What makes an element a d-block element?

D-block elements have their highest energy electron in a d subshell. Normally, it is the same thing to say ‘outer electron’ and ‘highest energy electron’. However, things aren’t quite so simple in the d-block. A diagram of orbital energy versus distance out from the nucleus is useful in understanding this point.

Notice that the energy of the 3d-orbital lies between the energies of the 4s and 4p orbitals. This means that when the element is calcium (atomic number 20), the next available orbital is one of the 3d-orbitals, not the 4p.
So, for **scandium** (atomic number 21), the 21st electron goes into the 3d subshell, which is the first point in the periodic table when the outermost electron is not the same thing as the 'highest energy electron.'

<table>
<thead>
<tr>
<th>1s</th>
<th>2s</th>
<th>2p</th>
<th>3s</th>
<th>3p</th>
<th>3d</th>
<th>4s</th>
<th>4p</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Definition:** A d-block element should be defined as ‘one whose highest energy electron is in a d-orbital.’
D-block electronic configurations – atoms.

For the first row of d-block elements, all configurations consist of 1s\(^2\)2s\(^2\)2p\(^6\)3s\(^2\)3p\(^6\) followed by a number of electrons in the 3d subshell and the 4s subshell.

A quick and easy method to work out d-block electron configurations is:

- Count how far the element is across the d-block.
- Put this number of electrons in the d subshell.
- If the element is chromium or copper, move one electron from the 4s to the 3d subshell.

Chromium and copper have unusual configurations, as they are 4s\(^{1}\) rather than 4s\(^{2}\). This is because the half-full and full d-subshell configurations carry additional stability, which is associated with their symmetry.

D-block electronic configurations – ions.

When D-block elements are ionised, the 4s electrons are removed before any in the 3d subshell. Some common ion configurations are shown below:

Chromium and copper have unusual configurations, as they are 4s\(^{1}\) rather than 4s\(^{2}\). This is because the half-full and full d-subshell configurations carry additional stability, which is associated with their symmetry.
What makes an element a transition element?

**Definition:** A transition element is one that can form at least one ion/oxidation state/compound with a partially full d-subshell.

Scandium and zinc are not transition elements:

- Scandium always forms Sc$^{3+}$, which has an *empty* d-subshell. If more electrons were lost, the stable noble gas structure would be broken. The high energy required to do this would not be recouped by any lattice or bonds formed in such a compound.

- Zinc always forms Zn$^{2+}$, which has a *completely full* d-subshell. The stable full d-subshell in zinc is not disrupted, for the same reasons as the Noble gas configuration in the explanation for Sc above. (NB this argument does not apply to copper, which typically does allow its full d-subshell to be disrupted to form Cu$^{2+}$).

Compounds of transition elements, which have partially full d-subshells, have unusual properties as a result of the partially filled d subshell.

Note that in the s and p blocks of the periodic table, inner shells of electrons always consist of bunched groups of full subshells. In the first row of the D-block however, all but Sc and Zn can form compounds in which they have partially filled d-subshells. The presence of unpaired electrons and empty orbitals in the subshell are what give rise to the unusual properties of transition elements, such as paramagnetism and coloured ions.

Note that whether a D-block element is transitional or not depends on the ions that it can form, not the electronic configuration of the element. So both copper and zinc have completely full d-subshells as elements, but zinc never forms Zn$^{3+}$ or higher oxidation states, so it is non transitional. Copper on the other hand can form Cu$^{2+}$, which has a partially full d-subshell, so copper is a transition element.
D-block

Using electronic configurations to explain certain observations.

Why is Fe$^{2+}$ easier to oxidise to Fe$^{3+}$ than is the case for Mn$^{2+}$ to Mn$^{3+}$?

Looking at the electronic configurations of the ions in question...

Fe$^{2+}$ has a repulsion between two electrons in the same orbital. Loss of this electron creates a stable and symmetrical half-full d-subshell, which accounts for the relative ease with which Fe$^{2+}$ can be oxidised to Fe$^{3+}$.

So, although ionisation of Fe$^{2+}$ to Fe$^{3+}$ is endothermic, it is less endothermic than might otherwise be expected.

The opposite is true for Mn however, Mn$^{2+}$ has the stable and symmetrical half-full d-subshell, so is reluctant to lose an electron to become Mn$^{3+}$, as this will disrupt its stable electron configuration.

So, ionisation of Mn$^{2+}$ to Mn$^{3+}$ is more endothermic than expected.

NB So-called stable half-full and full d-subshells are small-fry compared to noble gas electron structures. Sometimes the preservation of stability is a useful argument, sometimes it is not.

For example, both Mn$^{2+}$ and Fe$^{2+}$ are oxidised on exposure to air to Mn$^{3+}$ and Fe$^{3+}$ respectively, despite the so-called ‘reluctance’ of Mn$^{2+}$ to do so based on its electron configuration.

For example, when writing the configuration of Cr, we move one electron from the 4s to the 3d, to make half-full d-subshell stability. However, when writing the configuration for Fe$^{2+}$ ([Ar]3d$^6$) we do not move one electron from the 3d to the 4s to do the same.

For example, the electronic configuration of copper, [Ar] 3d$^{10}$ 4s$^1$ does not restrict it to an oxidation state of +1 in all of its compounds. It does help explain why copper is the first-row d-block element to exist with significant stability in the +1 oxidation state however, all the others have +2 or +3 as their lowest oxidation state.

