

5.1 The Periodic Table: chemical periodicity

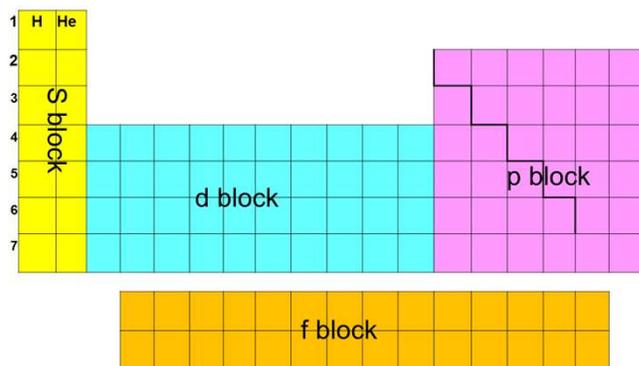
Periodicity is the repeating pattern of physical or chemical properties going across the periods

Classification of elements in s, p, d blocks

Elements are classified as s, p or d block, according to which orbitals the highest energy electrons are in.

Period 2 = Li, Be, B, C, N, O, F, Ne

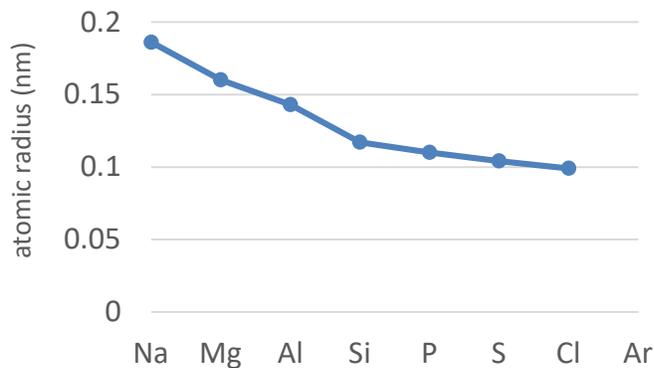
Period 3 = Na, Mg, Al, Si, P, S, Cl, Ar



Atomic radius

The atomic radii of the period 3 elements **decrease** going from left to right across a period. This is because the **increased number of protons** create more positive charge attraction for **electrons, which are in the same shell** with similar shielding.

There is exactly the same trend shown in period 2



Ionic radius

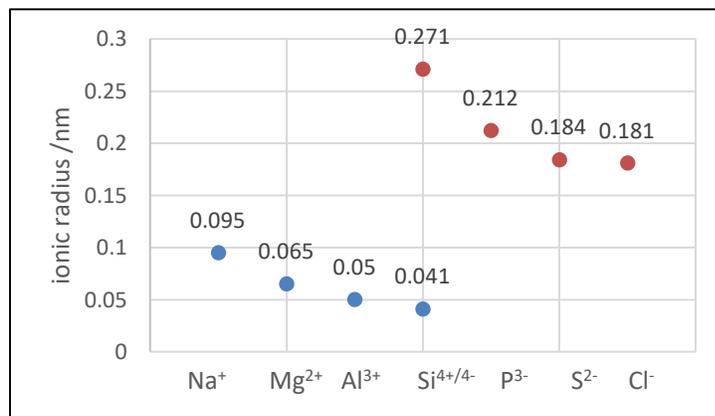
Na^+ Mg^{2+} Al^{3+} Si^{4+} all have the same electronic structure (of the noble gas Ne)

There are increasing numbers of protons from Na to Si but the same number of electrons. The effective nuclear attraction per electron therefore increases and ions get smaller.

Positive ions are smaller compared to their atoms because they have one less shell of electrons and the ratio of protons to electrons has increased. Therefore there is a greater net force on the remaining electrons holding them more closely.

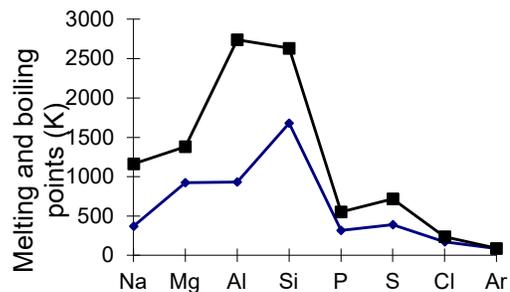
Similarly Si^{4-} P^{3-} S^{2-} Cl^- all have the same electronic structure (of the noble gas Ar)

There are increasing numbers of protons from Si to Cl but the same number of electrons. The effective nuclear attraction per electron therefore increases and ions get smaller.



