

1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 02 (Class XI – Semester 02)
Module Name/Title	s block elements – Part 2
Module Id	kech_21002
Pre-requisites	Periodic table and periodic properties of elements, properties of alkali metals
Objectives	After going through this module, the learner will be able to: <ul style="list-style-type: none">• Describe the general characteristics of the s block group 2 elements and their compounds.• Explain preparation, properties and uses of industrially important calcium compounds• Diagnol relationship between beryllium and aluminium• Differentiate between alkali and alkaline earth metals• Explain the biological significance of calcium and magnesium
Keywords	Alkaline Earth Metals, Calcium Compounds, Atomic Radii, Ionic Radii, Ionization Enthalpy, Oxidation State, Electrode Potential, Chemical Reactivity

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1. Introduction

The group 2 elements comprise beryllium, magnesium, calcium, strontium, barium and radium. They follow alkali metals in the periodic table. These (except beryllium) are known as alkaline earth metals. The first element beryllium differs from the rest of the members and shows diagonal relationship to aluminium.

Like alkali metals, these elements are also very reactive, hence are distributed in nature in combined form as carbonate, phosphates, silicates and sulphates.

2. Properties of GROUP 2 ELEMENTS : ALKALINE EARTH METALS

The atomic and physical properties of the alkaline earth metals are shown in Table 1.

Property	Beryllium Be	Magnesium Mg	Calcium Ca	Strontium Sr	Barium Ba	Radium Ra
Atomic number	4	12	20	38	56	88
Atomic mass (g mol^{-1})	9.01	24.31	40.08	87.62	137.33	226.03
Electronic configuration	[He] $2s^2$	[Ne] $3s^2$	[Ar] $4s^2$	[Kr] $5s^2$	[Xe] $6s^2$	[Rn] $7s^2$
Ionization enthalpy (I) / kJ mol^{-1}	899	737	590	549	503	509
Ionization enthalpy (II) / kJ mol^{-1}	1757	1450	1145	1064	965	979
Hydration enthalpy (kJ/mol)	- 2494	- 1921	-1577	- 1443	- 1305	-
Metallic radius / pm	111	160	197	215	222	-
Ionic radius M^{2+} / pm	31	72	100	118	135	148
m.p. / K	1560	924	1124	1062	1002	973
b.p. / K	2745	1363	1767	1655	2078	(1973)
Density / g cm^{-3}	1.84	1.74	1.55	2.63	3.59	(5.5)
Standard potential E^\ominus / V for (M^{2+}/M)	-1.97	-2.36	-2.84	-2.89	- 2.92	-2.92
Occurrence in lithosphere	2*	2.76**	4.6**	384*	390 *	10^{-6} *

*ppm (part per million); ** percentage by weight

Table1: Atomic and Physical Properties of the Alkaline Earth Metals

2.1 Electronic Configuration

These elements have two electrons in the orbital of the valence shell (Table 2). Their general electronic configuration may be represented as [noble gas] ns^2 . Like alkali metals, the compounds of these elements are also predominantly ionic. These show similar physical and chemical properties because of same valence shell electronic configuration.

Element	Symbol	Electronic configuration
Beryllium	Be	$1s^2 2s^2$
Magnesium	Mg	$1s^2 2s^2 2p^6 3s^2$
Calcium	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Strontium	Sr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$
Barium	Ba	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$ or [Xe] $6s^2$
Radium	Ra	[Rn] $7s^2$

Table 2; Electronic configuration of Group 2 metals

2.2 Atomic and Ionic Radii

The atomic and ionic radii of the alkaline earth metals are smaller than those of the corresponding alkali metals in the same periods. This is due to the increased nuclear charge in these elements. Within the group, the atomic and ionic radii increase with increase in atomic number due to addition of extra shell of electrons in each succeeding element and hence the screening effect.

2.3 Ionization Enthalpies

The alkaline earth metals have low ionization enthalpies due to fairly large size of the atoms. Since the atomic size increases down the group, their ionization enthalpy decreases (Table 1). The first ionisation enthalpies of the alkaline earth metals are higher than those of the corresponding Group 1 metals. This is due to their small size as compared to the corresponding alkali metals. It is interesting to note that the second ionisation enthalpies of the alkaline earth metals are smaller than those of the corresponding alkali metals. This could be due to the fact that in alkali metals second electron is to be removed from a cation, which has already achieved a noble gas configuration and in alkaline earth metals it is to be removed from a cation, which is yet to achieve a noble gas configuration.

