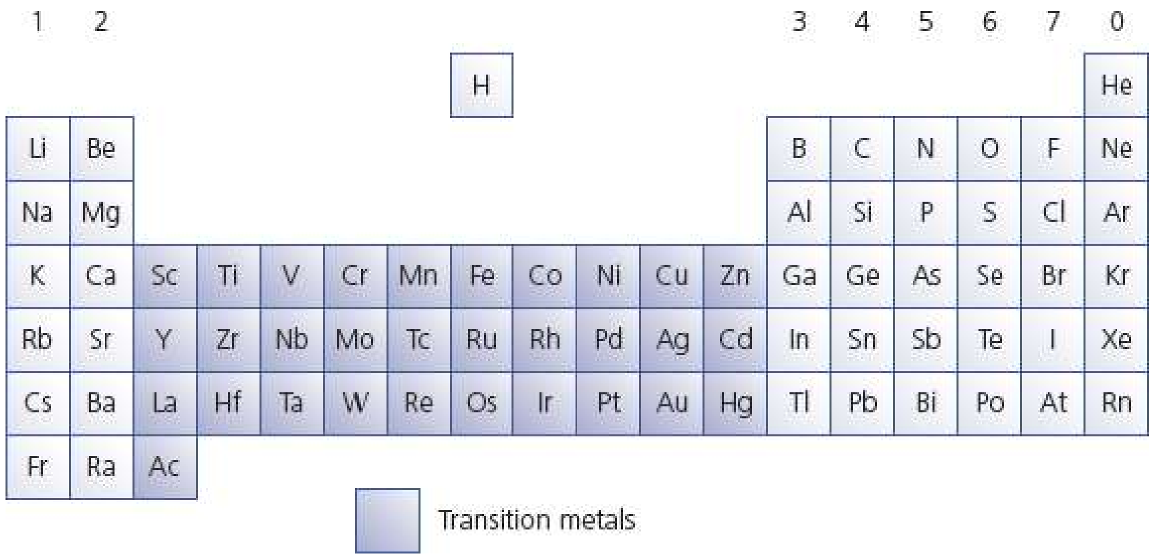
28 Chemistry of transition elements

Electronic structures and physical properties

Although you can probably identify the block of elements that make up the transition elements in the Periodic Table (Figure 28.1), you need to know *why* these elements are different from other metals, and what makes them special.



1	2											3	4	5	6	7	0
							H										He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

▨ Transition metals

Figure 28.1 The Periodic Table

The **transition elements** are shaded and represent the filling of the d-electron orbitals in each of the 3d-, 4d- and 5d-orbitals.

KEY TERM

A **transition element** is defined as a metal that forms one or more stable ions with incompletely filled d-orbitals.

You only really need to know details about the 3d elements – scandium, Sc, to zinc, Zn.

You can see this best by looking at the electronic configurations of the elements and ions of this group of elements (Figure 28.2).

