The s-Block Elements

Presented by
Mrs. Shashi Jit
Associate Professor
Chemistry Department
PGGCG, Sector 11,
Chandigarh
Members of the s-Block Elements

<table>
<thead>
<tr>
<th>IA</th>
<th>IIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>Be</td>
</tr>
<tr>
<td>Na</td>
<td>Mg</td>
</tr>
<tr>
<td>K</td>
<td>Ca</td>
</tr>
<tr>
<td>Rb</td>
<td>Sr</td>
</tr>
<tr>
<td>Cs</td>
<td>Ba</td>
</tr>
<tr>
<td>Fr</td>
<td>Ra</td>
</tr>
</tbody>
</table>

IA Alkali metals
IIA Alkaline Earth metals
Chapter summary

• 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 form complexes
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

<table>
<thead>
<tr>
<th></th>
<th>Group I</th>
<th>Group II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1.0</td>
<td>Be</td>
</tr>
<tr>
<td>Na</td>
<td>0.9</td>
<td>Mg</td>
</tr>
<tr>
<td>K</td>
<td>0.8</td>
<td>Ca</td>
</tr>
<tr>
<td>Rb</td>
<td>0.8</td>
<td>Sr</td>
</tr>
<tr>
<td>Cs</td>
<td>0.7</td>
<td>Ba</td>
</tr>
<tr>
<td>Fr</td>
<td>0.7</td>
<td>Ra</td>
</tr>
</tbody>
</table>
# Basic oxides, hydroxides

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Hydroxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$O</td>
<td>LiOH</td>
</tr>
<tr>
<td>Na$_2$O, Na$_2$O$_2$</td>
<td>NaOH</td>
</tr>
<tr>
<td>K$_2$O$_2$, KO$_2$</td>
<td>KOH</td>
</tr>
<tr>
<td>Rb$_2$O$_2$, RbO$_2$</td>
<td>RbOH</td>
</tr>
<tr>
<td>Cs$_2$O$_2$, CsO$_2$</td>
<td>CsOH</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Hydroxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>Be(OH)$_2$</td>
</tr>
<tr>
<td>MgO</td>
<td>Mg(OH)$_2$</td>
</tr>
<tr>
<td>CaO</td>
<td>Ca(OH)$_2$</td>
</tr>
<tr>
<td>SrO</td>
<td>Sr(OH)$_2$</td>
</tr>
<tr>
<td>BaO, Ba$_2$O$_2$</td>
<td>Ba(OH)$_2$</td>
</tr>
</tbody>
</table>
Oxides, Peroxide, Superoxide

Reaction with water:

Oxide: \( \text{O}^{2-} + \text{H}_2\text{O} \rightarrow 2\text{OH}^- \)

Peroxide: \( \text{O}_2^{2-} + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^- \)

Superoxide: \( 2\text{O}_2^- + 2\text{H}_2\text{O} \rightarrow 2\text{OH}^- + \text{H}_2\text{O}_2 + \text{O}_2 \)

Li does not form peroxide or super oxide

\( \text{Li}_2\text{O}_2 \rightarrow \text{Li}_2\text{O} + \frac{1}{2} \text{O}_2 \)
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

\[ \text{Na}^+ \text{Cl}^- (g) \rightarrow \text{Na} (g) + \text{Cl} (g) \]
\[ \text{Na} (g) \rightarrow \text{Na}^* (g) \]
\[ [\text{Ne}]3s^1 \quad [\text{Ne}]3p^1 \]
\[ \text{Na}^* (g) \rightarrow \text{Na} (g) + h\nu (589\text{nm}, \text{yellow}) \]
Flame test

Li  deep red
Na  yellow
K   lilac
Rb  bluish red
Cs  blue
Ca  brick red
Sr  blood red
Ba  apple green

HCl(aq)  sample
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)

<table>
<thead>
<tr>
<th>Element</th>
<th>Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>0.152</td>
</tr>
<tr>
<td>Na</td>
<td>0.186</td>
</tr>
<tr>
<td>Mg</td>
<td>0.160</td>
</tr>
<tr>
<td>K</td>
<td>0.231</td>
</tr>
<tr>
<td>Ca</td>
<td>0.197</td>
</tr>
<tr>
<td>Rb</td>
<td>0.244</td>
</tr>
<tr>
<td>Sr</td>
<td>0.215</td>
</tr>
<tr>
<td>Cs</td>
<td>0.262</td>
</tr>
<tr>
<td>Ba</td>
<td>0.217</td>
</tr>
<tr>
<td>Fr</td>
<td>0.270</td>
</tr>
<tr>
<td>Ra</td>
<td>0.220</td>
</tr>
</tbody>
</table>
# Ionization Enthalpy

