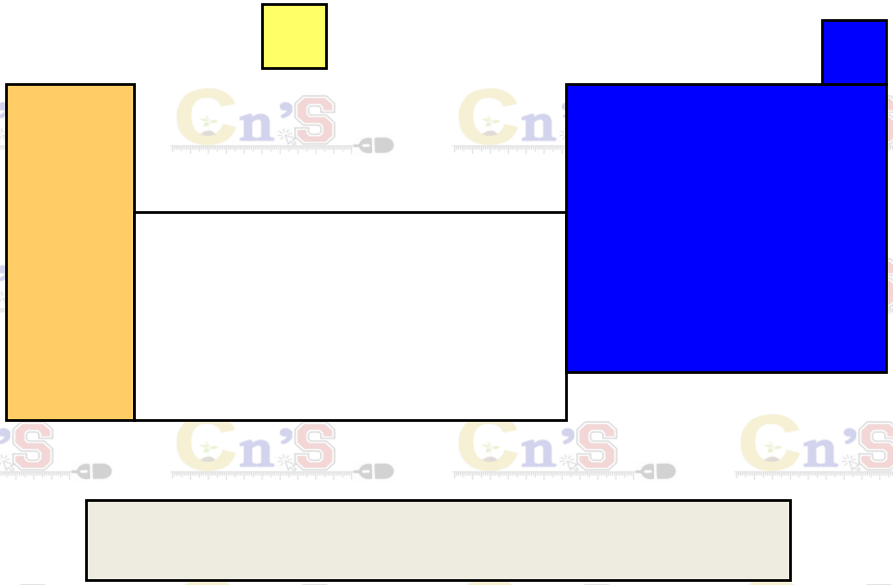
The S-Block Elements

Members of the s-Block Elements

IA	IIA
Li	Be
Na	Mg
K	Ca
Rb	Sr
Cs	Ba
Fr	Ra



IA Alkali metals

IIA Alkaline Earth metals

Objectives

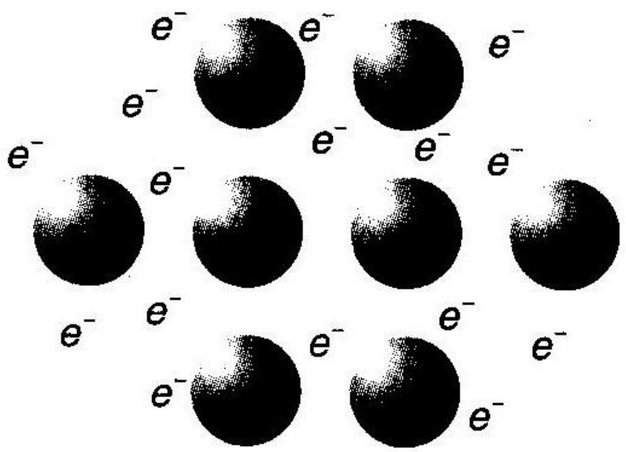
- Characteristic properties of the s-block elements
- Variation in properties of the s-block elements
- Variation in properties of the s-block compounds
- Uses of compounds of the s-block elements

Characteristic properties of s-block elements

- Metallic character
- Low electronegativity
- Basic oxides, hydroxides
- Ionic bond with fixed oxidation states
- Characteristic flame colours
- Weak tendency to from complex

Metallic character

- High tendency to lose e^- to form positive ions
- Metallic character increases down both groups



Electronegativity

- Low nuclear attraction for outer electrons
- Highly electropositive
- Small electronegativity

Group I	Group II
Li 1.0	Be 1.5
Na 0.9	Mg 1.2
K 0.8	Ca 1.0
Rb 0.8	Sr 1.0
Cs 0.7	Ba 0.9
Fr 0.7	Ra 0.9

Basic oxides, hydroxides

Oxide	Hydroxides
Li_2O	$LiOH$
Na_2O, Na_2O_2	$NaOH$
K_2O_2, KO_2	KOH
Rb_2O_2, RbO_2	$RbOH$
Cs_2O_2, CsO_2	$CsOH$

Oxide	Hydroxides
BeO	$Be(OH)_2$
MgO	$Mg(OH)_2$
CaO	$Ca(OH)_2$
SrO	$Sr(OH)_2$
BaO, Ba_2O_2	$Ba(OH)_2$

Oxides, Peroxide, Superoxide

Reaction with water:

Oxide: $O^{2-} + H_2O \rightarrow 2OH^-$
Peroxide: $O_2^{2-} + 2H_2O \rightarrow H_2O_2 + 2OH^-$
Superoxide: $2O_2^- + 2H_2O \rightarrow 2OH^- + H_2O_2 + O_2$

```
 ..   .. 2-
:O:O:
 ..  ..
```

Peroxide ion

```
 .   . -
:O:.O:
 ..  ..
```

Super oxide

Li does not form peroxide or super oxide
$Li_2O_2 \rightarrow Li_2O + ½ O_2$

Hydroxides

Group I hydroxides	Li	Na	K	Rb	Cs

All are soluble, base strength increase.

Group II hydroxide	Be	Mg	Ca	Sr	Ba

Solubility increase, from Amphoteric to basic, base strength increase

Predominantly ionic with fixed oxidation state

Group I: Most electropositive metals.
Low first I.E. and extremely high second I.E.
Form predominantly ionic compounds with non-metals by losing one electron.
Fixed oxidation state of +1.

Group II: Electropositive metals.
Low first and second I.E. but very high third I.E.. Have a fixed oxidation state of +2.
Be and Mg compounds possess some degree of covalent character.

Characteristic flame colours

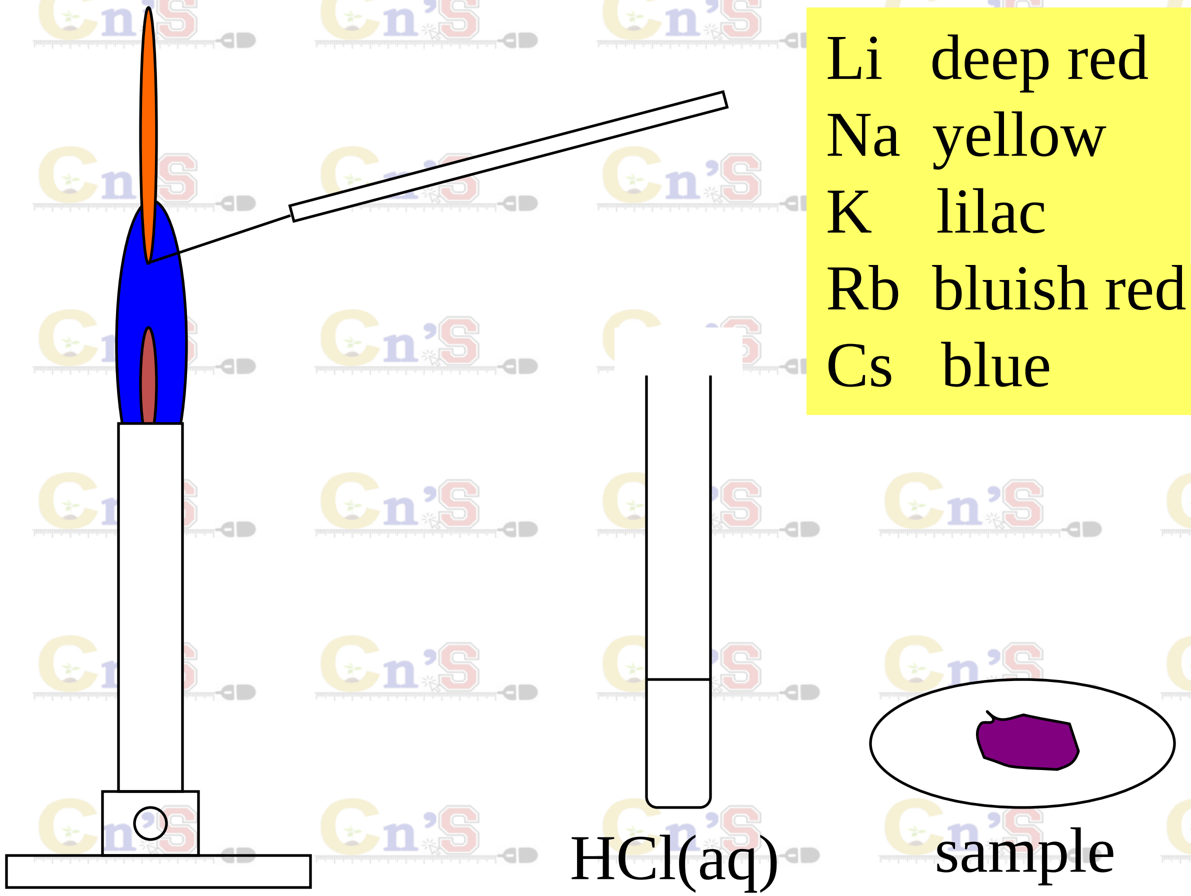
$Na^+ Cl^- (g) \rightarrow Na (g) + Cl (g)$

