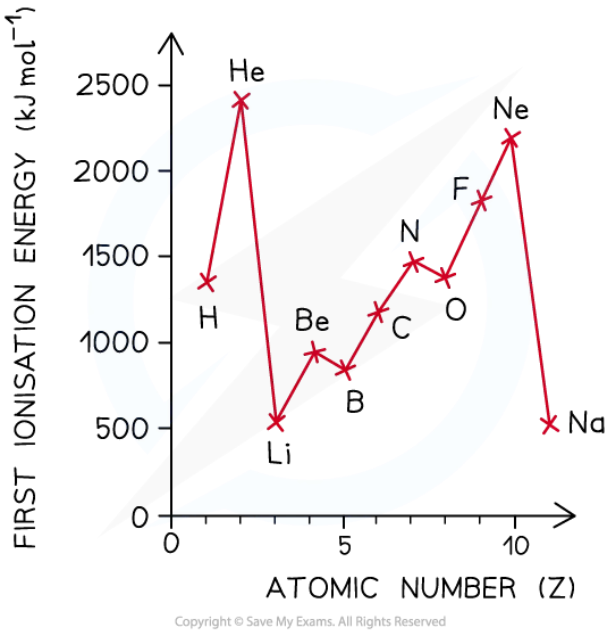
Ionisation Energy Trends Across a Period

- The trends in ionisation energy across a period and down a group have been discussed in our revision note on Periodicity
    - Trends in ionisation energy across a period provide evidence for the existence of energy sublevels

Graph showing Ionisation Energies From H to Ne



A graph showing the ionisation energies of the elements hydrogen to sodium

- The ionization energy across a period increases due to the following factors:
    - Across a period the nuclear charge increases
    - The distance between the nucleus and outer electron remains reasonably constant
    - The shielding by inner shell electrons remains the same
- There is a rapid decrease in ionisation energy between the last element in one period and the first element in the next period caused by:
    - The increased distance between the nucleus and the outer electrons
    - The increased shielding by inner electrons
    - These two factors outweigh the increased nuclear charge

Exceptions to the general trend in ionisation energy

- There are discontinuities in the general trend which are caused by the following:
    - There is a slight decrease in 1st I.E. between beryllium and boron as the fifth electron in boron is in the 2p subshell which is further away from the nucleus than the 2s subshell of beryllium
        - Beryllium has a first ionisation energy of 900 kJ mol-1 as its electron configuration is 1s2 2s2
        - Boron has a first ionisation energy of 801 kJ mol-1 as its electron configuration is 1s2 2s2 2p1
    - There is a slight decrease in 1st I.E. between nitrogen and oxygen due to spin-pair repulsion in the 2p subshell of oxygen

- Nitrogen has a first ionisation energy of 1402 kJ mol^{-1} as its electron configuration is $1s^2\ 2s^2\ 2p^3$
- Oxygen has a first ionisation energy of 1314 kJ mol^{-1} as its electron configuration is $1s^2\ 2s^2\ 2p^4$

Summary of Ionisation Energy Trends across a Period & going down a Group Table

Across a Period: Ionisation Energy Increases	Down a Group: Ionisation Energy Decreases
Increase in nuclear charge	Increase in nuclear charge
Shell number is the same The distance of the outer electron to the nucleus is the same	Increase in shells Distance of outer electron to nucleus increases The shielding effect increases, therefore, the attraction of valence electrons to the nucleus decreases
Shielding remains reasonably constant	Increased shielding
Deceased atomic/ionic radius	Increases atomic/ionic radius
The outer electron is held more tightly to the nucleus so it gets harder to remove it	The outer electron is held more loosely to the nucleus so it gets easier to remove it

Characteristic Properties of 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
  - High melting points
  - Have magnetic properties
  - Behave as catalysts
    - Use in catalytic converters and as biological catalysts
  - Form coloured compounds
  - Form complex ions with ligands
- These properties are a result of having an incomplete d sublevel

For more information about the electrical conductivity and high melting points of transition metals, see our revision note on the Physical Properties of Transition Elements

