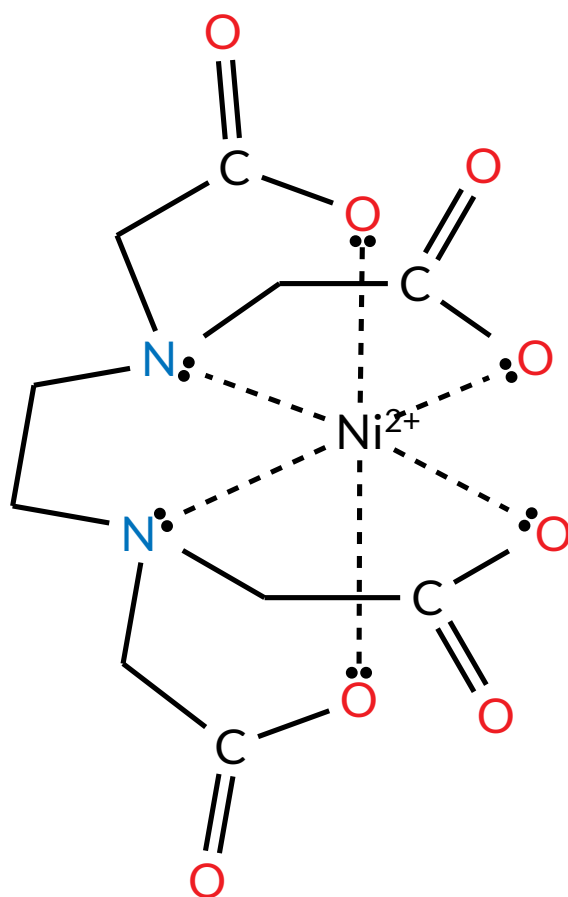


# Inorganic Chemistry



Chapters 20 to 23



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## PART I

# Group II

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## 1 Overview

Group II 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

All compounds containing group II metals have them at a fixed oxidation state of +2, and all group II metals have 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 II metals form +2 compounds two reasons; first, the 3rd ionisation energy (to get to a +3 state) is significantly greater than either the 1st or 2nd – this required energy 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 II metals *increase* down the group, due simply to the increasing number of quantum shells.

## 2.3 Ionisation Energy

As should be expected, the first and second ionisation energies of the elements in the group *decrease* progressively. This is due to the increasing number of electron shells between the nucleus and the valence electron shell. Thus, the shielding effect increases, the electrostatic force of attraction decreases, and less energy is required to remove the two valence electrons.

## 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, leading to weaker electrostatic forces between the delocalised electron cloud and the ions – hence weaker metallic bonding.

There is unfortunately no simple explanation for the irregularity in the trend.

### 2.4.2 Comparison with Group I Metals

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

## 2.5 Solubility of Hydroxides and Sulphates

The solubility of group II hydroxides *increases* down the group, while the solubility of the sulphates *decrease* down the group;  $\text{Mg}(\text{OH})_2$  and  $\text{BaSO}_4$  are insoluble, while  $\text{MgSO}_4$  and  $\text{Ba}(\text{OH})_2$  are soluble.

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

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

For the sulphates, the anionic radius is far larger than the cationic radius, hence the lattice energy remains relatively constant down the group. However, looking at the enthalpy change of hydration, the increasing cationic radius decreases the  $\Delta H_{\text{hyd}}$ . Hence, the overall effect is that  $\Delta H_{\text{sol}}$  increases down the group, becoming *less exothermic*, and hence solubility decreases.

For the hydroxides, the reverse is true; the anionic radius is small compared to the cation, so the lattice energy decreases down the group as the cationic radius has a greater effect. Thus, combined with the decreasing  $\Delta H_{\text{hyd}}$ , solubility for the hydroxides increases down the group.



## 3 Chemical Properties of the Elements

### 3.1 Redox Reactivity

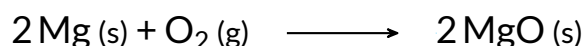
Due to the decrease in first two ionisation energies down the group, the group II metals are more easily oxidised down the group. Therefore, their strength as reducing agents also increases down the group.

Behold a table of  $E_{ox}^*$  values (lol you thought you had escaped them, didn't you):

Reaction	$E_{ox}^*/V$
$\text{Be (s)} \rightarrow \text{Be}^{2+} + 2 \text{e}^-$	+1.99
$\text{Mg (s)} \rightarrow \text{Mg}^{2+} + 2 \text{e}^-$	+2.37
$\text{Ca (s)} \rightarrow \text{Ca}^{2+} + 2 \text{e}^-$	+2.87
$\text{Sr (s)} \rightarrow \text{Sr}^{2+} + 2 \text{e}^-$	+2.89
$\text{Ba (s)} \rightarrow \text{Ba}^{2+} + 2 \text{e}^-$	+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.

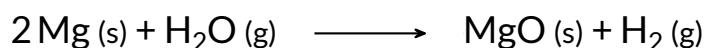


Barium reacts at room temperature quickly, so it is stored under oil to prevent rapid tarnishing. Beryllium on the other hand needs to be burning before *any* reaction takes place; its curiosities will be explored later.

### 3.3 Reaction with Water

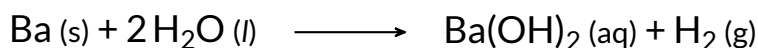
Again, the reactivity of the metals with water increase down the group; they reduce water to hydrogen gas. Note that beryllium does not react with water (or steam), even when heated.

All the metals form hydroxides with the exception of magnesium — when reacting with steam, it forms MgO directly, and reacts slowly with cold water otherwise to form Mg(OH)<sub>2</sub>.



The hydroxide formed, since it is only sparingly soluble, acts as a protective layer than slows down the further reaction of the underlying metal with water.

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



Note that the solubility of Ca(OH)<sub>2</sub> 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 II hydroxides are basic (duh), except for beryllium hydroxide (Be(OH)<sub>2</sub>) which is amphoteric.

## 4 Chemical Properties of the Oxides

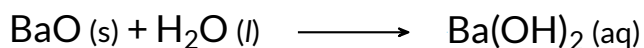
### 4.1 Physical Properties

Strictly does not belong in this section, but whatever. All group II oxides are solid at room temperature, are white, are 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 II oxides react with water to form their respective hydroxides (hence they are basic oxides), except 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.



## 5 Thermal Stability of Group II Compounds

### 5.1 Overview

All group II 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.

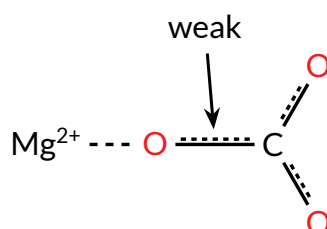
Element	MCO <sub>3</sub>	M(NO <sub>3</sub> ) <sub>2</sub>	M(OH) <sub>2</sub>
Mg	400 °C	450 °C	300 °C
Ca	900 °C	575 °C	390 °C
Sr	1280 °C	635 °C	466 °C
Ba	1360 °C	675 °C	700 °C

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 II metals, they are able to *polarise* the covalent bonds *within the anion*, weakening them.

This weakening of the covalent bonds in the anion allows said bond to break when heat is applied, typically resulting in a metal oxide as the product.



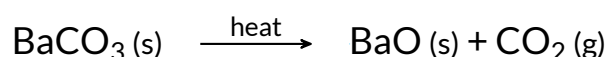
In this case, when heat is applied, the weak bond will be broken, leading to the formation of MO and CO<sub>2</sub>. Generally speaking this is why metal oxides are usually formed.

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.

Clearly, only polyatomic anions can be decomposed; monatomic anions cannot be broken down further by heat.

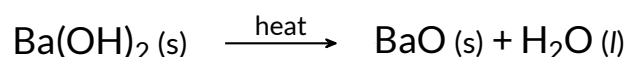
### 5.2.1 Carbonates

The thermal decomposition of group II carbonates generally produces the metal oxide, and carbon dioxide gas.



### 5.2.2 Hydroxides

Decomposing hydroxides produces the metal oxide and water.



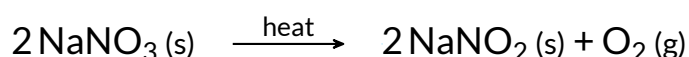
### 5.2.3 Nitrates

The thermal decomposition of nitrates generally yields the metal oxide, as well as nitrogen and oxygen gas.

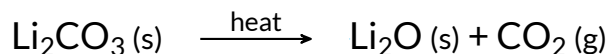


## 5.3 Comparison with Group I Metals

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



Lithium is the exception to this rule — it has a sufficiently high charge density (due to its tiny ionic radius) to polarise nitrates fully to decompose in the same way as group 2 ions, and can also polarise carbonates.



## 6 Beryllium Being Boneheaded

Nice alliteration, eh?

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  $\text{BeCl}_2$ , 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 reacts with neither water nor oxygen, leading to its unreactivity.

