3.3 First-row d-block elements (HL)

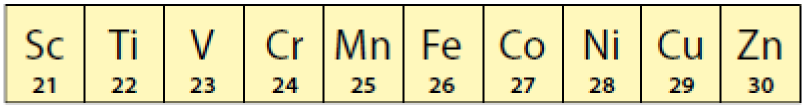
Learning objectives

- Describe the characteristic properties of transition metals • Explain why transition metals have variable oxidation numbers
- Explain the formation and describe the shape of complex ions
- Explain why transition metal complex ions are coloured
- Explain the factors that affect the colour of a transition metal complex
- Understand the magnetic properties of transition metal atoms and ions
- Describe some uses of transition metals and their compounds as catalysts

Understandings:

- Transition elements have variable oxidation numbers, form complex ions with ligands, have coloured compounds, and display catalytic and magnetic properties.
- Zn is not considered to be a transition element as it does not form ions with incomplete d orbitals.
- Transition elements show an oxidation number of +2 when the s electrons are removed.

The first-row d-block elements are:



Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
21	22	23	24	25	26	27	28	29	30

They are called ‘d-block’ elements because the subshell being filled across this series is the 3d subshell. The electron configurations range from [Ar]$4s^2 3d^1$ for scandium to [Ar]$4s^2 3d^{10}$ for zinc.

Write the electronic configuration for each element in the table in the short form

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
[Ar]$4s^2 3d^1$									

Qn. In what ways are Sc and Zn different from the rest?

A transition element is an element that forms at least one stable ion with a partially filled d subshell

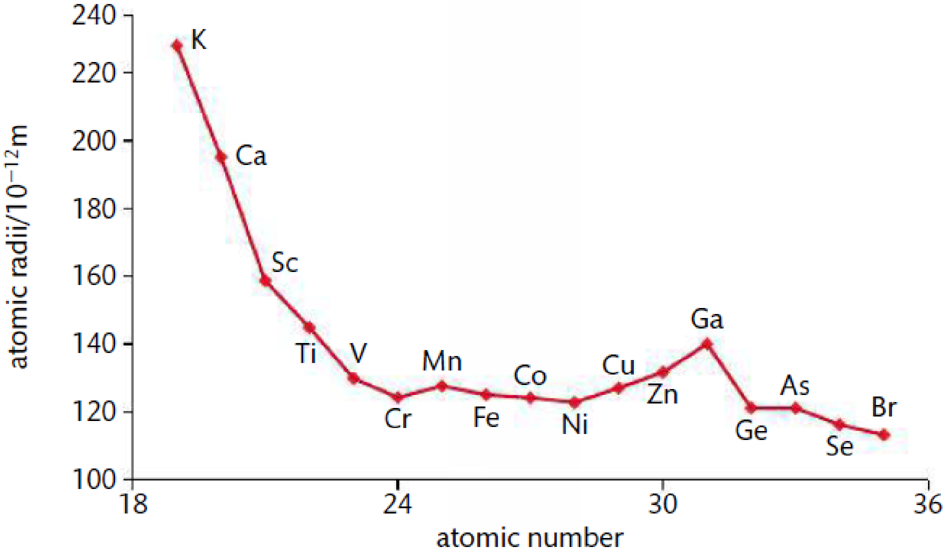
According to this definition, zinc is not counted as a transition element because the only ion it forms is the 2+ ion, with electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ (full d subshell).The classification of scandium is more controversial.

Properties of transition elements

Transition elements are all typical metals – they have high melting points and densities.

- Transition elements can exhibit more than one oxidation number in compounds/complexes.
- Transition elements form complex ions.
- Transition elements form coloured compounds/complexes.
- Transition elements and their compounds/complexes can act as catalysts in many reactions.
- Compounds of transition elements can exhibit magnetic properties.

Atomic radius across the d-block elements



The relatively small decrease in atomic radii across the d block is due to the correspondingly small increase in effective nuclear charge experienced by the outer 4s electrons. The increase in nuclear charge due to the added proton is largely offset by the addition of an electron in an *inner* 3d sub-level.

