

Topic 3: Periodicity

3.1 The periodic table

- U1 The periodic table is arranged into four blocks associated with the four sublevels—s, p, d, and f.
- U2 The periodic table consists of groups (vertical columns) and periods (horizontal rows).
- U3 The period number (n) is the outer energy level that is occupied by electrons.
- U4 The number of the principal energy level and the number of the valence electrons in an atom can be deduced from its position on the periodic table
- U5 The periodic table shows the positions of metals, non-metals and metalloids.
- A1 Deduction of the electron configuration of an atom from the element's position on the periodic table, and vice versa.

The elements are arranged in the periodic table in increasing order of atomic mass from left to right. Going down one row increase the number of electron shells by one. Going one column to the right increases atomic mass by 1.

Group - a group is a vertical column of elements in the Periodic Table. The atoms of the elements in the group all have the same outer shell structure but an increasing number of inner shells.

Period – a period is a horizontal row of elements in the Periodic Table. Within a period, the atoms of the elements have the same number of shells but with an increasing number of electrons in the outer shell.

Before calcium ($Z = 20$),

- group number = number of valence electrons
- period number = number of electron shells

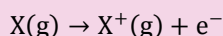
Electron Configurations in the Periodic Table

3.2 Periodic trends

- U1 Vertical and horizontal trends in the periodic table exist for atomic radius, ionic radius, ionization energy, electron affinity and electronegativity.
- U2 Trends in metallic and non-metallic behaviour are due to the trends above.
- U3 Oxides change from basic through amphoteric to acidic across a period.
- A1 Prediction and explanation of the metallic and non-metallic behaviour of an element based on its position in the periodic table.
- A2 Discussion of the similarities and differences in the properties of elements in the same group, with reference to alkali metals (group 1) and halogens (group 17).
- A3 Construction of equations to explain the pH changes for reactions of Na_2O , MgO , P_4O_{10} , and the oxides of nitrogen and sulfur with water.

IB definitions

First ionisation energy – the first ionization energy is the minimum energy required to remove a mole of electrons from a mole of gaseous atoms to form a mole of univalent cations in the **gaseous** state.



Electronegativity – ability of an atom to attract electrons towards itself (man-made scale from 4.0 to 0)

Atomic Radius

The **atomic radius** is defined as the distance from the nucleus to the outermost electron or, in practice, half the distance between two bonded nuclei.

- In a period: atomic size decreasing, as larger Z_{eff} (same amount of shielding but more proton numbers)
- In a group: from top to bottom, the atom size increases (adding more energy level, so the amount of shielding increases, so Z_{eff} decreases)

Ionic Radius

- Positive ion' radius is smaller than its atom: losing an electron means less outermost electrons, larger forces experienced by each outermost electrons (effective nuclear charges increase), so the radius gets smaller.
- Negative ion' radius is larger than its atom: gaining an electron means more outermost electrons, smaller forces experienced by each outermost electrons (effective nuclear charges decrease), so the radius gets larger

Electron Affinity

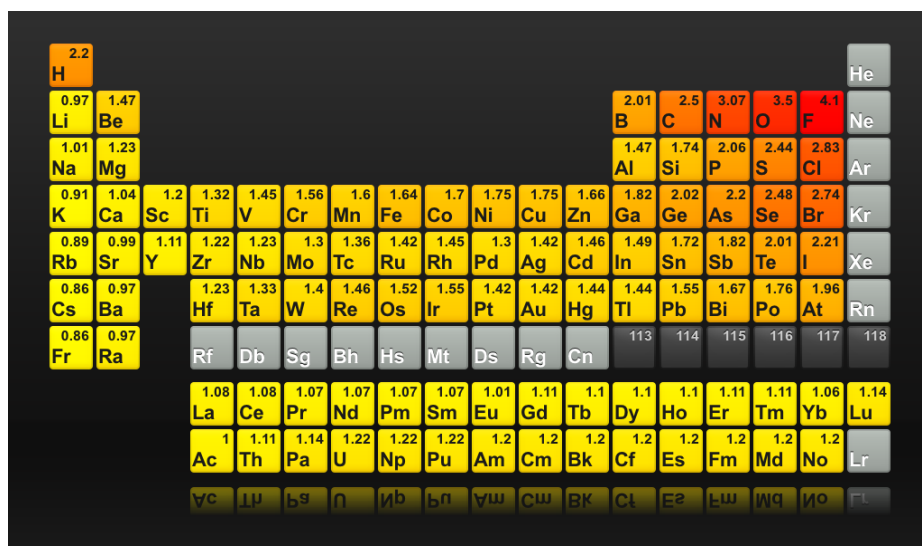
Value of electron affinity is negative because energy is released (-ve), not represents magnitude

