Edexcel

A - Level

Chemistry

CODE: (WCH11)

Topic 17

Organic chemistry – Transition metals and their chemistry

17A 1 Transition metal electronic configuration

WHICH ELEMENTS ARE THE TRANSITION METALS?

WHERE ARE THEY FOUND IN THE PERIODIC TABLE?

The Periodic Table is a classification system for elements, with groups like Group 1 and noble gases in Group 0 or 8. Period 4 reveals elements between Groups 2 and 4, including **transition metals**. These elements are classified as belonging to the d-block of the Periodic Table.

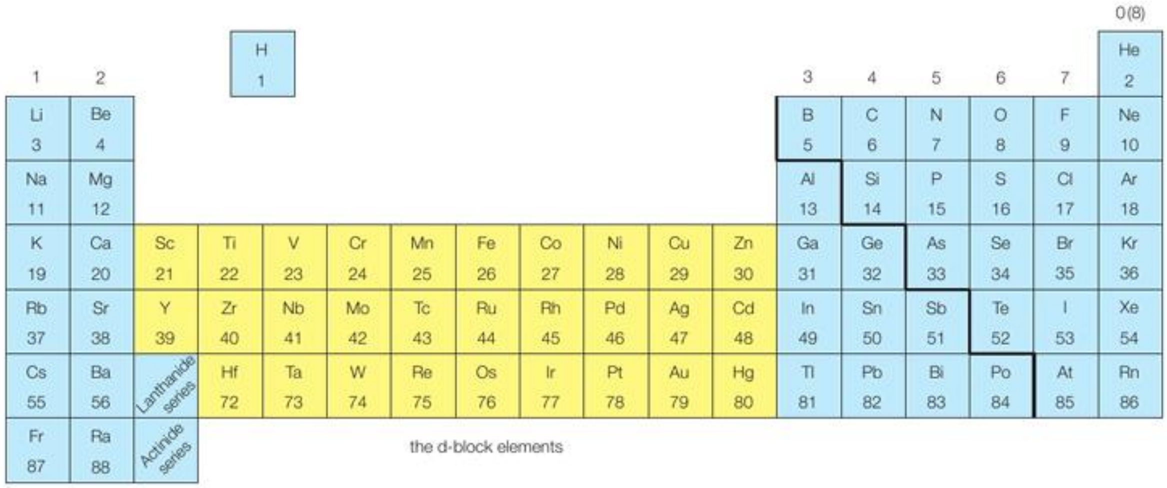


fig A The position of the transition metals in the periodic table.

WHAT IS A TRANSITION METAL?

Transition metals are d-block elements that form stable ions with incompletely filled d-orbitals. They are easier to list their characteristics than fully explain their nature, as their location is based on their electronic configurations.

CHARACTERISTICS OF TRANSITION METALS

Transition metals:

- are hard solids
- have high melting and boiling temperatures
- can act as catalysts
- form coloured ions and compounds
- form ions with different oxidation numbers
- form ions with incompletely filled d-orbitals.

fig B Transition metals include precious metals such as silver and gold, along with familiar metals such as copper, iron and zinc. Each transition metal has more than one oxidation state, and their salts form coloured solutions in water.

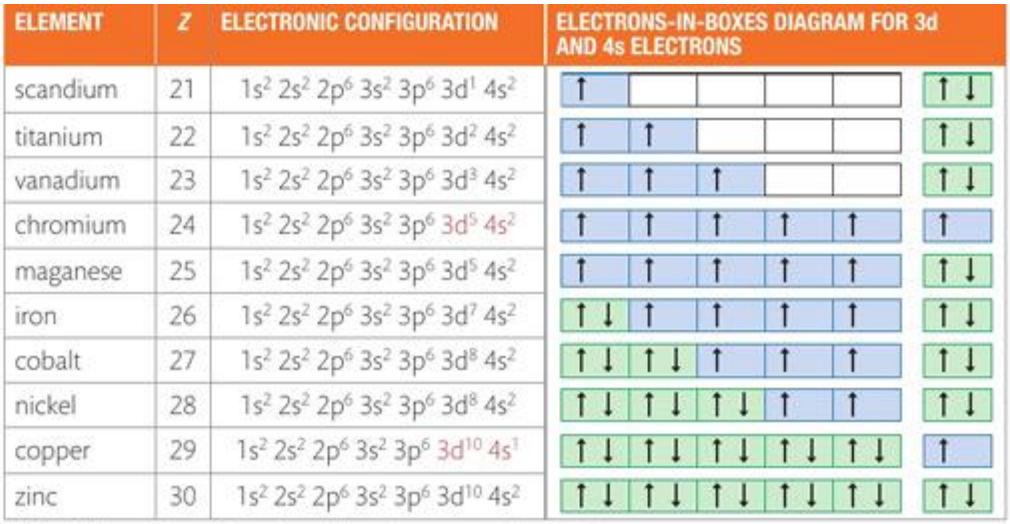
ELECTRONIC CONFIGURATIONS

THE ELEMENTS

Topic 2 (Book 1: IAS) explains how to write electronic configurations of elements from hydrogen to krypton, including ten d-block elements in Period 4. Table A shows these in full using spdf notation, with electrons-in-box diagrams. Copper and chromium irregularities are shown in red. Abbreviated shorter forms of electronic configuration can be used.

THE IONS

When these elements form ions, they lose one or more electrons. Scandium loses both of its 4s electrons and its only 3d electron, forming the Sc^{3+} ion. Zinc loses both of its 4s electrons and none of its 3d electrons, forming the Zn^{2+} ion. Because these two elements form only one ion each, and these ions have no incompletely filled d-orbitals, they are not classified as transition metals.



ELEMENT	Z	ELECTRONIC CONFIGURATION	ELECTRONS-IN-BOXES DIAGRAM FOR 3d AND 4s ELECTRONS					
scandium	21	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$	↑					↑↓
titanium	22	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$	↑	↑				↑↓
vanadium	23	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$	↑	↑	↑			↑↓
chromium	24	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$	↑	↑	↑	↑	↑	↑
maganese	25	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$	↑	↑	↑	↑	↑	↑↓
iron	26	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$	↑↓	↑	↑	↑	↑	↑↓
cobalt	27	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$	↑↓	↑↓	↑	↑	↑	↑↓
nickel	28	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$	↑↓	↑↓	↑↓	↑	↑	↑↓
copper	29	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$	↑↓	↑↓	↑↓	↑↓	↑↓	↑
zinc	30	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

table A Electronic configurations of the elements scandium to zinc.

The eight elements form ions by losing their 4s electrons before their 3d electrons, resulting in ions with different oxidation numbers. Higher oxidation numbers are not found in simple ions and typically contain an electronegative element, often oxygen.

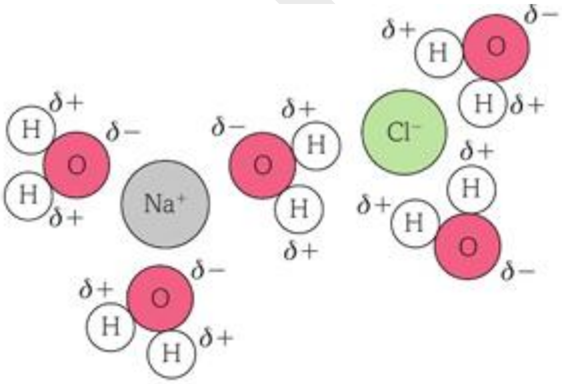
SUBJECT VOCABULARY

transition metal an element that forms one or more stable ions with incompletely filled d-orbitals

17A 2 Ligands and complexes

SYMBOLS AND EQUATIONS WITHOUT LIGANDS

Na^+, the sodium ion, is a symbol for metal ions and is dissolved in water. The process involves attracted oxygen atoms in water molecules, keeping sodium ions in solution. Na^+ is surrounded by water molecules, with water molecules changing.



▲ **fig A** Positive sodium ions surrounded by δ− oxygen atoms in water molecules, and negative chloride ions surrounded by δ+ hydrogen atoms in water molecules.

When you write equations for the reactions of transition metal ions you can sometimes use the same method. For example, the iron(II) ion can be shown as Fe2+, or as Fe2+(aq) to show that it is dissolved in water.

The equation for a displacement reaction involving a transition metal ion is:

$$Mg(s) + Fe^{2+}(aq) \rightarrow Mg^{2+}(aq) + Fe(s)$$

SYMBOLS AND EQUATIONS WITH LIGANDS

Non-transition metal ions have larger radii than transition metal ions, like K^+ and Fe2+. Transition metal ions attract electron-rich species, like water molecules, forming six bonds, forming a structure represented in diagrams. This allows for more strong attraction.

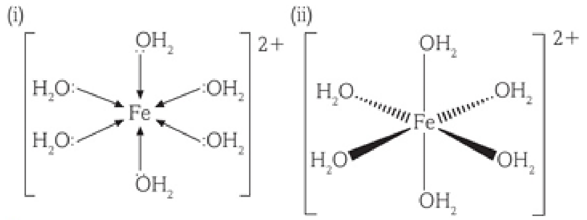


fig B Here are two ways to represent a complex ion: (i) shows one of the lone pairs of electrons on the oxygen atoms and the dative covalent bonds with arrows; (ii) shows the 3D arrangement of bonds and water molecules around the metal ion.

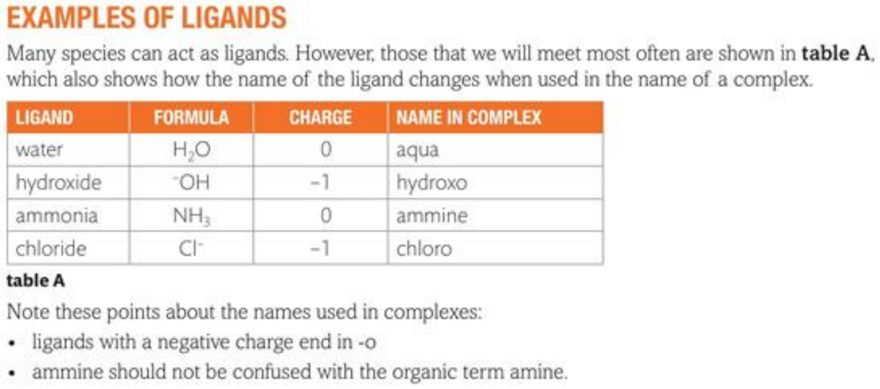
In fig B (i):

- the bonds are shown with arrowheads, indicating that they are **dative (coordinate) bonds** - one of the lone pairs of electrons on each oxygen atom is used to form the bond
- the whole structure is shown inside square brackets, and the original charge of the Fe2+ ion is shown outside the bracket
- the water molecules are arranged in a regular pattern around the Fe - this arrangement can be explained in terms of the electron pair repulsion theory.