These last points illustrate an important aspect of A-level chemistry, and that is that explanations often apply to one particular situation and are non very ‘portable’ for want of a better word.

So, if you are asked to suggest why zinc always forms Zn$^{2+}$ ions, then the full stable d-subshell is a good thing to bring up. Don’t however, worry about the fact that this argument does not apply to copper, which happily disrupts its full d-subshell in order to form Cu$^{2+}$. Copper is a different element, it turns out that it is ‘worth it’ for copper to disrupt its full d-subshell in order to make Cu$^{2+}$ ions but it is not worth it for zinc to do the same to make Zn$^{3+}$ ions.
Complex ion formation

Basics

**Definition:** Complex ions are constructed from a central atom or ion and a number of species known as ligands, which datively covalently bond to it.

**Definition:** Ligands are neutral or negatively charged atoms or molecules that can datively covalently bond to a central metal atom or ion.

Monodentate describes a ligand than makes a single dative bond, bidentate ligands make two dative bonds, etc.

Some typical ligands are:

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>aqua (or aquo)</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>ammine</td>
</tr>
<tr>
<td>CO</td>
<td>carbonyl</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>hydroxo</td>
</tr>
<tr>
<td>CN(^-)</td>
<td>cyano</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>chloro</td>
</tr>
<tr>
<td>O(^2-)</td>
<td>oxo</td>
</tr>
<tr>
<td>NH(_2)CH(_2)CH(_2)NH(_2)</td>
<td>‘en’</td>
</tr>
</tbody>
</table>

Complex ions are written with square brackets, e.g. [Fe(H\(_2\)O)\(_6\)]\(^{3+}\).

Complex ion geometry

Complex ions in the d-block exist with six, four or two ligands. The geometries are as follows:

- six ligands – always octahedral
  e.g. [Cu(H\(_2\)O)\(_6\)]\(^{2+}\)
- four ligands – might be tetrahedral
  e.g. [CuCl\(_4\)]\(^{-}\)
- four ligands – might be square planar
  e.g. [Cu(CN)\(_4\)]\(^{-}\)
- two ligands – always linear
  e.g. [Cu(NH\(_3\))\(_2\)]\(^{+}\)

Strictly speaking, the shapes of complex ions in the D-block should not be predicted in terms of repulsions between pairs of electrons. However, at A-level you might be expected to explain any of the shapes in this manner, other than square planar, as these shapes are consistent with those that would be expected from simple repulsion between the ligand pairs of electrons. The square planar geometry for complex ions cannot be explained in this way however, and it is not at all analogous to the existence of XeF\(_4\) as a square planar geometry with lone pairs at the top and bottom.

**Exam Tip:** When you sketch a complex ion, remember to illustrate the shape and the presence of dative covalent bonds.

*Diagram of shapes of complexes*
Oxidation states and naming of complex ions

It is important to understand the relationship between the species that constitute a complex ion, and the overall charge that the complex ion will have.

- \([\text{Fe}(\text{H}_2\text{O})_6]^{3+}\)
  In this species, the water molecules are neutral, so the overall charge is the same as the charge on the metal ion, which is +3. The oxidation state of the iron is +3. The name of this complex is hexaaquairon(III).

- \([\text{Fe}((\text{CN})_6]^{4-}\)
  Here the CN ligands each carry a negative charge. The overall charge is 4-, so the charge on the iron is +2 (Check: +2 – 6 = -4). The oxidation state of the iron is +2. The name of this complex is hexacyanoferrate(II). The use of ferrate rather than iron is to indicate that this complex has an overall negative charge.

- \([\text{Cu}((\text{NH}_3)_2])^+\)
  Ammine ligands have no charge, so the charge on the copper, and its oxidation state, is +1. The name of this complex is diamminecopper(I).

- \([\text{Cu}(\text{Cl})_2]^\)
  Chloro ligands have a negative charge, and the overall charge of the complex ion is -1. So, the copper must carry a charge of +1 (Check: +1 – 1 = -1). The name of this complex is dichlorocuprate(I). Note the change from copper in the previous example, to cuprate in order to denote the overall negative charge of the complex.

- \([\text{Co}(\text{Cl})_3(\text{H}_2\text{O})_4]^{+}\)
  The overall charge of the Co atom is +3. The name of this complex ion is tetraaquadichlorocobalt(III). When naming multiple ligands, they are named alphabetically.

All of the above are ions, so another rule is needed if their name is to be included in the full name of a whole compound, for example, \(\text{K}_4[\text{Fe}((\text{CN})_6]^\). In this compound, the potassium ions are known to have a charge of +1 each, so the charge on the complex ion is -4, making the oxidation state of the iron to be +2. The name of this compound is potassium hexacyanoferrate(II), so the additional rule is cations are named before anions in compounds. You have been doing this for ages though, for example NaCl is sodium chloride. \([\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_3\) would be hexaaquairon(III) chloride.

All of the complexes above are ions, so their compounds are ionic. The above example has electrostatic attractions between the \([\text{Fe}(\text{H}_2\text{O})_6]^\) ions and the Cl ions. When a compound exists as a neutral complex however, it can be named in one word.