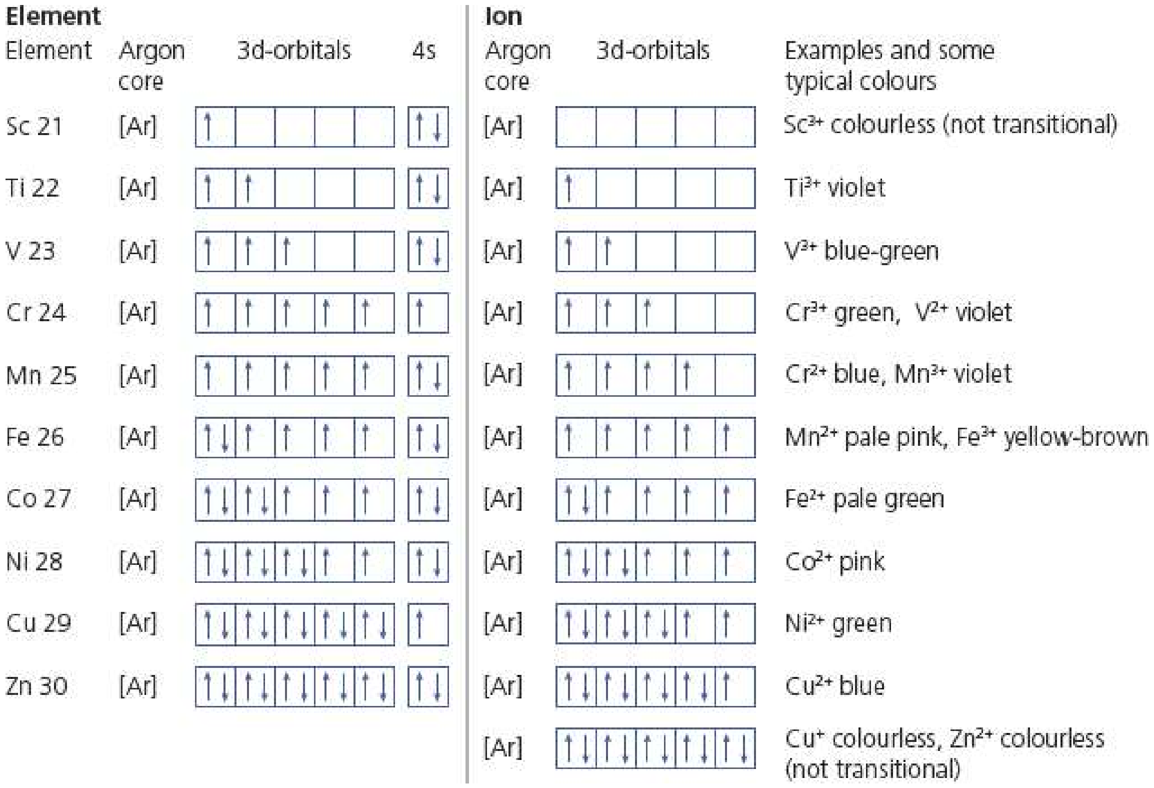


Figure 28.2 Electronic configurations of the elements and some ions of transition metals

Table 28.1 shows some of the common properties of the elements scandium to zinc. If you look first at the electronic configurations of the elements, you can see that all except copper and zinc have incompletely filled d-orbitals.

Table 28.1

Property	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Melting point/°C	1541	1668	1910	1857	1246	1538	1495	1455	1083	420
Density/ g cm^{-3}	2.99	4.54	6.11	7.19	7.33	7.87	8.90	8.90	8.92	7.13
Atomic radius/ pm	161	145	132	125	124	124	125	125	128	133
M^{2+} ionic radius/pm	n/a	90	88	84	80	76	74	72	69	74
M^{3+} ionic radius/pm	81	76	74	69	66	64	63	62	n/a	n/a
Common oxidation states	+3	+2, +3, +4	+2, +3, +4, +5	+2, +3, +6	+2, +3, +4, +6, +7	+2, +3, +6	+2, +3	+2, +3	+1, +2	+2
Outer electronic configuration	$3d^{1}4s^{2}$	$3d^{2}4s^{2}$	$3d^{3}4s^{2}$	$3d^{5}4s^{1}$	$3d^{5}4s^{2}$	$3d^{6}4s^{2}$	$3d^{7}4s^{2}$	$3d^{8}4s^{2}$	$3d^{10}4s^{1}$	$3d^{10}4s^{2}$
First ionisation energy/ kJ mol^{-1}	632	661	648	653	716	762	757	736	745	908

NOW TEST YOURSELF

1 Study the data in Table 28.1.

a Give **two** pieces of data that show scandium differing from a typical transition metal.

b Give **two** pieces of data that show zinc differing from a typical transition metal.

Considering the common oxidation states, you can see that Sc^{3+} ions have no d-electrons, and that Zn^{2+} ions have full d-orbitals. Based on this evidence there is a case for saying that scandium is a transition element, but that no case can be made for zinc.

On examining the common stable ions of the transition elements you can see that, with the exception of scandium, all the elements lose their two 4s-electrons to form a 2+ ion:

- For elements that have two to five 3d-electrons, the loss of these, together with the 4s electrons, gives the highest oxidation state (the ion with the highest positive charge).
- Note that there are no d^4 or d^9 arrangements for chromium or copper *atoms*. This is because half-full and completely full d-orbitals are favoured energetically.

You might be asked to state the electronic configuration of a given transition element and suggest its stable ions. You can do this from the Periodic Table:

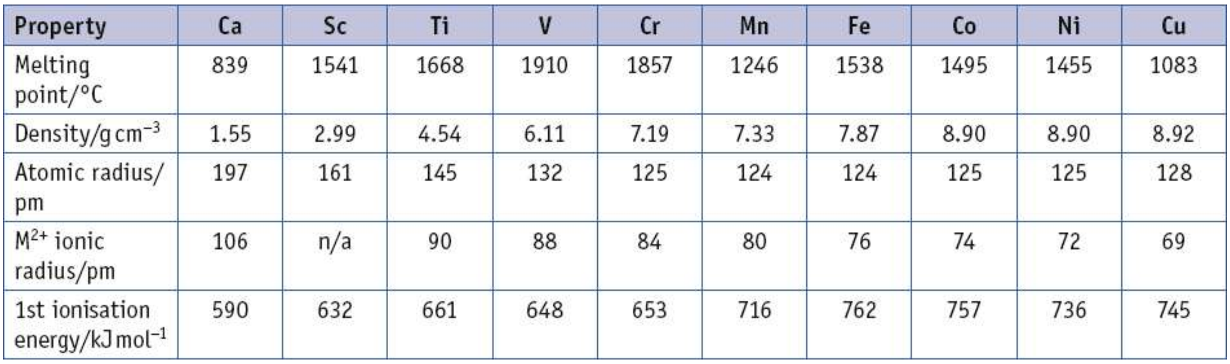
- Use the proton (atomic) number to work out the total number of electrons.
- Then put the electrons into orbitals, bearing in mind the exceptions mentioned above.

