HL # d-block elements (first row)

THE FIRST ROW TRANSITION ELEMENTS

Element	(Sc)	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	(Zn)
Electron configuration [Ar]	$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$	$4s^23d^7$	$4s^23d^8$	$4s^13d^{10}$	$4s^23d^{10}$

A transition element is defined as an element that possesses an incomplete d sub-level in one or more of its oxidation states. Scandium is not a typical transition metal as its common ion Sc^{3+} has no d electrons. Zinc is not a transition metal as it contains a full d sub-level in all its oxidation states. (Note: for Cr and Cu it is more energetically favourable to half-fill and completely fill the d sub-level respectively so they contain only one 4s electron).

Variable oxidation states

The 3d and 4s sub-levels are very similar in energy. When transition metals lose electrons they lose the 4s electrons first. All transition metals can show an oxidation state of +2. Some of the transition metals can form the +3 or +4 ion (e.g. Fe^{3+}, Mn^{4+}) as the ionization energies are such that up to two d electrons can also be lost. The M^{4+} ion is rare and in the higher oxidation states the element is usually found not as the free metal ion but either covalently bonded or as the oxyanion, such as MnO_4^-. Some common examples of variable oxidation states in addition to +2 are:
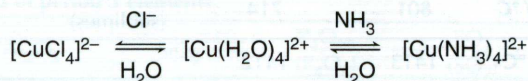
Cr(+3)	$CrCl_3$	chromium(III) chloride
Cr(+6)	$Cr_2O_7^{2-}$	dichromate(VI) ion
Mn(+4)	MnO_2	manganese(IV) oxide
Mn(+7)	MnO_4^-	manganate(VII) ion
Fe(+3)	Fe_2O_3	iron(III) oxide
Cu(+1)	Cu_2O	copper(I) oxide

CHARACTERISTIC PROPERTIES OF TRANSITION ELEMENTS

Formation of complex ions

Because of their small size d-block ions attract species that are rich in electrons. Such species are known as **ligands**. Ligands are neutral molecules or anions which contain a non-bonding pair of electrons. These electron pairs can form co-ordinate covalent bonds with the metal ion to form **complex ions**.

A common ligand is water and most (but not all) transition metal ions exist as hexahydrated complex ions in aqueous solution, e.g. $[Fe(H_2O)_6]^{3+}$. Ligands can be replaced by other ligands. A typical example is the addition of ammonia to an aqueous solution of copper(II) sulfate to give the deep blue colour of the tetraaminecopper(II) ion. Similarly if concentrated hydrochloric acid is added to a solution of Cu^{2+}(aq) the yellow tetrachlorocopper(II) anion is formed. Note: in this ion the overall charge on the ion is –2 as the four ligands each have a charge of –1.

$$[CuCl_4]^{2-} \underset{H_2O}{\overset{Cl^-}{\rightleftharpoons}} [Cu(H_2O)_4]^{2+} \underset{H_2O}{\overset{NH_3}{\rightleftharpoons}} [Cu(NH_3)_4]^{2+}$$

The number of lone pairs bonded to the metal ion is known as the **co-ordination number**. Compounds with a co-ordination number of six are octahedral in shape, those with a co-ordination number of four are tetrahedral or square planar, whereas those with a co-ordination number of two are usually linear.
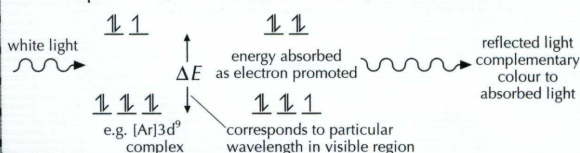
Co-ordination number	6	4	2
Examples	$[Fe(CN)_6]^{3-}$	$[CuCl_4]^{2-}$	$[Ag(NH_3)_2]^+$
	$[Fe(OH)_3(H_2O)_3]$	$[Cu(NH_3)_4]^{2+}$	

Coloured complexes

In the free ion the five d orbitals are degenerate (of equal energy). However, in complexes the d orbitals are split into two distinct levels. The energy difference between the levels corresponds to a particular wavelength or frequency in the visible region of the spectrum. When light falls on the complex, energy of a particular wavelength is absorbed and electrons are excited from the lower level to the higher level.

Cu^{2+}(aq) appears blue because it is the complementary colour to the wavelengths that have been absorbed. The amount the orbitals are split depends on the nature of the transition metal, the oxidation state, the shape of the complex, and the nature of the ligand, which explains why different complexes have different colours. If the d orbital is completely empty, as in Sc^{3+}, or completely full, as in Cu^+ or Zn^{2+}, no transitions within the d level can take place and the complexes are colourless.

white light → energy absorbed as electron promoted → reflected light complementary colour to absorbed light

ΔE

e.g. [Ar]$3d^9$ complex — corresponds to particular wavelength in visible region

Catalytic behaviour

Many transition elements and their compounds are very efficient catalysts. A catalyst increases the rate of a reaction by providing an alternative reaction pathway with a lower activation energy. Transition metal complexes are able to do this because they can exist in a variety of oxidation states. Reactants can be brought into close contact with each other by becoming reversibly attached to the catalyst. Some common examples include:

Iron in the Haber process
$$3H_2(g) + N_2 \overset{Fe(s)}{\rightleftharpoons} 2NH_3(g)$$

Vanadium(V) oxide in the Contact process
$$2SO_2(g) + O_2(g) \overset{V_2O_5(s)}{\rightleftharpoons} 2SO_3(g)$$

Nickel in hydrogenation reactions
$$C_2H_4(g) + H_2(g) \overset{Ni(s)}{\longrightarrow} C_2H_6(g)$$

Manganese(IV) oxide with hydrogen peroxide
$$2H_2O_2(aq) \overset{MnO_2(s)}{\longrightarrow} 2H_2O(l) + O_2(g)$$