The small increase in effective nuclear charge also accounts for the small range in first ionization energies across the first transition series.

Ionisation of transition elements

Transition elements form positive ions.

Complete the table below to show the electron configuration for the ions of the transition elements

Element	Electron configuration	Ion	Electron configuration
Cr		Cr^{2+}	
		Cr^{3+}	
Mn		Mn^{2+}	
Fe		Fe^{2+}	
		Fe^{3+}	
Co		Co^{2+}	
Cu		Cu^{+}	
		Cu^{2+}	

The 4s electrons are always removed before the 3d electrons when an ion is formed.

Chemical properties

The chemical properties of the transition metals are very different from those of the s-block metals. Transition metals:

- form compounds with more than one oxidation number
- form a variety of complex ions
- form coloured compounds
- act as catalysts when either elements or compounds.

Variable oxidation numbers

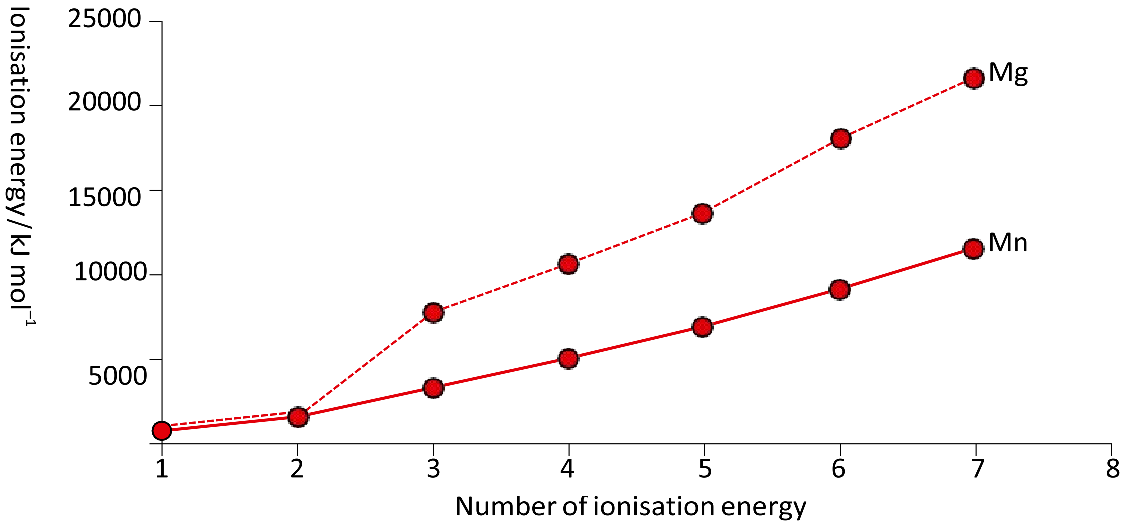
One of the key features of transition metal chemistry is the wide range of oxidation numbers that the metals display in their compounds.

Points to note:

- All the transition metals show both the +2 and +3 oxidation states.
- The maximum oxidation state of the elements increases in steps of +1 and reaches a maximum at manganese. Maganese has the electron configuration [Ar]$4s^2 3d^5$ and therefore a maximum oxidation number of +7. These states correspond to the use of both the 4s and 3d electrons in bonding
- Oxidation states above +3 generally show covalent character. Ions of higher charge have such a large charge density that they polarize negative ions and increase the covalent character of the compound
- Compounds with higher oxidation states tend to be oxidizing agents for example potassium dichromate (VI) ($K_2Cr_2O_7$).

Why more than one oxidation number?

The 4s and 3d subshells are close in energy, and there are no big jumps in the successive ionisation energies when the 4s and 3d electrons are removed.



It can be seen that there is a very large jump between the second and third ionisation energies of magnesium, but that there are no such jumps for manganese.

Magnetic properties of transition metal compounds

Every spinning electron in an atom or molecule can behave as a tiny magnet. Electrons with opposite spins behave like minute bar magnets with opposing orientation and so have no net magnetic effect. Some transition metals and their compounds are unusual in having some electrons that remain unpaired, which when aligned lead to magnetic properties.