In fig B (ii):

- solid wedges represent bonds coming out of the plane of the paper
- striped wedges represent bonds going behind the plane of the paper.

These water molecules, and other electron-rich species that can form dative bonds in the same way, are called **ligands**. The complete formulae are called **complexes**. As most complexes have charges, they are often called **complex ions**, but where there is no overall charge, it is better to use the term 'complex'. The total number of dative bonds around the metal ion is called the **coordination number.**



EXAMPLES OF LIGANDS

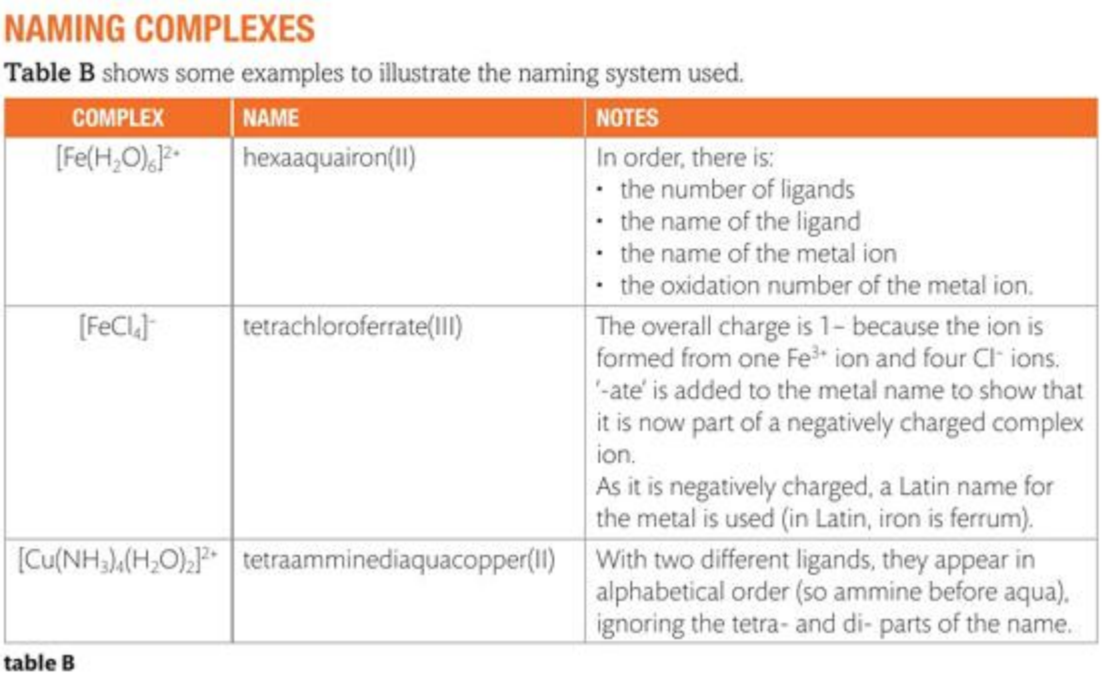
Many species can act as ligands. However, those that we will meet most often are shown in **table A**, which also shows how the name of the ligand changes when used in the name of a complex.

LIGAND	FORMULA	CHARGE	NAME IN COMPLEX
water	H_2O	0	aqua
hydroxide	^-OH	−1	hydroxo
ammonia	NH_3	0	ammine
chloride	Cl^-	−1	chloro

table A

Note these points about the names used in complexes:

- ligands with a negative charge end in -o
- ammine should not be confused with the organic term amine.

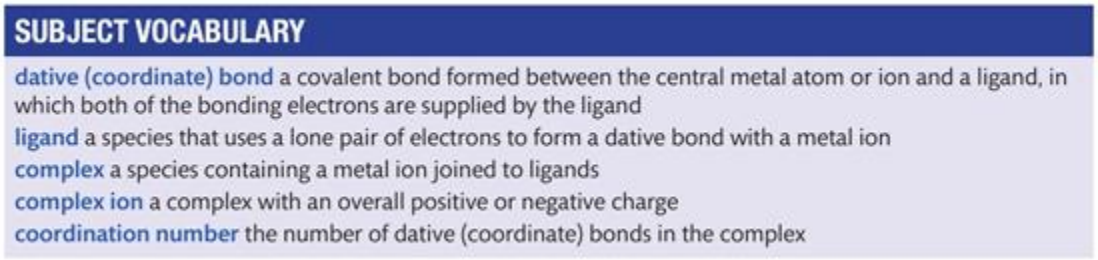


NAMING COMPLEXES

Table B shows some examples to illustrate the naming system used.

COMPLEX	NAME	NOTES
$[Fe(H_2O)_6]^{2+}$	hexaaquairon(II)	In order, there is: • the number of ligands • the name of the ligand • the name of the metal ion • the oxidation number of the metal ion.
$[FeCl_4]^-$	tetrachloroferrate(III)	The overall charge is 1− because the ion is formed from one Fe^{3+} ion and four Cl^- ions. '-ate' is added to the metal name to show that it is now part of a negatively charged complex ion. As it is negatively charged, a Latin name for the metal is used (in Latin, iron is ferrum).
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	tetraamminediaquacopper(II)	With two different ligands, they appear in alphabetical order (so ammine before aqua), ignoring the tetra- and di- parts of the name.

table B



SUBJECT VOCABULARY

dative (coordinate) bond a covalent bond formed between the central metal atom or ion and a ligand, in which both of the bonding electrons are supplied by the ligand

ligand a species that uses a lone pair of electrons to form a dative bond with a metal ion

complex a species containing a metal ion joined to ligands

complex ion a complex with an overall positive or negative charge

coordination number the number of dative (coordinate) bonds in the complex

17A 3 The origin of colour in complex

A COMPLEX EXPLANATION!

Colour is very important in our world - think of traffic lights, paint charts, clothing and the colours of flowers. There are scientific explanations for colour in plants, paints and dyes. However, these explanations are often specific to the type of chemical substance being considered.

As far as transition metal complexes are concerned, a full explanation includes three main concepts:

- the electromagnetic spectrum and the colour wheel
- the connection between colour, energy and wavelength
- the electronic configurations of transition metal ions.

THE ELECTROMAGNETIC SPECTRUM

We first need to find out about the electromagnetic spectrum (fig A). You are probably familiar with the idea that the visible part of the electromagnetic spectrum (sometimes described as 'white light') is made up of a mixture of colours (sometimes described as the colours of the rainbow).

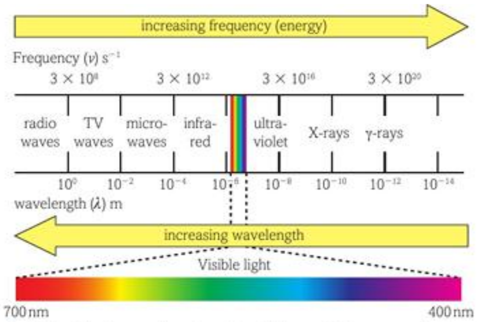


fig A The diagram shows how the visible part of the spectrum fits into the complete electromagnetic spectrum.

So, how many colours make up white light? A traditional answer is seven:

red orange yellow green blue indigo violet

THE COLOUR WHEEL

THE COLOURS IN A COLOUR WHEEL

Now consider the colours in the visible spectrum shown as a wheel, with the red and violet ends of the spectrum next to each other. There are many different colour wheels with varying numbers of colours (just try a web search), but fig B shows one that contains seven colours corresponding to those listed above. Clockwise from the top, they are shown in order from red to violet.

COMPLEMENTARY COLOURS

In colour wheels, complementary colours are the colours shown opposite each other. In this one, red is opposite blue and green. When white light is passed through a solution containing a transition metal complex, some wavelengths of light are absorbed by the complex. The light emerging will therefore contain proportionately more of the complementary colour. So, if a complex absorbs red light, the light emerging will look blue or green (fig C).

fig B This is one example of a colour wheel.

fig C A range of transition metal solutions. From left to right: Ti^{2+}, V^{3+}, VO^{2+}, Cr^{3+}, $Cr_2O_7^{2-}$, Mn^{2+}, MnO_4^-, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}.

COLOUR DEPENDS ON ELECTRONS IN 3d ENERGY LEVELS

The color difference in aqueous solutions of metal ions is a complex process, but the basic explanation is that the difference in color is caused by the presence of zinc and copper ions. The electronic configurations of Zn2+ and Cu2+ ions are shown in fig D.

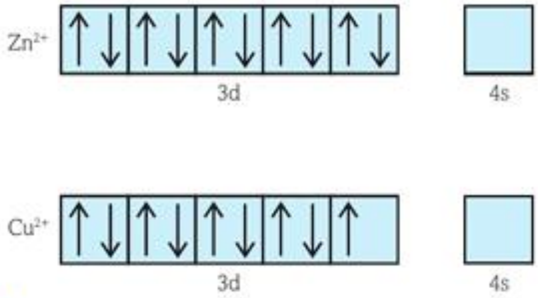


fig D The diagram shows the configurations of the 3d and 4s electrons in Zn^{2+} and Cu^{2+}.

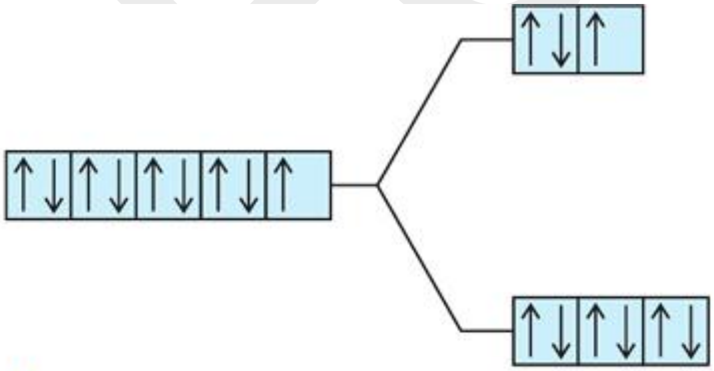


fig E In the Cu^{2+} ion, the water ligands split the 3d energy level into lower and higher energy levels.