Variable Oxidation States

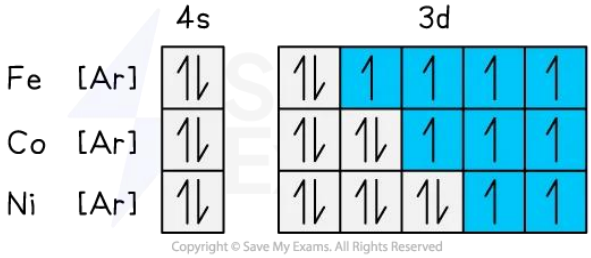
- Like other metals on the periodic table, the transition elements will lose electrons to form positively charged ions
- However, unlike other metals, transition elements can form more than one positive ion
  - They are said to have variable oxidation states

- Because of 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

Magnetic Properties

- Magnetism in transition metals is due to the presence of unpaired electrons in the d-orbitals
- Spinning electrons create a tiny magnetic dipole
- When paired electrons orientate themselves, the magnetic dipoles act in opposite directions, which means that there is no overall magnetic effect
- Most materials have paired electrons arranged like this, making them non-magnetic
- Some transition elements have unpaired electrons
- These unpaired electrons can be aligned in an external field resulting in magnetic properties
- The transitions elements iron, cobalt and nickel have strong magnetic properties
    - The alloy steel also has strong magnetic properties because it contains iron
- They contain unpaired electrons in their d orbitals

Arrangement of electrons in orbitals for iron, cobalt and nickel



Iron, cobalt and nickel have strong magnetic properties because they contain unpaired electrons in their d orbitals

- If iron, cobalt and nickel are heated and cooled in a magnetic field, the magnetic field of the electrons remains
- Magnetic regions within the metal that are aligned magnetically are known as domains
- Banging or heating a permanent magnet will weaken the magnetism

Examiner Tips and Tricks

- Previous specifications required you to know about the three types of magnetism:
    - Diamagnetism
    - Paramagnetism
    - Ferromagnetism
- The current specification states that "knowledge of different types of magnetism will not be assessed "

Transition elements as catalysts

- Transition metals are often used as catalysts in the elemental form or as compounds
- The ability of transition metals to form more than one stable oxidation state means that they can accept and lose electrons easily
- This enables them to catalyse certain redox reactions

    - They can be readily oxidised and reduced again, or reduced and then oxidised again
    - This is a consequence of transition metals having variable oxidation states
- There are two types of catalyst:
    - A heterogeneous catalyst is in a different physical state (phase) from the reactants
        - The reaction occurs at active sites on the surface of the catalyst
        - An example is the use of iron, Fe, in the Haber process for making ammonia
          $N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$
- A homogeneous catalyst is in the same physical state (phase) as the reactants

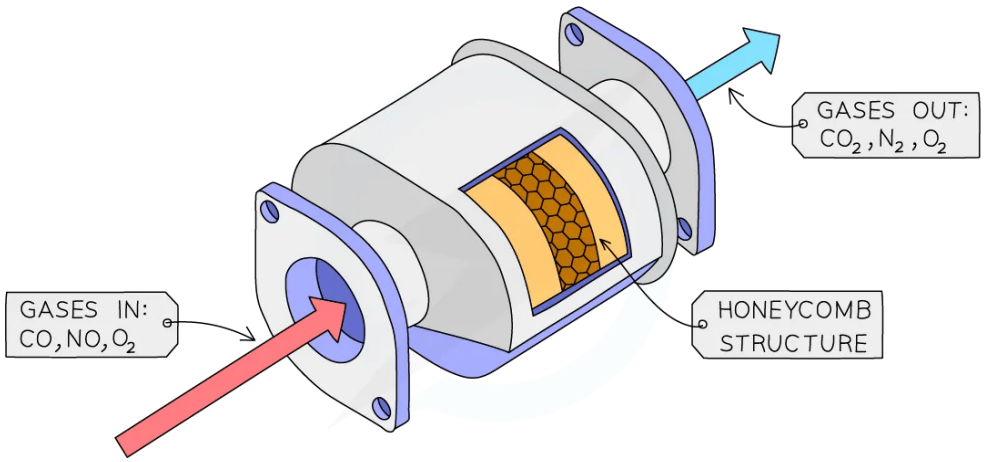
Further examples of transition metal catalysts

- The hydrogenation or reduction of alkenes makes use of a nickel catalyst
  $CH_2{=}CH_2\ (g) + H_2\ (g) \rightarrow CH_3CH_3\ (g)$
- The same reaction is used in the hydrogenation of vegetable oils
- The decomposition of hydrogen peroxide is a common reaction in the study of chemical kinetics and uses manganese(IV) oxide as the catalyst
  $2H_2O_2\ (g) \rightarrow\ 2H_2O\ (aq) + O_2\ (g)$

