GROUPS I and II

Introduction

Elements in Group I *(alkali metals)* and Group II *(alkaline earths)* are known as **s-block elements** because their valence (bonding) electrons are in s orbitals.

	Li	*Na*	*K*	*Rb*	*Cs*
Atomic Number	3	11	19	37	55
Electronic configuration	$1s^2 2s^1$	[Ne] $3s^1$	[Ar] $4s^1$	[Kr] $5s^1$	[Xe] $6s^1$

	Be	*Mg*	*Ca*	*Sr*	*Ba*
Atomic Number	4	12	20	38	56
Electronic configuration	$1s^2 2s^2$	[Ne] $3s^2$	[Ar] $4s^2$	[Kr] $5s^2$	[Xe] $6s^2$

PHYSICAL PROPERTIES

Atomic Radius

Increases down each group electrons are in shells further from the nucleus

	Li	*Na*	*K*	*Rb*	*Cs*
Atomic radius / nm	0.152	0.186	0.231	0.244	0.262

Group II values are smaller increased nuclear charge ‘pulls in’ the electrons

	Be	*Mg*	*Ca*	*Sr*	*Ba*
Atomic radius / nm	0.106	0.140	0.174	0.191	0.198

Ionic Size

Increases down the group

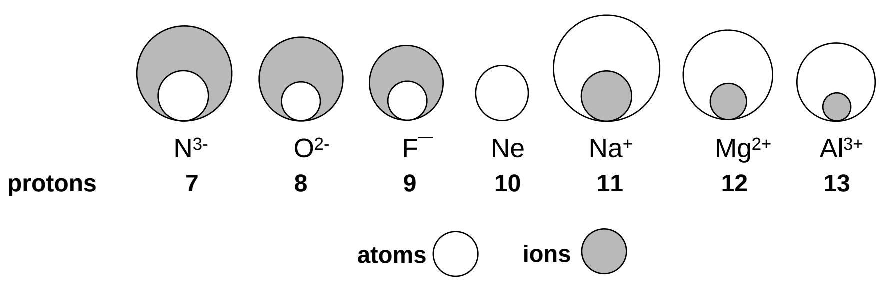
	Li^+	*Na^+*	*K^+*	*Rb^+*	*Cs^+*
Ionic radius / nm	0.060	0.095	0.133	0.148	0.169

Group II ions are smaller due to the greater nuclear charge

	Be^{2+}	*Mg^{2+}*	*Ca^{2+}*	*Sr^{2+}*	*Ba^{2+}*
Ionic radius / nm	0.030	0.064	0.094	0.110	0.134

Positive ions are smaller than the original atom because the **nuclear charge exceeds the electronic charge**. **Negative ions are bigger** than the original atom due to repulsion between electrons in the outer shell.

Species isoelectronic with neon



Melting Points **Decrease down each group** metallic bonding gets weaker due to increased size

Each atom contributes the outer (valence) electrons to the delocalised cloud.

Melting points tend not to give a decent trend as different crystalline structures affect the melting point.

	Li	*Na*	*K*	*Rb*	*Cs*
Melting point / °C	180	98	64	39	29

Group II values are higher Each atom contributes two electrons to the cloud

	Be	*Mg*	*Ca*	*Sr*	*Ba*
Melting point / °C	1283	650	850	770	710

Ionisation Energy **Decreases down the group** atomic size increases

Values for Group I are low because the electron has just gone into a new level and is shielded by filled inner levels. This makes them reactive. **Group II values are higher than their Group I equivalents due to the increased nuclear charge.**

Group I **large increase for the 2nd I.E.** as the electron is now being removed from a **shell nearer the nucleus** and there is **less shielding**.

	Li	*Na*	*K*	*Rb*	*Cs*
Ist I.E. / kJ mol $^{-1}$	519	494	418	402	376
2nd I.E. / kJ mol $^{-1}$	**7300**	**4560**	**3070**	**2650**	**2420**
3rd I.E. / kJ mol $^{-1}$	11800	6940	4600	3850	

Group II **large increase for the 3rd I.E.** as the third electron is being removed from a **shell nearer the nucleus**.