$Na(g) \rightarrow Na^* (g)$

$[Ne]3s^1 \quad [Ne]3p^1$

$Na^*(g) \rightarrow Na(g) + h\upsilon$ (589nm, yellow)

Flame test



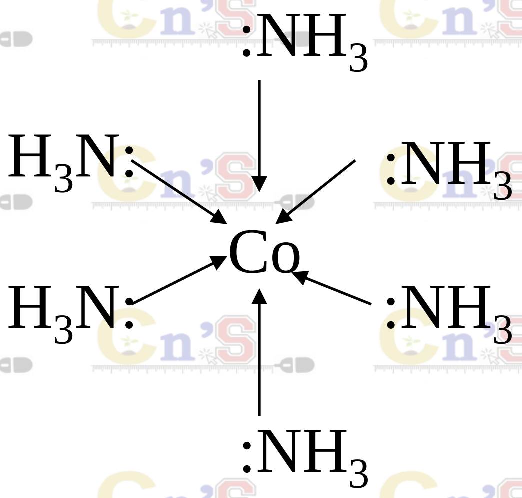
Li deep red
Na yellow
K lilac
Rb bluish red
Cs blue

Ca brick red
Sr blood red
Ba apple green

Weak tendency to form complex

Complex formation is a common feature of d-block element. e.g. $Co(NH_3)_6^{3+}$

s-block metal ions have no low energy vacant orbital available for bonding with lone pairs of surrounding ligands, they rarely form complexes.

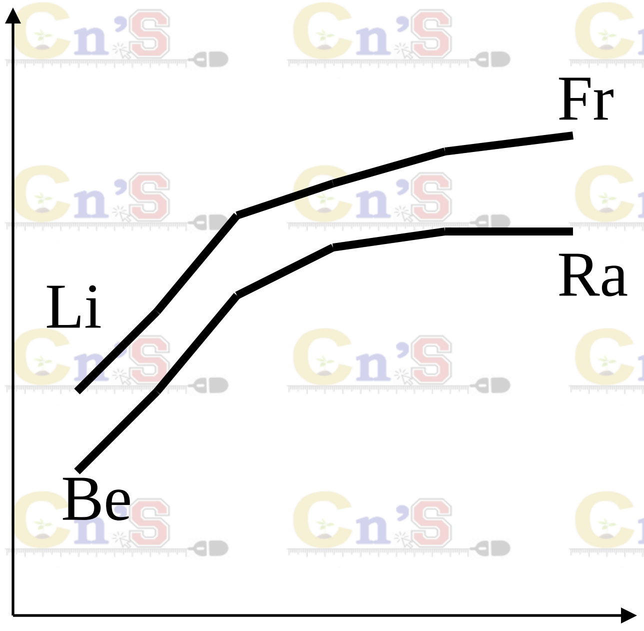


Variation in properties of elements

- Atomic radii
- Ionization enthalpies
- Hydration enthalpies
- Melting points
- Reactions with oxygen, water, hydrogen and chlorine

Atomic radii (nm)

Li	0.152	Be	0.112
Na	0.186	Mg	0.160
K	0.231	Ca	0.197
Rb	0.244	Sr	0.215
Cs	0.262	Ba	0.217
Fr	0.270	Ra	0.220

