The s-Block Elements

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Members of the s-Block Elements



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 sblock 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		Oxide	Hydroxides
Li ₂ O	LiOH		BeO	Be(OH) ₂
Na ₂ O,	NaOH		MgO	Mg(OH) ₂
Na ₂ O ₂			CaO	Ca(OH) ₂
K_2O_2, KO_2	КОН		SrO	Sr(OH) ₂
Rb_2O_2 , RbO_2	RbOH		BaO, Ba ₂ O ₂	Ba(OH) ₂
Cs_2O_2 ,	CsOH			
CsO 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: $2O_2^{-} + 2H_2O \rightarrow 2OH^- + H_2O_2 + O_2$



Li does not form peroxide or super oxide $Li_2O_2 \rightarrow Li_2O + \frac{1}{2}O_2$

Hydroxides



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

$$\begin{split} &Na^+ \operatorname{Cl}^-(g) \to \operatorname{Na}(g) + \operatorname{Cl}(g) \\ &Na(g) \to \operatorname{Na}^*(g) \\ &[\operatorname{Ne}]3s^1 \quad [\operatorname{Ne}]3p^1 \\ &Na^*(g) \to \operatorname{Na}(g) + \operatorname{hu}(589\mathrm{nm}, \mathrm{yellow}) \end{split}$$



Flame test



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	k	
Na	0.186	Mg	0.160		F
K	0.231	Ca	0.197		R
Rb	0.244	Sr	0.215		
Cs	0.262	Ва	0.217	Be	
Fr	0.270	Ra	0.220		

Ionization Enthapy

Group I	1st I.E.	2nd I.E.	Group I	1st I.E.	2nd I.E.	3 rd I.E.
Li	519	7300	Be	900	1760	14800
Na	494	4560	Mg	736	1450	7740
K	418	3070	Ca	590	1150	4940
Rb	402	2370	Sr	548	1060	4120
Cs	376	2420	Ba	502	966	3390





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.
- 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

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





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

Group I	Structure	Group II	Structure
Li	B.C.C.	Be	H.C.P.
Na	B.C.C.	Mg	H.C.P.
K	B.C.C.	Ca	C.C.P.
Rb	B.C.C.	Sr	C.C.P.
Cs	B.C.C.	Ba	B.C.C.

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		F	Peroxide		Superoxide		
Structure	 :O: 	2-		2- :O-O: 			 :0:.0: 	
Formed by	Li and Group II		1	Na and Ba		K,	Rb, Cs	

Reaction with water

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

Li	-3.05 volt	
Na	-2.71	
Κ	-2.93]
Rb	-2.99	I
Cs	-3.20	(
		1



Energetic vs. Kinetic Factor

Reaction with hydrogen

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 BeH₂ and MgH₂ 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 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)+ H₂O(l) → H₂(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.

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°C) All other group I carbonates are stable at ~800°C

 $\begin{array}{ll} \operatorname{BeCO}_3 \to \operatorname{BeO} + \operatorname{CO}_2 & (\mbox{ at } 100^\circ \mathrm{C}) \\ \operatorname{MgCO}_3 \to \operatorname{MgO} + \operatorname{CO}_2 & (\mbox{ at } 540^\circ \mathrm{C}) \\ \operatorname{CaCO}_3 \to \operatorname{CaO} + \operatorname{CO}_2 & (\mbox{ at } 900^\circ \mathrm{C}) \\ \operatorname{SrCO}_3 \to \operatorname{SrO} + \operatorname{CO}_2 & (\mbox{ at } 1290^\circ \mathrm{C}) \\ \operatorname{BaCO}_3 \to \operatorname{BaO} + \operatorname{CO}_2 & (\mbox{ at } 1360^\circ \mathrm{C}) \end{array}$

Thermal Stability of hydroxides

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

 $\begin{array}{ll} \text{Be}(\text{OH})_2(\text{s}) \rightarrow \text{BeO}(\text{s}) + \text{H}_2\text{O}(\text{g}) & \Delta\text{H} = +54 \text{ kJ/mol} \\ \text{Mg}(\text{OH})_2(\text{s}) \rightarrow \text{MgO}(\text{s}) + \text{H}_2\text{O}(\text{g}) & \Delta\text{H} = +81 \text{ kJ/mol} \\ \text{Ca}(\text{OH})_2(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{g}) & \Delta\text{H} = +109 \text{ kJ/mol} \\ \text{Sr}(\text{OH})_2(\text{s}) \rightarrow \text{SrO}(\text{s}) + \text{H}_2\text{O}(\text{g}) & \Delta\text{H} = +127 \text{ kJ/mol} \\ \text{Ba}(\text{OH})_2(\text{s}) \rightarrow \text{BaO}(\text{s}) + \text{H}_2\text{O}(\text{g}) & \Delta\text{H} = +146 \text{ kJ/mol} \end{array}$

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*.

- 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.







Relative solubility of Group II hydroxides

Compound	Solubility / mol per 100g water
Mg(OH) ₂	0.020 x 10 ⁻³
Ca(OH) ₂	1.5 x 10 ⁻³
Sr(OH) ₂	3.4 x 10 ⁻³
Ba(OH) ₂	15 x 10 ⁻³

Solubility of hydroxides increases down the group.

Solubility of Group II sulphates

Compound	Solubility / mol per 100g water
MgSO ₄	3600 x 10 ⁻⁴
CaSO ₄	11 x 10 ⁻⁴
SrSO ₄	0.62 x 10 ⁻⁴
BaSO ₄	0.009 x 10 ⁻⁴

Solubility of sulphates increases up the group.

Explanation of solubility



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

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.

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

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

2. For Group II subhates, the cations are much smaller than the anion ot cause a store to $1/(r_+ + r_-)$. However, the $\Delta H_{hydration}$ (prescontermic, a descending the second states) $MgSO_4$ $SrSO_4$



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

3. For the smaller size anions, OH^{-} .

Down the Group, less break the lattice as the However the change smaller due to the lat As a result, $\Delta H_{solution}$ and the solubility inc



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 $-OCH_2CH_2$ — 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⁺

K^+F^-

not soluble in benzene



K+F−

benzene

add 18-crown-6



18-crown-6 complex of K⁺ dissolves in benzene



F⁻ carried into benzene to preserve electroneutrality

+ F-

Thank You