# TOPIC 13: THE PERIODIC TABLE – The transition metals

**13. 1 First-row d-block elements**

E.I.: The transition metals have characteristic properties; these properties are related to their all having incomplete *d* sublevels.

**Nature of science** 3.1 Looking for trends and discrepancies – transition elements follow certain patterns of behavior. The elements Zn, Cr and Cu do not follow these patterns and are therefore considered anomalous in the first-row d-block.

|  |
| --- |
| Understandings* 13.1 U1 Transition elements have variable oxidation states, form complex ions with ligands, have coloured compounds, and display catalytic and magnetic properties.
* 13.1 U2 Zn is not considered to be a transition element as it does not form ions with incomplete d-orbitals.
* 13.1 U3 Transition elements show an oxidation state of +2 when the s-electrons are removed.
 |
| Applications and skills* 13.1 AS1 Explanation of the ability of transition metals to form variable oxidation states.
* 13.1.AS2 Explanation of the nature of the coordinate bond within a complex ion.
* 13.1 AS3 Deduction of the total charge given the formula of the ion and ligands present.
* 13.1 AS4 Explanation of the magnetic properties in transition metals in terms of unpaired electrons.
 |

**Electronic configuration**

The first-row d-block contains 10 elements because the 3d sub-level has 5 orbitals each accommodating two electrons. These 10 elements, although they are in the same row and therefore in different groups, show a lot of similarities but also some changes. However, as you move across the row these changes are only very gradual (=transitional) as opposed to the more pronounced changes when you go across periods 2 and 3.

The reasons why these elements share properties so closely must be found in their electronic structures and the relative energy levels within their atoms.

The following are characteristic properties of transition elements:

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **variable oxidation states** | **complex ion formation** | **coloured** **compounds** | **catalytic properties** | **magnetic properties** |

To be able to explain these properties, we need to know the electronic configuration of these first row transition metals. Complete the electronic configurations below using the Aufbau rules of the first 10 transition elements.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  3d |  |  |  |  4s |
| Sc | [Ar] |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |
| Ti | [Ar] |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |
| V | [Ar] |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |
| Cr | [Ar] |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |
| Mn | [Ar] |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |
| Fe | [Ar] |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |
| Co | [Ar] |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |
| Ni | [Ar] |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |
| Cu | [Ar] |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |
| Zn | [Ar] |  |  |  |  |  |  |  |  |

Exceptions to the general patterns in the electron arrangement are:

|  |
| --- |
| 1. Cr: [Ar] 3d5 4s1 instead of [Ar] 3d4 4s2 as the first is the preferred arrangement and appears to be more stable in terms of energy; the 3d sub-level is half-filled (a half-filled or filled or empty orbital has greater stability than a partially filled orbital although this does not always apply) which gives a lower total energy; because the 3d and 4s are so close together they can be considered as degenerate orbitals. This 3d54s1 only happens in the electronic configuration of Cr atoms.
2. Cu: [Ar] 3d10 4s1 instead of [Ar] 3d9 4s2 because filling up of 3d is a more stable arrangement.
 |

Electronic configuration of transition metal ions

You recall that when filling up orbitals, the 4s orbital is filled before the 3d orbitals. This is because in the empty atom, the 4s orbital has a lower energy than 3d orbitals. However, once the electrons are actually in the 4s orbitals, the energy order changes; the 4s electrons repel each other and this increases the 4s energy level beyond the 3d energy level. When the 3d sublevel is being filled it is at an energy level below 4s.

As a result in all the chemistry of the transition elements, the 4s orbital behaves as the outermost, highest energy orbital when it has electrons in it. So the reversed order of the 3d and 4s orbitals only applies to building the atom up in the first place. In all other respects, you treat the 4s electrons as being the outer electrons.

As the 3d electrons are on a slightly lower energy level than the 4s electrons when the transition metal atoms ionise, it are the 4s electrons (they are also shielded from the nuclear charge by the 3d electrons) which are removed first before the 3d electrons.