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>519</td>
<td>7300</td>
<td>Be</td>
<td>900</td>
<td>1760</td>
<td>14800</td>
</tr>
<tr>
<td>Na</td>
<td>494</td>
<td>4560</td>
<td>Mg</td>
<td>736</td>
<td>1450</td>
<td>7740</td>
</tr>
<tr>
<td>K</td>
<td>418</td>
<td>3070</td>
<td>Ca</td>
<td>590</td>
<td>1150</td>
<td>4940</td>
</tr>
<tr>
<td>Rb</td>
<td>402</td>
<td>2370</td>
<td>Sr</td>
<td>548</td>
<td>1060</td>
<td>4120</td>
</tr>
<tr>
<td>Cs</td>
<td>376</td>
<td>2420</td>
<td>Ba</td>
<td>502</td>
<td>966</td>
<td>3390</td>
</tr>
</tbody>
</table>
Ionization Enthalpy

1st I.E.

Li  Na  K  Rb  Cs

1st IE

2nd IE

Be⁺  Ca⁺  Ba⁺

Be  Ca  Ba
Ionization Enthalpy

Group I

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

2. Removal of a 2\textsuperscript{nd} 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 3\textsuperscript{rd} 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

-600 to -300

Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺

-2250 to -1500

Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺
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.
## Variation in Melting Points

<table>
<thead>
<tr>
<th>Group I</th>
<th>Structure</th>
<th>Group II</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>B.C.C.</td>
<td>Be</td>
<td>H.C.P.</td>
</tr>
<tr>
<td>Na</td>
<td>B.C.C.</td>
<td>Mg</td>
<td>H.C.P.</td>
</tr>
<tr>
<td>K</td>
<td>B.C.C.</td>
<td>Ca</td>
<td>C.C.P.</td>
</tr>
<tr>
<td>Rb</td>
<td>B.C.C.</td>
<td>Sr</td>
<td>C.C.P.</td>
</tr>
<tr>
<td>Cs</td>
<td>B.C.C.</td>
<td>Ba</td>
<td>B.C.C.</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th></th>
<th>Normal Oxide</th>
<th>Peroxide</th>
<th>Superoxide</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Structure</strong></td>
<td>.. 2-</td>
<td>.. 2-</td>
<td>.. -</td>
</tr>
<tr>
<td>:O:</td>
<td>..</td>
<td>:O-O:</td>
<td>:O::O:</td>
</tr>
<tr>
<td><strong>Formed by</strong></td>
<td>Li and Group II</td>
<td>Na and Ba</td>
<td>K, Rb, Cs</td>
</tr>
</tbody>
</table>
Reaction with water

\[ \text{M(s)} \rightarrow \text{M}^+(\text{aq}) + \text{e}^- \]
\[ \text{H}_2\text{O}(l) + \text{e}^- \rightarrow \text{OH}^-(\text{aq}) + \frac{1}{2} \text{H}_2(\text{g}) \]

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 s-block elements except Be react directly with hydrogen.

\[ 2\text{Na}(s) + \text{H}_2(g) \rightarrow 2\text{NaH}(s) \]
\[ \text{Ca}(s) + \text{H}_2(g) \rightarrow \text{CaH}_2(s) \]

The reactivity increases down the group.

Only \( \text{BeH}_2 \) and \( \text{MgH}_2 \) are covalent, others are ionic.
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.
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 hydroxide
Reactions of oxides and hydroxides

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

   Oxide: $\text{O}^{2-} + \text{H}_2\text{O} \rightarrow 2\text{OH}^-$
   Peroxide: $\text{O}_2^{2-} + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^-$
   Superoxide: $2\text{O}_2^- + 2\text{H}_2\text{O} \rightarrow 2\text{OH}^- + \text{H}_2\text{O}_2 + \text{O}_2$

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 $\text{Be(OH)}_2(s)$ and $\text{HCl(aq)}$.
   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:\[\text{H}^-\](s)+ H\text{2}O(l) \rightarrow \text{H}2(g)+ \text{OH}^-\text{(aq)}

Hydride ions are also good reducing agent. They can be used to prepare complex hydrides such as LiAlH\text{4} and NaBH\text{4} which are used to reduce C=O in organic chemistry.
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$_2$CO$_3$ → Li$_2$O + CO$_2$ (at 700°C)
All other group I carbonates are stable at ~800°C

BeCO$_3$ → BeO + CO$_2$ (at 100°C)
MgCO$_3$ → MgO + CO$_2$ (at 540°C)
CaCO$_3$ → CaO + CO$_2$ (at 900°C)
SrCO$_3$ → SrO + CO$_2$ (at 1290°C)
BaCO$_3$ → BaO + CO$_2$ (at 1360°C)
Thermal Stability of hydroxides

