Inorganic Chemistry

Fe-EDTA Complex

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Group 2

1 Overview

Group 2 metals are the *alkaline earth metals*, and have this name for two reasons; their oxides form alkaline solutions when dissolved in water, and some another mostly irrelevant and historical reason. Mainly the alkaline solution thing.

2 Physical Properties

2.1 Electronic Configuration

Group 2 metals are present in compounds with a fixed oxidation state of $+2$, with a fully filled outermost s subshell:

Be: $1s^2 2s^2$
Mg: $1s^2 2s^2 2p^6 3s^2$
Ca: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Sr: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$
Ba: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$

Group 2 metals form $+2$ compounds for two reasons; first, the 3rd ionisation energy (to get to a $+3$ state) is significantly greater than either the 1st or 2nd, which cannot be sufficiently compensated for by an exothermic lattice energy.

Secondly, they do not exist in the $+1$ state because in many cases, the lattice energy of compounds containing the metal in the $+2$ state is more exothermic, thus favouring the more stable MX_2 compound as opposed to the MX compound.

2.2 Ionic and Atomic Radii

Naturally, both the ionic and atomic radii of the group 2 metals *increase* down the group, due to the increasing number of quantum shells.

2.3 Ionisation Energy

The first and second ionisation energies of the elements *decrease* down the group. This is due to the increasing number of electron shells between the nucleus and the valence electron shell, increasing the shielding effect.

Recall that the shielding effect decreases the attractive electrostatic forces between the valence electrons and the nucleus, so less energy is required to remove said electron.

2.4 Melting and Boiling Points

2.4.1 General Trend

Generally speaking, the melting and boiling points decrease down the group, although there are rather large irregularities in the trend. The broad reason for decreasing melting and boiling points is the increasing cationic size down the group, which leads to weaker electrostatic forces between the delocalised electron cloud and the ions. Thus, the strength of the metallic bond decreases.

2.4.2 Comparison with Group 1 Metals

In the same period, group 2 metals have higher melting and boiling points than group 1 metals, primarily due to the increase in nuclear charge ($+1$ to $+2$) along with more electrons in the delocalised cloud, leading to stronger metallic bonding.

2.5 Solubility of Hydroxides and Sulphates

The solubilities of group 2 hydroxides *increase* down the group, while the solubilities of the sulphates *decrease*; $Mg(OH)_2$ and $BaSO_4$ are insoluble, while $MgSO_4$ and $Ba(OH)_2$ are soluble.

$$\Delta H_{sol} = -LE + \Delta H_{hyd}$$

$$LE \propto \frac{q_+ \times q_-}{r_+ + r_-} \qquad \Delta H_{hyd} \propto \frac{q_+}{r_+} + \frac{q_-}{r_-}$$

For the sulphates, the anionic radius is far larger than the cationic radius, hence the LE remains relatively constant down the group. However, looking at the enthalpy change of hydration, the increasing cationic radius decreases the ΔH_{hyd}. Overall, ΔH_{sol} increases down the group and is *less exothermic*, decreasing solubility.

For the hydroxides, the reverse is true; the anionic radius is small compared to the cation, so the the cationic radius has a greater effect and LE decreases. Thus, combined with the decreasing ΔH_{hyd}, hydroxides become increasingly soluble down the group.

3 Chemical Properties of the Elements

3.1 Redox Reactivity

Due to the decrease in the first two ionisation energies down the group, the ease of oxidation increases as well — implying that group 2 metals increase in strength as reducing agents as well.

Behold a table of $E^{\ominus}_{ox}$ values:

Reaction	$E^{\ominus}_{\text{ox}}$/V
Be $_{(s)}$ $\longrightarrow$ Be^{2+} + 2 e^{-}	+1.99
Mg $_{(s)}$ $\longrightarrow$ Mg^{2+} + 2 e^{-}	+2.37
Ca $_{(s)}$ $\longrightarrow$ Ca^{2+} + 2 e^{-}	+2.87
Sr $_{(s)}$ $\longrightarrow$ Sr^{2+} + 2 e^{-}	+2.89
Ba $_{(s)}$ $\longrightarrow$ Ba^{2+} + 2 e^{-}	+2.91

3.2 Reaction with Oxygen

The trend of the metals' reactions with oxygen is simply a product of their increasing reducing power down the group. They all tarnish in air (before exploding) without external agents, and the reactivity increases down the group.

$$2\,\text{Mg}_{(s)} + \text{O}_2{}_{(g)} \longrightarrow 2\,\text{MgO}_{(s)}$$
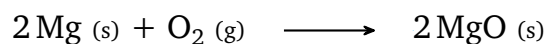
Barium reacts at room temperature quickly, so it is stored under oil to prevent rapid tarnishing. Beryllium on the other hand needs to be burning before *any* reaction takes place; its curiosities will be explored later.

Reaction	Flame Colour	Reactivity
2 Mg $_{(s)}$ + O$_2$ $_{(g)}$ $\longrightarrow$ 2 MgO $_{(s)}$	brilliant white	very slow
2 Ca $_{(s)}$ + O$_2$ $_{(g)}$ $\longrightarrow$ 2 CaO $_{(s)}$	brick red	slow
2 Sr $_{(s)}$ + O$_2$ $_{(g)}$ $\longrightarrow$ 2 SrO $_{(s)}$	crimson red	fast
2 Ba $_{(s)}$ + O$_2$ $_{(g)}$ $\longrightarrow$ 2 BaO $_{(s)}$	green	very fast

3.3   Reaction with Water

The reactivities of the metals with water increase down the group, reducing water to hydrogen gas. Note that Be does not react with water (or steam), even when heated.

All the metals form hydroxides with the exception of Mg — when reacting with steam, it forms MgO directly, and ptherwise reacts slowly with cold water to form $Mg(OH)_2$.

$$2\,Mg_{\ (s)} + H_2O_{\ (g)} \longrightarrow MgO_{\ (s)} + H_{2\ (g)}$$
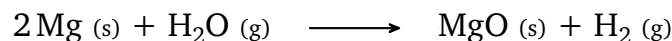
The hydroxide formed, since it is only sparingly soluble, acts as a protective layer that slows down the further reaction of the underlying metal with water.

For the rest of the metals, hydroxides are formed directly with increasing vigour.

$$Ba_{\ (s)} + 2\,H_2O_{\ (l)} \longrightarrow Ba(OH)_{2\ (aq)} + H_{2\ (g)}$$
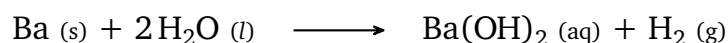
Note that the solubility of $Ca(OH)_2$ is an equilibrium, and exists as either slaked lime in the solid form, or limewater in the aqueous form. The latter is produced when reacted with excess water.

Finally, all the group 2 hydroxides are basic, except for beryllium hydroxide ($Be(OH)_2$) which is amphoteric.

4   Properties of the Oxides

4.1   Physical Properties

All group 2 oxides are solid at room temperature, white, basic, and have very high melting and boiling points. Melting and boiling points for the oxides decrease down the group, due to a decreasing lattice energy.

4.2   Reaction with Water

All group 2 oxides react with water to form their respective hydroxides (hence they are basic oxides). The exeption is BeO which is amphoteric but does not react with water.

The vigour of the reaction increases down the group, since the magnitude of the lattice energy of the ionic oxide decreases. In particular, magnesium oxide reacts *very slowly* with cold water.

$$BaO_{\ (s)} + H_2O_{\ (l)} \longrightarrow Ba(OH)_{2\ (aq)}$$
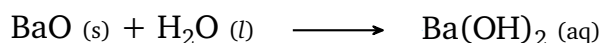
5 Thermal Stability of Group 2 Compounds

5.1 Overview

All group 2 hydroxides, carbonates and nitrates thermally decompose at appropriate temperatures. The trend for all 3 is that the temperature required *increases* down the group, aka. the stability of these ionic compounds increases down the group.

The data for beryllium is generally sparse, so... it's not there. Oops.

Element	MCO_3	$M(NO_3)_2$	$M(OH)_2$
Mg	400 °C	450 °C	300 °C
Ca	900 °C	575 °C	390 °C
Sr	1280 °C	635 °C	466 °C
Ba	1360 °C	675 °C	700 °C

The main factor affecting the thermal stability is the polarising power of the ion, which depends on charge density — this decreases down the group, leading to more stable ionic compounds.

5.2 Mechanism of Action

The decomposition of all 3 categories of ionic compounds follow the same principle. Given the relatively high charge density of the group 2 metals, they are able to *polarise* the covalent bonds *within the anion*, weakening them.

This weakening of the covalent bonds in the anion allows it to break when heat is applied, typically resulting in a metal oxide as the product.
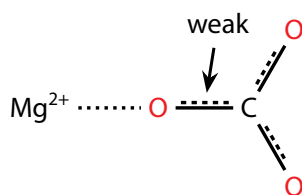
The concept is similar for nitrates and hydroxides, and shows why the product is usually the metal oxide.

When heat is applied, the weak bond will be broken, leading to the formation of MgO and CO_2.

As the polarising power of the metal ion decreases down the group (due to increasing radius but constant charge), the bond is weakened to a lesser degree, leading to a higher stability.

5.2.1 Carbonates

The thermal decomposition of group 2 carbonates produces the metal oxide and carbon dioxide gas.

$$BaCO_3 \text{ (s)} \xrightarrow{\text{heat}} BaO \text{ (s)} + CO_2 \text{ (g)}$$
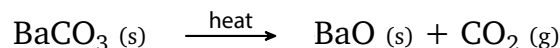
5.2.2 Hydroxides

Thermally decomposing hydroxides produces the metal oxide and water.

$$Ba(OH)_2 \text{ (s)} \xrightarrow{\text{heat}} BaO \text{ (s)} + H_2O \text{ (l)}$$
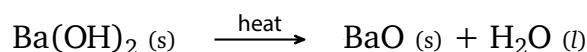
5.2.3 Nitrates

The thermal decomposition of nitrates yields the metal oxide, nitrogen, and oxygen.

$$2\,Ba(NO_3)_2 \text{ (s)} \xrightarrow{\text{heat}} 2\,BaO \text{ (s)} + 4\,NO_2 \text{ (g)} + O_2 \text{ (g)}$$
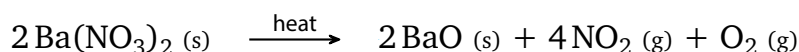
5.3 Comparison with Group 1 Metals

Most group 1 metals do not have sufficient charge density to polarise the carbonate anion, however they do polarise the nitrate ion enough for some decomposition:

$$2\,NaNO_3 \text{ (s)} \xrightarrow{\text{heat}} 2\,NaNO_2 \text{ (s)} + O_2 \text{ (g)}$$
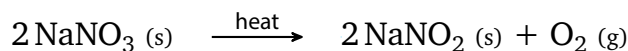
Lithium is the exception to this rule — it has a sufficiently high charge density (due to its tiny ionic radius) to polarise nitrates fully, decomposing them in the same way as group 2 ions, and can also do the same to carbonates.

$$Li_2CO_3 \text{ (s)} \xrightarrow{\text{heat}} Li_2O \text{ (s)} + CO_2 \text{ (g)}$$
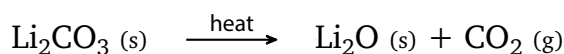
6   Beryllium Being Boneheaded

The majority of the discrepancies with beryllium can be attributed to the highly covalent character of bonds formed with Be, partially due to its high charge density which can polarise the electron cloud of anions.

Compounds with large anions, such as $BeCl_2$, are completely covalent.

6.1   Non-reaction with Water and Oxygen

Similar to magnesium but more extreme, beryllium forms an *impervious* oxide layer when exposed to oxygen — this layer reacts with neither water nor oxygen, leading to beryllium's unreactivity.

6.2   Amphoteric Nature

Beryllium oxides and hydroxides are amphoteric unlike its other group 2 compatriots, due to the partially covalent nature of the bonds with Be.

- Acid: $BeO + 2\,NaOH + H_2O \longrightarrow Na_2[Be(OH)_4]$
- Base: $BeO + H_2SO_4 \longrightarrow BeSO_4 + H_2O$

Note the formation of the $[Be(OH)_4]^{2-}$ complex, which will be discussed below.

6.3   Formation of Be complexes

6.3.1   Hydrated Ions

As will be discussed later, Mg^{2+} has sufficient charge density to form hydrated complex ions in water ($[Mg(H_2O)_6]^{2+}$). Thus, it is clear that Be should form these complexes as well, and it does — $[Be(H_2O)_4]^{2+}$.

However, Be^{2+} is only 4-coordinate, due to the lack of vacant d-orbitals (there is no 2d subshell). By making do with only the 2s and 2p orbitals, it bonds with 4 ligands. By contrast Mg^{2+} has a 3d subshell, allowing for up to 6 ligands.

6.3.2 Other Complexes

While Be^{2+} can form complexes, Be can also form complexes when bonded with other atoms, since it still has 2 vacant p-orbitals that can be used to bond with ligands.