### 6.2 Amphoteric Nature

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

- Acid:  $\text{BeO} + 2 \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2[\text{Be}(\text{OH})_4]$
- Base:  $\text{BeO} + \text{H}_2\text{SO}_4 \rightarrow \text{BeSO}_4 + \text{H}_2\text{O}$

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

### 6.3 Formation of Be complexes

#### 6.3.1 Hydrated Ions

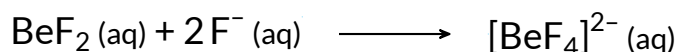
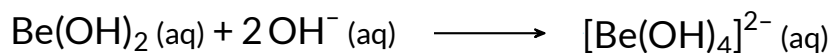
As will be discussed later,  $\text{Mg}^{2+}$  has sufficient charge density to form hydrated complex ions in water ( $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ ). Thus, it is clear that Be should form these complexes as well, and it does –  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ .

However,  $\text{Be}^{2+}$  is only 4-coordinate, due to the lack of vacant d-orbitals (there is no 2d subshell). Hence, by using the 2s and 2p orbitals, it can form 4 bonds with ligands. By contrast  $\text{Mg}^{2+}$  has a 3d subshell, allowing for more ligands.

### 6.3.2 Other Complexes

While  $\text{Be}^{2+}$  can form complexes, Be can also form complexes when bonded with other atoms, since it still has 2 vacant p-orbitals to fill with ligand bonds.

An example seen above is the formation of  $[\text{Be}(\text{OH})_4]^{2-}$  when  $\text{Be}(\text{OH})_2$  is exposed to more  $\text{OH}^-$ , and the formation of  $[\text{BeF}_4]^{2-}$ .



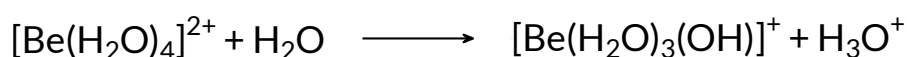
A point to note is that  $[\text{Be}(\text{OH})_4]^{2-}$  is created from  $\text{Be}(\text{OH})_2$ , which is itself formed from the hydrolysis of a beryllium salt in water (since  $\text{BeO}$  does not react with water).

On adding a base (aka  $\text{OH}^-$ ), the hydrated  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$  complex acts as an acid, forming the  $[\text{Be}(\text{OH})_4]^{2-}$  by losing 4  $\text{H}^+$  ions. This behaviour is conveniently discussed below.

## 6.4 Acidity of Beryllium Salts

Similar to other cations of high charge density like  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  (and to a certain extent  $\text{Mg}^{2+}$ ),  $\text{Be}^{2+}$  forms a hydrated complex in water,  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ , which was seen above.

Just like the other complexes, it can hydrolyse to give  $\text{H}_3\text{O}^+$ , making it acidic in water.



Naturally it can undergo further hydrolysis to finally form  $[\text{Be}(\text{OH})_4]^{2-}$ . This behaviour is what enables beryllium to react with bases, and be amphoteric.

## PART II

# Group VII

---

## 1 Overview

As should be familiar by now, group VII elements are the *halogens*, and are the most reactive group of non-metals. They are reactive to the point of not occurring as free elements ( $\text{Cl}_2$ ,  $\text{F}_2$ ) in nature, almost always being found as part of other compounds in an ionic state.

## 2 Physical Properties

### 2.1 Electronic Configuration

Halogens have a  $np^5$  valence shell, and so tend to form  $X^-$  ions.

F:  $1s^2 2s^2 2p^5$

Cl:  $1s^2 2s^2 2p^6 3s^2 3p^5$

Br:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^5$

I:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2 5p^5$

### 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, which is half the distance between the two atomic centres in  $X_2$ , 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 Bond Energy

Generally speaking the bond energies of the halogens decrease down the group, as the atomic radius increases and hence the orbital overlap decreases; this leads to a lengthening of the covalent bond, which makes it weaker.

Element	X–X bond energy/kJ mol <sup>-1</sup>
F	159
Cl	242
Br	193
I	151

The discrepancy in the F–F bond energy is due to electrostatic repulsion between the lone pairs on each F atom, which naturally would weaken the bond. This repulsion is due to the length of the bond and the size of the atoms.

## 2.4 Electron Things

### 2.4.1 First Ionisation Energy

Although the ionisation energy for halogens is typically not of great interest, it is still useful to know their trend. The trend is completely regular, with the ionisation energy decreasing down the group.

This is due to the increasing distance between the valence shell and the nucleus, increasing the shielding effect and thus reducing the energy needed to remove one valence electron.

### 2.4.2 First Electron Affinity

Of more interest is the first electron affinity, which measures the enthalpy change when adding one mole of electrons to one mole of gaseous atoms, forming one mole of singly-charged anions (if you do not recall).

In short, it is the enthalpy change to in creating  $X^-$  from X by adding  $e^-$ .

Element	First Electron Affinity/kJ mol <sup>-1</sup>
F	-328
Cl	-349
Br	-325
I	-295



The general trend is that the electron affinity decreases down the group (becomes less exothermic) since the electrostatic attraction between the new electron to be added and the nucleus decreases with increasing atomic radius.

Again, 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.

### 2.4.3 Electronegativity

The trend for electronegativity is fairly regular in decreasing down the group; fluorine is the most electronegative element (ever), and iodine is the least electronegative in the group.

The decrease in electronegativity is explained by the increasing distance between the bond pair of electrons and the nucleus, which reduces the electrostatic force attracting the electrons to the nucleus.

## 2.5 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.

Naturally, as non-polar molecules the polarisability depends only on the number of electrons. As the number of electrons increase, then so does the intermolecular force, and hence so does the melting and boiling point.

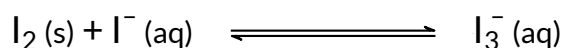
TL;DR: melting and boiling points increase down the group.  $F_2$  and  $Cl_2$  are gasses at room temperature,  $Br_2$  is a liquid, and  $I_2$  is a solid.

## 2.6 Solubility

### 2.6.1 In 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 soluble complex  $I_3^-$  in the presence of  $I^-$  ions:



## 2.6.2 In Non-polar Solvents

It should be no surprise that the solubility of the halogens in non-polar solvents is simply a function of their polarisability, and as with their melting and boiling points, said solubility increases down the group.

## 2.7 Colours

Generally speaking the colour of the halogens increase in intensity down the group.

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

Note that when concentrated in aqueous solution, the colour intensity naturally increases. Also, the  $I_3^-$  complex is brown in colour when aqueous.

## 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 have *low-lying* d-orbitals (in the number 3, 4, and 5 quantum shells respectively) that can accommodate more electrons and form more bonds. Thus, they can exist in the +1, +3, +5 and +7 oxidation states.

Examples of compounds with the halogen in positive oxidation states include  $\text{HClO}$ ,  $\text{ClF}$ ,  $\text{HClO}_2$ ,  $\text{HClO}_3$ , and  $\text{HClO}_4$ .

### 3.2 Oxidising Power

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

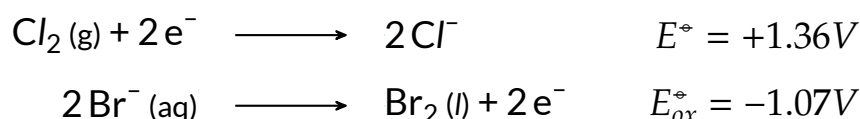
Reaction	$E^\circ/\text{V}$
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.80
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.36
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.07
$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+0.54

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.

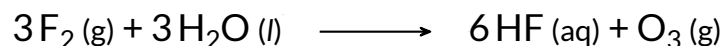
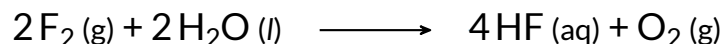
For example, with  $\text{Cl}_2$  displacing  $\text{Br}^-$ :



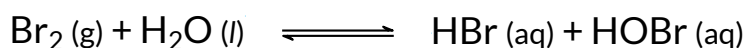
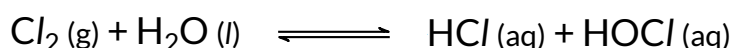
Since the  $E_{\text{cell}}^\circ$  value ( $1.36 + (-1.07) = +0.29\text{V}$ ) is positive, the reaction is feasible. Naturally were the conditions reversed, nothing would happen; bromine would not displace chloride.

### 3.4 Reaction with Water

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



Chlorine and bromine, on the other hand, undergo a disproportionation reaction in water, in an equilibrium reaction:



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.

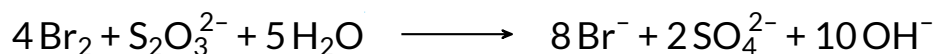
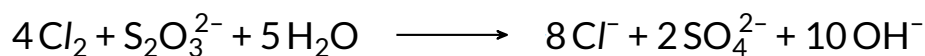
### 3.5 Reaction with Aqueous $\text{Fe}^{2+}$ Ions

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

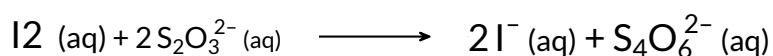
Fluorine would first explode, so it cannot react with the *aqueous* solution.

