PERIOD 3 : INORGANIC CHEMISTRY

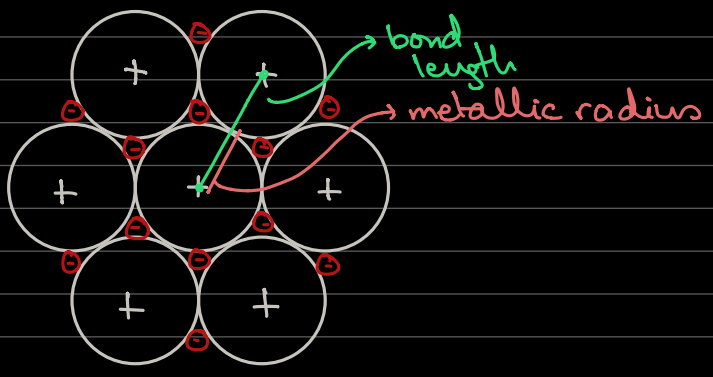
Na	Mg	Al	Si	P	S	Cl	Ar
11	12	13	14	15	16	17	18

Metals — Metalloid — Non-metals

Trends in physical properties across the period

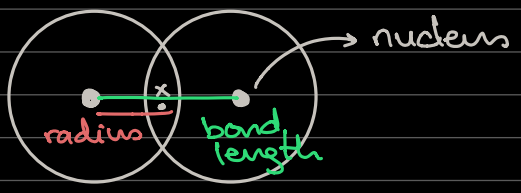
1. Atomic and Ionic Radii
   - Metals have metallic radii
   - Non-metals (other than Ar) have covalent radii
   - Ar has van der waals radius

Metallic Radius



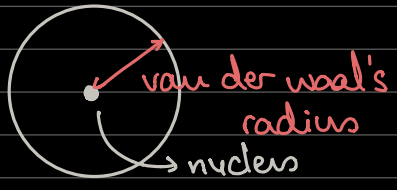
Metallic radius = $\frac{\text{Bond length}}{2}$

Covalent Radius



Covalent radius = $\frac{\text{distance bw. nuclei}}{2}$

Van der Waal's radius



Atomic Radii

→ Atomic radius decreases across the period

- As proton number increases, electrons enter the same shell and are at the same distance from the nucleus

↳ But the nuclear charge increases, so the outer electrons feel a greater nuclear charge and the electron cloud shrinks, decreasing the atomic radius

Ionic Radii

CATIONS

- Metals form cations by losing electrons

$Na \longrightarrow Na^{+} + e^{-}$
$Mg \longrightarrow Mg^{2+} + 2e^{-}$
$Al \longrightarrow Al^{3+} + 3e^{-}$
$Si \longrightarrow Si^{4+} + 4e^{-}$

- Cation radius is smaller than the corresponding atomic radius as the cation has one less shell of electrons than the neutral atom

- And the remaining electrons feel a greater effective nuclear charge as there are more protons than electrons