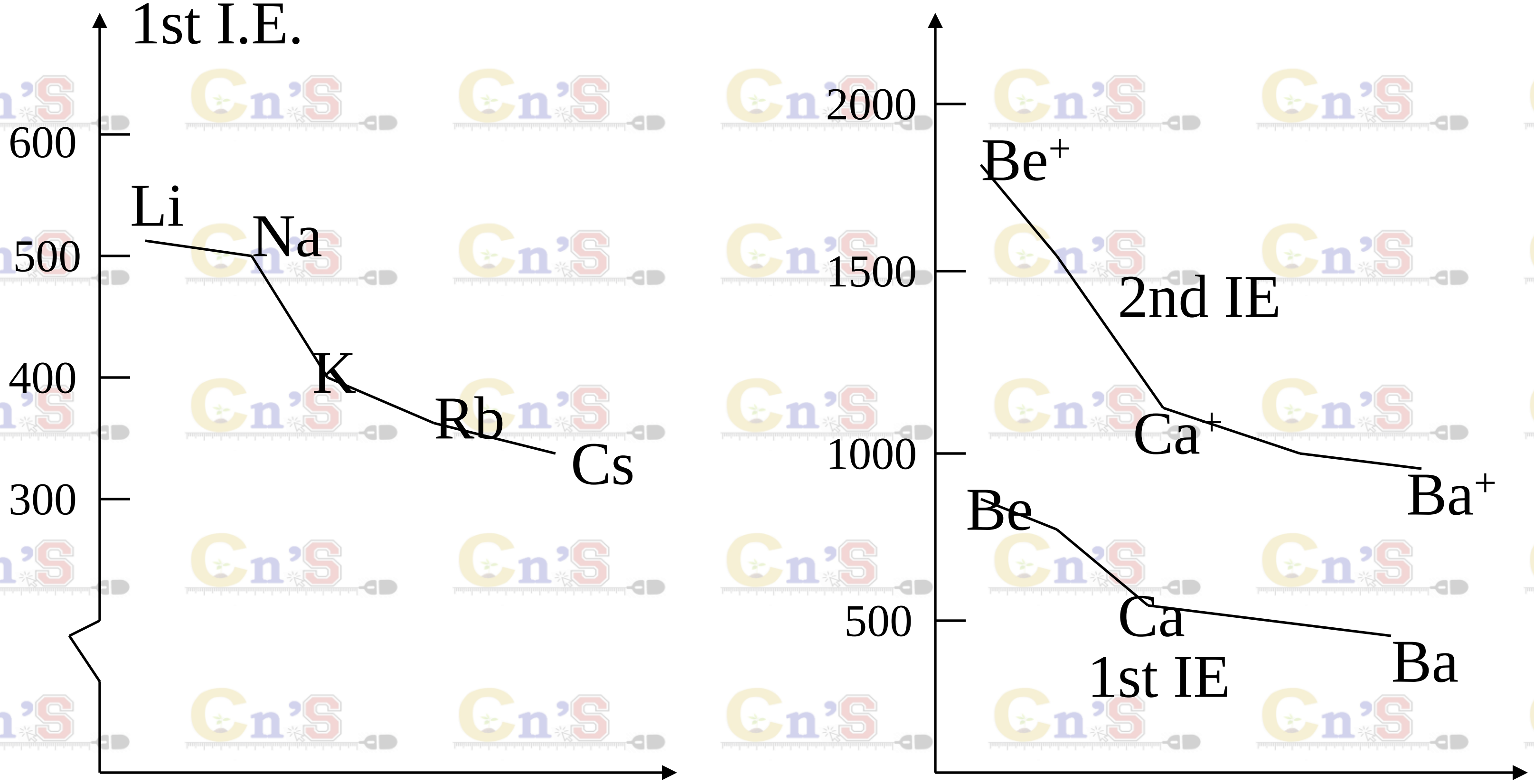


Ionization Enthapy

Group I	1st I.E.	2nd I.E.
Li	519	7300
Na	494	4560
K	418	3070
Rb	402	2370
Cs	376	2420

Group I	1st I.E.	2nd I.E.	3rd I.E.
Be	900	1760	14800
Mg	736	1450	7740
Ca	590	1150	4940
Sr	548	1060	4120
Ba	502	966	3390

Ionization Enthalpy



Ionization Enthalpy

Group I

1. Have generally low 1st I.E. as it is well shielded from the nucleus by inner shells.

2. Removal of a 2nd electron is much more difficult because it involves the removal of inner shell electron.

3. I.E. decreases as the group is descended.
   As atomic radius increases, the outer e is further away from the well-shielded nucleus.

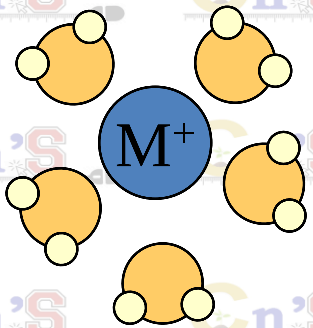
Ionization Enthalpy

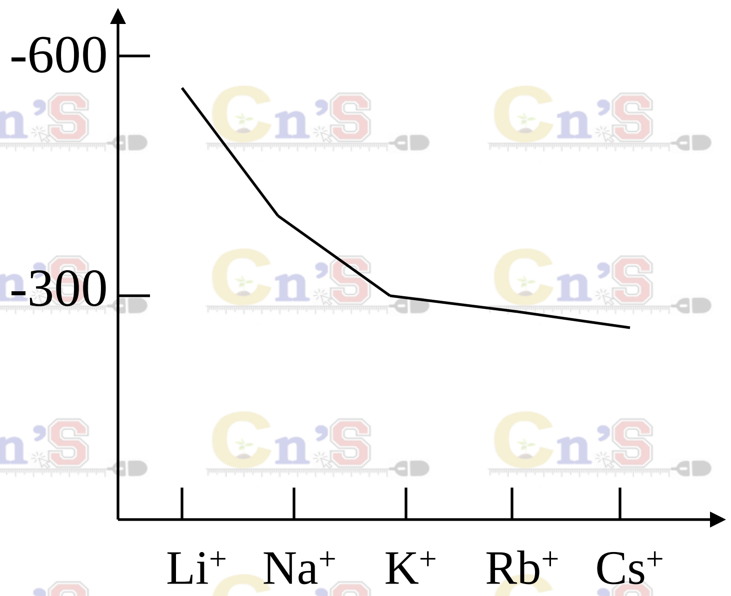
Group II

1. Have low 1st and 2nd IE.
2. Removal of the 3rd electron is much more difficult as it involves the loss of an inner shell electron.
3. IE decrease as the group is descended.
4. IE of the group II is generally higher than group I.

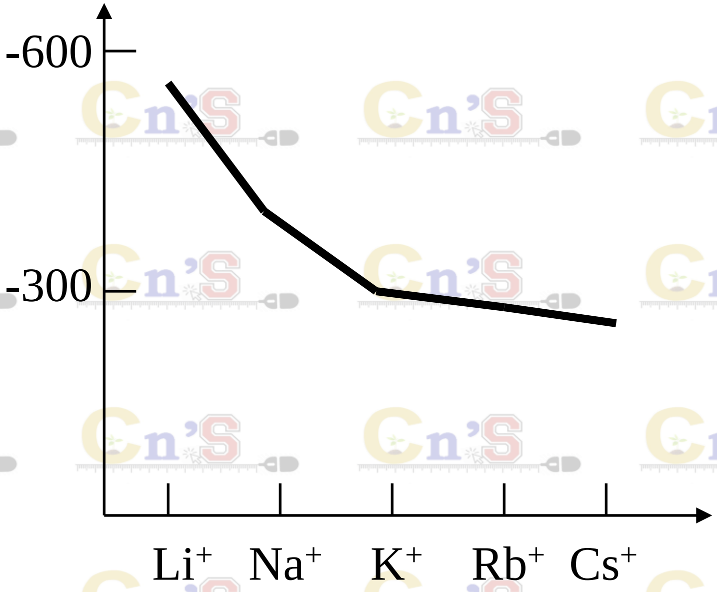
Hydration Enthalpy

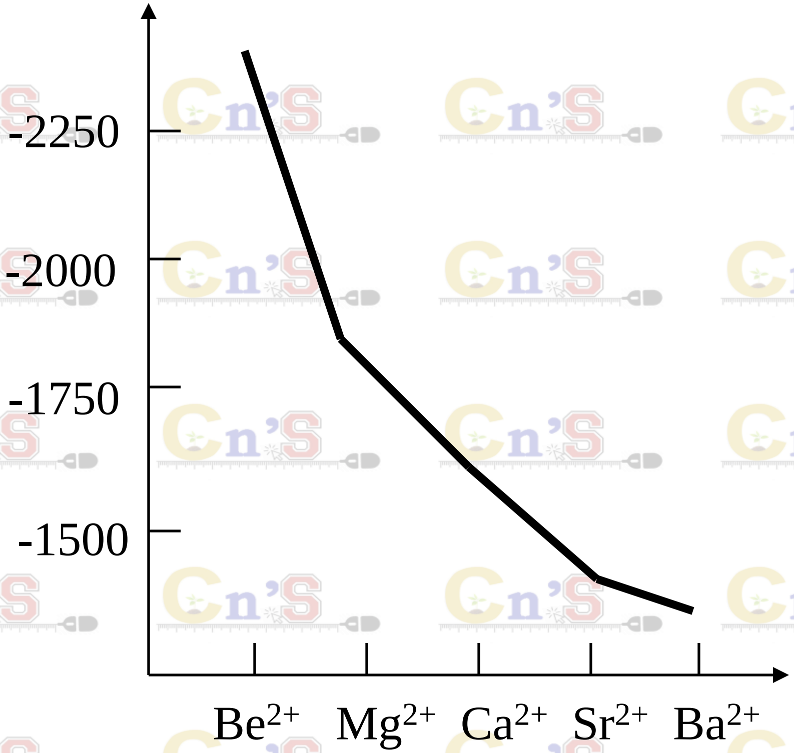
$$M^+(g) + \text{aqueous} \rightarrow M^+(aq) + \text{heat}$$