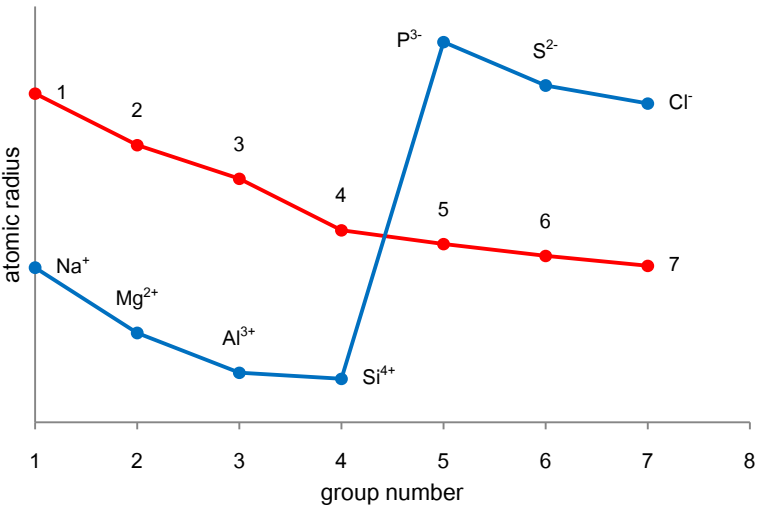
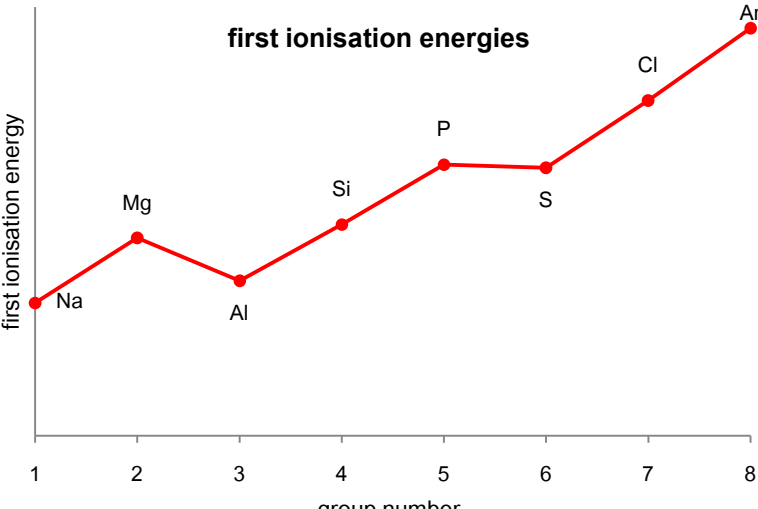
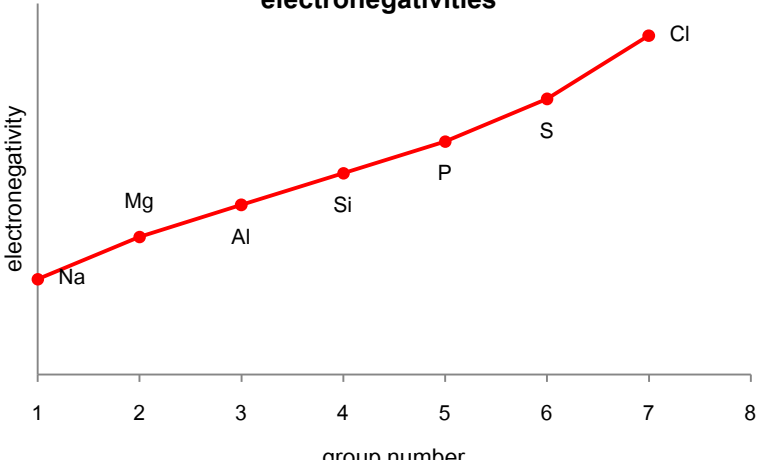
- From period 2 to period 3, electron affinity increases: putting electrons in $n=2$ shell (maximum hold 8 electrons), electrons will face relatively larger repulsion, so it needs more energy to hold the electrons in place, that means less energy will be released. However, in the case of $n=3$ shell (maximum hold 18 electrons), there is more space for electrons to move, so it takes relatively less energy to hold the electrons in place, that means more energy will be released. (inter electron repulsion)
- Group 17 have largest electron affinity value: outer energy level will be fulfilled, so F^- will be more stable than F, releasing a lot of energy
- Electron affinity is opposite from first ionisation energy
- In a period: Electron affinity generally increases (more protons but same shielding, larger Z_{eff} , larger attraction to electrons) However, for example nitrogen has no EA value, because nitrogen itself is stable (half-filled orbitals); Beryllium also doesn't have EA value, because adding an electron in will create a new 2p orbitals for beryllium, the distance from the nucleus and more electron shielding makes it very energy-consuming. Lithium EA value is larger than boron, that is because electron is added into 2s sub-shell, which is closer to the nucleus than 2p sub-shell. Remember, distance matters most; so the attraction from the nucleus to electron is far more larger
- In a group, electron affinity generally decreases as Z_{eff} decreases except the case discussed above from period 2 to period 3 which has more space and less inter electron repulsion.
- Group 18 elements don't have EA value – they are already stable