Melting and boiling points of period 3 elements.

For **Na, Mg, Al**- these all have metallic bonding : This is strong bonding hence the high melting points. The metallic bonding gets stronger the more electrons there are in the outer shell that are released to the sea of delocalised electrons. The successive ions are also smaller and have more protons. There is therefore a stronger electrostatic attraction between the positive metal ions and the delocalised electrons and higher energy is needed to break bonds.



Si is macromolecular: It has many strong covalent bonds between atoms. High energy is needed to break the many covalent bonds so silicon has a very high melting point and boiling point



Similar trend in period 2

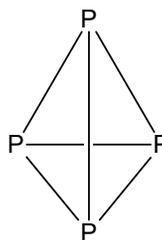
Li, Be have metallic bonding with high melting points
B,C are macromolecular substances with very high melting points.

N₂, O₂ are molecular gases with low melting points because they have small London intermolecular forces.
Ne monoatomic gas (very low mp)

Cl₂(g), S₈(s), P₄(s) are all **simple molecular** substances :
There are weak **London intermolecular forces between molecules**, so little energy is needed to break them resulting in low melting points and boiling points.

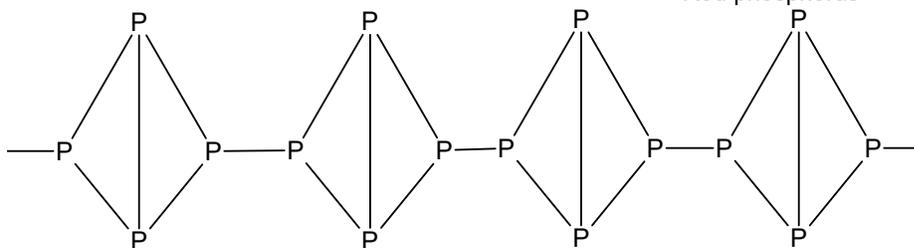
Allotropes of Phosphorus

White phosphorus has the formula P₄ and is simple molecular. It is highly reactive and spontaneously combustible in air. It was used in incendiary bombs in the second world war.

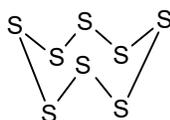


Red phosphorus

Red phosphorus is macromolecular and has a higher melting point. It is still reactive and reacts with oxygen, but it is not spontaneously combustible.



Sulfur in its S₈ form has a higher melting point than P₄ because it has more electrons (S₈=128)(P₄=60) so has stronger London forces between molecules.



Argon is monoatomic and only has very weak London forces between atoms.



Electrical conductivity

Elements with metallic bonding

Sodium, magnesium and aluminium are all good conductors of electricity. The conductivity increases as you go from sodium through to aluminium, as they have successively more delocalized electrons per atom.

Macromolecular

Silicon is a semiconductor.

Simple molecular P₄ S₈ Cl₂, mono atomic Ar

These do not conduct electricity. There are no free electrons to move.

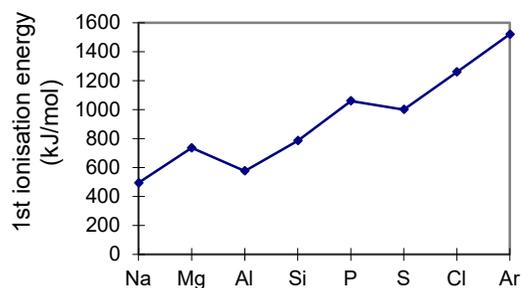
1st ionisation energy

The general trend across the period is to increase. This is due to increasing number of protons as the electrons are being added to the same shell.

There is a small drop between magnesium and aluminium. Magnesium has its outer electrons in the 3s sub shell, whereas aluminium is starting to fill the 3p subshell. Aluminium's outer electron is slightly easier to remove because the 3p electrons are higher in energy.

There is a small drop between phosphorous and sulfur. Sulfur's outer electron is being paired up with another electron in the same 3p orbital.

When the second electron is added to an orbital, there is a slight repulsion between the two negatively charged electrons which makes the second electron easier to remove.



