A Level
Inorganic chemistry

24 The 3d block

In this topic we study the 3d block, which includes many familiar metals such as iron and copper. The chemical properties of these metals and their compounds contrast with those of the metals in the s and p blocks. For example, the 3d-block elements can exist in several oxidation states and their ions are coloured, whereas the s- and p-block elements usually show only one oxidation state and have colourless ions. The complicated chemistry of the 3d block can be explained in terms of their electronic configurations and in particular by the closeness in energy of the 3d, 4s and 4p orbitals.

Learning outcomes

By the end of this topic you should be able to:

12.1a) explain what is meant by a *transition element*, in terms of d-block elements forming one or more stable ions with incomplete d orbitals

12.1b) sketch the shape of a d orbital

12.1c) state the electronic configuration of each of the first row transition elements and of their ions

12.1d) contrast, qualitatively, the melting points and densities of the transition elements with those of calcium as a typical s-block element

12.1e) describe the tendency of transition elements to have variable oxidation states

12.1f) predict from a given electronic configuration, the likely oxidation states of a transition element

12.2a) describe and explain the reactions of transition elements with ligands to form complexes, including the complexes of copper(II) and cobalt(II) ions with water and ammonia molecules and hydroxide and chloride ions

12.2b) define the term *ligand* as a species that contains a lone pair of electrons that forms a dative bond to a central metal atom/ion including monodentate, bidentate and polydentate ligands, define the term *complex* as a molecule or ion formed by a central metal atom/ion surrounded by one or more ligands, describe transition metal complexes as linear, octahedral, tetrahedral or square planar, and state what is meant by co-ordination number and predict the formula and charge of a complex ion, given the metal ion, its charge, the ligand and its co-ordination number

12.2c) explain qualitatively that ligand exchange may occur, including the complexes of copper(II) ions with water and ammonia molecules and hydroxide and chloride ions

12.2d) describe and explain the use of Fe^{3+}/Fe^{2+}, MnO_4^-/Mn^{2+} and $Cr_2O_7^{2-}/Cr^{3+}$ as examples of redox systems (see also Topic 23)

12.2e) predict, using $E^\ominus$ values, the likelihood of redox reactions

12.3a) describe the splitting of degenerate d orbitals into two energy levels in octahedral and tetrahedral complexes

12.3b) explain the origin of colour in transition element complexes resulting from the absorption of light energy as an electron moves between two non-degenerate d orbitals

12.3c) describe, in qualitative terms, the effects of different ligands on absorption, and hence colour, using the complexes of copper(II) ions with water and ammonia molecules and hydroxide and chloride ions as examples

12.3d) apply the above ideas of ligands and complexes to other metals, given information

12.4a) describe the types of stereoisomerism shown by complexes, including those associated with bidentate ligands: *cis-trans* isomerism, e.g. *cis-* and *trans*-platin $Pt(NH_3)_2Cl_2$, and optical isomerism, e.g. $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$

12.4b) describe the use of cisplatin as an anticancer drug and its action by binding to DNA in cancer cells, preventing cell division

12.5a) describe and explain ligand exchanges in terms of competing equilibria (also see Topic 22)

12.5b) state that the stability constant, K_{stab}, of a complex ion is the equilibrium constant for the formation of the complex ion in a solvent from its constituent ions or molecules

12.5c) deduce expressions for the stability constant of a ligand substitution

12.5d) explain ligand exchange in terms of stability constants, K_{stab}, and understand that a large K_{stab} is due to the formation of a stable complex ion.

24.1 Introduction

The elements from scandium to zinc inclusive comprise the **3d block**. The 3d subshell contains five orbitals, each able to accommodate two electrons (see Topic 2), and so this block contains ten elements. The electronic configuration of scandium is $[Ar]3d^1 4s^2$ and that of zinc is $[Ar]3d^{10} 4s^2$. A 3d-block element is sometimes defined as one of the elements in which the 3d subshell is being progressively filled. This is not strictly speaking correct, because copper has the electronic configuration $[Ar] 3d^{10} 4s^1$. It is more accurate to state that the 3d block contains elements with electronic configurations from $[Ar] 3d^1 4s^2$ to $[Ar]3d^{10} 4s^2$ inclusive.

Originally this block was known as the 'transition metals', because some of their properties show a gradual change between those of the reactive metal calcium in Group 2 to the much less reactive metal gallium in Group 13. The term **transition metal** is now reserved for those metals in the block that show properties characteristically different from those in the s and p blocks: they can exist in more than one oxidation state, and eir ions are often coloured. We exclude both scandium and zinc from the class of transition metals, for the following reasons.

- Scandium forms only the colourless Sc^{3+} ion, which is isoelectronic with the Ca^{2+} ion and has no electrons in the 3d subshell.
- Zinc forms only the colourless Zn^{2+} ion, which is isoelectronic with the Ga^{3+} ion and has 10 electrons in the 3d subshell.

It is the elements that form ions with *some* electrons in the 3d subshell that exhibit the special properties of transition metals.


The 3d elements and the transition metals

- The **3d block** contains elements in which the 3d subshell is being progressively filled.
- The 3d block includes all the elements with the electronic configurations $[Ar]3d^1 4s^2$ to $[Ar]3d^{10} 4s^2$ inclusive.
- The **transition metals** form some compounds containing ions with an incomplete d subshell.

The 4s subshell is filled before the 3d subshell because it is lower in energy (see section 2.12), even though the 4s subshell is part of a shell whose average distance is further away from the nucleus. The difference in energy between 4s and 3d is very small, however, which means that both s and d electrons may be involved in bonding.

The order of energy levels 4s < 3d holds only as far as calcium. With the increasing nuclear charge from 21 in scandium to 30 in zinc, the energy levels of both the 4s and 3d orbitals decrease, but the 3d level decreases faster than the 4s (see Figure 24.1 and Figure 2.25, page 34). At scandium their energy levels are almost the same, but subsequently the order changes so that 3d is slightly lower than 4s. When an ion is formed, the 4s electrons are removed before the 3d electrons. The reason for this reversal in energy levels is discussed in the next section.

Figure 24.1 The 3d and 4s energy levels on crossing the 3d block. The graph is not to scale.
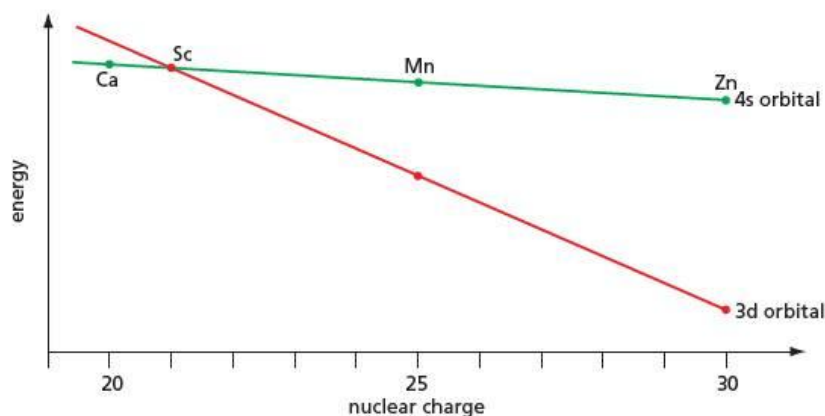
24.2 Properties of the metals