Electronegativity

Ability of an atom to attract electrons towards itself

- Electronegativity is all about effective nuclear charge, higher Z_{eff} higher electronegativity
- In a period: electronegativity increases (more protons but same shielding, Z_{eff} increases)
- In a group: from top to bottom, electronegativity decreases (electrons are further from the nucleus and more shielding effect, Z_{eff} decrease)
- Fluorine has highest electronegativity value 4.0 --- least shielding, closer to nucleus



Trend	Explanation
<p style="text-align: center;">atomic and ionic radii</p>  <p>1 2 3 4 5 6 7 8</p> <p>group number</p>	<p>Across the period the number of protons in the nucleus increases (so there is a greater attractive force) but there is the same amount of shielding effect. The effective nuclear charge therefore increases across the period, pulling the energy levels closer. This means that atomic nuclei decrease across the period. The same trend is observed with ionic radii except because the cations have 1 shell fewer they have a smaller radius.</p> <p>The graph shows the Si^{4+} ion (radius: 42), the Si^{4-} ion also exists with a radius of 271.</p>
<p style="text-align: center;">first ionisation energies</p>  <p>1 2 3 4 5 6 7 8</p> <p>group number</p>	<p>As mentioned previously, the effective nuclear charge increases across the period. Because of this, the first ionisation energies generally increase across the period.</p> <p>There are, however, two decreases:</p> <ul style="list-style-type: none"> From Mg to Al – electrons in p orbitals are of higher energy and further away from the nucleus, thus easier to remove From P to S – an electron in a doubly occupied orbital is repelled by its partner and so is easier to remove than an electron in a half-filled orbital <p>Mg: $[\text{Ne}] 3s^2$ Al: $[\text{Ne}] 3s^2 3p^1$ P: $[\text{Ne}] 3s^2 3p_x^1 3p_y^1 3p_z^1$ S: $[\text{Ne}] 3s^2 3p_x^2 3p_y^1 3p_z^1$</p>
<p style="text-align: center;">electronegativities</p>  <p>1 2 3 4 5 6 7 8</p> <p>group number</p>	<p>The electronegativity increases across the period as the size of the atoms decreases</p>

Group 1 – the alkali metals

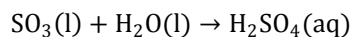
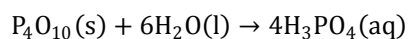
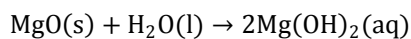
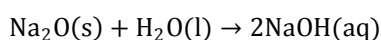
- they are very reactive metals
- they form ionic compounds with non-metals
- the elements further down the group are more reactive than the higher ones since the valence electron is further from nucleus and has more shielding
- they react with water to form hydrogen and metal hydroxide alkaline solution
- they react with halogens to form ionic salts

Group 7 - halogens

- they are very reactive non-metals
- reactivity decreases down group
- they form ionic compounds with metals and covalent compounds with other non-metals
- higher halogens can displace lower ones from compounds

Reactions with water

The reactions specified by the syllabus are:



