Chapter 10

The s-Block Elements (For Advanced)

INTRODUCTION

The elements found in the s-block of the Periodic Table are characterized by having their last electron enter the outermost s-orbital. In our study, we will delve into the compounds formed by these s-block elements, exploring their applications, uses, and overall significance.

S- Block Elements Introduction

The s-block is positioned at the far-left side of the periodic table. Due to the limitation of the s-orbital to accommodate only two electrons, elements with one electron in their outermost s-orbital are grouped into Group 1, while those with two electrons occupy Group 2.

Group 1 of the periodic table consists of Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Caesium (Cs), and Francium (Fr). These elements collectively belong to the category of alkali metals because, upon reacting with water, they form hydroxides that are strongly alkaline in nature. While Sodium and Potassium are abundant in nature, Lithium, Rubidium, and Caesium have lower abundance. Francium, the final element in Group 1, is radioactive.

Group 2 encompasses Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba), and Radium (Ra). With the exception of Beryllium, the other elements in Group 2 are referred to as alkaline earth metals. This nomenclature is attributed to the alkaline nature of their oxides and hydroxides, which are found in the Earth's crust. Beryllium is not classified as an alkaline earth metal due to the amphoteric nature of its oxide, BeO, as demonstrated in reactions with both acids and alkalies:

$$BeO + 2HCl \rightarrow BeCl_2 + H_2O$$

$$BeO + 2NaOH + H_2O \rightarrow \underset{\text{sodium beryllate}}{Na_2[Be(OH)_4]}$$

Among the alkaline earth metals, Calcium and Magnesium are ranked 5th and 6th, respectively, in abundance in the Earth's crust. Strontium and Barium have comparatively lower abundance, Beryllium is rare, and Radium is the rarest of all alkaline earth metals.

The general electronic configuration for alkali metals is [noble gas] ns, and for alkaline earth metals, it is [noble gas] ns^2. The first element in each group exhibits anomalous behavior compared to other members of the respective group, owing to factors such as smaller atomic size, higher ionization enthalpies, higher electronegativities, and the absence of vacant d-orbitals in their valence shells. These anomalous properties bear a resemblance to the second element of the next group.

For example, lithium exhibits similarities to magnesium, and beryllium shares common traits with Aluminium in many of their properties, a phenomenon known as the diagonal relationship.

Cause of Diagonal Relationship

As one progresses along a period from left to right on the periodic table, the electropositive character of elements decreases.

Conversely, when moving down a group, the electro positivity of elements increases. These two opposing effects partially offset each other when moving diagonally from the top left to the bottom right of the periodic table.

Consequently, elements that are diagonally related in this manner exhibit similar properties. This phenomenon, known as the diagonal relationship, is primarily attributed to the similarity in ionic sizes.

Biological fluids contain a substantial number of ions, including Na^+, K^+, Mg^{2+}, and Ca^{2+}. These ions play a crucial role in maintaining ion balance and facilitating nerve impulse conduction.

Lithium exhibits a diagonal relationship with magnesium because they share similar polarizing power, which is the ratio of charge to size. Lithium resembles magnesium in several aspects, including:

1. Their atomic sizes, with Li at 1.34 A and Mg at 1.36 A, are quite similar.
2. The ionic sizes of Li^+ (0.60 A) and $Mg^2 +$ (0.65 A) are almost identical.

Their polarizing power, defined as the ratio of ionic charge to ionic radius of Li^+ and Mg^{2+}, is approximately the same.

Their electro negativities, with Li at (1.00) and Mg at (1.20), are not significantly different.

Both lithium and magnesium are classified as hard metals.

They both decompose water only when heated.

Both elements combine with oxygen to form monoxides.

LiOH and $Mg\ (OH)_2$ are both weak bases.

LiCl and $MgCl_2$ are predominantly covalent and, as a result, are soluble in organic solvents such as alcohol and pyridine.

Both lithium and magnesium form nitrides, namely Li_3N and Mg_3N_2, when they react with nitrogen.

Carbonates, chlorides, oxalates, and phosphates of both lithium and magnesium are sparingly soluble in H_2O.

The hydroxides and carbonates of both lithium and magnesium decompose when heated, forming their respective oxides.

Heating nitrates of both lithium and magnesium results in the evolution of NO_2 and O_2, leaving their oxides behind.