Electrons move from lower energy levels to higher energy levels through **promotion or excitation**. The energy gained depends on the difference in energy between the two levels. The energy gained is directly proportional to the frequency of the absorbed light and inversely proportional to the wavelength. In the case of Cu2+ ions, low frequency radiation is absorbed from the red end, resulting in blue light transmission.

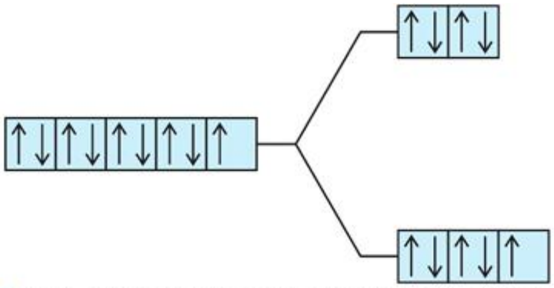


fig F Note that one electron has moved from the lower energy level to the higher energy level.

SUBJECT VOCABULARY

electromagnetic spectrum the range of all wavelengths and frequencies of all the types of radiation
complementary colours colours opposite each other on a colour wheel
promotion (or **excitation**) when an electron moves from a lower energy level to a higher energy level

17A 4Common shapes of complexes

PREDICTING THE SHAPES OF COMPLEXES

USING ELECTRON PAIR REPULSION THEORY

The electron pair repulsion theory can be applied to predict and explain the shapes of complexes by focusing on the number of electron pairs donated by ligands to the central metal ion. This theory can be applied to both simple molecules and transition metal complexes.

NUMBER OF LIGANDS	ELECTRON PAIRS DONATED	SHAPE	BOND ANGLE	EXAMPLE OF A COMPLEX ION	EXAMPLE OF A SIMPLE MOLECULE
6	6	octahedral	90°	$[Co(NH_3)_6]^{2+}$	SF_6
4	4	tetrahedral	109.5°	$[CuCl_4]^{2-}$	CH_4
2	2	linear	180°	$[Ag(NH_3)_2]^+$	$BeCl_2$

table A The electron pair repulsion theory can predict the shapes of simple molecules and complex ions.

OCTAHEDRAL COMPLEXES

The most common ligands in most octahedral complexes are water, ammonia and the hydroxide ion. These ligands have different numbers of lone pairs of electrons (ammonia has one, water has two and the hydroxide ion has three). However each ligand uses only one lone pair to form a coordinate bond with the transition metal ion. As they contain six ligands, the complexes are sometimes described as having **six-fold coordination**.

ABBREVIATED FORMULA	NAME	COLOUR
$[Mn(H_2O)_6]^{2+}$	hexaaquamanganese(II)	very pale pink (usually described as colourless)
$[Fe(H_2O)_4(OH)_2]$	tetraaquadihydroxoiron(II)	pale green
$[Cr(OH)_6]^{3-}$	hexahydroxochromate(III)	green

table B Examples of octahedral complexes.

Fig A shows the shapes of these complexes.

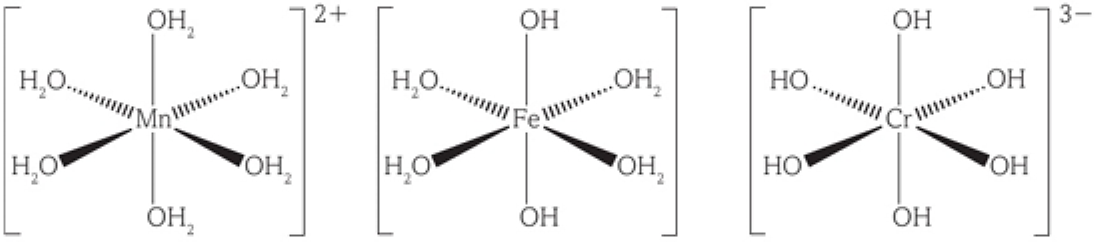


fig A The structures of some octahedral complexes.

Note that:

- Solid and striped wedge bonds are used to indicate the shapes, although the 3D shape can be shown in other ways.
- The overall charges are all different - this depends on the charge on the original transition metal ion and on how many negatively charged ligands there are.
- All three structures use square brackets, although these are sometimes left out when the complex is neutral.
- The water ligands are shown as both H2O and OH2- the important point is that the bond must be shown to come from oxygen because it supplies the lone pair of electrons for the dative bond.

TETRAHEDRAL AND LINEAR COMPLEXES

Tetrahedral complexes are less common than octahedral complexes, with chloride ions acting as ligands in $[CuCl_4]^{2-}$ ion. Due to chlorine's Period 3 element size, six chloride ions are usually not enough. The only linear complex is the reactive ion in Tollens' reagent, which has only two ligands due to silver's transition metal behavior in Period 5.

Fig B shows the shapes of these two complexes.

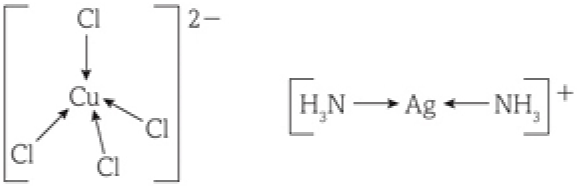


fig B The structures of a tetrahedral complex and a linear complex.

SUBJECT VOCABULARY

six-fold coordination complexes in which there are six ligands forming coordinate bonds with the transition metal ion

17A 5 Squar planar complexes

SQUARE PLANAR MOLECULES

The electron pair repulsion theory predicts the shapes of simple molecules and ions, but a **square planar** shape is seen in xenon tetrafluoride (XeF_4). Xenon atoms have eight electrons, and fluorine atoms form covalent bonds. The outer energy shell contains 12 electrons, arranged in six pairs, with two lone pairs repelling each other.

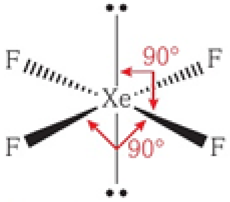


fig A The square planar shape of the xenon tetrafluoride molecule.

cis-PLATIN

Square planar complexes, like cis-platin, are less common than octahedral and tetrahedral complexes. This complex's square planar shape is due to its transition metal behavior in Period 6, which differs from Period 4 transition metals. Its effective treatment for testicular cancer is noteworthy.

CIS-TRANS ISOMERS

You have learned about E-Z and cis-trans isomerism in Topic 5 (Book 1: IAS). Your understanding of this type of isomerism can now be applied to inorganic compounds such as cis-platin and its isomer, trans-platin. These consist of a platinum(II) ion, two ammonia ligands and two chloride ion ligands.

Fig B shows the structures of these isomers and the relationship between them.

- The cis- prefix indicates that identical ligands are next to each other.
- The trans-prefix indicates that they are opposite each other.

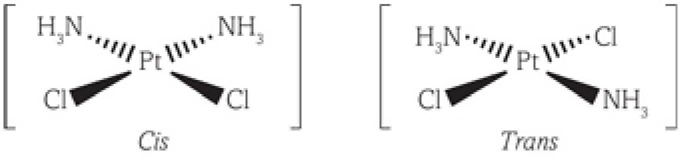


fig B Structures of *cis*-platin and *trans*-platin.

ANTI-CANCER ACTION

A full understanding of how cis-platin kills cancer cells is beyond the aims of this book. Put simply:

- All cells, including cancer cells, contain deoxyribonucleic acid (DNA).
- During cell division, the two strands of DNA must separate from each other to form more DNA.
- The structure of cis-platin enables it to form a bond between the two strands of DNA (fig C), which prevents them from separating and so prevents the cancer cells from dividing.

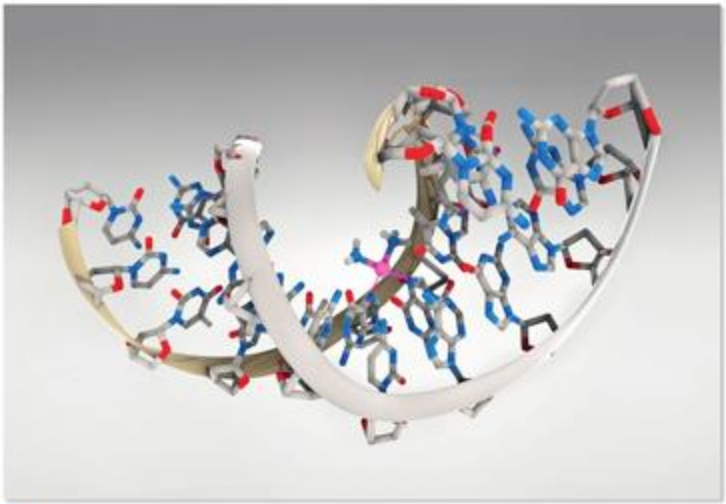


fig C DNA strands are shown in grey and *cis*-platin in pink.

trans-PLATIN

The isomers trans-platin and cis-platin have different structures. The difference in structure means that trans-platin is a much less effective cancer treatment than cis-platin. It is also more toxic. So, it is important to use only the cis-isomer in the cancer treatment.

SUBJECT VOCABULARY

square planar this shape contains a central atom or ion surrounded by four atoms or ligands in the same plane and with bond angles of 90°

17A 6Multidentate ligands

DENTICITY

When ligands were introduced earlier in this book we could have described them as **monodentate ligands**. You can think of monodentate as meaning 'one tooth' or 'one bite', which means that the ligand uses one lone pair of electrons on one atom to form the dative bond with the metal ion.

Now for **bidentate ligands**. Bi means two, so a bidentate ligand has two atoms, each of which can use a lone pair of electrons to form a dative bond with the metal ion. You can imagine that a bidentate ligand has two atoms that can 'bite' onto the metal ion.