Table 24.1 The main properties of the elements in the 3d block

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronic configuration [Ar]	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
Melting point/°C	1541	1660	1887	1857	1244	1535	1495	1453	1083	420
Boiling point/°C	2831	3287	3377	2672	1962	2750	2870	2732	2567	907
Density/$g\,cm^{-3}$	2.99	4.54	6.11	7.19	7.44	7.87	8.90	8.90	8.96	7.13
Metallic radius/nm	0.164	0.146	0.135	0.129	0.132	0.126	0.125	0.124	0.128	0.135
Conductivity/$mS\,m^{-1}$	1.6	1.2	4.0	7.9	0.54	10.2	16.0	14.6	59.9	16.9
M^{2+} radius/nm	—	0.090	0.079	0.073	0.067	0.061	0.078	0.070	0.073	0.075
M^{3+} radius/nm	0.083	0.067	0.064	0.062	0.062	0.055	0.053	0.056	—	—
ΔH_{at}/$kJ\,mol^{-1}$	378	470	514	397	281	416	425	430	338	131
First IE/$kJ\,mol^{-1}$	632	661	648	653	716	762	757	736	745	908
Second IE/$kJ\,mol^{-1}$	1240	1310	1370	1590	1510	1560	1640	1750	1960	1730
Third IE/$kJ\,mol^{-1}$	2390	2720	2870	2990	3250	2960	3230	3390	3350	3828
$E^{\ominus}(M^{2+}/M)$/V	—	−1.63	−1.20	−0.91	−1.18	−0.44	−0.28	−0.25	+0.34	−0.76
$E^{\ominus}(M^{3+}/M^{2+})$/V	—	−0.37	−0.26	−0.41	+1.49	+0.77	+1.82	—	—	—
Electronegativity	1.36	1.54	1.63	1.66	1.55	1.83	1.88	1.91	1.90	1.65

Electronic configuration

As the proton number increases by one unit, an extra electron is usually added to the 3d subshell. There are two exceptions to this general trend:

- chromium is $[Ar]3d^5 4s^1$, and not $[Ar]3d^4 4s^2$
- copper is $[Ar]3d^{10} 4s^1$, and not $[Ar]3d^9 4s^2$.

This suggests that $3d^5$ (with a half-filled subshell) and $3d^{10}$ (with a full subshell) are energetically preferred configurations, avoiding the inter-electron repulsion in the 4s orbital that occurs with the $4s^2$ configuration. Both these configurations have a symmetrical 3d cloud of electrons that screens the nucleus more effectively than other configurations.

## Melting points, boiling points and conductivities

The melting and boiling points of the 3d-block metals are generally much higher than those of the s- and p-block metals. This indicates that not only the 4s electrons but also the 3d electrons are involved in the metallic bonding. When melting and boiling points are plotted against proton number, both graphs have two maxima, with an intermediate minimum at manganese (see Figure 24.2). These minima suggest that the half-filled subshell of 3d electrons is not readily available for metallic bonding. We might expect the same effect in chromium, but it occurs to a lesser degree because the nuclear charge is lower.

The conductivities of the 3d-block metals are similar to those of calcium ($29.2\,mS\,m^{-1}$); the conductivity of copper is particularly high.

Metallic radii, ionic radii and densities

The metallic radii tend to decrease across the block as the increasing nuclear charge attracts the outer electrons more strongly. There are minor variations to this trend that can be rationalised in terms of the different strengths of the metallic bonding – for example, the metallic radii of both copper and zinc are larger than those of the preceding metals, and their metallic bonding is weaker, as shown by their comparatively low melting points. This decrease in metallic radius means that the densities of the transition metals are higher than that of calcium ($1.55\,g\,cm^{-3}$); those at

Figure 24.2 Melting and boiling points of the 3d-block metals
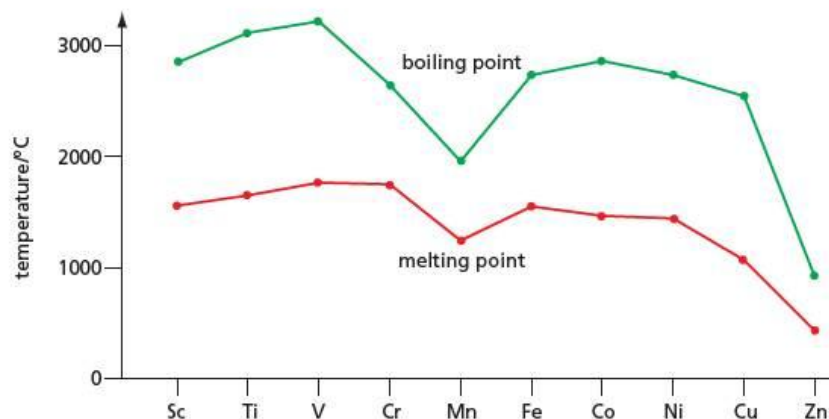

the end of the block have the highest densities, as they have the smallest atomic radii and the highest relative atomic masses.

There is no obvious trend in the M^{2+} ionic radii, but the M^{3+} ionic radii tend to decrease across the block as the nuclear charge increases and attracts the electrons more strongly. This decrease in ionic radius is accompanied by an increase in charge density of the ion, leading to an increased stability of the complexes formed towards the right of the block.

Ionisation energies

A graph of ionisation energies against proton number (see Figure 24.3) shows three main features.

Figure 24.3 Ionisation energies of the 3d-block metals
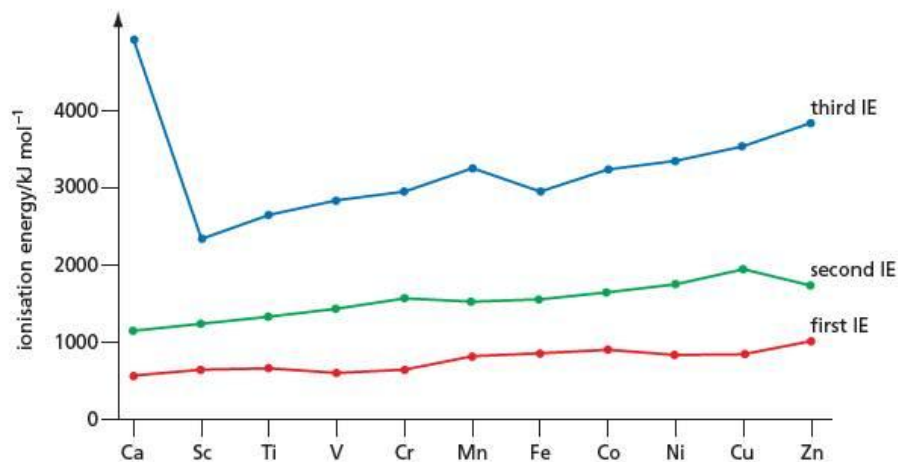
- The first and second ionisation energies increase only slightly across the block.
- The second ionisation energies are only slightly higher than the first.
- The third ionisation energies are significantly higher, and show a characteristic d-subshell pattern.

The first ionisation energies involve the removal of a 4s electron. This is outside the 3d subshell and is partially screened by it. As the nuclear charge increases across the block, the additional d electrons shield the effect of the increasing nuclear charge so that the 4s electron experiences only a small extra attraction. The same effect is shown by the second ionisation energies, with the exception of those for chromium and copper – these have rather higher second ionisation energies because the second electron being removed is a 3d electron, which does experience the increased nuclear charge.

The third ionisation energies involve the removal of a 3d electron. The pattern of five values steadily rising, followed by a drop and then five more steadily rising, mirrors the ionisation energies involving the removal of 2p electrons on crossing

the second period (see Figure 2.33, page 41). The drop from manganese to iron is a reflection of the fact that two electrons in the same orbital repel each other (see Figure 24.4).

Figure 24.4 The electronic configurations of manganese and iron. The formation of the Fe^{3+} ion involves the removal of an electron from a doubly occupied 3d orbital; this electron is more easily removed because it is repelled by the other electron in the orbital.

3d and 4s energy levels

The relative energies of the 3d and 4s orbitals change on crossing the block (see Figure 24.1). Up to calcium, the energy of the 4s orbital is lower than that of the 3d, even though, on average, the electron is further away from the nucleus. This is because the 4s electron spends some time very near to the nucleus, where it experiences the full attraction of the unscreened nuclear charge. A 4s electron is said to be more **penetrating** than a 3d electron.