GROUP-1 ELEMENTS: ALKALI METALS

Electropositive Character or Metallic Character

The electropositive or metallic character is determined by the ease of removing electrons, as reflected in the ionization potential. Thanks to their larger size, these elements can readily shed their six outermost electrons to form M^+ ions. This electropositive property increases from lithium (Li) to cesium (Cs).

Flame Test

Alkali metals and their salts exhibit distinctive colors when introduced to a Bunsen flame. The energy within the flame excites the outermost electron, which, upon returning to its ground state, emits absorbed energy in the form of visible light.

Ex. Li-Crimson red Na-Golden yellow K-Violet
Rb-Red violet Cs-Blue

Reaction with NH_3

(a) $2Li + NH_3 \rightarrow Li_2NH$(Lithimide)

$2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2 \uparrow$ (So, amide)

(b) Solubility in Liquid Ammonia

1. Alkali metals all dissolve in liquid ammonia (NH3) to form blue solutions.
2. These blue solutions exhibit electrical conductivity and possess strong reducing properties, mainly due to the presence of ammoniated electrons.

$$Na_{(s)} + (x+y)\,NH_3 \rightarrow [Na(NH_3)_x]^+ + \underset{\text{Ammoniated electron}}{[e(NH_3)_y]^-}$$

3. The diluted solutions exhibit paramagnetic properties.

Physical and Chemical Properties of Alkali Metals

Physical Properties

Alkali metals exhibit a characteristic silvery-white coloration and generally possess a soft and lightweight nature. The softness observed in alkali metals is a consequence of the weak metallic bonding within them, primarily influenced by the large size of their atoms. This softness trend intensifies as one descends the group, with potassium surpassing sodium in terms of softness. While alkali metals share low densities, the pattern follows an increasing trend down the group, except for an anomaly where potassium is lighter than sodium. Lithium, being the lightest metal with a density of 0.534 g/cm^3, presents a unique challenge as it cannot be stored in kerosene oil due to its tendency to float on the surface. Instead, it is kept enveloped in paraffin wax.

The low density of alkali metals can be attributed to their expansive atomic size and the resultant weak metallic bond. Interestingly, as one progresses down the group, both atomic size and atomic mass increase. However, the corresponding rise in atomic mass is not entirely offset by the increase in atomic volume, leading to a gradual elevation in the ratio of mass to volume, i.e., density.

Alkali metals also exhibit low melting and boiling points. The low melting points result from their larger atomic size, which translates to lower binding energies among atoms in the crystal lattice. Furthermore, the increase in atomic size as the group descends contributes to a decrease in the strength of the metallic bond, thereby causing a decline in melting points. This consistent trend is mirrored in the boiling points of alkali metals, as the same factors govern their order along the group.

Chemical Properties

The alkali metals exhibit a remarkable degree of reactivity, which can be attributed to specific factors. Firstly, their heightened chemical reactivity arises from a combination of factors, including.

(i) a notably low value of first ionization enthalpy.
(ii) their relatively large size.
(iii) a low heat of atomization.

These factors collectively contribute to the propensity of alkali metals to readily undergo chemical reactions. Moreover, as one progresses down the group of alkali metals, their reactivity intensifies, underscoring the trend of increasing reactivity within this chemical group.

The significance of the chemical properties of alkali metals is underscored by the following points:

1. Elevated temperatures prompt alkali metals to form metallic hydrides, a process that involves the release of ions.
2. Alkali metals exhibit the ability to generate nitrides through their reaction with atmospheric nitrogen.
3. Upon interacting with atmospheric oxygen, alkali metals undergo a transformation where they lose their luster and oxidize. Interestingly, the nature of the oxides produced varies.
4. The interaction of alkali metals with water leads to the generation of basic hydroxides, accompanied by the release of hydrogen. This reaction is exothermic, and the enthalpy increases in a progressive manner from lithium to cesium.

Flame Coloration

When alkali metals and their salts are subjected to heating in the oxidizing flame of a Bunsen burner, they exhibit distinct colors in the flame. This occurrence is a result of the heat generated by the flame exciting the outermost orbital electron, causing it to transition to a higher energy level. Subsequently, when the excited electron returns to the ground state, it emits radiation in the visible region, leading to the characteristic colors observed.

