Cambridge (CIE) A Level Chemistry

Your notes

General Physical & Chemical Properties of the First Row of Transition Elements, Titanium to Copper

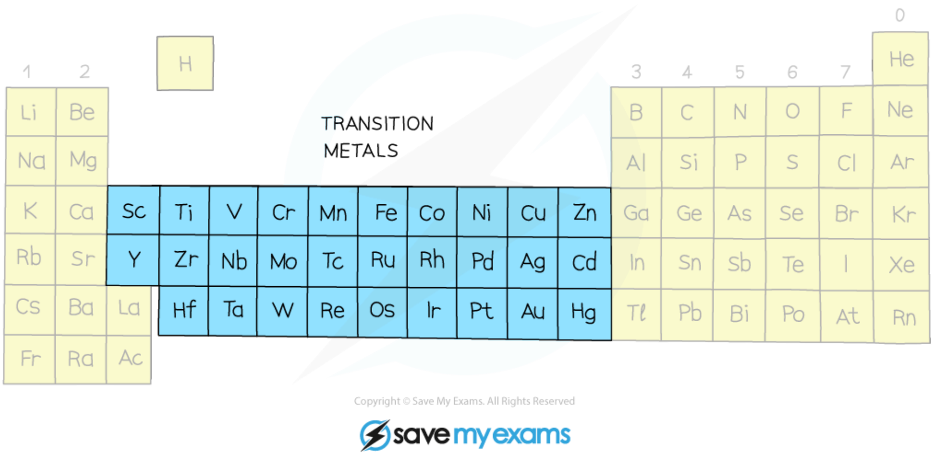
Contents

- The Transition Elements: Titanium to Copper
- Oxidation States of Transition Metals

Definition of a Transition Element

- **Transition elements** are d-block elements which form **one** or **more stable ions** with an **incomplete d subshell**
- They are all metals found in the d-block of the Periodic Table, between Groups 2 and 13
  - Sometimes they are referred to as transition metals
- Not all d-block elements are classed as transition elements: scandium and zinc, for example, are not classed as transition elements, despite being in the d-block
- **Scandium** is not classed as a transition element because:
  - It only forms **one** ion, Sc^{3+}
  - The Sc^{3+} ion has **no electrons** in its 3d subshell; it has the electronic configuration of [Ar]
- **Zinc** is also not classed as a transition element because:
  - It also forms only **one** ion, Zn^{2+}
  - The Zn^{2+} ion has a **complete** 3d subshell; it has the electronic configuration $[Ar]3d^{10}$

The transition elements on the periodic table



The transition elements are in the central d-block on the Periodic Table

Shape of 3d(xy) & 3d(z2) Orbitals

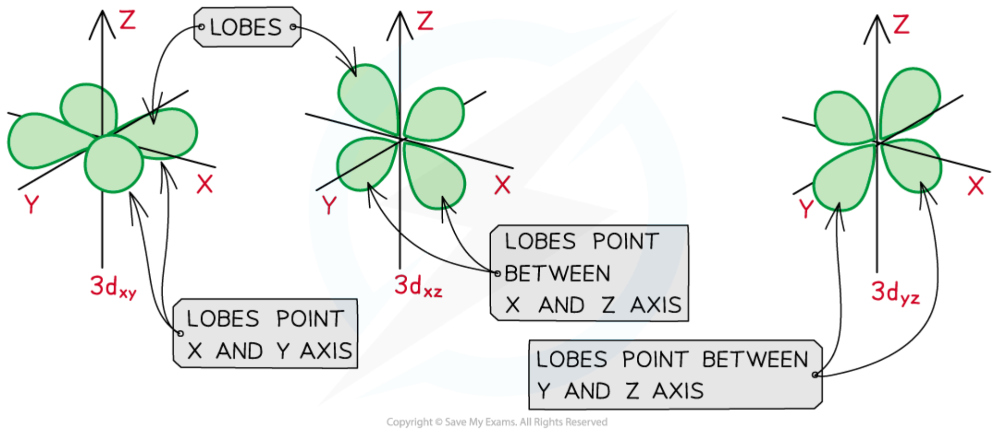
- The transition elements all have **incomplete** d subshells
- There are five orbitals in a d subshell. Some of these orbitals may have similar **shapes** but different **orientations**, whereas others may have completely different **shapes**

