GROUP -1 (ALKALI METALS)

1. Electronic configuration : ns^1
2. Physical state : Silvery white, soft and light
3. Atomic and ionic radii, volume : Atomic and ionic radii increases from Li to Fr due to presence of extra shell of electrons. Volume increases from Li to Cs
4. Density : Densities are quite low and increases from Li to Cs. K is lighter than Na due to unusual increase in atomic size. Li, Na and K are lighter than water
5. Melting point and boiling points: Decrease in melting and boiling point from to Li to Cs due to weak intermetallic bonding
6. Metallic character : Increases from Li to Cs
7. Conductivity: Good conductor.
8. Oxidation state : +1 oxidation state
9. Ionization enthalpy: Ionization enthalpy decreases from Li to Cs due to decrease in atomic size
10. Hydration of ions: Smaller the size of cation, greater degree of hydration $Li^+ > Na^+$, $K^+ > Rb^+ > Cs^+$
11. Hydration energy : Hydration energy of alkalimetals decreases from Li^+ to Cs^+
12. Flame colouration:

Li	Crimson
Na	Yellow
K	Pale violet
Rb	Red violet
Sc	Blue

When an alkali metal is heated in a flame the electrons absorbs energy from flame and are excited to next higher level. When these excited electrons returns back to their original position they emit energy in the form of visible radiations which impart a characteristics colour to the flame

13. Reducing property: Strong reducing agent. Li is strongest reducing agent in solution
14. Complex formation: Alkali metals have little tendency to form complexes. Since Lithium has a small size, it forms certain complexes. Alkali metals form stable complexes with polydentate ligand such as crown ether.

15. Action of air: Stability of peroxides and superoxide increases from Li to Cs. It can be explained by stabilization of larger anion by larger cation through lattice energy. Peroxides and superoxides are important oxidizing agent
16. Nature of hydroxide and halide: Thermal stability of Group-I hydrides decreases down the group, hence reactivity increases from LiH to CsH. Melting and boiling point of halides follows order: Fluorides > Chlorides > Bromides > iodides.
    The ease of formation of alkali metal halides increases from Li to Cs
17. Nature of oxide and hydroxide: Alkali metal oxides are basic in nature and their basic character increases gradually on moving down the group. The basic character of alkali metal hydroxide
    LiOH < NaOH < KOH < RbOH < CsOH
18. Nature of carbonates and bicarbonates: Alkali metal carbonates and bicarbonate stability increases down the group. Since electropositive character increases from Li to Cs
    All carbonates and bicarbonate are water soluble and their solubility increases from Li to Cs

CHEMICAL PROPERTIES

Alkalimetals are highly reactive due to low ionization energy. Reactivity decreases down the group

i) Reaction with oxygen and air

The alkali metals tarnish in air due to formation of carbonates , oxides and hydroxides at their surface and hence kept in kerosene oil or paraffin wax. When burnt in oxygen lithium form Li_2O

Sodium form peroxide Na_2O_2 and other alkali metals form super oxide MO_2 (M = K, Rb, Cs)

Lithium when burnt in air it form nitride by reacting with nitrogen along with Lithium oxide

$6Li\ (s) + N_2(g) \rightarrow 2Li_3N\ (s)$

Other alkali metals do not react with Nitrogen

Lithium oxide is very stable due to small size of lithium and O^{2-} ions and have higher charge density

Sodium peroxide and KO are stable because of ions are of comparable size.

Increasing stablility of peroxide and super oxide is due to stabilization of larger anions by larger cation through lattice energy

Superoxide ion (O^{2-} has a three-electron bond which makes it paramagnetic and coloured where as peroxides are diamagnetic and colour less.
Both peroxide add oxide acts as a oxidizing agents.
Alkali metal oxides are basic in nature and basic character increases down the group

ii) Reaction with water:

Alkali metals reacts vigorously and readily with water to form hydroxides with liberation of hydrogen

The reactivity increases down the group due to increased electro positivity.

K, Rb, Cs lower alkali metals in group reacts so vigorously that evolved hydrogen catches fire spontaneously. Because of their high reactivity they are kept in kerosene.

Alkali metals reacts with compound containing acidic hydrogen atoms such as alcohol and acetaldehyde

$2M + 2\,C_2H_5OH \rightarrow H_2 + 2C_2H_5OM$ (metal ethoxide)

$2M + HC \equiv CH \rightarrow H_2 + M - C \equiv C - M$ (alkali metal acetylide)

Alkali metal hydroxides are strong basic. Basic character increases from LiOH to CsOH

LiOH < NaOH < KOH < RbOH < CsOH.