Exactly the same trend in period 2 with drops between Be & B and N to O for same reasons- make sure change 3s and 3p to 2s and 2p in explanation!

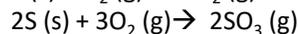
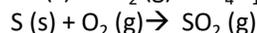
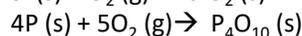
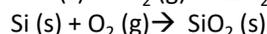
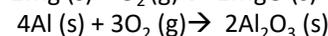
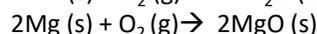
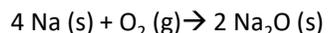
Trends in the reactions of the elements Na, Mg, Al, Si, P and S with oxygen

The elements all react with oxygen to form oxides.

Sodium burns with a **yellow flame** to produce a **white solid**.

Magnesium, aluminium, silicon and phosphorus all burn with a **white flame** to give **white solid** smoke.

Sulfur burns with a **blue flame** to form an acidic **choking gas**.



Sodium is stored under oil and white phosphorus under water. This is to stop these elements coming into contact and reacting with air.

Note: the highest oxidation number of the element in the oxide is the same as the number of valence electrons in the element

oxide	O.N.
Na ₂ O	+1
MgO	+2
Al ₂ O ₃	+3
SiO ₂	+4
P ₄ O ₁₀	+5
SO ₃	+6

A survey of the properties of the oxides of Period 3 elements

Ionic oxides

The metal oxides (Na_2O , MgO , Al_2O_3) are ionic. They have high melting points. They have **ionic giant lattice structures**: strong forces of attraction between ions and so have high melting points. They are ionic because of the large electronegativity difference between the metal and oxygen.

The increased charge on the cation from sodium to aluminium makes the ionic forces stronger (bigger lattice enthalpies of dissociation) going so leading to increasing melting points.

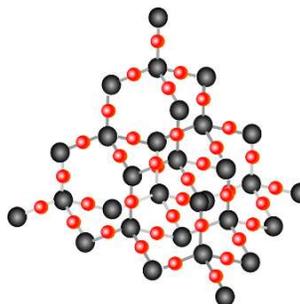
Aluminium oxide (Al_2O_3) is ionic but does show some covalent character. This can be explained by the electronegativity difference being less big or alternatively by the small aluminium ion with a high charge being able to get close to the oxide ion and distorting the oxide charge cloud.

Aluminium metal is protected from corrosion in moist air by a thin layer of aluminium oxide. The high lattice strength of aluminium oxide and its insolubility in water make this layer impermeable to air and water.

Macromolecular oxides

Silicon dioxide, SiO_2 , is macromolecular: it has a tetrahedral arrangement. Each silicon atom forms 4 covalent bonds to an oxygen. Each oxygen forms two covalent bonds to silicon

It has many very strong covalent bonds between atoms. High energy is needed to break the many strong covalent bonds. It therefore has a very high melting point.



Ceramics

Magnesium oxide (giant ionic), aluminium oxide (giant ionic) and silicon dioxide (giant covalent) can all be classed as ceramics. They have important properties in common that are useful.

High melting points and strength - high

For ionic ones the melting points are high because of giant lattice of ions with strong electrostatic forces between oppositely charged ions.

For giant covalent ones- high- because of many strong covalent bonds in macromolecular structure. It takes a lot of energy to break the many strong bonds .

Electrical conductivity –low

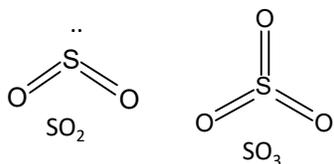
For ionic ones poor: the ions can't move and are fixed in the lattice

For giant covalent ones- poor, because electrons cannot move (localised)

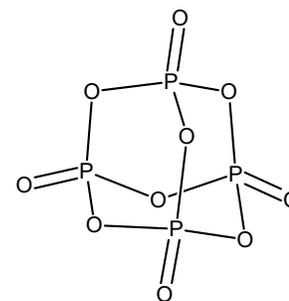
Simple molecular oxides:

Solid phosphorus(V) oxide, P_4O_{10} , and gaseous sulfur dioxide, SO_2 , are simple molecular substances with weak intermolecular forces between molecules (London forces+ permanent dipoles forces) so they have lower melting points than the other period 3 oxides. They are covalent because of the small electronegativity difference between the non-metal and oxygen atoms.