Complete the table below

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| species | electronic configuration |  | species | electronic configuration |
| Sc3+ |  |  | Fe2+ |  |
| Ti4+ |  |  | Fe3+ |  |
| V5+ |  |  | Co2+ |  |
| Cr3+ |  |  | Ni2+ |  |
| Cr6+ |  |  | Cu+ |  |
| Mn2+ |  |  | Cu2+ |  |
| Mn3+ |  |  | Zn2+ |  |

**Variable oxidation states (except zinc). Why? Similar successive ionization energies of 3d and 4s electrons**

* Oxidation state of a transition element in a compound or molecular ion = number of electrons released/sharing in either covalent (sometimes the bonds formed have a greater covalent character) or ionic bonds.
* When writing an oxidation state we write the sign first then the number e.g. +3 unlike an ionic charge which as number first and then the sign e.g. 3+.
* **All transition elements**, except Sc (+3 only) and Zn (+2 only), **have more than one stable oxidation state.**
* **Common oxidation state:**  as first and second ionization energies are very similar in all transition elements, all first row d-block elements have + 2 as an oxidation state which corresponds with the loss of the 4s electrons. Exceptions are Cr and Cu that lose the single 4s electron and one 3d electron to have +2 as their oxidation state. Similar trends occur in other rows of transition metals.
* You should be familiar with the following oxidation states (in brackets are their configurations):

|  |  |  |
| --- | --- | --- |
| Cu |  +1 (=[Ar] 3d10 ) | +2 (=[Ar] 3d 9) |
| Cr | +3 (=[Ar] 3d3 ) |  +6 (=[Ar] ) |
| Mn | +4 (=[Ar] 3d3 ) |  +7 (=[Ar]) |
| Fe | +3 (=[Ar] 3d5 ) | +2 (=[Ar] 3d6) |

* Transition metals have variable oxidation states because **the 3d and 4s electrons have similar successive ionization energies (only a gradual increase) because** the five inner d orbitals are at a similar energy level as the single 4s orbital.
* The only gradual increase in successive ionization energies is because there is less repulsion every time an electron is removed so electrons are attracted more strongly by the nucleus. However, the decrease in repulsion is also only gradual.

One first row d-block element is not considered a transition element

The definition below is a recent development as the part about an atom has been added which now means that scandium is considered a transition element with its [Ar] 4s23d1 which it was not before this change in the definition.

**A transition element is a d-block element that has an atom with a partially filled d-sub-level or that forms at least one stable cation that has a partially filled d-sub-level.**

As Zn does not have neither an atom or a stable ion, Zn2+, with a partially-filled d-sub-level Zn is not considered a transition metal. Zinc also **does not form any coloured compounds**, only **has one oxidation state** and has **no catalytic activity**. Many of these properties also fit scandium but this is now considered a transition metal a it has an atom with a partially-filled d sub-level.

**Formation of complexes or complex ions (result of the high charge density of the metal ion)**

A complex or complex ion has a metal ion at its centre around which there are a number of other molecules or negative ions. A complex is a compound that is formed when a ligand, that has been attracted by the charge of the transition metal ion, donates an electron pair (= dative bond) into an empty low energy orbital (3d, 4s or 4p) of the metal ion.

These complexes/complex ions are usually formed when transition metals are dissolved in water; or become hydrated. However, these complexes also form in other circumstances.

When the complex is charged it is called a complex ion; the charge on the ion is delocalised over the entire complex as indicated by the square brackets.

Transition metals can form complexes because their ions have a high charge density:

* they have quite a large nuclear charge but are relatively small;
* the 3d electrons are not so effective (as 2s or 2p electrons) at shielding the effect of the ionic charge which really comes from the nucleus.

Molecules like water, ammonia and negative molecular ions can all act as ligands as they have at least one lone pair.

**A ligand = a molecule or negative ion which contains a non-bonding electron pair which it uses to form a dative bond with the central ion in a complex.**

### Different types of ligands

Ligands can be classified according to their number of atoms that can donate non-bonding pairs and therefore the number of coordinate bonds that they can form:

* monodentate ligands can only form 1 coordinate bond as they have only one atom that can donate non-bonding pair/form coordinate bond. Example are water (only oxygen atom can), ammonia and any halide ion.
* polydentate ligands can form 2 or more coordinate bonds as they have 2 or more atoms that can donate non-bonding pairs e.g. EDTA, 1,2-ethanediamine as both molecules have 2 nitrogen atoms in them. EDTA can make 6 coordinate bonds so one EDTA molecule can make a complex ion with an iron (II) or iron (III) ion.

