Transition Elements

Electronic Structure

The transition elements are :

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Ac	Unq	Unp	Unh	Uns					

They have incomplete d orbitals in at least one of their ions
e.g. the first transition series

Sc $1S^2$ $2S^2$ $2P^6$ $3S^2$ $3P^6$ $4S^2$ $3d^1$

Ti $1S^2$ $2S^2$ $2P^6$ $3S^2$ $3P^6$ $4S^2$ $3d^2$

V $1S^2$ $2S^2$ $2P^6$ $3S^2$ $3P^6$ $4S^2$ $3d^3$

Cr $1S^2$ $2S^2$ $2P^6$ $3S^2$ $3P^6$ $4S^1$ $3d^5$

Mn $1S^2$ $2S^2$ $2P^6$ $3S^2$ $3P^6$ $4S^2$ $3d^5$

Fe $1S^2$ $2S^2$ $2P^6$ $3S^2$ $3P^6$ $4S^2$ $3d^6$

Co $1S^2$ $2S^2$ $2P^6$ $3S^2$ $3P^6$ $4S^2$ $3d^7$

Ni $1S^2$ $2S^2$ $2P^6$ $3S^2$ $3P^6$ $4S^2$ $3d^8$

Cu $1S^2$ $2S^2$ $2P^6$ $3S^2$ $3P^6$ $4S^1$ $3d^{10}$

**Zn** $1S^2$ $2S^2$ $2P^6$ $3S^2$ $3P^6$ $4S^2$ $3d^{10}$

Since the outer electrons in these transition metals all fill the same sub-level (3d) the atoms all have a similar size. One consequence of this is the identical lattice structures of similar transition metal salts e.g. $Fe^{2+}(F^-)_2$ and $Ni^{2+}(F^-)_2$.

The vacant d orbitals are the reason that many transition metals are heterogeneous catalysts

e.g. Iron catalyses the Haber process :

$$3H_2 \quad + \quad N_2 \quad -> \quad 2NH_3$$
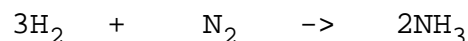
When the H_2 and N_2 become adsorbed on the catalyst surface electrons flow out of the H-H and $N \equiv N$ bonds into the vacant d orbitals on the Iron atoms. Thus the H-H and $N \equiv N$ bonds are weakened lowering the activation energy.
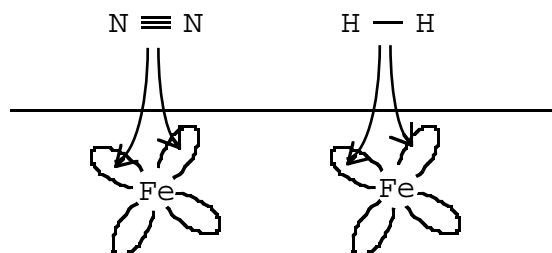

The energies of the 3d and 4S orbitals are very similar. It is a fact that electrons in a d orbital repel each other more than electrons in an S orbital. In a neutral atom the electrons in the 3d orbital are therefore further from the nucleus (higher energy) than the electrons in the 4S orbital. When electrons are removed from the atom to form an ion the electron-electron repulsions are reduced and the 3d orbital actually falls below the 4S orbital in energy.

Electrons are, in effect, removed from the 4S orbital <u>before</u> the 3d orbitals.

e.g. the formation of the Mn^{2+} ion

$$Mn \ (4S^2 \ 3d^5) \quad -> \quad Mn^{2+} \ (4S^0 \ 3d^5)$$
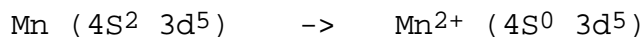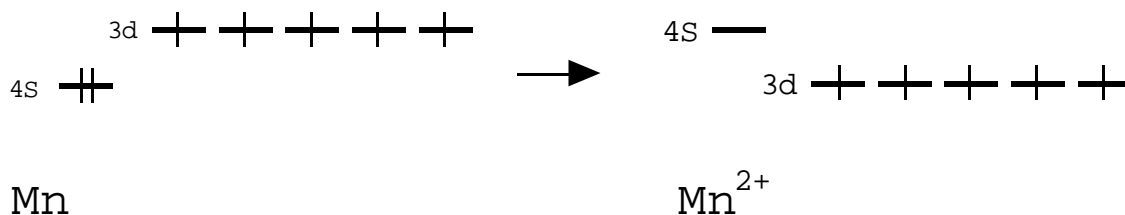
The 2+ valency (oxidation state) is therefore the most common in transition elements but, because of the close proximity of the 3d orbitals, the third ionisation energy is low, resulting in the easy removal of a third electron :