As metal ion size increases down the group distance between metal ion and OH group increases. Thus more basic hydroxides down the group also thermal stability of hydroxide increases down the group.

iii) Reaction with hydrogen:

Hydrogen reacts with alkali metals to form hydride M^+H^-. Reactivity increases down the group as electro positive character increases down the group. And thermal stability decreases and heat of formation decreases down the group.

Hydrides liberate hydrogen at anode on electrolysis. Therefore they are used as reducing agent.

$LiH(s) + H_2O \rightarrow LiOH(aq) + H_2(g)$

$NaH + CH_3OH \rightarrow CH_3ONa + H_{2(g)}$

iv) Reaction with halogens

The alkali metals combine readily with halogens(X_2) forming halides

$2M + X_2 \rightarrow 2M^+X^-$. The ease of formation of halides increases down the group

Li < Na < K < Rb < Cs

Reactivity of halogen towards particular alkali metal follows the order

$F_2 > Cl_2 > Br_2 > I_2$

Except halides of Li all are ionic and are soluble in water.
K, Rb, C forms simple and mixed polyhalides because of large size e.g CsI_3, KI_3, CsI_2Cl, $RbIBr_2$, $RbClI_4$. Polyhalides of Cs are thermally more stable.
Melting point nad boiling point of particular alkali metal follow the order Fluorides > Chlorides > Bromides > Iodides.
Lithium halides LiBr and LiI are covalent compound.
LiF is soluble in non-polar solvents like kerosene.

v) Solubility in liquid ammonia

Alkali metals dissolves and form solution in liquid ammonia. When alkali metals are dissolved in liquid ammonia, there is a considerable expansion in total volume hence such solutions are called expanded metals.

$M \rightarrow M^+ + \text{electron}$

$M^+ + xNH_3 \rightarrow [M(NH_3)_x]^+$ (Ammoniated metal ion)

Electron + yNH_3 -- > $[e(NH_3)_y]^-$ (Ammoniated electron)

Colour of such solution is blue . Solution is paramagnetic and has electrical conductivity due to presence of unpaired electron in the cavities of ammonical solution and ammoniated cations and electrons respectively.
The free ammoniated electrons make the solution a very powerful reducing agent. Thus ammonical solution of an alkali metal is preferred as reducing agent than its aqueous solution because in aqueous solution evolution of hydrogen from water takes place (thus H_2O acts as a oxidizing agent). While its solution in ammonia is quite stable

vi) Reaction with oxoacids

Alkali metal hydroxide being basic in nature react with oxoacid (such as H_2CO_3), H_3PO_4 HNO_3 , H_2SO_4 etc.) to form different slats such as metal carbonates, bicarbonates, sulphates, nitrates, etc.
Alkali metal carbonates and bicarbonates are highly stable towards heat and their stability increases down the group, since electropositive character increases from Li to Sc. However Li_2CO_3 is less stable and readily decomposes to form oxide.

$Li_2CO_3 \rightarrow Li_2O + CO_2$

Alkali metal bicarbonates on heating decompose to give respective carbonates

$2MHCO_3 \rightarrow M_2CO_3 + CO_2 + H_2O$

All carbonates and bicarbonates are water soluble. Their solubility increases down the group since their lattice energy decreases more rapidly than their hydration energy in the group.

Alkali metal nitrates (MNO_3) decompose on strong heating to corresponding nitrite and O_2 except $LiNO_3$ which decomposes to its oxides

$2NaNO_3 \rightarrow 2NaNO_2 + O_2$

But $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$

ANOMALOUS BEHAVIOUR OF LITHIUM

Lithium, the first member of alkali metals differs in many properties from the other alkali-metals due to the following reasons:

i) Li has smallest atomic and ionic size in the group
ii) Li^+ has highest polarizing power in its group which makes its compounds covalent
iii) Li has highest ionization energy, high heat of hydration, highest electro-negativity or minimum electropositive character in its group.
iv) Li does not have d-orbitals also.