Examples include the formation of $[Be(OH)_4]^{2-}$ when $Be(OH)_2$ is exposed to more OH^-, and the formation of $[BeF_4]^{2-}$:

$$Be(OH)_{2\ (aq)} + 2\,OH^-_{\ (aq)} \longrightarrow [Be(OH)_4]^{2-}_{\ (aq)}$$

$$BeF_{2\ (aq)} + 2\,F^-_{\ (aq)} \longrightarrow [BeF_4]^{2-}_{\ (aq)}$$
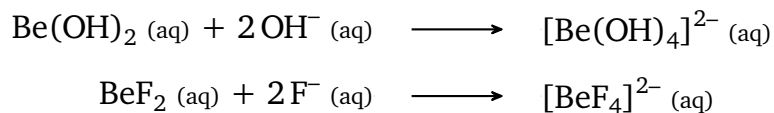
A point to note is that $[Be(OH)_4]^{2-}$ is created from $Be(OH)_2$, which is itself formed from the hydrolysis of a beryllium salt in water (since BeO does not react with water).

On adding a base (aka OH^-), the hydrated $[Be(H_2O)_4]^{2+}$ complex acts as an acid, forming $[Be(OH)_4]^{2-}$ by losing 4 H^+ ions.

6.4 Acidity of Beryllium Salts

Similar to other cations of high charge density like Al^{3+}, Fe^{3+} and Cr^{3+} (and to a certain extent Mg^{2+}), Be^{2+} forms a hydrated complex in water, $[Be(H_2O)_4]^{2+}$, which was seen above.

Just like the other complexes, it can hydrolyse to give H_3O+, making it acidic in water.

$$[Be(H_2O)_4]^{2+} + H_2O \longrightarrow [Be(H_2O)_3(OH)]^+ + H_3O^+$$
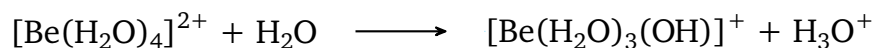
$[Be(H_2O)_3(OH)]^+$ can undergo further hydrolysis three more times, to finally form $[Be(OH)_4]^{2-}$. This enables beryllium to react with bases, and hence be amphoteric.

Group 7

1 Overview

Group 7 elements are also known as *halogens*, and are the most reactive group of non-metals. They are reactive to the point of rarely occurring as free elements (Cl_2, F_2) in nature.

2 Physical Properties

2.1 Electronic Configuration

Halogens have a $n\text{p}^5$ valence shell, and so tend to form X^- ions.

F: $1\text{s}^2 2\text{s}^2 2\text{p}^5$
C*l*: $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^5$
Br: $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 4\text{s}^2 4\text{p}^5$
I: $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^{10} 4\text{s}^2 4\text{p}^6 5\text{s}^2 5\text{p}^5$

2.2 Various Radii

All the halogens exist as diatomic molecules with a covalent bond between the two atoms. Both the ionic radii, and the covalent radii (defined as half the distance between two atomic centres), increase down the group as expected.

The ionic radius for any halogen is always greater than its corresponding covalent radius, since the anion has one more electron, leading to greater interelectronic repulsion and hence a larger radius.

2.3 First Ionisation Energy

As expected, the ionisation energies decrease down the group, due to the increased shielding effect caused by the addition of electron shells.

2.4   First Electron Affinity

Recall that the first electron affinity is the enthalpy change created by adding one mole of electrons to one mole of gaseous atoms of a given element. This is of particular interest for halogens since they tend to ionise to X^- forms.

Element	First EA / $kJ\,mol^{-1}$
F	-328
Cl	-349
Br	-325
I	-295

The trend is that electron affinity decreases down the group (becomes less exothermic), since the electrostatic attraction between the joining electron and the nucleus decreases with increasing atomic radius.

The anomaly for fluorine is due to its small size and electron lone pairs — it takes slightly more energy to fit a new electron into the already crowded area around the fluorine atom.

2.5   Bond Energy

Generally speaking, the bond energies of the halogens decrease down the group as the atomic radii increase. The orbital overlap thus decreases, which lengthens the covalent bond and hence weakens it.

Element	bond energy / $kJ\,mol^{-1}$
F	159
Cl	242
Br	193
I	151

The discrepancy in the $F-F$ bond energy is due to the small atomic radius (and hence bond length) of the F atom, which leads to abnormally-high levels of electrostatic repulsion between its lone pairs.

2.6   Electronegativity

Electronegativity decreases down the group; fluorine is the most electronegative element, and iodine is the least electronegative in the group.

The decrease in electronegativity is explained by the increasing atomic distnace which reduces the electrostatic force attracting valence electrons to the nucleus.

2.7   Melting and Boiling Points

The melting and boiling points of the halogens are largely determined by their atomic size, and hence number of electrons. Since they exist as covalent diatomic molecules, the only intermolecular attractions are instantaneous dipole – induced dipole interactions.; as the number of electrons increase, so do the strength of the id-id interactions, leading to higher melting and boiling points.

All that is to say that melting and boiling points increase down the group; F_2 and Cl_2 are gases at room temperature, Br_2 is a liquid, and I_2 is a solid.

2.8   Colours

Generally speaking the colours of the halogens increase in intensity down the group:

Element	Gaseous	Liquid/Solid	Aqueous	Non-polar
F	pale yellow	-	- boom -	very pale yellow
Cl	yellow-green	-	pale yellow	very pale green
Br	reddish-brown	reddish-brown	yellow	orange
I	dark purple	shiny black	brown	violet

Note that colour intensity increases with concentration as well.

2.9   Solubility

2.9.1   Polar Solvents (Water)

Generally, all the halogens except fluorine dissolve in water to *some* extent. Fluorine reacts explosively due to its high reduction potential, and oxidises water.

Chlorine and bromine react to form a number of ionic products in water in a disproportionation equilibrium, which will be discussed later. Iodine neither dissolves in water nor disproportionates (due to its low reduction potential), but can form a *brown* soluble complex I_3^- in the presence of I^- ions:

$$I_{2\ (s)} + I^-_{\ (aq)} \rightleftharpoons I^-_{3\ (aq)}$$
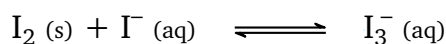
2.9.2   Non-polar Solvents

The solubility of the halogens in non-polar solvents is simply a function of their polarisability, and as with their melting and boiling points, increases down the group.

3 Chemical Properties of the Elements

3.1 Oxidation State

The most stable oxidation state for the halogens is of course -1, due to having a filled valence shell. However, chlorine, bromine and iodine can often be found in positive oxidation states, particularly when bonded to oxygen or other halogens.

The primary reason for this behaviour is the fact that halogens other than fluorine are no longer the most electronegative, so more electronegative elements like oxygen can attract electrons away from the halogen atom. Examples include ClF, ClO^-, and ClO_2^-.

3.2 Oxidising Power

As explained above, the electronegativities of the elements decrease down the group, and since they describe basically the same fundamental electron behaviour, it is no surprise that the reduction potentials decrease down the group as well.

Reaction	$E^{\ominus}/V$
$F_2 + 2\,e^- \longrightarrow 2\,F^-$	+2.80
$Cl_2 + 2\,e^- \longrightarrow 2\,Cl^-$	+1.36
$Br_2 + 2\,e^- \longrightarrow 2\,Br^-$	+1.07
$I_2 + 2\,e^- \longrightarrow 2\,I^-$	+0.54

This means that oxidising power decreases down the group as well.

3.3 Halogen Displacement

A halogen that is more reactive (ie. has a higher reduction potential) can oxidise a less reactive halogen and itself get reduced, thereby *displacing* the less reactive halogen.

For example, with Cl_2 displacing Br^-:

$$Cl_{2\,(g)} + 2\,e^- \longrightarrow 2\,Cl^- \qquad E^{\ominus} = +1.36\,V$$

$$2\,Br^-_{\,(aq)} \longrightarrow Br_{2\,(l)} + 2\,e^- \qquad E^{\ominus}_{ox} = -1.07\,V$$
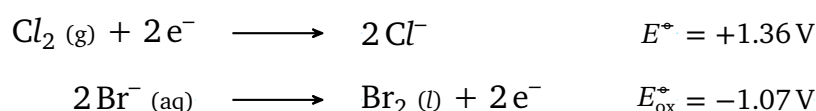
Since the $E^{\ominus}_{cell}$ value $(1.36\,V + (-1.07\,V) = +0.29\,V)$ is positive, the reaction is feasible. Naturally were the conditions reversed, nothing would happen; bromine would not displace chloride.

3.4 Reaction with Water

Fluorine reacts with water to form hydrogen fluoride and a mixture of oxygen and ozone, explosively — even when cold.

$$2\,F_2\text{ (g)} + 2\,H_2O\text{ (l)} \longrightarrow 4\,HF\text{ (aq)} + O_2\text{ (g)}$$

$$3\,F_2\text{ (g)} + 3\,H_2O\text{ (l)} \longrightarrow 6\,HF\text{ (aq)} + O_3\text{ (g)}$$
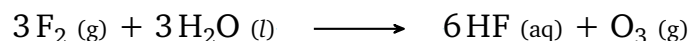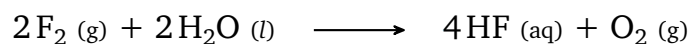
Chlorine and bromine, on the other hand, undergo a disproportionation reaction in water, in an equilibrium reaction:

$$Cl_2\text{ (g)} + H_2O\text{ (l)} \rightleftharpoons HCl\text{ (aq)} + HOCl\text{ (aq)}$$

$$Br_2\text{ (g)} + H_2O\text{ (l)} \rightleftharpoons HBr\text{ (aq)} + HOBr\text{ (aq)}$$
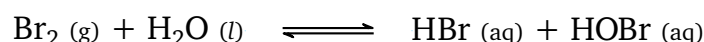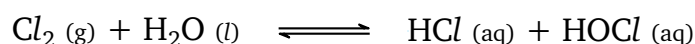
Of note is that HOCl is the primary agent responsible for the bleaching mechanism in chlorine water. Also, the position of equilibrium for bromine's disproportionation is further to the left than chlorine, aka. disproportionation occurs to a *smaller* extent.

Iodine does not react with pure water.

3.5 Reaction with Aqueous Fe^{2+} Ions

A simple calculation of the $E^{\bullet}_{cell}$ values for the reaction would show that only chlorine and bromine are able to oxidise Fe^{2+} (aq) to Fe^{3+} (aq) (producing the relevant colour change). Iodine does not oxidise Fe^{2+}.

Fluorine would first explode, so it cannot react with the *aqueous* solution.

3.6 Reaction with Thiosulphate (S$_2$O$_3^{2-}$) Ions

Thiosulphate ions can be oxidised by chlorine and bromine to give sulphate ions:

$$4\,Cl_2\text{ (aq)} + S_2O_3^{2-}\text{ (aq)} + 5\,H_2O\text{ (aq)} \longrightarrow 8\,Cl^-\text{ (aq)} + 2\,SO_4^{2-}\text{ (aq)} + 10\,OH^-\text{ (aq)}$$

$$4\,Br_2\text{ (aq)} + S_2O_3^{2-}\text{ (aq)} + 5\,H_2O\text{ (aq)} \longrightarrow 8\,Br^-\text{ (aq)} + 2\,SO_4^{2-}\text{ (aq)} + 10\,OH^-\text{ (aq)}$$
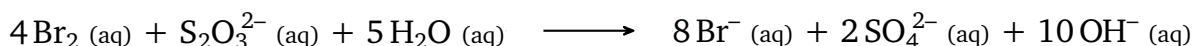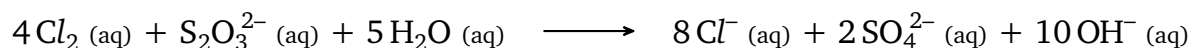
Above, sulphur is oxidised from a +2 oxidation state in thiosulphate to a +6 state in sulphate. However, iodine, given its weaker oxidation strength, can only oxidise thiosulphate to a +2.5 oxidation state, forming S$_4$O$_6^{2-}$.

$$I_2\text{ (aq)} + 2\,S_2O_3^{2-}\text{ (aq)} \longrightarrow 2\,I^-\text{ (aq)} + S_4O_6^{2-}\text{ (aq)}$$
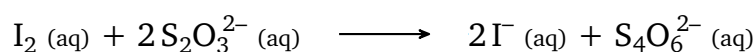
3.7   Disproportionation in Alkaline Solutions

Chlorine and bromine disproportionate readily and non-reversibly in alkaline solutions, to form ions in the +1 and -1 oxidation states:

$$Cl_{2\ (aq)} + 2\,OH^-_{\ (aq)} \longrightarrow Cl^-_{\ (aq)} + ClO^-_{\ (aq)} + H_2O_{\ (l)}$$

$$Br_{2\ (aq)} + 2\,OH^-_{\ (aq)} \longrightarrow Br-_{\ (aq)} + BrO^-_{\ (aq)} + H_2O_{\ (l)}$$

Simultaneously, the hypochlorite and hypobromite ions (ClO^- and BrO^- respectively) themselves undergo a disproportionation reaction to form the halogens in -1 and +5 oxidation states:

$$3\,BrO^- \longrightarrow 2\,Br^- + BrO_3^-$$
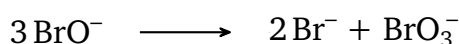
The hypohalite ion is thermally unstable, and decomposes through the secondary disproportionation reaction. Its stability decreases down the group, due to the increased bond length which decreases bond strength. Since the reactions are simultaneous, the proportion each product is dependent on the rate of each reaciton.