Catalytic converters

- Catalytic converters are used in car exhaust boxes to reduce air pollution
- They usually consist of a mixture of finely divided platinum and rhodium supported on a ceramic base

Catalytic converter diagram



The transition metal catalyst is on an inert support medium in a vehicle catalytic converter

- Carbon monoxide, nitrogen dioxide and unburnt hydrocarbons are sources of pollution in car exhaust
- The transition metal catalysts facilitate the conversion of these pollutants into less harmful products:
  $2NO\ (g) + 2CO\ (g) \rightarrow N_2\ (g) + 2CO_2\ (g)$
  $CH_3CH_2CH_3\ (g) + 5O_2\ (g) \rightarrow 3CO_2\ (g)\ + 4H_2O\ (g)$
- Some transition metals are precious metals so they can be very expensive

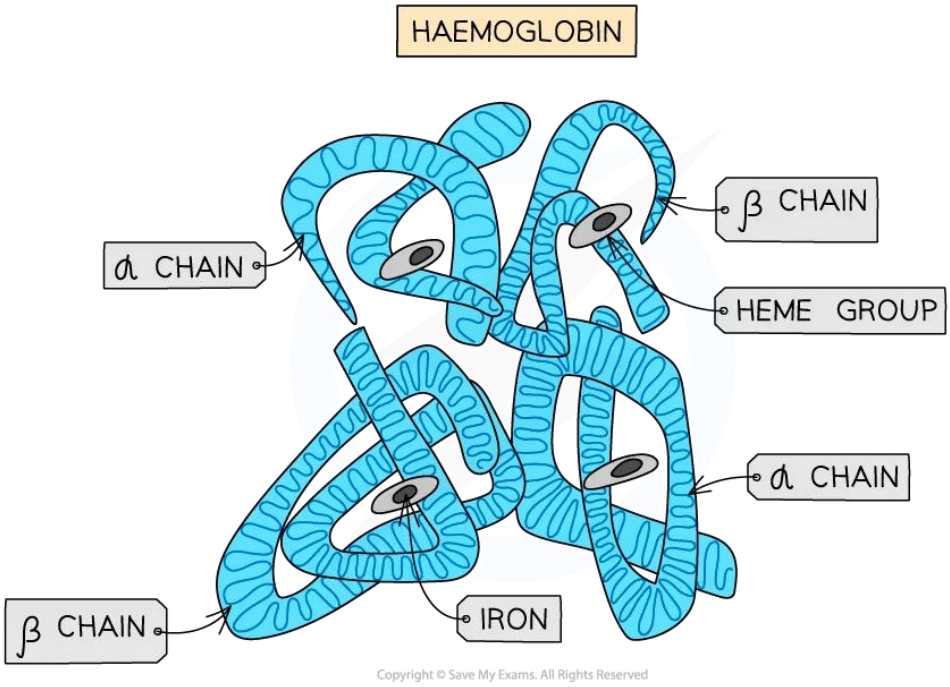
- In order to minimise the cost and maximise the efficiency of the catalyst the following measures can be taken:
  - Increasing the surface area of the catalyst
  - Coating an inert surface medium with the catalyst to avoid using large amounts of the catalyst

- This is achieved by spreading the catalyst over a hollow matrix such as a honeycomb-like structure

Biological catalysts

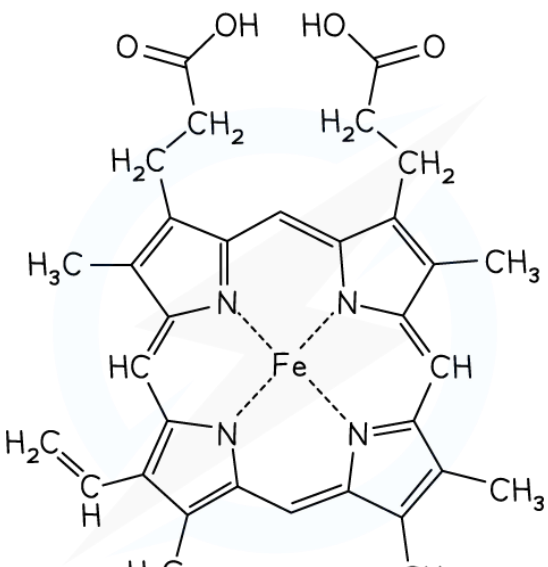
- Many of the enzyme catalysed reactions in the body make use of homogeneous transition metal catalysts
- An example of this is haemoglobin, abbreviated to Hb, which transports oxygen around the blood:

Haemoglobin structure diagram



Haemoglobin contains haem units that are responsible for transporting oxygen

The structure of haem



The haem unit contains an iron(II) ion

- The iron(II) ion is in the centre of a large heterocyclic ring called a porphyrin
- The iron has a coordination number of four, is square planar and can bind to one oxygen molecule
- The Hb molecule contains four porphyrin rings so each Hb can transport four oxygen molecules

Forming coloured compounds

- 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 state of Cr is +3) is dark green
    - Whereas the colour of the $[Cr(NH_3)_6]^{3+}$ complex (the oxidation state of Cr is still +3) is purple

For more information about transition metals as coloured compounds, see our revision note on Colour in Transition Metal Complexes

Forming Complex Ions

- Another property of transition elements caused by their ability to form variable oxidation states is the ability to form complex ions
- A complex ion consists of a central metal atom or ion, with a number of molecules or ions surrounding it
    - A molecule or ion surrounding the central metal atom or ion is called a ligand
- 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

For more information about complex ions and transition metals, see our revision notes on Coordinate Bonds

Variable Oxidation States in Transition Elements

Electron Configuration

- The full electronic configuration of the first-row transition metals is shown in the table below
- Following the Aufbau Principle electrons occupy the lowest energy subshells first
    - The 4s overlaps with the 3d subshell so the 4s is filled first
- Remember: You can abbreviate the first five subshells, 1s-3p, to [Ar] representing the configuration of argon (known as the argon core)

Table showing the electronic configuration of the first d-series transition elements

Transition metal	Electronic configuration	Noble gas core electronic configuration
Ti	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$	$[Ar]\ 3d^2\ 4s^2$
V	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$	$[Ar]\ 3d^3\ 4s^2$
Cr	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$	$[Ar]\ 3d^5\ 4s^1$
Mn	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$	$[Ar]\ 3d^5\ 4s^2$
Fe	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$	$[Ar]\ 3d^6\ 4s^2$
Co	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$	$[Ar]\ 3d^7\ 4s^2$
Ni	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$	$[Ar]\ 3d^8\ 4s^2$
Cu	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$	$[Ar]\ 3d^{10}\ 4s^1$

- There are two exceptions to the Aufbau Principle in the first row of the d-block:
    - Chromium
    - Copper
- In both cases, an electron is promoted from 4s to 3d to achieve a half-full and full d-subshell, respectively
- Chromium and copper have the following electron configurations, which are different to what you may expect:
    - Cr is $[Ar]\ 3d^5\ 4s^1$ not $[Ar]\ 3d^4\ 4s^2$
    - Cu is $[Ar]\ 3d^{10}\ 4s^1$ not $[Ar]\ 3d^9\ 4s^2$
- This is because the [Ar] 3d5 4s1 and $[Ar]\ 3d^{10}\ 4s^1$ configurations are energetically more stable and are preferred configurations
- When forming cations, remove the 4s electrons first

Worked Example

Deducing the electronic configuration of transition element ions
State the full electronic configuration of:

1. Cu
2. Mn(III) ions
3. V^{4+}

Answer 1 - Cu:

- Cu atomic number = 29
- $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}4s^1$ OR $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1 3d^{10}$
- Remember: Copper atoms prefer a complete d subshell

Answer 2 - Mn(III):

- Step 1: Write out the electron configuration of the atom first:
    - Mn atomic number = 25
    - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2 3d^5$
- Step 2: Subtract the appropriate number of electrons starting from the 4s subshell
    - Mn(III) = 22 electrons
    - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4$

Answer 3 - V^{4+}:

- Step 1: Write out the electron configuration of the atom first:
    - V atomic number = 23
    - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \ 3d^3\ 4s^2$
- Step 2: Subtract the appropriate number of electrons starting from the 4s subshell
    - V^{4+} = 19 electrons
    - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$
- When transition elements forms ions they lose electrons from the 4s subshell first

