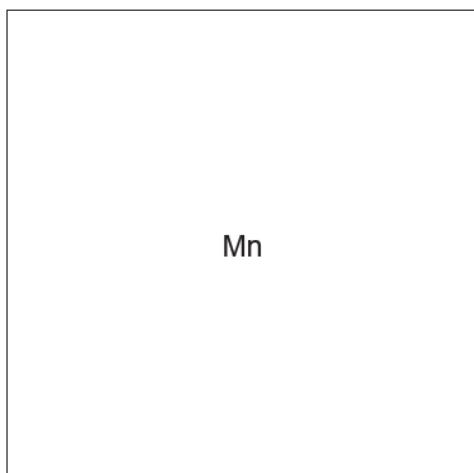
Label one 180° bond angle on your diagram.

[1]

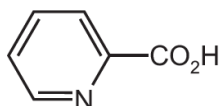


31. The $[\text{MnCl}_4]^{2-}$ complex does **not** contain any 180° bond angles.
 Draw a three-dimensional diagram to show the shape of the $[\text{MnCl}_4]^{2-}$ complex.
 State one bond angle on your diagram.

[2]



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, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, 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. $\text{Be}(\text{OH})_2$ is soluble in aqueous solutions containing an excess of hydroxide ions and forms the complex ion $[\text{Be}(\text{OH})_4]^{2-}$. This complex ion has a similar shape to that of $[\text{CuCl}_4]^{2-}$.
 Draw a three-dimensional diagram to show the structure of the complex ion $[\text{Be}(\text{OH})_4]^{2-}$.
 Name the shape of the $[\text{Be}(\text{OH})_4]^{2-}$ 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 $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ions. If an excess of concentrated hydrochloric acid is added to this solution, a ligand exchange reaction occurs and $[\text{CuCl}_4]^{2-}$ complex ions are formed.

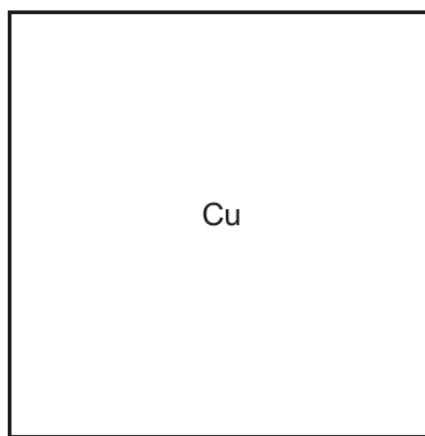
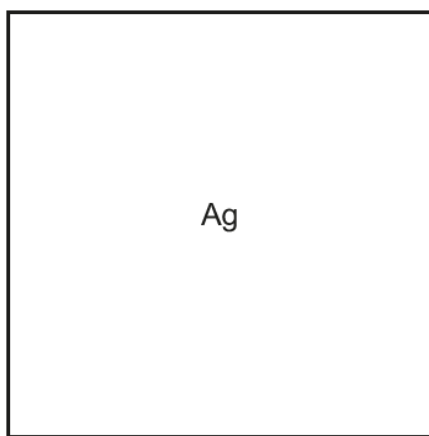
(i) Complete Table 5.1 to state the geometry, the coordination number of copper, and one bond angle in each of the two complex ions. [3]

Table 5.1

complex ion	geometry	coordination number	bond angle
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$			
$[\text{CuCl}_4]^{2-}$			

(ii) Draw a three-dimensional diagram to show the structure of the complex ion $[\text{CoCl}_4]^{2-}$.

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



36. Name the shape of the complex ion $[\text{Ag}(\text{NH}_3)_2]^+$.
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 $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.
Explain your answer.

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

38. Fig. 4.1 shows another ruthenium complex.

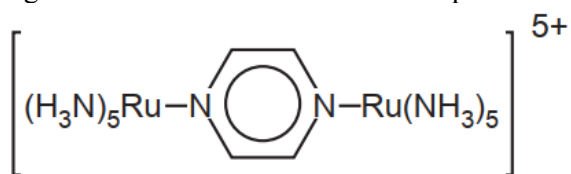
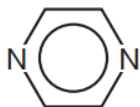


Fig. 4.1

This complex contains the neutral ligand pyrazine.

pyrazine



Suggest how pyrazine is able to bond to two separate ruthenium ions.

