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Group 2 Elements- Alkaline Earth Metals

Group 2 of Periodic Table contains in all six elements, namely beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra) of which Ra is radioactive. These elements follow alkali metals in the periodic table.

The oxides and hydroxides of these elements are strongly alkaline in nature. They are found in earth crust and are infusible like soil. Hence, these elements (except beryllium) are also called Alkaline earth metals.

The first element beryllium differs from the rest of the members of its group and shows diagonal relationship to aluminium.

The atomic and physical properties of the alkaline earth metals are as under-

Atomic Properties

(1) Electronic Configuration

The general electronic configuration these metals is [noble gas] ns^2. These elements have two electrons in the s -orbital of the valence shell. They readily loose these electron to form divalent M^{2+} ions.

ELEMENT	SYMBOL	ELECTRONIC CONFIRGURATION
Berylium	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	$[Rn] 7s^2$

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.

On moving down the group, the atomic and ionic radii goes on increasing due to addition of new shells one by one.

3. Ionization Enthalpies

Due to fairly larger atomic size, the alkaline earth metals have relatively low ionization enthalpies. The first ionization enthalpies of the alkaline earth metals are higher than those of the corresponding Group 1 metals. This is due to their smaller atomic size as compared to the corresponding alkali metals. However, the second

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ionization enthalpies of the alkaline earth metals are smaller than those of the corresponding alkali metals.

The ionization enthalpy decreases on moving down the group. It is because of the increases of the atomic size down the group.

Atomic and Physical Properties of the Alkaline Earth Metals						
PROPERTY	**Be**	**Mg**	**Ca**	**Sr**	**Ba**	**Ra**
Atomic number	4	12	20	38	56	88
Atomic mass	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	727	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 of 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^0 for M^{+2}/M (V)	-1.97	-2.36	-2.84	-2.89	-2.92	-2.92

4. Hydration Enthalpies

Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group and follows following order-

$$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$$

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 $MgCl_2.6H_2O$ and $CaCl_2 \cdot 6H_2O$ while NaCl and KCl do not form such hydrates.

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Physical Properties-

(1) Appearance

The alkaline earth metals, in general, are silvery white in appearance with metallic lusture. Beryllium and magnesium appear some what greyish.

(2) Density

These are relatively soft but harder than the alkali metals.

(3) Melting and Boiling point

The melting and boiling points of these metals are higher than the corresponding alkali metals due to their smaller atomic sizes. The trend is, however, not systematic.

(4) Flame Colouration

Calcium, strontium and barium impart characteristic colour to an oxidizing flame (Bunsen flame). For example,

Elements	Ca	Sr	Ba
Flame colour	Brick red	Crimson red	Apple or grassy green

In fact, in Bunsen flame, the valence electrons of these elements get excited to a higher energy level by absorbing energy. When these electrons drop back to the ground state, they emit energy in the form of visible light.

The electrons in beryllium and magnesium are too strongly bound to get excited by Bunsen flame. Hence, these elements do not impart any colour to the flame i.e. they do not show the phenomenon of Flame colouration.

The flame test for Ca, Sr and Ba is helpful in their detection in qualitative analysis and estimation by flame photometry.

Because of the relatively low ionization enthalpies, these elements are strongly electropositive in nature. The electropositive character increases down the group from Be to Ba.

(5) Electrical and thermal conductances

The alkaline earth metals like those of alkali metals have high electrical and thermal conductivities which are typical characteristics of metals.

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Chemical Properties

(1) Reactivity towards air and water-

The alkaline earth metals are less reactive than the alkali metals. The reactivity of these elements increases on going down the group. Beryllium and magnesium are 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.

These elements also react with water with increasing vigour even in cold to form hydroxides.