For chlorine, the primary reaction is fast below $20\,°C$, while the secondary reaction dominates above $70\,°C$. For bromine, the first reaction is fast fast around $20\,°C$ as well, but the hypobromite ion is already unstable and the secondary reaction dominates; at $0\,°C$, it is slow enough for BrO^- to be the primary product.
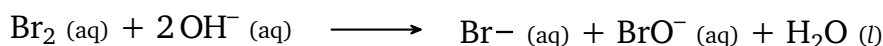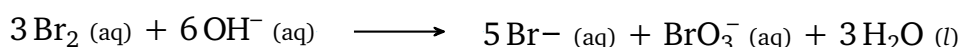
$$3\,Cl_{2\ (aq)} + 6\,OH^-_{\ (aq)} \longrightarrow 5\,Cl^-_{\ (aq)} + ClO_3^-_{\ (aq)} + 3\,H_2O_{\ (l)}$$

$$3\,Br_{2\ (aq)} + 6\,OH^-_{\ (aq)} \longrightarrow 5\,Br-_{\ (aq)} + BrO_3^-_{\ (aq)} + 3\,H_2O_{\ (l)}$$

The overall reaction at high temperatures (respectively for each species)

Note that the hypoiodite ion is thermally unstable enough to spontaneously decompose to directly form the iodate ion at any temperature.

3.8   Reaction with Metals

Given that the halogens are oxidising agents, they can easily oxidise most reactive metals to give ionic compounds. Fluorine exceptionally can react directly with all metals, including traditionally unreactive ones such as gold and silver (with heating); the vigour of the reaction reduces down the group.

3.8.1   Reaction with Sodium

All 4 halogens can react with sodium, which results in the metal burning with a *bright orange* flame, forming a solid ionic salt NaX.

$$X_{2\ (g)} + 2\,Na_{\ (s)} \longrightarrow 2\,NaX_{\ (s)}$$
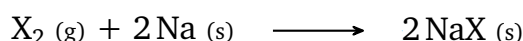
3.8.2 Reaction with Iron

Fluorine, chlorine, and bromine can oxidise iron metal from oxidation state 0 directly to oxidation state +3:

$$3\,X_{2\ (g)} + 2\,Fe_{\ (s)} \longrightarrow 2\,FeX_{3\ (s)}$$

Iodine can only oxidise iron to oxidation state +2:

$$I_{2\ (g)} + Fe_{\ (s)} \longrightarrow FeI_{2\ (s)}$$
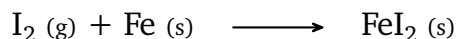
3.9 Reaction with Phosphorus

All of the halogens can react vigorously and irreversibly with solid phosphorus at room temperature to give phosphorus trihalide:

$$3\,X_{2\ (g)} + 2\,P_{\ (s)} \longrightarrow 2\,PX_{3\ (l)}$$
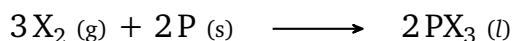
In the case of chlorine and bromine, there exists an equilibrium in excess halogen that results in the formation of PX_5.

$$PX_{3\ (l)} + X_{2\ (g)} \rightleftharpoons PX_{5\ (s)}$$
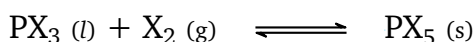
These compounds should be familiar as chlorinating and brominating agents in the nucleophilic substitution of OH groups in organic chemistry.

3.10 Reaction with Hydrogen

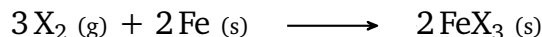The halogens react with hydrogen gas with *decreasing vigour* down the group to form the respective hydrogen halide.

$$X_2 + H_2 \longrightarrow 2\,HX$$
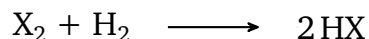
As usual, the reaction with fluorine is explosive even at $-200\,°C$ and in the dark; chlorine reacts explosively in sunlight, and rapidly otherwise. Bromine reacts slowly, and typically requires heating at $300\,°C$ with a Pt catalyst.

Iodine's reaction is reversible and occurs slowly. The reaction is typically incomplete and a mixture of HI and I_2 is obtained; this is due to the positive enthalpy change of formation of HI.

4 Chemical Properties of Hydrogen Halides

4.1 Physical Properties

The hydrogen halides are polar, diatomic molecules. The melting and boiling points generally increase down the group, due to the larger electron cloud, which at larger sizes is the main determinant of the intermolecular attraction force (as opposed to permanent dipole interactions)

Thing	Melting Point / °C	Boiling Point / °C
HF	-80	20
HCl	-115	-85
HBr	-89	-67
HI	-51	-35

The large discrepancy with HF is due to its ability to form *hydrogen bonds*, which are stronger than the pd-pd interactions (and id-id interactions) of the other halogens. Note that HCl is generally unable to form hydrogen bonds (even though it has similar electronegativity to O and N) due to the atomic size of Cl.

4.2 Thermal Stability

The weaker hydrogen halides can be decomposed back into X_2 and H_2 when heated. Naturally the temperature that is required for this decomposition decreases down the group, due to the decreasing strength of the $H-X$ bond. HF and HCl cannot even be decomposed when heated strongly.

- HF and HCl do not decompose
- HBr decomposes on strong heating, yielding reddish-brown fumes of $Br_{2 \; (g)}$
- HI decomposes simply by contact with a hot metal rod, yielding violet fumes of $I_{2 \; (g)}$.

4.3 Acid Strength

HCl, HBr and HI are strong acids that dissociate fully in water to give $H^+_{\; (aq)}$ ions.

The acid strength *increases* down the group, since the $H-X$ bond becomes weaker, which allows for easier dissociation. However, HF notably behaves as a weak acid due to incomplete dissociation which can be attributed to the high strength of the $H-F$ bond.

At high (approaching 100%) concentrations however, HF undergoes autoionisation and homoassociation to form the strong acid HF_2^-:

$$3\,HF \; \rightleftharpoons \; H_2F^+ + HF_2^-$$
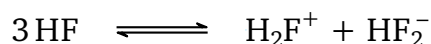
HF_2^- (or FHF^-) is stablised by the strong hydrogen bond between HF and H.

5 Chemical Properties of Halide Ions

5.1 Precipitation Reactions

Silver ions react with halide ions in an equilibrium reaction to form insoluble AgX.

$$Ag^+ \text{ (aq)} + X^- \text{ (aq)} \longrightarrow AgX \text{ (s)}$$

As discussed in previous chapters, the solubility of the AgX salt depends on the concentration of Ag^+ and X^- ions in the solution; recall that ionic product = $[Ag^+][I^-]$. If IP is less than K_{sp}, then the salt will dissolve; otherwise, the salt will precipitate out of the solution.

Upon adding NH_3 (aq), a complex ion is formed with the silver ions.

$$Ag^+ \text{ (aq)} + NH_3 \text{ (aq)} \longrightarrow [Ag(NH_3)_2]^+ \text{ (aq)}$$

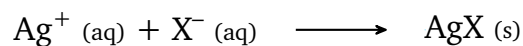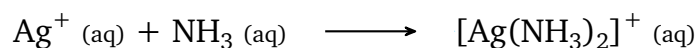The formation of this complex reduces the concentration of Ag^+ in the solution, thus decreasing the value of IP in the original reaction. When the ionic product becomes smaller than K_{sp}, the precipitate will dissolve.

For AgCl, dilute NH_3 (aq) is enough to lower the ionic product below K_{sp}, and allow the salt to dissolve. For AgBr, concentrated NH_3 (aq) must be used to lower the ionic product below the K_{sp} of AgBr.

For AgI, the K_{sp} value is so small that no amount of NH_3 (aq) will lower the concentration of Ag^+ enough for the salt to dissolve.

Ion	Colour of AgX	Required NH_3 (aq)	K_{sp} / $mol^2\,dm^{-6}$
Cl^-	white	dilute	1.6×10^{-10}
Br$^-$	cream	concentrated	7.7×10^{-13}
I$^-$	yellow	nothing works	8.3×10^{-17}

5.2 Reaction with Lead (II) Ions

As you might know, lead halides are insoluble. Only lead iodide (PbI_2) is yellow, while the precipitates of the other halides are white.

$$Pb^{2+}\text{ (aq)} + 2\,X^-\text{ (aq)} \longrightarrow PbX_2\text{ (s)}$$
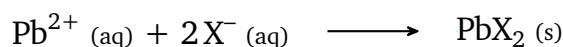
Addition of excess X^- will cause the precipitate to re-dissolve, since the soluble complex ion $[PbX_4]^{2-}$ is formed.

$$Pb^{2+}\text{ (aq)} + 4\,X^-\text{ (aq)} \longrightarrow [PbX_4]^{2-}\text{ (aq)}$$
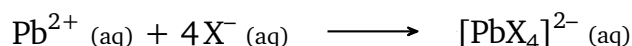
5.3 Reaction with Concentrated H_2SO_4

Generally speaking, X^- ions can act as a Brønsted base, accepting H^+ ions from acids. When concentrated sulphuric acid is added to solid halide salts, this indeed occurs:

$$NaX\text{ (s)} + H_2SO_4\text{ (l)} \longrightarrow HX\text{ (g)} + NaHSO_4\text{ (s)}$$

However, H_2SO_4 is also a strong oxidising agent; thus, it is able to oxidise the HBr and HI formed in the acid-base reaction above. Note that it is insufficiently strong to oxidise HF and HC*l*.
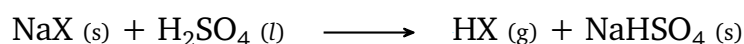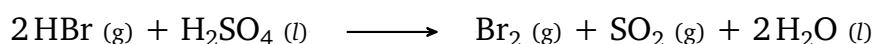
$$NaBr\text{ (s)} + H_2SO_4\text{ (l)} \longrightarrow HBr\text{ (g)} + NaHSO_4\text{ (s)}$$
$$2\,HBr\text{ (g)} + H_2SO_4\text{ (l)} \longrightarrow Br_2\text{ (g)} + SO_2\text{ (g)} + 2\,H_2O\text{ (l)}$$
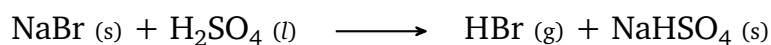
In this reaction, most of the HBr remains unreacted, and some Br_2 (g) is produced, leading to the observation of slight reddish-brown fumes.

Below, H_2SO_4 continues to oxidise HI in a complex and frankly ridiculous manner:

$$NaI\text{ (s)} + H_2SO_4\text{ (l)} \longrightarrow HI\text{ (g)} + NaHSO_4\text{ (s)}$$
$$2\,HI\text{ (g)} + H_2SO_4\text{ (l)} \longrightarrow I_2\text{ (g)} + SO_2\text{ (g)} + 2\,H_2O\text{ (l)}$$
$$6\,HI\text{ (g)} + H_2SO_4\text{ (l)} \longrightarrow 3\,I_2\text{ (g)} + S\text{ (s)} + 4\,H_2O\text{ (l)}$$
$$8\,HI\text{ (g)} + H_2SO_4\text{ (l)} \longrightarrow 4\,I_2\text{ (g)} + H_2S\text{ (g)} + 4\,H_2O\text{ (l)}$$
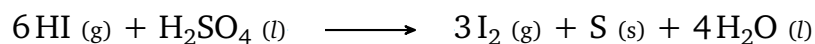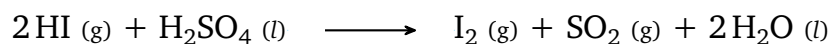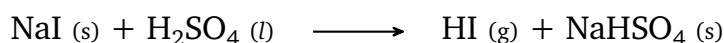
Due to the ease of oxidising HI, H_2SO_4 is itself reduced, with sulphur going from a +6 oxidation state to a -2 state in H_2S (which smells like rotten eggs). Furthermore, SO_2 is also a pungent gas — this is a smelly reaction.

Most of the HI is oxidised, thus there will be a large output of violet fumes, with some white fumes of HI.

5.3.1 Reaction in the Presence of MnO_2

Manganese dioxide is a stronger oxidising agent than H_2SO_4, and thus it can serve to oxidise the HCl that sulphuric acid cannot:

$$NaCl_{(s)} + H_2SO_4{}_{(l)} \longrightarrow HCl_{(g)} + NaHSO_4{}_{(s)}$$

$$4\,HCl_{(g)} + MnO_2{}_{(l)} \longrightarrow Cl_2{}_{(g)} + MnCl_2{}_{(g)} + 2\,H_2O_{(l)}$$
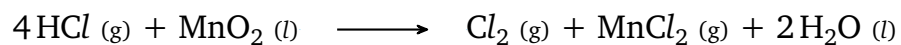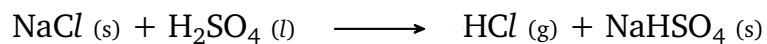
5.3.2 H_3PO_4 as a Weaker Oxidising Agent

Given that sulphuric acid will obliterate HBr and HI, a less powerful oxidising agent can be used to obtain these instead of getting Br_2 and I_2 — concentrated phosphoric acid is such an acid:

$$NaX_{(s)} + H_3PO_4{}_{(l)} \longrightarrow HX_{(g)} + NaH_2PO_4{}_{(s)}$$
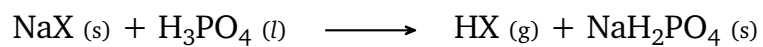
The Third Period

1 Overview

This chapter will examine the 7 elements in the third period; sodium (Na), magnesium (Mg), aluminium (A*l*), silicon (Si), phosphorus (P), sulphur (S), and chlorine (C*l*). Argon is... inert. Mostly.