.....

 [1]

The overall charge of the ruthenium complex in Fig. 4.1 is 5+. Deduce the possible oxidation states of the two ruthenium ions in the complex.

..... [1]

Ligand Exchange Reactions

39. An excess of aqueous ammonia is added to dilute copper(II) sulfate solution. A dark blue complex, $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$, is formed.

(i) Write an ionic equation for this reaction.

..... [1]

40. (a) Aqueous copper(II) sulfate, CuSO_4 , contains the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ion.

(i) A few drops of $\text{NH}_3(\text{aq})$ are added to $\text{CuSO}_4(\text{aq})$.

Describe any observations made.

..... [1]

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

..... [1]

(b) (i) An excess of $\text{NH}_3(\text{aq})$ is added to $\text{CuSO}_4(\text{aq})$.

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]

41. Samples of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ are reacted separately with an excess of solution **A** and with an excess of solution **B**.

The reaction of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ with solution **A** is a precipitation reaction.

The reaction of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ 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]

42. An aqueous solution of copper(II) sulfate is a blue colour due to the presence of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ions.

(i) Write an equation for the reaction between $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions and $\text{NaOH}(\text{aq})$.

..... [1]

(ii) Write an equation for the reaction between $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions and an excess of conc. HCl .

..... [1]

43. $\text{Cu}(\text{NO}_3)_2$ is added to water to form solution A.

Fig. 1.1 shows some reactions of solution A.

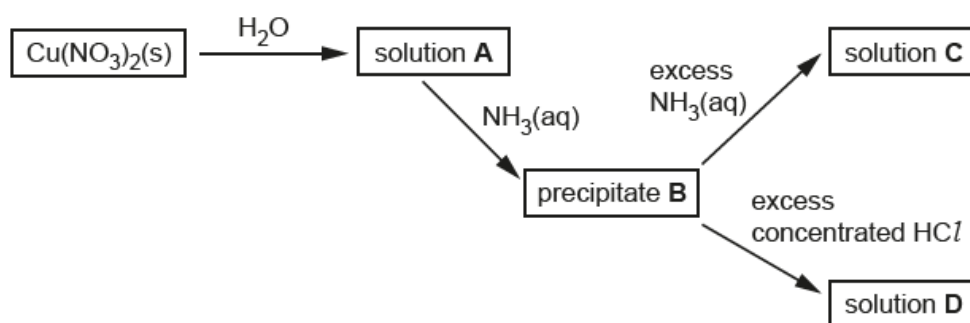


Fig. 1.1

- (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		

44. **a)** Samples of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ 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: $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ with an excess of aqueous sodium hydroxide
- colour and state of the copper-containing species
- ionic equation
- type of reaction [3]
- (ii)** reaction 2: $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ 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]
45. Aqueous solutions of copper(II) salts contain $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions.
Equilibrium 3 and equilibrium 4 show two reactions of these ions.
- equilibrium 3 $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightleftharpoons \text{Cu}(\text{OH})_2(\text{s}) + 6\text{H}_2\text{O}(\text{l})$
- equilibrium 4 $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
- (i)** State the colour of $\text{Cu}(\text{OH})_2(\text{s})$ and $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq})$.
- colour of $\text{Cu}(\text{OH})_2(\text{s})$
- colour of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq})$ [1]
- (ii)** Use Le Chatelier's principle to explain why a precipitate is formed when $\text{NaOH}(\text{aq})$ is added dropwise to $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$.
-
-
- [1]
46. Aqueous manganese(II) ions show similar chemical properties to aqueous copper(II) ions when reacted separately with $\text{NaOH}(\text{aq})$ and with concentrated HCl .
- (i)** Write the ionic equation, and state the type of reaction, for the reaction of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ with $\text{NaOH}(\text{aq})$.
- ionic equation
- type of reaction [2]

(ii) Write the ionic equation, and state the type of reaction, for the reaction of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ with concentrated HCl.

ionic equation

type of reaction [2]

47. State the colour of the solution of $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

..... [1]

48. The solution of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is heated gently in a fume cupboard so that NH_3 is released. Some NH_3 remains in solution and some forms NH_3 gas. The colour of the solution changes; a precipitate of $\text{Cu}(\text{OH})_2$ forms and is collected.