The specific colors for each alkali metal are detailed below:

Metal	Color	Wavelength (λ/nm)
Lithium (Li)	Crimson red	670.8 nm
Sodium (Na)	Yellow	589.2 nm
Potassium (K)	Violet	766.5 nm
Rubidium (Rb)	Red violet	780.0 nm
Cesium (Cs)	Blue	455.5 nm

This distinctive property of alkali metals proves valuable in their identification through flame tests. The quantification of these colors can be achieved through analytical techniques such as flame photometry or atomic absorption spectroscopy.

Example: What is the reason behind the distinctive coloration of the flame when alkali metals are present?

Solution: The phenomenon is attributed to the elevation of the outermost orbital electron to a higher energy level due to the heat generated by the flame. As this excited electron returns to its ground state, it emits radiation within the visible spectrum, giving rise to the characteristic coloration observed in the flame.

Photoelectric Effect

(a) The atomic size of potassium (K), rubidium (Rb), and cesium (Cs) is significantly large, resulting in very low ionization potentials.

(b) Because of their remarkably low ionization potentials, the valence shell electrons of these elements can be easily excited by absorbing visible light. This is why cesium (Cs) is employed in photoelectric cells.

Atomic and Physical Properties of Alkali Earth Metals

Atomic Size

(a) In their respective periods, atomic size is largest for all elements except noble gases.

(b) The atomic size increases from Li to Fr as an extra shell is added.

$$\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs} < \text{Fr}$$

Physical Characteristics

(a) They are characterized by having a single electron in their outermost shell, with a general formula of ns^1.

(b) Francium is an element within the alkali metals group that is radioactive.

(c) All alkali metals possess a silvery-white appearance.

(d) These metals are known for being lightweight, soft, malleable, and ductile, exhibiting a metallic luster.

(e) Alkali metals display paramagnetic or diamagnetic properties and appear colorless when in the form of ions.

Atomic and Ionic Radii

The atoms belonging to alkali metals exhibit the largest size within their respective periods, and this atomic radius expands as one descends the group. The underlying reason for this trend is the progressive addition of new energy shells as the group is traversed. Despite an increase in nuclear charge along the group, the predominant influence stems from the addition of new shells. Consequently, the atomic radii of alkali metals follow an increasing pattern when moving down the group from the top to the bottom.

Alkali metals undergo a transformation into positively charged ions by relinquishing one valence electron. These resulting monovalent ions (M^+) exhibit a size smaller than that of the parent atom. Within the group, there exists a correlation between ionic radii and atomic number, with the ionic radii expanding as the atomic number increases.

Ionization Energy in Alkaline Earth Elements

Alkaline earth elements exhibit a notable capability to donate all their valence electrons, aiming to attain an octet noble gas configuration.

This results in two distinct ionization energies:

(i) First Ionization Energy, (ii) Second Ionization Energy

First Ionization Energy

The initial ionization energy, concerning the removal of the first electron from a neutral alkaline earth metal atom, is influenced by factors such as smaller radii and electrons being closely held by a higher nuclear charge. This energy requirement surpasses that of alkali metal atoms. Notably, electrons are withdrawn from a completely filled subshell, contributing to the stability of the resulting cation.

Second Ionization Energy

The second ionization energy, required for the removal of the second electron from the cation in alkaline earth metals, surpasses the first ionization energy of the atom but falls below the second ionization energy of alkali metals. Despite the formidable nature of ionization energy, the removal of both electrons occurs due to several factors:

1. The atom adopts a noble gas configuration.
2. The compact packing of atoms or ions in solids aids in overcoming the higher ionization energy by increasing lattice energy.
3. Liquids, benefiting from greater solvation, exhibit higher hydration energy.

All alkaline earth elements in group two manifest as divalent electropositive metals with a consistent oxidation state of 2. Notably, the diminutive beryllium atom necessitates the highest ionization energy to remove its valence electron. The protective influence of inner electrons, as the atomic size increases, facilitates easier removal of the valence electron with less energy.

Consequently, the ionization energy experiences a decrease as the atomic number or size of the alkaline earth elements increases.

Hydration Energy (Heat of Hydration)

(a) The solubility of alkali metal salts in water is primarily attributed to the hydration of cations by water molecules.