2 Elemental Reactions

Generally speaking, the reactivity of the elements with both oxygen and chlorine *decrease* across the period. Since reducing power decreases across the period, elements are less likely to be oxidised by oxygen and chlorine.

2.1 Reaction with Oxygen

2.1.1 Sodium

Sodium metal tarnishes rapidly in air, and burns readily with a *bright yellow* flame.

$$2\,\text{Na}_{\text{(s)}} + \tfrac{1}{2}\,\text{O}_2\,_{\text{(g)}} \longrightarrow \text{Na}_2\text{O}_{\text{(s)}}$$
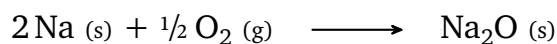
2.1.2 Magnesium

Magnesium metal tarnishes in air, albeit less readily than sodium. It burns very strongly with a *bright white* flame, and its combustion is highly exothermic.

$$\text{Mg}_{\text{(s)}} + \tfrac{1}{2}\,\text{O}_2\,_{\text{(g)}} \longrightarrow \text{MgO}_{\text{(s)}}$$
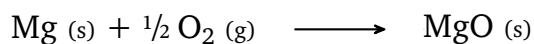
2.1.3 Aluminium

Aluminium metal is readily oxidised by air, and forms a protective layer of aluminium oxide (Al_2O_3) that shields the metal inside from further oxidation.

High temperatures (above 800 °C) are required to fully oxidise aluminium.

$$2\,Al_{\text{ (s)}} + \tfrac{3}{2}\,O_{2\text{ (g)}} \longrightarrow Al_2O_{3\text{ (s)}}$$
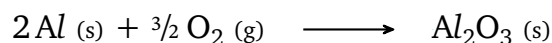
2.1.4 Silicon

Silicon *does not* react with oxygen at room temperature. When strongly heated, some silicon dioxide (SiO_2) can be formed. Silicon is a giant covalent molecule, so large amounts of energy need to be supplied to allow any reaction to take place.

$$Si_{\text{ (s)}} + O_{2\text{ (g)}} \longrightarrow SiO_{2\text{ (s)}}$$
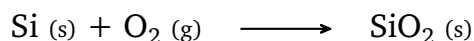
2.1.5 Phosphorus

There are two predominant forms of elemental phosphorus; white phosphorus, which are discrete molecules of P_4, and red phosphorus, which takes a polymeric form.

The former *spontaneously combusts* in air with a bright white flame, due to the strained tetrahedral bonds in the molecule. On the other hand, red phosphorus is more stable, and will burn on heating with a soft orange flame; the products for both forms of phosphorus are identical:

$$P_{4\text{ (s)}} + 3\,O_{2\text{ (g)}} \longrightarrow P_4O_{6\text{ (s)}}$$
$$P_{4\text{ (s)}} + 5\,O_{2\text{ (g)}} \longrightarrow P_4O_{10\text{ (s)}}$$
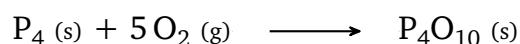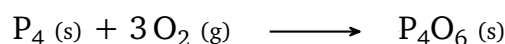
With limited oxygen, the predominant product will be P_4O_6; in excess oxygen, the major product will be P_4O_{10}.

2.1.6 Sulphur

Sulphur is stable at room temperature, and requires some heating to burn — with a pale blue flame:

$$S_{(s)} + O_{2\,(g)} \longrightarrow SO_{2\,(g)}$$
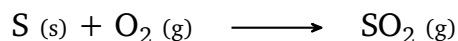
With a catalyst (eg. vanadium oxide V_2O_5), SO_2 can be further oxidised:

$$SO_{2\,(g)} + \tfrac{1}{2}\,O_{2\,(g)} \longrightarrow SO_{3\,(g)}$$
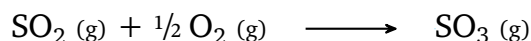
2.1.7 Chlorine

Chlorine rarely reacts directly with oxygen, because it is a stronger oxidising agent than oxygen and hence unlikely to be oxidised.

2.2 Reaction with Chlorine

2.2.1 Sodium

Sodium metal is readily oxidised by chlorine and burns in it, with highly exothermic reaction:

$$2\,Na_{(s)} + Cl_{2\,(g)} \longrightarrow NaCl_{(s)}$$
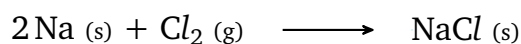
2.2.2 Magnesium

Magnesium's reaction with chlorine is similar to that of sodium:

$$Mg_{(s)} + Cl_{2\,(g)} \longrightarrow NaCl_{(s)}$$
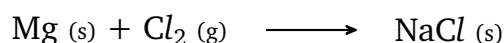
2.2.3 Aluminium

Aluminium does not *quite* react readily with chlorine. The reaction can be sped up by passing *dry* chlorine gas over heated aluminium foil (larger surface area):

$$Al_{(s)} + \tfrac{3}{2}\,Cl_{2\,(g)} \longrightarrow AlCl_{3\,(s)}$$

$AlCl_3$ typically sublimes into the gaseous state.

2.2.4 Silicon

The reaction of silicon with chlorine is even slower than with aluminium, but if heated silicon powder is used, the reaction can be sped up slightly.

$$Si_{(s)} + 2\,Cl_{2\,(g)} \longrightarrow SiCl_{4\,(l)}$$
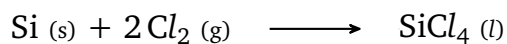
Silicon tetrachloride is a liquid at room temperature.

2.2.5 Phosphorus

White phosphorus (P_4) burns vigorously in chlorine gas to form PCl_3 and PCl_5:

$$P_{4\,(s)} + 6\,Cl_{2\,(g)} \longrightarrow 4\,PCl_{3\,(l)}$$
$$P_{4\,(s)} + 10\,Cl_{2\,(g)} \longrightarrow 4\,PCl_{5\,(s)}$$
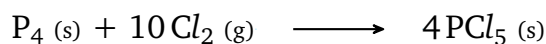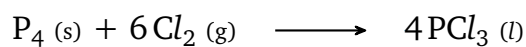
The formation of PCl_5 occurs in an equilibrium, so excess chlorine gas should be used to favour the production of the latter, or limited chlorine to prefer the former:

$$PCl_{3\,(l)} + Cl_{2\,(g)} \rightleftharpoons PCl_{5\,(s)}$$

2.2.6 Sulphur

Heated sulphur can react with chlorine gas:

$$2\,S_{(s)} + Cl_{2\,(g)} \longrightarrow S_2Cl_{2\,(l)}$$
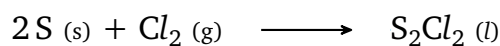
2.3 Reaction with Water

2.3.1 Sodium

Sodium, characteristic of group 1 metals, reacts vigorously even with cold water.

$$2\,\text{Na}_{(s)} + 2\,\text{H}_2\text{O}_{(l)} \longrightarrow 2\,\text{NaOH}_{(aq)} + \text{H}_{2\,(g)}$$
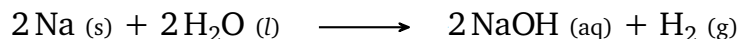
2.3.2 Magnesium

Magnesium reacts slowly with cold water, due to the formation of a mostly-insoluble hydroxide layer around the metal.

$$\text{Mg}_{(s)} + 2\,\text{H}_2\text{O}_{(l)} \longrightarrow \text{Mg(OH)}_{2\,(s)} + \text{H}_{2\,(g)}$$
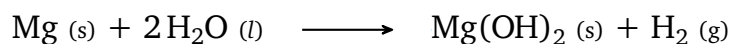
With steam however, magnesium reacts directly to form magnesium oxide:

$$\text{Mg}_{(s)} + \text{H}_2\text{O}_{(g)} \longrightarrow \text{MgO}_{(s)} + \text{H}_{2\,(g)}$$
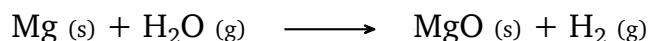
2.3.3 Aluminium

Aluminium does not appear to react with with water, but this is due to the strong and unreactive layer of Al_2O_3 on the surface, which is formed by the fast oxidation of aluminium by oxygen in the air.

If the coating is not present, aluminium will form $Al(\text{OH})_3$ and H_2 as usual.

2.3.4 Silicon

Silicon is fairly unreactive towards water, due to the strong bonds in its giant covalent structure. However, when heated strongly with steam, silicon dioxide can be formed:

$$\text{Si}_{(s)} + 2\,\text{H}_2\text{O}_{(g)} \longrightarrow \text{SiO}_{2\,(s)} + \text{H}_{2\,(g)}$$
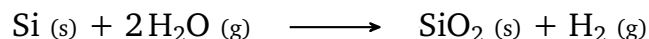
2.3.5 Phosphorus and Sulphur

Neither phosphorus nor sulphur react with water.

2.3.6 Chlorine

Chlorine disproportionates reversibly in water, as covered in the previous chapter on halogens:

$$Cl_{2\,(g)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}Cl_{(aq)} + \text{HO}Cl_{(aq)}$$
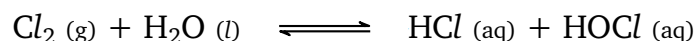
3 Properties of the Oxides

In general, the acidities of the oxides increase across the period. Sodium and magnesium oxide are basic, aluminium oxide is amphoteric, and the other oxides are acidic. This is due to the decreasing ionic character, or conversely, the increasing covalent character in the bonding of the oxides.

The sections below will also cover the reactions of the hydroxides when appropriate.

3.1 Bonding, Structure, and Melting Points

Across the period, the bonding in the oxides moves from ionic to covalent. This is due to the decreasing difference in electronegativity between the element and oxygen; thus it is less likely to *completely lose* electrons, and hence covalent bonds become prevalent.

The change in bonding naturally creates a change in structure, from ionic lattices to discrete covalent molecules. Hence, this also causes a general decrease in melting points across the period.

Thing	Structure	Melting Point / °C
Na_2O	ionic	1130
MgO	ionic	2850
Al_2O_3	ionic	2070
SiO_2	giant covalent	1700
P_4O_6	covalent	24
P_4O_{10}	covalent	360 (sublimes)
SO_2	covalent	-75
SO_3	covalent	17

The melting point of MgO is much larger than that of Na_2O due to the much higher charge density of Mg^{2+}, which greatly increases the lattice energy of MgO.

However, the *even higher* charge density of Al^{3+} instead serves to *polarise* the O^{2-} ion, resulting in some *covalent character*, hence *reducing* the lattice energy of Al_2O_3.

The reason for the high melting point of silicon dioxide is simply due to its giant covalent structure.

3.2   Sodium Oxide

Sodium oxide dissolves completely in water to give OH⁻ ions, and as such a it will give a pH of around 13. This reaction is vigorous and exothermic, occurring even with cold water.

Sodium oxide also reacts directly with acids, to give an aqueous salt solution.

$$Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2\,Na^+_{(aq)} + 2\,OH^-_{(aq)}$$

$$Na_2O_{(s)} + 2\,H^+_{(aq)} \longrightarrow 2\,Na^+_{(aq)} + H_2O_{(l)}$$
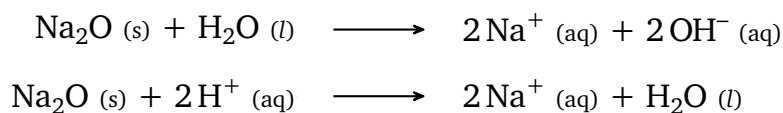
3.3   Magnesium Oxide

Magnesium oxide dissolves much less readily in water, and reacts *very slowly*. This is due to the high lattice energy of MgO, which naturally needs a lot of energy to break to create ions.

Furthermore, whatever pithy amounts of $Mg(OH)_2$ formed *barely* dissociates to give OH⁻ ions, and so the reaction mixture is a mostly solid lump with a slightly-higher-than-neutral pH of around 9. This is due to the similarly high lattice energy of $Mg(OH)_2$.

$$MgO_{(s)} + H_2O_{(l)} \longrightarrow Mg(OH)_{2\,(s)}$$

$$Mg(OH)_{2\,(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2\,OH^-_{(aq)}$$

On the other hand, both MgO and $Mg(OH)_2$ can react directly with acids to form aqueous salt solutions:

$$MgO_{(s)} + 2\,H^+_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + H_2O_{(l)}$$

$$Mg(OH)_{2\,(s)} + 2\,H^+_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + 2\,H_2O_{(l)}$$
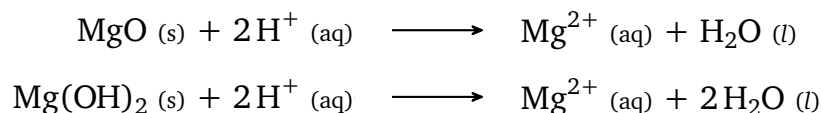
3.4 Aluminium Oxide

Aluminium oxide, Al_2O_3, is partially covalent, due to the polarising power of the Al^{3+} ion. Thus, the combination of ionic and covalent characters allows Al_2O_3, as well as $Al(OH)_3$, to be amphoteric; ie. they react with both acids and bases.