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

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

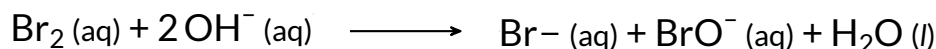
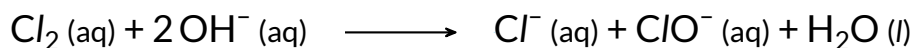


Above, sulphur is oxidised from a +2 oxidation state in thiosulphate to a +6 state in sulphate. However, iodine, given its weaker oxidation strength, can only oxidise thiosulphate to a +2.5 (yes, that's right) oxidation state, forming  $\text{S}_4\text{O}_6^{2-}$ .

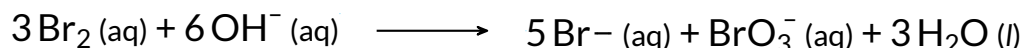
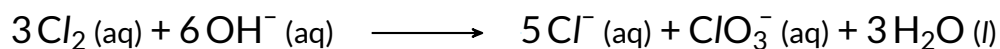


### 3.7 Disproportionation in Alkaline Solutions

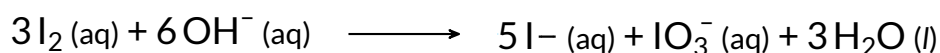
Chlorine, bromine and iodine disproportionate readily and non-reversibly in alkaline solutions to give various ions. Under cold conditions, both  $\text{Cl}_2$  and  $\text{Br}_2$  disproportionate to form the halogen in the +1 oxidation state.



The maximum temperature for the formation of  $\text{ClO}^-$  is around room temperature, while that for  $\text{BrO}^-$  is around  $0^\circ\text{C}$ . When heated, the halogen enters the +5 oxidation state instead of the +1 oxidation state.



Iodine being iodine, it enters the +5 oxidation state to form  $\text{IO}_3^-$  regardless of temperature.



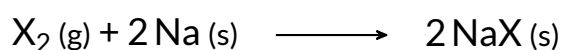
## 3.8 Reaction with Metals

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.

Unsurprisingly the vigour of the reaction reduces down the group.

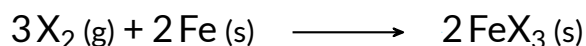
### 3.8.1 Reaction with Sodium

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

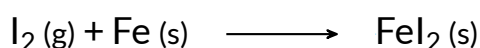


### 3.8.2 Reaction with Iron

The first 3 halogens, fluorine, chlorine, and bromine, can oxidise iron metal from the 0 oxidation state directly to the +3 oxidation state.

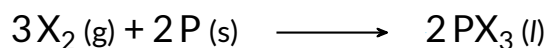


Naturally, iodine being what it is, can only oxidise iron to the +2 oxidation state.

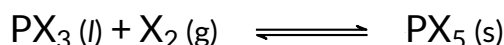


### 3.9 Reaction with Phosphorus

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



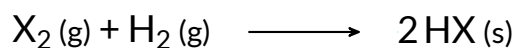
In the case of chlorine and bromine, there exists an equilibrium in excess halogen that results in the formation of  $\text{PX}_5$ .



These compound 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.



As usual, the reaction with fluorine is explosive even at  $-200\text{ }^\circ\text{C}$  and in the dark, while chlorine reacts explosively in sunlight and rapidly otherwise. Bromine reacts slowly, and typically requires heating at  $300\text{ }^\circ\text{C}$  with a Pt catalyst.

As usual, iodine's reaction is reversible and occurs slowly; the reaction is typically incomplete and a mixture of HX and  $\text{I}_2$  is obtained; this is due to the positive enthalpy change of formation.

## 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.

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 of course *id-id* interactions of the other halogens.

Note that other than electronegativity, the size of the negative atom also contributes to the ability to form hydrogen bonds, which is why HCl is not considered to be able to form them even though it has similar electronegativity to nitrogen and oxygen.

### 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.

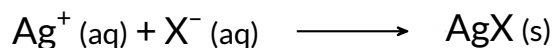
The acid strength *increases* down the group, since the  $H-X$  bond becomes weaker, which allows for easier dissociation. However, HF notably behaves as a weak acid due to incomplete dissociation which can be attributed to the high strength of the  $H-F$  bond.



## 5 Chemical Properties of Halide Ions

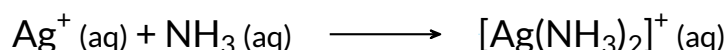
### 5.1 Precipitation Reactions

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



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

Upon adding  $\text{NH}_3 (\text{aq})$ , a complex ion is formed with the silver ions.



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

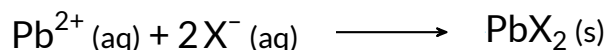
For AgCl, dilute  $\text{NH}_3 (\text{aq})$  is enough to lower the ionic product below  $K_{sp}$ , and allow the salt to dissolve. For AgBr, concentrated  $\text{NH}_3 (\text{aq})$  must be used to lower the concentration of  $\text{Ag}^+$  enough such that the ionic product becomes smaller than the  $K_{sp}$  of AgBr.

For AgI, the  $K_{sp}$  value is so small that no amount of  $\text{NH}_3 (\text{aq})$  will lower the concentration of  $\text{Ag}^+$  enough for the salt to dissolve.

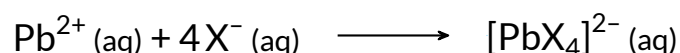
Ion	Colour of AgX	Required $\text{NH}_3 (\text{aq})$	$K_{sp}/\text{mol}^2 \text{ dm}^{-6}$
$\text{Cl}^-$	white	dilute	$1.6 \times 10^{-10}$
$\text{Br}^-$	cream	concentrated	$7.7 \times 10^{-13}$
$\text{I}^-$	yellow	nothing works	$8.3 \times 10^{-17}$

## 5.2 Reaction with Lead (II) Ions

As you might know, lead halides are insoluble. Only lead iodide ( $\text{PbI}_2$ ) is yellow, while the precipitates of the other halides are white.

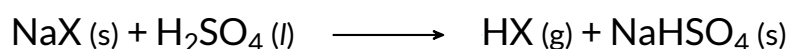


Addition of excess  $\text{X}^{-}$  will cause the precipitate to re-dissolve, since a soluble complex ion,  $[\text{PbX}_4]^{2-}$  is formed.

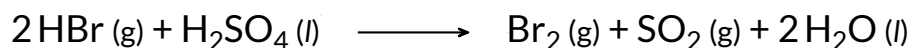
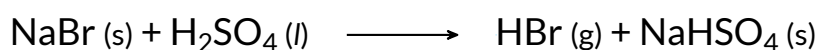


## 5.3 Reaction with Concentrated $\text{H}_2\text{SO}_4$

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

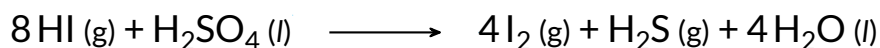
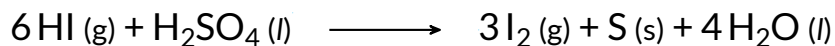
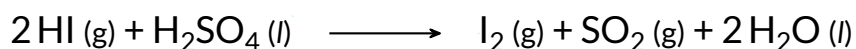
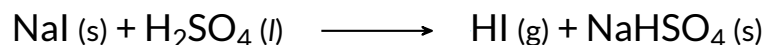


However,  $\text{H}_2\text{SO}_4$  is also a strong oxidising agent; thus, it is able to oxidise the  $\text{HBr}$  and  $\text{HI}$  formed in the acid-base reaction above. Note that it is insufficiently strong to oxidise  $\text{HF}$  and  $\text{HCl}$ .



In this reaction, most of the  $\text{HBr}$  remains untouched, and some  $\text{Br}_2(\text{g})$  is produced, leading to the observation of slight reddish-brown fumes.

Below,  $\text{H}_2\text{SO}_4$  continues to oxidise HI in a complex and frankly ridiculous manner.

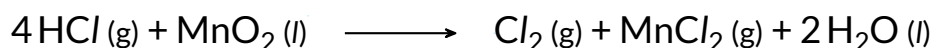
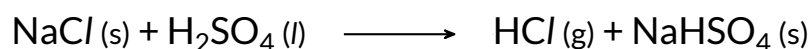


Due to the ease of oxidising HI,  $\text{H}_2\text{SO}_4$  is itself reduced, with sulphur going from a +6 oxidation state to a -2 state in  $\text{H}_2\text{S}$ . As a sidenote, it is  $\text{H}_2\text{S}$  that smells like rotten eggs. Furthermore,  $\text{SO}_2$  is also a pungent gas. This is a smelly reaction.

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

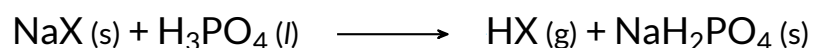
### 5.3.1 Reaction in the Presence of $\text{MnO}_2$

Manganese dioxide is a stronger oxidising agent than  $\text{H}_2\text{SO}_4$ , and thus it can serve to oxidise the HCl that sulphuric acid cannot.



### 5.3.2 $\text{H}_3\text{PO}_4$ 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  $\text{Br}_2$  and  $\text{I}_2$  – concentrated phosphoric acid is such an acid.