- \(\text{Cr(OH)}_3(\text{H}_2\text{O})_3\) is called triaquatrihydroxochromium(III)
- \(\text{Ni}((\text{CO})_4)\) is called tetracarbonylnickel(0).
Only iron, copper and silver have special Latin names to use if they are negatively charged (ferrate, cuprate and argentate). Other elements simply have their normal name with –ate at the end.

For species such as chromate(VI) and manganate(VII), the suffix ‘-ate’ **without specification of a ligand** in the name indicates the presence of O$^{2-}$ as the ‘ligand’, with just as many being used as are sufficient to make the overall charge negative, given the oxidation state of the metal atom. For manganate(VII), four O$^{2-}$ ‘ligands’ are needed to tip the charge over to -1 overall.

Check $+7 - 2 \times 4 = -1$.

For chromate (VI), four O$^{2-}$ ‘ligands’ are needed to tip the charge over to -2 overall.

Check $+6 - 2 \times 4 = -2$.

I have put the term ‘ligand’ in inverted commas here as MnO$_4^{-}$ is generally not regarded as consisting of an Mn atom with a +7 charge surrounded by four O$^{2-}$ ligands. It is perhaps more usual to think of covalent bonds from oxygen to manganese in a +7 oxidation state, but this will be looked at properly in the next section.

**Electronic structure of complex ions**

You might be asked to give the electronic structure of a complex ion, showing ‘which electrons come from the metal atom and which from the ligands clearly’. The method is as follows.

- Identify the Oxidation State of the metal atom.
- Draw the electrons in boxes configuration for this ion, leaving space to draw boxes for 4p and 4d in case it is necessary.
- Fill in an empty box with a pair of electrons from each ligand present, starting at the lowest available energy.

Using [Fe(H$_2$O)$_6$]$^{2+}$ as an example:

The Oxidation State of iron here is +2, so the outer 4s electrons must be lost.

Six boxes are needed for the ligands, each with a pair of electrons in.

Bold electrons come from the ligands, non-bold from the iron.

Note that had the example been [Fe(CN)$_6$]$^{+}$, the electronic structure would have been no different. Each CN$^{-}$ simply provides a pair of electrons, just like an H$_2$O would.
Using \([\text{V(H}_2\text{O)}_6]^{3+}\) as an example:

This example illustrates the need to use boxes of the lowest available energy.

For the previous example, the oxidation states of the metal atoms were quite low, +2 and +3 respectively. When up to four electrons are lost, it is easy to imagine the structure in terms of a simple cation, surrounded by ligands.

With a species such as \(\text{MnO}_4^-\), however, the Oxidation State of Mn is +7 and there is an alternative way of representing the electronic structure of this ion. Rather than losing seven electrons to form an \(\text{Mn}^{7+}\) ion, which would be very energetically unfavourable, the Mn atom could promote its 4s electron into the 4p orbital, enabling it to make seven covalent bonds with its electrons.

Now the manganese needs to bond with four O atoms. One of the oxygen atoms already has a single negative charge, so it will only make one covalent bond with the manganese atom. The others will each make a double bond.

Of course, you may prefer to represent the structure as a complex with an \(\text{Mn}^{7+}\) ion and four \(\text{O}^{2-}\) ligands each. In this case the electronic structure would be:
Isomerism in complex ions

Structural isomers occur when the molecular formula is the same but the bonds are different so they have different structural formulae.

- For example, isomers with the molecular formula CoCl$_3$(H$_2$O)$_n$.

With this formula there are altogether nine species capable of acting as ligands, but only room for six around the Co in any one structure. Three structures exist.

- [Co(H$_2$O)$_6$]Cl$_3$ Here the charge on the complex ion is $+3$, as the water ligands are neutral, and there are three Cl$^-$ on the outside.

- [Co(H$_2$O)$_5$Cl]Cl$_2$H$_2$O Here one Cl$^-$ acts as a ligand, whereas the other two are simply counter-ions and are not part of the complex ion structure.

- [Co(H$_2$O)$_4$Cl$_2$]Cl.2H$_2$O Here two Cl$^-$ ions are acting as ligands and only one is outside the complex ion structure.

If any of these substances is added to water, it is found that only the Cl$^-$ ions which are not acting as ligands from free Cl$^-$ (aq) ions, the ligand Cl$^-$ ions remain firmly bonded as part of the complex ion structure.

The isomers can be distinguished by dissolving separately a fixed mass of each in water and adding excess silver(I) nitrate solution. Cl$^-$ ions that are not acting as ligands are precipitated as AgCl. Clearly the first isomer will produce three times the mass of precipitate that the third produced.
Coloured ions

Many compounds of transition elements are coloured, for example the hexaaquocopper(II) ion is turquoise, \([\text{Cu}(\text{H}_2\text{O})_6]^{2+}\). One way in which compounds of transition elements may be coloured is known as d-d transitions. The essential features of this are:

- The repulsion between ligands and the d-orbitals causes the exact energy of the d-subshell to split into two levels (don’t worry about why yet!).
- If the d subshell is partially full of electrons (d⁷ through to d⁹), then electrons are promoted from the lower to the upper levels when photons of light carrying the right amount of energy (or the right frequency) interact with them.
- These photons are absorbed by the electron being promoted, so are missing from the remaining transmitted or reflected light.
- The remaining photons of other energies/frequencies are seen by the eye, mixing together to give the complementary colour to that of the photons absorbed.