Difference between lithium and other alkali metals

i) Lithium is harder and higher than other alkali metals due to strong metallic bonding.
ii) Its m.pt. And b.pt are higher than the rest of alkali metals
iii) Li on burning in air or oxygen forms monoxide while other alkali metals form higher oxides like peroxides and superoxides
iv) Li forms nitride with nitrogen whereas other alkali metals do not $6Li + N_2 \rightarrow 2Li_3N$
v) Some lithium salts like LiF, Li_2CO_3 and Li_3PO_4 are sparingly soluble in water where as corresponding slats of other alkali metals are freely soluble
vi) Li form imide (LiNH) with ammonia while other alkali metals form amides (MNH_2)
vii) $LiHCO_3$ does not exist as solid but it occurs in solution. Other alkali metals bicarbonates are known in solid state.
viii) Unlike other alkali metals Li does not form alum

Similarities between and magnesium or diagonal relationship between lithium and magnesium

Lithium and magnesium resemble in number of properties due to similarity in their atomic and ionic size. The properties of resemblance are as follows

i) Both Li and Mg form monoxides Li_2O and MgO on heating with air or oxygen.

ii) Both Li and Mg form ionic nitrides when heated in nitrogen

$6Li + N_2 \rightarrow 2Li_{3N}$

$3Mg + N_2 \rightarrow Mg_3N_2$

iii) Hydroxides, carbonates and nitrates of both Li and Mg decomposes on heating to yield respective oxide

$2LiOH \rightarrow Li_2O + H_2O$

$Mg(OH)_2 \rightarrow MgO + H_2O$

$Li_2CO_3 \rightarrow Li_2O + CO_2$

$MgCO_3 \rightarrow MgO + CO_2$

$4LiNO_3 \rightarrow 2Li_2 + 4NO_2 + O_2$

$2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$

iv) Fluorides, carbonates, oxalates and phosphates of both metals are sparingly soluble in water.

v) Both LiCl and $MgCl_2$ are deliquescent salts.

SOME IMPORTANT COMPOUNDS OF ALKALI METALS

SODIUM CHLORIDE, NaCl (Common salt)

NaCl obtained from sea water may have impetrates like $CaSO_4$, Na_2SO_4, $CaCl_2$, $MgCl_2$ etc. $MgCl_2$ and $CaCl_2$ are deliquescent in nature (absorbs moisture from air) hence impure common salt gets wet in rainy reason. Pure NaCl can be prepared by passing HCl gas into saturated solution of commercial salt. Pure salt gets precipitated due to common ion effect.
NaCl is used as table salt
NaCl is used in preparation of number of compounds such as Na_2CO_3, NaOH, Na_2O_2 etc

SODIUM HYDROXIDE, NaOH (CAUSTIC SODA)
Sodium hydroxide is known as caustic soda, since it breaks down the protein of skin to a pasty mass.

PREPARATION
1**. Causticization process (Gossage process)**
This process involves heating of sodium carbonate with milk of lime
$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons CaCO_3 \downarrow + 2NaOH$

2**. Electrolysis of NaCl**
Electrolysis of saturated aqueous solution of NaCl gives NaOH , Cl_2 and H_2

$$NaCl(aq) \xrightarrow{electrolysis} Na^+ + Cl^-$$

At anode: $2Cl^- \rightarrow Cl_2 + 2e^-$
At cathode : $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$
$Na^+ + OH^- \rightarrow NaOH$
Cl_2 gas, one of the byproduct reacts with NaOH to form other byproduct
$2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$

3. **Porous diaphragm process (Nelson cell process)**
In this process a perforated cathode made up of steel lined up with asbestos is used. In this process Cl_2 formed at anode is taken out so that extent of impurities in NaOH is quite low

4**. Castner-kellner cell (Mercury cathode process)**
This process involves the electrolysis of conc. Brine solution in such a way so that reaction between NaOH and Cl_2 does not takes place. In this process three compartments are made in electrolytic cell and mercury used as cathode moves freely from one compartment to another. Graphite rods are used as anode.

Properties
NaOH is deliquescent, white crystalline solid which absorbs moisture and carbon dioxide from atmosphere to form aq.NaOH layer around pellet first and finally white powder of Na_2CO_3.
$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$
NaOH dissolves readily in water to yield higher alkaline solution which is corrosive, soapy in touch and bitter in test.
Uses :
NaOH is widely used in soap industry, paper industry, textile industry (for mercerization of cotton)
It is used in the manufacture of dyes and drugs
NaOH is used for absorbing acids and gases, in petroleum refining and as a regent in laboratories.