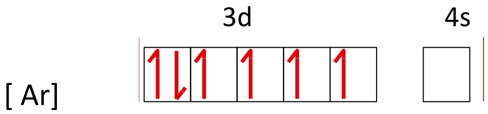
Substances can be distinguished by their response to externally applied magnetic fields

Materials are classified as diamagnetic, paramagnetic, or ferromagnetic based on their behaviour when placed in an external magnetic field.

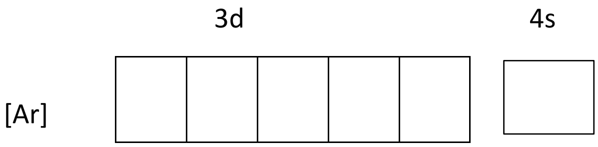
- **Diamagnetism** is a property of all materials and produces a very weak opposition to an applied magnetic field.
- **Paramagnetism**, which only occurs with substances which have unpaired electrons, is stronger than diamagnetism. It produces magnetization proportional to the applied field and in the same direction.
- **Ferromagnetism** is the largest effect, producing magnetizations sometimes orders of magnitude greater than the applied field.

Consider the electron configurations of the following metal ions and classify them by magnetic behaviors above.

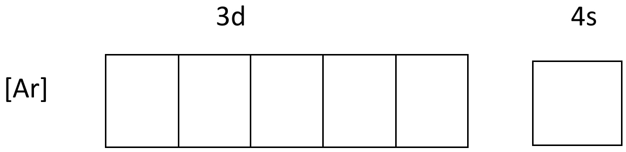
(a) Fe2+



(b) Cr^{3+}



(a) Cu^{2+}



Iron, cobalt, and nickel are ferromagnetic

Iron, nickel, and cobalt are ferromagnetic; the unpaired d electrons in large numbers of atoms line up with parallel spins in regions called **domains**. The domains are generally randomly oriented with respect to each another, but can become more ordered if exposed to an external magnetic field.

Complex ions

A complex ion consists of a central metal ion surrounded by **ligands** – transition metal ions form many complexes. **Ligands are negative ions or neutral molecules that have lone pairs of electrons. They use the lone pairs to bond to a metal ion to form a complex ion. Coordinate covalent bonds (dative bonds) are formed between the ligand and the transition metal ion.**

A complex ion is formed when ligands bond to a transition metal ion. The ligands donate lone pairs into vacant orbitals (3d, 4s or 4p) on the transition metal ion.
The complex ion [Fe(H2O)6]$^{3+.}$The water molecules are ligands as they form coordinate bonds to the central ion.

Draw the structure of this complex

The number of coordinate bonds from the ligands to the central ion is called the **coordination number**. As complexes often have distinctive colours they can be used in qualitative analysis.
All transition elements, with the exception of titanium, form an octahedral complex ion with the formula [M(H2O)6]2+ in aqueous solution.

Complex ions can undergo substitution reactions in which, for example, H2O ligands are replaced by other ligands. For example, in the addition of concentrated hydrochloric acid to blue copper(II) sulfate solution:

$$[Cu(H2O)6]^{2+}(aq) + 4Cl^{-}(aq) \leftrightarrow [CuCl4]^{2-}(aq) + 6H2O(l)$$

Blue yellow

The oxidation number of a transition metal in a complex ion

The oxidation number of a transition metal in a complex ion can be worked out from the charges on the ligands. Ligands may be either neutral or negatively charged.

In $[Fe(H_2O)6]^{2+}$ all the ligands are neutral water molecules. The overall charge on the ion is just due to the iron ion, so the oxidation number of iron must be +2.

In $[Ni(CN)_4]^{2-}$ all the ligands have a 1^- charge, so the total charge from all four ligands is 4^-. The overall charge on the ion is 2^-; so, the oxidation number of nickel must be +2 to cancel out 2^- from the 4^- charge.