Due to the high lattice energy of both Al_2O_3 and $Al(OH)_3$, they are insoluble in water. However, they both react with acids to form an aqueous salt solution containing Al^{3+} ions:

$$Al_2O_{3\ (s)} + 6\,H^+_{\ (aq)} \longrightarrow Al^{3+}_{\ (aq)} + 3\,H_2O_{\ (l)}$$

$$Al(OH)_{3\ (s)} + 3\,H^+_{\ (aq)} \longrightarrow Al^{3+}_{\ (aq)} + 3\,H_2O_{\ (l)}$$
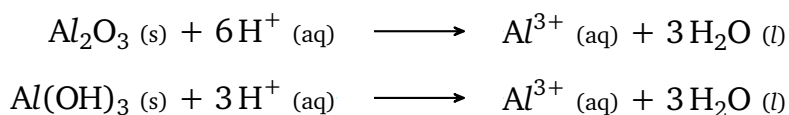
They can react with strong bases as well, to form *aluminate complex ions*, $[Al(OH)_4]^-$:

$$Al_2O_{3\ (s)} + 2\,OH^-_{\ (aq)} \longrightarrow 2\,[Al(OH)_4]^-_{\ (aq)}$$

$$Al(OH)_{3\ (s)} + OH^-_{\ (aq)} + 3\,H_2O_{\ (l)} \longrightarrow [Al(OH)_4]^-_{\ (aq)}$$
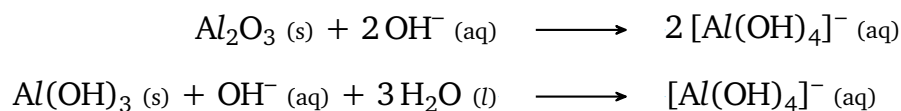
3.5 Silicon Dioxide

Silicon dioxide neither reacts with nor dissolves in water, due to the strong covalent bonds between the Si and O atoms. In fact, it does not succumb even when heated with aqueous bases. For any reaction to take place, there must be strong heating with concentrated bases, eg. NaOH.

$$SiO_{2\ (s)} + 2\,OH^-_{\ (l)} \longrightarrow SiO_3^{2-}_{\ (aq)} + H_2O_{\ (l)}$$
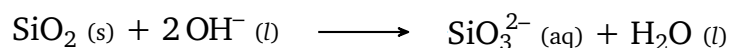
When it does react, a silicate ion is formed.

3.6   Phosphorus Oxides

Both forms of phosphorus oxide, P_4O_6 and P_4O_{10}, react with water to give acidic solutions. Both react with cold water, although the reaction of P_4O_{10} is a lot more violent than that for P_4O_6.

$$H_3PO_3 \qquad\qquad\qquad\qquad H_3PO_4$$

H_3PO_3 and H_3PO_4 are both weak acids. H_3PO_3 is a diprotic acid, and its pK_a values are 1.1 and 6.7; H_3PO_4 is a triprotic acid, with pK_a values of 2.15, 7.20, and 12.32. Note that the third hydrogen in H_3PO_3 isn't attached to anything electronegative, so it does not dissociate.

$$P_4O_6 \text{ (s)} + 6\,H_2O \text{ (l)} \longrightarrow 4\,H_3PO_3 \text{ (aq)}$$

$$H_3PO_3 \text{ (aq)} \rightleftharpoons H_2PO_3^- \text{ (aq)} + H^+ \text{ (aq)}$$

$$H_2PO_3^- \rightleftharpoons HPO_3^{2-} \text{ (aq)} + H^+ \text{ (aq)}$$

$$P_4O_{10} \text{ (s)} + 6\,H_2O \text{ (l)} \longrightarrow 4\,H_3PO_4 \text{ (aq)}$$

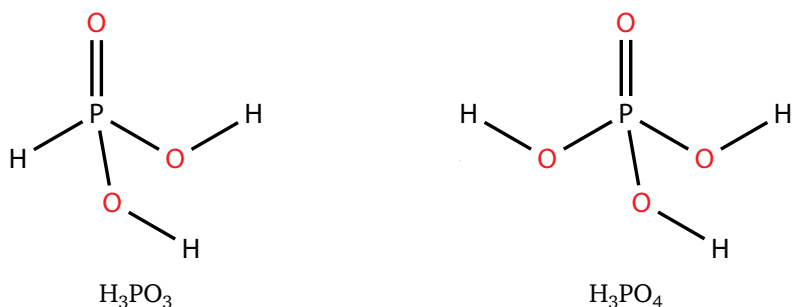$$H_3PO_4 \text{ (aq)} \rightleftharpoons H_2PO_4^- \text{ (aq)} + H^+ \text{ (aq)}$$

$$H_2PO_4^- \text{ (aq)} \rightleftharpoons HPO_4^{2-} + H^+ \text{ (aq)}$$

$$HPO_4^{2-} \text{ (aq)} \rightleftharpoons PO_4^{3-} \text{ (aq)} + H^+ \text{ (aq)}$$
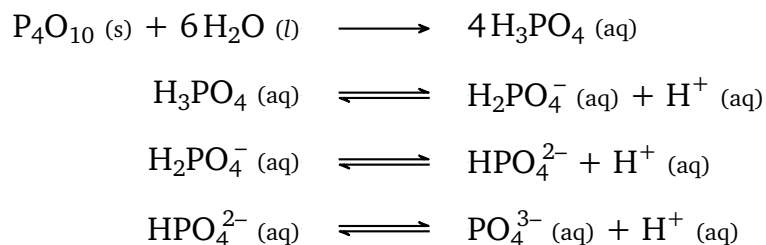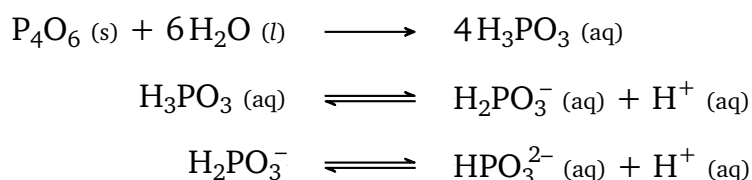
Both P_4O_6 and P_4O_{10} can react directly with bases to give a salt solution, containing anions of the fully deprotonated acids (HPO_3^{2-} and PO_4^{3-} respectively):

$$P_4O_6 \text{ (s)} + 8\,OH^- \text{ (aq)} \longrightarrow 4\,HPO_4^{2-} \text{ (aq)} + 2\,H_2O \text{ (l)}$$

$$P_4O_{10} \text{ (s)} + 12\,OH^- \text{ (aq)} \longrightarrow 4\,PO_4^{3-} \text{ (aq)} + 6\,H_2O \text{ (l)}$$
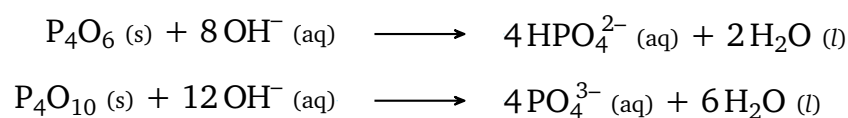
3.7 Sulphur Oxides

3.7.1 Sulphur Dioxide (SO_2)

Sulphur dioxide is mostly soluble in water, giving a solution of the weak diprotic sulphurous acid, H_2SO_3. It has a pK_a value of around 1.8, so it is slightly stronger than H_3PO_3 and H_3PO_4.

Sulphurous acid, H_2SO_3

$$SO_{2\ (g)} + H_2O_{\ (l)} \longrightarrow H_2SO_{3\ (aq)}$$

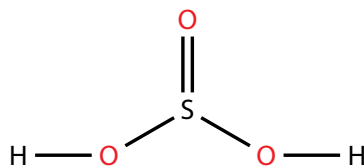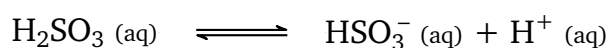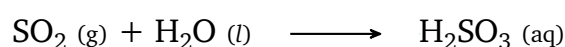$$H_2SO_{3\ (aq)} \rightleftharpoons HSO_3^-{}_{\ (aq)} + H^+{}_{\ (aq)}$$

$$HSO_3^- \rightleftharpoons SO_3^{2-}{}_{\ (aq)} + H^+{}_{\ (aq)}$$

$SO_{2\ (g)}$ can react directly with bases to form a salt solution containing the sulphite ion, SO_3^{2-}, which is the fully deprotonated version of the acid.

$$SO_{2\ (g)} + 2\,OH^-{}_{\ (l)} \longrightarrow SO_3^{2-}{}_{\ (aq)} + H_2O_{\ (l)}$$
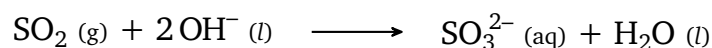
3.7.2 Sulphur Trioxide (SO_3)

Sulphur trioxide, on the other hand, reacts violently with water, producing a mist of H_2SO_4 droplets.
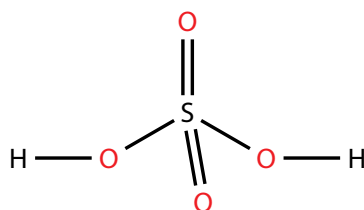
Sulphuric acid, H_2SO_4

Sulphuric acid is the strong acid that we know and love; $SO_{3\ (g)}$ can also react directly with bases to form an aqueous salt solution with sulphate ions.

$$SO_{3\ (g)} + 2\,OH^-{}_{\ (l)} \longrightarrow SO_4^{2-}{}_{\ (aq)} + H_2O_{\ (l)}$$
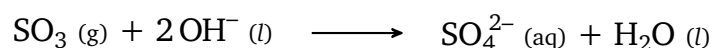
It should be noted that while the first proton of H_2SO_4 is a undoubtedly a strong acid with a pK_a of -3, the second proton (from HSO_4^-) has a pK_a of only 1.99, which is technically a weak acid. In most cases however, H_2SO_4 will still fully deprotonate to give the sulphate ion.

4 Properties of the Chlorides

4.1 Bonding, Structure, and Melting Points

The trend for the chlorides is mostly identical to that for the oxides; bonding moves from ionic to covalent due to decreasing electronegativity difference between the element and chlorine, causing a shift from ionic solids to discrete covalent molecules.

Thing	Structure	Melting Point / °C	Boiling Point / °C
$NaCl$	ionic	801	1413
$MgCl_2$	ionic	714	1412
$AlCl_3$	discrete covalent	—	180 (sublimes)
$SiCl_4$	discrete covalent	-70	58
PCl_3	discrete covalent	-112	76
PCl_5	discrete covalent	—	160 (sublimes)
SO_2	discrete covalent	-72	-10
SO_3	discrete covalent	16.9	45

4.1.1 Aluminium Chloride

In the solid state (at room temperature), it is a very pale solid, and exists as an ionic lattice with a *very high* degree of covalent character.

However, at around 180 °C, the heat causes the ionic lattice to expand, dissolving the ionic character of the compound. Thus, $AlCl_3$ sublimes immediately into a gas, since the electrostatic forces have now disappeared, leaving only id-id interactions for intermolecular bonding.

A caveat, however, is that the Al atom in $AlCl_3$ is *electron deficient*, having only 3 electron pairs. Thus, it tends to form dative bonds with another molecule of $AlCl_3$, creating a dimer of Al_2Cl_6.
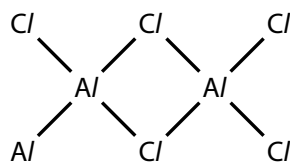
The dimer Al_2Cl_6.

$AlCl_3$ and Al_2Cl_6 actually exist in an equilibrium:

$$2\,AlCl_3 \text{ (g)} \quad \rightleftharpoons \quad Al_2Cl_6 \text{ (g)}$$
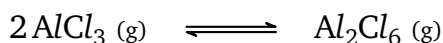
At higher temperatures, the equilibrium shifts to the left, and $AlCl_3$ exists predominantly as discrete molecules, with no dimerisation.

4.2 Sodium Chloride

Sodium chloride, $NaCl$, should be familiar; it unremarkably dissolves in water to give Na^+ (aq) and Cl^- (aq) ions:

$$NaCl \text{ (s)} \xrightarrow{\text{water}} Na^+ \text{ (aq)} + Cl^- \text{ (aq)}$$

The pH of the solution is 7 — neutral.

4.3 Magnesium Chloride

Magnesium chloride, $MgCl_2$, dissolves in water as well to give Mg^{2+} (aq) and Cl^- (aq) ions. Note that because of magnesium's somewhat high charge density, it forms a hydrated aqua complex in water:

$$MgCl_2 \text{ (s)} + 6\,H_2O \text{ (l)} \longrightarrow [Mg(H_2O)_6]^{2+} \text{ (aq)} + 2\,Cl^- \text{ (aq)}$$
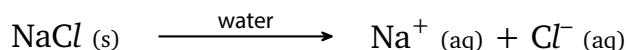
In a mechanism similar to that of the hydrolysis of aqua complex ions of metals with high charge density, magnesium is strong enough to polarise the $O-H$ bond slightly, forming a slightly acidic solution:

$$[Mg(H_2O)_6]^{2+} \text{ (aq)} + H_2O \quad \rightleftharpoons \quad [Mg(H_2O)_5OH]^+ \text{ (aq)} + H_3O^+ \text{ (aq)}$$

Note that the polarising power is much weaker than, for instance, Al^{3+} or Cr^{3+}, so the pH of such a solution is only around 6.5.