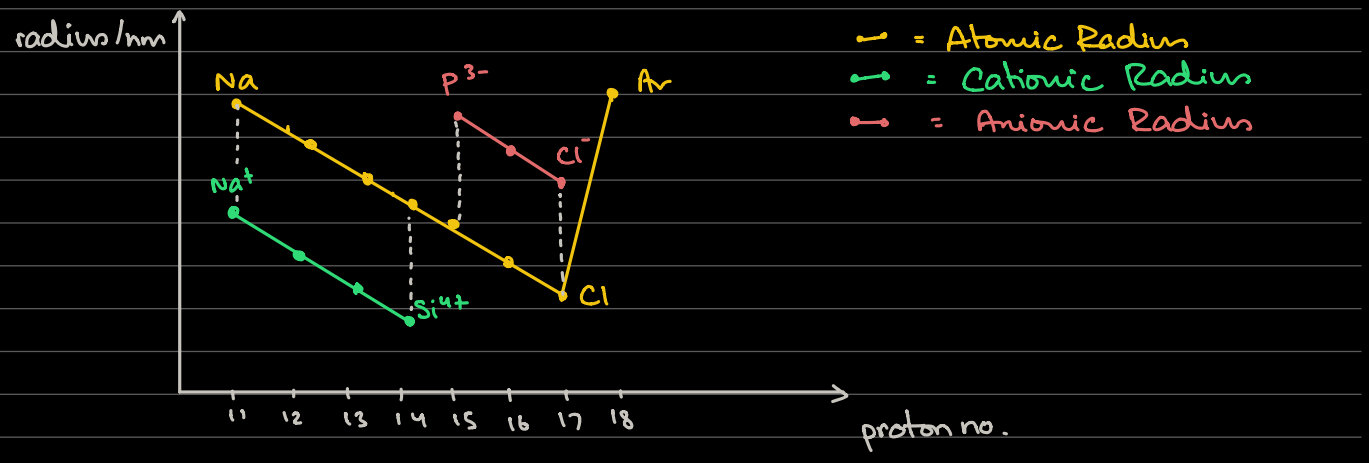
ANIONS

- Anionic radii are larger than their atomic radii

- Anions have more electrons than protons, hence the attractive force on the outer (valence) electrons is less than that in the neutral atom

↳ the outer electrons are held less tightly, and the electron cloud expands

- Anions are bigger than cations, as anions have one extra shell of electrons



2. Melting Point

- Melting point depends on the bonds that must be weakened and broken for melting, and then boiling, to take place.

- Na, Mg, Al have a giant metallic structure with strong metallic bonds

  ↳ Metallic bonds become stronger when the number of electrons available to the "sea of delocalised electrons" increase

  - Metallic bonds are also stronger when the atomic radius is smaller

Na Mg Al | Si | P_4 S_8 Cl Ar

Metals
- Giant metallic structure
- metallic bonds

Metalloid
- Giant covalent structure
- Covalent bonds

Non-metals
- Simple molecular
- Covalent bonds

Na, Mg, Al

- Na < Mg < Al ↦ Melting points

From Na → Al, the melting point increases as the metallic bonds become stronger, so more energy is required to break them

Silicon

- Si has an even higher melting point than Aluminium, as it has a giant covalent structure and a lot of energy is required to break the strong covalent bonds

P_4, S_8, Cl_2, Ar

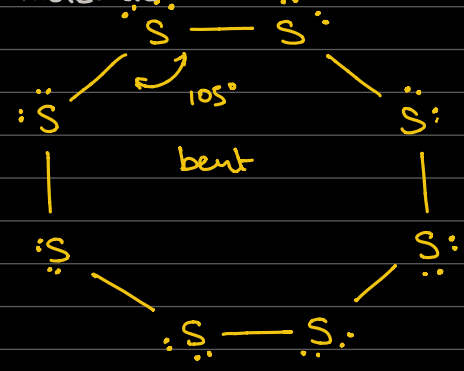
- non-polar
- ID-ID forces of attraction between the molecules

Ar < Cl_2 < P_4 < S_8 ↦ Melting points

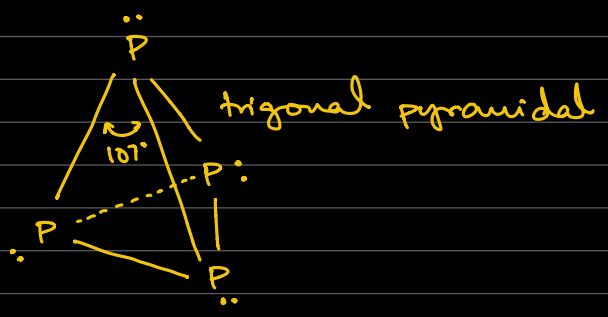
- Melting point depends on the strength of the ID-ID forces of attraction