Look at the rows in Table 28.1 that give data about atomic radii, ionic radii and first ionisation energies. You can see that across the transition elements there is a relatively small change in each of these properties.

Comparison with calcium

You are also expected to be able to contrast the properties of the transition elements with those of the s-block metal, calcium (Table 28.2).

Table 28.2



Property	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Melting point/°C	839	1541	1668	1910	1857	1246	1538	1495	1455	1083
Density/g cm^{-3}	1.55	2.99	4.54	6.11	7.19	7.33	7.87	8.90	8.90	8.92
Atomic radius/pm	197	161	145	132	125	124	124	125	125	128
M^{2+} ionic radius/pm	106	n/a	90	88	84	80	76	74	72	69
1st ionisation energy/kJ mol^{-1}	590	632	661	648	653	716	762	757	736	745

- You can see from the melting points and densities that the transition elements are much more similar to each other than they are to calcium. This is also borne out by the atomic and M^{2+} ionic radii and, to a lesser extent, by the first ionisation energies.
- The syllabus also refers to conductivity, but comparisons are harder to make here because all metals are much better electrical conductors than semi-conductors or non-metals.

Oxidation states

- As you can see from Table 28.1, most of the transition elements form more than one ion or oxidation state. You can see the details more clearly in

Figure 28.3.

- The reason that these other oxidation states exist is that there is not a large energy barrier to the removal of subsequent electrons.

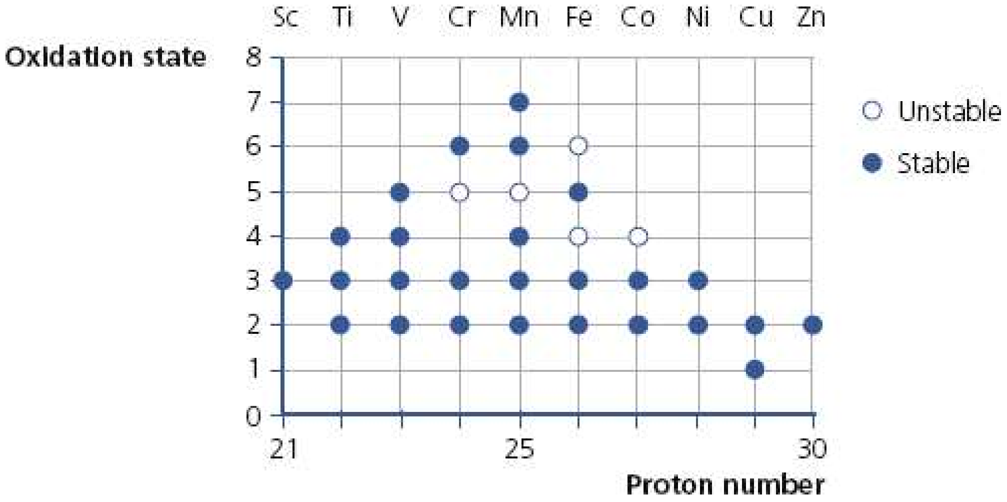


Figure 28.3 Oxidation states in transition metals

- You can see an example of these differences in ionisation energies if you compare the first four ionisation energies of calcium with those of chromium and manganese (Table 28.3).

Table 28.3

Element	Proton number	1st IE/kJ mol^{-1}	2nd IE/kJ mol^{-1}	3rd IE/kJ mol^{-1}	4th IE/kJ mol^{-1}
Calcium	20	590	1150	4940	6480
Chromium	24	653	1590	2990	4770
Manganese	25	716	1510	3250	5190

- It is clear from the data in Table 28.3 that to remove the third electron from calcium requires about as much energy as removing the fourth from chromium or manganese.
- However, it is not as simple as just comparing ionisation energies. Having ionised the metal, it then has to react to form a compound.
- There are two key enthalpies to consider – the lattice energy (if a solid is being formed) and the enthalpies of hydration of the ions (if an aqueous solution is being formed).
- The more highly charged an ion, the more electrons have to be removed and the more ionisation energy has to be provided.
- Offsetting this, however, the more highly charged the ion, the more energy is released, either as lattice energy or as the hydration enthalpy of the

metal ion.