4.4 Aluminium Chloride

The reactions of $AlCl_3$ with water differ mainly based on the amount of water or base used.

4.4.1 Limited Water

When *a few drops* of water are added to $AlCl_3$, white fumes of HCl are formed, leaving behind a white precipitate of $Al(OH)_3$. The aluminium hydroxide formed is insoluble in water.

$$AlCl_3 \text{ (s)} + 3\,H_2O \text{ (l)} \longrightarrow Al(OH)_3 \text{ (s)} + 3\,HCl \text{ (g)}$$
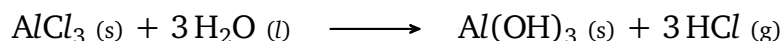
4.4.2 Excess Water

In excess water, $AlCl_3$ instead forms the hydrated aluminium complex ion, and chloride ions:

$$AlCl_3 \text{ (s)} + 6\,H_2O \text{ (l)} \longrightarrow [Al(H_2O)_6]^{3+} \text{ (aq)} + 3\,Cl^- \text{ (aq)}$$

As covered previously, this hydrated aluminium ion can undergo hydrolysis to give an acidic solution:

$$[Al(H_2O)_6]^{3+} \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons [Al(H_2O)_5OH]^{2+} \text{ (aq)} + H_3O^+ \text{ (aq)}$$

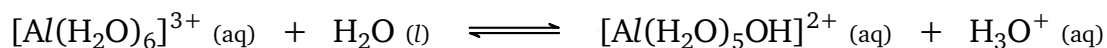The extent of hydrolysis is much greater than for $[Mg(H_2O)_6]^{2+}$, so the pH is typically around 3.

4.4.3 Limited OH$^-$

When a limited amount of base (OH$^-$) is added, $[Al(H_2O)_6]^{3+}$ (aq) behaves as a triprotic acid, being able to release 3 H$^+$ (aq) ions before being depleted and forming a precipitate of $[Al(H_2O)_3(OH)_3]$ (s).

$$[Al(H_2O)_6]^{3+} \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons [Al(H_2O)_5OH]^{2+} \text{ (aq)} + H_3O^+ \text{ (aq)}$$

$$[Al(H_2O)_5OH]^{2+} \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons [Al(H_2O)_4(OH)_2]^+ \text{ (aq)} + H_3O^+ \text{ (aq)}$$

$$[Al(H_2O)_4(OH)_2]^+ \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons [Al(H_2O)_3(OH)_3] \text{ (s)} + H_3O^+ \text{ (aq)}$$
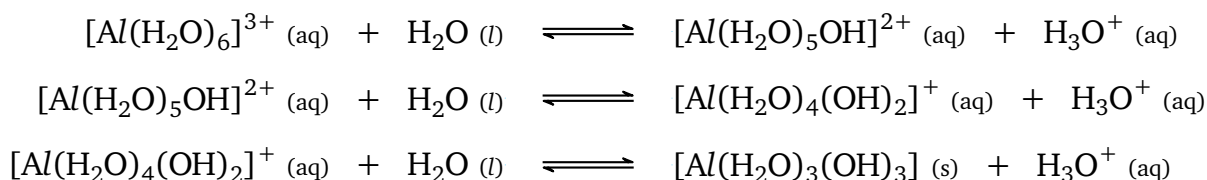
A solution of $[Al(H_2O)_6]^{3+}$ (aq) is usually acidic enough to react with carbonate ions to liberate carbon dioxide gas (which, remember, neither alcohols nor phenols can do), forming the insoluble precipitate.

4.4.4 Excess OH$^-$

When faced with excess amounts of base, the white precipitate of $[Al(H_2O)_3(OH)_3]$ (s) will appear to dissolve, instead forming the aluminate complex ion $[Al(OH)_4]^-$ (aq).

$$[Al(H_2O)_3(OH)_3] \text{ (s)} + OH^- \text{ (aq)} \rightleftharpoons [Al(OH)_4]^- \text{ (aq)} + 3\,H_2O \text{ (l)}$$
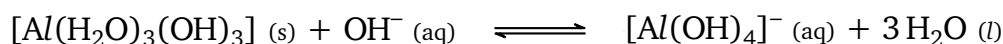
Note that, since this is an equilibrium reaction, the concentration of OH$^-$ must be high enough to move the position of equilibrium to the right, to favour the formation of the soluble aluminate ion.

4.5   Silicon Chloride

Silicon chloride *readily* and *violently* hydrolyses in water completely, forming HCl, which can either effervesce away as gaseous hydrogen chloride, or dissolve in the water to form a strongly acidic solution of pH 1.

$$\text{Si}Cl_4 \text{ (l)} + 2\,\text{H}_2\text{O (l)} \longrightarrow \text{SiO}_2 \cdot 2\,\text{H}_2\text{O (s)} + 4\,\text{H}Cl \text{ (aq)}$$
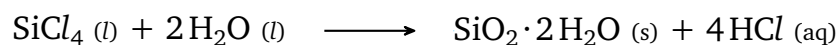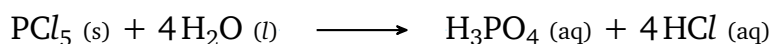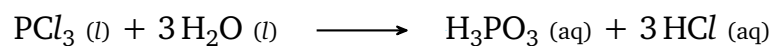
$\text{SiO}_2 \cdot 2\,\text{H}_2\text{O}$ (s) is a hydrated form of silicon dioxide, but it is still in the solid state.

4.6   Phosphorus Chlorides

Both phosphorus chlorides, PCl_3 and PCl_5, completely hydrolyse in water in a similar fashion to silicon chloride, forming HCl and hence a strongly acidic solution.

$$\text{P}Cl_3 \text{ (l)} + 3\,\text{H}_2\text{O (l)} \longrightarrow \text{H}_3\text{PO}_3 \text{ (aq)} + 3\,\text{H}Cl \text{ (aq)}$$

$$\text{P}Cl_5 \text{ (s)} + 4\,\text{H}_2\text{O (l)} \longrightarrow \text{H}_3\text{PO}_4 \text{ (aq)} + 4\,\text{H}Cl \text{ (aq)}$$

Note that, of course, the contributions of H_3PO_3 and H_3PO_4 to the pH of the solution will not be forgotten, but they are quite insignificant in the face of HCl.

Furthermore, on dropwise addition of water with PCl_5, it tends to form POCl_3, phosphorus oxychloride, instead.

$$\text{P}Cl_5 \text{ (s)} + \text{H}_2\text{O (l)} \longrightarrow \text{PO}Cl_3 \text{ (l)} + 2\,\text{H}Cl \text{ (g)}$$
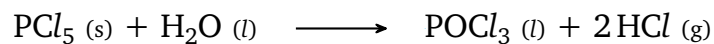
Transition Metals

1 Overview

Transition metals are d-block elements with atoms that have a *partially-filled* d-subshell, or form cations with incomplete d-subshells.
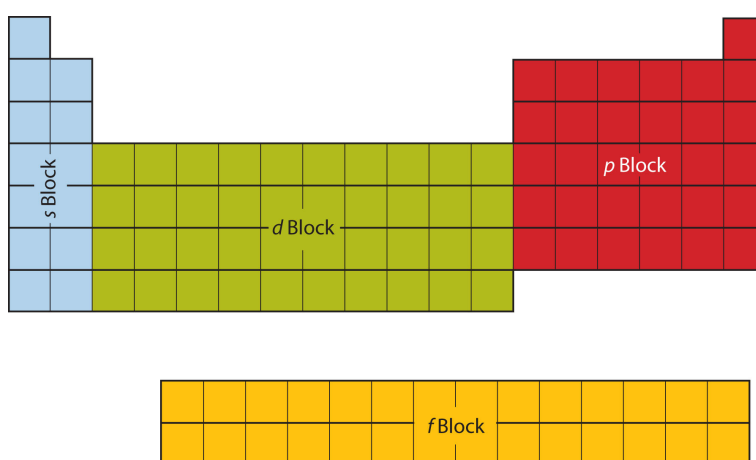
The d-block is in green.

Even though zinc and scandium are in the d-block, they are generally not considered transition metals, and do not exhibit many of the typical properties of transition metals.

1.1 Electronic Configuration

The electronic configurations of the period 4 d-block elements are laid out below. For reference, the electronic configuration of argon is $1s^2 2s^2 2p^6 3s^2 3p^6$.

Moving down the periodic table, most of the "rules" and "trends" that govern electrons start to break down — especially when involving transition metals. It becomes more useful to observe experimental data and come up with explanations, rather than creating predictions and making exceptions.

1.1.1 Atomic Configuration

These are the atomic configurations of the first period of transition metals.

Element	Atomic Configuration
Sc	[Ar] $3d^1 4s^2$
Ti	[Ar] $3d^2 4s^2$
V	[Ar] $3d^3 4s^2$
Cr	[Ar] $3d^5 4s^1$
Mn	[Ar] $3d^5 4s^2$
Fe	[Ar] $3d^6 4s^2$
Co	[Ar] $3d^7 4s^2$
Ni	[Ar] $3d^8 4s^2$
Cu	[Ar] $3d^{10} 4s^1$
Zn	[Ar] $3d^{10} 4s^2$

Notably, Chromium and Copper seem out of place with their $4s^1$ configurations. While the *generally accepted* explanation is that half-full and fully-filled subshells ($3d^5$ and $3d^{10}$ respectively) are more stable, in reality there is no extra stability conferred to this configuration.
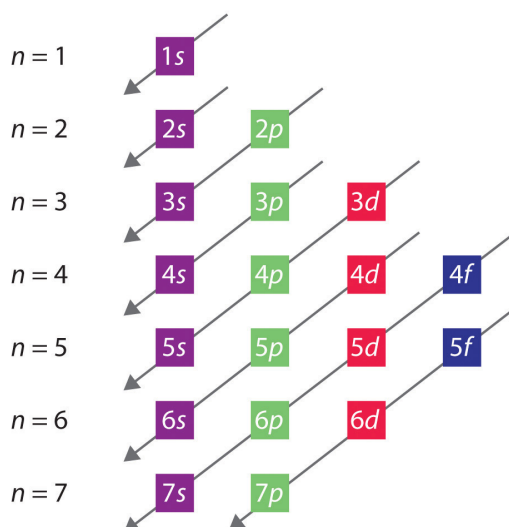
A more complete explanation can be found in the appendix, but the TL;DR is that the *alternative* configurations are less stable (due to a number of factors — electronic repulsion, exchange energy, atomic radius), so the electrons end up in that arrangement.

1.1.2 Ionic Configuration

As previously mentioned, transition metals exist in multiple oxidation states, so it is futile to list them all. However, it is important to note that the 4s electrons are removed first, before the 3d electrons.

Ion	Ionic Configuration
Sc^{3+}	[Ar] $3d^0$
Cr^{3+}	[Ar] $3d^3$
Co^{2+}	[Ar] $3d^7$
Cu^{2+}	[Ar] $3d^9$
Zn^{2+}	[Ar] $3d^{10}$

The electron shells are filled in this order (commonly known as the Madelung rule):

$n = 1$ 1s

$n = 2$ 2s   2p

$n = 3$ 3s   3p   3d

$n = 4$ 4s   4p   4d   4f

$n = 5$ 5s   5p   5d   5f

$n = 6$ 6s   6p   6d

$n = 7$ 7s   7p

However, there is nothing that implies electrons must be removed in the corresponding order (like a stack). It must be noted that the electron state of an Fe^{2+} is not simply that of an Fe^{3+} ion with one extra electron. In the ground state, an empty 4s subshell does have a lower energy than an empty 3d subshell, so the former is filled first, across the period.

However, the subsequent addition of electrons to the 3d subshell lowers its energy below that of the 4s (but it's already full, so it doesn't matter). Thus, when electrons are removed, they are pulled from the higher-energy orbitals — so the 4s subshell is the first to go.

The key appreciation is that the 3d and 4s subshells are very close together in terms of energy levels, such that certain stabilising or destabilising effects can have enough impact to move an electron across a subshell.

2   Physical Properties

2.1   Atomic Radii

Generally speaking, the atomic radii across the transition metals remain relatively constant. Physically, the 4s electrons are the valence electrons; hence, since subsequent electrons are added to the 3d subshell, the increase in the shielding effect somewhat mitigates the increase in nuclear charge.
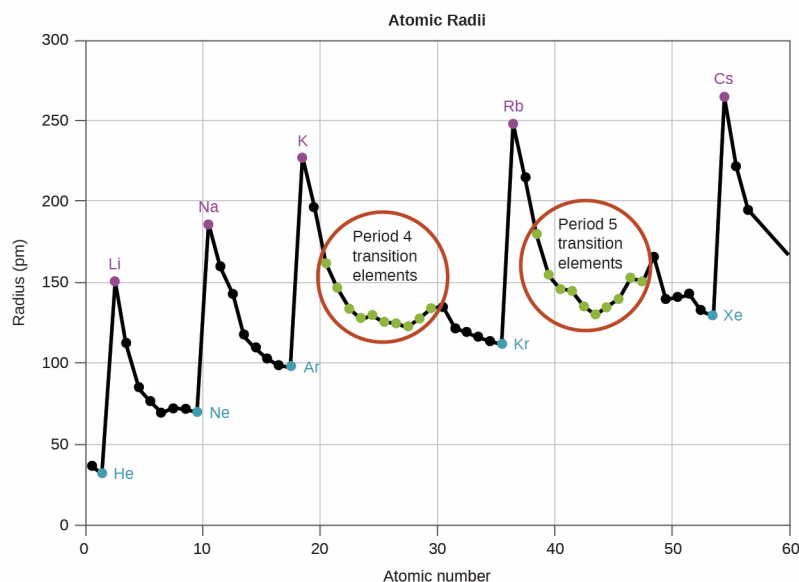
Hence, the atomic radius remains relatively constant across the d-block elements. In comparison with potassium and calcium, the radii of the d-block elements are *much smaller*; this is due to the fact that the shielding effect of the 3d-subshell is quite poor, due to its *diffuse nature*.