Phosphorus(V) oxide is a molecule containing 4P's and 10 O's. As phosphorus(V) oxide is a bigger molecule and has more electrons than SO_2 it will have larger London forces between molecules and a higher melting point.

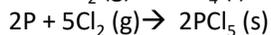
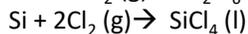
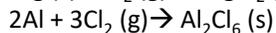
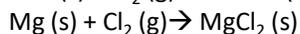
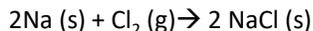


P_4O_{10} is commonly called phosphorus pentoxide but actually contains 10 oxygens



Reactions of the elements Na, Mg, Al, Si, P and S with chlorine

The elements of period 3 all react with chlorine to form chlorides.



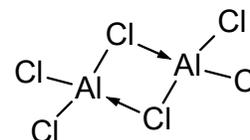
Note: the highest oxidation number of the element in the chloride is the same as the number of valence electrons in the element

oxide	O.N.
NaCl	+1
MgCl ₂	+2
Al ₂ Cl ₆	+3
SiCl ₄	+4
PCl ₅	+5

Bonding in period 3 chlorides

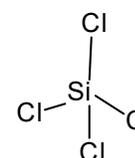
The metal chlorides (Na and Mg) are ionic. Ionic giant lattice structures have strong forces of attraction between oppositely charged ions so these chlorides have higher melting points than the other period 3 chlorides.

Aluminium chloride is a simple covalent molecule because of the relatively small difference in electronegativity between aluminium and chlorine. Aluminium chloride exists as a dimer Al₂Cl₆

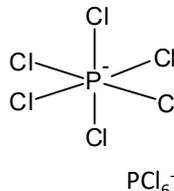
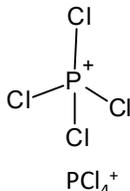
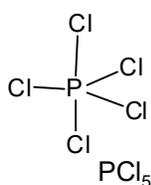


The non-metal chlorides are simple molecular

Silicon tetrachloride (SiCl₄) is simple molecular. It has weak intermolecular forces (London forces) so has a lower melting point than the other period 3 chlorides.

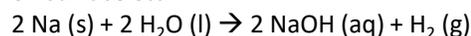


Phosphorus pentachloride (PCl₅) has a higher than expected melting point because in solid phase it exists as an ionic structure of PCl₄⁺ PCl₆⁻

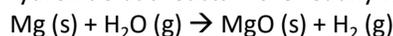


Trends in the reactions of the elements with water, limited to sodium and magnesium

Sodium reacts with cold water. It fizzes around on surface etc.



Magnesium reacts very slowly with cold water to form the hydroxide but reacts more readily with **steam** to form the oxide.

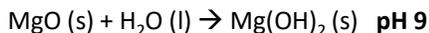


The reactions of the oxides of the elements Na → S with water

Metal ionic oxides tend to react with water to form hydroxides which are alkaline.



The ionic oxides are basic as the oxide ions accept protons to become hydroxide ions in this reaction (acting as a bronsted lowry base).



Mg(OH)_2 is only slightly soluble in water as its lattice is stronger so there are fewer free OH^- ions produced and so lower pH.

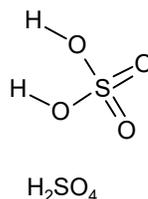
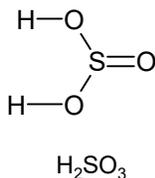
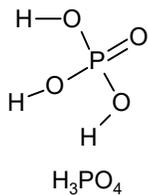
Magnesium oxide, MgO , and magnesium hydroxide, Mg(OH)_2 , are better than sodium hydroxide, NaOH , for treating acid in rivers and the stomach because they are only sparingly soluble and weakly alkaline. Using an excess of magnesium hydroxide would not make the water excessively alkaline.

Al_2O_3 and SiO_2 **do not dissolve** in water because of the high strength of the Al_2O_3 ionic lattice and the SiO_2 macromolecular structure, so they give a neutral **pH 7**

The non-metal, **simple molecular**, covalent, oxides react with water to produce acids.