2.4 Hydration Enthalpies

Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group.



Due to their smaller size, the hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Thus, compounds of alkaline earth metals are more extensively hydrated than those of alkali metals, e.g., MgCl_2 and CaCl_2 exist as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ while NaCl and KCl do not form such hydrates.

2.5 Physical Properties

The alkaline earth metals, in general, are silvery white, lustrous and relatively soft but harder than the alkali metals. Beryllium and magnesium appear to be somewhat greyish. The melting and boiling points of these metals are higher than the corresponding alkali metals due to smaller sizes. The trend is, however, not systematic. Because of the low ionisation enthalpies, they are strongly electropositive in nature. The electropositive character increases down the group from Be to Ba. These metals exhibit oxidation state +2 in their compounds. The alkaline earth metals like those of alkali metals have high electrical and thermal conductivities which are typical characteristics of metals.

2.6 Flame colouration: Calcium, strontium and barium impart characteristic brick red, crimson and apple green colours respectively to the flame. In flame the electrons are excited to higher energy levels and when they drop back to the ground state, energy is emitted in the form of visible light. The flame test for Ca, Sr and Ba is helpful in their detection in qualitative analysis and estimation by flame photometry.

The electrons in beryllium and magnesium are strongly bound to the nucleus and so are not excited by the flame. Hence, these elements do not impart any colour to the flame.

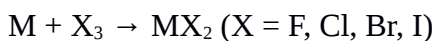
2.7 Chemical Properties

The alkaline earth metals, due to the low ionization energies and high negative values of standard electrode potential are highly reactive metals. The reactivity of these elements increases on going down the group. However, these metals are less reactive than the alkali metals.

(i) Reactivity towards air and water: These metals are less electropositive than alkali metals hence these react with air or oxygen slowly as compared to alkali metals. The reactivity towards oxygen increases on moving down the group. Beryllium and magnesium are kinetically inert to oxygen and water because of the formation of an oxide film on their surface. However, powdered beryllium burns brilliantly on ignition in air to give BeO and Be_3N_2 . Magnesium is more electropositive and burns with dazzling brilliance in air to give MgO and Mg_3N_2 . Calcium,

strontium and barium are readily attacked by air to form the oxide and nitride. They also react with water with increasing vigour even in cold to form hydroxides.

(ii) Reactivity towards the halogens:All the alkaline earth metals combine with halogen at elevated temperatures forming their halides.

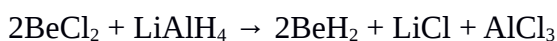


Thermal decomposition of $(NH_4)_2BeF_4$ is the best route for the preparation of BeF_2 . $BeCl_2$ is conveniently made from the oxide.



(iii) Reactivity towards hydrogen:All the elements except beryllium combine with hydrogen upon heating to form their hydrides, MH_2

BeH_2 , however, can be prepared by the reaction of $BeCl_2$ with $LiAlH_4$.



(iv) Reactivity towards acids:The alkaline earth metals readily react with acids liberating dihydrogen.



(v) Reducing nature:Like alkali metals, the alkaline earth metals are strong reducing agents. This is indicated by large negative values of their reduction potentials (Table 1). However their reducing power is less than those of their corresponding alkali metals. Beryllium has less negative value compared to other alkaline earth metals. However, its reducing nature is due to large hydration energy associated with the small size of Be^{2+} ion and relatively large value of the atomization enthalpy of the metal. Reducing character of alkaline earth metals increases on moving down the group.

(vi) Solutions in liquid ammonia:Like alkali metals, all the alkaline earth metals dissolve in liquid ammonia to give deep blue black solutions forming ammoniated ions.



On evaporating these solutions, the ammoniates, $[M(NH_3)_6]^{2+}$ can be recovered, which decompose to give corresponding amides. The concentrated solutions are bronze coloured because of metal cluster formation.

2.8 Uses

Beryllium: Beryllium is used in the manufacture of alloys.