The increase in nuclear charge from Ca to Sc without a correspondingly significant change in the shielding effect leads to a sharp decrease in atomic radius, by virtue of being able to attract the valence electrons closer to the nucleus.

## 2.2   Melting and Boiling Points

There is no singular trend, but generally speaking the melting and boiling points for the transition elements are all higher than the s-block metals. This is due to the increased number of electrons available for metallic bonding — transition metals can use both the 3d and 4s electrons, due to the small difference in their energy levels.

From vanadium to manganese however, there is a decrease in melting and boiling points, which is due to the stability of the singly-filled 3d-subshell, which reduces their availability for metallic bonding.

Somewhat similarly, from iron to zinc, the melting and boiling points start to decrease, as paired electrons are again less available for bonding.

2.3 First Ionisation Energy

The trend for the first IE is somewhat similar to the trend for atomic radii. For s- and p-block elements, additional electrons do not contribute significantly to the shielding effect as they are added to the valence shell. Hence, with an increasing nuclear charge, it becomes more difficult to remove a valence electron.
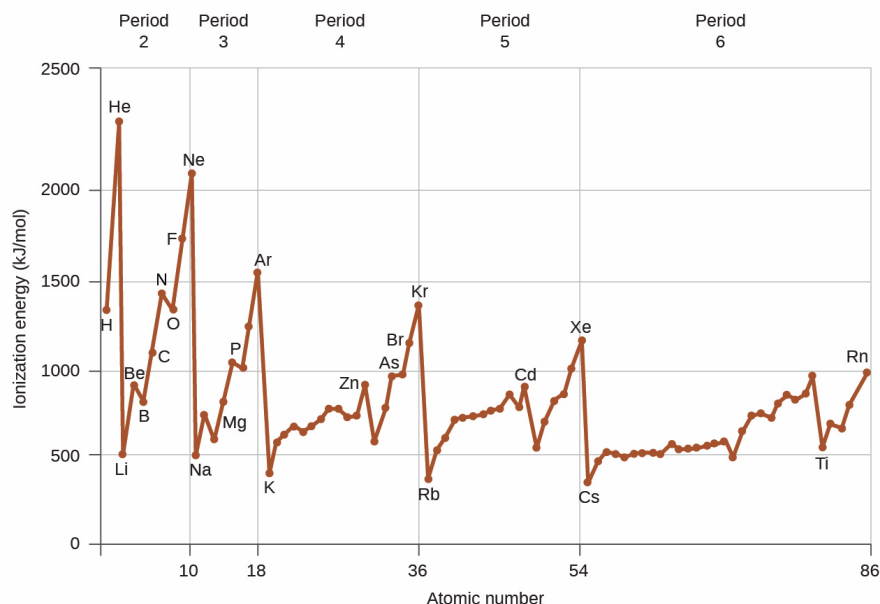
By contrast, electrons are added to the inner 3d-subshell across the transition elements, leading to an increase in the shielding effect. Thus mostly negates the increasing nuclear charge, since the valence electron, which is the one being removed, is in the 4s-subshell.

Hence, first IE increases only *slightly* across the transition metals.

2.4 Other things

Other than the 3 main trends, transition metals are generally denser than s-block metals, mostly due to their increased atomic mass and smaller atomic radii.

Furthermore, they are generally better conductors (lower resistance) due to the larger number of delocalised electrons.

3 Chemical Properties

3.1 Variable Oxidation States

The primary reason for transition metals having variable oxidation states is the relatively small difference in energy levels of the 3d and 4s subshells. Thus, once the 4s electrons are removed, not much more energy is needed to start removing electrons from the 3d subshell.

Conversely, for s-block metals, the next subshell to remove electrons from would be the p-subshell, which is at a far higher energy level, and hence is not easily removed — thus s-block metals tend to only have one oxidation state, the one where all the 4s electrons are removed.

Generally speaking, the 2+ ion is usually more stable than the 3+ ion, due to the need to remove an extra electron. Iron is an exception here, due to the existence of 6 electrons in its 3d subshell, with 1 electron pair and 4 unpaired electrons, which is less stable than having 5 unpaired electrons; hence Fe^{3+} is more stable than Fe^{2+}.

3.1.1 Trends in Oxidation States

Across the period, the number of possible oxidation states increases, and peaks at manganese (having up to +7), before decreasing back to +2 in zinc.

The reason for the first part in the trend is attributable to the increasing number of 3d electrons, all of which can be removed or involved in bonding to increase the oxidation state. Hence, manganese, with 5 electrons in the 3d-subshell and 2 in the 4s-subshell, can have 7 electrons removed, or involved in bonding (typically the latter)

In the second half, electrons in the d-subshell start pairing up, reducing the possible number of electrons that can participate in covalent bonding, hence the number of possible oxidation states decrease.

3.1.2 Bonding in Various Oxidation States

Transition metals at relatively low oxidation states, from +1 to +3, typically exist as ions, and form ionic solids. In this respect they behave like normal s-block metals. For example, $FeCl_3$, $CuSO_4$ have Fe^{3+} and Cu^{2+} ions.

However, at higher oxidation states, it is unstable to have exposed ions with high charge, so the transition metals at such high oxidation states are typically *covalently bonded* (yes, that's right) with oxygen, forming covalent molecules or oxy-anions. Examples include MnO_4^- and $Cr_2O_7^{2-}$.

3.2 Catalytic Properties

3.2.1 Heterogeneous Catalysis

The main reason transition metals are able to act as heterogeneous catalysts is due to the presence of a *partially-filled* d-subshell. This lets them either *accept* or *donate* electron pairs, allowing for the adsorption of reactant molecules.

The detailed mechanism is covered elsewhere, but suffice to say this ability to accept or donate electrons can weaken the bonds in the reactant, lowering the activation energy.
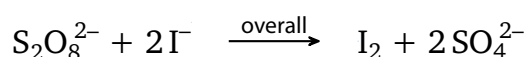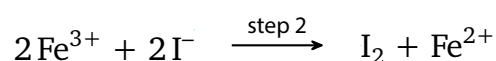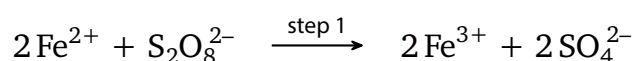
Some examples of heterogeneous catalysts include:

- Finely divided Fe powder, *Haber Process*: $3\,H_2 + N_2 \longrightarrow 2\,NH_3$
- V_2O_5, *Contact Process*: $2\,SO_2 + O_2 \longrightarrow 2\,SO_3$
- Nickel, *Reduction of Alkenes*: $RCH{=}CH_2 + H_2 \longrightarrow RCH_2CH_3$

3.2.2 Homogeneous Catalysis

The ability for transition metals to act as homogeneous catalysts is due to an entirely different reason; it is a result of the ease of converting between different oxidation states. This is often useful when there is a need to react two negatively-charged ions — the transition metal ion can act as an intermediary.

A common example is the oxidation of I^- to I_2 by $S_2O_8^{2-}$.

$$2\,Fe^{2+} + S_2O_8^{2-} \xrightarrow{\text{step 1}} 2\,Fe^{3+} + 2\,SO_4^{2-}$$

$$2\,Fe^{3+} + 2\,I^- \xrightarrow{\text{step 2}} I_2 + Fe^{2+}$$

$$S_2O_8^{2-} + 2\,I^- \xrightarrow{\text{overall}} I_2 + 2\,SO_4^{2-}$$

Here, the Fe^{2+} ion and the $S_2O_8^{2-}$ ion can easily react, because they are oppositely charged. Fe^{2+} is oxidised by the peroxodisulphate ion to Fe^{3+}, forming one of the products, SO_4^{2-}.

The Fe^{3+} produced then proceeds to oxidise the I^- ion, forming the other product, I_2, and regenerating the Fe^{2+} catalyst.

Without the catalyst, the need to react two negatively charged ions directly ($S_2O_8^{2-}$ and I^-) would lead to an abysmal rate of reaction.

Note that the order of the two sub-reactions is irrelevant, so Fe^{3+} can be used as the catalyst as well.

4 Complexes

4.1 Overview

A complex consists of a central metal atom or cation, datively-bonded to surrounding ligands, which are anions or molecules with at least one lone pair.

While all metal cations can form complexes, transition metals form them more readily than other metals. This is due to their relatively higher charge density than s-block metals (smaller atomic radius, with similar or higher nuclear charge), as well as empty orbitals for dative bonding.

Note that aluminium fulfils both of these criteria, and expectedly forms complex ions; $[Al(OH)_4]^-$ and the hydrated ion $[Al(H_2O)_6]^{3+}$ are examples. The Al^{3+} ion has entirely empty 3s-, 3p-, and 3d-subshells, which can accept electron pairs from ligands.

In transition metals as well as aluminium for instance, empty subshells are typically *hybridised* into identical orbitals with the same energy levels; aluminium hybridises the 3s, 3p, and 3d subshells, while transition metals typically can hybridise the 4s, 4p, and 4d subshells as well.
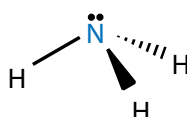
4.2 Ligand Dentateness

While a fair number of ligands are monodentate, ie. they form a single dative bond with the central atom, there are also a number of *polydentate* ligands, forming more than one dative bond.
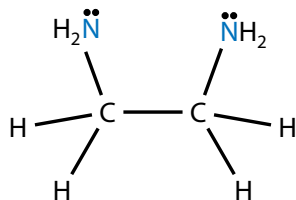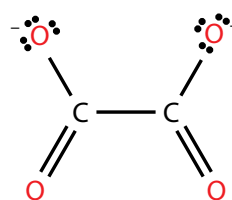
Monodentate Ligands
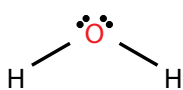
water   cyanide   hydroxide

Bidentate Ligands
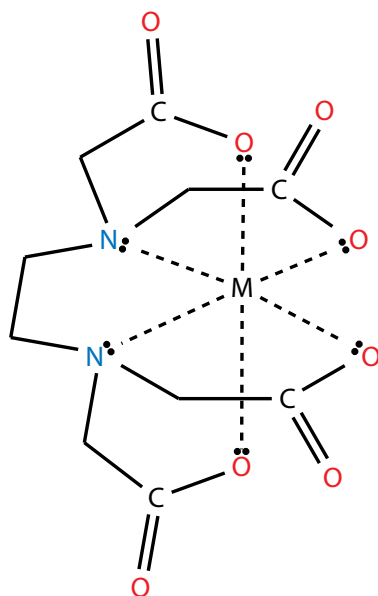

ethane-1,2-diamine (abbrv. en)   ethanedioate

These bidentate ligands form two dative bonds per molecule of ligand.

Hexadentate Ligands

The prime example of a hexdentate ligand is ethylenediaminetetraacetate, otherwise known as EDTA. It is on the cover page.


ethylenediaminetetraacetate (abbrv. EDTA)

4.3 Complex Charges

Ironically it is not very complex to determine the charge of a complex; simply sum the oxidation number of the central metal atom and the ionic charges of the ligands. It is possible to have neutral complexes, either by having balanced charges, or with a neutral metal atom and neutral ligands.

A compound containing a complex ion typically has *counter ions* that serve to balance the charge. In an aqueous solution, the counter ions dissociate from the complex ion as expected. The complex ion is treated as a *single, polyatomic ion*.
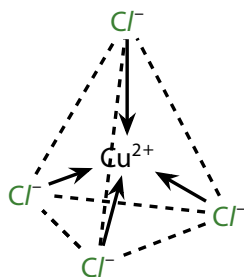
4.4   Coordination Number

The coordination number of a complex determines the number of ligands around the central atom, as well as their arrangement around the central atom, in a manner similar to VSEPR theory.
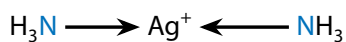
$[Ag(NH_3)_2]^+$, linear, CN: 2
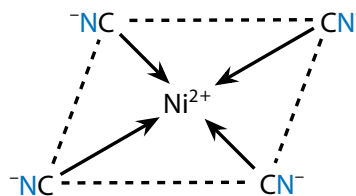
$[Ni(CN)_4]^{2-}$, square planar, CN: 4

$[CuCl_4]^{2-}$, tetrahedral, CN: 4

$[Fe(CN)_6]^{3-}$, square planar, CN: 4
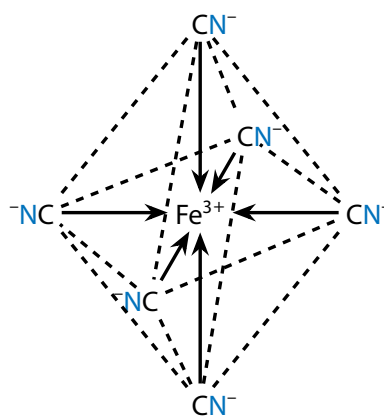
4.5   Hydrated Complex Ions

Otherwise known as aqua complexes, these ions are formed when a transition metal, or any metal with a sufficiently high charge density, is dissolved in water. Essentially these are complexes where the water molecules act as ligands. This is because transition metal cations have high charge density and thus polarising power, preferring the formation of covalent bonds as opposed to ionic interactions.