You can work out for yourself what a **multidentate ligand** is - a ligand with several atoms, each of which uses a lone pair of electrons to form a dative bond with the metal ion. The most common example you are likely to meet has six such atoms, so it could be described as a **hexadentate ligand.**

BIDENTATE LIGANDS

The most likely bidentate ligand you will meet in your chemistry course is the organic compound with the structural formula $NH_2CH_2CH_2NH_2$. Its correct name is 1,2-diaminoethane, although for a reason we will soon see, it is sometimes called ethylenediamine - the ethylene comes from the CH_2CH_2 part, and it is correctly described as a diamine because there are two amino groups. Its structure is:

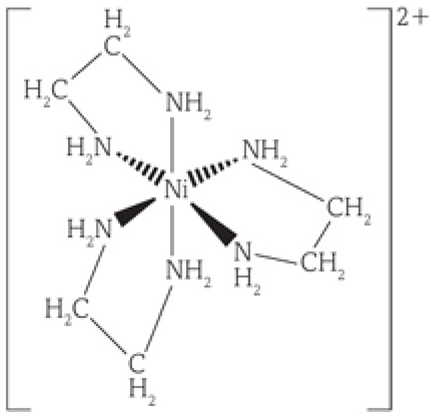


fig B The structure of the complex formed when Ni^{2+} reacts with three molecules of 1,2-diaminoethane.

If this complex were formed by the reaction between a hexaaqua metal ion and 1,2-diaminoethane, this abbreviated equation could be written:

$$[Ni(H_2O)_6]^{2+} + 3en \rightarrow [Ni(en)_3]^{2+} + 6H_2O$$

MULTIDENTATE LIGANDS

The most likely multidentate ligand you will see in your chemistry course is an organic ion with a rather complicated structure.

First, consider the structure of 1,2-diaminoethane. Next, imagine that each of the four hydrogen atoms on the two nitrogens are replaced by $-CH_2COOH$ (this is ethanoic acid bonded to the nitrogens via the CH_3 group), as shown in fig C.

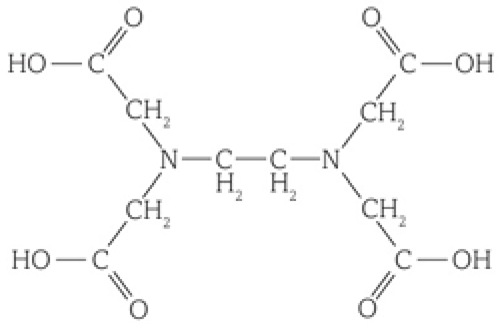


fig C The structure of the EDTA molecule.

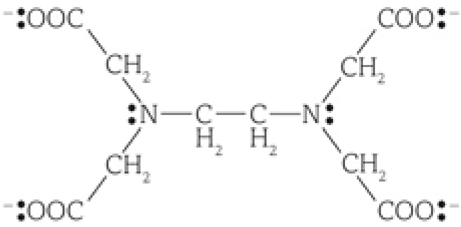


fig D The structure of the EDTA^{4-} ion.

Ethanoic acid, previously known as acetic acid, can be renamed ethylenediaminetetraacetic acid due to its structure. The compound's abbreviation is 'EDTA', which is formed when each ethanoic acid group loses its H+ ion, resulting in a hexadentate ligand with four negative charges, referred to as EDTA^{4-}.

The advantage of displaying the EDTA^{4-} ion in this way is that it clearly shows the six lone pairs of electrons that are used to form the dative bonds when the ion acts as a ligand (two pairs on the nitrogen atoms and four pairs on the oxygen atoms). **Fig E** uses a skeletal formula to show the complex formed between one M^{2+} ion and one EDTA^{4-} ion.

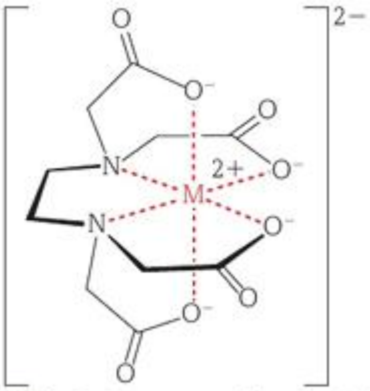


fig E The structure of the complex formed between M^{2+} and EDTA^{4-}.

THE STABILITY OF COMPLEXES

Most complexes are stable, in the sense that they do not decompose easily. In this heading, 'stability' does not refer to complexes containing transition metal ions with unstable oxidation numbers, such as +2 in scandium (Sc2+). Instead, it refers to a comparison of the stabilities of two complexes in which the number of ligands has changed. For a discussion of 'stability' see Topic 12. Consider this ligand exchange reaction in which a monodentate ligand is replaced by a bidentate ligand:

$$[Cu(H_2O)_6]^{2+} + 3en \rightarrow [Cu(en)_3]^{2+} + 6H_2O$$

When a monodentate ligand is replaced by a bidentate or
hexadentate ligand, the increase in stability is even greater, as in this example with EDTA^{4-}:

$$[Cu(H_2O)_6]^{2+} + EDTA^{4-} \rightarrow [Cu(EDTA)]^{2-} + 6H_2O$$

Here, six water ligands are replaced by one EDTA4- ligand, so the total number of species has increased from two to seven.

HAEMOGLOBIN AND OXYGEN TRANSPORT

You may know that haemoglobin is a protein in red blood cells that plays a vital role in transporting oxygen through the bloodstream in humans and other animals. Here is a simplified explanation of the role of haemoglobin in oxygen transport, without including details of its structure and of the haem group that it contains:

- Haemoglobin consists of three main parts, the largest of which is protein (the 'globin' part).
- Within the protein, there are four haem groups that are made up mostly of carbon and hydrogen atoms.
- Inside each haem group, there are four nitrogen atoms that hold an Fe2+ ion by forming dative bonds with it in a square planar structure.
- There is a fifth dative bond from the protein to the Fe2+ ion.
- When blood passes through the lungs, haemoglobin collects oxygen molecules and transports them to cells, where it is released.
- When haemoglobin collects oxygen, the oxygen molecule acts as a ligand by using one of its lone pairs of electrons to form a dative bond with one of the Fe2+ ions.

Fig F is a very simplified diagram showing the six dative bonds in oxyhaemoglobin.

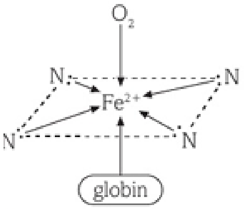


fig F Part of the structure of oxyhaemoglobin, showing the dative covalent bonds to the central metal ion.

HAEMOGLOBIN AND CARBON MONOXIDE

Carbon monoxide acts as a ligand, forming a weak dative bond with haemoglobin. This allows oxygen to be released easily. However, carbon monoxide replaces oxygen in haemoglobin, causing a ligand substitution reaction. The strong dative bond prevents easy breakage, potentially causing too little oxygen to support life.

Put very simply, this reaction is reversible:

haemoglobin + oxygen ⇌ oxyhaemoglobin

but this reaction is not easily reversible

haemoglobin + carbon monoxide → carboxyhaemoglobin

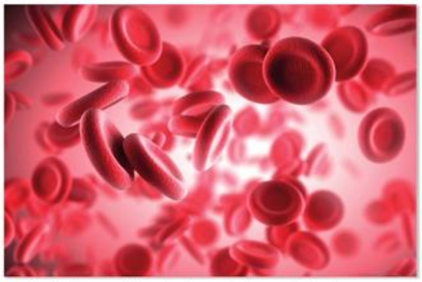


fig G These red blood cells contain haemoglobin that transports oxygen from the lungs to the cells in the body.

SUBJECT VOCABULARY

monodentate ligand	a molecule or ion that forms one dative bond with a metal ion
bidentate ligand	a molecule or ion that forms two dative bonds with a metal ion
multidentate ligand	a molecule or ion that forms several dative bonds with a metal ion
hexadentate ligand	a molecule or ion that forms six dative bonds with a metal ion

17B 1 Different types of reactions

TYPES OF REACTIONS

So far, we have considered the origin of colour in transition metal ions. We can now consider why there are often colour changes when transition metal ions take part in reactions. Four main types of reactions can occur:

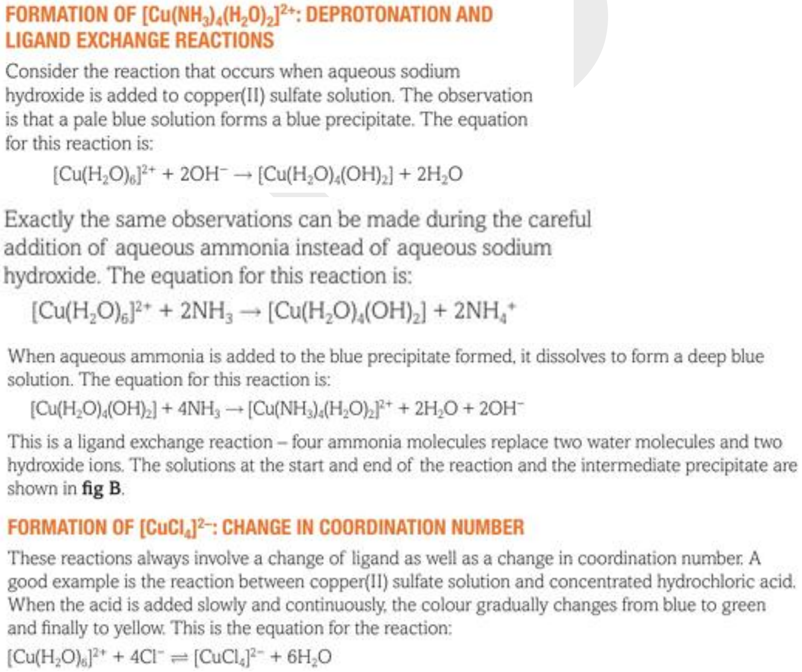
- redox- the oxidation number of the transition metal ion changes
- **deprotonation**-one or more of the ligands gains or loses a hydrogen ion (proton)
- **ligand exchange** - one or more of the ligands around the transition metal ion is replaced by a different ligand
- coordination number change - the number of ligands changes. Any one of these types of reactions can cause a change in the colour of the complex. Some reactions involve more than one of these types of reactions.

CHANGE IN OXIDATION NUMBER

An aqueous solution containing Fe2+(aq) ions is pale green, but when it is exposed to air it gradually turns yellow or brown, as the oxidation number of iron increases from +2 to +3. The type and number of ligands remain unchanged in this oxidation reaction.