Chemical reactions of NaOH

$$NaOH \xrightarrow{Co_2} Na_2CO_3$$
$$NaOH \xrightarrow{Co} HCOONa$$
$$NaOH \xrightarrow{SO_2} Na_2SO_3$$
$$NaOH \xrightarrow{S,} Na_2S_2O_3$$
$$NaOH \xrightarrow{P_4} NaH_2PO_2 + PH_3$$
$$NaOH \xrightarrow{M(M = B,\ Al)} NaMO_2$$
$$NaOH \xrightarrow{X_2(Hot)} NaX + NaXO_3 + H_2O$$
$$NaOH \xrightarrow{X_2(Cold)} NaX + NaXO + H_2O$$
$$NaOH \xrightarrow{Zn\ or\ ZnO_2} Na_2ZnO_2$$
$$NaOH \xrightarrow{Sio_2} Na_2SiO_3$$
$$NaOH \xrightarrow{Al_2O_3\ or\ Al(OH)_3} NaAlO_2$$
$$NaOH \xrightarrow{Sn} Na_2SnO_3$$
$$NaOH \xrightarrow{ZnSO_4} Zn(OH)2 \xrightarrow{NaOH} Na_2ZnO_2$$
$$NaOH \xrightarrow{FeCl_3} Fe(OH)_3\downarrow + NaCl$$
$$NaOH \xrightarrow{NH_4Cl} NH_3\uparrow + NaCl + H_2O$$

SODIUM CARBONATE, Na_2CO_3 (WASHING SODA)
Sodium carbonate exists in various forms such as:
Na_2CO_3 - soda ash or light ash
$Na_2CO_3 . H_2O$ - Monohydrate, widely used in glass manufacturing
$Na_2CO_3 . 7H_2O$ - Hepta hydrate
$Na_2CO_3 . 10H_2O$ - Washing soda or sal soda (used in soap and detergents)

PREPARATION

Sodium carbonate is manufactured by Solvay process which is efficient and economic. In this process compounds used as raw material are brine (NaCl), NH_3 and $CaCO_3$

Solvay process involves following reaction

$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3$ (ammonium bicarbonate)

$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$

$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$ (at $150^{O}C$)

CO_2 is obtained by decomposition of $CaCO_3$

$CaCO_3 \rightarrow CaO + CO_2$ (at $1100^{O}C$)

CaO forms slaked lime with water which decomposes NH_4Cl to ammonia thus NH_3 is recycled.

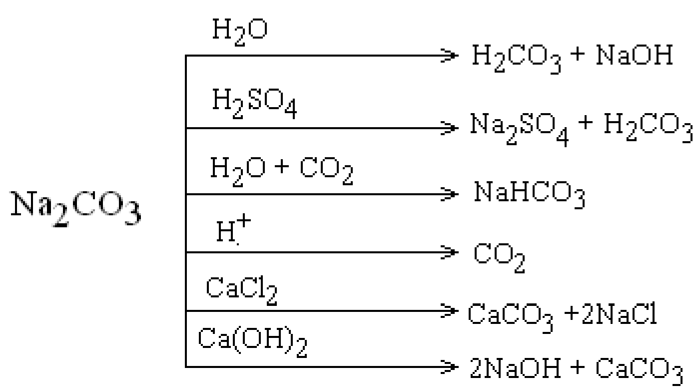
$CaO + H_2O \rightarrow Ca(OH)_2$

$Ca(OH)_2 + 2NH_4Cl \rightarrow 2NH_3 + 2H_2O + CaCl_2$

PROPERTIES

Sodium carbonate is a white crystalline solid which readily dissolves in water. Its solubility decreases with increase in temperature.

Chemical reactions of Na_2CO_3



Uses

Sodium carbonate is used in laundries as washing soda
It is also used to remove hardness of water
Na_2CO_3 is used to manufacture glass, caustic soda etc
It is used in petroleum refining and in textile industry

SODIUM BICARBONATE, $NaHCO_3$ (BAKING SODA)

Preparation:
Sodium bicarbonate or sodium hydrogen carbonate is obtained as intermediate compound in Solvay process
It can also be prepared by passing CO_2 through solution of sodium carbonate
$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$

Properties

$NaHCO_3$ on heating decomposes to produce bubbles of CO_2 which make the cakes and pastries fluffy
$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$
It is amphiprotic i.e. it can acts as H^+ donor as well as H^+ acceptor
$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

USES
$NaHCO_3$ is used in the preparation of baking powder
[Baking powder = $NaHCO_3$ (30%) + $Ca(H_2PO_4)_2$ (10%) + Starch (40%) + $NaAl(SO_4)_2$]
It is used in fire extinguisher : $NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$
Such kind of fire extinguisher are known as soda-fire extinguisher
It is used as antacid and mild antiseptic

MICROCOSMIC SALT, $Na(NH)_4HPO_4 . 4H_2O$

Microcosmic salt exists in colourless crystalline solid form. It is prepared by dissolving NH_4Cl nad Na_2HPO_4 in 1:1 ,molar ratio in hot water.