Copper-beryllium alloys are used in the preparation of high strength springs.

Metallic beryllium is used for making windows of X-ray tubes.

Magnesium: Magnesium forms alloys with aluminium, zinc, manganese and tin.

Magnesium-aluminium alloys being light in mass are used in aircraft construction.

Magnesium (powder and ribbon) is used in flash powders and bulbs, incendiary bombs and signals.

A suspension of magnesium hydroxide in water (called milk of magnesia) is used as antacid in medicine.

Magnesium carbonate is an ingredient of toothpaste.

Calcium: Calcium is used in the extraction of metals from oxides which are difficult to reduce with carbon.

Calcium and barium metals, owing to their reactivity with oxygen and nitrogen at elevated temperatures, have often been used to remove air from vacuum tubes.

Barium: Barium sulphate being insoluble in water and opaque to X-rays is used as barium meal to take a shadow of stomach on X-ray film to diagnose ulcers.

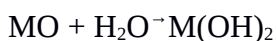
Radium salts are used in radiotherapy, for example, in the treatment of cancer.

3. General Characteristics of Compounds of the Alkaline Earth Metals

The dipositive oxidation state (M^{2+}) is the predominant valence of Group 2 elements. The alkaline earth metals form compounds which are predominantly ionic but less ionic than the corresponding compounds of alkali metals. This is due to increased nuclear charge and smaller size. The oxides and other compounds of beryllium and magnesium are more covalent than those formed by the heavier and large sized members (Ca, Sr, Ba). The general characteristics of some of the compounds of alkali earth metals are described below.

(i) Oxides and Hydroxides: The alkaline earth metals burn in oxygen to form the monoxide, MO which, except for BeO, have rock-salt structure. The enthalpies of formation of these oxides are quite high and consequently they are very stable to heat. The BeO is essentially covalent in nature. While oxides of other elements are ionic in nature. All these oxides except BeO are basic

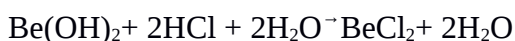
in nature and react with water to form sparingly soluble hydroxides. BeO is amphoteric in nature.



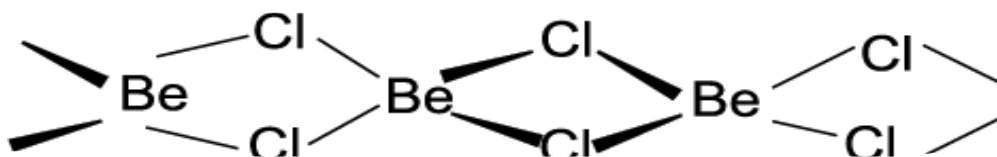
The solubility, thermal stability and the basic character of these hydroxides increase with increasing atomic number from $\text{Mg}(\text{OH})_2$ to $\text{Ba}(\text{OH})_2$. The alkaline earth metal hydroxides are, however, less basic and less stable than alkali metal hydroxides. Beryllium hydroxide is amphoteric in nature as it reacts with acid and alkali both.



Beryllate ion



(ii) Halides: The alkaline earth metals combine with halogens to form their halides MX_2 at appropriate temperatures. Except for beryllium halides, all other halides of alkaline earth metals are ionic in nature. Ionic character of these halides increases as the size of metal ion increases. Beryllium halides are essentially covalent and soluble in organic solvents. Beryllium chloride has a polymeric structure in the solid state as shown below:



In the vapour phase BeCl_2 tends to form a chloro-bridged dimer which dissociates into the linear monomer at high temperatures of the order of 1200 K. The tendency to form halide hydrates gradually decreases (for example, $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) down the group. The dehydration of hydrated chlorides, bromides and iodides of Ca, Sr and Ba can be achieved on heating; however, the corresponding hydrated halides of Be and Mg on heating suffer hydrolysis. The fluorides are relatively less soluble than the chlorides owing to their high lattice energies.