After calcium, the 4s electrons are screened from the effect of the increasing nuclear charge by the addition of the 3d electrons, which are nearer to the nucleus. The energy of the 4s electrons therefore decreases only slightly on crossing the 3d block. This small decrease in energy explains the small increase in first and second ionisation energies on crossing the 3d block from scandium to zinc. The 3d electrons, however, are not screened to the same extent and so experience a greater effective nuclear charge, becoming progressively more tightly held by the nucleus. The energy of the 3d electrons therefore decreases significantly on crossing the 3d block, as is shown by the sharper rise in the third ionisation energies (see Figure 24.3). (From scandium to zinc, the second ionisation energies increase by 40%, whereas the third ionisation energies increase by 60%.)

Worked example 1

Using [Ar] to represent the argon core, give the electronic configurations of the following species.
a Cr   **b** Cu^{2+} **c** V^{2+}

Answer
a $[Ar]3d^5 4s^1$ **b** $[Ar]3d^9$ **c** $[Ar]3d^3$

Now try this

1 Using [Ar] to represent the argon core, give the electronic configurations of the following species.
   a Cu   **b** Co^{2+} **c** Ti^{3+}
2 Briefly explain the following.
   a The second ionisation energy of copper is higher than the second ionisation energy of zinc.
   b It is difficult to oxidise $Mn^{2+}(aq)$ to $Mn^{3+}(aq)$.
   c On passing from scandium to titanium, the increase in the third ionisation energy is much larger than the increase in the first ionisation energy.

Briefly explain the following observations.

a The first ionisation energy of cobalt is only slightly larger than the first ionisation energy of iron.
b The third ionisation energy of iron is much lower than the third ionisation energy of manganese.
c The metallic radius of vanadium is smaller than that of titanium.

Answer

a The increase in nuclear charge from 26 to 27 is screened by the addition of an extra 3d electron. The effective nuclear charge, and hence the attraction of the 4s electrons, therefore increases only slightly.
b The third electron is being removed from a d^6 configuration, which has two electrons in one d orbital. These two electrons repel each other, making each one easier to remove.
c The increase in nuclear charge from 22 to 23 makes the inner clouds of electrons contract, and the radius of the atom decreases.

24.3 Variable oxidation states

Table 24.2 shows the more familiar oxidation states of some of the 3d elements. Many other oxidation states are known which can be stabilised under special conditions.

Table 24.2 The more familiar oxidation states of some of the 3d elements are marked ●. Other oxidation states are known but are formed only under special conditions. All the elements have an oxidation state of 0 in the metal.

Oxidation state	Cr	Mn	Fe	Cu	Zn
VII		●			
VI	●				
V					
IV					
III	●		●		
II		●	●	●	●
I				●	

Table 24.2 shows the following main features.

● Chromium and manganese show their highest oxidation state in CrO_4^{2-} and MnO_4^{-}. In these, their oxidation numbers are equal to the sum of the numbers of 3d and 4s electrons; this shows that all of these electrons are used in the bonding.
● Manganese, iron, copper and zinc all form M^{2+} ions by loss of the $4s^2$ electrons.
● Chromium and iron form M^{3+} ions as their third ionisation energies are relatively low.
● Copper forms Cu(I) compounds as it has a single 4s electron.

The presence of a high and a low oxidation state in chromium, manganese and iron means that these elements have important uses in redox chemistry, as is shown by the values of $E^⊖$ in Table 24.3.

Table 24.3 Values of $E^⊖$ for three common redox systems. The use of manganate(VII) and acid dichromate(VI) is discussed in Topic 16. Titrations using MnO_4^{-} are discussed in section 7.4.

Redox system	$E^⊖/V$
$Cr_2O_7^{2-}/Cr^{3+}$	+1.33
MnO_4^{-}/Mn^{2+}	+1.52
Fe^{3+}/Fe^{2+}	+0.77

In titrations, dichromate(VI) and manganate(VII) are always used in acidic solution.

1 Write the half-equation (i.e. including electrons) showing the reduction of each of these oxidants in acidic solution.
2 Write the balanced ionic equation for the reaction between each of these oxidants with Fe^{2+} ions, and calculate the $E^⊖_{cell}$ value for each reaction.

🔁 24.4 Complex formation

Ligands

The 3d metal ions are relatively small and have a high charge density. They therefore attract groups containing lone pairs of electrons. These groups are known as **ligands**. Ligands are bases, and also nucleophiles (see Table 15.1, page 270), and their ability to be attracted to metal ions follows a similar pattern to the nucleophilic strength found in organic chemistry. For common ligands an approximate order of attraction is as follows:

$$H_2O < \text{halide ions} < NH_3 < CN^-$$
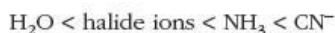
The ligand bonds to the metal ion to form a **complex ion**. Six, four or two ligands combine with one metal ion, so the formation of a complex ion may be represented as the donation of six or four or two pairs of electrons to the metal ion. A dative covalent bond (co-ordinate bond) is formed between each ligand and the metal ion.

Ligands contain atoms of p-block elements that are more electronegative than the 3d-block atom. This means that the ligand attracts the electrons of the bond away from the metal. The result is that the metal atom is approximately neutral, and the charge is spread to the outside of the ion (see Figure 24.5).

Figure 24.5 The formation of a complex ion. Water is shown as the ligand in this example. The metal ion could be M^{2+} rather than M^{3+}.

donation of electrons   or   final structure
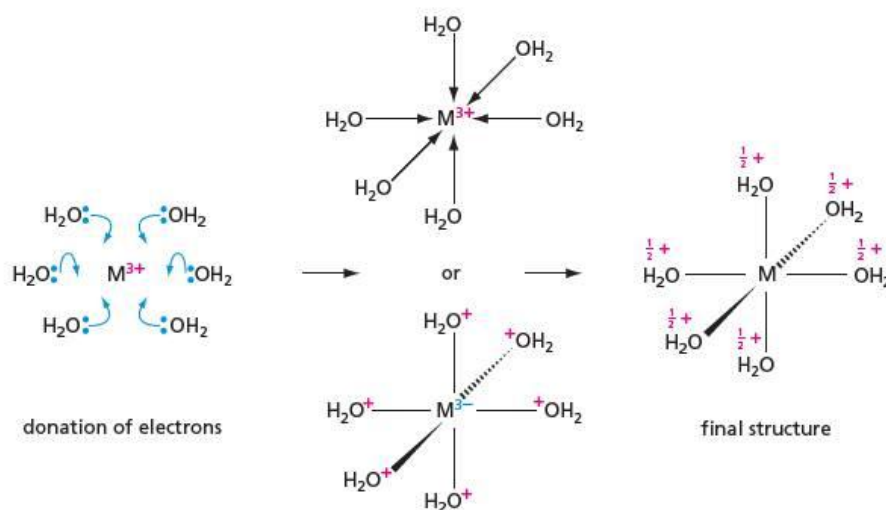
In the example in Figure 24.5, the oxidation number of the metal is simply the same as the charge on the complex ion. If the ligand is charged, for example a Cl^- ion, the oxidation number of the metal is found in the same way as in any other ion (see section 7.2). If the oxidation number of copper in the $CuCl_4^{2-}$ ion is x, then:

$$x + 4 \times (-1) = -2 \quad \text{and} \quad x = +2$$

So the oxidation number of copper in this complex ion is +2. If a simple formula does not make it clear which groups are attached to the metal ion, it is common practice to enclose the complex ion in square brackets. An example of this is $Cr(H_2O)_6Cl_3$, which does not make it clear which ligands are attached to the chromium ion. It could, for example, be $[Cr(H_2O)_6]Cl_3$ (which has no chlorine ligands but has three free chloride ions) or $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (which has one chlorine ligand and two free chloride ions).

A **complex ion** is formed when **ligands** donate a pair of electrons to a metal ion. The 3d-block metals form stable complex ions for the following reasons.