Hydration Enthalpy





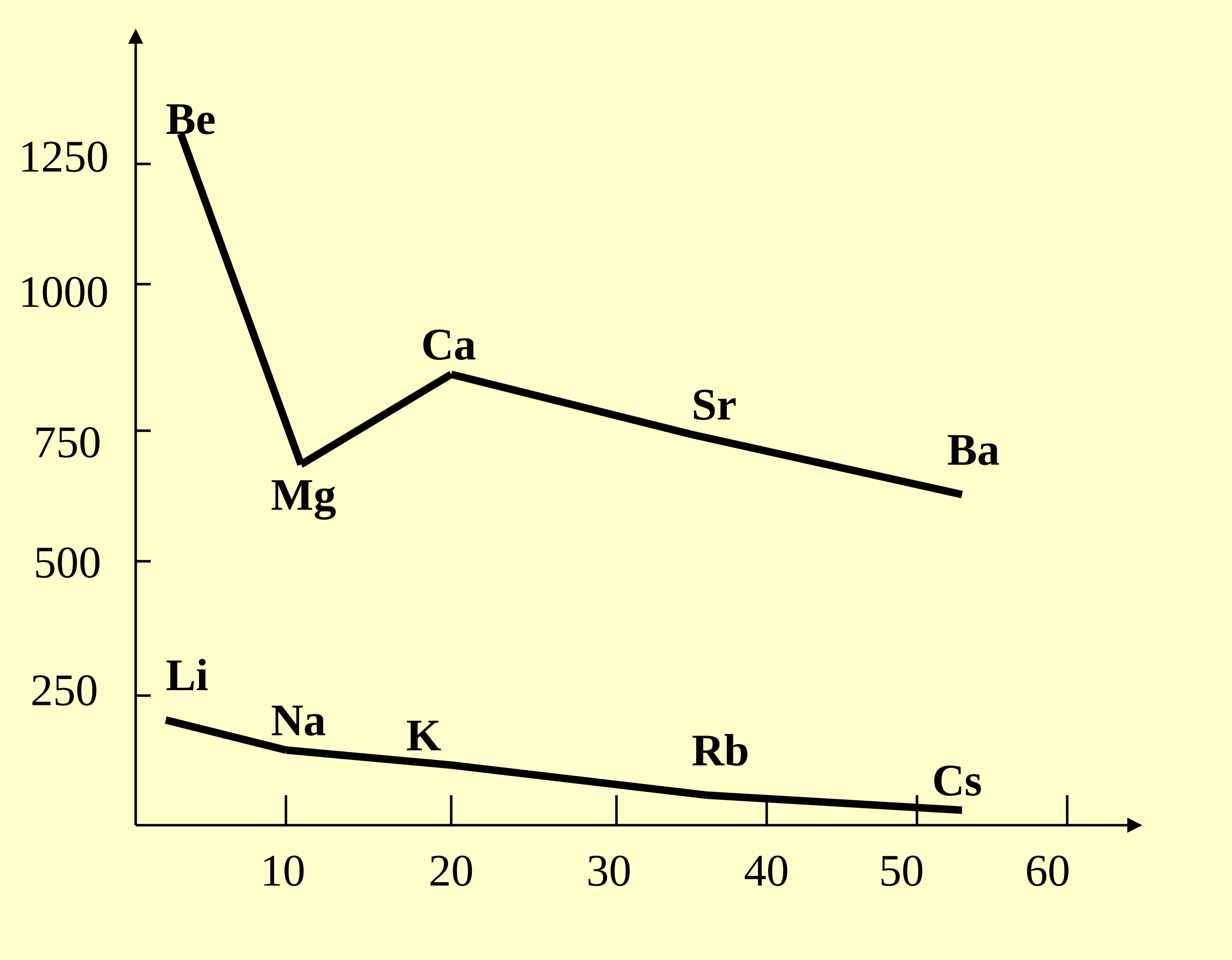
Hydration Enthalpy

General trends:

1. On going down both groups, hydration enthalpy decreases.
   (As the ions get larger, the charge density of the ions decreases, the electrostatic attraction between ions and water molecules gets smaller.)

2. Group 2 ions have hydration enthalpies higher than group 1.
   (Group 2 cations are doubly charged and have smaller sizes)

Variation in Melting Points



Variation in Melting Points

Strength of metallic bond depends on:

1. Ionic radius
2. Number of e^- contributed to the electron sea per atom
3. Crystal lattice structure

Note: The exceptionally high m.p. of calcium is due to contribution of d-orbital participation of metallic bonding.

Reactions with oxygen

S-block elements are strong reducing agents.
Their reducing power increases down both groups.
(As the atomic size increases, it becomes easier to remove the outermost electron)

S-block elements reacts readily with oxygen.
Except Be and Mg, they have to be stored under liquid paraffin to prevent contact with the atmosphere.

Reactions with oxygen

	Normal Oxide	Peroxide	Superoxide
Structure	.. 2- :O: ..	.. .. 2- :O-O:	. . - :O:.O: .. ..
Formed by	Li and Group II	Na and Ba	K, Rb, Cs

Sodium burns in oxygen with an orange flame to produce a white solid mixture of sodium oxide and sodium peroxide.

- For the simple oxide:

$$4Na + O_2 \longrightarrow 2Na_2O$$

- For the peroxide

$$2Na + O_2 \longrightarrow Na_2O_2$$

b. Magnesium

- Magnesium burns in oxygen with an intense white flame to give while solid of Magnesium oxide. :

$$2Mg + O_2 \longrightarrow 2MgO$$

- Note: If Magnesium burns in air rather than in pure Oxygen, it also reacts with the Nitrogen in the air forming a mixture of Magnesium oxide and Magnesium nitride.

$$2Mg + N_2 \longrightarrow Mg_3N_2$$

There are several reactions of group I metals with air/O_2.

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$

$$2Na(s) + \text{Excess } O_2(g) \text{ -----------------} \ Na_2O_2(s)$$

$$2Na(s) + 2H_2O(g) \rightarrow 2NaOH(s) + H_2(g)$$

K, Rb and Cs readily react with O_2 forming superoxides.

$$K(s) + O_2(g) \overset{\text{Excess}}{\text{-----------}} KO_2(s)$$

When a clean piece of Mg ribbon and a small cut piece of Na are exposed to air Na tarnishes faster than Mg. Hence it is clear that the reactivity of Mg is lower than Na.

Accordingly it can be said that relative to metals of group I, the reactivity of group II metals with air is lower.

Metals of Group II when heated in air burn forming oxides.

$$2Mg(s) + O_2(g) \text{ ------------------- } 2MgO(s)$$

For Be to react it should be heated to a very high temperature.

With N_2

Lithium and Group II metals form metal nitrides by reacting with N_2 gas or N_2 presents in air.

$$6Li(s) + N_2(g) \rightarrow 2Li_3N(s)$$

$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$$

When heated in air only Li of Group I reacts with nitrogen.