- The five orbitals are
  - $3d_{yz}$
  - $3d_{xz}$
  - $3d_{xy}$
  - $3d_{x^2-y^2}$
  - $3d_{z^2}$
- Note that students are required to sketch the shapes of the **$3d_{xy}$** and **$3d_{z^2}$** orbitals **only**

Shapes of the 3d orbitals

- The $3d_{yz}$, $3d_{xz}$, and $3d_{xy}$ orbitals are orbitals which lie in the y-z, x-z and x-y plane respectively
  - They all have **four lobes** that point **between** the two axes

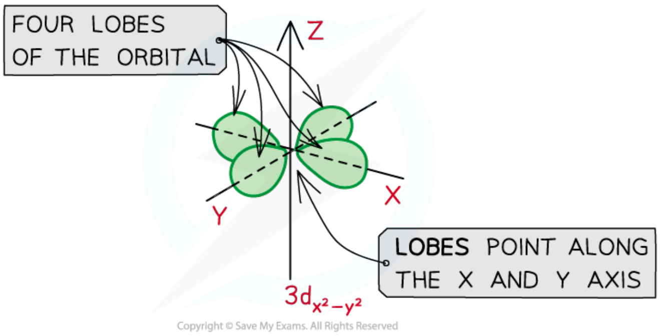
The $3d_{yz}$, $3d_{xz}$, and $3d_{xy}$ orbitals



The 3dyz, 3dxz, and 3dxy orbitals all have four lobes which are similar in shape but point between different axes

- The $3d_{x2-y2}$ orbital looks like the $3d_{yz}$, $3d_{xz}$, and $3d_{xy}$ orbitals, as it also consists of **four lobes**
- The difference is that these lobes point **along** the x and y axes and **not** between them

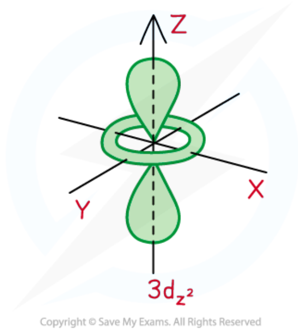
The $3d_{x^2-y^2}$ orbital



The four lobes in a 3dx2-y2 orbital point along the axes

- The $3d_{z^2}$ orbital is different from the other orbitals, as there are two main lobes which form a **dumbbell shape**
- The two main lobes point **along** the z-axis and there is a "doughnut" ring around the centre

The $3d_{z^2}$ orbital



The 3dz2 orbital has a dumbbell shape with a ring around the centre

Properties of the Transition Elements

- Although the **transition elements** are metals, they have some properties unlike those of other metals on the periodic table, such as:
  - Variable **oxidation states**
  - Behave as **catalysts**
  - Form **complex ions**
  - Form **coloured compounds**

Ions of transition metals

- Like other metals on the periodic table, the transition elements will lose electrons to form positively charged ions
- However, unlike other metals, transition elements can form more than one positive ion

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- They are said to have **variable oxidation states**
- Due to this, Roman numerals are used to indicate the oxidation state of the metal ion
  - For example, the metal sodium (Na) will only form Na^+ ions (no Roman numerals are needed, as the ion formed by Na will always have an oxidation state of +1)
  - The transition metal iron (Fe) can form Fe^{2+} (Fe(II)) **and** Fe^{3+} (Fe(III)) ions
- The table below shows the most common oxidation states of a few transition metals

Oxidation states of transition elements table

Transition element	Common oxidation states
Ti	+3, +4
V	+2, +3, +4, +5
Cr	+3, +6
Mn	+2, +4, +6, +7
Fe	+2, +3
Ni	+2
Cu	+1, +2