- Their ions are small and have a high charge density.
- They have 3d orbitals of low energy that can accommodate electrons donated by the ligands.

The shapes of complex ions

The number of atoms surrounding a central atom is called the **co-ordination number**. Thus a complex such as $[Cr(H_2O)_6]^{3+}$ has a co-ordination number of 6. A complex of formula ML_6^{3+} has six pairs of electrons and its shape using VSEPR arguments (see section 3.9) is a regular octahedron (see Figure 24.6).

Figure 24.6 The shapes of complex ions with six ligands, with four ligands and with two ligands

octahedral   tetrahedral   square planar   linear
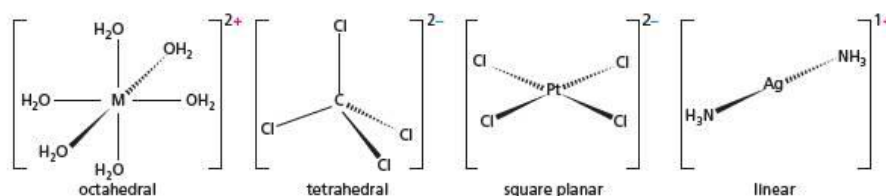
If the complex contains two ligands (co-ordination number 2), it is linear; examples are the $CuCl_2^-$ and $[Ag(NH_3)_2]^+$ ions. With four ligands, VSEPR arguments predict that the complex is tetrahedral and this is usually the case; examples are the $CoCl_4^{2-}$ and $[Zn(NH_3)_4]^{2+}$ ions. However, there are complexes with four ligands that are square planar, which shows that factors other than electron repulsion must be taken into account. An example of a square planar complex is cisplatin, which is discussed on page 410.

Bonding in complex ions

In aqueous solution, Cu^{2+} ions hydrate to give the $Cu(H_2O)_6^{2+}$ ion. Each water molecule is bonded to the central Cu^{2+} ion by a dative covalent bond. In order to form this ion, there need to be six empty orbitals to receive the six lone pairs from the six water molecules. There are also nine 3d electrons in the free Cu^{2+} ion that need five orbitals to accommodate them. Thus at least 11 orbitals are required in all. These are obtained by hybridising the six ligand lone-pair orbitals, together with the one 3s, the three 3p and the five 3d orbitals of the metal ion.

The energies and geometries of all of the resulting orbitals need not concern us, except for one important outcome: under the influence of the ligand lone pairs, the five 3d orbitals split into two groups with different energies. In the simple Cu^{2+} ion, the five 3d orbitals all have the same energy (they are said to be **degenerate**), but in the presence of six ligands spaced octahedrally, the orbitals divide into two groups – a group of two, called the e_g, and a group of three, called the t_{2g} (see Figure 24.7). The lobes of the three t_{2g} orbitals are directed in between the six ligands (see Figure 24.8), and their energy is only slightly increased when the complex is formed. The two e_g orbitals, however, have lobes which point in the direction of the six ligands; this means that any electrons in these orbitals will experience inter-electron repulsion with the ligand lone pairs when the complex is formed, and so their energy is higher than that of electrons in the t_{2g} orbitals.

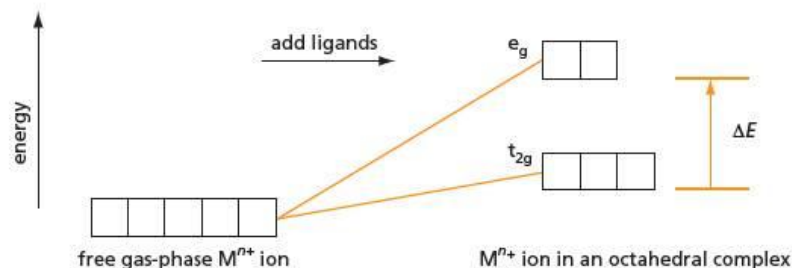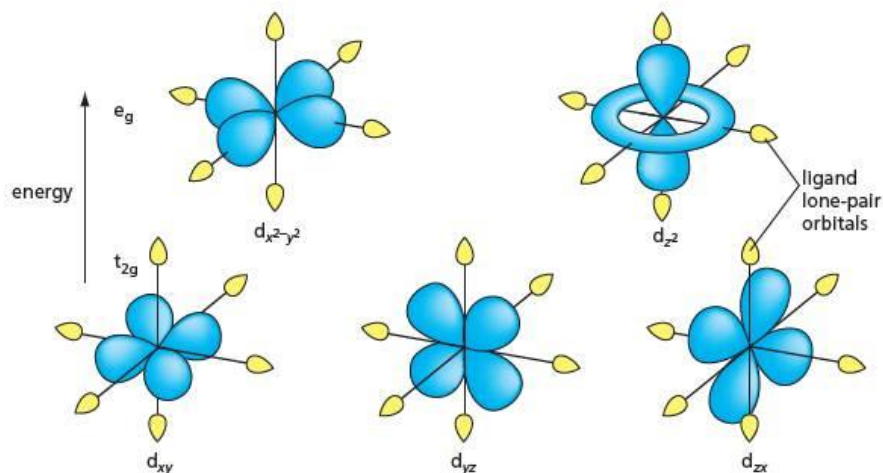**Figure 24.7** The splitting of the 3d orbitals in an octahedral field

free gas-phase M^{n+} ion M^{n+} ion in an octahedral complex

Figure 24.8 The shapes of the three t_{2g} and the two e_g orbitals. The t_{2g} orbitals point in between the ligands; the e_g orbitals point towards the ligands.

In tetrahedral complexes, the changes in the energy levels of the e_g and t_{2g} orbitals is reversed. The t_{2g} orbitals now point towards the ligands. This means that they can be used to form strong bonds, but it also means that any electrons that are already in the orbitals will be strongly repelled. The e_g orbitals now lie between the ligands and any electrons in them are relatively unaffected by the formation of a complex.

Ligand-exchange reactions

When ammonia is added to a solution containing aqueous Cu^{2+} ions, four of the water molecules are substituted by ammonia, producing the cuprammonium ion. This is an example of a **ligand-exchange reaction**, the substitution of one ligand by another:

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

This is a reversible reaction and if the purple complex $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)]$ is diluted, the pale blue colour of the $[Cu(H_2O)_6]^{2+}(aq)$ ion is restored. There is competition between the H_2O and NH_3 molecules to attach themselves to the copper ion. We have an equilibrium with a constant given by the expression:

$$K = \frac{[Cu(NH_3)_4(H_2O)_2]^{2+}][H_2O]^4}{[Cu(H_2O)_6]^{2+}[NH_3]^4}$$

As $[H_2O]$ is in large excess and virtually a constant, we can include it in the equilibrium constant and write:

$$K_{stab} = \frac{[[Cu(NH_3)_4(H_2O)_2]^{2+}]}{[Cu(H_2O)_6][NH_3]^4}$$

where K_{stab} is known as the **stability constant**. Strictly speaking, there are stability constants for each of the equilibria as H_2O molecules are progressively substituted by NH_3 molecules, but here we will only consider the overall constant. The value of K_{stab} depends on how firmly the ligands bind to the metal atom. In general, atoms with high electronegativity bond weakly and those with lower electronegativity bind more strongly. Thus water (which binds via the very electronegative oxygen atom) forms weak bonds while the CN^- ion (which binds via the carbon atom that has much lower electronegativity) forms strong bonds and will have a large value of K_{stab} (see Table 24.4). A high charge on the metal ion also makes K_{stab} larger; compare $\frac{[[Fe(CN)_6]^{3-}]}{[Fe^{3+}][CN^-]^6}$ and $\frac{[[Fe(CN)_6]^{4-}]}{[Fe^{2+}][CN^-]^6}$.

Table 24.4 Values of K_{stab} for some complexes. The values are usually so large that they are often given in the form $\log K_{stab}$.