For example, for aqueous copper(II) ions, the d-subshell contains 9 electrons in total. When the six water molecules surround it, the five 3d-orbitals are split into two sets.

\[
\text{Cu}^{2+} \quad \begin{array}{c}
\text{3d} \\
\| \| \| \| \| \\
\end{array} \quad \begin{array}{c}
\| \| \| \\
\end{array}
\]

Two of the d-orbitals point directly at the orbitals, so are repelled to a higher level than the other three, which are not repelled as much. At A-level, the above diagram is usually simplified to that shown below.

\[
\text{Cu}^{2+} \quad \begin{array}{c}
\text{3d} \\
\| \| \| \| \| \\
\end{array} \quad \begin{array}{c}
\| \| \| \\
\end{array}
\]

It amounts to the same thing, there is an energy gap between the lower and upper set of d-orbitals.

Check with you teacher whether you need to know the shapes of the d-orbitals. If you do, it’s quite easy to see that two of the orbitals are pointing right at the ligands as they are drawn along the xyz axes (d_{x²y²} and d_{z²}), and the other three are pointing between the ligands as they are drawn between the xyz axes (d_x, d_y and d_z).
D-block

So, in the case of aqueous copper(II) ions, the energy gap between the two sets of d-orbitals corresponds to that carried by photons of red visible light. When photons of red light land on electron in the lower set of d-orbitals, the electron is promoted to the upper set and the photons of red light are removed from the spectrum.

If you imagine white light to consist of a mixture of red, green and blue light, like the dots on a TV screen if you get too close to it, then this process has removed the red photons. The remaining photons, which pass through the solution of Cu\(^{2+}\)(aq) and enter the viewers eye, are green and blue. This is why Cu\(^{2+}\)(aq) is turquoise, which is after all, a greeny-blue colour!

**Factors which affect the colour seen**

Anything that affects the value of the energy difference between the two sets of d-orbitals will affect the colour seen.

The identity of the metal ion – e.g. Fe\(^{2+}\)(aq) is green, Cu\(^{2+}\)(aq) is turquoise.

The oxidation state of the metal – e.g. V\(^{2+}\)(aq) is lilac, V\(^{3+}\)(aq) is green.

The identity of the ligands – e.g. [Cu(H\(_2\)O)\(_6\)]\(^{2+}\) is turquoise, [Cu(NH\(_3\))\(_6\)]\(^{2+}\) is deep blue.

**Taking things a little further**

*Are all species with a partially filled d subshell and ligands going to be coloured?*

No, a colour is only seen if the energy gap corresponds to a frequency of visible light. If the energy gap were larger, it may well correspond to UV light, in which the d-d transitions would be occurring but no colour would be seen, as no colour has been removed from the visible range of the electromagnetic spectrum.

*What happens to the photons of red light that are absorbed by the Cu\(^{2+}\)(aq) in the previous example?*

The red photons are in fact emitted immediately as the promoted electron drops back down from the upper set of orbitals. They are however emitted in all directions, so they are effectively scattered and very few enter the viewer’s eye compared to the number of green and blue photons that pass to it straight through the solution of Cu\(^{2+}\)(aq).

*Why is Cu\(_2\)O brick red, when Cu\(^+\) has a full d subshell?*

The d-d transitions are only the most typical means by which transition elements can exhibit coloured ions or compounds. Other methods involve transfer of charge between the d-orbitals and-orbitals on the ligands. Check with you teacher to see if you need to know about this.
Variable oxidation states

Transition elements are noted for their ability to exist in several different oxidation states. For example, iron exists commonly as Fe$^{2+}$ and Fe$^{3+}$, and sometimes as Fe(VI) in compounds such as BaFeO$_4$.

By contrast, s-block elements are restricted to the ‘group valency’, i.e. +1 for metals in group one and +2 for metals in group two. Aluminium (in the p block) is restricted to +3.

A graph of ionisation energy versus number of electrons removed is useful in understanding what is going on. Comparing vanadium (a transition element) and calcium (an s block element).

For calcium, there is a large discontinuity in the successive ionisation energies after two electrons are removed. This is because subsequent electrons come from a stable noble gas configuration, so large amounts of energy would be required.

For vanadium, there is no discontinuity, the successive ionisation energies increase gradually. This is because after loss of the 4s electrons, subsequent electrons do not come from a stable noble gas structure, instead they come from the d subshell.

With a transition element, the gradual increases in ionisation energy can be compensated for in the compounds formed. For example, compounds with V$^{3+}$ ions would have higher lattice energies than those with V$^{2+}$, or the V$^{3+}$ ion has a more exothermic hydration energy than V$^{2+}$.

Note that Sc and Zn do not show variable oxidation states, Sc always forms Sc$^{3+}$ and Zn always forms Zn$^{2+}$, for reasons discussed earlier.

Also note that lots of elements in the p-block show variable oxidation states, for example the elements of group four all show +2 and +4, chlorine goes from −1 to +7, so variable oxidation states do not exist solely for transition metals. If you are trying to highlight this aspect of transition metals, you should obviously contrast them to a simple s-block metal such as calcium.
Catalytic activity

**Definition:** A catalyst is a substance that speeds up a reaction, without being used up or chemically changed by it. Catalysts provide an alternative pathway that has a lower activation energy, so more molecules have enough energy to react.