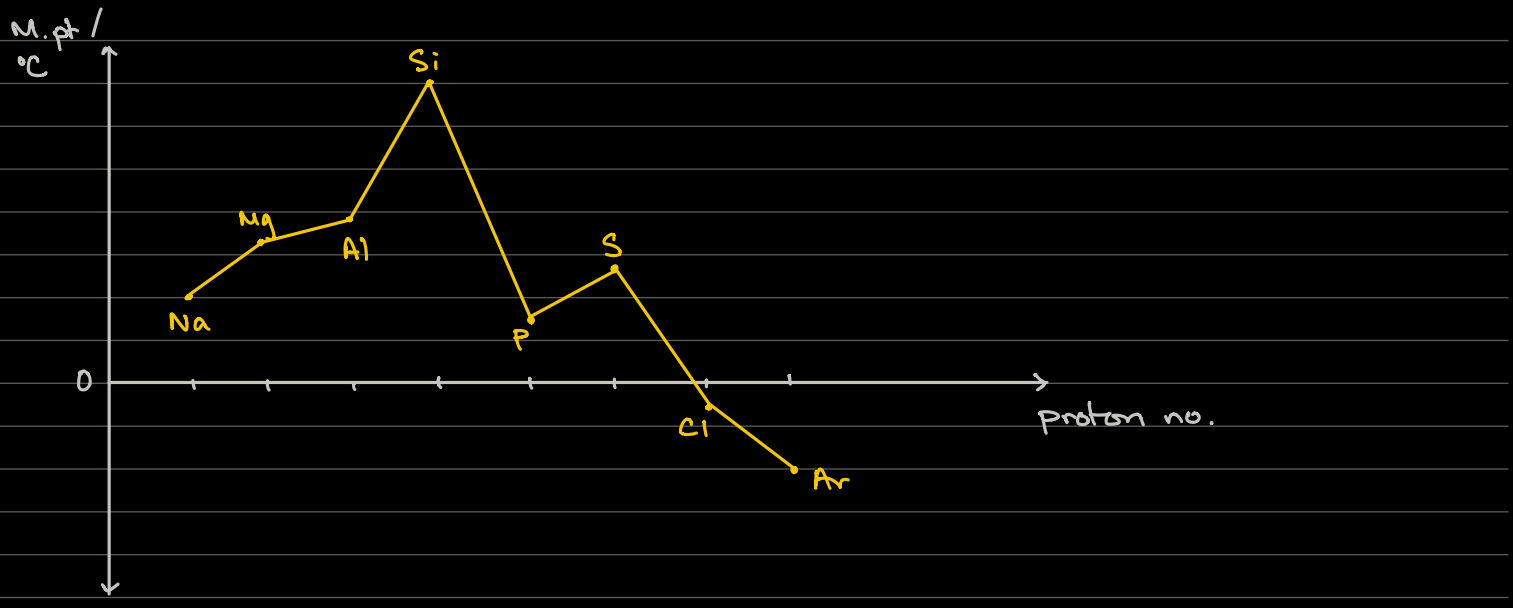
- S_8 has the highest melting point as it has the highest Mr, more polarisable electrons, which makes ID-ID the strongest

S_8 molecule:



P_4 molecule:





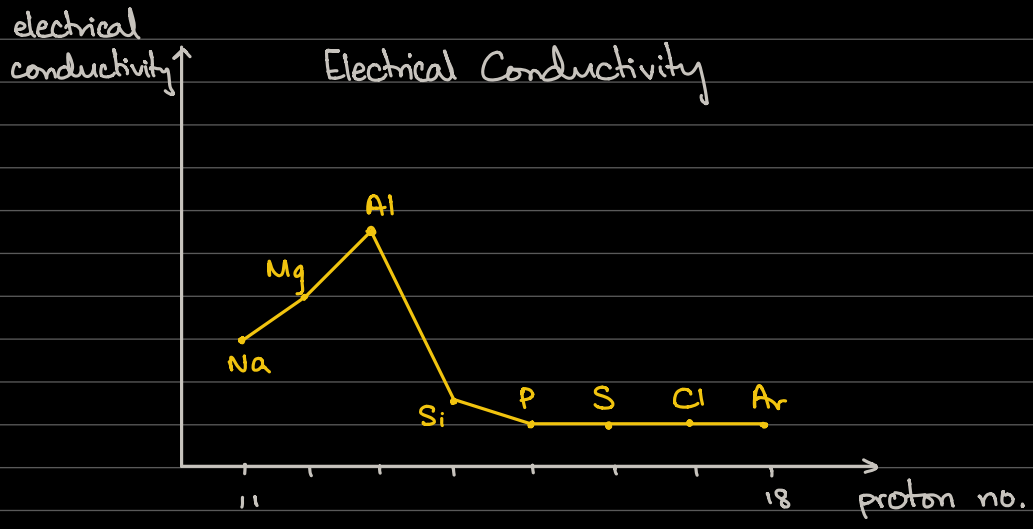
- The melting point of Al is only slightly higher than that of Mg, as the metallic bond in aluminum is only slightly stronger
  - ↳ because Al has a smaller metallic radius and therefore a high charge density, so it tends to attract the sea of delocalised back towards itself, which reduces the strength of the metallic bond.