NOW TEST YOURSELF

2 The graph in Figure 28.4 was obtained for one of the first row transition metals. Explain the important points on the graph and identify the metal.

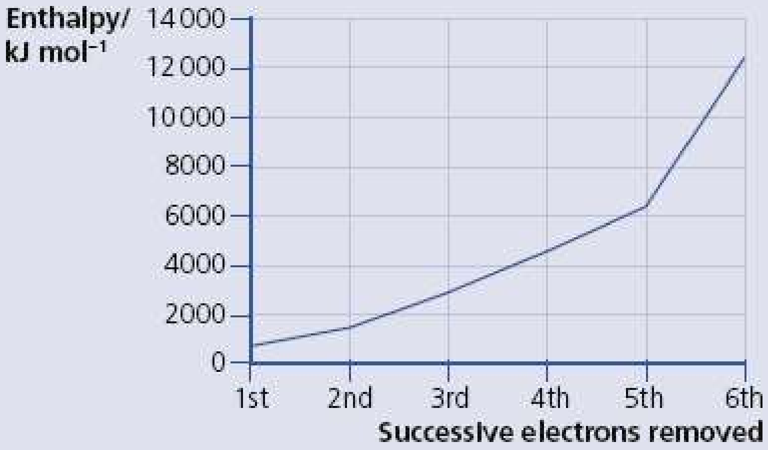


Figure 28.4

Redox systems

There are three important redox systems that you need to know about and also for the practical syllabus: Fe^{3+}/Fe^{2+}, MnO_4^-/Mn^{2+} and $Cr_2O_7^{2-}/Cr^{3+}$. You have already looked at some simple redox processes in Chapter 6.

Reaction between acidified manganate(VII) ions and iron(II) ions

- This reaction is used to estimate iron(II) ions quantitatively.
- It is self-indicating – on the addition of a standard solution of potassium manganate(VII) to an iron(II) solution, decolorisation of manganate(VII) occurs as the almost colourless manganese(II) ion (a very pale pink) is formed.
- The end point is when the first permanent pale pink is seen with one drop excess of the manganate(VII).

- The dilute sulfuric acid prevents the formation of a manganese(IV) oxide precipitate and ensures the reduction of manganate(VII) ions to manganese(II) ions.
- The two half-equations are:

$$\mathrm{MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)} \qquad E^\ominus = +1.52\ \mathrm{V}$$

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

- Because each iron(II) ion supplies one electron, each manganate(VII) ion can oxidise five iron(II) ions. Thus, the overall equation is:

$$\mathrm{MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)}$$

Reaction between acidified dichromate(VI) ions and iron(II) ions

- As with potassium manganate(VII), a standard solution of potassium dichromate(VI) can be used to estimate iron(II) ions in solution quantitatively. In this case, however, a redox indicator must be used to detect the end point.
- The indicator changes colour when oxidised to another form, but only after the iron is oxidised, i.e. it is not as easily oxidised as $\mathrm{Fe^{2+}}$ – the $E^\ominus$ of the indicator is more positive than that of $\mathrm{Fe^{2+}}$ but lower than that for the dichromate(VI) ions.
- Hence, it is oxidised by the dichromate to show the end point.
- The two half-equations are:

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

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

- Because each iron(II) ion supplies one electron, each dichromate(VI) ion can oxidise six iron(II) ions. The overall equation is:

$$\mathrm{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)}$$

Other redox reactions

The transition metals take part in a range of redox reactions, some of which could form part of the titrimetric work you may asked to carry out in the practical paper. You might also be asked to predict whether or not a given reaction will take place based on $E^\ominus$ data. If you are not sure how to do this, read Chapter 6 again.

The important things to remember are:

- Metals react by electron loss (oxidation state increases) to form positive cations (e.g. sodium ion, Na^+). So, as the electron-loss potential increases, the reactivity of the metal increases.
- Non-metallic elements react by electron gain (oxidation state decrease) to form single covalent bonds (e.g. HCl) or the negative anion (e.g. chloride ion Cl^- in NaCl). So, as the electron-accepting power decreases, so does the reactivity of the element.
- For a reaction to be feasible, the E_{cell} value must be *positive*. So if you calculate it to be negative, the reverse reaction will be the feasible one.

