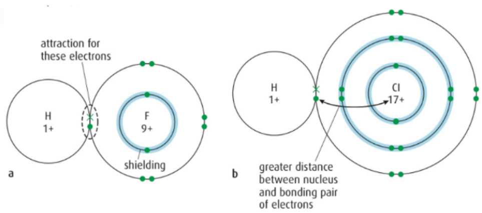
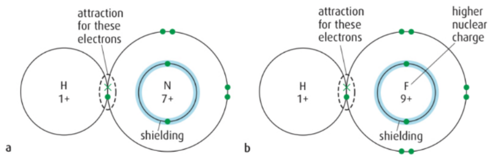
UNIT 9 - PERIODICITY

Physical Properties

<u>Electronegativity</u>



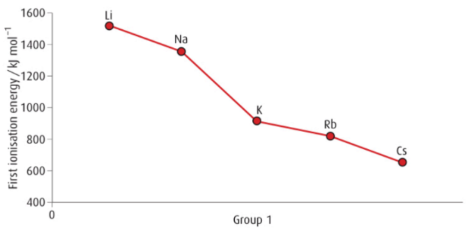


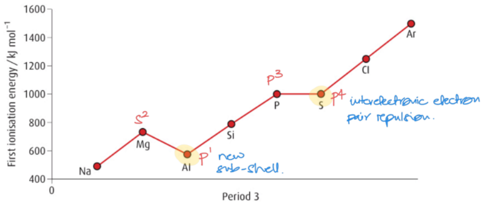
Electronegativity is how strongly the electrons are attracted to the atom's nuclei. It depends on the size of the individual atoms and their nuclear charge.

Electronegativity decreases down a group because:
- Atomic radius increases (number of shells increases)
- The amount of shielding by inner electrons increases
- Nuclear attraction decreases

Electronegativity increases across a period because:
- Atomic radius decreases (the number of shells stays to same but they are pulled closer to the nucleus as nuclear charge increases)
- The amount of shielding by inner electrons stays the same
- Nuclear attraction increases

<u>First Ionisation Energy</u>

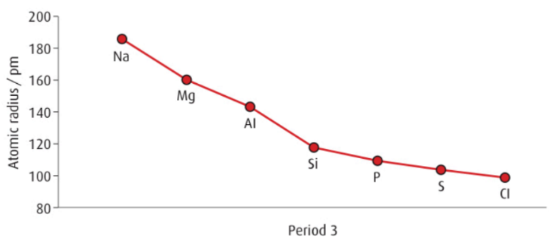


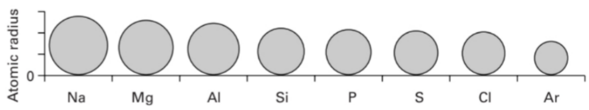


First Ionisation Energy decreases down a group because:
- The size of the atom increases
- outer electron is further away from the nucleus…
- … and is, therefore, less strongly attracted by the nucleus

First Ionisation Energy across a period increases from left to right because:
- Nuclear charge increases
- The electrons are removed from the same energy level
- Shielding is negligible

<u>Atomic Radii</u>



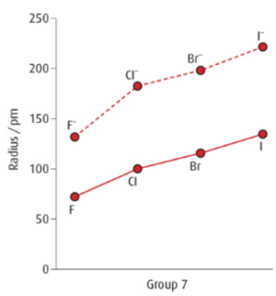


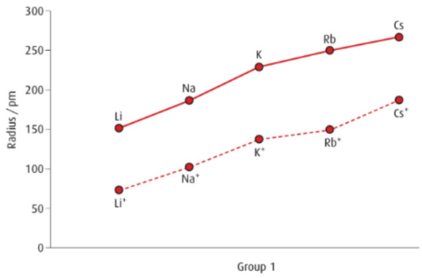
The atomic radii are basically used to describe the size of an atom. The atomic radius is usually taken to be half the internuclear distance in the element.