	Be	*Mg*	*Ca*	*Sr*	*Ba*
Ist I.E. / kJ mol $^{-1}$	899	738	590	550	500
2nd I.E. / kJ mol $^{-1}$	1800	1500	1100	1100	1000
3rd I.E. / kJ mol $^{-1}$	**14849**	**7733**	**4912**	**4120**	**3390**

Electronegativity **Decreases down the group**

Increased shielding makes the shared pair attracted less strongly to the nucleus

	Li	*Na*	*K*	*Rb*	*Cs*
Electronegativity (Pauling)	1.0	0.9	0.8	0.8	0.7

Group II values are larger

	Be	*Mg*	*Ca*	*Sr*	*Ba*
Electronegativity (Pauling)	1.5	1.2	1.0	0.95	0.89

Hydration Enthalpy

This is a measure of an ion's attraction for water

Decreases *(gets less negative)* **down each group**

Charge density of the ions decreases thus reducing the attraction for water

	Li^+	Na^+	K^+	Rb^+	Cs^+
Hydration Enthalpy / kJ mol $^{-1}$	-519	-406	-322	-301	-276

Group II values are greater increased charge density of 2^+ ions

	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Hydration Enthalpy / kJ mol $^{-1}$		-1920	-1650	-1480	-1360

Physical strength

Get softer down a group Metallic bonding is weaker as the ions get bigger

Group II metals are harder Electron cloud has a greater concentration

FLAME TESTS

Colour

- cations of the metals in Groups I and II give characteristic colours
- arises due to **electronic transitions** within the cation.

When a compound is heated, electrons are given energy and are sent to higher energy levels. They can then fall back, emitting energy in the form of light.

COLOURS OF IONS

Li^+	*carmine red*		
Na^+	*bright yellow*		
K^+	*lilac*	Ca^{2+}	*brick red*
Rb^+	*red*	Sr^{2+}	*red*
Cs^+	*blue*	Ba^{2+}	*apple green*

Compounds are used in fireworks to provide colour.

CHEMICAL PROPERTIES

Oxygen
- **react with increasing vigour down the group as size increases**

GROUP I
- **Ionic oxides (M_2O)** are formed — $4K_{(s)} + O_{2(g)} \longrightarrow 2K_2O_{(s)}$
  They are strong bases and react with water to give a strongly alkaline solution — $K_2O_{(s)} + H_2O_{(l)} \longrightarrow 2KOH_{(aq)}$
- **Peroxides (M_2O_2)** can also be formed — $2K_{(s)} + O_{2(g)} \longrightarrow K_2O_{2(s)}$
  They are also strong bases but produce oxygen as well — $2K_2O_{2(s)} + 2H_2O_{(l)} \longrightarrow 4KOH_{(aq)} + O_{2(g)}$
- **Superoxides (MO_2)** are also possible — $K_{(s)} + O_{2(g)} \longrightarrow KO_{2(s)}$

N.B. Peroxides and superoxides are coloured

GROUP II
- **Ionic oxides** are also produced — $2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO_{(s)}$
  see below for details

Water
- react with increasing vigour down each group
- Group I metals are more reactive than their Group II equivalents

GROUP I
- Group I metals are powerful reducing agents
- produce the metal hydroxide and hydrogen.

e.g. $2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$

- hydroxides are white crystalline solids
- basic strength increases down the group due to the lower attraction between hydroxide ions and larger uni-positive ions (lower charge density).

GROUP II
- Less reactive due to higher ionisation energies

Be — does not react with water or steam

Mg — reacts very slowly with cold water

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

but reacts quickly with steam

$Mg_{(s)} + H_2O_{(g)} \longrightarrow MgO_{(s)} + H_{2(g)}$

Ca, Sr, Ba — react with cold water with increasing vigour

e.g. $Ca_{(s)} + 2H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)} + H_{2(g)}$

- hydroxides are not as basic as those in Group I
- this is due to the greater charge density of the M^{2+} ion.

Chlorine
- chlorides may be made by direct combination under the influence of heat
- white ionic solids and are water soluble.
- lithium and beryllium chlorides have a degree of covalent character - *Fajan's Rules*

e.g. $2Na_{(s)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)}$

$Ca_{(s)} + Cl_{2(g)} \longrightarrow CaCl_{2(s)}$

COMPOUNDS

Oxides
- white crystalline ionic solids

GROUP I
- very soluble in water
- form strongly alkaline solutions in water

e.g. $Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)}$

GROUP II
- partially soluble in water (increases down the group - see below)
- form weak alkalis

e.g. $CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)}$

Hydroxides
- white crystalline solids
- solubility in water increases down the Group

$Be(OH)_2$	*insoluble*	
$Mg(OH)_2$	*sparingly soluble*	
$Ca(OH)_2$	*slightly soluble*	- an aqueous solution is known as 'lime water'
$Sr(OH)_2$	*quite soluble*	
$Ba(OH)_2$	*very soluble*	