$$Mn^{2+} \ (4S^0 \ 3d^5) \quad -> \quad Mn^{3+} \ (4S^0 \ 3d^4)$$
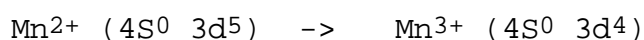
Ions with charges greater than 4+ are unknown. The energy required
to pull 4 electrons completely off an atom is just too great.
Subsequent electrons can however be released from the d orbitals
to form **polar covalent bonds** resulting in many compounds and
ions in which Manganese, like all the transition metals, exhibits
a variable valency:

e.g. manganate(VII) ion MnO_4^-

An electrovalent structure for this ion would be impossible. The
highly positive Mn^{7+} ion would attract electrons from the O^{2-} ions
resulting in the formation of covalent bonds between Mn and O :
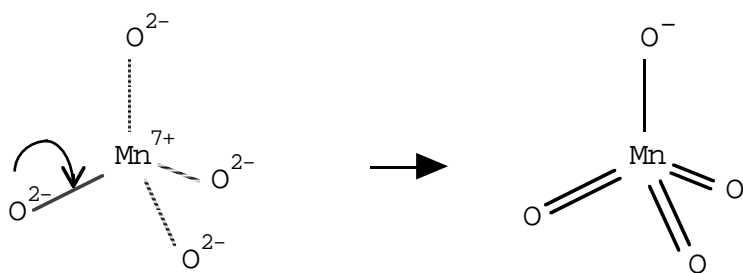
The electrovalent model is nevertheless useful : we can imagine
the Mn^{7+} ion protected by a cage of O^{2-} ions. Take away the
protection and you have a highly effective oxidising agent, Mn^{7+}.
e.g. Oxidation of chloride by acidified manganate(VII) :

$$MnO_4^- \quad + \quad H^+ \quad + \quad Cl^- \quad -> \quad Mn^{2+} \quad + \quad H_2O \quad + \quad Cl_2$$
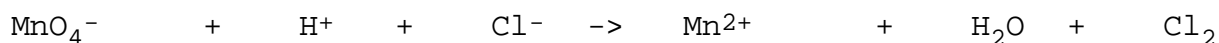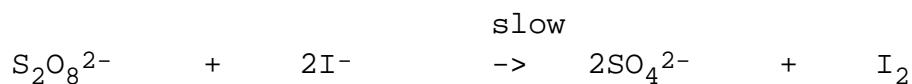
The oxidation state of Mn decreases from 7 to 2 as it is reduced
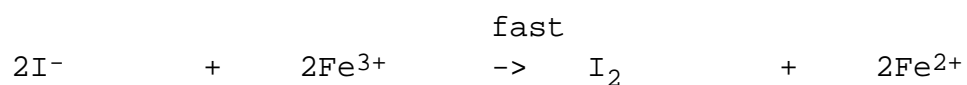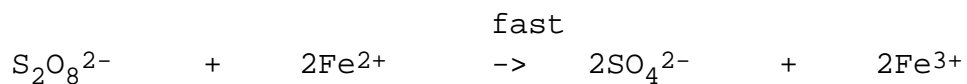in this reaction.
Manganese exhibits the greatest variety of oxidation states of all
the transition metals :

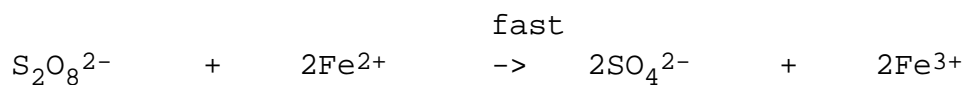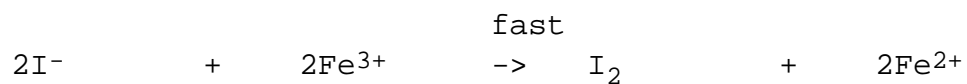| Oxidation state	Examples
2	Mn^{2+}, $MnCl_4^{2-}$
3	Mn^{3+}
4	MnO_2, $MnCl_6^{2-}$
5	MnO_4^{3-}
6	MnO_4^{2-}
7	MnO_4^-, MnO_3^+