(iii) Salts of Oxoacids: The alkaline earth metals also form salts of oxoacids. Some of these are :

Carbonates: Carbonates of alkaline earth metals are insoluble in water and can be precipitated by addition of a sodium or ammonium carbonate solution to a solution of a soluble salt of these metals. The solubility of carbonates in water decreases as the atomic number of the metal ion increases. All the carbonates decompose on heating to give carbon dioxide and the corresponding metal oxide. Beryllium carbonate is unstable and can be kept only in the atmosphere of CO_2 . The thermal stability increases with increasing cationic size.

Sulphates: The sulphates of the alkaline earth metals are all white solids and stable to heat. Calcium, magnesium and beryllium sulphate crystallize in the hydrate form whereas strontium and barium crystallize without any water of crystallization. BeSO_4 , and MgSO_4 are readily soluble in water; the solubility decreases from CaSO_4 to BaSO_4 . The greater hydration enthalpies of Be^{2+} and Mg^{2+} ions overcome the lattice enthalpy factor and therefore their sulphates are soluble in water.

Nitrates: The nitrates are made by dissolution of the carbonates in dilute nitric acid. Magnesium nitrate crystallises with six molecules of water, whereas barium nitrate crystallises as the anhydrous salt. This again shows a decreasing tendency to form hydrates with increasing size and decreasing hydration enthalpy. All of them decompose on heating to give the oxide like lithium nitrate.



(M = Be, Mg, Ca, Sr, Ba)

Problem

Why does the solubility of alkaline earth metal hydroxides in water increase down the group?

Solution

Among alkaline earth metal hydroxides, the anion being common and small the cationic radius will influence the lattice enthalpy. Since lattice enthalpy decreases much more than the hydration enthalpy with increasing ionic size, the solubility increases as we go down the group.

Problem

Why does the solubility of alkaline earth metal carbonates and sulphates in water decrease down the group?

Solution

The size of anions being much larger compared to cations, the lattice enthalpy will remain almost constant within a particular group. Since the hydration enthalpies decrease down the group, solubility will also decrease on moving down the group for alkaline earth metal carbonates and sulphates.

4. Anomalous Behaviour of Beryllium

Beryllium, the first member of the Group 2 metals, shows anomalous behaviour as compared to magnesium and rest of the members. Further, it shows diagonal relationship to aluminium which is discussed subsequently. The main reasons for anomalous behaviour of beryllium are due to:

(i) Exceptionally small size of its atoms and ions

(ii) High ionisation enthalpy

(iii) Absence of d orbitals

4.1 Difference between beryllium and other alkaline earth metals

- i. Because of high ionisation enthalpy and small size beryllium forms compounds which are largely covalent and get easily hydrolysed.
- ii. Beryllium does not exhibit coordination number more than four as in its valence shell there are only four orbitals. The remaining members of the group can have a coordination number of six by making use of d-orbitals.
- iii. The oxide and hydroxide of beryllium, unlike the hydroxides of other elements in the group, are amphoteric in nature.

4.2 Diagonal Relationship between Beryllium and Aluminium

The ionic radius of Be^{2+} is estimated to be 31 pm and that of Al^{3+} is 50 pm; as a result the charge/radius ratio of both the ions is very similar. Hence beryllium resembles aluminium in some ways. Some of the similarities are:

- i. Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.
- ii. Beryllium hydroxide dissolves in excess of alkali to give a beryllate ion, $[\text{Be}(\text{OH})_4]^{2-}$ just as aluminium hydroxide gives aluminate ion, $[\text{Al}(\text{OH})_4]^-$. Oxides and hydroxide of both Be and Al are amphoteric in nature.
- iii. The chlorides of both beryllium and aluminium are covalent and have Cl-bridged structure in vapour phase. Both the chlorides are soluble in organic solvents and are strong Lewis acids. They are used as Friedel Craft catalysts.
- iv. Beryllium and aluminium ions have strong tendency to form complexes, BeF_4^{2-} , AlF_6^{3-} .

5. Some Important Compounds of Calcium

Important compounds of calcium are calcium oxide, calcium hydroxide, calcium sulphate, calcium carbonate and cement. These are industrially important compounds. The large scale preparation of these compounds and their uses are described below.