Iron(II) sulphate ($FeSO^4$) Iron(III) sulphate ($Fe2(SO^4)^3$)

▲ **fig A** Solid samples clearly show colour differences between ions.



FORMATION OF $[Cu(NH_3)_4(H_2O)_2]^{2+}$: DEPROTONATION AND LIGAND EXCHANGE REACTIONS

Consider the reaction that occurs when aqueous sodium hydroxide is added to copper(II) sulfate solution. The observation is that a pale blue solution forms a blue precipitate. The equation for this reaction is:

$$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow [Cu(H_2O)_4(OH)_2] + 2H_2O$$

Exactly the same observations can be made during the careful addition of aqueous ammonia instead of aqueous sodium hydroxide. The equation for this reaction is:

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

When aqueous ammonia is added to the blue precipitate formed, it dissolves to form a deep blue solution. The equation for this reaction is:

$$[Cu(H_2O)_4(OH)_2] + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 2H_2O + 2OH^-$$

This is a ligand exchange reaction – four ammonia molecules replace two water molecules and two hydroxide ions. The solutions at the start and end of the reaction and the intermediate precipitate are shown in **fig B**.

FORMATION OF $[CuCl_4]^{2-}$: CHANGE IN COORDINATION NUMBER

These reactions always involve a change of ligand as well as a change in coordination number. A good example is the reaction between copper(II) sulfate solution and concentrated hydrochloric acid. When the acid is added slowly and continuously, the colour gradually changes from blue to green and finally to yellow. This is the equation for the reaction:

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$$

▲ **fig B** The pale blue solution contains $[Cu(H_2O)_6]^{2+}$, the pale blue precipitate contains $[Cu(H_2O)_4(OH)_2]$ and the deep blue solution contains $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

▲ **fig C** The pale blue solution contains $[Cu(H_2O)_6]^{2+}$, the yellow solution on the right contains $[CuCl_4]^{2-}$ and the green solution in the middle contains a mixture of the two.

SUBJECT VOCABULARY

deprotonation the removal of one or more hydrogen ions (protons) from a complex ion

ligand exchange when one ligand in a complex ion is replaced by a different ligand

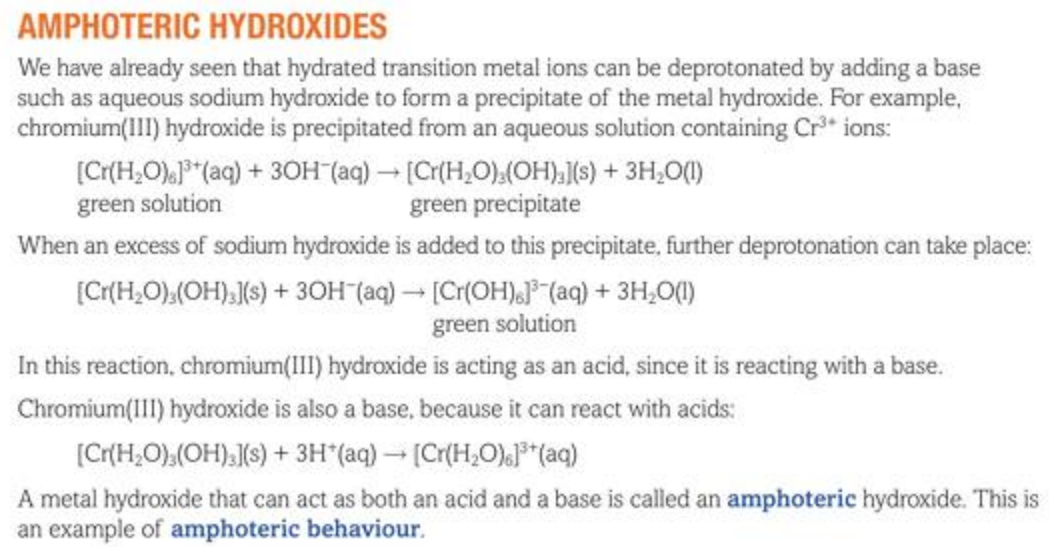
amphoteric (substance) a substance that can act both as an acid and as a base

amphoteric behaviour the ability of a species to react with both acids and bases

The state symbols, all (aq), have been left out for clarity.

You can see that all six water ligands have been replaced by four chloride ions. This reaction is also an example of a change in coordination number, from 6 to 4. Note that although the charge on the complex has changed from 2+ to 2-, there has been no change in oxidation number.

The arrow shows that the reaction is reversible, which helps to explain the colour change observed. The hexaaquacopper(II) ion is blue and the tetrachlorocuprate(II) ion is yellow, so the green colour is due to a mixture of the blue and yellow complex ions. The solutions at the start and end of the reaction and the intermediate mixture are shown in fig C.



AMPHOTERIC HYDROXIDES

We have already seen that hydrated transition metal ions can be deprotonated by adding a base such as aqueous sodium hydroxide to form a precipitate of the metal hydroxide. For example, chromium(III) hydroxide is precipitated from an aqueous solution containing Cr^{3+} ions:

$$\underset{\text{green solution}}{[Cr(H_2O)_6]^{3+}(aq)} + 3OH^-(aq) \rightarrow \underset{\text{green precipitate}}{[Cr(H_2O)_3(OH)_3](s)} + 3H_2O(l)$$

When an excess of sodium hydroxide is added to this precipitate, further deprotonation can take place:

$$[Cr(H_2O)_3(OH)_3](s) + 3OH^-(aq) \rightarrow \underset{\text{green solution}}{[Cr(OH)_6]^{3-}(aq)} + 3H_2O(l)$$

In this reaction, chromium(III) hydroxide is acting as an acid, since it is reacting with a base.

Chromium(III) hydroxide is also a base, because it can react with acids:

$$[Cr(H_2O)_3(OH)_3](s) + 3H^+(aq) \rightarrow [Cr(H_2O)_6]^{3+}(aq)$$

A metal hydroxide that can act as both an acid and a base is called an **amphoteric** hydroxide. This is an example of **amphoteric behaviour**.

17B 2 reactions of cobalt and iron complex

REACTIONS INVOLVING COBALT COMPLEXES

▲ **fig A** The bright colour of these glass bottles is caused by blue cobalt compounds.

REACTION WITH ALKALIS

Consider the reaction that occurs when aqueous sodium hydroxide is added to a solution containing the hexaaquacobalt(II) ion until no further change is seen. The observation is that a pink solution forms a blue precipitate. The equation for this reaction is:

$$[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow [Co(H_2O)_4(OH)_2] + 2H_2O$$

The same observations can be made when aqueous ammonia is used as the alkali. However, when aqueous ammonia is added to excess, there is an observation not made with aqueous sodium hydroxide- the precipitate dissolves to form a pale yellow solution. The equation for the deprotonation reaction is:

$$[Co(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Co(H_2O)_4(OH)_2] + 2NH_4^+$$

The equation for the ligand exchange reaction forming the pale yellow solution is:

$$[Co(H_2O)_4(OH)_2] + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 4H_2O + 2OH^-$$

REACTION WITH CONCENTRATED HYDROCHLORIC ACID

This reaction is very like the one with the $[Cu(H_2O)_6]^{2+}$ ion. When concentrated hydrochloric acid is slowly added to a solution containing the hexaaquacobalt(II) ion, the pink solution gradually changes to blue. This is the equation for the reaction:

$$[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$$

You can see that all six water ligands have been replaced by four chloride ions. This reaction is also an example of a change in coordination number, from 6 to 4. Note that although the charge on the complex has changed from 2+ to 2-, there has been no change in oxidation number.

REACTIONS INVOLVING IRON COMPLEXES

REACTION OF IRON (II) COMPLEXES WITH ALKALIS

Consider the reaction that occurs when aqueous sodium hydroxide is added to a solution containing the hexaaquairon(II) ion until no further change is seen. The observation is that a pale green solution forms a green precipitate. The equation for this reaction is:

$$[Fe(H_2O)_6]^{2+} + 2OH^- \rightarrow [Fe(H_2O)_4(OH)_2] + 2H_2O$$

As with copper and cobalt, this is a deprotonation reaction - the two hydroxide ions have removed hydrogen ions from two of the water ligands and converted them into water molecules. The two water ligands that have lost hydrogen ions are now hydroxide ligands.

The same observations can be made when aqueous ammonia is used as the alkali. The equation for the deprotonation reaction is:

$$[Fe(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Fe(H_2O)_4(OH)_2] + 2NH_4^+$$

Upon standing, the colour of the green precipitate gradually changes to brown as oxygen from the atmosphere causes oxidation, forming $[Fe(H_2O)_3(OH)_3]$ – this is the triaquatrihydroxoiron(III) complex.

REACTION OF IRON (III) COMPLEXES WITH ALKALIS

Consider the reaction that occurs when aqueous sodium hydroxide is added to a solution containing the hexaaquairon(III) ion until no further change is seen. The observation is that a yellow-brown solution forms a brown precipitate. The equation for this reaction is:

$$[Fe(H_2O)_6]^{3+} + 3OH^- \rightarrow [Fe(H_2O)_3(OH)_3] + 3H_2O$$

As with iron(II), this is a deprotonation reaction - the three hydroxide ions have removed hydrogen ions from three of the water ligands and converted them into water molecules. The three water ligands that have lost hydrogen ions are now hydroxide ligands.

The same observations can be made when aqueous ammonia is used as the alkali. The equation for the deprotonation reaction is:

$[Fe(H_2O)_6]^{3+} + 3NH_3 \rightarrow [Fe(H_2O)_3(OH)_3] + 3NH_4^+$

There are no further reactions when an excess of either aqueous sodium hydroxide or aqueous ammonia is added and no further changes upon standing.

17B 3 Chemistry of chromium

INTRODUCTION

Some of the reactions of chromium are similar to those we have already met for the ions of copper, cobalt, iron(II) and iron(III). However, chromium has ions in which the metal has an oxidation number of +6, so reactions involving these ions must be considered in a different way.

A WORD OF WARNING

The spectrum of visible light contains infinite colors, sometimes referred to as the seven of the rainbow. Human perception of colors varies, with specific colors being described differently by different individuals.
The situation with the colours used to describe chromium compounds is further complicated by these factors:

- Some compounds have different colours as solids and aqueous solutions.
- The colour of a solution depends on concentration.
- The presence of dissolved oxygen in an aqueous solution can affect the colour observed.