The variable valencies of transition metals allows them to act as homogeneous catalysts in redox reactions e.g. both Fe^{2+} and Fe^{3+} catalyse the reaction :

$$S_2O_8{}^{2-} \quad + \quad 2I^- \quad \xrightarrow{\text{slow}} \quad 2SO_4{}^{2-} \quad + \quad I_2$$

Mechanism with Fe^{2+} catalyst :

$$S_2O_8{}^{2-} \quad + \quad 2Fe^{2+} \quad \xrightarrow{\text{fast}} \quad 2SO_4{}^{2-} \quad + \quad 2Fe^{3+}$$

$$2I^- \quad + \quad 2Fe^{3+} \quad \xrightarrow{\text{fast}} \quad I_2 \quad + \quad 2Fe^{2+}$$

Mechanism with Fe^{3+} catalyst :

$$2I^- \quad + \quad 2Fe^{3+} \quad \xrightarrow{\text{fast}} \quad I_2 \quad + \quad 2Fe^{2+}$$

$$S_2O_8{}^{2-} \quad + \quad 2Fe^{2+} \quad \xrightarrow{\text{fast}} \quad 2SO_4{}^{2-} \quad + \quad 2Fe^{3+}$$

Complex Ions

The vacant d orbitals in a transition metal ion leaves it open to attack by **ligands** - negative ions or neutral molecules with **lone pairs**. The ligand forms a bond to the metal ion by donating its lone pair into an empty d orbital e.g. reaction of Water with Cu^{2+} :
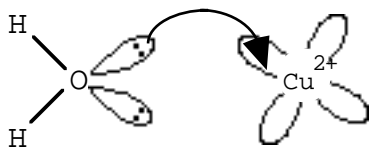

Six Water ligands may become attached to the Cu^{2+} ion forming the blue hexaaquacopper(II) ion which has an octahedral shape :
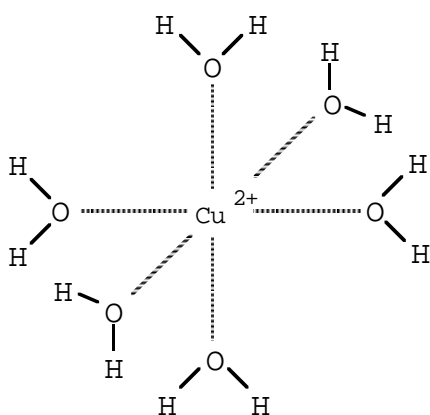

The number of ligands grouped around the metal ion is known as the ion's **coordination number** - 6 in this case.

Similarly Ammonia can behave as a ligand : When a solution of Ammonia in Water is added to a solution of Copper(II) sulphate in Water the Water ligands are displaced by the Ammonia and a deep blue solution containing the tetraamminediaquacopper(II) ion is formed :

$$4NH_3 \quad + \quad Cu^{2+}(H_2O)_6 \quad -> \quad 4H_2O \quad + \quad Cu^{2+}(NH_3)_4(H_2O)_2$$
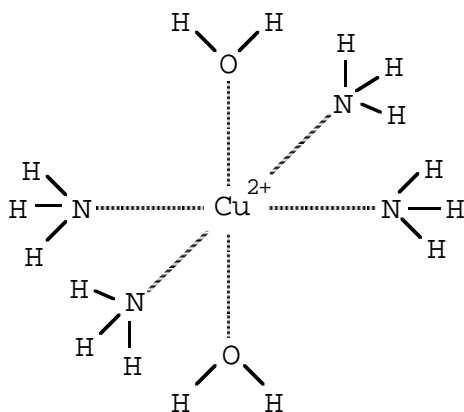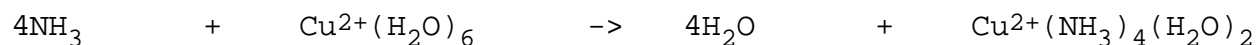
Both H_2O and NH_3 are **monodentate** ligands - they have only one donor site.