3. Electrical Conductivity

Na Mg Al	Si	P S Cl Ar
· good conductors because they have mobile / delocalised electrons to carry charge		· low conductivity / non-conductors · simple molecular · no free electrons to carry charge

- moderate conductivity
- semiconductor
- metalloid
- It conducts when other metals are added to it as impurities

Na → Al conductivity increases, as Al has more electrons available in the sea of delocalised electrons



4. 1st Ionisation Energy
— Already done previously

CHEMICAL PROPERTIES OF PERIOD 3 ELEMENTS

1. Reaction of the elements with oxygen

SODIUM (Na)

$4Na + O_2 \xrightarrow{\text{burn}} 2Na_2O$ Ionic Oxide
↳ white solid

- Na burns with a yellow flame
- Na_2O, a white ionic oxide is formed
- Na tarnishes when exposed to air at RTP (passive oxidation)

MAGNESIUM (Mg)

$2Mg + O_2 \xrightarrow{\text{burn}} 2MgO$ Ionic Oxide
↳ white ash

- Mg burns with an intense (bright) white flame
- Superficial oxidation (ie. just on the surface) occurs at RTP

ALUMINUM (Al)

$4Al + 3O_2 \longrightarrow 2Al_2O_3$ Ionic Oxide
↳ white solid

- Burns with a white flame
- Superficial oxidation at RTP

SILICON (Si)

$Si + O_2 \xrightarrow[\text{strongly}]{\text{heat}} SiO_2$ Covalent oxide
↳ white solid

- no reaction at RTP

PHOSPHOROUS (P)

$P_4 + \underset{\text{excess}}{5O_2} \xrightarrow{\text{burn}} P_4O_{10}$ Covalent Oxide
↳ dense white fumes

- burns with a white flame
- P_4O_{10} is one of the more stable oxides that P forms
  ↳ phosphorous (V) oxide

$P_4 + \underset{\text{limited}}{3O_2} \xrightarrow{\text{burn}} P_4O_6$ Covalent Oxide
↳ phosphorous (III) oxide

SULFUR (S)

$S + O_2 \xrightarrow{\text{burn}} SO_2$ Covalent oxide (stable)

- burns with a blue flame

$2SO_2 + O_2 \rightleftharpoons 2SO_3$ use excess oxygen and V_2O_5 as catalyst

CHLORINE (Cl)
ARGON (Ar) → No reaction

OXIDATION STATES OF THE OXIDES

- Correspond to the number of valence electrons used for bonding by the metal
- Oxidation state increases to a maximum across the period

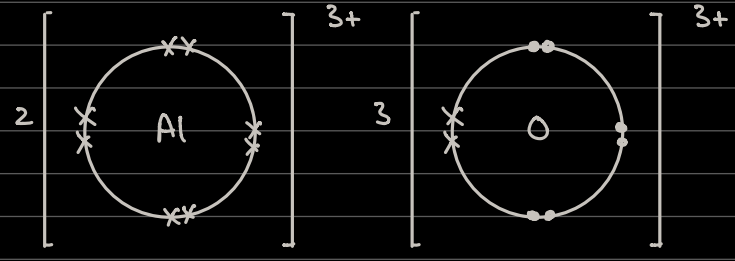
$\overset{+1}{Na_2}\overset{-2}{O}$ $\overset{+2}{Mg}\overset{-2}{O}$ $\overset{+3}{Al_2}\overset{-2}{O_3}$ $\overset{+4}{Si}\overset{-2}{O_2}$ $\overset{+3}{P_4}\overset{-2}{O_6}$ $\overset{+5}{P_4}\overset{-2}{O_{10}}$ $\overset{+4}{S}\overset{-2}{O_2}$ $\overset{+6}{S}\overset{-2}{O_3}$ $\overset{+7}{Cl_2}\overset{-2}{O_7}$ (not by burning)