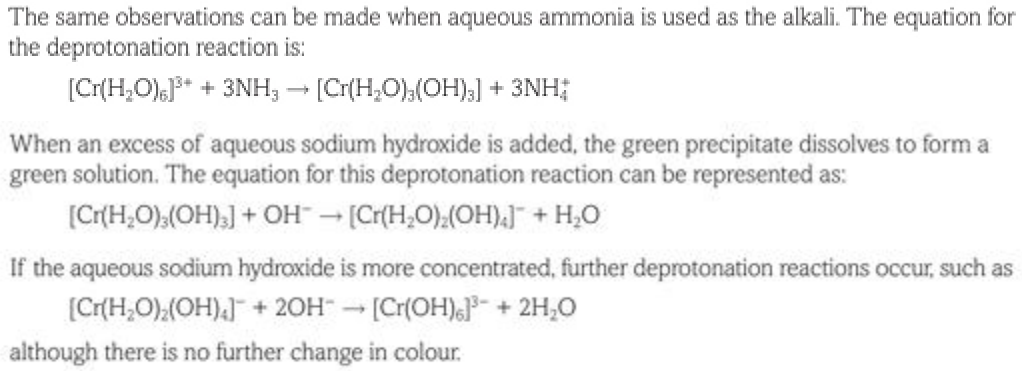
This means that the colours used in this book may not always correspond to those in other books, and may be different from those observed in test tube reactions that you see.

REACTIONS INVOLVING CHROMIUM(III) COMPLEXES

REACTION OF CHROMIUM(III) COMPLEXES WITH ALKALIS

Consider the reaction that occurs when aqueous sodium hydroxide is added to a solution containing the hexaaquachromium(III) ion until no further change is seen. The observation is that a green solution forms a green precipitate. The equation for this reaction is:

$[Cr(H_2O)_6]^{3+} + 3OH^- \rightarrow [Cr(H_2O)_3(OH)_3] + 3H_2O$



The same observations can be made when aqueous ammonia is used as the alkali. The equation for the deprotonation reaction is:

$$[Cr(H_2O)_6]^{3+} + 3NH_3 \rightarrow [Cr(H_2O)_3(OH)_3] + 3NH_4^+$$

When an excess of aqueous sodium hydroxide is added, the green precipitate dissolves to form a green solution. The equation for this deprotonation reaction can be represented as:

$$[Cr(H_2O)_3(OH)_3] + OH^- \rightarrow [Cr(H_2O)_2(OH)_4]^- + H_2O$$

If the aqueous sodium hydroxide is more concentrated, further deprotonation reactions occur, such as

$$[Cr(H_2O)_2(OH)_4]^- + 2OH^- \rightarrow [Cr(OH)_6]^{3-} + 2H_2O$$

although there is no further change in colour.

The reactions involving hydroxide ions can be reversed by the addition of acid, illustrating the amphoteric nature of the neutral complex.

When an excess of aqueous ammonia is added to the green precipitate, the precipitate is slow to dissolve, but eventually a violet or purple solution forms:

$$[Cr(H_2O)_3(OH)_3] + 6NH_3 \rightarrow [Cr(NH_3)_6]^{3+} + 3H_2O + 3OH^-$$

In all of the reactions so far, the oxidation number of chromium has remained unchanged at +3. However, provided that the solutions are alkaline, oxidation is easily achieved by the addition of the oxidising agent hydrogen peroxide. In this reaction the solution changes from green to yellow as the chromate(VI) ion, with oxidation number +6, is formed. The equation for this oxidation is:

2[Cr(OH),]3+ 3H2O2 → 2CrO2 + 20H + 8H2O

Note that although the chromate(VI) ion is a complex, it is not enclosed in square brackets.

CHROMATE(VI) AND DICHROMATE(VI) IONS

Chromate(VI) ions are stable in alkaline solution, but in acidic conditions the dichromate(VI) ion is more stable. So, if acid is added there is a colour change from yellow to orange as the following reaction occurs:

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

This reaction is easily reversed by adding alkali. When considering redox reactions, it is often easier to use simplified formulae by leaving out square brackets and ligands that do not undergo redox reactions, especially water.

REDUCTION OF DICHROMATE(VI) IONS

When zinc metal is added to an acidic solution containing dichromate(VI) ions, reduction reactions occur in which the oxidation number of chromium decreases first to +3 and then to +2.

The first stage of the reduction involves a colour change from orange to green, as this reaction occurs:

$$Cr_2O_7^{2-} + 14H^+ + 3Zn \rightarrow 2Cr^{3+} + 7H_2O + 3Zn^{2+}$$

The second stage of the reduction involves a colour change from green to blue, as this reaction occurs:

$$2Cr^{3+} + Zn \rightarrow 2Cr^{2+} + Zn^{2+}$$

EXPLANATION OF REDOX REACTIONS USING ER VALUES

It is often helpful to explain why redox reactions occur by considering the standard electrode potentials of the different redox systems involved. For chromium, we need to consider these values:

1	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	$E^\circ = -0.76\,V$
2	$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	$E^\circ = -0.41\,V$
3	$CrO_4^{2-} + 4H_2O + 3e^- \rightleftharpoons Cr(OH)_3 + 5OH^-$	$E^\circ = -0.13\,V$
4	$H_2O_2 + 2e^- \rightleftharpoons 2OH^-$	$E^\circ = +1.24\,V$
5	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	$E^\circ = +1.33\,V$

If you have already learned about standard electrode potentials earlier in this book you may remember that when half-equations are arranged from high negative E° values at the top to high positive values at the bottom, then the best reducing agent is at the top and on the right, and the best oxidising agent is at the bottom and on the left.

EXPLAINING OXIDATION FROM +3 TO +6

The simplified equation for the oxidation of chromium(III) by hydrogen peroxide in alkaline conditions is:

$$2Cr(OH)_3 + 3H_2O_2 + 4OH^- \rightarrow 2CrO_4^{2-} + 8H_2O$$

How can this equation be obtained from the half-equations?

The relevant half-equations are 3 and 4 (see previous page). In these equations, the best reducing agent is $Cr(OH)_3$, and the best oxidising agent is H_2O_2. For these two species to react together, we need to add half-equation 3 (reversed) to half-equation 4. When adding half-equations, they may need to be multiplied so that the number of electrons is the same in both. In this example, we need to multiply equation 3 by 2, and equation 4 by 3, so as to obtain $6e^-$ in both:

$$2Cr(OH)_3 + 10OH^- \rightleftharpoons 2CrO_4^{2-} + 8H_2O + 6e^-$$

$$3H_2O_2 + 6e^- \rightleftharpoons 6OH^-$$

Adding the half-equations and cancelling identical species on both sides gives:

$$2Cr(OH)_3 + 3H_2O_2 + 4OH^- \rightarrow 2CrO_4^{2-} + 8H_2O$$

Since the $E^\ominus$ value for half-equation 3 is more negative than the $E^\ominus$ value for half-equation 4, $Cr(OH)_3$ is electron releasing with respect to H_2O_2, and therefore the reaction is thermodynamically feasible. If the solution is then acidified by adding dilute sulfuric acid, the chromate(VI) ion is converted into the dichromate(VI) ion:

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

EXPLAINING REDUCTION FROM +3 TO +6

The simplified equation for the reduction of chromium(VI) by zinc in acidic conditions is:

$$Cr_2O_7^{2-} + 14H^+ + 3Zn \rightarrow 2Cr^{3+} + 7H_2O + 3Zn^{2+}$$

How can this equation be obtained from the half-equations?

The relevant half-equations are 1 and 5 (see previous page). In these equations, the best reducing agent is Zn and the best oxidising agent is $Cr_2O_7^{2-}$. For these two species to react together, we need to add half-equation 1 (reversed) to half-equation 6, bearing in mind multiplying half-equations:

$$3Zn \rightleftharpoons 3Zn^{2+} + 6e^-$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$$

As in the previous example, adding gives:

$$Cr_2O_7^{2-} + 14H^+ + 3Zn \rightarrow 2Cr^{3+} + 7H_2O + 3Zn^{2+}$$

Since the $E^\ominus$ value for half-equation 1 is more negative than the $E^\ominus$ value for half-equation 5, Zn is electron releasing with respect to $Cr_2O_7^{2-}$, and therefore the reaction is thermodynamically feasible.

EXPLAINING REDUCTION FROM +3 TO +2

The simplified equation for the reduction of chromium(III) by zinc in acidic conditions is:

$$2Cr^{3+} + Zn \rightarrow 2Cr^{2+} + Zn^{2+}$$

How can this equation be obtained from the half-equations?

The relevant half-equations are 1 and 2. In these equations, the best reducing agent is Zn and the best oxidising agent is Cr^{3+}. For these two species to react together, we need to add half-equation 1 (reversed) to half-equation 2, bearing in mind multiplying half-equations:

$$Zn \rightleftharpoons Zn^{2+} + 2e^-$$

$$2Cr^{3+} + 2e^- \rightleftharpoons 2Cr^{2+}$$

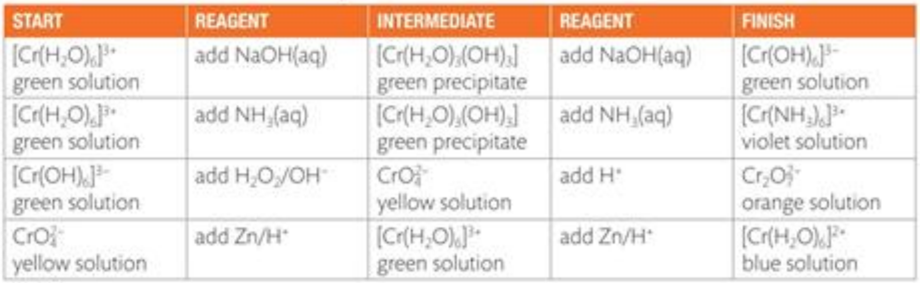
As in the previous example, adding gives:

$$Cr^{3+} + Zn \rightarrow 2Cr^{2+} + Zn^{2+}$$

Since the $E^\ominus$ value for half-equation 1 is more negative than the $E^\ominus$ value for half-equation 2, Zn is electron releasing with respect to Cr^{3+}, and therefore the reaction is thermodynamically feasible.