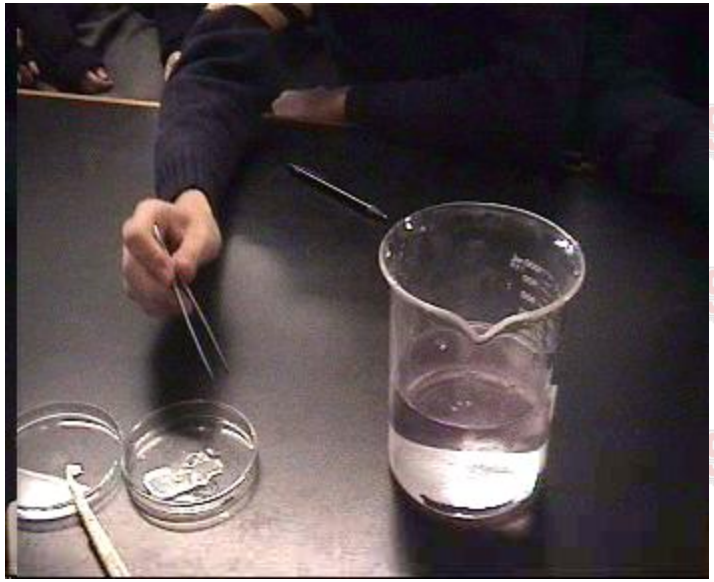
Metals of Group II when heated in air burn forming nitrides.

Reaction with water

$M(s) \rightarrow M^{+}(aq) + e^{-}$
$H_2O(l) + e^{-} \rightarrow OH^{-}(aq) + \frac{1}{2} H_2(g)$

Li	-3.05 volt
Na	-2.71
K	-2.93
Rb	-2.99
Cs	-3.20

Be	-1.85 volt
Mg	-2.38
Ca	-2.87
Sr	-2.89
Ba	-2.90



Energetic vs. Kinetic Factor

- All the elements of the first group react with water liberating hydrogen and become hydroxides.

  Example : Na reacts rapidly with water liberating hydrogen.

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

- When a small piece of K is added into water it reacts while burning. As K reacts with water more rapidly than Na, it can be concluded that the rate of reaction with water increases down the group.

- A reaction is not seen when a clean piece of Mg is added into water. When the water with Mg is warmed, it is seen to react slowly.
- $Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(s) + H_2(g)$
- As the reactivity shown by Mg with water is lower compared to Na, it can be said that the metals of group II compared to metals of group I show a lower reactivity. Be does not react with water. Ca, Sr, and Ba react with water liberating hydrogen and forming the hydroxides.
- $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$

- Be and Mg react with steam to form the oxides.
- $Be(s) + H_2O(g) \rightarrow BeO(s) + H_2(g)$
- $Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$

Reaction with Chlorine

a. Sodium

- Sodium burns in chlorine with a bright orange flame. White solid sodium chloride is produced.

$$2Na + Cl_2 \longrightarrow 2NaCl$$

b. Magnesium

- Magnesium burns with its usual intense white flame to give white magnesium chloride.

$$Mg + Cl_2 \longrightarrow MgCl_2$$

With acids

As the metals of the group I react with acids liberating large quantity of heat, an explosion takes place. Therefore it should not be tested.

$$2\,Na(s) + H_2\overset{dil}{SO_4}(aq) \rightarrow Na_2SO_4(aq) + H_2(g)$$

Group II metals reacts with dilute acids to liberate H_2 rapidly.

$$Mg(s) + H_2\overset{dil}{SO_4}(aq) \rightarrow MgSO_4(aq) + H_2(g)$$

Group II metals can be oxidised by concentrated acids.

$$Mg(s) + 2H_2\overset{conc.}{SO_4}(aq) \rightarrow MgSO_4(aq) + SO_2(g) + 2H_2O(l)$$

$$Mg(s) + 4H\overset{conc.}{NO_3}(aq) \rightarrow Mg(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

Reaction with hydrogen

- **With H_2** *s* Block elements form metal hydrides by reacting with H_2 gas.

$$2Li(s) + H_2(g) \rightarrow 2LiH(s)$$

$$2Na(s) + H_2(g) \rightarrow 2NaH(s)$$

$$Mg(s) + H_2(g) \rightarrow MgH_2(s)$$

All the s-block elements except Be react directly with hydrogen.

$$2Na(s) + H_2(g) \rightarrow 2NaH(s)$$

$$Ca(s) + H_2(g) \rightarrow CaH_2(s)$$

The reactivity increases down the group.

Only BeH_2 and MgH_2 are covalent, others are ionic.

- Because *s* block elements easily remove their electrons and form cations they are considered as good reducing agents.
- While atomic radius increases down the group nuclear attraction decreases. Consequently, reducing ability of the elements also increases.

Reaction with chlorine

All the s-block metals react directly with chlorine to produce chloride.

All group I chlorides are ionic.

$BeCl_2$ is essentially covalent, with comparatively low m.p.

The lower members in group II form essentially ionic chlorides, with Mg having intermediate properties.

Although lithium has highly negative E^o, it only reacts slowly with water. This illustrates the importance of the role of kinetic factors in determining the rate of a chemical reaction.

Lithium has a higher m.p., this increases the activation energy required for dissolution in aqueous solution.
It does not melt during the reaction as Na and K do, and thus it has a smaller area of contact with water.

Variation in properties of the compounds

- Reactions of oxides and hydroxides
- Reactions of chlorides
- Reactions of hydrides
- Relative thermal stability of carbonates and hydroxides
- Relative solubility of sulphate(VI) and hydroxde

Reactions of oxides and hydroxides

1. All group I oxides reacts with water to form hydroxides

   Oxide: $O^{2-} + H_2O \rightarrow 2OH^-$
   Peroxide: $O_2^{2-} + 2H_2O \rightarrow H_2O_2 + 2OH^-$
   Superoxide: $2O_2^- + 2H_2O \rightarrow 2OH^- + H_2O_2 + O_2$

2. All group I oxides/hydroxides are basic and the basicity increases down the group.

Reactions of oxides and hydroxides

3. Group II oxides/hydroxides are generally less basic than Group I. Beryllium oxide/hydroxide are amphoteric.

Reactions of chlorides

1. All group I chlorides are ionic and readily soluble in water. No hydrolysis occurs.

2. Group II chlorides show some degree of covalent character.
   Beryllium chloride is covalent and hydrolysis to form $Be(OH)_2(s)$ and $HCl(aq)$.
   Magnesium chloride is intermediate, it dissolves and hydrolysis slightly.
   Other group II chlorides just dissolve without hydrolysis.

Reactions of hydrides

They all react readily with water to give the metal hydroxide and hydrogen due to the strong basic property of the hydride ion, $H:^-$

$$H:^-(s) + H_2O(l) \rightarrow H_2(g) + OH^-(aq)$$

Hydride ions are also good reducing agent. They can be used to prepare complex hydrides such as $LiAlH_4$ and $NaBH_4$ which are used to reduce C=O in organic chemistry.

Covalent Character:.

Small cation and large anion favors covalency.

Order: LiCl > NaCl > KCl > RbCl > CsCl & . LiI > LiBr > LiCl > LiF

Greater the charge on the cation greater is its polarizing power and hence larger is the covalent character: $Na^{+}Cl^{-} < Mg^{+2}Cl_2 < Al^{+3}Cl_3$

Greater the charge on the anion, more easily it gets polarized thereby imparting more covalent character to the compound formed eg covalent character increase in the order. $NaCl < Na_2SO_4 < Na_3PO_4$

Thermal Stability

Thermal stability refers to decomposition of the compound on heating. Increased thermal stability means a higher temperature is needed to decompose the compound.