NOW TEST YOURSELF

3 Work out the overall equation for the reaction of manganate(VII) ions with hydrogen peroxide in acid solution.

Geometry of the d-orbitals

In Chapter 1 we looked at the shape and symmetry of s- and p-orbitals, which can hold two and six electrons respectively. In considering the transition elements you need to understand the shape and symmetry of the d-orbitals, which can hold up to ten electrons.

The d-orbitals can be divided into two groups.

- Each of the first group (Figure 28.5(a)) is similar to a pair of p-orbitals at right angles to one another, and as you can see the lobes lie between the x and y, y and z and z and x axes.
- The second group (Figure 28.5(b)) is different, in that the lobes lie on the x, y and z axes. You do *not* need to know *why* they are these shapes, only the shapes and symmetry of the five orbitals.

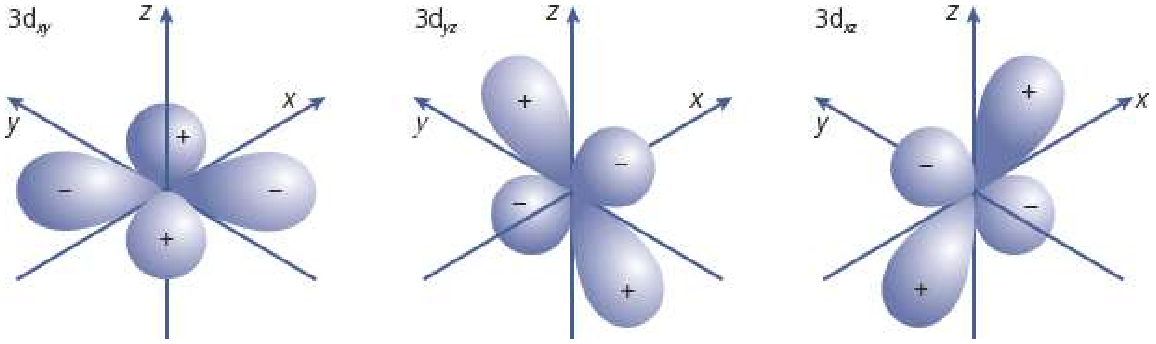


Figure 28.5(a)

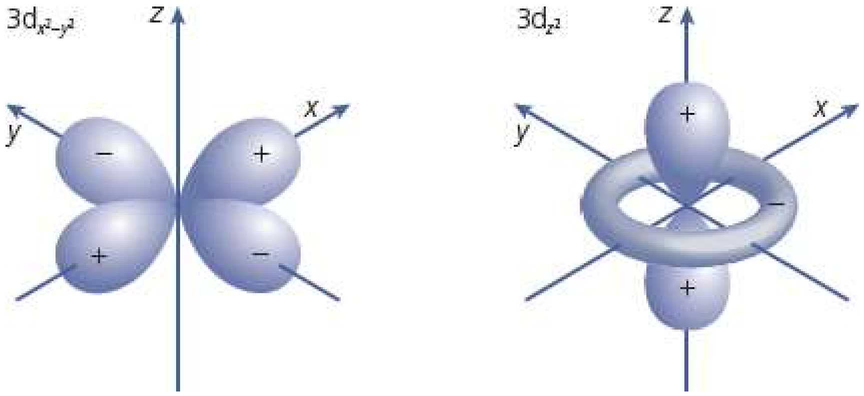


Figure 28.5(b)

The shape and symmetry of these orbitals are important when transition metal cations react to form **complexes**.

The metal cations do this by interacting with **ligands**.

Imagine electron-rich ligands approaching a transition metal ion with electrons in its d-orbitals. There will be some repulsion, raising the energy of some d-orbitals more than that of others.

In a ‘bare’ transition metal ion with no ligands attached, all of the d-orbitals have the same energy and are said to be **degenerate**. As ligands approach the transition metal ion, some of the d-orbitals will be repelled more than others by the ligand electrons. The particular orbitals involved will depend on where four or six ligands are attracted to the transition mental ion. When the d-orbitals have different energies they are said to be **non-degenerate**.

KEY TERMS

A **complex** is a transition metal ion bound to a number of ligands (see below), usually four or six, which reacts as a large ion.

A **ligand** is an atom, ion or molecule that can act as an electron-pair donor, and usually forms a dative covalent or coordinate bond with the central metal ion. Ligands can be monodentate, bidentate or polydentate depending on the number of dative bonds they form with the transition metal ion.

Degenerate electron orbitals are ones in which, for example, all d electrons have the same energy. **Non-degenerate** electron orbitals are ones in which the presence of a ligand causes some of the orbitals to have different energies (see Figure 28.6).

Look at Figure 28.6.