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

Be(OH)$_2$(s) → BeO(s) + H$_2$O(g)  \[\Delta H = +54 \text{ kJ/mol}\]
Mg(OH)$_2$(s) → MgO(s) + H$_2$O(g)  \[\Delta H = +81 \text{ kJ/mol}\]
Ca(OH)$_2$(s) → CaO(s) + H$_2$O(g)  \[\Delta H = +109 \text{ kJ/mol}\]
Sr(OH)$_2$(s) → SrO(s) + H$_2$O(g)  \[\Delta H = +127 \text{ kJ/mol}\]
Ba(OH)$_2$(s) → BaO(s) + H$_2$O(g)  \[\Delta H = +146 \text{ kJ/mol}\]
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. Compounds are more stable if the charge increases and size decreases.
4. For compounds with large polarizable anions, thermal stability is affected by the polarizing power of the cations.
Explanation of Thermal Stability

Decreasing polarizing power

Increasing stability
Explanation of Thermal Stability

\[
\text{Mg}^{2+} \xrightarrow{\text{O} \cdots \text{C} \cdots \text{O}^{-}} \text{Mg}^{2+} \text{O}^{2-} + \text{CO}_2
\]

\[
\text{Mg}^{2+} \xrightarrow{\text{O} \cdots \text{H}} \xrightarrow{\text{H} \cdots \text{O}} \text{Mg}^{2+} \text{O}^{2-} + \text{H}_2\text{O}
\]
Explanation of Thermal Stability

\[ \text{MgCO}_3 \rightarrow \text{MgO} \]

\[ \text{BaCO}_3 \rightarrow \text{BaO} \]

Diagram showing the transition of MgCO$_3$ to MgO and BaCO$_3$ to BaO with a graph indicating the stability of MgO and BaO.
Relative solubility of Group II hydroxides

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility / mol per 100g water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(OH)(_2)</td>
<td>0.020 x 10(^{-3})</td>
</tr>
<tr>
<td>Ca(OH)(_2)</td>
<td>1.5 x 10(^{-3})</td>
</tr>
<tr>
<td>Sr(OH)(_2)</td>
<td>3.4 x 10(^{-3})</td>
</tr>
<tr>
<td>Ba(OH)(_2)</td>
<td>15 x 10(^{-3})</td>
</tr>
</tbody>
</table>

Solubility of hydroxides increases down the group.
Solubility of Group II sulphates

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility / mol per 100g water</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO$_4$</td>
<td>$3600 \times 10^{-4}$</td>
</tr>
<tr>
<td>CaSO$_4$</td>
<td>$11 \times 10^{-4}$</td>
</tr>
<tr>
<td>SrSO$_4$</td>
<td>$0.62 \times 10^{-4}$</td>
</tr>
<tr>
<td>BaSO$_4$</td>
<td>$0.009 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Solubility of sulphates increases up the group.
Explanation of solubility

\[ \text{MX(s)} \xrightarrow{\text{aqueous}} \text{M}^+(\text{aq}) + \text{X}^-(\text{aq}) \]

\[ \Delta H_{\text{solution}} \]

\[ -\Delta H_{\text{lattice}} \]

\[ \text{M}^+(\text{g}) + \text{X}^-(\text{g}) \]

\[ \Delta H_{\text{hydration}} \]

\[ \Delta H_{\text{solution}} = -\Delta H_{\text{lattice}} + \Delta H_{\text{hydration}} \]
Explanation of solubility

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

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

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

2. For Group II sulphates, the cations are much smaller than the anions, not causing a significant change in \(\Delta H_{\text{lattice}}\) (proportional to \(1/(r_+ + r_-)\)). However, the changing in size of cations does cause \(\Delta H_{\text{hydration}}\) (proportional to \(1/r_+\) and \(1/r_-\)) to become less exothermic, and the solubility decreases when descending the Group.
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.

\[
\Delta H_{\text{solution}} = -\Delta H_{\text{lattice}} + \Delta H_{\text{hydration}}
\]
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
**Crown Ethers**

**Structure**
- cyclic polyethers derived from repeating \(--\text{OCH}_2\text{CH}_2--\) units

**Properties**
- form stable complexes with metal ions

**Applications**
- synthetic reactions involving anions
negative charge concentrated in cavity inside the molecule
negative charge concentrated in cavity inside the molecule
forms stable Lewis acid/Lewis base complex with $K^+$
forms stable Lewis acid/Lewis base complex with $K^+$
Ion-Complexing and Solubility

$K^+ F^-$

not soluble in benzene
Ion-Complexing and Solubility

\[ \text{add 18-crown-6} \]

\[ \text{K}^+ \text{F}^- \rightarrow \text{benzene} \]
Ion-Complexing and Solubility

18-crown-6 complex of K⁺ dissolves in benzene
Ion-Complexing and Solubility

F⁻ carried into benzene to preserve electroneutrality

+ F⁻
Thank You