Coloured complex

- Another characteristic property of transition elements is that their compounds are often **coloured**
  - For example, the colour of the $[Cr(OH)_6]^{3-}$ complex (where the oxidation number of Cr is +3) is **dark green**
  - Whereas the colour of the $[Cr(NH_3)_6]^{3+}$ complex (where the oxidation number of Cr is still +3) is **purple**

Colours of common transition metal complexes

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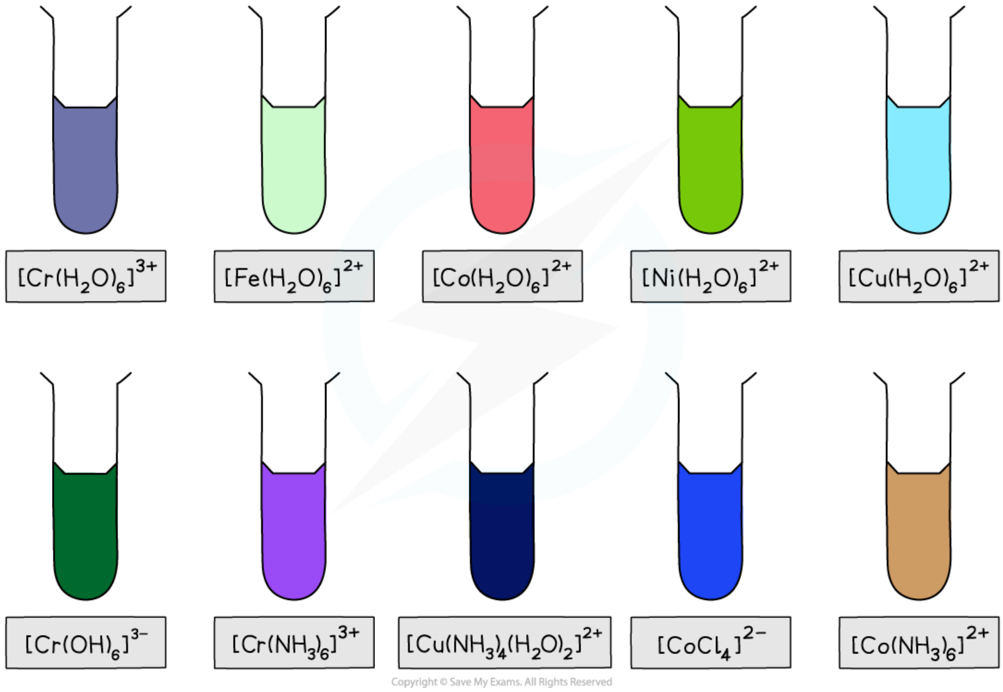

Examples of some transition metal ions and their coloured complexes

Transition elements as catalysts

- Since transition elements can have variable oxidation states, they make excellent **catalysts**
- During catalysis, the transition element can change to various oxidation states by gaining electrons or donating electrons from reagents within the reaction
  - For example, iron (Fe) is commonly used as a catalyst in the Haber Process, switching between the +2 and +3 oxidation states
- Substances can also be adsorbed onto their surface and activated in the process

Complex ions

- Another property of transition elements caused by their ability to form variable oxidation states is their ability to form **complex ions**
- A complex ion is a molecule or ion, consisting of a central metal atom or ion, with a number of molecules or ions surrounding it
- The molecules or ions surrounding the central metal atom or ion are called **ligands**
- Due to the different oxidation states of the central metal ions, a different number and wide variety of ligands can form bonds with the transition element
  - For example, the chromium(III) ion can form $[Cr(NH_3)_6]^{3+}$, $[Cr(OH)_6]^{3-}$ and $[Cr(H_2O)_6]^{3+}$ complex ions

Effects of the 3d & 4s Subshells on Oxidation States of the Transition Elements

- Transition elements can have **variable oxidation states**
- These variable oxidation states can be formed as the 3d and 4s atomic orbitals are **similar in energy**
- This means that a similar amount of energy is needed to remove a different number of electrons
- When the transition elements form **ions**, the electrons of the 4s subshell are lost first, followed by the 3d electrons
- The most common oxidation state is +2, which is usually formed when the two 4s electrons are lost