- It shows that for the formation of a tetrahedral complex, three orbitals have higher energy ($3d_{xy}$, $3d_{yz}$ and $3d_{zx}$), whereas for an octahedral complex the reverse is true ($3d_{x^2-y^2}$ and $3d_{z^2}$).
- This is because in octahedral complexes the ligands approach the central metal ion along the axes, and there is repulsion between the electrons on the ligands and those in the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals.
- In tetrahedral complexes the four ligands approach the central metal ion between the axes and now there is repulsion between the electrons on the ligands and those in the $3d_{xy}$, $3d_{yz}$ and $3d_{zx}$ orbitals.

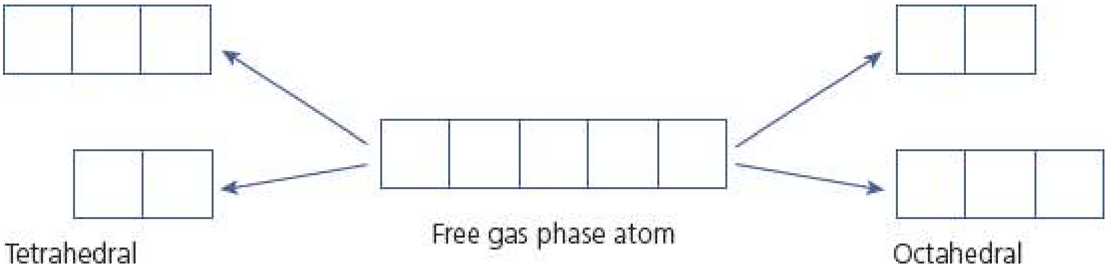


Figure 28.6 Splitting of d-orbitals in transition metal complexes

NOW TEST YOURSELF

4 Sketch the arrangement of the five d-orbitals in

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

b $[CuCl_4]^{2-}$

Formation of complexes

- As well as forming simple compounds, such as oxides and salts, one of the characteristic properties of transition metals is their ability to form complex ions, many of which have distinctive colours.
- The reason for the colour is the absorption of light from different parts of the electromagnetic spectrum.
- This absorption occurs because of the movement of an electron from a lower energy d-orbital to one of higher energy (see Figure 28.6).
- In the case of aqueous copper(II) ions the transition is shown in Figure 28.7.

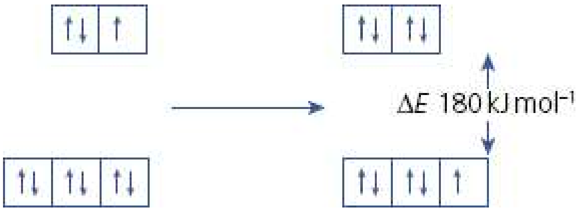


Figure 28.7 Promotion of an electron in copper(**II**)

The promotion of this electron requires 180 kJ mol^{-1}, and the frequency corresponding to this lies in the red-orange region of the spectrum. As a result, these colours are absorbed, leaving yellow, green, blue and purple to be transmitted, resulting in the familiar pale-blue colour of aqueous Cu(II) ions.

The **colour** of a complex depends on the energy gap in the d-orbitals, which is a result of two factors:

- the nature of the metal and its oxidation state
- the nature of the ligand

STUDY TIP

The **colour** you observe for a complex ion is what remains from white light (the complementary colour) after the energy required to promote an electron from one group of d-orbitals to the other group has been removed.

You are familiar with the colours of the two common oxidation states of iron, Fe^{2+} and Fe^{3+} in aqueous solution – Fe^{2+} is pale green and Fe^{3+} is yellow-brown.

When copper ions are dissolved in water, they form the complex ion $[Cu(H_2O)_6]^{2+}$, which is pale blue. On adding aqueous ammonia to this solution until the ammonia is present in an excess, the solution turns a deep blue:

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

The deepening blue is a sign of a bigger energy gap between the two sets of orbitals (Figure 28.8).

Figure 28.8 Energy gap in copper(**II**) complexes

Other ligands can have a bigger or smaller energy gap, and some indication of the order is given in Figure 28.9.

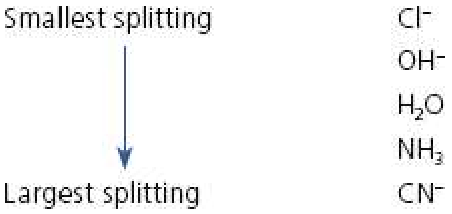


Figure 28.9

NOW TEST YOURSELF

5 Three octahedral complexes of chromium are coloured blue, green and purple. Each complex contains one type of ligand – ammonia, water or hydroxide ions.