Equations showing
formation of ions in
solution



Displayed formulae of acids



Reaction of P_4O_{10} with water

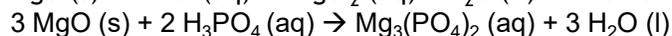
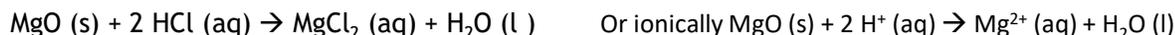
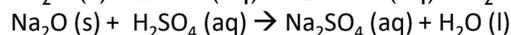
The overall trends are:

- **ionic metal oxides** show **basic** behaviour
- **non-metal covalent** oxides show **acidic** behaviour.

The slightly intermediate nature of the bonding in aluminium oxide is reflected in its amphoteric behaviour: it can act as both a base and an acid.

Acid base reactions between period 3 oxides and simple acids and bases.

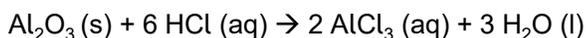
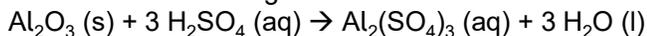
The **basic oxides** react with acids to make salts



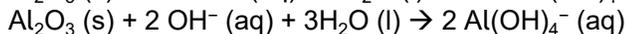
Amphoteric Oxides

Aluminium oxide can act as both an acid and an alkali and is therefore called amphoteric

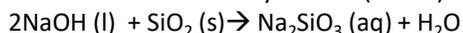
Aluminium oxide acting as a **base**



Aluminium oxide acting as a **acid**.

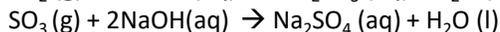
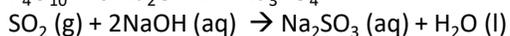
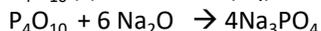
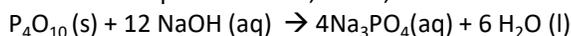


Silicon dioxide (SiO_2) has a **giant covalent structure** with very strong covalent bonds. This stops SiO_2 dissolving or reacting with water and weak solutions of alkali. It will, however, react with very concentrated sodium hydroxide (NaOH).

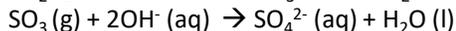
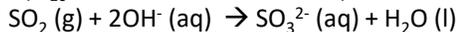
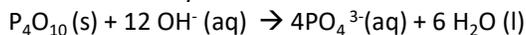


It is still classed as an acidic oxide

The other simple molecular, acidic, oxides react with bases to form salts.

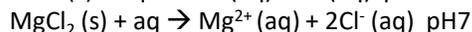
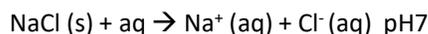


Or show ionically



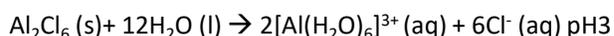
The reactions of the chlorides of the elements Na → P with water

The ionic chlorides e.g. sodium and magnesium **dissolve** (and not hydrolyse) in water to form aqueous ions and **neutral** solutions.

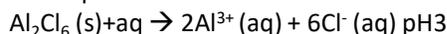


The covalent chlorides **react with water (hydrolyse)** to form **acidic** solutions.

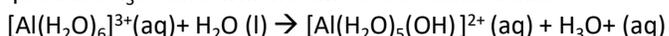
Aluminium chloride has covalent character. It dissolves in water to form an acidic solution. (Unlike Na and Mg which form neutral solutions when they dissolve in water.)



Or simplified to



The $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ then reacts (hydrolyses) with water to produce H_3O^+ ions which make the solution acidic



Note: Aluminium acts more like the non-metals because its chloride is covalent.

$\text{SiCl}_4 (\text{l}) + 4\text{H}_2\text{O} (\text{l}) \rightarrow \text{Si}(\text{OH})_4 (\text{s}) + 4\text{H}^+ (\text{aq}) + 4\text{Cl}^- (\text{aq}) \quad \text{pH}0$
Observation: this is a vigorous exothermic reaction and a white solid/gel forms.

$\text{PCl}_5 (\text{s}) + 4\text{H}_2\text{O} (\text{l}) \rightarrow \text{H}_3\text{PO}_4 (\text{aq}) + 5\text{H}^+ (\text{aq}) + 5\text{Cl}^- (\text{aq}) \quad \text{pH}0$
Observation: this is a vigorous exothermic reaction.