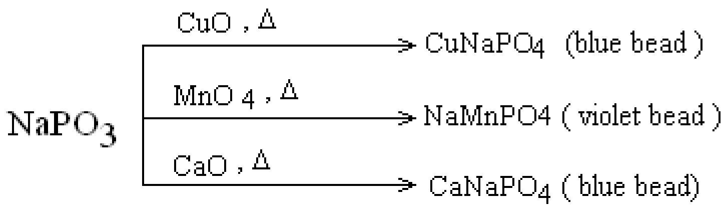
$NH_4Cl + N_2HPO_4 \rightarrow Na(NH_4)HPO_4 + NaCl$

USES

It is used for performing 'bead test' (like borax) for detecting colour ions in qualitative analysis.

On heating microcosmic salt form $NaPO_3$ which form coloured beads of orthophosphates with oxides of transition metal and cloudy bead with SiO_2

Na(NH$_4$) → $NaPO_3 + H_2O + NH_3$



BIOLOGICAL SIGNIFICANCE OF SODIUM AND POTASSIUM

Na^+ and K^+ are essential for proper functioning of human body
Different ratio of Na^+ to K^+ inside and outside cells produce an electrical potential across the cell membrane which is essential for functioning of nerve and muscle cells.
These ions activate many enzymes
These ions primarily help in transmission of nerve signals in regulating the flow of water across cell membrane, transport of sugars and amino acids into cells, etc.

GROUP –II (ALKALINE EART METAL)

1. Electronic configuration : ns^2
2. Physical state: Grayish white luster when freshly cut, malleable and ductile.
3. Atomic and ionic radii, volume : Small compared to Group_I (due to extra nuclear charge). Atomic and ionic radii increases from Be to Ra. Volume increases from Be to Ra
4. Density: Greater than alkali metals. Do not show regular trend due to difference in crystal structure. Decreases from Be to Ca and increases upto Ra
5. Melting point and boiling points: Decreases from Be to Ba
6. Metallic character : Less compared to group-I. Increases from Be to Ra
7. Conductivity: Good conductor
8. Oxidation state : +2 oxidation state
9. Ionization enthalpy: Greater than alkali metals. Decreases down the group
10. Hydration of ions: Smaller the size of cation, greater hydration
$$Be^{+2} > Mg^{+2} > Ca^{+2}, Sr^{+2} > Ba^{+2} > Ra^{+2}$$
11. Hydration energy : Hydration energy decreases from Be^{2+} to Ra^{2+}, Number of molecules of water of crystallization decreases as ion becomes larger
12. Flame colouration:

Ca	Brisk red
Sr	Crimson red
Ba	Grassy green
Ra	Crimson

Beryllium and Magnesium do not impart any colour to the flame as their atoms are smaller and consequently require higher energies for excitation of the electrons to higher levels.

13. Strong reducing agent but weaker as compared to Group-I
14. Complex formation: Be^{+2} being smallest in size shows a great tendency to form complexes such as $[BeF_3]^-$, $[BeF_4]^{-2}$ Tendency of other ions to form complexes decrease with the increase of size of M^{2+} ion
15. Action of air: the reactivity of oxygen increases as we go down the group since their electropositive character increases. The tendency to form peroxides increases down the group.
16. Nature of hydroxide and halide: Group-II hydrides are all reducing agent CaH_2, SrH_2 and BaH_2 are ionic and BeH_2 are ionic and BeH_2 and MgH_2 are covalent. Halides of Group-II are ionic and ionic character increases down the group. Solubility of halides in water decreases from Be to Ba
17. Nature of oxide and hydroxide: Alkaline earth metals are basic in nature. Their basic strength is BaO > SrO > CaO > BeO.
    Basic character of Group II hydroxide is $Ba(OH)_2 > Sr(OH)_2 > Ca(OH)_2 > Mg(OH)_2 > Be(OH)_2$
18. Nature of carbonates and bicarbonates: Solubility of carbonates decreases down the group from Be to Ba. Thermal stability of carbonates of alkaline earth metal increases as we go down group from Be to Ba

CHEMICAL PROPERTIES

Due low ionization energy and high negative value of standard electrode potential alkaline earth metals are highly reactive.

Since ionization energy decreases and electrode potential become more negative therefore reactivity of alkaline earth metal increases from Be to Ba.

Alkaline earth metals have higher ionization energy than corresponding alkali metals

i) Reaction with oxygen and air

Since electropositive nature of increases down the group reactivity with oxygen increases.