Complex	K_{stab}	$\log K_{stab}$
$[CuCl_4]^{2-}$	4.2×10^5	5.62
$[Cu(NH_3)_4]^{2+}$	1.3×10^{13}	13.1
$[Fe(CN)_6]^{3-}$	10×10^{31}	31
$[Fe(CN)_6]^{4-}$	1.0×10^{24}	24
$[Ag(NH_3)_2]^+$	1.7×10^7	7.23

Now try this

1 A solution of copper sulfate had ammonia added until $[NH_3] = 0.050\,mol\,dm^{-3}$. Calculate the ratio of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ to $[Cu(H_2O)_6]$ under these conditions.
2 (Harder – use the Nernst equation on page 389.)

$E^{\ominus}_{cell}$ for $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ is $+0.77\,V$

Calculate $E^{\ominus}_{cell}$ for $[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN_6)]^{4-}$.

A more complicated ligand-exchange reaction occurs when concentrated hydrochloric acid is added to aqueous Cu^{2+} ions. Here, four H_2O ligands are replaced by Cl^- ions, but the remaining two water molecules are expelled, leaving the tetrahedral tetrachlorocopper(II) ion (see Figure 24.9):

$$Cu(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightarrow [CuCl_4]^{2-}(aq) + 2H_2O(l)$$
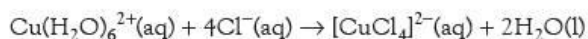
Figure 24.9 Solutions containing **a** the $Cu(H_2O)_6^{2+}$ ion and **b** the $[CuCl_4]^{2-}$ ion


a

b
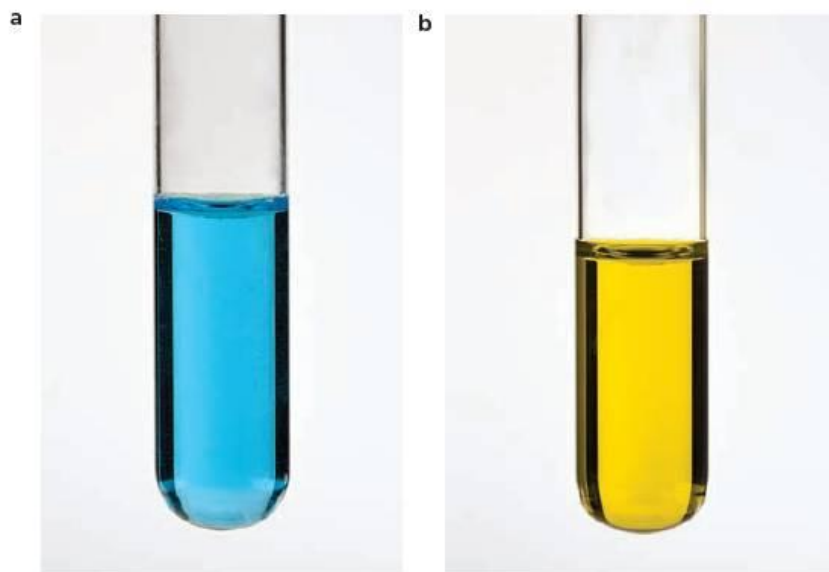
Deprotonation reactions

The water molecules in the hydrated complex ions play an important role. When sodium hydroxide solution is added to a solution containing $Fe^{3+}(aq)$ ions, a precipitate of iron(III) hydroxide, $Fe(OH)_3(s)$, is formed. At first this looks like a simple precipitation reaction:
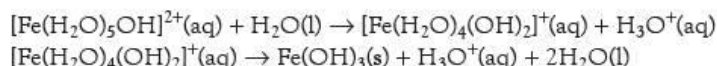
$$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$$
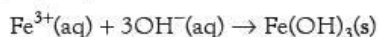
This equation suggests that the reaction is similar to the precipitation of, for example, barium sulfate when $SO_4^{2-}(aq)$ ions and $Ba^{2+}(aq)$ ions are mixed together:

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$
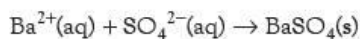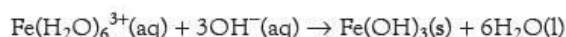
However, this ignores the role of the water molecules. The positive charge of the $Fe(H_2O)_6^{3+}$ ion is partially spread over the surface of the complex. This enables the $Fe(H_2O)_6^{3+}$ ion to act as a weak acid ($K_a = 10^{-5}\,mol\,dm^{-3}$) and to undergo an acid–base reaction with water molecules:

$$Fe(H_2O)_6^{3+}(aq) + H_2O(l) \rightarrow [Fe(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$$
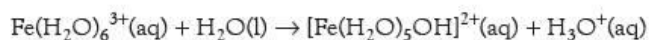
If the H_3O^+ ions are removed by the addition of a strong base such as sodium hydroxide, further acid–base reactions can take place:

$$[Fe(H_2O)_5OH]^{2+}(aq) + H_2O(l) \rightarrow [Fe(H_2O)_4(OH)_2]^+(aq) + H_3O^+(aq)$$
$$[Fe(H_2O)_4(OH)_2]^+(aq) \rightarrow Fe(OH)_3(s) + H_3O^+(aq) + 2H_2O(l)$$

The overall reaction with hydroxide ions is:

$$Fe(H_2O)_6^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s) + 6H_2O(l)$$

The result is that the $Fe(H_2O)_6^{3+}$ ion has been **deprotonated** by a series of acid–base reactions and water ligands have been released.

Worked example 1
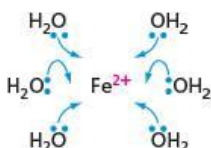
a State the number of d electrons in the Fe^{2+} ion.
b Show, using curly arrows, the formation of the $Fe(H_2O)_6^{2+}$ ion.
c Write an equation for the conversion of $Fe(H_2O)_6^{2+}$ into the $[Fe(CN)_6]^{4-}$ ion on the addition of aqueous KCN.
d State the type of reaction represented by this change.

Answer

a 6
b See Figure 24.10.

Figure 24.10

c $Fe(H_2O)_6^{2+}(aq) + 6CN^-(aq) \rightarrow [Fe(CN)_6]^{4-}(aq) + 6H_2O(l)$
d This is a ligand-exchange reaction.

Worked example 2

a Write an equation for the action of aqueous sodium hydroxide on the $Cu(H_2O)_6^{2+}(aq)$ ion.
b State the type of reaction that is represented by this change.

Answer

a $Cu(H_2O)_6^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s) + 6H_2O(l)$
b This is a deprotonation or acid–base reaction.

Complex ions nomenclature

When naming a complex ion, the following rules apply.

- A cation has the usual metal name, for example, copper.
- An anion has the metal name with an 'ate' ending, for example, chromate.
- The oxidation state is indicated in the usual way, for example, iron(III).
- The ligands are given specific names, for example, chloro (Cl^-), aqua (H_2O), hydroxo (OH^-), ammine (NH_3), cyano (CN^-).
- The number of ligands is indicated by the prefixes di-, tri-, tetra-, penta-, hexa-.

So the complex ion $Fe(H_2O)_6^{3+}$ is the hexaaquairon(III) ion, and $Cu(NH_3)_4^{2+}$ is tetraamminecopper(II).