CHROMIUM CHEMISTRY SUMMARY

Table A summarises the important reactions of chromium complexes in four sequences. Some of the coloured solutions are shown in **fig A**.



START	REAGENT	INTERMEDIATE	REAGENT	FINISH
$[Cr(H_2O)_6]^{3+}$ green solution	add NaOH(aq)	$[Cr(H_2O)_3(OH)_3]$ green precipitate	add NaOH(aq)	$[Cr(OH)_6]^{3-}$ green solution
$[Cr(H_2O)_6]^{3+}$ green solution	add $NH_3(aq)$	$[Cr(H_2O)_3(OH)_3]$ green precipitate	add $NH_3(aq)$	$[Cr(NH_3)_6]^{3+}$ violet solution
$[Cr(OH)_6]^{3-}$ green solution	add H_2O_2/OH^-	CrO_4^{2-} yellow solution	add H^+	$Cr_2O_7^{2-}$ orange solution
CrO_4^{2-} yellow solution	add Zn/H^+	$[Cr(H_2O)_6]^{3+}$ green solution	add Zn/H^+	$[Cr(H_2O)_6]^{2+}$ blue solution

table A

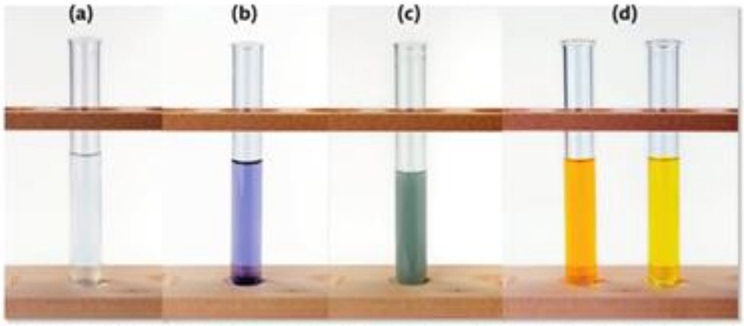


fig A Tube (a) contains the very pale blue $[Cr(H_2O)_6]^{2+}$ ion, produced by reduction using zinc. Tube (b) contains the $[Cr(H_2O)_6]^{3+}$ ion, which is normally green, but can appear violet in the presence of other ions, as here. Tube (c) contains the $[Cr(OH)_6]^{3-}$ ion, which is also green, present in alkaline solutions. The tubes in (d) contain chromium with oxidation number +6. The orange solution contains the $Cr_2O_7^{2-}$ ion and the yellow solution contains the CrO_4^{2-} ion.

17B 4Reactions of manganese complexes

REACTIONS OF MANGANESE(II) COMPLEXES WITH ALKALIS

Consider the reaction that occurs when aqueous sodium hydroxide is added to a solution containing the hexaaquamanganese(II) ion until no further change is seen. The observation is that a pale pink solution forms a pale brown precipitate. The equation for the reaction is:

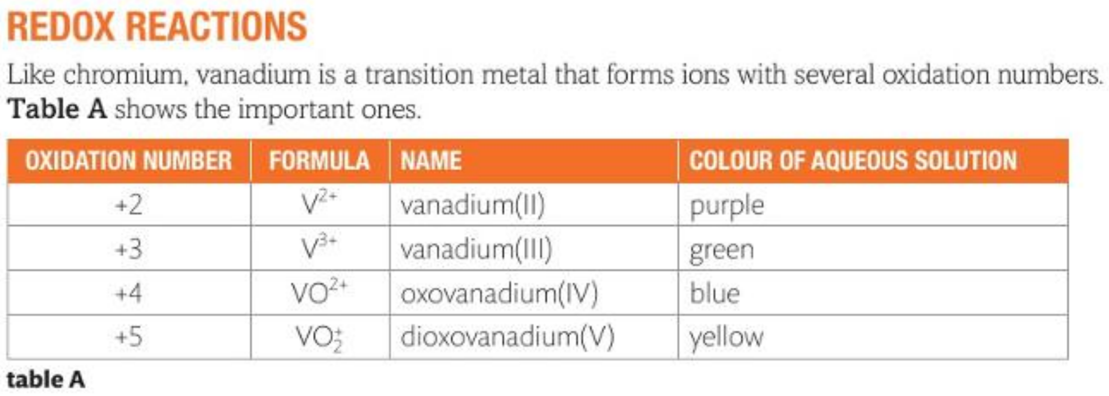
$$[Mn(H_2O)_6]^{2+} + 2OH^- \rightarrow [Mn(H_2O)_4(OH)_2] + 2H_2O$$

This is a deprotonation reaction – the two hydroxide ions have removed hydrogen ions from two of the water ligands and converted them into water molecules. The two water ligands that have lost hydrogen ions are now hydroxide ligands. The pale brown precipitate turns darker brown on standing in air as it is oxidised to $[Mn(H_2O)_3(OH)_3]$, and then turns very dark brown, forming hydrated manganese(IV) oxide, $MnO_2.xH_2O$.

The precipitate does not dissolve in excess aqueous sodium hydroxide.
The same observations are made when aqueous ammonia is used as the alkali. The equation for this deprotonation reaction, forming the pale brown precipitate, is:

$$[Mn(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Mn(H_2O)_4(OH)_2] + 2NH_4^+$$

17B 5 Chemistry of vanadium



REDOX REACTIONS

Like chromium, vanadium is a transition metal that forms ions with several oxidation numbers. **Table A** shows the important ones.

OXIDATION NUMBER	FORMULA	NAME	COLOUR OF AQUEOUS SOLUTION
+2	V^{2+}	vanadium(II)	purple
+3	V^{3+}	vanadium(III)	green
+4	VO^{2+}	oxovanadium(IV)	blue
+5	VO_2^+	dioxovanadium(V)	yellow

table A

The focus here is on redox reactions with vanadium, as it has distinct colors for each oxidation number in its compounds. The feasibility of these reactions is considered in terms of E values, with complex species and water ligands excluded for clarity.

REDUCING VANADIUM FROM +5 TO +2

The usual source of vanadium with oxidation number +5 is the compound ammonium vanadate(V), NH_4VO_3. An acidic solution of this compound contains the dioxovanadium(V) ion, $VO2^+$. When zinc is added to this solution, reduction begins and there is a gradual colour change from yellow, through blue and green, to purple as the oxidation number decreases from +5 to +2. All of these colours are of solutions - there are no precipitates involved. The test tubes in fig A show the colours.

▲ **fig A** The tube on the left (yellow) contains the VO_2^+ ion. The second tube (blue) contains the VO^{2+} ion. The third tube (green) contains the V^{3+} ion. The tube on the right (purple) contains the V^{2+} ion.

EXPLANATION USING E° VALUES

For vanadium, we need to consider these values:

1	$V^{2+} + 2e^- \rightleftharpoons V$	$E^\circ = -1.18\,V$
2	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	$E^\circ = -0.76\,V$
3	$V^{3+} + e^- \rightleftharpoons V^{2+}$	$E^\circ = -0.26\,V$
4	$VO_2^+ + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	$E^\circ = +0.34\,V$
5	$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	$E^\circ = +1.00\,V$

If you followed the explanations for the redox reactions of chromium in the previous topic, you should be able to understand a shortened explanation for each stage that just shows the two relevant half-equations and then the overall equation.

REDUCTION FROM +5 TO +4

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$$
$$Zn \rightarrow Zn^{2+} + 2e^-$$

Overall reaction:

$$2VO_2^+ + 4H^+ + Zn \rightarrow 2VO^{2+} + Zn^{2+} + 2H_2O$$

Since the E° value for half-equation 2 is more negative than the E° value for half-equation 5, Zn is electron releasing with respect to VO_2^+. Therefore, the reaction is thermodynamically feasible.

REDUCTION FROM +4 TO +3

$$VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$$
$$Zn \rightarrow Zn^{2+} + 2e^-$$

Overall reaction:

$$2VO^{2+} + 4H^+ + Zn \rightarrow 2V^{3+} + Zn^{2+} + 2H_2O$$

Since the E° value for half-equation 2 is more negative than the E° value for half-equation 4, Zn is electron releasing with respect to VO^{2+}. Therefore, the reaction is thermodynamically feasible.

REDUCTION FROM +3 TO +2

$$V^{3+} + e^- \rightarrow V^{2+}$$
$$Zn \rightarrow Zn^{2+} + 2e^-$$

Overall reaction:

$$2V^{3+} + Zn \rightarrow 2V^{2+} + Zn^{2+}$$

Since the E° value for half-equation 2 is more negative than the E° value for half-equation 3, Zn is electron releasing with respect to V^{3+}. Therefore, the reaction is thermodynamically feasible.

REDUCTION FROM +2 TO 0

$$V^{2+} + 2e^- \rightarrow V$$
$$Zn \rightarrow Zn^{2+} + 2e^-$$

Overall reaction:

$$2V^{2+} + Zn \rightarrow 2V + Zn^{2+}$$

Since the E° value for half-equation 2 is less negative than the E° value for half-equation 1, Zn is not electron releasing with respect to V^{2+}. Therefore, the reaction is not thermodynamically feasible.

PREDICTING OXIDATION REACTIONS

A similar method can be used to predict whether a given oxidising agent will oxidise a vanadium species to one with a higher oxidation number. You can see how to do this in Question 2 in this topic.

17B 6Reactions of nickel and zinc complex

REACTIONS OF NICKEL COMPLEXES WITH ALKALIS

Consider the reaction that occurs when aqueous sodium hydroxide is added to a solution containing the hexaaquanickel(II) ion until no further change is seen. The observation is that a green solution forms a green precipitate. The equation for the reaction is:

$$[Ni(H_2O)_6]^{2+} + 2OH^- \rightarrow [Ni(H_2O)_4(OH)_2] + 2H_2O$$

Hydroxide ions convert water ligands into hydroxide ligands, causing a deprotonation reaction. Excessive addition of aqueous ammonia results in a deep blue solution, unlike with aqueous sodium hydroxide, resulting in the same observations.