Acidity of oxides across period 3

Formula of oxide	Na_2O (s)	MgO (s)	Al_2O_3 (s)	SiO_2 (s)	P_4O_{10} (s) P_4O_6 (s)	SO_3 (l) SO_2 (g)	Cl_2O_7 (l) Cl_2O (g)
Acid-base character	basic		amphoteric	acidic			
Structure	giant ionic			giant covalent	molecular covalent		

- metal oxides are solid because they have strong ionic bonds and therefore form an ionic lattice
- sulphur dioxide is a macromolecular covalent structure like diamond
- the remaining three are molecular covalent
- ionic compounds conduct best because of the mobile charges in molten or aqueous phase

Period 3 chlorides

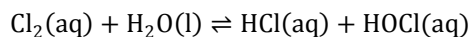
Formula of oxide	NaCl	MgCl ₂	AlCl ₃ / Al ₂ Cl ₆	SiCl ₄	PCl ₅ / PCl ₃	S ₂ Cl ₂	Cl ₂
Physical state	solid		solid / gas	liquid	solid / liquid	liquid	gas
Oxidation number	+1	+2	+3	+4	+5 / +3	+1	0
Electrical conductivity in molten state	high		poor	none			
Structure	giant ionic		molecular covalent				

- the more polar the substance is the better it conducts; ionic compounds conduct well
- the ionic compounds have the strongest forces of attraction and are therefore solid
- the non-metal chlorides have dipole-dipole or van der Waals' forces (depending on whether the dipoles cancel)

- Cl_2 is non-polar so the IMFs are weak, therefore it is a gas

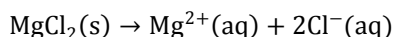
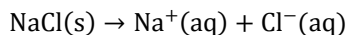
Reactions of period 3 chlorides with water

Chlorine reacts in a reversible disproportionation (both reduced and oxidised) reaction, producing hydrochloric acid and chloric(I) acid:



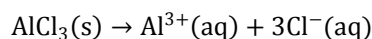
The solution is acidic. This is why chlorine turns damp litmus paper red.

Ionic chlorides split into ions in solution, which get surrounded by water molecules (partially charged oxygen to cation and partially charged hydrogen to anion). They become **hydrated**.



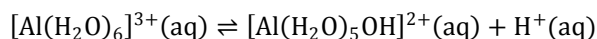
The pH of aqueous magnesium chloride is slightly less than 7 because the Mg^{2+} ion is polarising.

Aluminium chloride dissociates into ions when added to water:

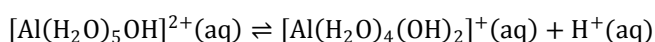


The aluminium ion has a high charge density due to it having a 3+ charge and a small ionic radius. The ion attracts water molecules which form **dative(or coordinate) bonds** with the ion to form an octahedral complex ion, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$

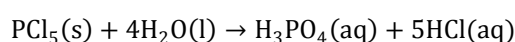
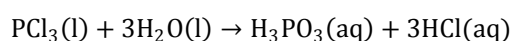
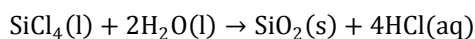
The hydrated ion is acidic as the Al^{3+} ion attracts the electrons of the OH bond of the surrounding water molecules, and releases the H^+ ion to form an acidic solution.



This process can go on:



Silicon and phosphorus react to form hydrochloric acid:



In summary:

Formula of oxide	NaCl	MgCl ₂	AlCl ₃ / Al ₂ Cl ₆	SiCl ₄	PCl ₅ / PCl ₃	S ₂ Cl ₂	Cl ₂
Acid-base character	neutral	weakly acidic	acidic				

Topic 13: The periodic table --- the transition metals (HL)

13.1 First-row d-block elements

U1	Transition elements have variable oxidation states, form complex ions with ligands, have coloured compounds, and display catalytic and magnetic properties.
U2	Zn is not considered to be a transition element as it does not form ions within complete d-orbitals.
U3	Transition elements show an oxidation state of +2 when the s-electrons are removed.
A1	Explanation of the ability of transition metals to form variable oxidation states from successive ionization energies.
A2	Explanation of the nature of the coordinate bond within a complex ion.
A3	Deduction of the total charge given the formula of the ion and ligands present.
A4	Explanation of the magnetic properties in transition metals in terms of unpaired electrons.