Beryllium metal is relatively unreactive but readily react with oxygen in powder form

$2Be + O_2$ (air) → 2BeO

Ba and Sr form peroxide on heating with excess of oxygen. The tendency to form peroxide increases as we move down the group, since larger cation stabilizes large anion

$$2BaO + O_2 \xrightarrow{773K} 2BaO_2$$

CaO_2 can also be prepared as the hydrate by treating $Ca(OH)_2$ with H_2O_2 and then dehydrating the product.

$Ca(OH)_2 + H_2O_2 \rightarrow CaO_2 . 2H_2O$

Crude MgO_2 has been made using H_2O_2 but peroxide of Beryllium is not known

Peroxides are white ionic solids containing $[O\text{-}O]^{2-}$ ion and can be regarded as salt of the weak acid hydrogen peroxide

Nature of alkaline earth metal oxides and peroxide

Oxides of Alkaline earth metals are basic in nature. Their basic character increases decreases the group

BaO > SrO > CaO > MgO > BeO

Size of Be^+ is small thus BeO is covalent in nature and occurs in polymeric form. Hence BeO has higher melting point and is harder than other oxides

On heating peroxides liberate oxygen and form monoxide MO. Their thermal stability increases with increasing cation size on moving down the group.

Formation of nitrides

All alkali metals burn in dinitrogen to form ionic nitrides of the formula, M_3N_2

(This is in contrast with alkali metal where only Li form Li_3N_2)

Their ionic character increases with the increase in the size of metal ion down the group.

Be_3N_2 being covalent is volatile while other nitrides are crystalline solids. All these nitrides on heating liberate NH_3 and on reacting with water.

$$Be_3N_2 \xrightarrow{\Delta} 3Be + N_2$$

$$Ca_3N_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2NH_3$$

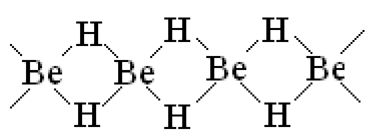
ii) Reaction with water (formation of hydroxides)

Alkali earth metals are less reactive with water as compared to alkali metals. Their reactivity with water increases down the group. Be. Does not react with water at all, magnesium reacts only with hot water while other metals Ca, Sr and Ba react with cold water.
Order of the reactivity with water Ba > Sr > Ca > Mg
$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$ or $Mg + H_2 \rightarrow Mg(OH)_2 + H_2$
Mg form a protective layer of oxide, it does not readily react, and reacts only on removal of oxide layer

Nature of Hydroxides: $Be(OH)_2$ is amphoteric, but the hydroxides of Mg, Ca Se and Ba are basic. Basic strength increases down the group. Solution of $Ca(OH)_2$ is called lime water and $Ba(OH)_2$ is called barty water. Aqueous suspension of $Mg(OH)_2$ is called milk of magnesia and is used as antacid

iii) Reaction with hydrogen (Formation of hydrides)
All alkaline earth metals except Be combine with hydrogen to form hydride MH_2 on heating.
CaH_2 is called hydrolith and is used for production of H_2 by action of water on it.

Nature of hydrides
Alkaline earth metal hydrides are reducing agent and are hydrolysed by water and dilute acids with evolution of hydrogen $CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$
CaH_2, SrH_2 and BaH_2 are ionic and contain the hydride ion H^-. beryllium and magnesium hydride are covalent compounds having polymeric structure in which hydrogen atom between beryllium atoms are held together by three centre-two electron bond



The structure involves three-centre bonds formation in which a ‘banana-shaped’ molecular orbital (or three-centre bond) covers three atoms Be … H … Be, and contains two electrons (this is called a three-centre two electron bond). This is an example of a cluster compound which is ‘electron deficient’

iv) Reaction with carbon
Alkali earth metal except Be or their oxides on heating with carbon form carbides of general formula MC_2

$$Ca + 2C \xrightarrow{1100^{O}C} CaC_2$$

$$CaO + 3C \xrightarrow{2000^{O}C} CaC_2 + CO$$

All the carbide are ionic in nature and have NaCl type structure. On treatment with water they liberate acetylene CH≡CH. Thus they are called as acetylides
On heating MgC_2 it changes to Mg_2C_3 and reacts with water to liberate propyne
On heating BeO with C at 1900-2000^{O}C a brick red coloured carbide of formula Be_2 C is formed, this has anti-fluotite structure