A sample of $\text{Cu}(\text{OH})_2$ is added to concentrated hydrochloric acid. A reaction takes place, forming a coloured copper complex, Y.

A sample of $\text{Cu}(\text{OH})_2$ is added to dilute sulfuric acid. A reaction takes place, forming a coloured copper complex, Z.

$[\text{Cu}(\text{NH}_3)_4]^{2+}$, Y and Z are different colours.

(b) Suggest an equation for the reaction of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ to form $\text{Cu}(\text{OH})_2$ as the aqueous solution of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is heated.

..... [1]

(c) Suggest an equation for the reaction of $\text{Cu}(\text{OH})_2$ 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

49. An aqueous solution of cobalt(II) chloride is a pink colour due to the presence of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ 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 $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions and NaOH(aq).

..... [1]

(iii) Write an equation for the reaction between $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions and an excess of conc. HCl.

..... [1]

50. A solution of cobalt(II) sulfate contains the complex ion $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.
 A solution containing $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is reacted separately with an excess of each of $\text{NaOH}(\text{aq})$, $\text{NH}_3(\text{aq})$ and $\text{NaCl}(\text{aq})$.
 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) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and an excess of $\text{NaOH}(\text{aq})$

equation

observation [2]

- (ii) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and an excess of $\text{NH}_3(\text{aq})$

equation

observation [2]

51. Aqueous solutions of cobalt(II) salts contain the complex ion $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.
 (i) Samples of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ 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.

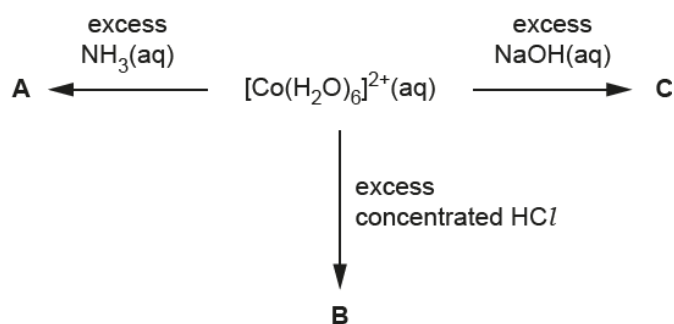


Fig. 2.1

Complete Table 2.1 about the reactions shown by $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. [4]

reagent added to $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$	formula of cobalt species formed	colour and state of cobalt species formed	type of reaction
an excess of $\text{NH}_3(\text{aq})$	A =		
an excess of concentrated HCl	B =		
an excess of $\text{NaOH}(\text{aq})$	C =		

52. Cobalt(II) nitrate, $\text{Co}(\text{NO}_3)_2$, is a reddish-brown crystalline solid. It dissolves in water to form a solution containing $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ 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 $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ cobalt-containing species formed

1 $\text{NaOH}(\text{aq})$

2 an excess of $\text{NH}_3(\text{aq})$

3 an excess of conc. $\text{HCl}(\text{aq})$

[2]

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

original colour of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$

final colour after addition of an excess of conc. $\text{HCl}(\text{aq})$ [1]

53. Samples of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ are reacted separately with aqueous sodium hydroxide and with an excess of aqueous ammonia.

Give the following information about these reactions.

●● the reaction of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ with aqueous sodium hydroxide

colour and state of the cobalt-containing species

ionic equation

type of reaction

●● the reaction of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ with an excess of aqueous ammonia

colour and state of the cobalt-containing species

ionic equation

type of reaction [6]

54. Transition metal atoms and transition metal ions form complexes by combining with species called ligands.

(a) When $\text{NaOH}(\text{aq})$ is added to an aqueous solution containing $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ 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 $\text{NaOH}(\text{aq})$.

(i) State the colour change seen in this precipitation reaction.

from to [1]

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

$[\text{Co}(\text{H}_2\text{O})_6]^{2+} + \dots + \dots$ [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, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, is added to an aqueous solution of cobalt(II) sulfate. Oxygen is then bubbled into the mixture forming a complex ion with the formula $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]^{3+}$.

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]

55. 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.