## PART III

# The Third Period

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## 1 Overview

This chapter will study the 7 elements in the third period; sodium (Na), magnesium (Mg), aluminium (Al), silicon (Si), phosphorus (P), sulphur (S), and chlorine (Cl). Argon is... inert.

## 2 Elemental Reactions

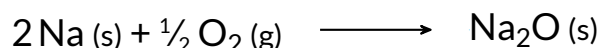
Generally speaking, the reactivity of the elements with both oxygen and chlorine *decrease* across the period. Both of them are oxidising agents, and since reducing power decreases across the period, they are less likely to be oxidised.

White phosphorus (P<sub>4</sub>) has a tetrahedral shape that incurs some strain in the bonds due to their angles, increasing its reactivity.

### 2.1 Reaction with Oxygen

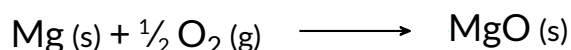
#### 2.1.1 Sodium

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



#### 2.1.2 Magnesium

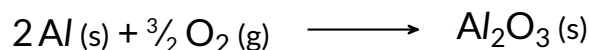
Magnesium metal tarnishes in air, albeit less readily than sodium. It burns very strongly with a *bright white* flame, and its combustion is highly exothermic.



### 2.1.3 Aluminium

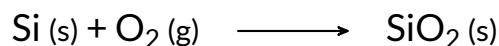
Aluminium metal is readily oxidised by air, and forms a protective layer of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) that protects the metal inside from further oxidation.

High temperatures (above  $800^\circ\text{C}$ ) are required to fully oxidise aluminium.



### 2.1.4 Silicon

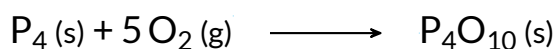
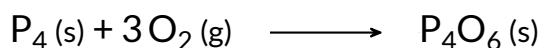
Silicon *does not* react with oxygen at room temperature. When strongly heated, some silicon dioxide ( $\text{SiO}_2$ ) can be formed. Silicon is a giant covalent molecule, so large amounts of energy need to be supplied to allow any reactions to take place.



### 2.1.5 Phosphorus

There are two predominant forms of elemental phosphorus; white phosphorus, which are discrete molecules of  $\text{P}_4$ , and red phosphorus, which takes a polymeric form.

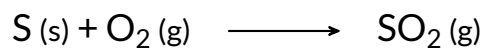
The former *spontaneously combusts* in air with a bright white flame, due to the strained tetrahedral bonds in the molecule. On the other hand, red phosphorus is more stable, and will burn on heating with a soft orange flame; the products for both forms of phosphorus are identical.



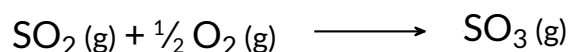
With limited oxygen, the predominant product will be  $\text{P}_4\text{O}_6$ ; in excess oxygen, the major product will be  $\text{P}_4\text{O}_{10}$ .

### 2.1.6 Sulphur

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



With a catalyst (eg. vanadium oxide  $\text{V}_2\text{O}_5$ ),  $\text{SO}_2$  can be further oxidised:



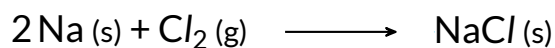
### 2.1.7 Chlorine

Chlorine does not directly react with oxygen, because it is unlikely for it to be oxidised by oxygen.

## 2.2 Reaction with Chlorine

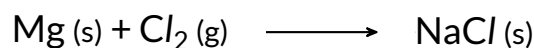
### 2.2.1 Sodium

Sodium metal is readily oxidised by chlorine and burns in the gas, in a highly exothermic reaction.



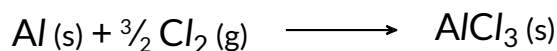
### 2.2.2 Magnesium

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



### 2.2.3 Aluminium

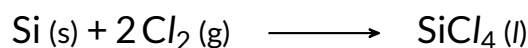
Aluminium does not react *that* readily with chlorine. The reaction can be sped up by passing *dry* chlorine gas over heated aluminium foil (larger surface area).



$\text{AlCl}_3$  typically sublimes into the gaseous state.

### 2.2.4 Silicon

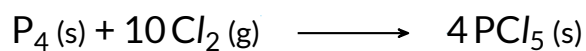
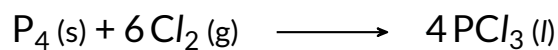
The reaction of silicon with chlorine is even slower than with aluminium, but if heated silicon powder is used, the reaction can be sped up slightly.



Silicon tetrachloride is a liquid at room temperature.

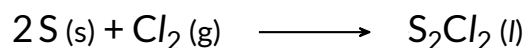
## 2.2.5 Phosphorus

White phosphorus ( $P_4$ ) burns vigorously in chlorine gas to form  $PCl_3$  and  $PCl_5$ . As covered previously, the formation of  $PCl_5$  occurs in an equilibrium, so excess chlorine gas should be used to favour the production of the latter, and limited chlorine to prefer the former.



## 2.2.6 Sulphur

Heated sulphur can react with chlorine gas.



## 2.2.7 Chlorine

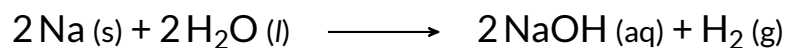
What did you expect to find in this section, really? Oh, of course; chlorine gas reacts vigorously with chlorine gas in an explosive reaction possessing the force of 100 megatons of TNT.



## 2.3 Reaction with Water

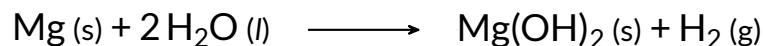
### 2.3.1 Sodium

Sodium, like group I metals, reacts vigorously even with cold water.

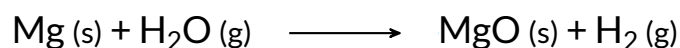


### 2.3.2 Magnesium

As covered in the chapter on the group II metals, magnesium reacts slowly with cold water, due to the low solubility of the hydroxide forming a layer around the metal.



However with steam, magnesium reacts directly to form magnesium oxide.

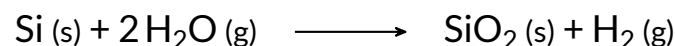


### 2.3.3 Aluminium

Aluminium does not appear to react with water, but this is mainly due to the strong and unreactive protective layer of  $\text{Al}_2\text{O}_3$  that is formed.

### 2.3.4 Silicon

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



### 2.3.5 Phosphorus

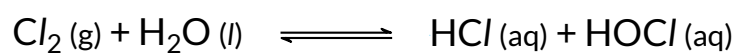
Phosphorus does not react with water.

### 2.3.6 Sulphur

Sulphur does not react with water.

### 2.3.7 Chlorine

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



### 3 Properties of the Oxides

In general, the acidity of the oxides increases 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, generally, a decrease in melting points across the period.

Thing	Structure	Melting Point/°C
Na <sub>2</sub> O	ionic	1130
MgO	ionic	2850
Al <sub>2</sub> O <sub>3</sub>	ionic	2070
SiO <sub>2</sub>	giant covalent	1700
P <sub>4</sub> O <sub>6</sub>	discrete covalent	24
P <sub>4</sub> O <sub>10</sub>	discrete covalent	360 (sublimes)
SO <sub>2</sub>	discrete covalent	-75
SO <sub>3</sub>	discrete covalent	17

Apparently chlorine oxides are not covered in this chapter, so they will not be talked about mostly because I don't know anything about them.

The melting point of MgO is much larger than that of Na<sub>2</sub>O due to the much higher charge density of Mg<sup>2+</sup>, which greatly increases the lattice energy of MgO.

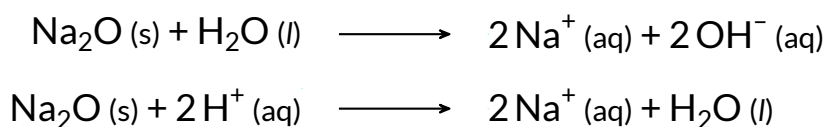
However, the *even higher* charge density of Al<sup>3+</sup> instead serves to *polarise* the O<sup>2-</sup> ion, resulting in some *covalent character*, hence reducing the lattice energy of Al<sub>2</sub>O<sub>3</sub>.

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  $\text{OH}^-$  ions, and as such 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.

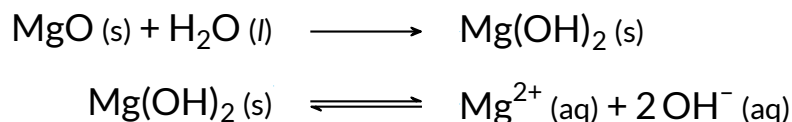


Sodium hydroxide... well we all know what sodium hydroxide is like. It is a strong base.

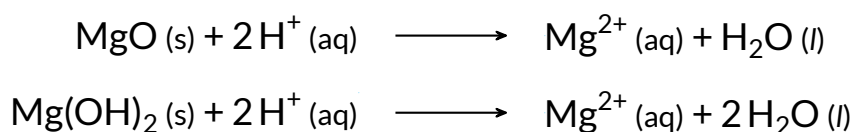
## 3.3 Magnesium Oxide

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

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



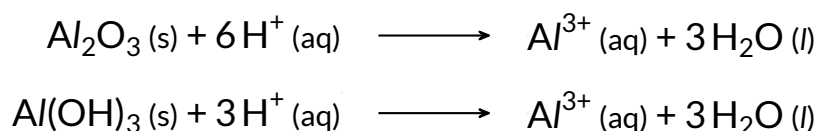
On the other hand, both  $\text{MgO}$  and  $\text{Mg(OH)}_2$  can react directly with acids to form aqueous salt solutions.