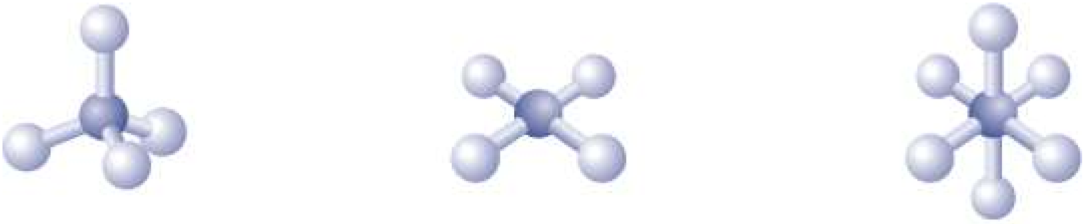
Identify the formula of each complex and match it to the correct colour, explaining your reasoning.

Coordination number

- You need to be able to say a little more about the structure of transition metal complexes.
- First, the **coordination number** is the number of coordinate bonds formed by the metal ion. In many cases this will be the same as the number of ligands, but some ligands can form more than one coordinate bond, so be careful. The most common coordination numbers are 4 and 6 (Figure 28.10).

KEY TERM

A **coordination number** is the number of coordinate bonds formed by a metal ion.



Tetrahedral Square planar Octahedral

Figure 28.10 Transition metal complexes with coordination numbers 4 and 6

- You also need to be able to predict the formula and charge of a complex ion given the metal ion, its charge, its ligand(s) and its coordination number.

NOW TEST YOURSELF

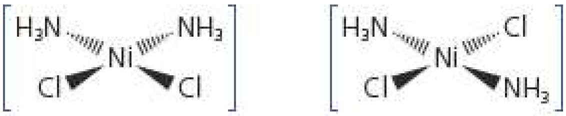
6 Predict the formula, including the overall charge, of the 4-coordinate complex of cobalt(II) with chloride ions.

- The ability of transition metals to form complexes with four or six coordinate bonds means that both *cis–trans* isomerism (Figure 28.11(a) and 28.11(b)) and **stereoisomerism** (Figure 28.12) can occur (see also

Chapters 13 and 29). This can occur with both monodentate and bidentate ligands.

KEY TERM

Stereoisomerism refers to the ability of transition metal complexes to form isomers that have different three-dimensional arrangements of ligands. Both *cis–trans* and optical isomerism are possible (see Chapters 13 and 29).



Cis

Trans

Figure 28.11(a) *Cis–trans* isomerism in square planar transition metal complexes

Cis-tetraammine cobalt dichloride

Trans-tetraammine cobalt dichloride

Figure 28.11(b) *Cis–trans* isomerism in octahedral transition metal complexes

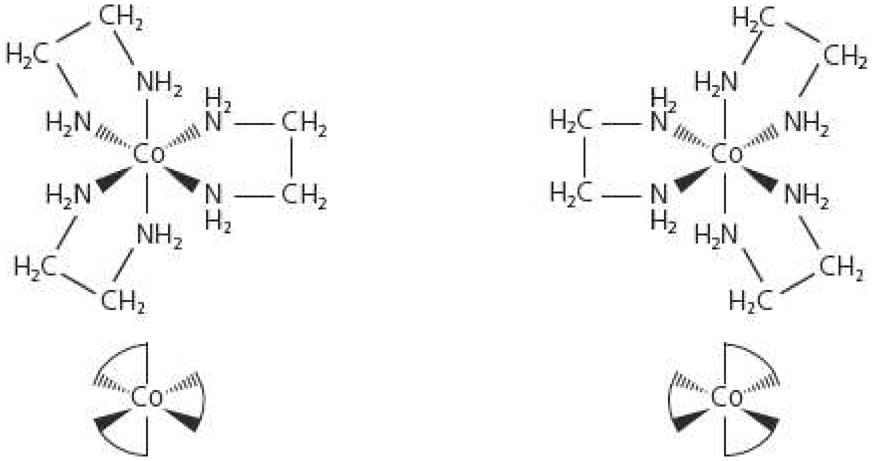


Figure 28.12 Optical isomerism in octahedral transition metal complexes

- The structure of different isomers can affect their properties, particularly in biochemical reactions.
- One example is '*cis*-platin' (see Figure 28.13) which is an important anticancer drug, whereas '*trans*-platin' is ineffective.

- *Cis*-platin works by binding to two guanine bases in the same strand of DNA and preventing replication of the DNA.