Catalytic ability

Transition elements and their compounds/complexes can act as catalysts. For example, finely divided iron is the catalyst in the **Haber process** in the production of ammonia:

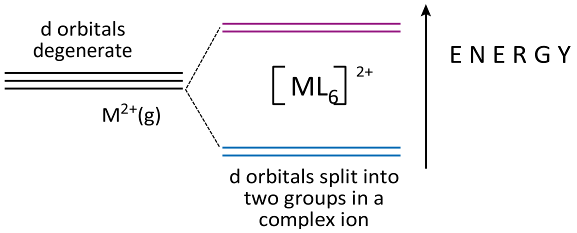
$$N2(g) + 3H2(g) \leftrightarrow 2NH3(g)$$

Iron in the above reaction is a heterogeneous catalyst (one that is in a different physical state to the reactants) but transition metal compounds often act as homogeneous catalysts (ones that are in the same phase as the reactants). The ability to act as a catalyst relies on a transition metal atom or ion having varying oxidation numbers and also being able to coordinate to other molecules/ions to form complex ions.

Coloured complexes (HL)

Complex ion	Colour
$[Cu(H_2O)_6]^{2+}$	blue
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	deep blue/violet
$[Fe(SCN)(H_2O)_5]^{2+}$	blood red
$[Ni(H_2O)_6]^{2+}$	green

In a gaseous transition metal ion, all the 3d orbitals have the same energy – that is, they are degenerate. However, when the ion is surrounded by ligands in a complex ion, these d orbitals are split into two groups. In an octahedral complex ion there are two orbitals in the upper group and three orbitals in the lower groups.

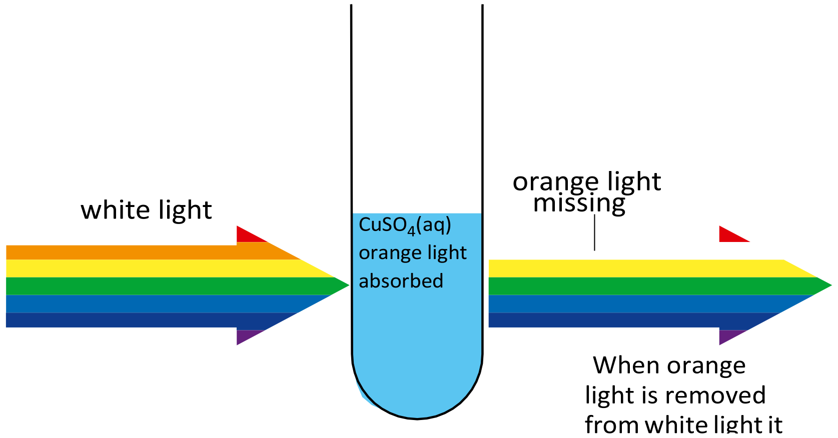


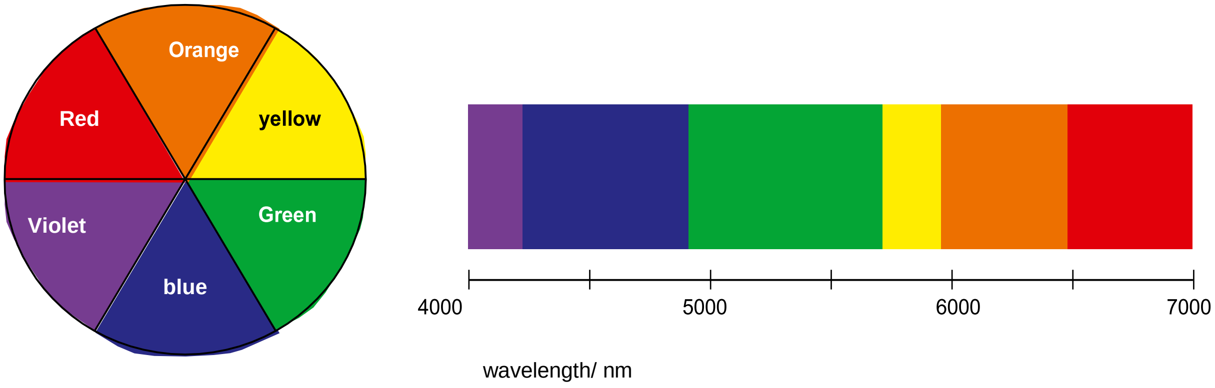
The splitting may be regarded as being caused by the repulsion between the electrons in the metal ion d orbitals and the lone pairs on the ligands.