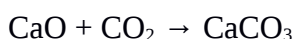
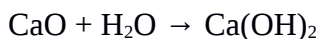
5.1 Calcium Oxide or Quick Lime, CaO

Preparation: It is prepared on a commercial scale by heating limestone (CaCO_3) in a rotary kiln at 1070-1270 K



The carbon dioxide is removed as soon as it is produced to enable the reaction to proceed to completion, as the reaction is reversible

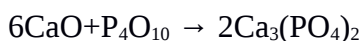
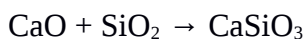
Properties: Calcium oxide is a white amorphous solid. It has a melting point of 2870 K. On exposure to atmosphere, it absorbs moisture and carbon dioxide.



Lime is generally obtained in the form of hard lumps. The addition of limited amount of water breaks the lump of lime. This process is called slaking of lime and fine powder obtained is known as slaked lime.

Quick lime slaked with caustic soda gives solid sodalime (CaO+NaOH).

Being a basic oxide, it combines with acidic oxides at high temperature.

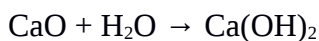


Uses:

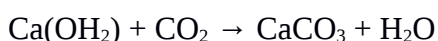
- (i) It is an important primary material for manufacturing cement and is the cheapest form of alkali.
- (ii) It is used in the manufacture of sodium carbonate from caustic soda.
- (iii) It is employed in the purification of sugar and in the manufacture of dye stuffs.
- (iv) It is used as flux in metallurgy.

5.2 Calcium Hydroxide (Slaked lime), Ca(OH)₂

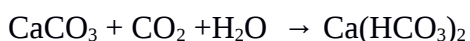
Preparation: Calcium hydroxide is prepared by adding water to quick lime, CaO.



Properties: It is a white amorphous powder. It is sparingly soluble in water. The aqueous solution is known as lime water and a suspension of slaked lime in water is known as milk of lime. When carbon dioxide is passed through lime water it turns milky due to the formation of calcium carbonate.



On passing excess of carbon dioxide, the precipitate dissolves to form calcium hydrogencarbonate.



Milk of lime reacts with chlorine to form hypochlorite, a constituent of bleaching powder.



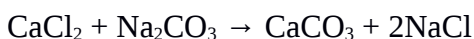
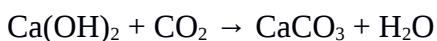
Uses:

- i. It is used in the preparation of mortar, a building material.
- ii. It is used in white wash due to its disinfectant nature.
- iii. It is used in glass making, in tanning industry, for the preparation of bleaching powder and for purification of sugar.
- iv. It is used as lime water to detect carbonates and CO₂.

5.3 Calcium Carbonate, CaCO₃

Calcium carbonate occurs in nature in several forms like limestone, chalk, marble etc.

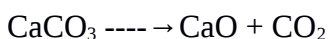
Preparation: It can be prepared by passing carbon dioxide through slaked lime or by the addition of sodium carbonate to calcium chloride.



Excess of carbon dioxide should be avoided since this leads to the formation of water soluble calcium hydrogencarbonate.

Properties: Calcium carbonate is a white fluffy powder. It is almost insoluble in water. When heated to 1200 K, it decomposes to evolve carbon dioxide.

1200K



It reacts with dilute acids liberating CO₂.

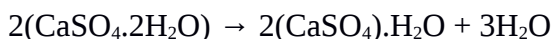
**Uses:**

- i. It is used as a building material in the form of marble and in the manufacture of quick lime.
- ii. Calcium carbonate along with magnesium carbonate is used as a flux in the extraction of metals such as iron.
- iii. Specially precipitated CaCO₃ is extensively used in the manufacture of high quality paper.
- iv. It is also used as an antacid, mild abrasive in tooth paste, a constituent of chewing gum, and a filler in cosmetics.

5.4 Calcium Sulphate (Plaster of Paris), CaSO₄·½ H₂O

It is a hemihydrate of calcium sulphate.

Preparation: It is obtained when gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is heated to 393 K



Above 393 K, no water of crystallization is left and anhydrous calcium sulphate, CaSO_4 is formed. This is known as 'dead burnt plaster'.

Properties: It is a white powder. It has a remarkable property of setting with water. On mixing with an adequate quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes. Addition of common salt increases the rate of setting and addition of borax or alum decreases it.