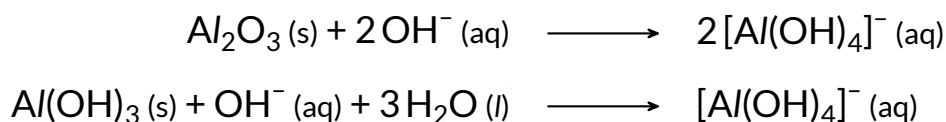
### 3.4 Aluminium Oxide

Aluminium oxide,  $\text{Al}_2\text{O}_3$ , is partially covalent, due to the polarising power of the  $\text{Al}^{3+}$  ion. Thus, the combination of ionic and covalent characters allow  $\text{Al}_2\text{O}_3$ , as well as  $\text{Al}(\text{OH})_3$ , to be amphoteric; ie. they react with both acids and bases.

Due to the high lattice energy of both  $\text{Al}_2\text{O}_3$  and  $\text{Al}(\text{OH})_3$ , both of them are insoluble in water. However, they both react with acids to form an aqueous salt solution containing  $\text{Al}^{3+}$  ions.

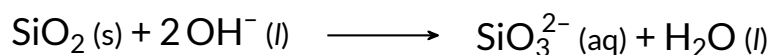


They can react with strong bases as well, to form *aluminate complex ions*,  $[\text{Al}(\text{OH})_4]^-$ .



### 3.5 Silicon Dioxide

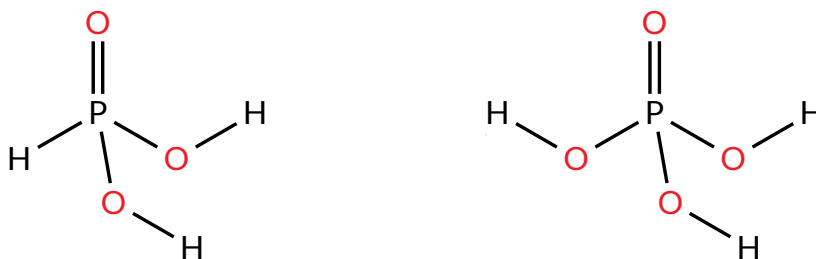
Silicon dioxide neither reacts nor dissolves in water, due to the strong covalent bonds between the Si and O atoms. In fact, it does not react even when heated with aqueous bases. For any reaction to take place, there must be strong heating with concentrated bases, eg. NaOH.



When it does react, a silicate ion is formed.

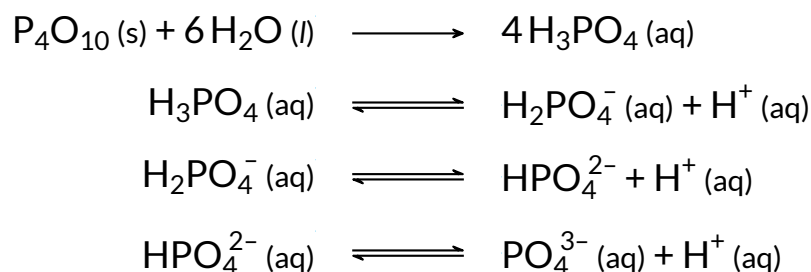
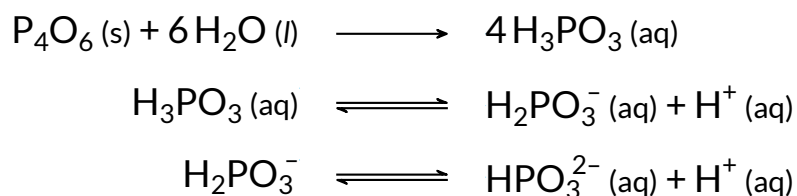
## 3.6 Phosphorus Oxides

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  $P_4O_6$ .

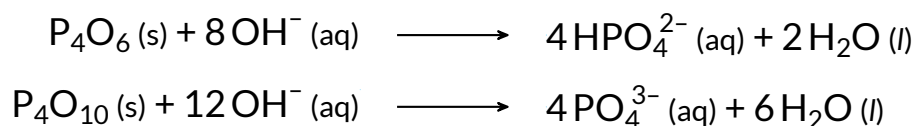


$H_3PO_3$  on the left,  $H_3PO_4$  on the right

$H_3PO_3$  and  $H_3PO_4$  are both weak acids, with the former having a  $pK_a$  value of 2.0, and a value of 2.15 for the former.  $H_3PO_4$  is a diprotic acid, while  $H_3PO_4$  is a triprotic acid. The third hydrogen in  $H_3PO_3$  isn't attached to anything electronegative, so it does not dissociate.



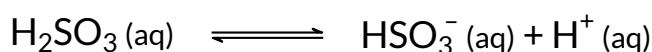
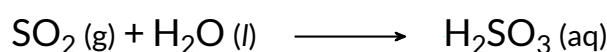
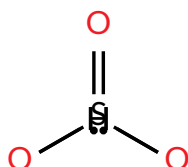
Both  $P_4O_6$  and  $P_4O_{10}$  can react directly with bases to give a salt solution, containing anions of the fully deprotonated acids ( $HPO_3^{2-}$  and  $PO_4^{3-}$  respectively).



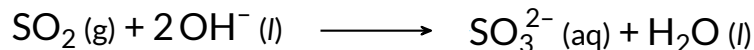
## 3.7 Sulphur Oxides

### 3.7.1 Sulphur Dioxide (SO<sub>2</sub>)

Sulphur dioxide is mostly soluble in water, giving a solution of the weak diprotic sulphurous acid, H<sub>2</sub>SO<sub>3</sub>. It has a  $pK_a$  value of around 1.8, so it is slightly stronger than H<sub>3</sub>PO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub>.

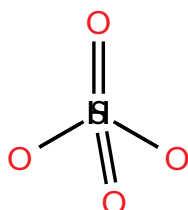


Naturally SO<sub>2</sub> (g) can react directly with bases to form a salt solution containing the sulphite ion, SO<sub>3</sub><sup>2-</sup>, which happens to be the fully deprotonated version of the acid.



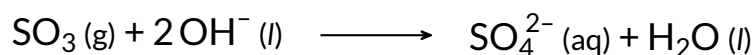
### 3.7.2 Sulphur Trioxide (SO<sub>3</sub>)

Sulphur trioxide, on the other hand, reacts violently with water, producing a mist of H<sub>2</sub>SO<sub>4</sub> droplets.



Sulphuric acid should be all too familiar.

Sulphuric is obviously a strong acid that ionises completely, and so there's no dissociation equation to show. SO<sub>3</sub> (g) can also react directly with bases to form an aqueous salt solution with sulphate ions.



## 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.

Again, it looks like sulphur chlorides are conveniently out-of-syllabus.

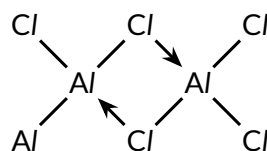
Thing	Structure	Melting Point/°C	Boiling Point/°C
NaCl	ionic	801	1413
MgCl <sub>2</sub>	ionic	714	1412
AlCl <sub>3</sub>	discrete covalent	180 (sublimes)	(sublimation)
SiCl <sub>4</sub>	discrete covalent	-70	58
PCl <sub>3</sub>	discrete covalent	-112	76
PCl <sub>5</sub>	discrete covalent	160 (sublimes)	(sublimation)

#### 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.

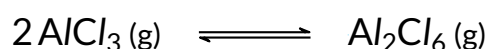
However, at around 180 °C, the heat causes the ionic lattice to expand, dissolving the ionic character of the compound. Thus, AlCl<sub>3</sub> sublimes immediately into a gas, since the electrostatic forces have now disappeared, leaving only *id-id* interactions for intermolecular bonding.

A caveat, however, is that the Al atom in AlCl<sub>3</sub> is *electron deficient*, having only 3 electron pairs. Thus, it tends to form dative bonds with another molecule of AlCl<sub>3</sub>, creating a dimer of Al<sub>2</sub>Cl<sub>6</sub>.



The dimer Al<sub>2</sub>Cl<sub>6</sub>.

AlCl<sub>3</sub> and Al<sub>2</sub>Cl<sub>6</sub> actually exist in an equilibrium:

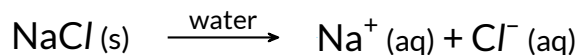


At higher temperatures, the equilibrium shifts to the left, and AlCl<sub>3</sub> exists predominantly as discrete molecules, with no dimerisation.



## 4.2 Sodium Chloride

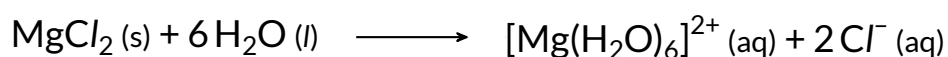
Sodium chloride,  $\text{NaCl}$ , should be familiar; it is unremarkable, and dissolves in water to give  $\text{Na}^+$  (aq) and  $\text{Cl}^-$  (aq) ions.