- This is because when the orbitals are occupied, the repulsion between electrons pushes the 4s into a higher energy state so that it now becomes slightly higher in energy than the 3d subshell
    - The 4s is now the outer shell and loses electrons first
- The loss of the 4s electrons means that +2 is a common oxidation state in transition metals
- The reason why the transition metals have variable oxidation states all comes down to energy

Table showing the common oxidation states of transition elements

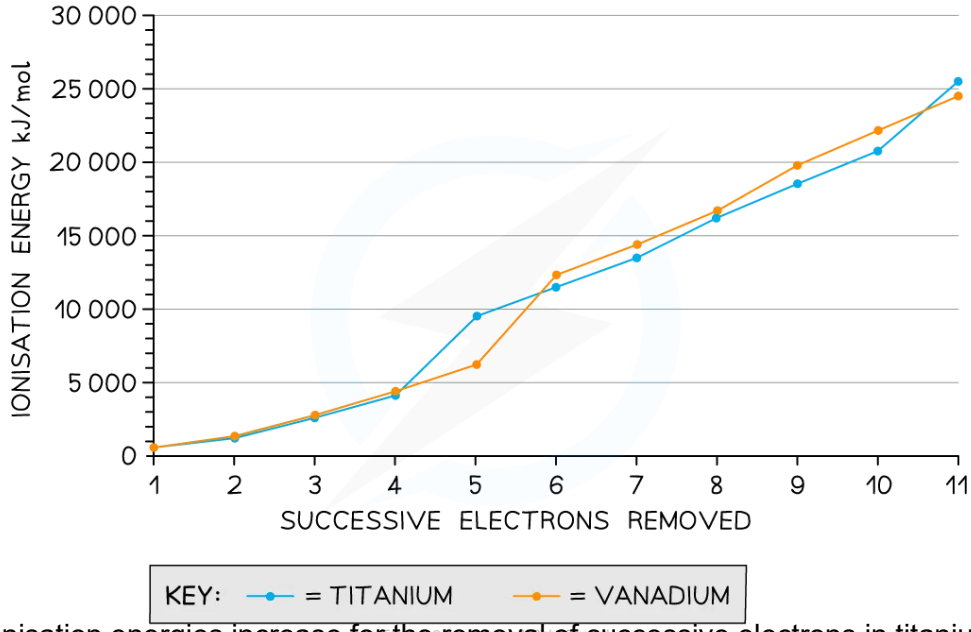
Element	Most common oxidation states
Ti	+3, +4
V	+3, +5
Cr	+3, +6
Mn	+2, +4, +7
Fe	+2, +3
Co	+2, +3
Ni	+2
Cu	+1, +2

Explaining variable oxidation states using successive ionisation energies

- Using titanium and vanadium as examples, the graph below shows that the first few ionisation energies are relatively small and relatively close together

- This means that the energy difference associated with removing a small number of electrons enables transition metals to vary their oxidation state with ease

Graph of titanium and vanadium ionisation energies



Ionisation energies increase for the removal of successive electrons in titanium and vanadium

- The +2 and +3 oxidation states are shown by all the transition elements
  - The +3 state is more stable in the elements up to chromium
  - The +2 state is more stable in the later elements
- Transition metal ions with oxidation state +3 and above tend to be polarising and have a degree of covalent character in the bonds they form
  - The ions have a high charge density and pull electrons towards themselves
- The maximum oxidation state possible corresponds to the total number of electrons in the 4s and 3d which reaches a maximum at manganese
  - An example you may be familiar with is the manganate(VII) ion, MnO_4^- which is a powerful oxidising agent

Examiner Tips and Tricks

- You may sometimes see electronic configurations with:
  - 3d electrons written before 4s
  - 4s electrons written before 3d
- Both ways are acceptable although putting the 3d electrons first is more conventional, even though 4s fills before 3d