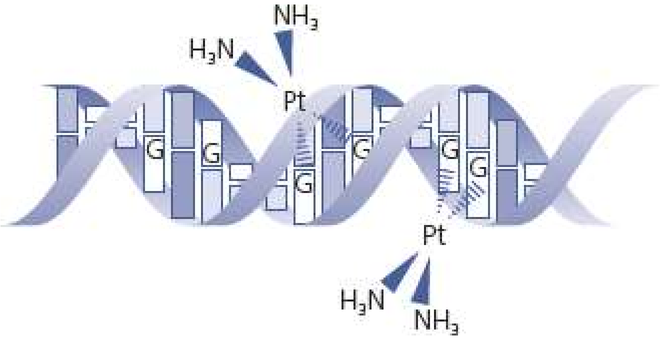


Figure 28.13 *Cis*-platin binding to DNA

Complex stability and ligand exchange

- The different colour changes seen on adding different reagents to aqueous solutions that contain transition metal ions occur because some complexes are more stable than others.
- Remember that most aqueous reactions involve equilibria and that using a high concentration of a reagent will change the position of equilibrium.
- However, this only becomes significant if the **stability constant** for the complex has a reasonable magnitude. The stability constant is the term used for the equilibrium constant for any change.
- You have already seen how, in the case of aqueous copper(II) ions and ammonia, the pale blue of the hexaaquacopper(II) ion is replaced by the much darker blue of the tetraamminediaquacopper(II) ion.
- Another example is the addition of aqueous hydroxide ions to a solution of Cu^{2+} ions in concentrated hydrochloric acid. The initial complex is $[CuCl_4]^{2-}$ which is yellow-green. On adding hydroxide ions the solution gradually turns pale blue as $[Cu(H_2O)_6]^{2+}$ ions are formed. As more hydroxide ions are added, a pale-blue precipitate is formed as the hydroxide ions displace water molecules in the complex.

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

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

- If you consider the reaction:

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

  the value of K_{stab} is 1.20×10^{13} mol^{-4} dm^3, which suggests that the equilibrium will lie to the right-hand side making the ammine complex the most stable.

KEY TERM

The **stability constant** of a complex, K_{stab}, is a equilibrium constant for the formation of a complex from its constituent ions or molecules, for a given solvent. The larger the value of K_{stab}, the more stable is the complex.

REVISION ACTIVITY

a Calcium and chromium are both metals in Period 4 of the Periodic Table. Explain why chromium is a transition metal but calcium is not.

b Give three properties shown by chromium not shown by calcium.

c What forms of isomerism are shown by transition metal complexes?

d Draw diagrams to show examples of each type.

END OF CHAPTER CHECK

By now you should be able to:

- define a transition element as a d-block element which forms one or more stable ions with an incomplete d shell; understand that transition elements have variable oxidation states, behave as catalysts (see Chapter 26), form complex ions and form coloured compounds

- sketch the shape of the $3d_{xy}$ and $3d_{z^2}$ orbitals and use the similarity in energy of the 4s and 3d sub-shells to explain why transition elements have variable oxidation states
- explain why transition elements behave as catalysts in terms of having more than one stable oxidation state and vacant d-orbitals that are energetically available allowing the formation of dative bonds with ligands to form complex ions
- describe and explain the reactions of transition elements with ligands to form complexes; define the term ligand as a species that contains a lone pair of electrons that forms a dative bond to the central metal atom/ion
- understand and use the terms monodentate, bidentate and polydentate to describe ligands; describe the geometry (shape and bond angles) of linear, square planar, tetrahedral or octahedral transition metal complexes
- state what is meant by coordination number, predict the formula and charge of a complex ion given the metal ion, its charge or oxidation state, the ligand and its coordination number or geometry
- predict, using $E^\ominus$ values, the feasibility of redox reactions involving transition elements or their ions
- describe the reactions of, and perform calculations (given suitable data) involving, $MnO_4^-/C_2O_4^{2-}$ in acid solution, MnO_4^-/Fe^{2+} in acid solution, Cu^{2+}/I^- and other redox systems
- describe the splitting of degenerate d-orbitals into two non-degenerate sets and use ΔE in octahedral and tetrahedral complexes; explain why transition elements form coloured compounds in terms of the frequency of light absorbed in promoting an electron between two non-degenerate d-orbitals
- describe the effects of different ligands on ΔE, frequency of light absorbed and hence the complementary colour that is observed; use complexes of Cu^{2+} and Co^{2+} with H_2O, NH_3, OH^- and Cl^- as examples of ligand exchange affecting the colour observed

- describe the types of stereoisomerism shown by complexes, including those related to bidentate ligands – geometrical (*cis*–*trans*) and optical isomerism; deduce the overall polarity of complexes
- define stability constant, K_{stab}, and write an expression for K_{stab} of a complex; use K_{stab} expressions to perform calculations; describe and explain ligand exchanges in terms of K_{stab} and understand that a large K_{stab} is due to the formation of a stable complex ion