On heating CaC_2 in an electric furnace with atomospheric dinitrogen at 100^{O}C, calcium cyanide CaNCN is formed, which is widely used as fertilizer
$CaC_2 + N_2 \rightarrow CaNCN + C$
BaC_2 also reacts with N_2 but forms cyanide $Ba(CN)_2$ and not cyanamide

v) Action of halogen

All Group 2 elements forms halides of MX_2 type either by the action of halogen acid (HX) on metals, metal oxides, hydroxide or carbonates or directly heating metal with halogen

$$M + 2HX \rightarrow MX_2 + H_2$$

$$MO + 2HX \rightarrow MX_2 + H_2O$$

$$M(OH)_2 + 2HX \rightarrow MX_2 + 2H_2O$$

$$MCO_3 + 2HX \rightarrow MX_2 + CO_2 + H_2O$$

$$M + X_2 \xrightarrow{\Delta} MX_2$$

Nature of Halides

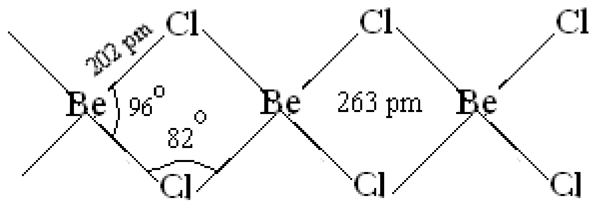
Beryllium halides are covalent and are soluble in organic solvents, due to small size and high charge density
The halides of all other alkaline earth metals are ionic. Their ionic character, however, increases as the size of the metal ion increases
They are hygroscopic, and fume in air due to hydrolysis. On hydrolysis, they produce acidic solution
Some of the halides are hydrated, but all chlorides are found in hydrated form e.g. $BeCl_2.4H_2O$, $MgCl_2.6H_2O$ etc.

Solubility of Halides

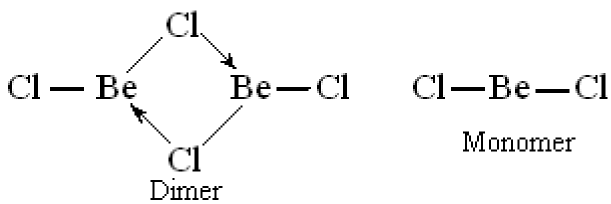
The halides of Beryllium (except BeF_2) being covalent in nature are insoluble in water (soluble in organic solvents) where as halides of other alkaline earth metals except fluorides are ionic solids and thus water soluble. The solubility in water decreases from Be to Ba due to the decrease in the hydration energy. The fluorides of alkaline earth metals (MF_2) except BeF_2 are insoluble in water owing to large values of lattice energy BeF_2 is readily soluble in water because of smaller size of Be^{2+}, large hydration energy is released which overcomes the lattice energy.

Structure of $BeCl_2$

In solid phase $BeCl_2$ has polymeric structure with halogen bridges in which a halogen atom bonded to one beryllium atom uses a lone pair of electrons to form a coordinate bond to another beryllium atom as shown below



In vapour phase it tends to form a chloro bridge dimer which dissociates into the liner triatomic monomer at high temperature (nearly 1200K)



vi) Reaction with acids

All alkali metals react with acids liberating H_2

$M + 2HCl \rightarrow MCl_2 + H_2$ (M = BE, Mg, Ca, Sr, Ba)

Since basic character of these metal increases down the group, their reactivity towards acid increases from Be to Ba. Be reacts slowly with acids, Mg reacts faster rate while Ca, Sr and Ba reacts explosively with acids

$Be + 2NaOH + 2H_2O \rightarrow H_2 + Na_2[Be(OH)_4]$ (sodium beryllate)

Mg, Ca, Sr and Ba do not reacts with NaOH. Illustrate basic character of group 2 elements increases on descending the group.

Be is redered passive with HNO_3 . As HNO_3 is strong oxidizing agent forms a layer of oxide on metal which protects the inner core of metal

vii) Solubility in liquid ammonia

All metals of group 2 dissolves in liquid ammonia to form bright blue coloured solution

$M \rightarrow M^{2+} + 2e^-$

$2NH_3 + 2e^- \rightarrow 2NH_2^- + H_2$

$M^{2+} + 2NH_2^- \rightarrow M(NH_2)_2$

Evaporation of ammonia from solution gives hexaammoniates of metal which slowly decomposes to give amides

$M(NH_3)_6 \rightarrow M(NH_2)_2 + 4NH_3\uparrow + H_2\uparrow$

Concentrated solution of meatl in ammonia are bronze coloured due to formation of metal clusters.

viii) Alkaline earth metal nitrates are prepared in solution and can be crystallized as hydrated salts by the action of HNO_3 on oxides, hydroxides and carbonates

Beryllium nitrate is unusual because it forms basic nitrate [$Be_4O(NO_3)_6$] in addition of the normal salt.

ix) Sulphates

The sulphates of alkaline earth metals (MSO_4 are prepared by the action of sulphuric acid on metals, metal oxides, hydroxides and carbonates.