Properties of transition elements

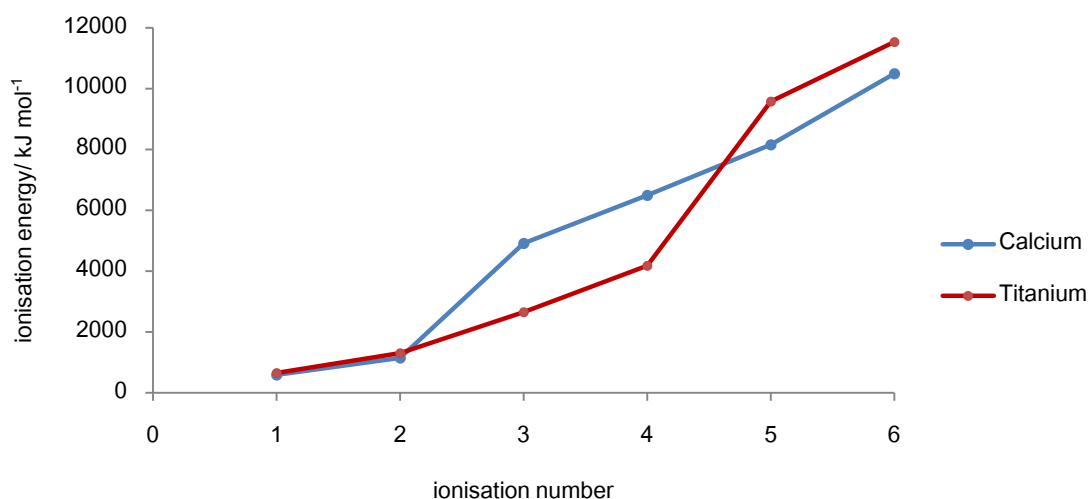
- variable oxidation states
- formation of complex ions
- coloured complexes
- catalytic behaviour
- the normal metallic properties (good conductors, malleable, ductile)
- formation of alloys
- high melting point and boiling point

Scandium and zinc

A transition metal is defined as an element that possesses an incomplete, or **partially filled, d sub-level** in one or more of its oxidation states. Scandium is not a typical transition metal as its common ion Sc^{3+} has no d electrons. Zinc is not a transition metal as it contains a full d sub-level in all its oxidation states.

Explanation of variable oxidation number of transition elements

The fact that transition metals can have various oxidation numbers has to do with ionisation energies. The diagram below shows the difference between calcium and titanium's ionisation energies.

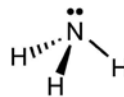


The increase in ionisation energies for titanium is more gradual as the 3d and 4s orbitals are close in energy level. Titanium can exist in +2, +3 and +4 oxidation states, but not +5 because the jump in ionisation energies is too large. Students should know that all transition elements can show an oxidation number of +2. In addition, they should be familiar with the oxidation numbers of the following: Cr (+3, +6), Mn (+4, +7), Fe (+3) and Cu (+1).

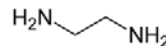
IB definitions

Ligand – an ion or molecule that donates **a pair of electrons** to a metal atom or ion in forming a coordination complex. Ligands are Lewis bases e.g. H_2O , CN^- , Cl^- and NH_3

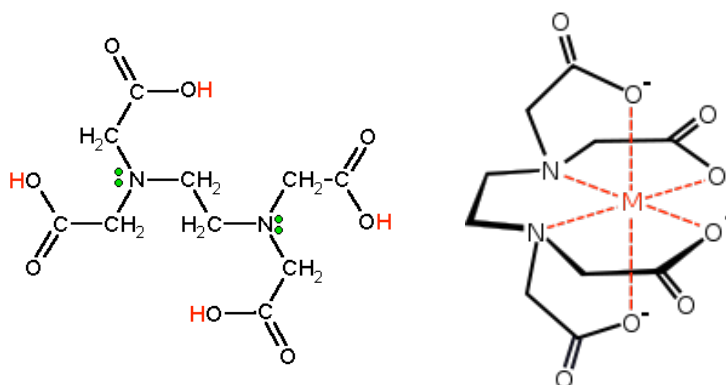
Monodentate ligand: it can form one co-ordinate bond in one molecule, such as NH_3 , H_2O



Bidentate ligand: it can form two co-ordinate bonds in one molecule, such as ethylenediamine



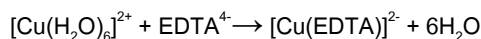
Polydentate ligand: it can form more than two co-ordinate bonds in one molecule, such as EDTA



It has potential to donate 6 of its electron pair and become EDTA^{4-} and a hexadentate ligand.