Worked example

Name the following complex ions.

a $Fe(CN)_6^{3-}$
b $[Cu(NH_3)_4(H_2O)_2]^{2+}$
c $[Fe(H_2O)_5OH]^{2+}$

Answer

a hexacyanoferrate(III) ion
b tetraamminediaquacopper(II) ion
c pentaaquahydroxoiron(III) ion

Now try this

Name the following complex ions.

a $Cr(NH_3)_6^{3+}$
b $CuCl_4^{2-}$
c $Zn(OH)_4^{2-}$
d $[CrCl_2(H_2O)_4]^+$
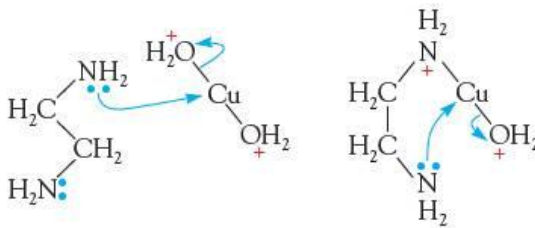
Chelates

Bidentate ligands

Ligands such as H_2O and CN^- are attached by one coordinate bond to the metal ion. If the ligand contains two groups that have a lone pair of electrons, it may form two bonds to the metal atom, forming a ring. Such a ligand is called a **chelate**, a name derived from the Greek word for a crab's claw. Stable complexes result if five- or six-membered rings are produced by the chelate and the metal ion.

Two ligands that readily form chelates are 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, and the ethanedioate ion, $^-O_2CCO_2^-$. These form five-membered rings (see Figure 24.11) and are called **bidentate** ligands because they join by two bonds.

Chelates form particularly stable complex ions, partly because they form strong bonds to the metal ion, but also because there is an additional entropy effect that adds to their stability. For example, a chelate is formed in which three ethanedioate ions bond to Fe^{3+}. Four species become seven after the reaction, so the formation of this chelate is accompanied by an increase in entropy:

$$Fe(H_2O)_6^{3+} + 3C_2O_4^{2-} \rightarrow Fe(C_2O_4)_3^{3-} + 6H_2O$$
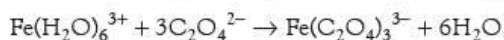
Another way of visualising the increase in entropy is to consider the effect after one end of the chelate has become bonded to the metal ion. Once this end is secured, it becomes much more likely that the other end will be in the right position to bond too.

Figure 24.11 Five-membered rings formed between 1,2-diaminoethane and the Cu^{2+} ion, and between the ethanedioate ion and the Fe^{3+} ion.

Multidentate ligands – edta

Some chelates form more than two bonds with the metal ion. A particularly important one is **e**thylene **d**iamine **t**etraacetic **a**cid, abbreviated as edta, which is used in the form of its disodium salt, containing $(edtaH_2)^{2-}$.

This has six pairs of electrons able to bond to a metal ion, and so forms a hexadentate chelate. edta is used to remove Ca^{2+} and Mg^{2+} ions from hard water.

$$Ca(H_2O)_6^{2+}(aq) + (edtaH_2)^{2-}(aq) \rightarrow Ca(edta)^{2-}(aq) + 2H+(aq) + 6H_2O(l)$$
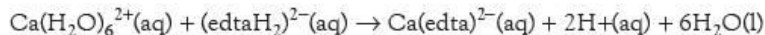
This trapping of metal ions is called **sequestering**. It alters the chemical properties of the metal ions, and can be used to counteract the effect of poisoning by heavy metal ions such as lead.

Analysing tap water

The formation of stable complexes between edta and Mg^{2+} and Ca^{2+} ions is used to estimate the hardness of water by titration with edta. A sample of the water being tested is mixed with a buffer solution at pH 10. A few drops of an indicator, solochrome black, are added and a solution of edta is run in from the burette.
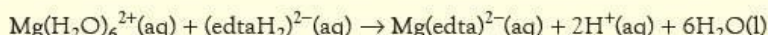
Solochrome black forms a red complex with magnesium ions. If solochrome black is represented as $HIn^{2-}(aq)$, the reaction is

$$MgIn^-(aq) + (edtaH_2)^{2-}(aq) \rightarrow Mg(edta)^{2-}(aq) + H^+(aq) + HIn^{2-}(aq)$$
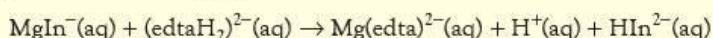
red complex   **blue solution**

During the titration, the free calcium and magnesium ions first react with the edta:

$$Mg(H_2O)_6^{2+}(aq) + (edtaH_2)^{2-}(aq) \rightarrow Mg(edta)^{2-}(aq) + 2H^+(aq) + 6H_2O(l)$$

When all the free calcium and magnesium ions have reacted with edta, the colour changes from red to blue as the $MgIn^-(aq)$ complex breaks down.

Worked example

A few drops of solochrome black indicator were added to $50.0\,cm^3$ of tap water. A $0.0100\,mol\,dm^{-3}$ solution of edta in a buffer at pH 10 was added from a burette and the indicator changed from red to blue after the addition of $7.55\,cm^3$.

a Suggest two substances that could be used to make the buffer solution.
b Calculate the total concentration of calcium and magnesium ions in the sample of hard water.

Answer
a Ammonia and an ammonium salt, for example, ammonium chloride (see section 22.3).
b $n(edta) = c \times \dfrac{V}{1000}$

$$= 0.0100 \times \frac{7.55}{1000}$$

$$= 7.55 \times 10^{-5}\,mol$$

This amount of edta reacted with $50.0\,cm^3$ of tap water. Since one mole of calcium or magnesium ions reacts with one mole of edta, the concentration of calcium and magnesium ions in the tap water is given by:

$$c(Ca^{2+} + Mg^{2+}) = \frac{1000}{V} \times n$$

$$= \frac{1000}{50} \times 7.55 \times 10^{-5}$$

$$= 1.51 \times 10^{-3}\,mol\,dm^{-3}$$

Isomerism in complex ions

Some of the types of isomerism found in organic chemistry (see section 12.6) are also found in complex ions. An example of structural isomerism occurs in compounds of formula $CrCl_3.6H_2O$. Three such compounds are known with different properties (see Table 24.5). In particular, they have different numbers of free Cl^- ions (as shown by their reactions with Ag^+ ions) and free water molecules (as shown by the number of water molecules that are easily removed by dehydration).

Table 24.5 The properties of the three isomers of $CrCl_3.6H_2O$

Colour	Number of free Cl^- Ions	Number of free H_2O molecules	Structure
purple	3	0	$[Cr(H_2O)_6^{3+}]3Cl^-$
blue-green	2	1	$[Cr(H_2O)_5Cl]^{2+}2Cl^-.H_2O$
green	1	2	$[Cr(H_2O)_4Cl_2]^+Cl^-.2H_2O$

Complexes can also show stereochemistry. A good example of this is the complex ion $[Ni(en)_2(NH_3)_2]^{2+}$, where 'en' is used as an abbreviation for 1,2-diaminoethane, $NH_2CH_2CH_2NH_2$. This complex can exist in *cis* and *trans* forms. The *cis* form (but not the *trans*) has a chiral centre (the nickel atom) and can be resolved into optical isomers (see Figure 24.12).

Figure 24.12 The stereochemistry of $[Ni(en)_2(NH_3)_2]^{2+}$
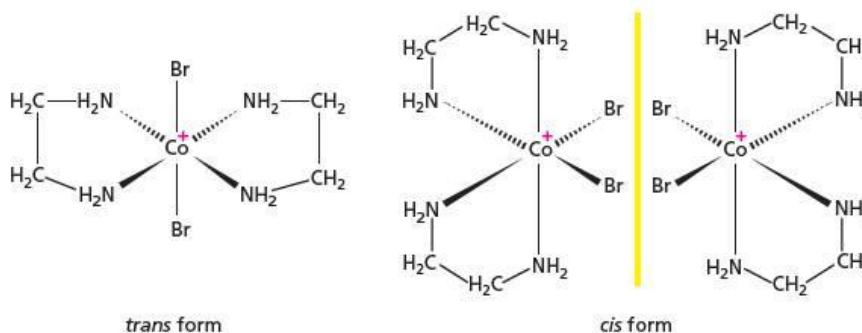
trans form   cis form

Ni^{2+} also forms a complex with three 1,2-diaminoethane ligands. This has only the *cis* form as the distance is too large for the ligand to stretch across the *trans* positions. The *cis* form can also be resolved into optical isomers (see Figure 24.13).