Transition metals can be involved in catalysis either as the elements themselves, or in compounds of the elements.

**Heterogeneous catalysis**

Heterogeneous catalysts are in a different phase to the reactants. For example, ethene and hydrogen gases being passes over a solid nickel catalyst, or gaseous SO\(_2\) and O\(_2\) being passed over finely divided V\(_2\)O\(_5\) on a support material.

Metals such as nickel absorb the reacting molecules on their surface by forming bonds, using their partially filled d-orbitals. This process weakens the bonds in the reacting molecules themselves, which is responsible for this pathway having a lower activation energy.

In addition, when molecules are absorbed onto a surface in this manner, they are brought closer together so their collision frequency can considered to have increased.

*Draw a diagram of heterogeneous catalysis (see flashcards).*

**NB** Catalysts of this sort are ‘poisoned’ by substances that bind to the catalyst irreversibly. Such substances block the catalyst’s ‘active sites’ and cause it to lose its catalytic activity. Lead from the tetraethyllead in leaded petrol blocks the Pt-Rh alloy catalysts in catalytic converters, which is why unleaded petrol must be used in conjunction with them. This is also the reason why gases must be clean and dry in industrial processes.
Compounds such as $V_2O_5$ change oxidation state in order to provide an alternative pathway.

In the un-catalysed reaction, $SO_2$ is oxidised by $O_2$ to $SO_3$. The overall reaction is...

$$SO_2(g) + 0.5O_2(g) \rightarrow SO_3(g)$$

The catalyst oxidises $SO_2$ to $SO_3$...

$$SO_2 + V_2O_5 \rightarrow SO_3 + 2VO_2$$

...then the catalyst is oxidised back to its original form by the $O_2$...

$$2VO_2 + 1/2O_2 \rightarrow V_2O_5$$

**Homogeneous catalysis**

In homogeneous catalysis the catalyst is present with the reactants in the same phase. For example the reaction shown below is aqueous, and is catalysed by aqueous $Fe^{2+}$ ions.

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

In the un-catalysed reaction, $I^-$ ions are oxidised by $S_2O_8^{2-}$ ions. In the catalysed steps, the $S_2O_8^{2-}$ instead oxidises the $Fe^{2+}$ to $Fe^{3+}$...

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

...then the $Fe^{3+}$ ions oxidise the $I^-$ to $I_2$.

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

Looking at the equations above, there is in this case an obvious reason why the above reactions might be faster than the un-catalysed reaction. In both of the catalysed steps the species reacting have opposite charges, and therefore attract each other. In the un-catalysed reaction however, the species have like-charges, and therefore repel one another.

Aside from the issue to like and unlike charges, the iron(II) salt has used the variable oxidation state of iron to provide an alternative pathway.

**NB** Homogeneous catalysts do not increase the collision frequency in the manner that a heterogeneous catalyst would, because they are in the same phase as the reactants.

**NB** Catalysts are by no means confined to the D-block or transition elements. The most common homogeneous catalyst would simply be $H^+$ ions, for example catalysing the hydrolysis of esters, or enzyme catalysts.
Ligand reactions

Acidity of aqueous solutions of d-block cations

D-block metal cations, typically +2 or +3 in charge, have a high charge density, which makes them polarising. This means that they are able to distort the electron clouds of atoms near them. In the same way as a Black Hole (which has a high mass density) sucks matter towards it, a cation with a high charge density sucks electron density towards it.

In aqua-cations, the O-H bonds in the water ligands are weakened by the polarising cation, with the result that other water molecules can remove H\(^+\) ions more easily.

\[
\text{[Fe(H}_2\text{O)}_6\text{]}^{3+}(aq) + \text{H}_2\text{O}(l) \quad \Leftrightarrow \quad \text{[Fe(H}_2\text{O)}_5\text{(OH)}\text{]}^{2+}(aq) + \text{H}_3\text{O}^+(aq)
\]
\[
\text{[Fe(H}_2\text{O)}_5\text{(OH)}\text{]}^{2+}(aq) + \text{H}_2\text{O}(l) \quad \Leftrightarrow \quad \text{[Fe(H}_2\text{O)}_4\text{(OH)}_2\text{]}^+(aq) + \text{H}_3\text{O}^+(aq)
\]

These reactions are acid-base reactions, the water molecules are behaving as bases by accepting protons from the aqua-cations. The reactions are also classified as deprotonation.

The process generates H\(_3\)O\(^+\) ions which lowers the pH of the solution, in other words aqua-cations of d-block metals are acidic.

In exam questions you wont always be told that an aqua cation is present. For example you might be asked to explain why a solution of chromium(II) chloride, CrCl\(_2\), has a pH below seven. After the water has been added, the ions present would be [Cr(H\(_2\)O\(_6\))\(^{2+}\)]\(^{2+}\) and Cl\(^-\). The trick is to realise that the question has got nothing to do specifically with chromium(II) chloride, but to do with the Cr(II) aqua cation. An appropriate equation to give would be...

\[
\text{[Cr(H}_2\text{O)}_6\text{]}^{2+}(aq) + \text{H}_2\text{O}(l) \quad \Leftrightarrow \quad \text{[Cr(H}_2\text{O)}_5\text{(OH)}\text{]}^+(aq) + \text{H}_3\text{O}^+(aq)
\]

Note that the charge on the cation decreases by one, in each equation, as one of the water ligands has been turned into an OH\(^-\) with each deprotonation.