1,2-Diaminoethane is a **bidentate** ligand with two donor sites e.g.
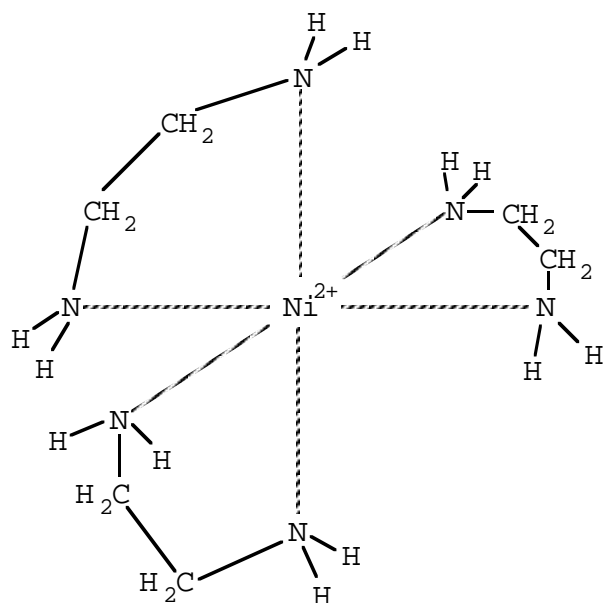
Tri 1,2-diaminoethane nickel(II)

In octahedral complexes like the hexaaquacopper(II) ion the ligands approach the central metal ion along the x, y and z axes repelling electrons in the $d_{x^2-y^2}$ and d_{z^2} orbitals which lie **directly along** the x, y and z axes. Thus the energies of the $d_{x^2-y^2}$ and d_{z^2} orbitals are increased relative to the d_{xy}, d_{yz} and d_{xz} orbitals which lie **between** the x, y and z axes :
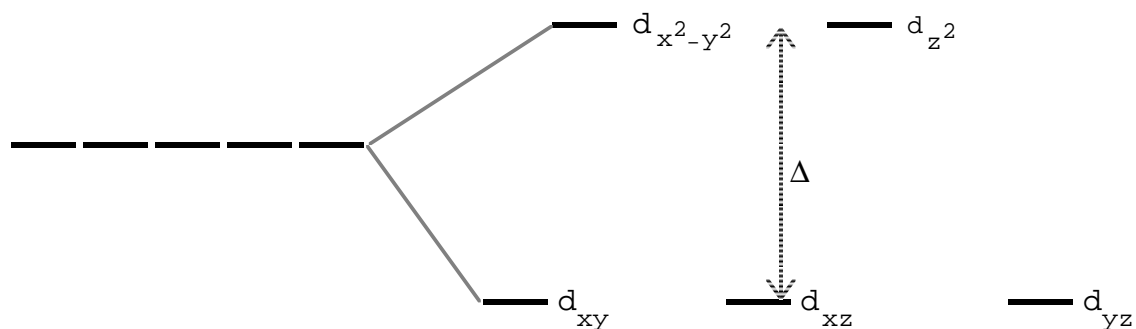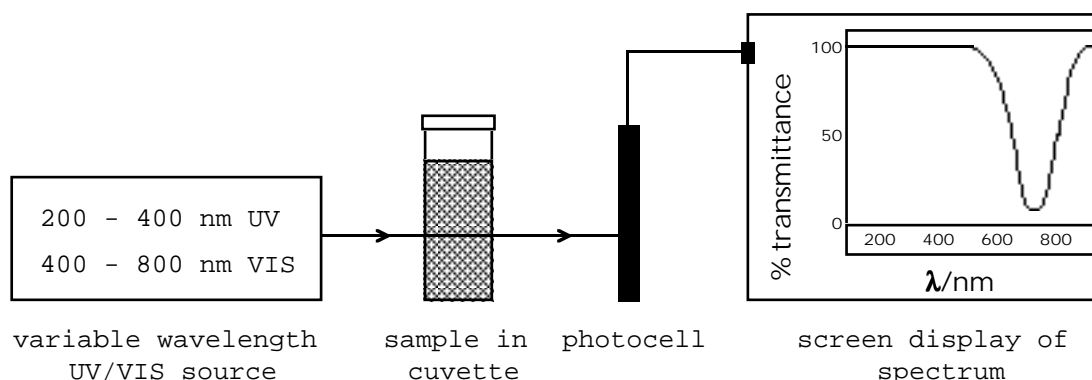
In $Cu^{2+}(H_2O)_6$ Δ = 2.6 x 10^{-19} kJ. This corresponds to a wavelength of 764 nm (red light). When red light of wavelength 764 nm strikes the $Cu^{2+}(H_2O)_6$ ion an electron in the lower levels (d_{xy}, d_{yz} and d_{xz}) is promoted into the higher levels ($d_{x^2-y^2}$ and d_{z^2}) and red light is absorbed ; all other colours are transmitted. We can deduce the resulting colour (cyan) using the **colour triangle** :
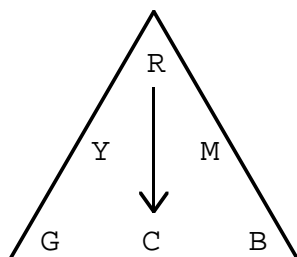
Ultra Violet and Visible Spectroscopy