Energy in the form of a certain frequency of visible light can be absorbed to promote an electron from the lower set of orbitals to the higher set.

Example:

When white light passes through copper sulfate solution (Figure **3.36**), orange light is absorbed, promoting an electron from the lower set of d orbitals to the higher set. This means that the light coming out contains all the colours of the spectrum except orange and so appears blue, the complementary colour to orange.





A colour wheel – along with the approximate wavelengths of visible light. Complementary colours are opposite each other in the colour wheel, therefore blue is complementary to orange and green is complementary to red.

For a substance to appear coloured, certain frequencies of light in the visible region of the spectrum must be absorbed.

The colour of a substance will appear to an observer as the **complementary colour** to the light that is absorbed.If we know the colour of the complex ion, the colour of light that is absorbed can be worked out, and vice versa. For example, because a solution of nickel(II) chloride is green, it must absorb red light – the complementary colour to green.

The formation of coloured substances requires the presence of a partially filled d subshell.

The Sc^{3+} ion or the Ti^{4+} ion both have no electrons in the 3d subshell and so are colourless, as it is not possible to absorb energy to promote a 3d electron.

The Cu^{+} ion and the Zn^{2+} ion both have ten 3d electrons (Figure **3.38**), and as there is no space in the upper set of orbitals it is not possible to promote an electron to the upper set of orbitals. No light in the visible region of the spectrum is absorbed and these ions are colourless.

Factors that affect the colour of transition metal complexes

1. Identity of the metal

Complexes of different metals in the same oxidation state have different colours. For example, Mn2+(aq) (3d5) is very pale pink/colourless but Fe2+(aq) (3d6) is pale green.

Different metal ions have different electron configurations and, because colours are caused by electron transitions, different arrangements of electrons give rise to different colours due to different amounts of repulsion between electrons.

A higher nuclear charge on the metal ion (26+ for Fe and 25+ for Mn) for the same number of electrons causes the ligands to be pulled in more closely in an Fe3+ complex, so that there is greater repulsion between the ligand electrons and the d electrons of the transition metal ion – and therefore greater splitting of the d orbitals.

2. Oxidation number

The same metal has different colours in different oxidation states. For example:

$[Fe(H_2O)_6]^{2+}(aq)$ is pale green and

$[Fe(H_2O)_6]^{3+}(aq)$ is pale violet.

There are two reasons for this:

- the electron configurations of the ions are different
- a higher charge on the metal ion causes the ligands to be pulled in more closely, so that there is greater repulsion between the ligand electrons and the d electrons of the transition metal ion – and therefore greater splitting of the d orbitals.
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In general, for complex ions containing the same metal and the same ligands, the greater the oxidation number of the transition metal, the greater the splitting of the d orbitals.

3. Nature of the ligand

The same metal ion can exhibit different colours with different ligands. This is mainly because of the different splitting of the d orbitals caused by different ligands. Ligands can be arranged into a **spectrochemical series** according to how much they cause the d orbitals to split:

$$I^- < Br^- < Cl^- < F^- < OH^- < H2O < NH3 < CO \approx CN^-$$

$[Cu(NH_3)_4(H_2O)_2]^{2+}$ has a larger energy gap between the two sets of d orbitals than $[Cu(H_2O)_6]^{2+}$ and absorbs a shorter wavelength of light.
$[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ is dark blue/ violet and absorbs more in the yellow–green (higher frequency) region of the visible spectrum. The fact that fluoride ions cause greater splitting of d orbitals than iodide ions can be explained in terms of **charge density** of the ligand – both F^- and I^- have the same charge but the F^- ion is much smaller and therefore causes greater repulsion of the metal ion d electrons and greater splitting of the d orbitals.