Also note that each equation is an equilibrium. These aqua-cations are weak acids. Unless a stronger base than water is added, the overall charge does not decrease to zero.

Adding stronger bases (OH\(^-\) and NH\(_3\)) to solutions of d-block cations

When stronger bases are added, they react with the H\(_3\)O\(^+\) ions and shift the above equilibria to the right hand side. In addition, they are strong enough to remove another H\(^+\) ion and create an electrically neutral hydroxo-complex, which precipitates from the solution as a solid. Equations representing this process are usually given from the simple hexaaqua cation.

\[
\text{[Fe(H}_2\text{O)}_6\text{]}^{3+}(aq) + 3\text{OH}(aq) \quad \Rightarrow \quad \text{Fe(H}_2\text{O)}_3\text{(OH)}_3(s) + 3\text{H}_2\text{O}(l)
\]
\[\text{yellow-brown solution foxy-red ppte}\]

\[
\text{[Fe(H}_2\text{O)}_6\text{]}^{2+}(aq) + 2\text{OH}^-(aq) \quad \Rightarrow \quad \text{Fe(H}_2\text{O)}_4\text{(OH)}_2(s) + 2\text{H}_2\text{O}(l)
\]
\[\text{pale green solution pale green ppte.}\]
D-block

Note that the number of hydroxide ions needed in the equation, and in the formula of the precipitate, is the same as the charge on the aqua-cation. As the charge from the OH\(^-\) ions exactly balances the charge on the metal cation, the complex formed has no overall charge and can not be hydrated by the polar water molecules. This is why the observation associated with deprotonation is formation of a precipitate.

If NH\(_3\) were used as the base at this point, the process is exactly the same. Instead of OH\(^-\) ions removing protons from H\(_2\)O ligands, NH\(_3\) molecules do it.

\[
[\text{Fe(H}_2\text{O)}_6\text{]}^{3+}(aq) + 3\text{NH}_3(aq) \rightarrow \text{Fe(H}_2\text{O)}_3(\text{OH})_3(s) + 3\text{NH}_4^+(aq)
\]

eyellow-brown solution  
foxy-red ppte

\[
[\text{Fe(H}_2\text{O)}_6\text{]}^{2+}(aq) + 2\text{NH}_3(aq) \rightarrow \text{Fe(H}_2\text{O)}_4(\text{OH})_2(s) + 2\text{NH}_4^+(aq)
\]
pale green solution  
pale green ppte.

Addition of excess OH\(^-\) ions: Further deprotonation

Some hydroxo-precipitates will dissolve when excess OH\(^-\) ions are added. These are those of Cr and Zn in the d-block, only Be in the s-block, and notably Al in the p-block.

The reaction occurring is still deprotonation of H\(_2\)O ligands to form OH\(^-\) ligands, but when it occurs after the precipitation of a hydroxo-complex it is referred to as further deprotonation.

\[
[\text{Cr(OH)}_3(\text{H}_2\text{O)}_3](s) + 3\text{OH}^-(aq) \rightarrow [\text{Cr(OH)}_4]^3-(aq) + 3\text{H}_2\text{O}(l)
\]
pale green ppte  
deep green solution.

\[
[\text{Zn(OH)}_2(\text{H}_2\text{O)}_2](s) + 2\text{OH}^-(aq) \rightarrow [\text{Zn(OH)}_4]^2-(aq) + 2\text{H}_2\text{O}(l)
\]
white ppte  
colourless solution.

The observation associated with further deprotonation is that the original precipitate dissolves, which is because now the complex is charged again, so can by hydrated by water molecules. NB If this reaction occurs, the metal hydroxide is classified as amphoteric.

Addition of excess NH\(_3\): Ligand Substitution

Some hydroxo-complexes dissolve in excess ammonia, in which case the reaction occurring is a complete swap of the ligands on the metal ion for the ammonia molecules.

\[
[\text{Cu(OH)}_2(\text{H}_2\text{O)}_4](s) + 4\text{NH}_3(aq) + 2\text{OH}^-(aq) \rightarrow [\text{Cu(NH}_3)_4(\text{H}_2\text{O)}_2]^{2+}(aq) + 2\text{H}_2\text{O}(l) + 2\text{OH}^-(aq)
\]
pale blue ppte  
deep blue solution

\[
[\text{Ni(OH)}_2(\text{H}_2\text{O)}_4](s) + 6\text{NH}_3(aq) \rightarrow [\text{Ni(NH}_3)_6]^{2+}(aq) + 4\text{H}_2\text{O}(l) + 2\text{OH}^-(aq)
\]
green ppte  
blue/purple solution

Don’t worry about the fact that not all of the ligands in copper are replaced by NH\(_3\).