Chelate effect

Complexes with polydentate ligand (e.g. EDTA) are most stable and favorable to be formed.



Because polydentate ligands have more binding sites, so it requires fewer moles of polydentate ligands to satisfy the “need” of the metal ions. As shown in the chemical equation, the reaction is moved from order to disorder (more moles of products than reactants), leading to a **highly positive value of entropy**.

According to the equation $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$, highly positive entropy will give an highly negative value of Gibb's free energy, so the reaction is spontaneous, meaning that the formation of $[\text{Cu}(\text{EDTA})]^{2-}$ is favourable.

Complexes

Transition metal ions have relatively high charges and small sizes allowing them to attract ligands' lone pairs of electrons. The number of dative bonds from ligands to the central ion is called the **coordination number**. Ligands can be exchanged.

Complexes: **co-ordinate bonds** between a metal ions and negative ions or substances with a lone pair.

Metal ion is Lewis acid – electron pair acceptor

Ligand is Lewis base – electron pair donor

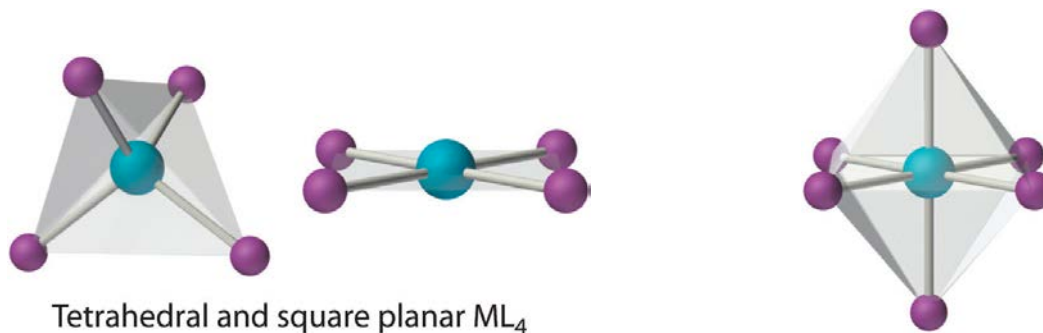
Coordination Number

Numbers of co-ordinate bonds around a metal ion in a complexes = coordination number

Coordination number = 2: The shape of the complexes is linear



Coordination number = 4: The shape of the complexes is tetrahedral or square planar



Coordination number = 6: The shape of the complexes is octahedral

When water is used as a ligand, it always forms a coordination number of 6 – octahedral shape.

13.2 Coloured complexes

- | | |
|----|---|
| U1 | The d sub-level splits into two sets of orbitals of different energy in a complex. |
| U2 | Complexes of d-block elements are coloured, as light is absorbed when an electron is excited between the d-orbitals. |
| U3 | The colour absorbed is complementary to the colour observed. |
| A1 | 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. |
| A2 | 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. |

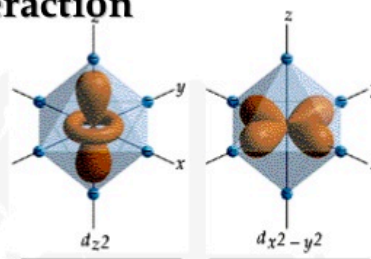
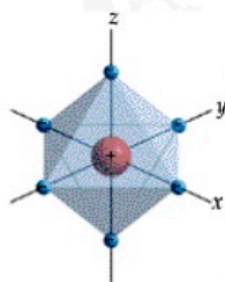
Splitting d-orbitals

When ligands approach the metal, in octahedral shape, they move in along the axis, so the orbital on the axis face more repulsion by electric field created by the incoming ligands. Therefore, they have more energy.