2. Reactions of the oxides with water

	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6 / P_4O_{10}	SO_2 / SO_3
type	Giant Ionic	Giant Ionic	Ionic, with some covalent character	Giant Covalent	← Simple Molecular →	
nature	Basic	Basic	Amphoteric	Acidic	Acidic	Acidic
pH in water	Alkaline ~13	Slightly Alkaline ~9	Insoluble ↑ in water ↑	Insoluble	Strongly Acidic ~2	Strongly Acidic ~2

- Na_2O and MgO are purely ionic compounds

but Al_2O_3 is ionic but with some covalent character



- Al^{3+} has a small ionic radius and a higher charge (+3), so it has a high charge density.
  - ↳ the Al^{3+} ion pulls the electron density back from the oxide ion, so Al_2O_3 ends up with a partial covalent character

SODIUM (Na_2O)

$$Na_2O + H_2O \longrightarrow 2NaOH$$

↳ alkaline solution of pH ~ 13-14

MAGNESIUM (MgO)

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

dissolves partially, pH ~9

ALUMINUM (Al_2O_3)
SILICON (SiO_2)
→ No rxn

PHOSPHOROUS (P_4O_6, P_4O_{10})

$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$ phosphorous acid pH ~ 2
$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$ phosphoric acid pH ~ 2

SULFUR (SO_2, SO_3)

$SO_2 + H_2O \longrightarrow H_2SO_3$ sulfurous acid pH ~ 1-2
$SO_3 + H_2O \longrightarrow H_2SO_4$ sulfuric acid pH ~ 1-2

↳ Highly exothermic

CHLORINE (Cl_2O_7)

$Cl_2O_7 + H_2O \rightleftharpoons 2HClO_4$ chloric (VII) acid

$Cl_2O + H_2O \rightleftharpoons 2HClO$ hypochlorous acid

3. Acid-Base reactions of the oxides

BASIC OXIDES react with acids to form salt and water

$Na_2O + 2HCl \longrightarrow 2NaCl + H_2O$

$Na_2O + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O$

$Na_2O + 2CH_3COOH \longrightarrow 2CH_3COONa + H_2O$

$MgO + 2HCl \longrightarrow MgCl_2 + H_2O$

$MgO + H_2SO_4 \longrightarrow MgSO_4 + H_2O$

$MgO + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2O$

AMPHOTERIC OXIDES react with both acids and alkali

$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + H_2O$
as base

$Al_2O_3 + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$
as base

$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2NaAl(OH)_4$
as acid — hot conc. — tetrahydroxy sodium aluminate

ACIDIC OXIDES react with bases to form salt and water

$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$
hot conc. — Sodium Silicate

$SiO_2 + CaO \longrightarrow CaSiO_3$
Calcium Silicate (slag)

$P_4O_6 + 12NaOH \longrightarrow 4Na_3PO_3 + 6H_2O$
sodium phosphite

$P_4O_{10} + 12NaOH \longrightarrow 4Na_3PO_4 + 6H_2O$
sodium phosphate

$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$
Sodium sulfite

$SO_3 + 2NaOH \longrightarrow Na_2SO_4 + H_2O$

sodium sulfate

$Cl_2O_7 + 2NaOH \longrightarrow 2NaClO_4 + H_2O$

sodium chlorate (VII)

4. Reactions of the elements with chlorine gas to form chlorides

SODIUM (Na)

$2Na(s) + Cl_2(g) \xrightarrow{heat} 2NaCl(s)$ ionic

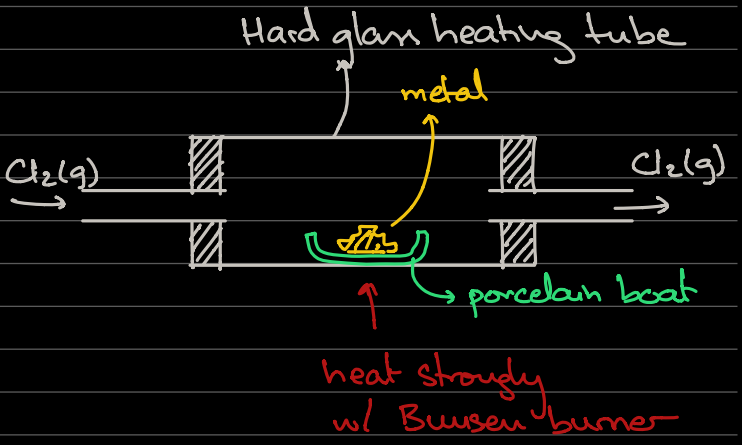
↳ white solid

↳ burns in chlorine with an orange flame

MAGNESIUM (Mg)