In the first row of the d-block, only the hydroxo-complexes of Co, Ni and Cu dissolve in excess ammonia.
Summary of ligand reactions:

The above reactions can be reversed easily. For example, the neutral precipitate \( \text{M}_(\text{H}_2\text{O})_3(\text{OH})_3 \) will dissolve in excess aqueous acid to reform the aqua-cation. The hydroxo anion \([\text{M}_(\text{OH})_6]^{3-}\) will reform the precipitate when acidified. The ammine cation might reform the aquo cation if the solution is made very dilute.
<table>
<thead>
<tr>
<th>aquo cation</th>
<th>dil. NaOH/NH₃</th>
<th>excess NaOH</th>
<th>excess NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Sc(H₂O)₆]³⁺(aq)</td>
<td>Sc(OH)₃(H₂O)₂(s) white ppte</td>
<td>no reaction</td>
<td>no reaction</td>
</tr>
<tr>
<td>[Ti(H₂O)₆]⁴⁺(aq)</td>
<td>Ti(OH)₃(H₂O)₂(s) white ppte</td>
<td>no reaction</td>
<td>no reaction</td>
</tr>
<tr>
<td>[V(H₂O)₆]³⁺(aq) lila soln</td>
<td>V(OH)₂(H₂O)₄(s) lilac ppte</td>
<td>no reaction</td>
<td>no reaction</td>
</tr>
<tr>
<td>[V(H₂O)₆]⁴⁺(aq) green soln</td>
<td>V(OH)₃(H₂O)₃(s) green ppte</td>
<td>no reaction</td>
<td>no reaction</td>
</tr>
<tr>
<td>[Cr(H₂O)₆]³⁺(aq) green or violet soln</td>
<td>Cr(OH)₃(H₂O)₃(s) green ppte</td>
<td>[Cr(OH)₆]³⁻(aq) deep green soln</td>
<td>no reaction</td>
</tr>
<tr>
<td>[Mn(H₂O)₆]²⁺(aq) pale pink soln</td>
<td>Mn(OH)₂(H₂O)₄(s) beige ppte²</td>
<td>no reaction</td>
<td>no reaction</td>
</tr>
<tr>
<td>[Fe(H₂O)₆]³⁺(aq) pale green soln</td>
<td>Fe(OH)₂(H₂O)₄(s) dirty green ppte³</td>
<td>no reaction</td>
<td>no reaction</td>
</tr>
<tr>
<td>[Fe(H₂O)₆]³⁺(aq) yellow-brown soln</td>
<td>Fe(OH)₃(H₂O)₃(s) foxy-red ppte</td>
<td>no reaction</td>
<td>no reaction</td>
</tr>
<tr>
<td>[Ni(H₂O)₆]²⁺(aq) green soln</td>
<td>Ni(OH)₂(H₂O)₄(s) green ppte</td>
<td>no reaction</td>
<td>[Ni(NH₃)₆]²⁺(aq) blue soln</td>
</tr>
<tr>
<td>[Co(H₂O)₆]²⁺(aq) pink soln</td>
<td>Co(OH)₂(H₂O)₄(s) pink ppte</td>
<td>no reaction</td>
<td>[Co(NH₃)₆]²⁺(aq) yellow-brown soln⁴</td>
</tr>
<tr>
<td>[Cu(H₂O)₆]²⁺(aq) pale blue soln</td>
<td>Cu(OH)₂(H₂O)₄(s) blue ppte⁵</td>
<td>no reaction</td>
<td>[Cu(NH₃)₄(H₂O)₂]²⁺(aq) deep blue soln⁶</td>
</tr>
<tr>
<td>[Zn(H₂O)₄]²⁺(aq) colourless soln</td>
<td>Zn(OH)₂(H₂O)₂(s) white ppte</td>
<td>[Zn(OH)₄]²⁻(aq) colourless soln</td>
<td>no reaction</td>
</tr>
<tr>
<td>[Al(H₂O)₆]³⁺(aq) colourless soln</td>
<td>Al(OH)₃(H₂O)₃(s) white ppte</td>
<td>[Al(OH)₃]³⁻(aq) colourless soln</td>
<td>no reaction</td>
</tr>
<tr>
<td>[Be(H₂O)₄]²⁺(aq) colourless soln</td>
<td>Be(OH)₂(H₂O)₂(s) white ppte</td>
<td>[Be(OH)₄]²⁻(aq) colourless soln</td>
<td>no reaction</td>
</tr>
</tbody>
</table>

Cr₂O₇²⁻(aq) orange soln, CrO₄²⁻(aq) yellow soln, MnO₄⁻(aq) purple soln, MnO₄²⁻(aq) green soln

1 The existence of a simple M⁴⁺(aq) cation is rare, typically an M⁴⁺ cation is too polarising for this to occur.
2 The ppte of Mn(OH)₂ goes brown as it is oxidised by the air to Mn(OH)₃.
3 The ppte of Fe(OH)₂ goes brown as it is oxidised by the air to Fe(OH)₃.
4 The solution slowly turns orange-brown as it oxidised by air to [Co(NH₃)₆]³⁺.
5 The ppte Cu(OH)₂ goes black is it dehydrates to form CuO.
6 The formula [Cu(NH₃)₄(H₂O)₂]²⁺ is equally acceptable.
7 Al (and Be) are not d-block but undergo the same ligand reactions.

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Vanadium exemplifies typical properties of transition elements, e.g. variable oxidation state, coloured ions, complex ions and catalytic activity ($V_2O_5$).