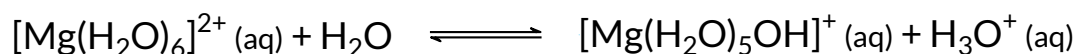
The  $pH$  of the solution is 7 – neutral.

## 4.3 Magnesium Chloride

Magnesium chloride,  $\text{MgCl}_2$ , dissolves in water as well to give  $\text{Mg}^{2+}$  (aq) and  $\text{Cl}^-$  (aq) ions. Note that because of magnesium's somewhat high charge density, it forms a hydrated aqua complex in water.



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.



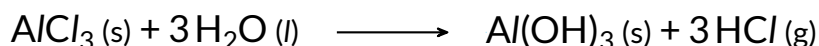
Note that the polarising power is much weaker than, for instance,  $\text{Al}^{3+}$  or  $\text{Cr}^{3+}$ , so the  $pH$  of such a solution is only around 6.5.

## 4.4 Aluminium Chloride

The reactions of  $\text{AlCl}_3$  with water differ mainly based on the amount of water or base used.

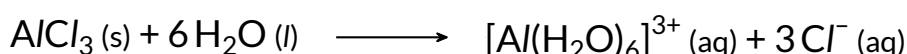
### 4.4.1 Limited Water

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

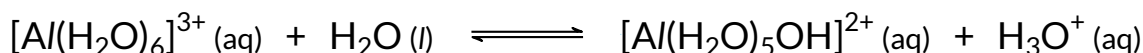


### 4.4.2 Excess Water

In excess water,  $\text{AlCl}_3$  instead forms the hydrated aluminium complex ion, and chloride ions.



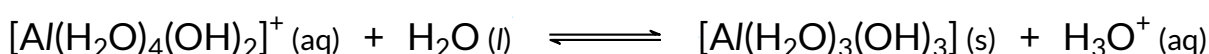
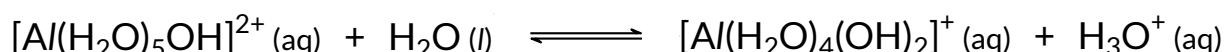
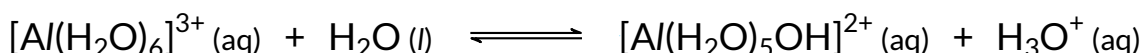
As covered previously, this hydrated aluminium ion can undergo hydrolysis to give an acidic solution.



The extent of hydrolysis is much greater than for  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ , so the *pH* of this solution is typically around 3.

### 4.4.3 Limited $\text{OH}^-$

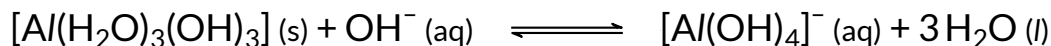
When a limited amount of base ( $\text{OH}^-$ ) is added,  $[\text{Al}(\text{H}_2\text{O})_6]^{3+} (\text{aq})$  typically behaves as a triprotic acid, being able to release 3  $\text{H}^+ (\text{aq})$  ions before being depleted and forming a precipitate of  $[\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3] (\text{s})$ .



A solution of  $[\text{Al}(\text{H}_2\text{O})_6]^{3+} (\text{aq})$  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 $\text{OH}^-$

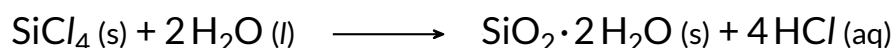
When faced with excess amounts of base, the white precipitate of  $[\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3] (\text{s})$  will appear to dissolve, instead forming the aluminate complex ion  $[\text{Al}(\text{OH})_4]^- (\text{aq})$ .



Note that, since this is an equilibrium reaction, the concentration of  $\text{OH}^-$  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

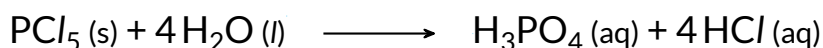
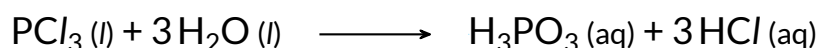
Silicon chloride *readily* and *violently* hydrolyses in water completely, forming  $\text{HCl}$ , which can either effervesce away as gaseous hydrogen chloride, or dissolve in the water to form a strongly acidic solution of  $\text{pH}$  1.



$\text{SiO}_2 \cdot 2 \text{H}_2\text{O} (\text{s})$  is a hydrated form of silicon dioxide, but it is still in the solid state.

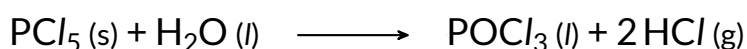
#### 4.6 Phosphorus Chlorides

Both phosphorus chlorides,  $\text{PCl}_3$  and  $\text{PCl}_5$ , completely hydrolyse in water in a similar fashion to silicon chloride, forming  $\text{HCl}$  and hence a strongly acidic solution.



Note that, of course, the contributions of  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_4$  to the  $\text{pH}$  of the solution will not be forgotten, but they are quite insignificant in the face of  $\text{HCl}$ .

Furthermore, on dropwise addition of water with  $\text{PCl}_5$ , it tends to form  $\text{POCl}_3$ , phosphorus oxy-chloride, instead.



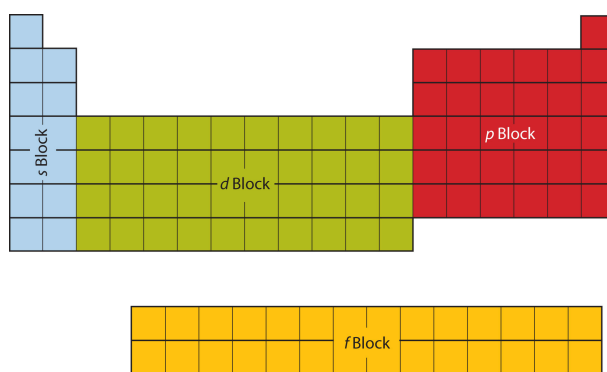
## PART IV

# Transition Metals

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## 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

### 1.1.1 Atomic Configuration

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

Scandium (Sc):	[Ar] $3d^1 4s^2$
Titanium (Ti):	[Ar] $3d^2 4s^2$
Vanadium (V):	[Ar] $3d^3 4s^2$
Chromium (Cr):	[Ar] $3d^5 4s^1$
Manganese (Mn):	[Ar] $3d^5 4s^2$
Iron (Fe):	[Ar] $3d^6 4s^2$
Cobalt (Co):	[Ar] $3d^7 4s^2$
Nickel (Ni):	[Ar] $3d^8 4s^2$
Copper (Cu):	[Ar] $3d^{10} 4s^1$
Zinc (Zn):	[Ar] $3d^{10} 4s^2$

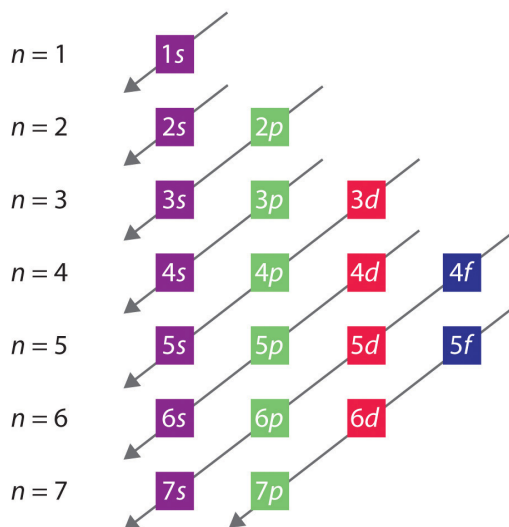
Note the strange configurations of Cu and Cr. Instead of having a  $3d^4 4s^2$  or  $3d^9 4s^2$  configuration, they instead have  $3d^5$  and  $3d^{10}$  configurations. The reason for this is the favourability, or lower energy level, of a configuration that minimises electron density.

Lower electron densities naturally mean less inter-electronic repulsion, which reduces the potential energy of the system and making it more stable.

## 1.1.2 Ionic Configuration

$\text{Sc}^{3+}$ :	$[\text{Ar}] 3d^0$
$\text{Ti}^{2+}$ :	$[\text{Ar}] 3d^2$
$\text{V}^{3+}$ :	$[\text{Ar}] 3d^2$
$\text{Cr}^{3+}$ :	$[\text{Ar}] 3d^3$
$\text{Mn}^{2+}$ :	$[\text{Ar}] 3d^5$
$\text{Fe}^{2+}$ :	$[\text{Ar}] 3d^6$
$\text{Co}^{2+}$ :	$[\text{Ar}] 3d^7$
$\text{Ni}^{2+}$ :	$[\text{Ar}] 3d^8$
$\text{Cu}^{2+}$ :	$[\text{Ar}] 3d^9$
$\text{Zn}^{2+}$ :	$[\text{Ar}] 3d^{10}$

Note how the 2 electrons in the 4s-subshell are lost first. The reason for this behaviour is due to the energy levels of the electron shells. The filling order proceeds in this manner:



The empty 4s subshell has a lower energy than the empty 3d subshell, so it is filled first. However, once the 4s subshell is filled, electrons go to the 3d subshell — the addition of electrons eventually lowers the energy level of the 3d subshell below that of the 4s.