Figure 24.13 Optical isomerism in the $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ ion
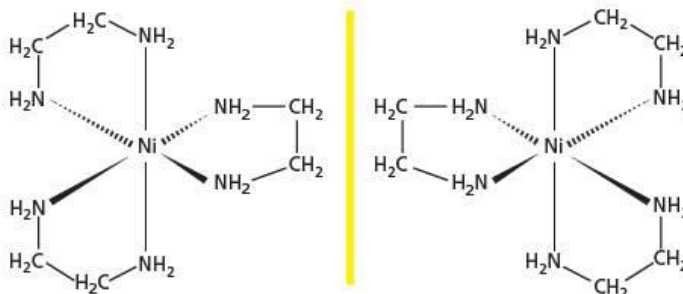
Cis- and *trans*-platin

An important example of *cis/trans* isomerism is the drug cisplatin. This has a Pt atom joined to two chlorine atoms and two ammonia molecules. It is a square planar complex and can, therefore, exist in both *cis* and *trans* forms.

cis-platin   trans-platin
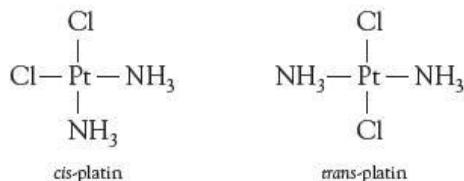
Cis-platin (but not *trans*-platin) is very effective in treating some forms of cancer. One of the chlorine atoms in *cis*-platin is easily hydrolysed to give the $[(NH_3)_2Cl(H_2O)]^+$ ion. This ion binds to one of the four bases in DNA, usually guanine (see Topic 27, page 489), to give the $[PtCl(guanine-DNA)(NH_3)_2]^+$ ion. This ion can cross-link with another DNA chain by displacement of the chlorine from the complex. The cross-linking inhibits

DNA replication, particularly in cancer cells that are undergoing rapid cell division, and the cell dies. There is no obvious reason why *trans*-platin is ineffective; one theory is that it becomes deactivated before it can attach itself to DNA.
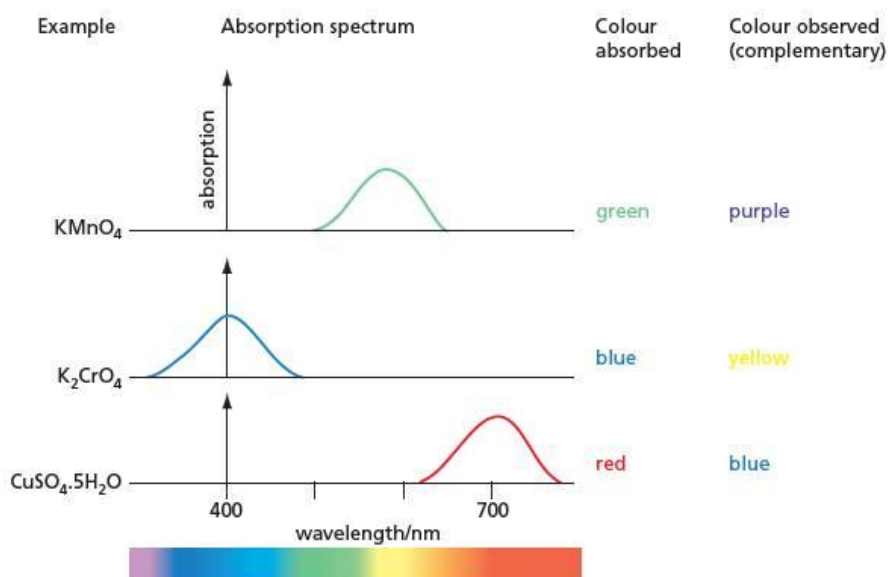
24.5 Colour in the d block

The origin of colour

All atoms and molecules absorb in the ultraviolet region of the spectrum because this radiation has enough energy to excite their outer electrons. The ultraviolet region is outside the visible range of the spectrum, so absorption in the ultraviolet leaves a substance colourless. Some substances, however, also have outer electron levels that are sufficiently close together for visible radiation to have enough energy to bring about electronic excitation. Under these circumstances, the substance appears coloured. The resulting colour seen is white light minus the colour being absorbed. The colour we see is therefore the **complementary** colour to the colour being absorbed (see Figure 24.14).

To absorb in the visible region, the substance must have two energy levels that are very close together. Close energy levels come about in two ways, namely **charge transfer** and **d-to-d transitions**.

Figure 24.14 The colours observed when absorption takes place in the visible region of the spectrum

Example	Absorption spectrum	Colour absorbed	Colour observed (complementary)
$KMnO_4$		green	purple
K_2CrO_4		blue	yellow
$CuSO_4.5H_2O$		red	blue

Charge transfer

If a substance contains bonds which are on the borderline between ionic and covalent, it may change from one bonding type to another by absorbing visible light. This effect is shown by some solids which are coloured (for example PbO, which is orange, and AgI, which is yellow) even though the ions they contain are colourless. In the d block, another example is CuO, which is black even though the Cu^{2+} ion is blue.

d-to-d transitions

In the d block, colour usually arises because of d-to-d electronic transitions. The t_{2g} and the e_g orbitals are close in energy, and electrons in the t_{2g} orbitals may be excited into the e_g orbitals by the absorption of a photon of visible light. Using the Planck equation,

$$\Delta E = hf$$

the frequency associated with the energy difference between the orbitals (ΔE in Figure 24.7) corresponds to the frequencies of visible light.

Ions that have no t_{2g} electrons, for example $Sc(H_2O)_6^{3+}$, are colourless because there are no t_{2g} electrons to promote. Similarly d^{10} ions, for example $Zn(H_2O)_6^{2+}$, are also colourless because there is no empty space in the e_g level to receive an extra electron (see Figure 24.15).

Figure 24.15 The electronic structures of the $Sc(H_2O)_6^{3+}$ and $Zn(H_2O)_6^{2+}$ ions

It is fairly easy to explain the colours of the Cu^{2+} complexes. This is because there is only a single space in the e_g orbitals to receive an excited electron, and as a result there is only one absorption band. The absorption is a band rather than a sharp line (as happens with atomic spectra in the gas phase) because the two energy levels are spread out under the influence of the adjacent ligands. The colour of the complex then depends on where the maximum of this absorption is in the visible spectrum.

- For the simple Cu^{2+} ion (anhydrous $CuSO_4$), the ligands create such a very weak field that the two energy levels are nearly the same; absorption is then in the infrared and this means that the substance is colourless.
- For the $[Cu(H_2O)_6]^{2+}$ ion, absorption is partially in the red end of the spectrum and the complex appears pale blue.
- For the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion, the absorption is in the green part of the spectrum and the colour is a more intense purple.

This change in the position of the absorption band is caused by the increase in the electrostatic field created by the ligands, which results in a larger splitting in the energy levels (ΔE in Figure 24.7) and a higher frequency of absorption (see Figure 24.16).

Figure 24.16 Colours of some Cu^{2+} compounds. As the ligand field becomes stronger, the splitting between the d orbitals increases and the absorption moves from the infrared into the visible region of the spectrum.

ligand	H_2O	NH_3	$H_2NCH_2CH_2NH_2$
absorption maximum/nm	800	620	530
colour	pale blue	deep blue	purple

24.6 Catalytic properties

The transition metals often act as catalysts. In the Haber process (see section 10.5) and the Contact process (see section 10.6), the catalysts are in the solid state. Transition metals can also act as catalysts in solution. A good example is the oxidation of iodide ions by peroxodisulfate(VI) ions:

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$
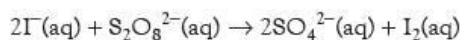
This reaction is normally quite slow, most likely because the negatively charged ions repel each other. However, it is catalysed by the addition of a number of d-block metal ions, for example $Fe^{2+}(aq)$. A possible mechanism is:

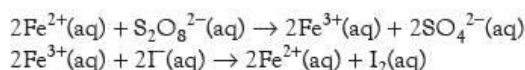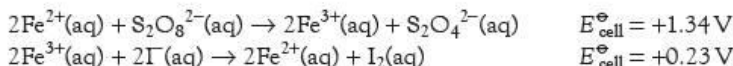$$2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$$
$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$$

Table 24.6 Relevant values of $E^\ominus$ for catalysis by Fe^{2+} ions

System	$E^\ominus$/V
$S_2O_8^{2-}/2SO_4^{2-}$	+2.01
Fe^{3+}/Fe^{2+}	+0.77
$I_2/2I^-$	+0.54

Each of the two parts of this mechanism involves a reaction between two ions of opposite charge, which is a favourable situation.