Colour in Transition Metal Complexes

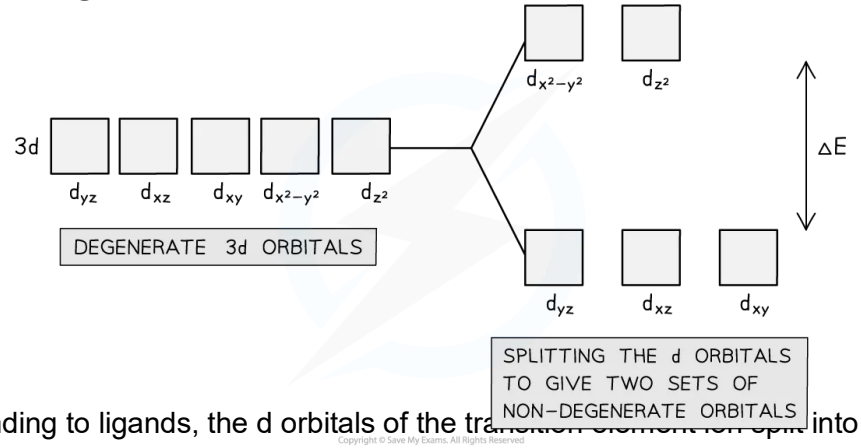
- Transition elements form coloured complexes when they bond with ligands
- Ligands are molecules, such as ammonia and water, or ions, such as ammonium or chloride ions that form a coordinate bond to a central metal ion
  - For more information, see our revision note on Coordination Bonds

Crystal Field Theory (CFT)

- The crystal field theory is a model based on electrostatic point charges and is used to explain colour in transition metal compounds

- In a transition metal atom, the five orbitals that make up the d-subshell all have the same energy
    - The term for this is degenerate
- However, when ligands are attached to a transition metal ion, the electric field formed by the lone pairs of electrons on the ligands repel the electrons in the d-subshell causing the d-orbitals to split in energy
- The dative bonding from the ligands causes the five d orbitals to split into two sets
- These two sets are not equal in energy and are described as being non-degenerate orbitals

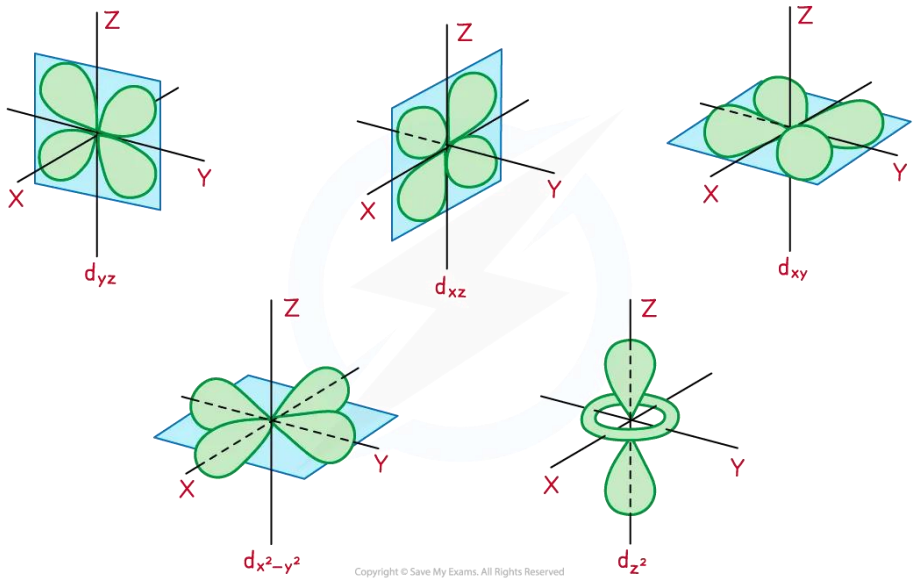
The effect of ligands on the d-orbitals of a central transition metal ion



Upon bonding to ligands, the d orbitals of the transition element ion split into two non-degenerate sets of orbitals

- The central metal ion in a complex has five d-orbitals for the electrons

Diagram showing the shapes and orientation of the five d-orbitals



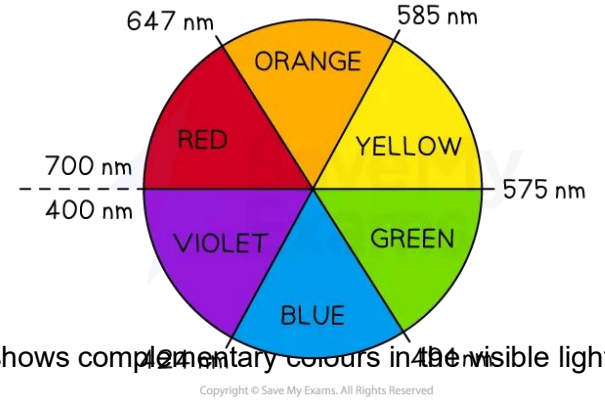
The names of the different d-orbitals are based on their position in the x, y and z planes. The shapes are shown here for reference only. You are not required to know the shapes of d-orbitals in the exam