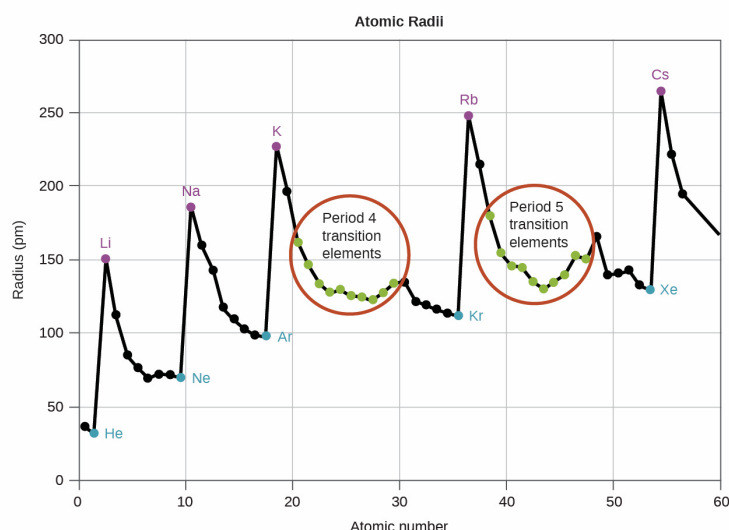
Hence, when removing electrons, the ones in the 4s subshell, which is now at a higher energy level than the 3d subshell, are the first to go.

Furthermore, from the configurations above it can be seen that  $\text{Sc}^{3+}$  only has an empty 3d-subshell, while  $\text{Zn}^{2+}$  has a fully-filled 3d-subshell. Thus, they are not considered transition metals.

## 2 Physical Properties

### 2.1 Atomic Radii

Generally speaking, the atomic radii across the transition metals remains relatively constant. Physically speaking, the 4s electrons are the valence electrons; hence, since new electrons are added to the 3d subshell, the increase in the shielding effect somewhat mitigates the increase in nuclear charge.



Hence, the atomic radii remains relatively constant across the d-block elements. Comparing with potassium and calcium, the radii of d-block elements are *much smaller* than the radii of s-block elements. This is due to the fact that the shielding effect of the 3d-subshell is quite poor due to its *diffuse nature*.

Thus, 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

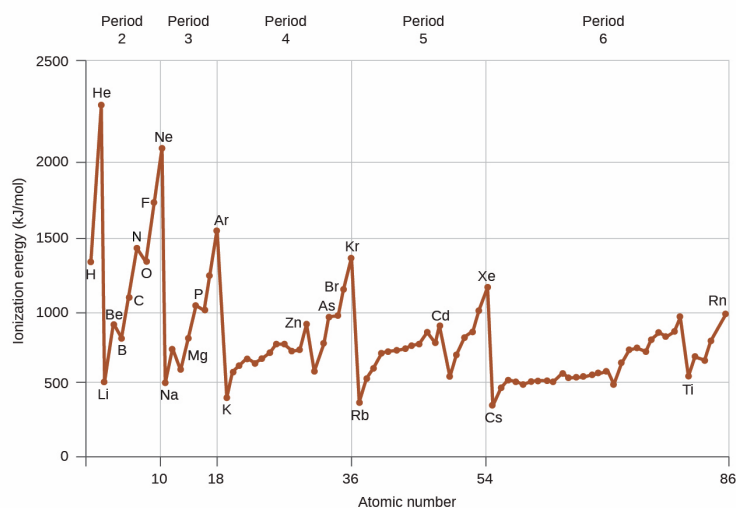
There is no singular trend, but generally speaking the melting and boiling points for the transition elements are all higher than the s-block metals. This is due to the increased number of electrons available for metallic bonding — transition metals can use both the 3d and 4s electrons, due to the small 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 (5 electrons out of 10, all with the same spin), 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.



In contrast, electrons are added to the inner 3d-subshell across the transition elements, leading to an increase in the shielding effect. This 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  $\text{Fe}^{3+}$  is more stable than  $\text{Fe}^{2+}$ .

#### 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,  $\text{FeCl}_3$ ,  $\text{CuSO}_4$  have  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  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  $\text{MnO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$ .



## 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 allows them to either *accept* electron pairs, or *donate* electron pairs, allowing for the adsorption of reactant molecules onto their surface.

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.

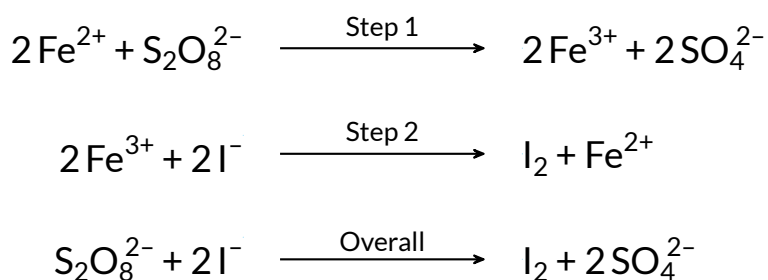
Some examples of heterogeneous catalysts include:

- Finely divided Fe powder, *Haber Process*:  $3 \text{H}_2 + \text{N}_2 \rightarrow 2 \text{NH}_3$
- $\text{V}_2\text{O}_5$ , *Contact Process*:  $2 \text{SO}_2 + \text{O}_2 \rightarrow 2 \text{SO}_3$
- Nickel, *Reduction of Alkenes*:  $\text{RCH}=\text{CH}_2 + \text{H}_2 \rightarrow \text{RCH}_2\text{CH}_3$

### 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  $\text{I}^-$  to  $\text{I}_2$  by  $\text{S}_2\text{O}_8^{2-}$ .



Here, the  $\text{Fe}^{2+}$  ion and the  $\text{S}_2\text{O}_8^{2-}$  ion can easily react, because they are oppositely charged.  $\text{Fe}^{2+}$  is oxidised by the peroxodisulphate ion to  $\text{Fe}^{3+}$ , forming one of the products,  $\text{SO}_4^{2-}$ .

The  $\text{Fe}^{3+}$  produced then proceeds to oxidise the  $\text{I}^-$  ion, forming the other product,  $\text{I}_2$ , and regenerating the  $\text{Fe}^{2+}$  catalyst.

Without the catalyst, the need to react two negatively charged ions directly ( $\text{S}_2\text{O}_8^{2-}$  and  $\text{I}^-$ ) would lead to an abysmal rate of reaction.

Note that the order of the two sub-reactions is irrelevant, so  $\text{Fe}^{3+}$  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.

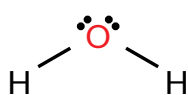
Note that aluminium fulfils both of these criteria, and expectedly forms complex ions;  $[\text{Al}(\text{OH})_4]^-$  and the hydrated ion  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  are examples. The  $\text{Al}^{3+}$  ion has entirely empty 3s-, 3p-, and 3d-subshells, which can accept electron pairs 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.

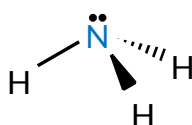
### 4.2 Ligand Denticity

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.

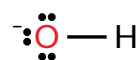
#### Monodentate Ligands



water

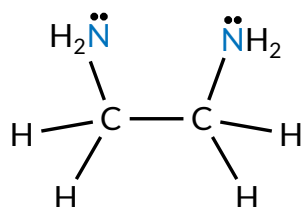


cyanide

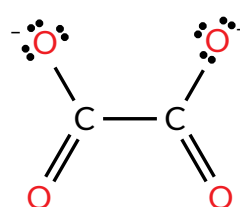


hydroxide

#### Bidentate Ligands



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

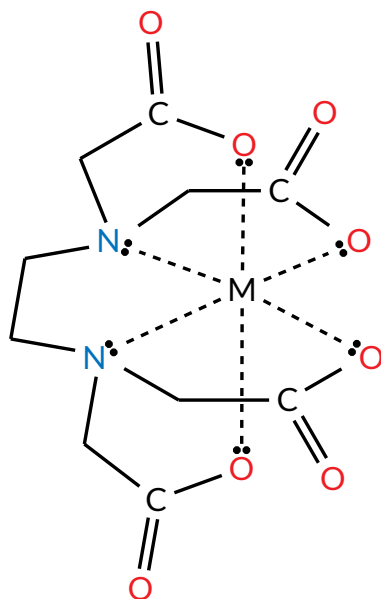


ethanedioate

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

## Hexadentate Ligands

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



ethylenediaminetetraacetate (abbrv. EDTA)

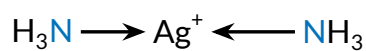
## 4.3 Complex Charges

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.