Thermal Stability of carbonates

$Li_2CO_3 \rightarrow Li_2O + CO_2$ (at 700^{o}C)
All other group I carbonates are stable at ~800^{o}C

$BeCO_3 \rightarrow BeO + CO_2$ (at 100^{o}C)
$MgCO_3 \rightarrow MgO + CO_2$ (at 540^{o}C)
$CaCO_3 \rightarrow CaO + CO_2$ (at 900^{o}C)
$SrCO_3 \rightarrow SrO + CO_2$ (at 1290^{o}C)
$BaCO_3 \rightarrow BaO + CO_2$ (at 1360^{o}C)

Thermal Stability of hydroxides

All group I hydroxides are stable except LiOH at Bunsen temperature.

$Be(OH)_2(s) \rightarrow BeO(s) + H_2O(g) \quad \Delta H = +54$ kJ/mol
$Mg(OH)_2(s) \rightarrow MgO(s) + H_2O(g) \quad \Delta H = +81$ kJ/mol
$Ca(OH)_2(s) \rightarrow CaO(s) + H_2O(g) \quad \Delta H = +109$ kJ/mol
$Sr(OH)_2(s) \rightarrow SrO(s) + H_2O(g) \quad \Delta H = +127$ kJ/mol
$Ba(OH)_2(s) \rightarrow BaO(s) + H_2O(g) \quad \Delta H = +146$ kJ/mol

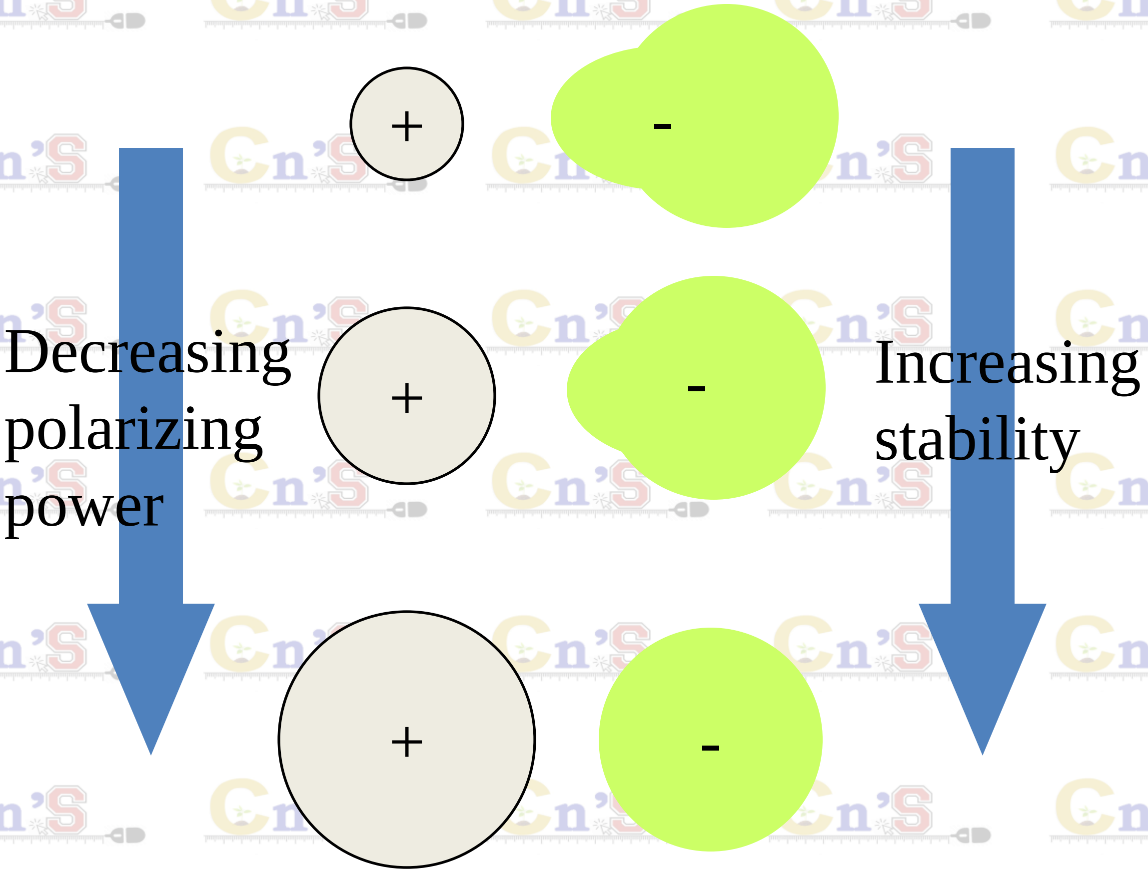
Thermal stability

1. Carbonates and hydroxides of Group I metals are as a whole more stable than those of Group II.
2. Thermal stability increases on descending the group.
3. Lithium often follow the pattern of Group II rather than Group I.
   This is an example of the *diagonal relationship*.

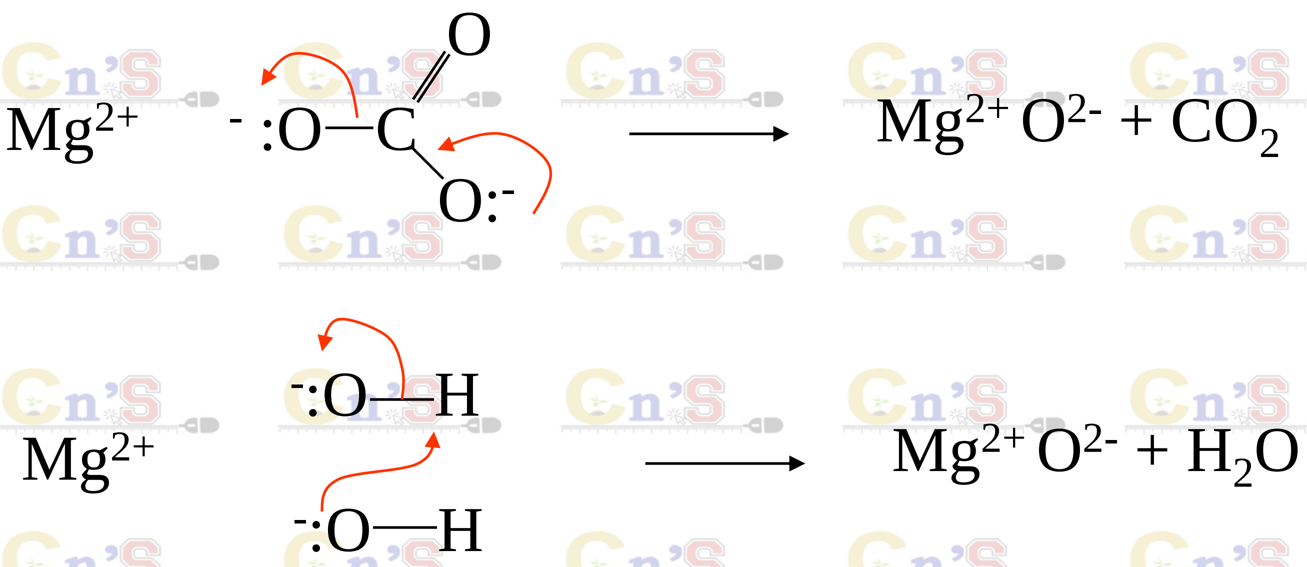
Explanation of Thermal Stability

1. Charge of the ions
2. Size of the ions
3. For compounds with large polarizable anions, thermal stability is affected by the polarizing power of the cations.
4. Compounds are more stable if the charge increases and size decreases.