Perception of colour

- +Most transition metal compounds appear coloured
- This is because the difference in energy between the non-degenerate orbitals allows electrons in the lower energy orbitals to be promoted into the higher energy orbitals

    - A larger splitting of the d-orbitals means that more energy is required to promote an electron
- This happens when the complex absorbs light energy with a wavelength corresponding to the energy gap between the orbitals
    - With a larger splitting of d-orbitals, light of a shorter wavelength and higher frequency is absorbed
- The amount of energy absorbed relates to certain parts of the visible electromagnetic spectrum
- The colour that is seen is complementary to the colour that is absorbed, i.e. it is made up of the parts of the visible spectrum that aren't absorbed
    - For example, a green compound will absorb all frequencies of the spectrum apart from green light, which is transmitted

The colour wheel



The colour wheel shows complementary colours in the visible light region of the electromagnetic spectrum

- Complementary colours are any two colours which are directly opposite each other in the colour wheel
    - For example, the complementary colour of red is green and the complementary colours of red-violet are yellow-green

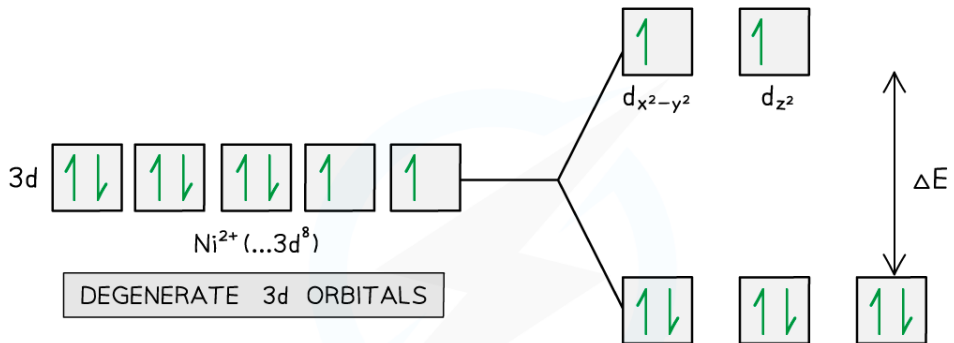
Examiner Tips and Tricks

- The colour wheel is given section 15 in the Data booklet, so there is no need to learn it
- There are different splitting patterns possible but you are not required to know different splitting patterns or their relation to coordination number.

Absorption of light

- When white light passes through a solution of aqueous nickel(II) sulfate, an electron in the lower energy d-orbitals is excited and jumps up into the higher energy d-orbitals
- A photon of red light is absorbed and light of the complementary colour (green) is transmitted
- This is why nickel(II) sulfate solution appears green
- The energy of the separation is ΔE corresponding to a wavelength of about 647 - 700 nm

Illustration of the electron promotion process in Nickel(II)



During electron promotion of a Ni(II) complex, an electron jumps from a dx orbital to a dx2-y2 orbital when light is shone on the solution

Worked Example

Titanium(III) sulfate forms a purple aqueous solution. Estimate the wavelength of light absorbed by this solution, using Section 15 of the data booklet.

Answer:

- Titanium(III) sulfate appears purple
- The complementary colour of yellow is absorbed
- The wavelength range of the complementary colour is 575 - 585 nm

Wavelength, frequency and energy

- A greater splitting of the d-orbitals results in a larger energy gap, ΔE
- This means that more energy is needed to promote an electron from a lower to a higher energy orbital
- Therefore, the light needs to have:
    - Shorter wavelength
    - Higher frequency
- The equations relating wavelength, frequency and energy are:

speed of light (3.00×10^8 m s^{-1})	=	frequency (s^{-1})	x	wavelength (m)

c		f		λ
energy (J)	=	Planck's constant (6.63×10^{-34} J s)	x	frequency (s^{-1})
E		h		f

- These are given in Section 1 of the Data Booklet, so there is no need to memorise them, although you do need to how to manipulate them and what the units are
- The constants are listed in Section 2 of the data Booklet