Atomic radius increases down a group because:
- Atoms have increasingly more electron shells
- Although the nuclear charge is higher, the number of electrons and hence the repulsion between electrons is also greater
- This counteracts the increased number of protons.

Atomic radius decreases across a period because:
- Atoms have the same number of electron shells
- The nuclear charge is higher and so pulls the shells closer to the nucleus
- This reduces the size of the atomic radii

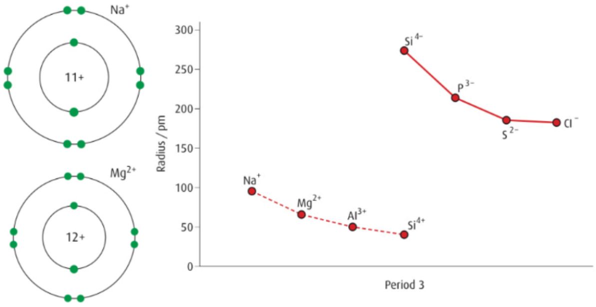
<u>Ionic Radii</u>



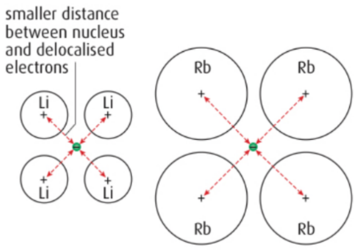


The ionic radius is the measure of the size of an ion. The ionic radii of positive ions are smaller than their atomic radii, and the ionic radii of negative ions are greater than their atomic radii. This is because negative ions gain electrons (so get bigger) and positive ions lose electrons (so get smaller).

The variation of ionic radius across a period is not a clear-cut trend, as the type of ion changes from one side to the other.



Melting point

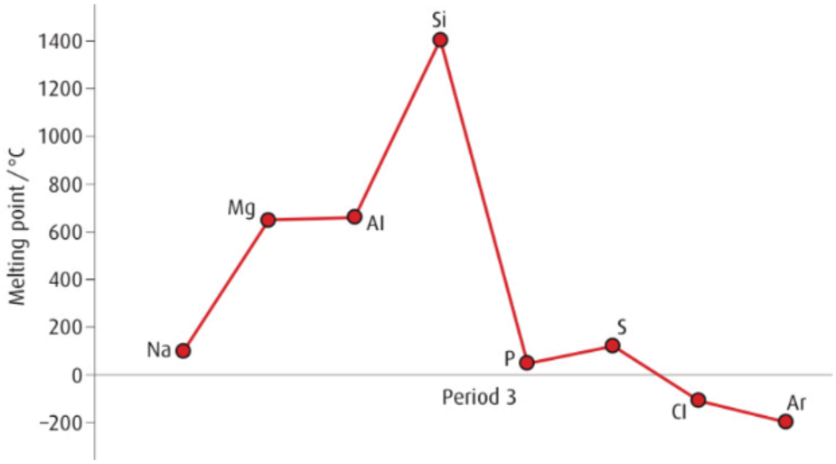


The variation of the melting point of the elements down a group changes from group to group and depends on the type of bonding in the element.

Group 1

The melting point decreases down Group 1. Due to the increase in ionic radii, the distance between the nuclei and delocalised electrons increases.

The melting points across Period 3 are as follows:



	Na	Mg	Al	Si	P	S	Cl	Ar
Melting point (°C)	98	649	660	1410	44	119	−101	−189
Boiling point (°C)	883	1090	2467	2355	280	445	−34	−186
Structure	metallic			giant covalent	covalent molecular			atomic
Species present	Na^+ ions	Mg^{2+} ions	Al^{3+} ions	Si atoms	P_4 molecules	S_8 molecules	Cl_2 molecules	Ar atoms

In Na, Mg and Al, the more electrons an atom contributes from its outermost shell to the shared delocalised electrons, the greater the cation's charge density, the stronger the bonding and the higher the melting point.