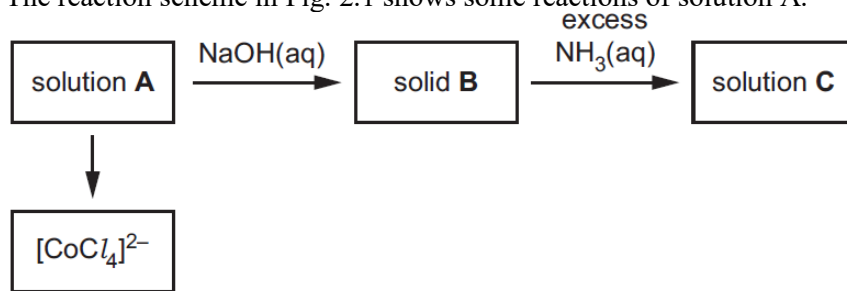


Fig. 2.1

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 $[\text{CoCl}_4]^{2-}$ from solution A.

..... [1]

56. (i) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and an excess of $\text{NaCl}(\text{aq})$

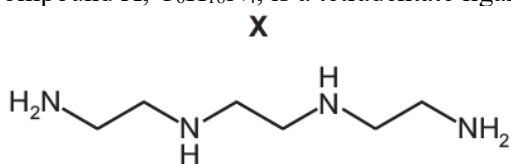
equation

observation [2]

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

..... [1]

57. Compound X, $\text{C}_6\text{H}_{18}\text{N}_4$, is a tetradentate ligand.



$\text{C}_6\text{H}_{18}\text{N}_4$ reacts with aqueous cobalt(II) ions, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, in a 1 : 1 ratio to form a new complex ion. Construct an equation for this reaction.

..... [1]

58. When an excess of $\text{CN}^-(\text{aq})$ ions is added to green $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ ions, yellow $[\text{Fe}(\text{CN})_6]^{4-}$ complex ions are formed.

Heating $[\text{Fe}(\text{CN})_6]^{4-}$ with dilute nitric acid and then neutralising the product with $\text{Na}_2\text{CO}_3(\text{aq})$ produces red crystals containing the $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ complex ion.

NO is a neutral, monodentate ligand.

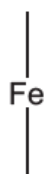
(i) State the shape of the $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ complex ion.

..... [1]

(ii) Write the equation for the reaction between $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ ions and an excess of $\text{CN}^-(\text{aq})$ ions.

..... [1]

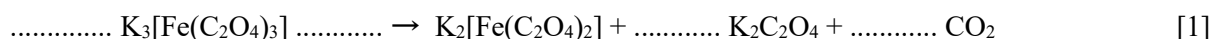
Complete the diagram to show the three-dimensional structure of the $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ complex ion.



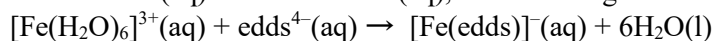
[1]

59. The anhydrous iron(III) compound $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ decomposes on heating to form a mixture of $\text{K}_2[\text{Fe}(\text{C}_2\text{O}_4)_2]$, $\text{K}_2\text{C}_2\text{O}_4$ and CO_2 .

Complete the equation for the decomposition of $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$.



60. When $\text{edds}^{4-}(\text{aq})$ is added to $\text{Fe}^{3+}(\text{aq})$, the following reaction occurs.



State the type of reaction that occurs.

..... [1]

61. Tollens' reagent can be used to distinguish between aldehydes and ketones. Tollens' reagent contains $[\text{Ag}(\text{NH}_3)_2]\text{OH}$, 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 $[\text{Ag}(\text{NH}_3)_2]\text{OH}$.

Construct equations for each of the steps in the preparation of $[\text{Ag}(\text{NH}_3)_2]\text{OH}$.

step 1

step 2 [2]

62. When 1.0 mol dm^{-3} $\text{NaCN}(\text{aq})$ 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 $\text{NaCN}(\text{aq})$ 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]

63. Write an ionic equation for the reduction of TiO_2^{+} by zinc metal in acidic conditions.

..... [1]

64. $[\text{Fe}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{4-}$ contains ligands which are anions of ethanedioic acid, $\text{HO}_2\text{CCO}_2\text{H}$. Complete the table to show any observations for the reactions of $\text{HO}_2\text{CCO}_2\text{H}$ with the named reagents. Where no change is observed, write 'none'. [2]

reagent	observations with $\text{HO}_2\text{CCO}_2\text{H}$
warm acidified manganate(VII)	
2,4-dinitrophenylhydrazine	
warm Tollens' reagent	