### Co-ordination number

The number of ligands that are attached to such a metal ion is referred to as the co-ordination number.

Common co-ordination numbers are:

Cu = 4 Fe = 6 Ag = 2

### Examples of common complex ions

 [Fe(H2O)6]3+ [Fe(CN)6]3- [CuCl4]2- [Cu(NH3)4]2+ [Ag(NH3)2]+

### Shapes of complex ions

Complexes also have shapes which we can predict using the VSEPR theory. The shape depends on the number of ligands:

* if co-ordination number = 6 then shape = octahedral
* if co-ordination number = 4 then shape = tetrahedral (or square planar = less common)
* if co-ordination number = 2 then shape = linear

Examples of octahedral ions from <http://www.chemguide.co.uk/inorganic/complexions/shapes.html>



**Magnetic properties**

In terms of magnetic properties (attracted or repelled by an external magnetic field) there are 3 types of materials:

* Paramagnetic materials are magnetic i.e. they are attracted weakly to a magnetic field.

In the case of the transition metals, atoms or ions that contain unpaired d electrons behave like small magnets. Because of their spin electrons create a magnetic field that can align itself to an external electric or magnetic field when exposed to it; unpaired electrons can do this because they can spin in any direction – they create a net magnetic moment. As a result atoms with unpaired d-electrons are weakly attracted to a magnet. The greater the number of unpaired electrons the more paramagnetic the material. The alignment is only temporary so they are only magnetic for a short period of time.

Examples of paramagnetic materials in the first row d-block:

* atoms: all apart from Zn.
* ions e.g. in compounds and complexes: e.g. Mg2+ has 5 unpaired electrons, Co2+ (3 unpaired

 electrons), Ni2+ (2 unpaired electrons), Fe2+ (unpaired electrons).

* Diamagnetic materials only have paired d-electrons and therefore create a magnetic field opposed or not aligned to an external field that is why they are weakly repelled by that external field. The paired electrons cancel out each other’s magnetic field so there is no net magnetic moment in the atom or ion.

Examples of diamagnetic materials: Zn and Zn2+.

* Ferromagnetic materials can be made into permanent magnets as their electron alignment caused by an external magnet can be made permanent e.g. by heating and cooling it in a magnetic field.

Examples of ferromagnetic materials are iron, cobalt and nickel.

**13.2 Coloured complexes**

E.I.: d-orbitals have the same energy in an isolated atom, but split into two sub-levels in a complex ion. The electric field of ligands may cause the d-orbitals in complex ions to split so that the energy of an electron transition between them corresponds to a photon of visible light.

**Nature of science** 1.10 Models and theories—the colour of transition metal complexes can be explained through the use of models and theories based on how electrons are distributed in d-orbitals.

4.1 Transdisciplinary—colour linked to symmetry can be explored in the sciences, architecture, and the arts.

|  |
| --- |
| Understandings* 13.2 U1 The d sub-level splits into two sets of orbitals of different energy in a complex ion.
* 13.2 U2 Complexes of d-block elements are coloured, as light is absorbed when an electron is excited between the d-orbitals.
* 13.2 U3 The colour absorbed is complementary to the colour observed.
 |
| Applications and skills* 13.2 AS1 Explanation of the effect of the identity of the metal ion, the oxidation number of the metal and the identity of the ligand on the colour of transition metal ion complexes.
* 13.2 AS2 Explanation of the effect of different ligands on the splitting of the d-orbitals in transition metal complexes and colour observed using the spectrochemical series
 |

d sub-level splitting

A compound that contains energy levels that are close together could absorb radiation in the visible light spectrum and therefore display a colour because the colour observed is complementary to the colour absorbed. This must be the case in d-block metals as their compounds are frequently coloured both in solid state (hydrated) and in solution.