Silicon's abnormally high melting point is due to its giant covalent structure as all the covalent bonds have to be broken.

P_4, S_8, Cl_2 & Ar have simple molecular structures held by weak van der Waals' forces forces resulting in low melting points, with S8 having the highest melting point of the four, due to the strongest induced van der Waals' forces as it has the most electrons.

Electrical Conductivity

Sodium, Magnesium, and Aluminum have a trend of increasing conductivity, due to increasing delocalized electrons.

Silicon is a semiconductor due to delocalized electrons present throughout the structure.

Phosphorus (P_4), Sulfur (S_8), Chlorine (Cl_2) and Argon (Ar) have simple molecular structures with no delocalized electrons and hence they do not conduct electricity.

Period 3

Reactions with water

Sodium reacts vigorously with cold water, giving o! hydrogen gas. It quickly dissolves, leaving a strongly alkaline solution of sodium hydroxide behind

$$2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH(aq) + H_{2(g)}$$

Magnesium only reacts very slowly with cold water, to produce hydrogen gas very weakly alkaline solution.

$$Mg_{(s)} + 2H_2O_{(l)} \rightarrow Mg(OH)_{2(aq)} + H_{2(g)}$$

Magnesium reacts vigorously with steam to make MgO and hydrogen gas:

$$Mg_{(s)} + H_2O_{(g)} \rightarrow MgO(s) + H_{2(g)}$$

Reactions with oxygen

All the elements in Period 3 except chlorine and argon react with oxygen directly forming their respective oxides. Oxygen being highly electronegative brings out the highest oxidation number of the elements.

The oxidation number of the element in their oxides is always positive and the maximum oxidation number in the oxide is the same as the Group number, corresponding to the number of electrons in the outermost shell.

ELEMENT	Na	Mg	Al	Si	P	S
FORMULA	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_2, SO_3
OXIDATION #	+1	+2	+3	+4	+5	+4, +6

basic oxide. amphoteric oxide acidic oxide.

Sodium burns vigorously in air with a yellow flame to form sodium oxide.

$$2Na_{(s)} + 1/2\ O_{2(g)} \rightarrow Na_2O_{(s)}$$

Magnesium also reacts vigorously when heated in oxygen with a bright white flame, forming magnesium oxide.

$$Mg_{(s)} + 1/2\ O_{2(g)} \rightarrow MgO_{(s)}$$

Aluminium metal is protected by a layer of aluminium oxide, but powdered aluminium does react well with oxygen and burns with a bright white flame.

$$4Al_{(s)} + 3O_{2(g)} \rightarrow 2Al_2O_{3(s)}$$

Silicon reacts with oxygen slowly when heated to form silicon (IV) oxide.

$$Si_{(s)} + O_{2(g)} \rightarrow SiO_{2(s)}$$

Phosphorus on heating burns with a yellow flame giving out white smoke of phosphorus(V) oxide.

$$P_{4(s)} + 5O_{2(g)} \rightarrow P_4O_{10(s)}$$

Sulphur on heating burns with a blue flame forming sulphur dioxide.

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$$

Sulphur dioxide may be converted to sulphur trioxide by reacting the gas with air in the presence of a catalyst.

$$SO_{2(g)} + 1/2O_{2(g)} \rightarrow SO_{3(g)}$$

ELEMENT	Na	Mg	Al	Si	P	S
FORMULA	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_2, SO_3
OXIDATION #	+1	+2	+3	+4	+5	+4, +6
TYPE	BASIC		AMPHOTERIC		ACIDIC	
BONDING	IONIC			COVALENT		
STRUCTURE	GIANT IONIC				SIMPLE COVALENT	
MELTING POINT	HIGH				LOW	

Oxides – basic, amphoteric, and acidic

Sodium and magnesium oxides produce alkaline solutions with water

$$Na_2O_{(s)} + H_2O_{(l)} \rightarrow 2NaOH_{(aq)}$$

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

$Mg(OH)_2$ is not very soluble in water resulting solution a less alkaline solution.