Questions about vanadium chemistry are often concerned with inter-conversions between the oxidation states in aqueous solution, and this topic integrates well with redox equilibria. It is important to be familiar with the formula of aqueous vanadium species.

\[
\begin{align*}
\text{Cl}_2 \text{ or } \text{MnO}_4^-/\text{H}^+ & \quad \text{Cl}_2 \text{ or } \text{MnO}_4^-/\text{H}^+ \\
\text{O}_2 & \quad \text{Fe}^{2+} \text{ or } \text{SO}_2/\text{SO}_3^{2-} \\
\text{H}_2\text{O} \text{ or } \text{H}^+ & \quad \text{Sn}^{2+} \\
\text{V}^{2+}(\text{aq}) \text{ blue} & \quad \text{Zn}^{2+} \text{ or } \text{H}^+ \\
\text{Cl}_2 \text{ or } \text{MnO}_4^-/\text{H}^+ & \quad \text{V}^{3+}(\text{aq}) \text{ green} \\
\text{VO}_2^+(\text{aq}) \text{ yellow} & \quad \text{Zn}^{2+} \text{ or } \text{H}^+ \\
\text{VO}^2+(\text{aq}) & \quad \text{V}^{2+}(\text{aq}) \text{ lilac} \\
\text{Fe}^{2+} \text{ or } \text{SO}_2/\text{SO}_3^{2-} & \quad \text{Sn}^{2+} \\
\end{align*}
\]

Note that if asked to specify reagents and conditions for these reactions you must be specific, for example…

- potassium manganate(VII) and dilute sulphuric acid rather than just MnO$_4^-$/$\text{H}^+$
- Zn and hydrochloric acid rather than just Zn/$\text{H}^+$

**NB** The species $V^{2+}(\text{aq})$ and $V^{3+}(\text{aq})$ are of course $[\text{V(H}_2\text{O})_6]^{2+}$ and $[\text{V(H}_2\text{O})_6]^{3+}$ respectively.
Vanadium(II) is strongly reducing, aqueous solutions containing $V^{2+}$ do not keep well as the $V^{2+}$ ion can reduce the water itself.

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$

$$V^{2+} \rightarrow V^{3+} + e^-$$

*Balance the equation*

This reaction is favoured by acidic conditions, as these use up $OH^-$ ions and favour the oxidising power of $H_2O$.

$$2H^+ + 2e^- \rightarrow H_2$$

$$2V^{2+} \rightarrow 2V^{3+} + 2e^-$$

*Balance the equation*

Vanadium(III) is stable in water but is oxidised by oxygen to vanadium(IV) in the form of $VO^{2+}$ (a $V^{4+}$ cation is too polarising to exist in aqueous solution).

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

$$V^{3+} + H_2O \rightarrow VO^{2+} + 2H^+ + e^-$$

*Balance the equation*

Vanadium(IV) is stable in air but is oxidised by strong oxidising agents such as chlorine or acidified potassium manganate solution. It is oxidised to vanadium(V) in the form of $VO_2^+$ (a $V^{5+}$ cation would also be too polarising to exist in aqueous solution).

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

$$VO^{2+} + H_2O \rightarrow VO_2^+ + 2H^+ + e^-$$

*Balance the equation using $MnO_4^-$*

*Balance the equation using $Cl_2$*
Vanadium(V) is mildly oxidising and can be reduced easily. Fe\(^{2+}\) or SO\(_2\)/SO\(_3\)\(^{2-}\) will reduce vanadium(V) in the form of VO\(_2^+\) to VO\(^{2+}\) and no further.

\[
\begin{align*}
\text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + e^- \\
\text{SO}_3^{2-} + \text{H}_2\text{O} & \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2e^- \\
\text{VO}_2^+ + 2\text{H}^+ + e^- & \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}
\end{align*}
\]

Balance the equation using Fe\(^{2+}\)

Balance the equation using SO\(_3^{2-}\)

Vanadium(IV) can be reduced to V(III) and no further by Sn\(^{2+}\) ions.

\[
\begin{align*}
\text{Sn}^{2+} & \rightarrow \text{Sn}^{4+} + 2e^- \\
\text{VO}^{2+} + 2\text{H}^+ + e^- & \rightarrow \text{V}^{3+} + \text{H}_2\text{O}
\end{align*}
\]

Balance the equation

The reducing agent Zn and hydrochloric acid can be used to reduce vanadium sequentially from +5 (in VO\(_2^+\)) to +2 (in V\(^{2+}\)). The desired oxidation state of vanadium can be obtained by quenching the reaction when the correct colour is seen. Quenching simply means stopping the reaction, in general it can be done by diluting the reaction mixture with cold distilled water.

NB although the colours of the ions go yellow → blue → green → lilac (+5, +4, +3, +2) the colour of the solution seen would be yellow → green → blue → green → lilac. The first green colour is simply a mixture of VO\(_2^+\) and VO\(^{2+}\) which are yellow and blue respectively.

An important compound of vanadium is ammonium vanadate(V), NH\(_4\)VO\(_3\). It is colourless and dissolves in acid to form a yellow solution.

\[
\begin{align*}
\text{VO}_3^- + 2\text{H}^+ & \rightarrow \text{VO}_2^+ + \text{H}_2\text{O} \\
\text{yellow}
\end{align*}
\]

Show that the above reaction is not a redox reaction.

Uses of vanadium include alloy steels where the vanadium makes the steel “springy”, and catalysis of the contact process by V\(_2\)O\(_5\), a brown solid.