65. Some reactions of TiO_2 are shown in Fig. 3.1. The anion, acac^- , is a bidentate ligand.

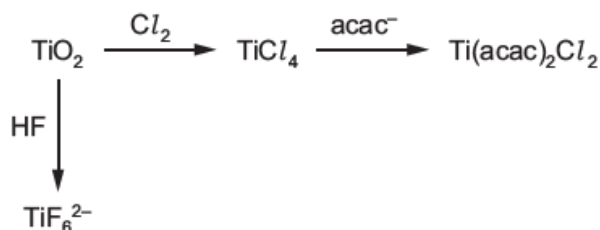


Fig. 3.1

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

..... [1]

66. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ decomposes readily on heating to form Cr_2O_3 , steam and an inert colourless gas. Construct an equation for the thermal decomposition of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$.

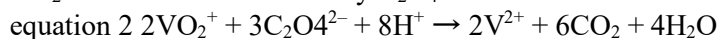
..... [1]

Calculations (Stoichiometry)

67. 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 .

$x = \dots\dots\dots$ [1]

68. VO_2^+ can be reduced to V^{2+} by $\text{C}_2\text{O}_4^{2-}$ in acidic conditions.



(i) In a titration, 25.00 cm^3 of $0.0300 \text{ mol dm}^{-3} \text{VO}_2^+(\text{aq})$ is added to 10 cm^3 of dilute sulfuric acid.

A solution of $0.0400 \text{ mol dm}^{-3} \text{C}_2\text{O}_4^{2-}(\text{aq})$ is then added from a burette until the end-point is reached.

The titration is repeated and concordant results are obtained, as shown in Table 3.1.

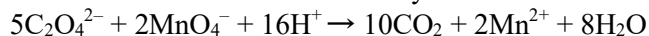
Table 3.1

	1	2
volume of $\text{C}_2\text{O}_4^{2-}(\text{aq})$ added / cm^3	28.15	28.10

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

[2]

69. The ethanedioate ion is oxidised by acidified KMnO_4 .



An experiment is performed to find the solubility of MgC_2O_4 in water.

A 40.0 cm^3 sample of saturated aqueous MgC_2O_4 requires 27.05 cm^3 of $0.00200 \text{ mol dm}^{-3}$ acidified KMnO_4 to oxidise all the $\text{C}_2\text{O}_4^{2-}$ ions.

Calculate the solubility, in mol dm^{-3} , of MgC_2O_4 in water. Show your working.

solubility = ...(Ans = 0.00338)..... mol dm^{-3} [3]

70. An impure sample of BaC_2O_4 , of mass 0.500 g, is added to 50.0 cm^3 of 0.0200 mol dm^{-3} acidified MnO_4^- (aq), an excess. A redox reaction takes place, and all the BaC_2O_4 reacts.
 The resulting solution, containing unreacted acidified MnO_4^- , is titrated with 0.0500 mol dm^{-3} Fe^{2+} (aq).
 The endpoint is reached when 30.40 cm^3 of 0.0500 mol dm^{-3} Fe^{2+} (aq) has been added.
 $\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 + 2\text{e}^-$
 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
 $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$
 Calculate the percentage by mass of BaC_2O_4 in the 0.500 g impure sample. Show your working.
 [Mr: BaC_2O_4 , 225.3]

- percentage by mass of BaC_2O_4 = ... [4]
71. The concentration of Cu^{2+} (aq) in a solution can be determined by the reaction of Cu^{2+} ions with I^- ions.
 reaction 1 $2\text{Cu}^{2+} + 4\text{I}^- \rightarrow 2\text{CuI} + \text{I}_2$
 The I_2 produced in reaction 1 is titrated against a solution containing thiosulfate ions, $\text{S}_2\text{O}_3^{2-}$, using a suitable indicator.
 reaction 2 $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$
 (i) A 25.0 cm^3 portion of a Cu^{2+} (aq) solution reacts with an excess of I^- (aq).
 The end-point of the titration occurs when 22.30 cm^3 of 0.150 mol dm^{-3} $\text{S}_2\text{O}_3^{2-}$ (aq) is added.
 Calculate the concentration of Cu^{2+} (aq) in the original solution.

concentration of Cu^{2+} (aq) = ... mol dm^{-3}

[2]

(ii) Identify a suitable indicator for the titration.