An Ultra violet/Visible spectrometer can be used to measure the
wavelength and intensity of the light absorbed:

| variable wavelength | sample in | photocell | screen display of |
| UV/VIS source | cuvette | | spectrum |

As the wavelength is increased from 200 nm the instrument measures
the intensity of the light passing through the sample and hitting
the photocell detector. The percentage of the light transmitted
through the sample is recorded. When no absorption occurs the %
transmittance is close to 100%.

A solution containing hexaaquacopper(II) ions would absorb at
764 nm. When the variable wavelength source reaches 764 nm the
solution would absorb some of the light causing a drop in the %
transmittance. The more light absorbed the lower the %
transmittance and the bigger the peak. The amount of light
absorbed depends on the concentration of the solution and can
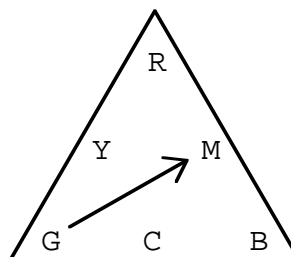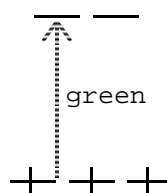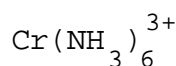therefore be used to measure solution concentration.

The Spectrochemical Series

The ligand field splitting energy, Δ, depends on the power of the ligand to squeeze the electrons in the $d_{x^2-y^2}$ and d_{z^2} orbitals. The spectrochemical series lists the ligands in order of increased splitting power:

$$CN^- > NH_3 > H_2O$$
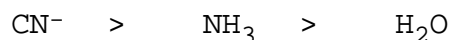
●   Compare the blue hexaaquachromium(III) and the magenta hexaamminechromium(III) ions :

$Cr(H_2O)_6^{3+}$ $Cr(NH_3)_6^{3+}$
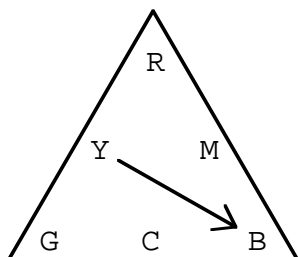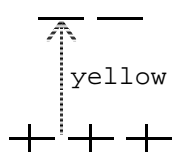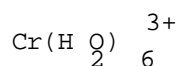
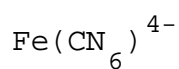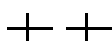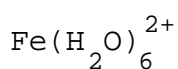yellow   green

Yellow light absorbed   Green light absorbed
Blue light transmitted   Magenta light transmitted

●   The hexaaquairon(II) ion contains unpaired electrons ; the hexacyanoiron(II) ion does not :

$Fe(H_2O)_6^{2+}$ $Fe(CN_6)^{4-}$

Δ is so great in the hexacyanoiron(II) ion that it is more favourable for electrons to pair up and share orbitals than jump up into the higher energy levels.