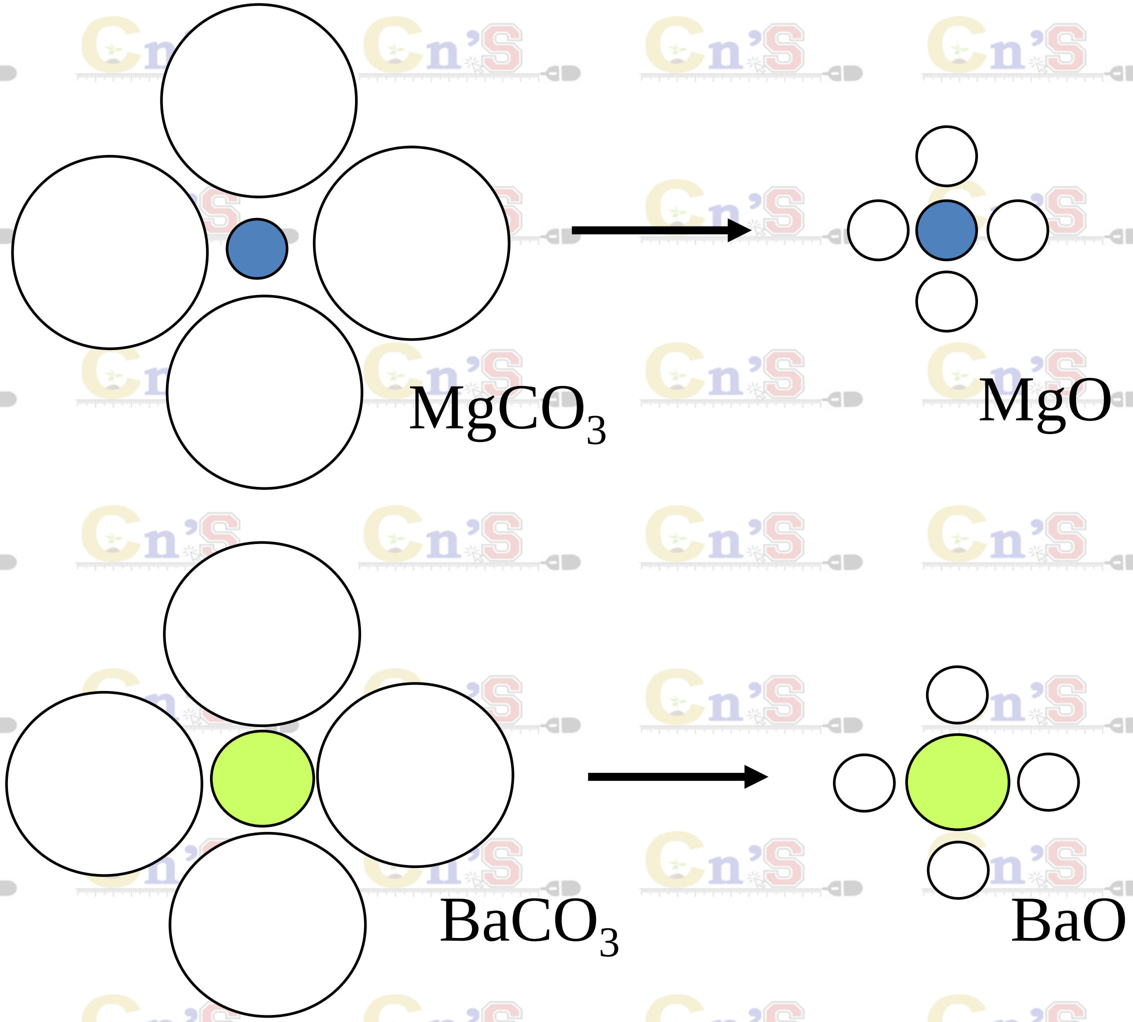
Explanation of Thermal Stability

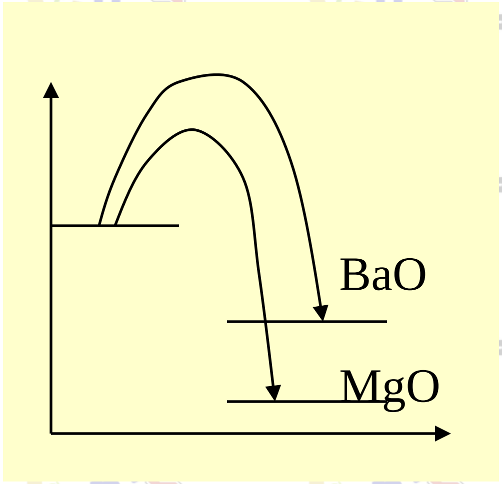


Explanation of Thermal Stability



Explanation of Thermal Stability





Relative solubility of Group II hydroxides

Compound	Solubility / mol per 100g water
$Mg(OH)_2$	0.020×10^{-3}
$Ca(OH)_2$	1.5×10^{-3}
$Sr(OH)_2$	3.4×10^{-3}
$Ba(OH)_2$	15×10^{-3}

Solubility of hydroxides increases down the group.

Solubility of Group II sulphates

Compound	Solubility / mol per 100g water
$MgSO_4$	3600×10^{-4}
$CaSO_4$	11×10^{-4}
$SrSO_4$	0.62×10^{-4}
$BaSO_4$	0.009×10^{-4}

Solubility of sulphates increases up the group.

Explanation of solubility

$$\begin{tikzcd} MX(s) \arrow[rr, "\text{aqueous}", "\Delta H_{\text{solution}}"'] \arrow[dr, "-\Delta H_{\text{lattice}}"'] & & M^+(aq) + X^-(aq) \\ & M^+(g) + X^-(g) \arrow[ur, "\Delta H_{\text{hydration}}"'] & \end{tikzcd}$$

$$\Delta H_{\text{solution}} = -\Delta H_{\text{lattice}} + \Delta H_{\text{hydration}}$$

Explanation of solubility

1. Group I compounds are more soluble than Group II because the metal ions have smaller charges and larger sizes. $\Delta H_{lattice}$ is smaller, and $\Delta H_{solution}$ is more exothermic.