(2) Reactivity towards the halogens

All the alkaline earth metals combine with halogen at elevated temperatures forming their halides of type MX_2.

$$M + X_2 \rightarrow MX_2 \quad (X = F, Cl, Br, I)$$

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

(3) 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 $LiAlH_4$.

$$2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$$

(4) Reactivity towards acids

The alkaline earth metals readily react with acids liberating dihydrogen.

$$M + 2HCl \rightarrow MCl_2 + H_2$$

(5) Reducing nature

Like alkali metals, the alkaline earth metals are strong reducing agents. This is indicated by large negative values of their reduction potentials. However their reducing power is less than those of their corresponding alkali metals.

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Beryllium has less negative value of its reduction potentials compared to other alkaline earth metals. Its reducing nature is due to large hydration enthalpy of small sized Be^{2+} ion and relatively large value of its atomization enthalpy.

(6) Solutions in liquid ammonia

Like alkali metals, the alkaline earth metals dissolve in liquid ammonia to give deep blue black solutions forming ammoniated ions.

$$M + (x+2y)NH_3 \rightarrow [M(NH_3)_x]^{2+} + 2[e(NH_3)_y]^-$$

From these solutions, the ammoniates, $[M(NH_3)_6]^{2+}$ can be recovered.

Uses-

(1) 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.

(2) Magnesium forms alloys with aluminium, zinc, manganese and tin. Magnesium-aluminium alloys being light in mass are used in air-craft 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.

(3) 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.

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

General Characteristics of Compounds of Alkaline Earth Metals

The compounds of alkaline earth metals 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.

(1) Oxides and Hydroxides

The alkaline earth metals burn in oxygen to form the ionic oxides of type, MO. These oxides, except BeO, have rock-salt structure.

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The BeO is essentially covalent in nature. The enthalpies of formation of these oxides are quite high and consequently they are very stable to heat. All these oxides are basic in nature except BeO, which is amphoteric.

These oxides react with water to form sparingly soluble hydroxides.

$$MO + H_2O \rightarrow M(OH)_2$$

The solubility, thermal stability and the basic character of these hydroxides increase with increasing atomic number from $Mg(OH)_2$ to $Ba(OH)_2$. The alkaline earth metal hydroxides are, however, less basic and less stable than alkali metal hydroxides.

Beryllium hydroxide is amphoteric in nature and reacts with both acid and alkali to form its salts.

$$Be(OH)_2 + 2HCl + 2H_2O \rightarrow [Be(OH)_4]Cl_2$$

$$Be(OH)_2 + 2OH^- \rightarrow [Be(OH)_4]^{2-}$$

Beryllate ion

(2) Halides

Except beryllium halides, all other halides of alkaline earth metals are ionic in nature. Beryllium halides are essentially covalent and soluble in organic solvents.

Beryllium chloride has a chain structure in the solid state**.** 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, $MgCl_2 \cdot 8H_2O$, $CaCl_2 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$) 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.

(3) Salts of Oxoacids

(i) Carbonates

All these elements form carbonates of type MCO_3. These carbonates are insoluble in water and can be easily precipitated by addition of a sodium or

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ammonium carbonate solution to a solution of a soluble salt of these metals. The solubility of carbonates in water decreases on moving down the group.

All the carbonates decompose on heating to give their oxides and carbon dioxide. Beryllium carbonate is highly unstable and therefore can be kept only in the atmosphere of CO_2. The thermal stability increases with increasing cationic size down the group.

(ii) Sulphates

All these elements form sulphates of type MSO_4. These all are white solids and stable to heat.

$BeSO_4$, and $MgSO_4$ are readily soluble in water. The water 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.

(iii) 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 these decompose on heating to give the oxide like lithium nitrate.

$$2M(NO_3)_2 \rightarrow 2MO + 4NO_2 + O_2$$

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

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

Ans. In hydroxides of alkaline earth metal, the anions are common. Hence, only the cationic radius influences 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.

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

Ans. In carbonates and sulphates anions are much larger as compared to cations. Hence, the lattice enthalpy remains almost constant within the group. Here, since the hydration enthalpy decreases down the group, the water solubility decreases on moving down the group.