..... [1]

72. Acidified manganate(VII) ions, MnO_4^- , can be used to analyse the content of iron tablets by titration. Two identical iron tablets are crushed and dissolved in distilled water. The resulting solution is made up to 150.0 cm^3 with distilled water. 25.0 cm^3 of this solution requires 18.60 cm^3 of $0.0500 \text{ mol dm}^{-3}$ acidified MnO_4^- to reach the end-point. All the Fe^{2+} ions are oxidised. The relevant half-equations are shown.
- $$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$$
- $$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$$

(i) Describe the colour change observed at the end-point of this titration.

from to [1]

(ii) Calculate the mass, in mg, of iron in one tablet.

Assume that all the iron in the tablets is Fe^{2+} .

Show your working.

mass of iron in one tablet = ... mg [4]

73. Ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, form complexes with transition element ions. The concentration of $\text{C}_2\text{O}_4^{2-}$ ions can be found by reaction with acidified $\text{Cr}_2\text{O}_7^{2-}$ ions. $\text{C}_2\text{O}_4^{2-}$ ions are protonated and form HOOC-COOH molecules, which are oxidised by $\text{Cr}_2\text{O}_7^{2-}$. The half-equations are shown.
- $$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$$
- $$2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HOOC-COOH}$$

(i) Construct an equation for the reaction between acidified $\text{Cr}_2\text{O}_7^{2-}$ and HOOC-COOH .

..... [1]

(ii) A 25.0 cm^3 sample of a solution of $\text{Na}_2\text{C}_2\text{O}_4$ reacts with exactly 16.20 cm^3 of an acidified solution of $0.0500 \text{ mol dm}^{-3}$ $\text{K}_2\text{Cr}_2\text{O}_7$.

Calculate the concentration of the solution of $\text{Na}_2\text{C}_2\text{O}_4$.

Solution:

$$n(\text{Cr}_2\text{O}_7^{2-}) = 16.20/1000 \times 0.0500 = 8.1 \times 10^{-4} \text{ moles}$$

From the above chemical equation,

$$n(\text{Cr}_2\text{O}_7^{2-}) / n(\text{C}_2\text{O}_4^{2-}) = 1:3$$

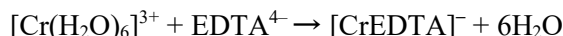
$$\text{or, } n(\text{C}_2\text{O}_4^{2-}) = 3 \times n(\text{Cr}_2\text{O}_7^{2-}) = 8.1 \times 10^{-4} \times 3 = 2.43 \times 10^{-3} \text{ moles}$$

$$[\text{Na}_2\text{C}_2\text{O}_4] = n/V = 2.43 \times 10^{-3} / 25 \times 1000 = 0.097 \text{ mol dm}^{-3}$$

$$[\text{Na}_2\text{C}_2\text{O}_4] = \dots\dots\dots (\text{ans} = 0.097 \text{ mol dm}^{-3}) \dots\dots\dots \text{mol dm}^{-3} [2]$$

74. 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, $\text{Cr}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, 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 $0.00800 \text{ mol dm}^{-3}$ aqueous EDTA^{4-} ions to reach the end-point.

The reaction occurs as shown.



Use the data to calculate the value of n in the formula of $\text{Cr}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$.

Show your working.

$n = \dots\dots\dots$

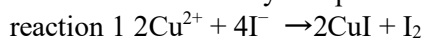
[3]

75. 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.

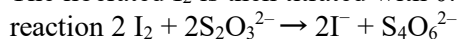
An excess of $\text{KI}(\text{aq})$ is added to a 25.0 cm^3 sample of this solution.

All of the copper is precipitated as white $\text{CuI}(\text{s})$.

Cu^{2+} ions are the only component in the solution that react with $\text{KI}(\text{aq})$. This is reaction 1.



The liberated I_2 is then titrated with $0.0200 \text{ mol dm}^{-3} \text{ S}_2\text{O}_3^{2-}$. This is reaction 2.



The titration requires 20.10 cm^3 of $0.0200 \text{ mol dm}^{-3} \text{ S}_2\text{O}_3^{2-}$ to reach the end-point.