$Mg(s) + Cl_2(g) \xrightarrow{heat\ strongly} MgCl_2(s)$

↳ burns in chlorine with a bright white flame



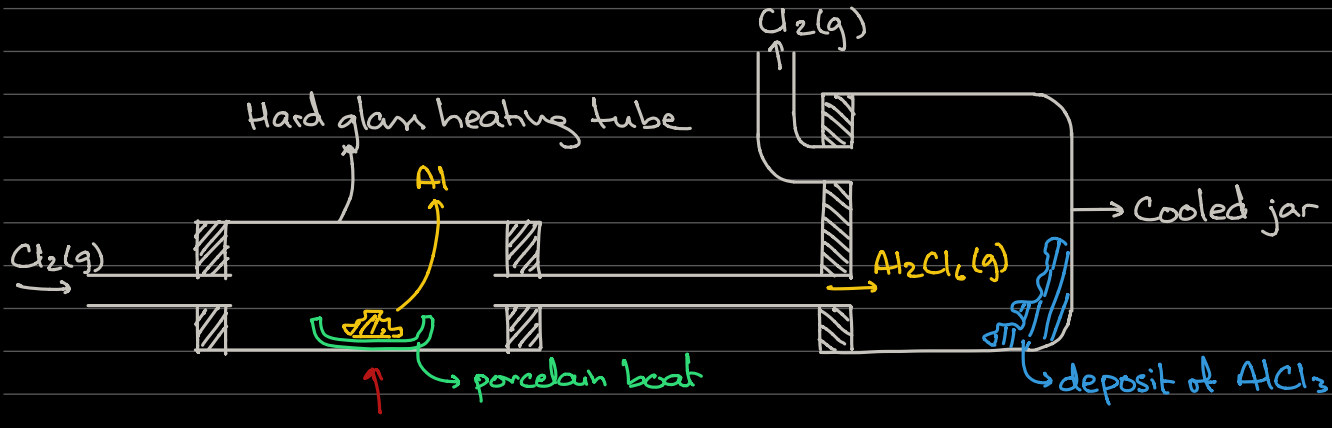
ALUMINUM (Al)

$2Al + 3Cl_2 \longrightarrow Al_2Cl_6(g)$ gas phase

↓ deposits

$2Al + 3Cl_2 \xrightarrow{RTP} 2AlCl_3(s)$

pale yellow solid



heat strongly w/ Bunsen burner

$$Al + Cl_2 \xrightarrow[\text{sublimes}]{180^\circ C} Al_2Cl_6\,(g) \xrightarrow[800^\circ C - 1000^\circ C]{\text{heat}} 2AlCl_3\,(g)$$

dimer

- $AlCl_3$ dimerises in the vapor phase to Al_2Cl_6 (at the sublimation temperature) and the dimer is held together by covalent (dative) bonds.
- $AlCl_3$ has a little bit of covalent character (explained previously)

SILICON (Si)

$$Si + 2Cl_2 \xrightarrow{\text{heat}} SiCl_4$$

Covalent chloride
liquid, collect by condensation

PHOSPHOROUS (P)

$$P_4 + 6Cl_2 \xrightarrow{\text{heat}} 4PCl_3$$

colourless, "fuming" liquid

$$PCl_3 + Cl_2 \xrightarrow{\text{heat}} PCl_5\,(s)$$

white, stable solid

Directly: $P_4 + 10Cl_2 \xrightarrow{\text{heat}} 4PCl_5\,(s)$

SULFUR (S)

$$2S + Cl_2 \xrightarrow{\text{heat}} S_2Cl_2$$

yellow solid

Disulfur dichloride
foul smelling orange liquid

5. Reactions of the chlorides with water

	$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3 / PCl_5	S_2Cl_2
Structure	Giant ionic with ionic bonds		Simple molecular / covalent bonds Small discrete molecules with van der waal's forces			