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Anomalous Behaviour of Beryllium

Beryllium shows anomalous behaviour. It shows dissimilarities in properties to rest of the members of the group but shows diagonal relationship to the aluminium. Some important anomalous properties of Be are as under-

(1) Beryllium has exceptionally small atomic and ionic sizes and therefore, it does not compare well with other members of the group.

(2) Because of high ionisation enthalpy and small size it forms compounds which are largely covalent and get easily hydrolysed.

(3) 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 present in their valence shell.

(4) The oxide and hydroxide of beryllium, unlike the hydroxides of other elements in the group, are amphoteric in nature.

Diagonal Relationship between Beryllium and Aluminium

The ionic radius of Be^{2+} is estimated to be 31 pm. Its charge/radius ratio is nearly the same as that of the Al^{3+} ion. Hence beryllium resembles aluminium in many respects, which are as under-

(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, $[Be(OH)_4]^{2-}$ just as aluminium hydroxide gives aluminate ion, $[Al(OH)_4]^-$.

(iii) The chlorides of both beryllium and aluminium have chloride bridge 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-}

Some Important Compounds of Calcium

(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.

$$CaCO_3 \rightarrow CaO + CO_2$$

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

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Properties

(i) Calcium oxide is a white amorphous solid.
(ii) It has a melting point of 2870 K.
(iii) On exposure to atmosphere, it absorbs moisture and carbon dioxide.

$$CaO + H_2O \rightarrow Ca(OH)_2$$
$$CaO + CO_2 \rightarrow CaCO_3$$

(iv) The addition of limited amount of water breaks the lump of lime. This process is called slaking of lime.
(v) Quick lime slaked with soda gives solid sodalime.
(vi) Being a basic oxide, it combines with acidic oxides at high temperature.

$$CaO + SiO_2 \rightarrow CaSiO_3$$
$$6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)$$

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.

(2) Calcium Hydroxide (Slaked lime), $Ca(OH)_2$

Preparation

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

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Properties

(i) It is a white amorphous powder.
(ii) 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.
(iii) When carbon dioxide is passed through lime water it turns milky due to the formation of calcium carbonate.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

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

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

(v) 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.

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(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.

(3) Calcium Carbonate, $CaCO_3$

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.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$$

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

Properties

(i) Calcium carbonate is a white fluffy powder.
(ii) It is almost insoluble in water.
(iii)When heated to 1200 K, it decomposes to evolve carbon dioxide.
(iv)It reacts with dilute acid to liberate carbon dioxide.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$
$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

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 $CaCO_3$ 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.

(4) Plaster of Paris, Calcium Sulphate hemihydrates, $CaSO_4 \cdot H_2O$

Chemically, calcium sulphate hemihydrate is called plaster of Paris.

Preparation

It is obtained by heating gypsum, $CaSO_4 \cdot 2H_2O$ to 393 K temperature.

$$2(CaSO_4.2H_2O) \rightarrow 2(CaSO)_4.H_2O + 3H_2O$$

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

Properties

(i) It has a remarkable property of setting with water.
(ii) On mixing with an adequate quantity of water it forms a plastic mass that sets into a hard solid in 5 to 15 minutes.

Uses

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

(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

CaO	50- 60%
SiO_2	20-25%
Al_2O_3	5-10%
MgO	2-3%
Fe_2O_3	1-2%
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 ($CaSO_4 \cdot 2H_2O$) to form cement.

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Thus, the important ingredients present in Portland cement are dicalcium silicate, Ca_2SiO_4 (26%), tricalcium silicate,Ca_3SiO_5(51%) and tricalcium aluminate, $Ca_3Al_2O_6$ (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.

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 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 plasma is regulated at about 100 mgL^{-1}. It is maintained by two hormones: calcitonin and parathyroid hormone. In fact, 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.

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