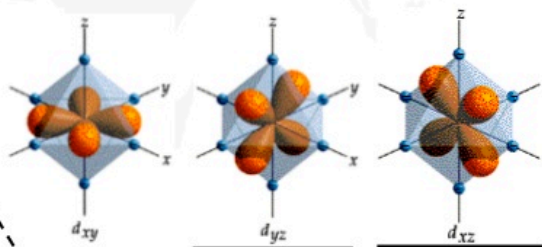
Similarly, orbitals between the axis are influenced less by the electric field created by incoming ligands, Therefore, they have less energy.

d-Orbitals and Ligand Interaction (Octahedral Field)

Ligands
approach
metal

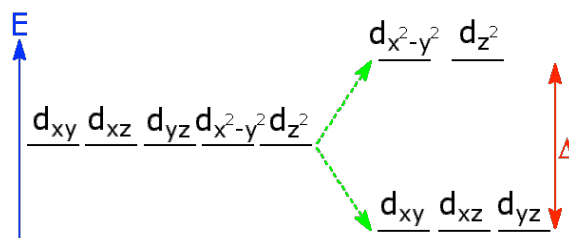


d-orbitals pointing directly at axis are
affected most by electrostatic interaction



d-orbitals not pointing directly at axis are least
affected (stabilized) by electrostatic interaction

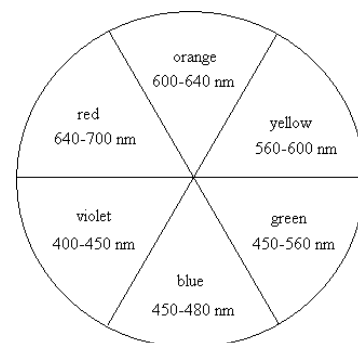
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The d-orbitals are split into two energy levels; the difference between two energy levels is denoted as Δ_o

Colour formation

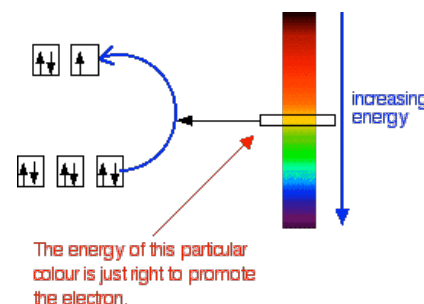
Colour of the light absorbed by the substance is **complementary** to the colour observed by us, showing on the colour wheel. For example, Fe^{2+} is green in colour, which means it must absorb red colour from the visible light.



When visible light passes through the substance, one electron will be excited to the higher energy d-orbital.

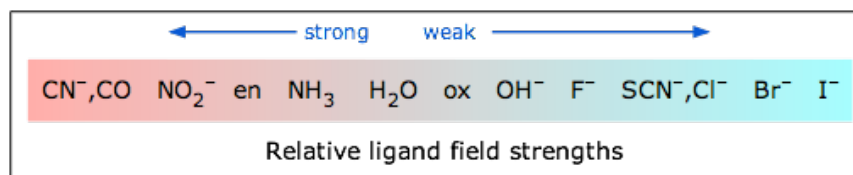
When it falls back, it gives out energy which falls in the visible light range due to the small gap between two d-orbital energy levels. This deexcitation will show colour.

The difference between the d-orbital energy levels (Δ_o) will affect the energy released by deexcitation, thereby showing different colours.



Factors affecting d-orbital splitting

- The nature of the ligand:
 - Stronger electric field (CO), more splitting, more energy will be absorbed, longer wavelength colour will be shown.**
 - Weaker electric field (I^-), less splitting, less energy will be absorbed, shorter wavelength colour will be shown.



- Electron configuration of metal ions (same elements)
 - Higher charge of the ions, more splitting, more energy will be absorbed, longer wavelength colour will be shown.** For example, Fe^{2+} has less charge, less splitting, red colour (less energy) is absorbed, so show green colour (shorter wavelength); Fe^{3+} has more charge, more splitting, green colour (more energy) is absorbed, so show red colour (longer wavelength).
- Nature of metal ions
 - More d-orbital electrons, more splitting, more energy will be absorbed, longer wavelength colour will be shown.** For example, Fe^{2+} has less d electrons, less splitting, red colour (less energy) is absorbed, so show green colour (shorter wavelength); Cu^{2+} has more d electrons, more splitting, orange colour (more energy) is absorbed.
- Geometry of complexes (tetrahedral/octahedral)

Magnetic properties of metals

The magnetic properties are about unpaired d-orbital electrons.

- Diamagnetic:** have all electrons paired up, so has no effects under magnetic field.
- Paramagnetic:** have unpaired electrons; slightly attracted by a magnetic field and the material does not retain the magnetic properties when the external field is removed.
- Ferromagnetic:** have unpaired electrons; exhibit a strong attraction to magnetic fields and are able to retain their magnetic properties after the external field has been removed.