
s-Block chemistry

26.1 The Group 1 elements

- The Group 1 elements are metallic solids with low melting points, low boiling points, and low enthalpies of atomization.
- The Group 1 metals are very reactive, and are readily oxidized to M^+ cations.
- Lithium and sodium are produced industrially by electrolysis of the molten chlorides, whereas potassium, rubidium, and caesium are obtained by reduction of their salts with sodium.

26.2 Group 1 compounds

- The Group 1 metals burn in air to form Li_2O , Na_2O_2 , KO_2 , RbO_2 , and CsO_2 as the major products.
- The Group 1 metals react violently with water to form H_2 gas and alkaline aqueous solutions of the hydroxides, MOH .
- The Group 1 metal halides are colourless ionic solids with the formulae MX .
- The Group 1 metals react with ethyne in liquid ammonia to form ethynides M_2C_2 , but only lithium forms a stable nitride, Li_3N .
- The hydrides and nitrides become less stable down the group due to the decrease in their lattice enthalpies.
- Peroxides, superoxides, nitrates, and carbonates become more stable down the group, due to the decreasing difference between their lattice enthalpies and those of their decomposition products.
- Generally, large cations stabilize large anions.
- The ionic nature of the bonding in Group 1 compounds means that enthalpy cycles can be used to investigate trends in the stabilities of the compounds going down the group.

26.3 Group 1 ions in solution

- For salts with large anions such as chlorides, bromides, and nitrates, the solubility in water decreases down Group 1.
- For salts with small anions such as fluorides and hydroxides, the solubility in water increases down Group 1.
- Generally compounds are soluble if they have small cations and large anions, or large cations and small anions.

26.4 Group 1 coordination chemistry

- Group 1 ions have low charge densities so they bind only weakly to most ligands.
- Group 1 ions form stable complexes with macrocyclic ligands such as crown ethers and cryptands. These ligands are size-selective, and form the most stable complexes with the metal ions that fit best into the cavity.

26.5 Reaction of Group 1 metals with liquid ammonia

- Group 1 metals dissolve in liquid ammonia to give blue solutions containing solvated electrons.
- These solutions are very strong reducing agents.

26.6 The Group 2 elements

- The Group 2 elements are metallic solids and typically form ionic compounds. Beryllium is exceptional in forming many covalent compounds.
- The Group 2 elements are less reactive than the Group 1 elements, but are readily oxidized to M^{2+} cations.
- The metals are produced by reduction of the oxides, but magnesium is also obtained from seawater.

26.7 Group 2 compounds

- The Group 2 metals burn in air to form the oxides, MO . For the later Group 2 metals, peroxides, MO_2 , are also formed.
- With the exception of beryllium, the Group 2 elements react with water to give the hydroxide, $M(OH)_2$, and H_2 gas.
- With the exception of beryllium, the Group 2 elements form ionic halides, MX_2 .

- The carbonates, nitrates, and hydroxides decompose on heating to oxides, with the decomposition temperature increasing down the group.

26.8 Group 2 coordination chemistry

- Group 2 ions have a more extensive coordination chemistry than Group 1 ions because of their greater charge density.
- Coordination numbers increase down the group with the increasing size of the M^{2+} ions.
- Be^{2+} compounds are acidic in solution due to hydrolysis of the $[Be(H_2O)_4]^{2+}$ ions.

26.9 Lithium and beryllium as exceptional elements

- The anomalous nature of lithium and beryllium is due to the small size of the Li^+ and Be^{2+} ions, and their high charge densities. Although this leads to the chemistry of these ions being very different from the other members of their groups, this behaviour fits with predictions from the ionic model.

26.10 Organometallic compounds

- Lithium and magnesium form organometallic compounds that are useful reagents in organic synthesis.
- Organolithium compounds RLi exist as oligomers. For example, the structure of methyl lithium contains $[MeLi]_4$ tetramers.
- Grignard reagents $RMgX$ contain tetrahedral metal centres and often crystallize with coordinated solvent molecules.
- Organometallic compounds are important in organic synthesis due to the carbon atoms being able to act as nucleophiles.

26.11 Diagonal relationships

- Since many trends work in different directions down groups and across rows, elements whose positions in the Periodic Table are diagonally related often have similar properties.
- The diagonal relationship between lithium and magnesium is particularly strong.

Learning outcomes

By the end of this chapter you should be able to do the following.

- Describe the preparation, uses, and reactivity of the *s*-block elements.
- Describe the synthesis and reactions of the *s*-block oxides, hydroxides, and halides.
- Explain why *s*-block compounds are largely ionic and rationalize the exceptions.
- Explain trends in reactivity and thermal stability using enthalpy cycles.
- Describe changes in the solubility of *s*-block compounds and explain these using the lattice Gibbs energies and hydration Gibbs energies.
- Justify why the chemistries of lithium and beryllium differ from those of the other elements in their groups.
- Explain the basis of the diagonal relationship between lithium and magnesium.
- Describe examples of *s*-block coordination complexes and explain why Group 2 coordination chemistry is more prevalent than Group 1 coordination chemistry.
- Use energy cycles to explain why some compounds don't exist.
- Describe examples of lithium and magnesium organometallic compounds.