Both basic oxides dissolve in acids to form salt and water.

$$Na_2O_{(s)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O_{(l)}$$

$$MgO_{(s)} + 2HCl_{(aq)} \rightarrow MgC_{l2(aq)} + H_2O_{(l)}$$

The insoluble oxide of aluminium shows its amphoteric nature by reacting and dissolving in both acidic and alkaline solutions.

$$Al_2O_{3(s)} + 6H^+ \rightarrow 2Al_3^+ + 3H_2O$$

$$Al_2O_{3(s)} + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

$$Al_2O_{3(s)} + 2OH^- + 3H_2O \rightarrow 2Al(OH)_4^-$$

$$Al_2O_{3(s)} + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$$

The covalently bonded non-metal oxides of phosphorus and sulfur dissolve and react in water to form acidic solutions.

$$P_4O_{10(s)} + 6H_2O \rightarrow 4H_3PO_4$$

$$SO_{2(g)} + H_2O \rightarrow H_2SO_3$$

$$SO_{3(g)} + H_2O \rightarrow H_2SO_4$$

These oxides also neutralise alkalis.

$$P_4O_{10(s)} + 12NaOH \rightarrow 4Na_3PO_4 + 6H_2O$$

$$SO_{2(g)} + 2NaOH \rightarrow Na_2SO_3 + H_2O$$

$$SO_{3(g)} + 2NaOH \rightarrow Na_2SO_4 + H_2O$$

Reactions with chlorine

ELEMENT	Na	Mg	Al	Si	P
FORMULA	NaCl	$MgCl_2$	Al_2Cl_6	$SiCl_4$	PCl_5
STRUCTURE	GIANT IONIC		SIMPLE COVALENT		
OXIDATION #	+1	+2	+3	+4	+5
STATE at RTP	solid	solid	solid	liquid	solid
PH	7	6.5	3	2	2
OBSERVATIONS WITH WATER	white solids dissolve to form colourless solutions			white fumes of HCl gas	

When sodium metal is heated with chlorine gas there is a vigorous reaction and a yellow flame is seen:

$$2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$$

Magnesium and aluminium also react vigorously with chlorine gas:

$$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)}$$

$$2Al_{(s)} + 3Cl_{2(g)} \rightarrow Al_2Cl_{6(s)}$$

Silicon reacts slowly with chlorine giving silicon(IV) chloride:

$$Si_{(s)} + 2Cl_{2(g)} \rightarrow SiCl_{4(l)}$$

Phosphorus also reacts slowly with excess chlorine gas:

$$P_{4(s)} + 10Cl_{2(g)} \rightarrow 4PCl_{5(l)}$$

<u>Period 3 chlorides and water</u>

The ionic chlorides of sodium and magnesium do not react with water; they just dissolve.

On adding Al_2Cl_6 to water, it breaks down forming Al^{3+} and Cl^- ions.

Al^{3+} is small and highly charged (high charge density), causing the water molecules bonded to it to lose one H^+ ion, making the resulting solution acidic.

$$[Al(H_2O)_6]^{3+}{}_{(aq)} \rightarrow [Al(H_2O)_5OH]^{2+}{}_{(aq)} + H^+{}_{(aq)}$$

The liquid chlorides, $SiCl_4$ and PCl_5, are hydrolysed in water, releasing white fumes of hydrogen chloride gas in a rapid reaction

$$SiCl_{4(l)} + 2H_2O_{(l)} \rightarrow SiO_{2(s)} + 4HCl_{(g)}$$

The SiO_2 is a white precipitate. Some of the HCl dissolves in the water, giving an acidic solution.

$$PCl_{5(l)} + 4H_2O_{(l)} \rightarrow H_3PO_{4(aq)} + 5HCl_{(g)}$$

Both H_3PO_4 and HCl are soluble in water and are highly acidic.