The equation for the deprotonation reaction forming the green precipitate is:

$$[Ni(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Ni(H_2O)_4(OH)_2] + 2NH_4^+$$

The equation for the ligand exchange reaction forming the blue solution is:

$$[Ni(H_2O)_4(OH)_2] + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 4H_2O + 2OH^-$$

REACTIONS OF ZINC COMPLEXES WITH ALKALIS

Consider the reaction that occurs when aqueous sodium hydroxide is added to a solution containing the hexaaquazinc(II) ion until no further change is seen. The observation is that a colourless solution forms a white precipitate. The equation for the reaction is:

$$[Zn(H_2O)_6]^{2+} + 2OH^- \rightarrow [Zn(H_2O)_4(OH)_2] + 2H_2O$$

This is a deprotonation reaction - the two hydroxide ions have removed hydrogen ions from two of the water ligands and converted them into water molecules. The two water ligands that have lost hydrogen ions are now hydroxide ligands.

When an excess of aqueous sodium hydroxide is added, the white precipitate dissolves to form a colourless solution. The equation for this deprotonation reaction is:

$$[Zn(H_2O)_4(OH)_2] + 2OH^- \rightarrow [Zn(H_2O)_2(OH)_4]^{2-} + 2H_2O$$

Zinc hydroxide also reacts with acid, showing its amphoteric behaviour:

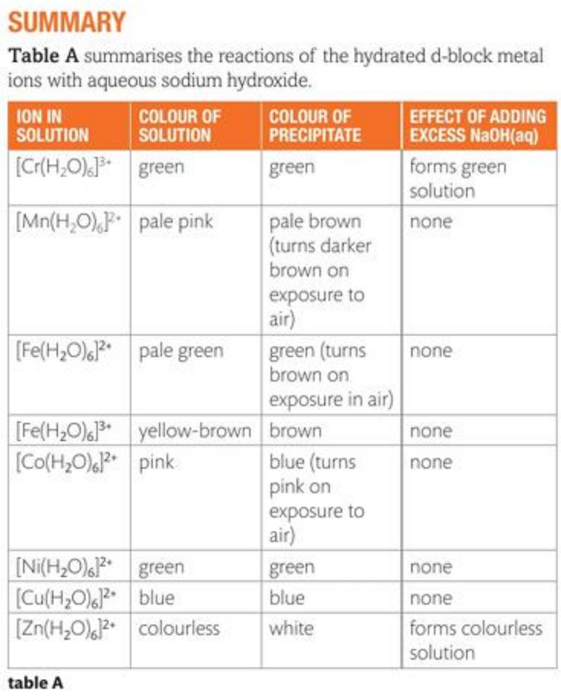
$$[Zn(H_2O)_4(OH)_2] + 2H^+ \rightarrow [Zn(H_2O)_6]^{2+}$$

Similar observations are made when aqueous ammonia is used as the alkali. The equation for the deprotonation reaction forming the white precipitate is:

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

The equation for the ligand exchange reaction forming the colourless solution is:

$$[Zn(H_2O)_4(OH)_2] + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2+} + 4H_2O + 2OH^-$$



SUMMARY

Table A summarises the reactions of the hydrated d-block metal ions with aqueous sodium hydroxide.

ION IN SOLUTION	COLOUR OF SOLUTION	COLOUR OF PRECIPITATE	EFFECT OF ADDING EXCESS NaOH(aq)
$[Cr(H_2O)_6]^{3+}$	green	green	forms green solution
$[Mn(H_2O)_6]^{2+}$	pale pink	pale brown (turns darker brown on exposure to air)	none
$[Fe(H_2O)_6]^{2+}$	pale green	green (turns brown on exposure in air)	none
$[Fe(H_2O)_6]^{3+}$	yellow-brown	brown	none
$[Co(H_2O)_6]^{2+}$	pink	blue (turns pink on exposure to air)	none
$[Ni(H_2O)_6]^{2+}$	green	green	none
$[Cu(H_2O)_6]^{2+}$	blue	blue	none
$[Zn(H_2O)_6]^{2+}$	colourless	white	forms colourless solution

table A

17C 1Hetrogeneous catalysis

DIFFERENT WAYS TO UNDERSTAND CATALYSIS

Catalysts are substances that increase reaction rate and remain unchanged at the end. Topic 9 (Book 1: IAS) introduced catalysis's effect on activation energy and Maxwell-Boltzmann energy distributions. This section and the next will explore catalysis's two main types: heterogeneous and homogeneous.

TRANSITION METALS AS HETEROGENEOUS CATALYSTS

A **heterogeneous catalyst** is a solid compound used in a reaction to produce oxygen gas by decomposing a liquid hydrogen peroxide solution. This type of catalysis is unique due to its phase difference from the reactants.

THE CONTACT PROCESS

Sulfuric acid is one of the most widely used chemicals, both in terms of the quantity produced and the number of industries that use it. Its biggest single use is in the manufacture of fertilisers. A complete description of the Contact process used to manufacture sulfuric acid is beyond the aims of this book, but the key reaction in the process is the conversion of sulfur dioxide to sulfur trioxide in this reaction:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

At the temperatures and pressures used in the process, all of the substances are in the gas phase, and the mixture of reactants is passed over a catalyst of vanadium(V) oxide, V2O5, usually known in industry as vanadium pentoxide (fig A).
fig A Sample of vanadium(V) oxide, as used as the catalyst in the Contact process.

SURFACE ADSORPTION THEORY

This theory is often used to explain the way that a heterogeneous catalyst works. It is usually considered as having three steps:

1 Adsorption, in which one or more reactants become attached to the surface of the catalyst.
2 Reaction, following the weakening of bonds in the adsorbed reactants.
3 Desorption, in which the reaction product becomes detached from the surface of the catalyst.

In the Contact process, the reaction step has two parts:
Part 1: sulfur dioxide adsorbs onto the vanadium(V) oxide and a redox reaction occurs:

$$V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$$

Note that the oxidation number of vanadium decreases from +5 to +4. The sulfur trioxide then desorbs.

Part 2: oxygen reacts with the V_2O_4 on the surface of the catalyst and another redox reaction occurs:

$$V_2O_4 + \frac{1}{2}O_2 \rightarrow V_2O_5$$

Note that the original catalyst is regenerated as the oxidation number increases from +4 to +5.

CATALYTIC CONVERTERS

THE PROBLEMS

One of the major problems associated with increased road vehicle usage over several decades is the increased amount of pollution from vehicle exhaust gases.

Although many different pollutants come from vehicle exhausts, two of the most significant are carbon monoxide and nitrogen monoxide.

- Carbon monoxide is a toxic gas that interferes with oxygen transport from the lungs through the bloodstream to vital organs in the body (see Section 17A.6).
- Nitrogen monoxide is easily oxidised in the atmosphere to nitrogen dioxide. It can act as a respiratory irritant and contribute to the formation of acid rain.

THE SOLUTIONS

Over 20 years, catalytic converters have been installed in cars worldwide to reduce vehicle emissions and improve air quality. The main transition metals used are platinum, rhodium, and sometimes palladium, which react to form carbon dioxide and nitrogen.

which are then desorbed from the surface of the catalyst. The overall reaction can be represented by this equation:

$$2CO + 2NO \rightarrow 2CO_2 + N_2$$

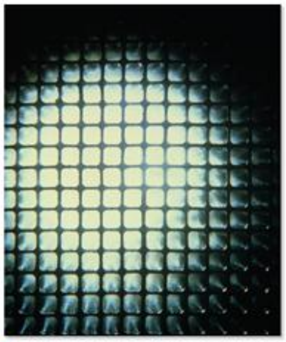


fig B View through the element of a catalytic converter from a car exhaust. The inner surface is coated with an alloy containing platinum, rhodium and palladium.

SUBJECT VOCABULARY

heterogeneous catalyst a catalyst that is in a different phase from the reactants
adsorption the process that occurs when reactants form weak bonds with a solid catalyst
desorption the process that occurs when products leave the surface of a solid catalyst

17C 2 Homogeneous catalysts

TRANSITION METALS AS HOMOGENEOUS CATALYSTS

A homogeneous catalyst is one that is in the same phase as the reactants. This means that they are either all gases, or more often, all in aqueous solution. You have not seen many examples of this type of catalyst, compared with those that take part in heterogeneous catalysis. Homogeneous catalysis is also much less common in industry.

A REACTION OF THE S2O2-ION

The ion with this formula has several names, the simplest of which is the 'persulfate ion', although it is often known as the 'peroxydisulfate ion'. We will not use the IUPAC name, which is very complicated! It acts as an oxidising agent in its reaction with iodide ions, the equation for which is:

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

One reason why this reaction is slow at room temperature is that the two reactant ions are both negatively charged and so repel each other.

STEPS IN THE CATALYSED REACTION

Step 1: The Fe2+ ions are not repelled by the S2O ions because they have the opposite charge. They react together as follows:

$$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$$

Step 2: The Fe^{3+} ions formed in Step 1 now react with the I^- ions (these also have opposite charges) as follows:

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$$

The iron(II) ions are used in Step 1 and regenerated in Step 2, so the two steps can repeat continuously.

The iron(II) ions are used in Step 1 and regenerated in Step 2, so the two steps can repeat continuously.

ALTERNATIVE MECHANISM

The reaction is also catalysed by Fe3+ ions, for which the following mechanism can be written. Step 1: 2Fe3+ + 21

The reaction is also catalysed by Fe^{3+} ions, for which the following mechanism can be written.

Step 1: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

Step 2: $S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$

The same two reactions are involved, but they occur in a different order.

The same two reactions are involved, but they occur in a different order.

OXIDATION OF ETHANEDIOATE IONS

You may know about titrations in which potassium manganate(VII) in acidic conditions acts as an oxidising agent. For these titrations to work well enough, it is important that the reactions are fast, so that the end point of the reaction can be accurately observed (fig A).

One example of a redox reaction that can be used in titrations is the oxidation of ethanedioate ions by potassium manganate(VII). The equation for this reaction is:

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 5CO_2 + 8H_2O$$

As with the $S_2O_8^{2-}/I^-$ reaction, the reacting species are both negatively charged. Therefore, the reaction is slow. However, as more potassium manganate(VII) solution is added, the reaction rate increases.

fig A (a) At the start of the titration, the colour of the potassium manganate(VII) solution takes some time to disappear; (b) the colour of the potassium manganate(VII) solution now disappears more quickly because there are Mn^{2+} ions to catalyse the reaction; (c) at the end of the titration, there are no more ethanedioate ions left to react, so the remaining potassium manganate(VII) solution gives the mixture a pink colour.