By contrast, most s-block metals (eg. sodium) do not form hydrated complexes, only ion-dipole interactions.

4.5.1 Hydrolysis of Hydrated Complexes

As discussed to death in previous sections, these hydrated complex ions are able to hydrolyse in water to some extent, producing H_3O^+ (aq) ions that make the solution acidic.

This ability is due to the high polarising power of the central cation, which can polarise and weaken $O-H$ bonds in the water ligand, eventually allowing another water molecule to attack the weakly-attached H atom, forming H_3O^+.

$$[Fe(H_2O)_6]^{3+} \text{ (aq)} \ + \ H_2O \text{ (l)} \ \rightleftharpoons \ [Fe(H_2O)_5OH]^{2+} \text{ (aq)} \ + \ H_3O^+ \text{ (aq)}$$

$$[Cr(H_2O)_6]^{3+} \text{ (aq)} \ + \ H_2O \text{ (l)} \ \rightleftharpoons \ [Cr(H_2O)_5OH]^{2+} \text{ (aq)} \ + \ H_3O^+ \text{ (aq)}$$
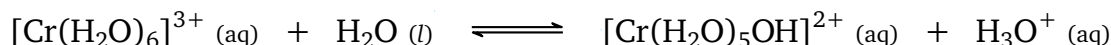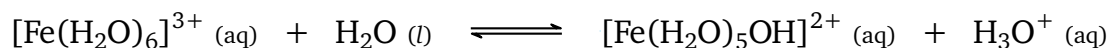
4.5.2 Cations with High Oxidation States

Transition metal cations with very high oxidation states, typically above $+3$, do not form hydrated complex ions. This is due to the extreme polarising power of the ion, which instead completely breaks the $O-H$ bonds, favouring the formation of oxy-anions.

As an example, aqueous chromium ions in the $+6$ oxidation state *do not* exist as $[Cr(H_2O)_6]^{6+}$. Instead, it forms CrO_4^{2-} and $Cr_2O_7^{2-}$, chromate and dichromate, which exist in an equilibrium.

$$2\,CrO_4^{2-} \text{ (aq)} + 2\,H^+ \text{ (aq)} \ \rightleftharpoons \ Cr_2O_7^{2-} \text{ (aq)} + H_2O \text{ (l)}$$
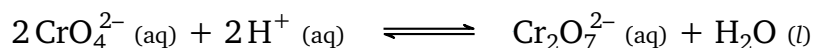
In acidic conditions, $[H^+]$ is high, so by Le Châtelier's Principle, the position of equilibrium moves to the right, favouring the production of orange dichromate. Conversely in an alkaline medium, the position of equilibrium moves to the left to favour yellow chromate.

<h1>4.6   Ligand Exchange</h1>

Ligand exchange reactions are simply reactions where one or more of the ligands of a complex are replaced by other ligands. That is all. The new complex can often have different properties, including reduction potential and colour.

<h2>4.6.1   Stability Constant, K_{stab}</h2>

K_{stab} is essentially another form of K_c for complex ions. For example, $[Cu(H_2O)_6]^{2+}$ were to replace its H_2O ligands with Cl^- ligands:

$$[Cu(H_2O)_6]^{2+} \text{ (aq)} + 4\,Cl^- \text{ (aq)} \rightleftharpoons [CuCl_4]^{2-} \text{ (aq)} + 6\,H_2O \text{ (l)}$$
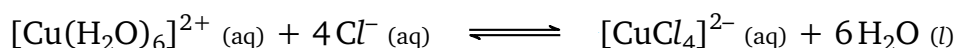
The K_{stab} equation would be as such:

$$K_{stab} = \frac{[[CuCl_4]^{2-}]}{[[Cu(H_2O)_6]^{2+}][Cl-]^4}$$

The higher the K_{stab} value, then, the greater the probability that ligand exchange will take place.

<h2>4.6.2   Effect on Reduction Potential</h2>

Ligands can affect the reduction potential of the central metal ion. For instance, $[Fe(H_2O)_6]^{3+}$ has a reduction potential of $+0.77\,V$, while $[Fe(CN)_6]^{3-}$ only has a reduction potential of $+0.36\,V$.

The primary difference lies in the stability of the complex formed, which affects the concentration of free metal ions in solution that can undergo reduction. Anionic ligands also have a stabilising effect on the metal cation, reducing their reduction potential electrostatically.

<h2>4.6.3   Ligand Exchange in Haemoglobin</h2>

Ligand exchange underlies the function of haemoglobin molecules in transporting oxygen to cells. Under normal circumstances, the haemoglobin molecule has a central Fe^{2+} ion, and can *reversibly* form dative bonds with O_2 molecules, creating *oxyhaemoglobin*.

When exposed to molecules of CO however, oxyhaemoglobin undergoes a ligand exchange reaction, replacing the O_2 ligand with a CO ligand. Unfortunately, the K_{stab} value of *carboxyhaemoglobin* is around *210 times* greater than that of oxyhaemoglobin.

Thus, the exchange is effectively *irreversible*, permanently disabling that particular molecule of haemoglobin. If enough molecules are disabled, oxygen fails to reach the cells and death occurs. I've heard it's painless, which is a slight consolation.

5   Colour of Complexes

5.1   Overview

As one might be aware, many complex ions are brightly coloured. Examples include $[Cu(H_2O)_6]^{2+}$, which is pale blue, $[Cu(NH_2)_4(H_2O)_2]^{2+}$, which is dark blue, and $[Fe(SCN)(H_2O)_5]^{2+}$, which is blood red.

There are a number of reasons for this, which will be explored below.

5.2   Quantum Theory of Light

What must first be explained is the quantum theory of light. It states that light consists of discrete particles — *photons*. When a photon interacts with an electron, it must be *completely* absorbed, in a one-to-one interaction. All of the energy of the photon must be absorbed at once, or not at all.

Next, electrons in atomic orbitals can only have certain, *fixed* energy levels. Thus, for an electron to absorb the energy of an oncoming photon, the energy of the photon must correspond *exactly* to a valid *energy gap* in the orbitals of the atom.

The energy of a photon is given as such:

$$E = \frac{hc}{\lambda}$$

E is the energy of the photon, h is the Planck Constant ($6.63 \times 10^{-34}\,\mathrm{m^2\,kg\,s^{-1}}$), c is the speed of light, and λ is the wavelength of the photon.

As one might know, the wavelength of light corresponds to the *colour* of that light. Hence, the energy of a photon depends on its colour.

The wavelengths of visible light lie between $400\,\mathrm{nm}$ and $700\,\mathrm{nm}$. Red has the longest wavelength, followed by orange, yellow, green, blue, then violet, at $400\,\mathrm{nm}$.

5.3 Crystal Field Theory

Crystal field theory, or CFT, is a theory that attempts to explain the reason for coloured complex ions. The primary idea underlying CFT is that complexes are formed because of an electrostatic attraction between the metal cation, and the lone pairs of electrons.

The 5 d-orbitals have the following shapes in 3d space:
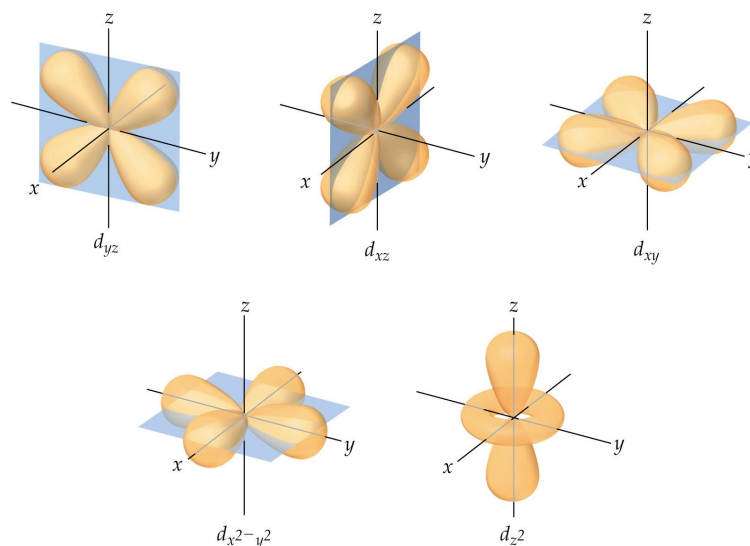
The 5 orbitals in the d subshell.

For an octahedral complex, the ligands will approach along the x, y, and z axes. Thus, they directly approach the lobes of the d_{z^2} and $d_{x^2-y^2}$ orbitals, leaving the lobes of the d_{yz}, d_{xz}, and d_{xy} orbitals between the ligands.

A theoretically free transition metal ion has 5 *degenerate* d-orbitals, that are all at the same energy level. However, due to their arrangement in space, the electrostatic repulsion between the ligands' lone pairs, and *some* of the d-orbitals, leads to a *splitting* of the orbitals, and a loss of degeneracy.
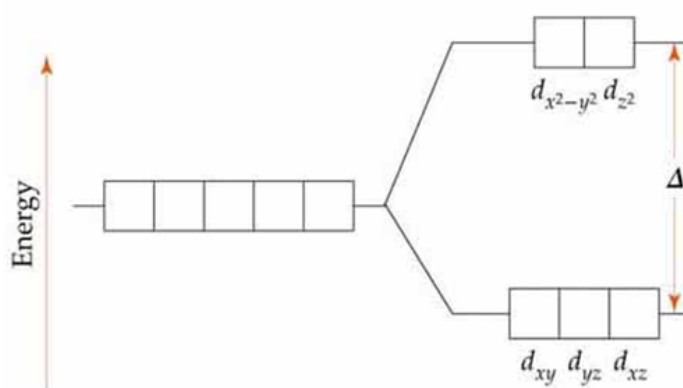
The 5 degenerate orbitals are split, into 2 and 3.

Note that the 2 higher energy orbitals correspond to those where there is electrostatic repulsion with the ligand, and the lower 3 are the orbitals between the axes.

5.3.1   d-d Electronic Transition

Going back to the quantum theory of light, a d-d electronic transition can occur when an electron in the lower-energy orbitals *absorbs* the energy of a photon corresponding to ΔE, and is *promoted* to the higher-energy orbital.

Hence, on average, the photons that pass through the complex molecule will be *missing* that particular wavelength of light, so the colour of the complex will appear to be the *complementary colour* of the one absorbed.

The complements of colours are below.

- Yellow / Violet

- Red / Green

- Orange / Blue

Conveniently, the value of ΔE for many complexes lie within the wavelength of visible light, so many of them appear coloured.

If ΔE lies beyond that, then d-d electronic transitions will still occur (absorption of UV light for example), but human eyes cannot detect them.

5.4 Charge-Transfer

Other than d-d electronic transfers, charge transfers — LMCT, or ligand-to-metal charge transfer, and MLCT, metal-to-ligand charge transfers — can also be the cause of coloured ions.

Notice that in MnO_4^-, the central Mn atom is at a +7 oxidation state, and has *no* d-electrons. Hence, d-d electronic transitions cannot be the cause of its *intense* purple colour. Instead, LMCT is the cause.

Similar concepts apply, including the quantum theory of light. Instead of ΔE being the difference in energy of the split d-orbitals, it is now the energy difference between the highest occupied molecular orbital of the donor, and the lowest unoccupied molecular orbital of the acceptor.

In other words, it is the first electron affinity of the acceptor less the first ionisation energy of the donor, plus corrections for electrostatic interactions.

$$\Delta E = E_A - E_I + J$$

Due to certain reasons which limit the kinds of electrons that can be promoted in a d-d electronic transition, the intensity of absorption for complexes whose colour depends on d-d transitions is usually small — hence most of the colours are somewhat less intense.

However, these restrictions (involving the quantum state of the electron) do not apply for charge transfers, so the intensity of light absorbed is much greater, leading to much more intense colours in these complexes.

5.5 Factors Affecting Complex Colours

5.5.1 Oxidation State of Cation

The oxidation state of the central metal atom will affect the number of electrons present in the d-subshell. This will thus affect the energy level of the orbitals in question, thus changing the value of ΔE.

Note that Sc^{3+}, Ti^{4+}, Cu^+ and Zn^{2+} are not coloured, even though titanium and copper are transition metals, because they either have fully-filled d-subshells, or empty d-subshells. The subshells are, in the case of titanium and copper, partially filled in other oxidation states.

5.5.2 Nature of Ligand

The nature of the ligand will also affect the value of ΔE. The bonds within the ligands themselves can affect the energy level of the lone pair of electrons, and thus change the degree of electrostatic repulsion faced by the orbitals.