- **basic strength also increases down group**
- the **metal ions get larger** so charge density decreases
- there is a lower attraction between the OH^- ions and larger unipositive ions
- the ions will split away from each other more easily
- there will be a greater concentration of OH^- ions in water

$$M(OH)_{2(s)} + \text{water} \longrightarrow M^{2+}_{(aq)} + 2OH^-_{(aq)}$$

'*The greater the concentration of OH^- ions in water the greater the alkalinity*'

- oxides of both groups dissolve in acid to form salts

e.g. $CaO_{(s)} + 2H^+_{(aq)} \longrightarrow Ca^{2+}_{(aq)} + H_2O_{(l)}$

Carbonates

GROUP I

- white crystalline solids
- readily soluble in water **EXC Li_2CO_3**
- resistant to fairly strong heating **EXC Li_2CO_3**

  This is due to the low charge and large size. Lithium, being smaller, has a larger charge density and favours combination with the high charge density oxide ion.

  Lithium carbonate decomposes on heating **$Li_2CO_{3(s)} \longrightarrow Li_2O_{(s)} + CO_{2(g)}$**

GROUP II

- white crystalline solids
- insoluble in water
- decompose on heating **$MgCO_{3(s)} \longrightarrow MgO_{(s)} + CO_{2(g)}$**

  higher charge density favours combination with O^{2-} rather than the larger carbonate ion.

Nitrates

GROUP I

- white crystalline solids
- readily soluble in water
- decompose on heating to give the nitrite **$2NaNO_{3(s)} \longrightarrow 2NaNO_{2(s)} + O_{2(g)}$**
- lithium nitrate behaves differently and acts more like a Group II nitrate **$4LiNO_{3(s)} \longrightarrow 2Li_2O_{(s)} + 4NO_{2(g)} + O_{2(g)}$**

GROUP II

- white crystalline solids
- readily soluble in water
- decompose on heating **$2Mg(NO_3)_{2(s)} \longrightarrow 2MgO_{(s)} + 4NO_{2(g)} + O_{2(g)}$**

Group II Sulphates

- white crystalline solids
- solubility in water decreases down the Group

Salt	*Ionic radius (M^{2+}) / nm*	*Hydration Enthalpy (M^{2+}) / kJ mol $^{-1}$*	*Solubility moles/100g*
$MgSO_4$	0.064	-1891	3600×10^{-4}
$CaSO_4$	0.094	-1562	11×10^{-4}
$SrSO_4$	0.110	-1413	0.62×10^{-4}
$BaSO_4$	0.134	-1273	0.009×10^{-4}

- reasons for solubility decreasing down the group ...
  - there is little change in the lattice enthalpy BUT
  - as the **cation gets larger** the **hydration enthalpy gets less negative**
  - a **larger cation** has a **lower charge density** and so is **less attracted to water**

THE ATYPICAL NATURE OF BERYLLIUM

Theory Beryllium differs from the other Group II elements; it has properties closer to that of aluminium - THE DIAGONAL RELATIONSHIP. Being the **head element** of a Group...

it has
- a much **smaller ionic size** (a **greater charge/size ratio** - **highly polarising**)
- a much **larger ionisation energies** than those elements below it

so
- is less likely to form ions
- compounds ($BeCl_2$) show covalent character
  - often soluble in organic solvents
  - have lower melting points
  - often hydrolysed by water
- maximum co-ordination number of 4 - due to small size
- beryllium hydroxide is AMPHOTERIC - dissolves in both acids and bases

$$\mathbf{Be(OH)_{2(s)} + 2H^+_{(aq)} + 2H_2O_{(l)} \longrightarrow [Be(H_2O)_4]^{2+}_{(aq)}}$$

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

Diagonal Relationship It is interesting to note how the chemistry of lithium (Group I) is closer to that of the Group II metal magnesium . This is often known as the *Diagonal Relationship* (it also occurs with beryllium and aluminium) and arises because the top element of a group has a much smaller ionic size and much larger ionisation energies than those below. This gives rise to a great degree of covalent character in the compounds because of the lower tendency to form ions. The chances of a compound being covalent can be predicted by applying Fajan's Rules. Compounds with a degree of covalent character have lower melting points and are often hydrolysed by water.

Lithium and magnesium are similar in the following ways

- hydroxides are only sparingly soluble in water
- carbonates decompose on heating to give oxide and carbon dioxide
- hydrogencarbonates do not exist in the solid state
- nitrates decompose on heating to give the oxide, nitrogen dioxide and oxygen
- form nitrides on strong heating in nitrogen e.g. $\mathbf{6Li + N_2 \longrightarrow 2Li_3N}$
- some salts are hydrolysed