Both theory and experiment can be used to support this mechanism.

- The relevant values of standard electrode potentials are given in Table 24.6. These show that the postulated mechanism is thermodynamically feasible.

$$2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + S_2O_4^{2-}(aq) \qquad E^\ominus_{cell} = +1.34\,V$$
$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq) \qquad E^\ominus_{cell} = +0.23\,V$$

- The two reactions can be tested experimentally. If a solution of $S_2O_8^{2-}$ ions is added to Fe^{2+} ions, Fe^{3+} ions are produced. If Fe^{3+} ions are added to I^- ions, iodine is liberated.
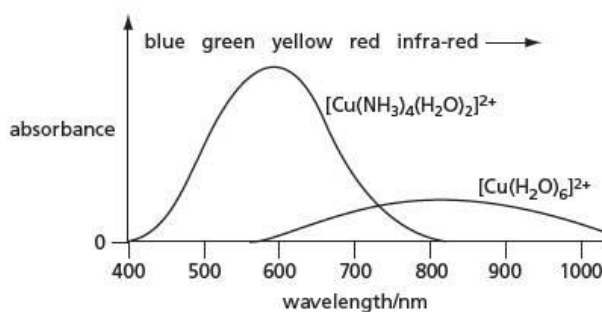
Summary

- The **3d block** includes the elements from scandium to zinc inclusive.
- The elements titanium to copper show features associated with **transition metals**, that is, variable oxidation states and coloured ions.
- The elements of the 3d block have high melting points, boiling points and densities.
- The first and second ionisation energies increase only slightly across the block from scandium to zinc, as 4s electrons are being removed which are shielded from the nuclear attraction by the inner 3d electrons. The third ionisation energies increase more rapidly as a 3d electron is being removed.
- Most of the elements form M^{2+} ions by loss of the 4s electrons, and some form M^{3+} ions as well.

- The elements chromium and manganese have a maximum oxidation number equal to the sum of the numbers of 3d and 4s electrons.
- The ions of all the 3d-block elements form **complex ions** by receiving electrons from two, four or six **ligands**.
- Complex ions may exist in different forms (isomerism) and in different shapes (stereoisomerism).
- The stability of the complex is measured by the stability constant, K_{stab}.
- Some ligands join onto the metal ions by more than one pair of electrons. These form **chelates**, which are especially stable.
- d^0 and d^{10} ions are colourless. Other d-block ions are coloured because of **d-to-d transitions** in the visible region of the spectrum.

Examination practice questions

Please see the data section of the CD for any A_r values you may need.

1 a Explain what is meant by the term *transition element*. [1]
   b Complete the electronic configuration of
      i   the vanadium atom, $1s^2\,2s^2\,2p^6$ ...
      ii the Cu^{2+} ion. $1s^2\,2s^2\,2p^6$ ... [2]
   c List the **four** most likely oxidation states of vanadium. [1]
   d Describe what you would see, and explain what happens, when dilute aqueous ammonia is added to a solution containing Cu^{2+} ions, until the ammonia is in an excess. [5]
   e Copper powder dissolves in an acidified solution of sodium vanadate(V), $NaVO_3$, to produce a blue solution containing VO^{2+} and Cu^{2+} ions.
      By using suitable half-equations from the data section on the CD, construct a balanced equation for this reaction. [2]
      [Cambridge International AS & A Level Chemistry 9701, Paper 4 Q3 June 2009]

2 One major difference between the properties of compounds of the transition elements and those of other compounds is that the compounds of the transition elements are often coloured.
   a Explain in detail why many transition element compounds are coloured. [3]

b The following graph shows the absorption spectrum of two complexes containing copper.

blue green yellow red infra-red ⟶

absorbance

$[Cu(NH_3)_4(H_2O)_2]^{2+}$

$[Cu(H_2O)_6]^{2+}$

0

400   500   600   700   800   900   1000
wavelength/nm

   i   State the colours of the following complex ions.
       • $[Cu(H_2O)_6]^{2+}$
       • $[Cu(NH_3)_4(H_2O)_2]^{2+}$
   ii Using the spectra above give **two** reasons why the colour of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion is deeper (more intense) than that of the $[Cu(H_2O)_6]^{2+}$ ion.

iii Predict the absorption spectrum of the complex $[Cu(NH_3)_2(H_2O)_4]^{2+}$, and sketch this spectrum on a copy of the graph. [6]

c Copper forms a complex with chlorine according to the following equilibrium.

$$Cu^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq)$$
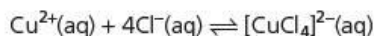
i Write an expression for the equilibrium constant, K_c, for this reaction, stating its units.

ii The numerical value of K_c is 4.2×10^5. Calculate the $[[CuCl_4]^{2-}]/[Cu^{2+}]$ ratio when $[Cl^-] = 0.20\,mol\,dm^{-3}$. [3]

[Cambridge International AS & A Level Chemistry 9701, Paper 41 Q3 November 2009]

3 a Complete the electronic structures of the Cr^{3+} and Mn^{2+} ions.

Cr^{3+} $1s^2\,2s^2\,2p^6$ ...
Mn^{2+} $1s^2\,2s^2\,2p^6$ ... [2]
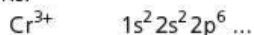
b i Describe what observations you would make when dilute $KMnO_4(aq)$ is added slowly and with shaking to an acidified solution of $FeSO_4(aq)$ until the $KMnO_4$ is in a large excess.

ii Construct an ionic equation for the reaction that occurs. [4]

c By selecting relevant $E^{\ominus}$ data from the data section on the CD explain why acidified solutions of $Fe^{2+}(aq)$ are relatively stable to oxidation by air, whereas a freshly prepared precipitate of $Fe(OH)_2$ is readily oxidised to $Fe(OH)_3$ under alkaline conditions. [4]

d Predict the organic products of the following reactions and draw their structures. You may use structural or skeletal formulae as you wish.

hot conc.
$MnO_4^- + H^+$

hot conc.
$MnO_4^- + H^+$

hot
$Cr_2O_7^{2-} + H^+$
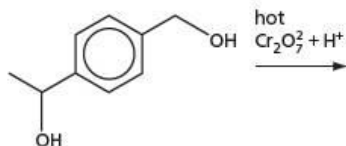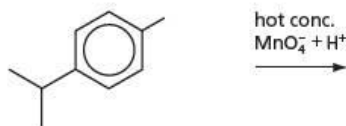
[4]

e $KMnO_4$ and $K_2Cr_2O_7$ are the reagents that can be used to carry out the following transformation.
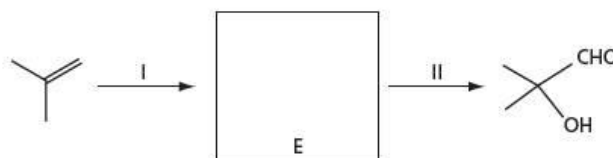
i Draw the structure of intermediate E.

ii Suggest reagents and conditions for reaction I, and for reaction II. [3]

[Cambridge International AS & A Level Chemistry 9701, Paper 42 Q4 June 2010]