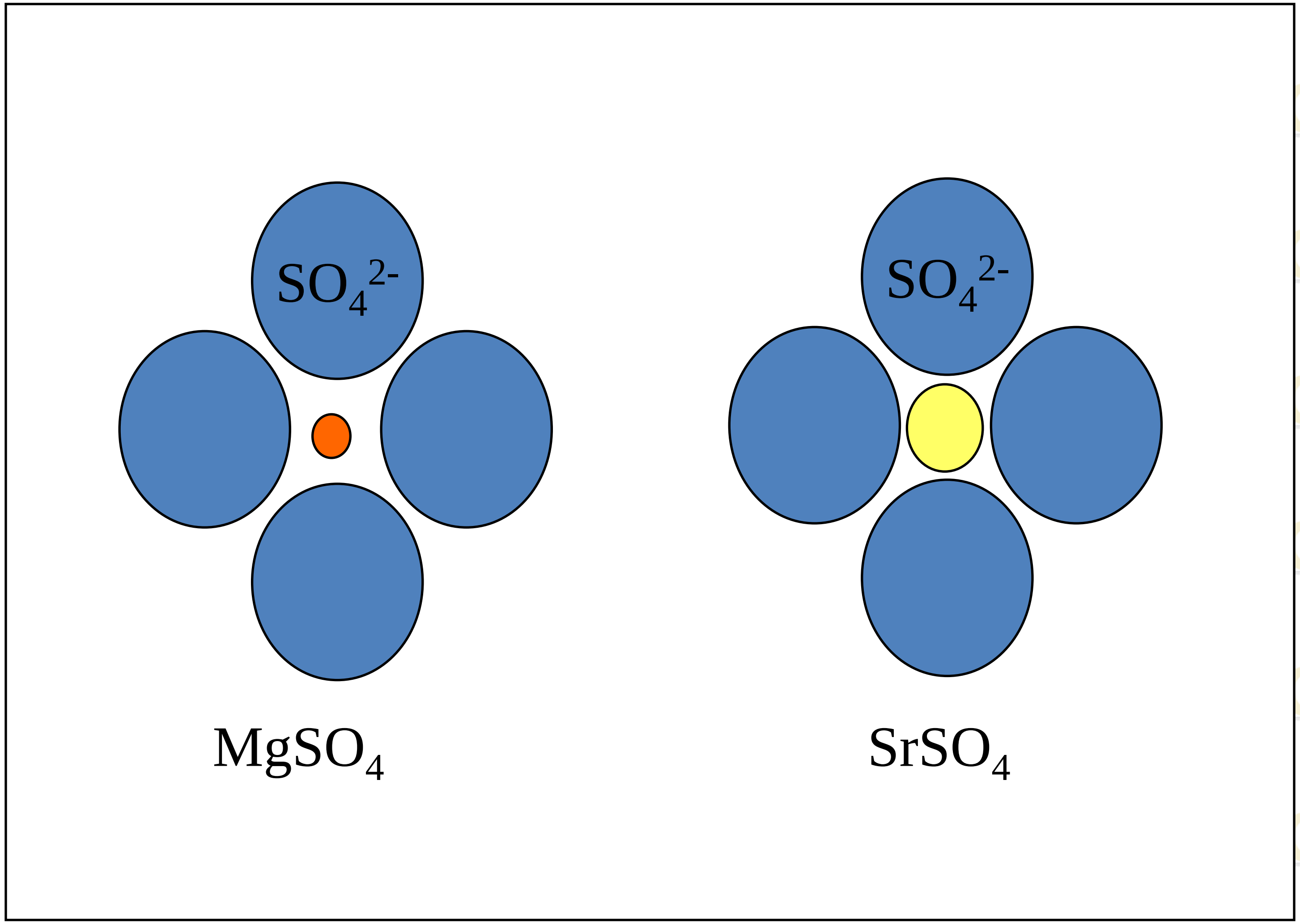
$$\Delta H_{solution} = -\Delta H_{lattice} + \Delta H_{hydration}$$

Explanation of s

$\Delta H_{solution} = -\Delta H_{lattice} + \Delta H_{hydration}$

2. For Group II sulphates, the cations are much smaller than the anions. The changing in size of cations does not cause a significant change in $\Delta H_{lattice}$ (proportional to $1/(r_+ + r_-)$).
   However, the changing in size of cations does cause $\Delta H_{hydration}$ (proportional to $1/r_+$ and $1/r_-$) to become less exothermic and the solubility decreases when
   descending the Group. Going down the size of the cation increases, so hydration become more difficult, $\Delta H_{hydration}$ becomes less negative/ less exothermic. Accordingly $\Delta H_{solution}$ too becomes less

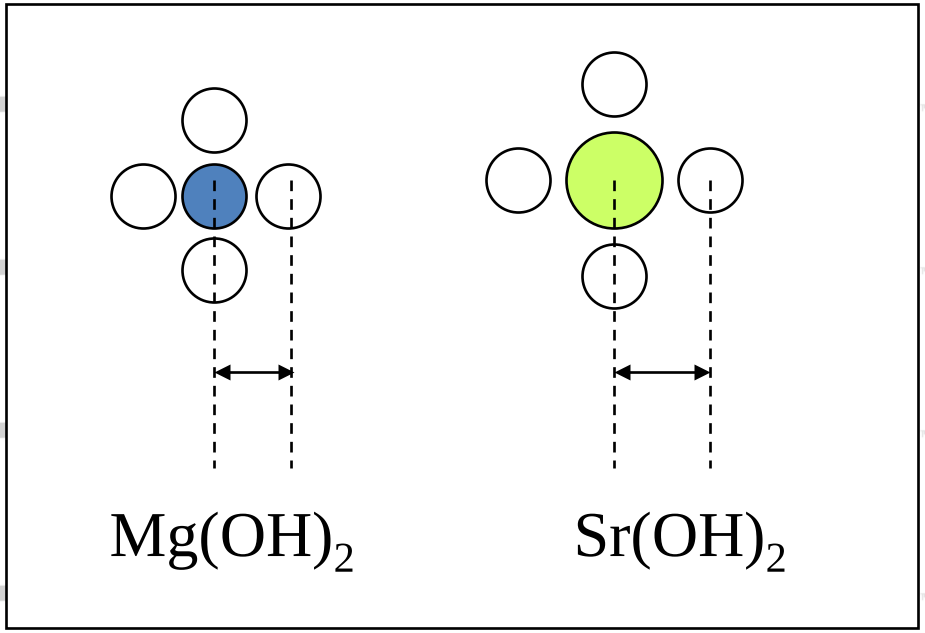
   exothermic, so the solubility decreases.


SO_4^{2-}
SO_4^{2-}
$MgSO_4$
$SrSO_4$

Explanation of solubility

$$\Delta H_{solution} = -\Delta H_{lattice} + \Delta H_{hydration}$$

3. For the smaller size anions, OH^-.
   Down the Group, less enthalpy is required to break the lattice as the size of cation increases.
   However the change in $\Delta H_{solution}$ is comparatively smaller due to the large value of $1/r_-$.
   As a result, $\Delta H_{solution}$ becomes more exothermic and the solubility increases down the Group.


$Mg(OH)_2$
$Sr(OH)_2$

	Cl^-	Br^-	I^-	OH^-	CO_3^{2-}	HCO_3^-	NO_2^-	NO_3^-	S^{2-}	SO_3^{2-}	SO_4^{2-}
Na^+	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
K^+	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
Be^{2+}	Soluble	Soluble	Soluble	Insoluble	Insoluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
Mg^{2+}	Soluble	Soluble	Soluble	Insoluble	Insoluble	Soluble	Soluble	Soluble	Soluble	Sparingly soluble	Soluble
Ca^{2+}	Soluble	Soluble	Soluble	Sparingly soluble	Insoluble	Soluble	Soluble	Soluble	Soluble	Insoluble	Sparingly soluble
Sr^{2+}	Soluble	Soluble	Soluble	Sparingly soluble	Insoluble	Soluble	Soluble	Soluble	Soluble	Insoluble	Insolubl
Ba^{2+}	Soluble	Soluble	Soluble	soluble	Insoluble	Soluble	Soluble	Soluble	Soluble	Insoluble	Insoluble

e

Uses of s-block compounds

- Sodium carbonate
  - Manufacture of glass
  - Water softening
  - Paper industry
- Sodium hydrocarbonate
  - Baking powder
  - Soft drink

Uses of s-block compounds

- Sodium hydroxide
  - Manufacture of soaps, dyes, paper and drugs
  - To make rayon and important chemicals
- Magnesium hydroxide
  - Milk of magnesia, an antacid
- Calcium hydroxide
  - To neutralize acids in waste water treatment
- Strontium compound
  - Fireworks, persistent intense red flame