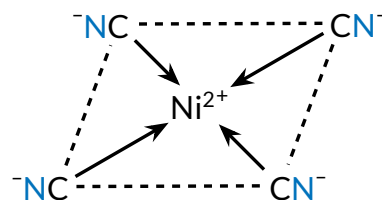
A compound containing a complex ion typically has *counter ions* that serve to balance the charge. In aqueous solution, the counter ions dissociate from the complex ion as expected. The complex ion is treated as a *single, polyatomic ion*.

## 4.4 Coordination Number

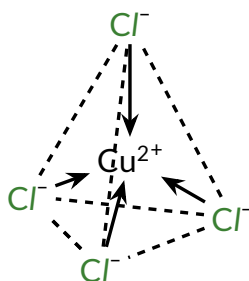
The coordination number of a complex determines the number of ligands around the central atom, as well as their arrangement around the central atom, in a manner similar to VSEPR theory.



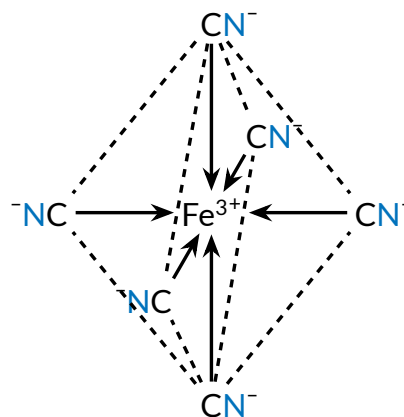
$[\text{Ag}(\text{NH}_3)_2]^+$ , linear, CN: 2



$[\text{Ni}(\text{CN})_4]^{2-}$ , square planar, CN: 4



$[\text{CuCl}_4]^{2-}$ , tetrahedral, CN: 4



$[\text{Fe}(\text{CN})_6]^{3-}$ , octahedral, CN: 6

## 4.5 Hydrated Complex Ions

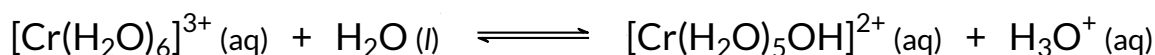
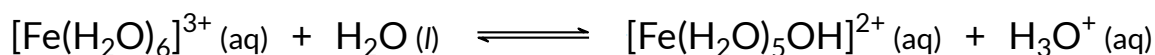
Otherwise known as aqua complexes, these ions are formed when a transition metal, or any metal with a sufficiently high charge density, is dissolved in water. Essentially these are complexes where the water molecules act as ligands.

In contrast, most s-block metals (eg. sodium) do not form hydrated complexes, only ion-dipole interactions. This is because the highly-charged and small transition metal cations have high polarising power, thus preferring the formation of covalent bonds versus ionic 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  $\text{H}_3\text{O}^+$  (aq) ions that make the solution acidic.

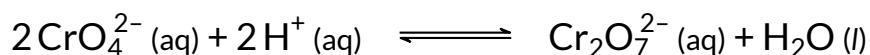
This ability is due to the high polarising power of the central cation, which can polarise and weaken O–H bonds in the water ligand, eventually allowing another water molecule to attack the weakly-attached H atom, forming  $\text{H}_3\text{O}^+$ .



### 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  $[\text{Cr}(\text{H}_2\text{O})_6]^{6+}$ . Instead, it forms  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$ , chromate and dichromate, which exist in an equilibrium.



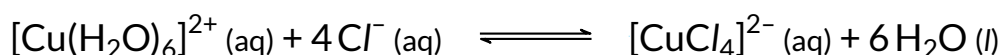
In acidic conditions,  $[\text{H}^+]$  is high, so by Le Châtelier's Principle, the position of equilibrium moves to the right, favouring the production of orange dichromate. Conversely in an alkaline medium, the position of equilibrium moves to the left to favour yellow chromate.

## 4.6 Ligand Exchange

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.

### 4.6.1 Stability Constant, $K_{stab}$

$K_{stab}$  is essentially another form of  $K_c$  for complex ions. For example, if an exchange between the  $\text{H}_2\text{O}$  ligands of  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  and  $\text{Cl}^-$  ligands were to happen:



The  $K_{stab}$  equation would be as such:

$$K_{stab} = \frac{[\text{CuCl}_4]^{2-}}{[\text{Cu}(\text{H}_2\text{O})_6]^{2+} [\text{Cl}^-]^4}$$

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

### 4.6.2 Effect on Reduction Potential

Different ligands can affect the reduction potential of the central metal ion. For instance,  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  has a reduction potential of +0.77 V, while  $[\text{Fe}(\text{CN})_6]^{3-}$  only has a reduction potential of +0.36 V.

The difference can be due to steric hindrance, or more likely in the case of  $[\text{Fe}(\text{CN})_6]^{3-}$ , the negative charge of the ligands increasing the energy needed for the electron to approach and successfully reduce the  $\text{Fe}^{3+}$  centre.

### 4.6.3 Ligand Exchange in Haemoglobin

Ligand exchange underlies the function of haemoglobin molecules in the blood that transport oxygen to cells. Under normal circumstances, the haemoglobin molecule has a central  $\text{Fe}^{2+}$  ion, and can *reversibly* form dative bonds with  $\text{O}_2$  molecules, creating *oxyhaemoglobin*.

When exposed to molecules of CO however, oxyhaemoglobin undergoes a ligand exchange reaction, replacing the  $\text{O}_2$  ligand with a CO ligand. Unfortunately, the  $K_{stab}$  value of *carboxyhaemoglobin* is around 210 times greater than oxyhaemoglobin.

Thus, the ligand exchange reaction is effectively *irreversible*, permanently disabling that molecule of haemoglobin. If enough molecules are disabled, death naturally 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  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ , which is pale blue,  $[\text{Cu}(\text{NH}_2)_4(\text{H}_2\text{O})_2]^{2+}$ , which is dark blue, and  $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$ , 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 explored 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 ( $6.63 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$ ),  $c$  is the speed of light, and  $\lambda$  is the wavelength of the photon.

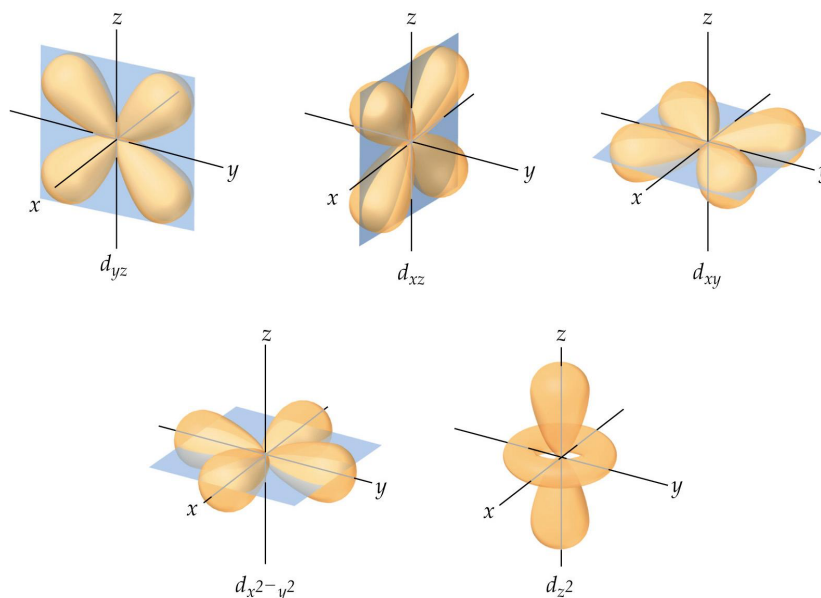
As one might know, the wavelength of light corresponds to the *colour* of that light. Hence, the energy of a photon depends on its colour.

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



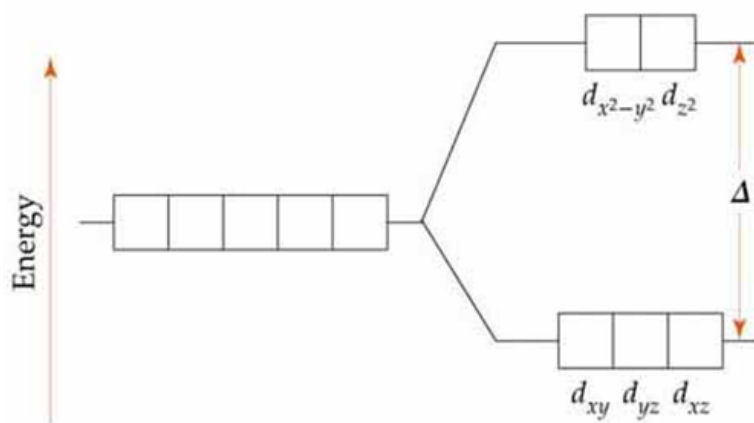
The 5 orbitals in the d subshell.

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.

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.





The 5 degenerate orbitals are split, into 2 and 3.

### 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  $\Delta E$ , 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  $\Delta E$  for many complexes lie within the wavelength of visible light, so many of them appear coloured.

If  $\Delta E$  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  $\text{MnO}_4^-$ , 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  $\Delta E$  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  $\Delta E$ .

Note that  $\text{Sc}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Cu}^+$  and  $\text{Zn}^{2+}$  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  $\Delta E$ . 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.