In the d-block metal ions in complexes in their ground state, the five orbitals in the 3d sub-level have the same energy (equivalent energy level) but in most of their compounds (usually complexes), these 5 equivalent orbitals are split in two or three different energy level (non-equivalent energy levels) with some orbitals on each level.

This splitting of the 3-d sublevel into two or more sets of orbitals is caused by the ligands as the electron clouds or non-bonding pairs around the ligand repel the electrons in the 3d orbitals of the metal ion. As a result the ligand electrons push the 3d electrons in the transition metal ion in orbitals closest to them to energy levels higher than the other orbitals that are not near the ligand. This creates sets of orbitals of different energy – non-equivalent - and this process is called field-splitting.

**d-to-d transition**

Although they are different in energy, the two sets of split orbitals are still close together. This allows an electron in a lower 3d orbital to become excited and absorb radiation (from the visible light spectrum) and be promoted (=transition) from a lower 3d orbital (low spin) to a higher 3d orbital (high spin). The amount of energy needed for this d-to-d transition (or the energy difference between the two sets of orbitals) corresponds to a photon within the visible light spectrum.

The colour shown by the transition metal ion complex is a mixture of the colours or radiation that it transmits after absorption of the frequencies for transition. **The colour observed is a mixture of the colours complementary to those colours that have been absorbed**. You should use a colour wheel to determine the complementary colour of a colour that has been absorbed.

Therefore for transition metal compounds to form coloured compounds, the transition metals ions must have partially-filled 3 d orbitals i.e. unpaired electrons.

The field splitting in a Cu2+ when it forms a complex with water is shown in the diagram below (from <http://www.chemguide.co.uk/inorganic/complexions/colour.html>). The symbol ΔE indicates the difference in energy between the two sets of orbitals. Using Planck’s constant and the frequencies of the complementary colours you should be able to calculate the amount of energy.

|  |  |
| --- | --- |
| dsplitcu | The colour of a transition metal complex depends on the size of ΔE (or split) in the diagram to the right which in its turn depends on:* The identity of the metal ion as this effects the nuclear charge which attracts the ligand; the identity also affects the number of ligands and the shape of the complex ions, how strongly ligands are attracted, all of which affect ΔE. Overall ΔE increases down a group in the d-block.
* The oxidation state/number of the metal ion as e.g. the more positive the oxidation state, the fewer the 3d electrons, the lower the amount of repulsion caused, the higher ΔE.
 |

|  |
| --- |
| * The identity of the ligand: each ligand has its own effect on the relative energies of the *d* electrons, e.g. NH3 has a greater effect than water because nitrogen has a lower electronegativity and therefore attracts its lone pair less strongly/less closely to the nucleus allowing it to repel more other electrons. NH3 is considered a stronger ligand than water. The stronger the ligand the more the electrons in the 3d split sub-level absorb towards the high-energy end of the visible light spectrum. Electronegativity cannot always be used to explain the difference as Cl- is a stronger ligand than I- as it has a higher charge density than I- (same ionic charge but greater ionic radius).
 |

Spectrochemical series

The spectrochemical series is a series that ranks various ligands in order of increasing ΔE values (large splitting). The series is based on experimental evidence. The further up the series the ligand, the more splitting of it causes, the higher the frequency/lower the wavelength of the radiation needed for a d-to-d transition.

Example of the effect of a ligand on the colour observed: hexaaquacopper (II) ions have a blue colour. As ammonia is a stronger ligand it displaces four of the water molecules and converts the complex ions into deep blue tetraaminediaquacopper (II) ions. This happens because ammonia as a stronger ligand causes greater repulsion and therefore a greater ΔE. As a result electrons in the tetraaminediaquacopper (II) complex need to absorb light of a higher energy/frequency to make any d-to-d transitions than in the hexaaquacopper (II) complex. This means the complementary colours that are observed also have higher frequencies.

Not all d-block compounds are coloured compounds

Compounds containing transition ions with empty d-orbitals (e.g. Sc3+, Ti4+) or full d orbitals (e.g. Zn2+) are colourless as no transition between split sub-levels or different sets of orbitals can occur (in the case of full orbitals there are no spaces).