Uses:

- (i) The largest use of Plaster of Paris is in the building industry as well as plasters.
- (ii) It is used for immobilising the affected part of organ where there is a bone fracture or sprain.
- (iii) It is also employed in dentistry, in ornamental work and for making casts of statues and busts.

5.5 Cement:

Cement is an important building material. It was first introduced in England in 1824 by Joseph Aspdin. It is also called Portland cement because it resembles with the natural limestone quarried in the Isle of Portland, England.

Cement is a product obtained by combining a material rich in lime, CaO with other material such as clay which contains silica SiO_2 along with the oxides of aluminium, iron and magnesium. The average composition of Portland cement is : CaO , 50-60%; SiO_2 , 20-25%; Al_2O_3 , 5-10%; MgO , 2-3%; Fe_2O_3 , 1-2% and SO_3 , 1-2%. For a good quality cement, the ratio of silica (SiO_2) to alumina (Al_2O_3) should be between 2.5 and 4 and the ratio of lime (CaO) to the total of the oxides of silicon (SiO_2) aluminium (Al_2O_3) and iron (Fe_2O_3) should be as close as possible to 2.

The raw materials for the manufacture of cement are limestone and clay. When clay and lime are strongly heated together they fuse and react to form 'cement clinker'. This clinker is mixed with 2-3% by weight of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to form cement. Thus important ingredients present in Portland cement are dicalcium silicate (Ca_2SiO_4) 26%, tricalcium silicate (Ca_3SiO_5) 51% and tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$) 11%.

Setting of Cement: When mixed with water, the setting of cement takes place to give a hard mass. This is due to the hydration of the molecules of the constituents and their rearrangement. The purpose of adding gypsum is only to slow down the process of setting of the cement so that it gets sufficiently hardened.

Uses:

Cement has become a commodity of national necessity for any country next to iron and steel. It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

6. Biological Importance of Magnesium and Calcium

An adult body contains about 25 g of Mg and 1200 g of Ca compared with only 5 g of iron and 0.06 g of copper. The daily requirement of calcium and magnesium ions in the human body has been estimated to be 200 – 300 mg.

All enzymes that utilise ATP in phosphate transfer require magnesium as the cofactor. The main pigment for the absorption of light in plants is chlorophyll which contains magnesium. About 99% of body calcium is present in bones and teeth. It also plays important roles in neuromuscular function, interneuronal transmission, cell membrane integrity and blood coagulation. The calcium concentration in blood plasma is regulated at about 100 mgL^{-1} by two hormones: calcitonin and parathyroid hormone. Do you know that bone is not an inert and unchanging substance but is continuously being solubilised and redeposited to the extent of 400 mg per day in man? All this calcium passes through the plasma. In normal adults this is balanced, but in elderly, net loss of bone calcium leads to a disease osteoporosis.

8. Summary

In this module we have learnt about the s-Block elements (Group-2) and their compounds. Group 2 (alkaline earth metals) constitute s block elements. The alkaline earth metals has two-electrons in the valence shell of their atoms. Their general electronic configuration may be $[\text{noble gas}]ns^2$.

There is a regular trend in the physical and chemical properties of the alkaline earth metals with increasing atomic numbers. The atomic and ionic sizes increase and the ionization enthalpies decrease systematically down the group. These are highly reactive metals, alkali metals forming mono positive (M^+) and divalent (M^{2+}) ions.

Beryllium shows similarities in properties to the second member of the next group. Such similarities are termed as the 'diagonal relationship' in the periodic table. As such it shows elements are anomalous as far as their group characteristics are concerned.

The chemistry of alkaline earth metals is very much like that of the alkali metals. However, some differences arise because of reduced atomic and ionic sizes and increased cationic charges in case of alkaline earth metals. Their oxides and hydroxides are less basic than the alkali metal oxides and hydroxides.

Industrially important compounds of calcium include calcium oxide (lime), calcium hydroxide (slaked lime), calcium sulphate (Plaster of Paris), calcium carbonate (limestone) and cement. Portland cement is an important constructional material. It is manufactured by heating a pulverised mixture of limestone and clay in a rotary kiln. The clinker thus obtained is mixed with some gypsum (2-3%) to give a fine powder of cement. All these substances find variety of uses in different areas.

Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.