(i) Calculate the number of moles of I_2 that are reduced in this titration.

number of moles of $\text{I}_2 = \dots\dots\dots \text{ mol}$ [1]

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

number of moles of copper = $\dots\dots\dots \text{ mol}$ [1]

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

percentage of copper = $\dots\dots\dots \%$ [1]

76. A solution contains 3.70 g of $\text{Na}_2[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ dissolved in 100 cm^3 of solution. A 25.0 cm^3 sample of this solution is warmed and then oxidised by $0.0100 \text{ mol dm}^{-3}$ acidified potassium manganate(VII). The equation for the redox reaction is shown.
- $$5\text{C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 10\text{CO}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$$
- Calculate the minimum volume of $0.0100 \text{ mol dm}^{-3}$ acidified potassium manganate(VII) needed to oxidise all of the ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, in the 25.0 cm^3 sample. Show all your working.
[Mr: $\text{Na}_2[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$, 321.5]

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

Calculations (electrode potentials)

77. Standard electrode potentials can be used to compare the stability of different complex ions for a given transition element.

Table 4.1 lists electrode potentials for some electrode reactions for $\text{Fe}^{3+} / \text{Fe}^{2+}$ systems.

Table 4.1

electrode reaction	E° / V
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{e}^- \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	+0.77
$[\text{Fe}(\text{CN})_6]^{3-} + \text{e}^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$	+0.36
$[\text{Fe}(\text{bipy})_3]^{3+} + \text{e}^- \rightleftharpoons [\text{Fe}(\text{bipy})_3]^{2+}$	+0.96

Use relevant data from Table 4.1 to state which iron(III) complex is hardest to reduce.

Explain your choice.

iron(III) complex

explanation

..... [1]

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

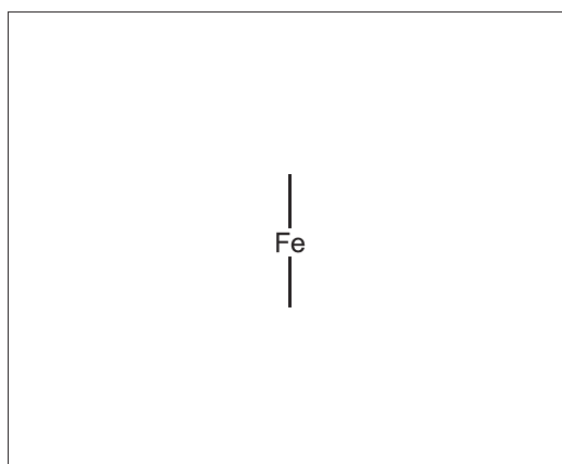
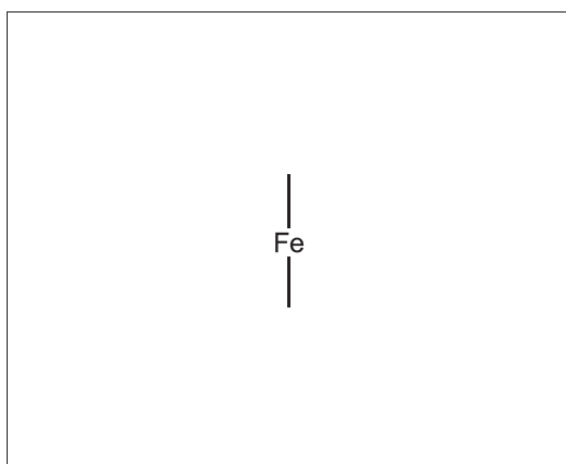
	half-equation	E^o / V
1	$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77
2	$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00
3	$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34
4	$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	-0.26

(i) Identify the vanadium species that forms when an excess of $H_2O_2(aq)$ reacts with $V^{2+}(aq)$ under standard conditions.

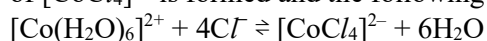
Explain your answer with reference to the data in Table 3.2.

.....

 [1]



79. (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.



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.

$$[Cd^{2+}(aq)] = 0.043 \text{ mol dm}^{-3}$$

$$[Cl^-(aq)] = 0.072 \text{ mol dm}^{-3}$$

Use your expression in (f)(ii) to calculate the concentration of $CdCl_4^{2-}(aq)$ in the equilibrium mixture.

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

*** ***

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