Melting Point	High	Sublimes at 180°C	Low melting points except for PCl_5, which is a solid
Effect of Water	Dissolve readily in water • pH = 7 • neutral solution	• pH ~ 6-5 • slightly acidic	Hydrolyse in water to give fumes of HCl pH ~ 3
			pH ~ 1-2

Why the difference in pH bw. NaCl and $MgCl_2$ in water?

$$NaCl(s) + (aq) \xrightarrow{\text{dissolves}} Na^+(aq) + Cl^-(aq) \quad pH\ 7$$

$$MgCl_2(s) + (aq) \xrightarrow{\text{dissolves}} Mg^{2+}(aq) + 2Cl^-(aq)$$

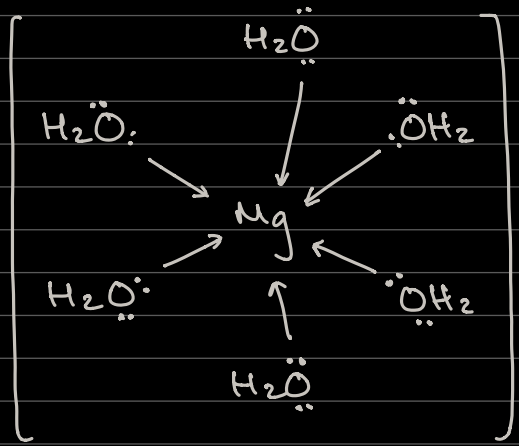
- Mg^{2+} is smaller than Na^+ and its surrounded by water molecules to form a complex ion
- Because it has a high charge density, it polarises water molecules and causes them to give up hydrogen ions, thus making the solution acidic

$$MgCl_2(s) + 6H_2O \rightleftharpoons [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$$

Complex ion
Hexa aqua magnesium (II)

$$[Mg(H_2O)_6]^{2+} \rightleftharpoons [(MgCH_2O_5)(OH)]^+ + H^+(aq)$$

↳ this makes the solution acidic
pH ~ 6.5



Dative bonds from H_2O to Mg^{2+}

what about the pH of $AlCl_3$?

- $AlCl_3$ hydrolyses in water to a greater extent, as the charge density of Al^{3+} is higher than that of Mg^{2+}

cation anion

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

$$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$$

more acidic pH ~ 3 as the concentration of H^+ is greater so pH is lower (more acidic)

- the highly charged Al^{3+} ion polarises water and makes it give up the H^+ ions to make the solution acidic

what about $SiCl_4$? (Important)

- Hydrolyses completely in water to give a strongly acidic solution

$$SiCl_4 + 2H_2O \longrightarrow \underset{\text{white ppt.}}{SiO_2(s)} + \underset{\text{white fumes}}{4HCl(g)}$$

PCl_3 and PCl_5:

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$
$$PCl_5 + 4H_2O \longrightarrow H_3OPO_4 + 5HCl$$

→ strongly acidic solutions

S_2Cl_2?

- very slow reaction with water
- forms decomposition products

$$S_2Cl_2 + H_2O \xrightarrow{\text{slow rxn.}} \underset{\text{white fumes}}{HCl(g)} + \underset{\text{yellow solid}}{S(s)} + \underset{\text{foul smelling gas}}{H_2S(g)}$$

and other products containing S

6. Reactions of the elements with water

SODIUM (Na)

$$2Na + 2H_2O \xrightarrow{rtp} 2NaOH + H_2$$

Observations:
- Violent reaction
- Na piece darts about the surface
- Na melts/dissolves
- Colourless gas evolved
- Alkaline solution is formed

MAGNESIUM (Mg)

$$Mg(s) + 2H_2O(l) \xrightarrow{rtp} Mg(OH)_2 + H_2$$

↳ $Mg(OH)_2$ forms a thin layer on the surface of Mg, therefore slowing down the reaction

$$Mg(s) + 2H_2O(g) \longrightarrow MgO(s) + H_2(g)$$

ALUMINUM (Al)

$$Al + H_2O(g) \xrightarrow{heat} Al_2O_3 + 3H_2(g)$$

$$Al + H_2O(l) \xrightarrow{rtp} \text{no rxn}$$

SILICON (Si)
PHOSPHOROUS (P)
SULFUR (S)
→ No rxn with water

CHLORINE (Cl)

$$Cl_2(g) + H_2O(l) \rightleftharpoons HCl + HOCl$$