Oxidation number at the start of the 3d transition elements

- At the **start** of the period, it is easier for the transition elements to lose the **maximum** number of electrons
- The maximum oxidation number of these transition elements involves all the 4s and 3d electrons in the atom
- For example, the maximum oxidation state of a titanium (Ti) ion is +3 or +4, as two 4s electrons and either 1 or 2 3d electrons are lost
  - Ti atom = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$
  - Ti^{3+} ion = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^1$
  - Ti^{4+} ion = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Oxidation number at the end of the 3d transition elements

- Towards the **end**, the 3d transition elements are more likely to adopt the +2 oxidation state
- This is because, across the d block, the 3d electrons become slightly **harder** to remove as the **nuclear charge** increases
  - The 3d electrons are attracted more strongly to the nucleus
  - The higher oxidation states become less stable
- Therefore, the elements are more likely to lose their 4s electrons only

- For example, nickel (Ni) is a transition element at the end of the period which only forms ions with oxidation state +2, due to the loss of the 4s electrons only
  - Ni atom = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$
  - Ni^{2+} ion = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^8$

Transition Elements: Catalysts

- Transition elements are often used as **catalysts** due to their ability to form ions with more than one **stable oxidation state**, and the fact that they contain **vacant d orbitals**

Oxidation states

- Transition element ions can adopt more than one **stable oxidation state**
- This means that they can accept and lose electrons easily to go from one oxidation state to another
- They can therefore catalyse **redox** reactions, by acting as both **oxidising agents** and **reducing agents**
- For example, iron (Fe) is often used as a catalyst due to its ability to form Fe(II) and Fe(III) ions, acting as an oxidising agent and a reducing agent
  - When Fe(II) acts as a reducing agent, it will reduce another species and become oxidised itself

$$\mathbf{Fe^{2+} \rightarrow Fe^{3+} + e^-}$$

- The Fe^{3+} formed in the catalytic cycle, can then also act as an oxidising agent by oxidising another species and getting reduced itself to reform the Fe^{2+} ion

$$\mathbf{Fe^{3+} + e^- \rightarrow Fe^{2+}}$$

- Transition element ions with high oxidation states make powerful oxidising agents because they will readily accept electrons
  - A common example of this is potassium permanganate (VII), where manganese has an oxidation state of +7

Vacant d orbitals

- When transition elements form ions, they have **vacant d orbitals** which are **energetically accessible**
  - The orbitals are not too high in energy
- This means that **dative bonds** can be formed between the transition element ion and **ligands**
  - Each ligand provides the pair of electrons required for the formation of a bond between the ion and the ligand
  - This pair of electrons is donated into the ion's vacant d orbital
- The table below shows the electron configuration of the transition element **atoms**

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- When they form ions, empty **d orbitals** are obtained which can be filled by the pairs of electrons donated by the ligands

Electronic configuration of transition elements table

Element	Electronic configuration
Ti	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$
V	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$
Cr	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
Mn	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$
Fe	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
Co	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$
Ni	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$
Cu	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

Transition Metals: Complex Ions

- A **complex** is a molecule or ion formed by a central metal atom or ion surrounded by one or more **ligands**
  - A complex can have an overall positive or negative charge, or it can be neutral
  - If a complex is charged overall, it is often called a **complex ion**
- Transition elements can easily form complex ions because they have **empty d orbitals** that are energetically accessible
  - The empty d orbitals are therefore not too high in energy and can accommodate a lone pair of electrons
- The transition element in the centre will accept pairs of electrons from the ligands into their empty d orbitals, forming **dative bonds**
  - The transition element in the centre is often referred to as the **central metal ion**, as all transition elements are metals, and it is often an ion in the centre
- For example, the titanium(III) (Ti^{3+}) ion, has an electronic configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^1$
  - This means that there are vacant d orbitals that can be occupied by electrons, from ligands such as H_2O for example, to form a $[Ti(H_2O)_6]^{3+}$ complex ion

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- 6 water ligands have each donated a pair of electrons, to form 6 dative bonds with the central metal ion

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