(b) The extent of cation hydration increases as the cation size decreases.

(c)

$$\underset{\xrightarrow{\hspace{8cm}}}{Li^+ \qquad Na^+ \qquad K^+ \qquad Rb^+ \qquad Cs^+}$$

Decrease in the extent of hydration
Reduction in hydration energy
Diminishing size of hydrated ions
Increased ionic conductance

Reduction Capability

(a) Alkali metals are exceptionally strong reducing agents due to their high standard oxidation potentials.

(b) The reducing ability increases as you move down the group in the gaseous or molten state, with the order:

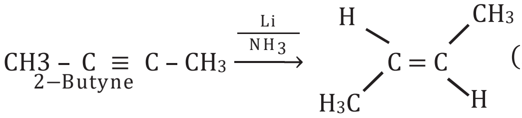
$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$$

(c) However, in an aqueous solution, the order changes to:

$$Li^+ > K^+ \quad Rb^+ > Cs^+ > Na^+$$

Reducing Property

The presence of unbound ammoniated electrons renders the solution highly effective as a potent reducing agent. In comparison to its aqueous counterpart, the ammoniacal solution of an alkali metal is preferred for its superior reducing capabilities. This preference arises from the fact that in an aqueous solution, the highly electropositive alkali metal tends to liberate hydrogen from water. Conversely, when dissolved in ammonia, the alkali metal solution remains relatively stable, assuming no catalyst is introduced.



(Birch Reduction)

Reaction with Sulfur and Phosphorus:

The interaction of metals with sulfur and phosphorus results in the formation of sulfides and phosphides, respectively. This chemical phenomenon is applicable to all metals.

Examples:

$$3Na + P \rightarrow \underset{\text{Sodium phosphide}}{Na_3P}$$

$$2Na + S \rightarrow \underset{\text{Sodium sulphide}}{Na_2S}$$

Reaction with Mercury:

Alkali metals exhibit a notable reaction with mercury, leading to the creation of amalgams. This chemical process is characterized by its highly exothermic nature.

Example:

$$Na + Hg \rightarrow \underset{\text{Sodium Amalgam}}{Na[Hg]}$$

In the presented reaction, sodium (Na) reacts with mercury (Hg), yielding sodium amalgam represented as Na[Hg]. The arrow (←) signifies the direction of the chemical transformation, and the square brackets denote the formation of an amalgam. The reaction is noted for its release of a significant amount of heat, indicating its exothermic characteristic

Uses of Group-1 Elements

1. Lithium finds application as a metallic component in various alloys, including an alloy with magnesium comprising approximately 14% lithium. This alloy exhibits exceptional toughness and corrosion resistance, making it suitable for applications such as armor plates and aerospace components. Additionally, lithium is employed in conjunction with lead to create a white metal and with aluminum for the production of aircraft parts.
2. Lithium hydroxide serves a crucial role in the ventilation systems of spacecraft and submarines, where it is utilized to absorb carbon dioxide, contributing to the maintenance of a controlled and breathable environment.

3. Lithium aluminum hydride ($LiAlH_1$) emerges as a potent reducing agent widely employed in organic synthesis due to its efficacy in facilitating various chemical reactions.
4. Liquid sodium or its alloys, often combined with potassium, functions as a coolant in nuclear reactors, demonstrating its utility in managing the temperature within these high-demand environments.
5. The sodium-lead alloy plays a pivotal role in the synthesis of tetraethyl lead ($Pb(C_2H_3)$), an anti-knocking agent used in petrol. The chemical reaction involving lead-sodium alloy, along with other components, leads to the formation of tetraethyl lead and sodium chloride.
6. Sodium is integral to the production of sodium vapor lamps, contributing to their efficient functioning in various lighting applications.
7. Potassium chloride finds application as a fertilizer, serving as a source of essential potassium nutrients for plant growth.
8. Potassium hydroxide is employed in the manufacturing process of soft soaps and functions as an absorbent for carbon dioxide, showcasing its versatility in different industrial applications.
9. Potassium ions play a vital and multifaceted role in biological systems, influencing various physiological processes essential for the proper functioning of living organisms.
10. Caesium is utilized in the construction of photoelectric cells, where its unique properties make it suitable for converting light energy into electrical energy.