Nature of sulphates

Sulphates of Be, Mg, and Ca are crystallize in the hydrated form where as sulphates of Sr and Ba crystallize without water of crystallization.

The solubility of sulphates decreases down the group mainly due to decrease in hydration energy from Be^{2+} to Ba^{2+} . thus high solubility of $BeSO_4$ and $MgSO_4$ can be attributed to high hydration energies of smaller Be^{2+} and Mg^{2+} ions.

Because of large size of sulphate ion lattice energy remains constant down the group

The sulphate decomposes on heating, giving the oxides:

$MgSO_4 \rightarrow MgO + SO_3$

More basic the metal, more stable is the sulphate. Basic nature of metals increases down the group thus thermal stability of sulphates increases on descending the group.

x) Carbonates and Bicarbonates

Carbonates of alkaline earth metals can be produced by passing CO_2 through their hydroxides

$M(OH)_2\ (aq) + CO_2(g) \rightarrow MCO_3(s) + H_2O(l)$

Alkaline earth metal carbonates are ionic but beryllium carbonates is unusual because of hydrated ion $[Be(H_2O)_4]^{2+}$ rather than Be^{2+}. The solubility of carbonates decreases down the group from Be to Ba. $MgCO_3$ is sparingly soluble in water but $BaCO_3$ is almost insoluble because hydration energy of metal cations decreases from Be^{2+} to Ba^{2+}. However all carbonates are more soluble in presence of CO_2 due to formation of corresponding bicarbonates

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

Thermal stability increases as we go down the group because size of the positive ion increases and polarizing ability decreases, causing more stability. If positive ion is small such as Be which distort electron cloud of carbonate ion makes $BeCO_3$ easily thermal decomposable.

Bicarbonates of alkaline earth metal do not exists in solid state. They exists in solution only. On heating, bicarbonates decomposes to carbonates with evolution of CO_2

$$M(HCO_3)_2 \xrightarrow{\Delta} MCO_3 + CO_2 + H_2O$$

ANOMALOUS BEHAVIOUR OF BERYLLIUM

Beryllium when compared to rest of the members anomalous behavior, mainly because of the following reasons

Small size of atom or its ion

Highly ionization energy, electronegativity and charge density, absence of d-orbital

Important difference between Beryllium and rest of the members

Beryllium is harder than other members

Beryllium does not reacts with water, even at elevated temperatures

It has higher boiling and melting points as compared to other members

It do not combine directly to form hydride, whereas other metals do so

Beryllium forms covalent compounds while other members form ionic compounds

With water, beryllium carbide gives methane while carbides of other members give acetylene

BeO is amphoteric in nature while oxides of other alkaline earth metals are basic

DIAGONAL SIMILARITIES OF BERYLLIUM AND ALUMINIUM

Due to diagonal relationship existing between beryllium and aluminium, they both show some similarities

Both Be and Al form covalent compounds

On treatment with concentrated HNO_3, both beryllium and aluminium are rendered passive.

Both form complexes

BeO and Al_2O_3 are amphoteric. They dissolve in acid as well as in base

$BeO + 2HCl \rightarrow BeCl_2 + H_2O$

$Be + 2NaOH \rightarrow Na_2BeO_2 + H_2O$

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$
$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2$ (sodium metaaluminate) + H_2O
The carbides of both B and Al liberate methane when reacts with water
$Be_2C + 2H_2O \rightarrow 2BeO + CH_4$
$Al_4C_4 + 6H_2O \rightarrow 2Al_2O_3 + 3CH_4$
Both the metals are weakly electropositive in nature
Beryllium and aluminium form fluoro complex anions $[BeF_4]^{2-}$ and $[AlF_6]^{3-}$ in aquepos solution. Stable fluoro complexes in solution are not formed by other metals of the group.
Beryllium dissolves in alkalies to give beryllate ion $[Be(OH)_4]^{2-}$ while aluminium dissolves to give $[Al(OH)_6]^{3-}$
$BeCl_2$ like Al_2Cl_6 has a bridged polymeric structure
Similar solubility are observed in halides of both beryllium and aluminium.

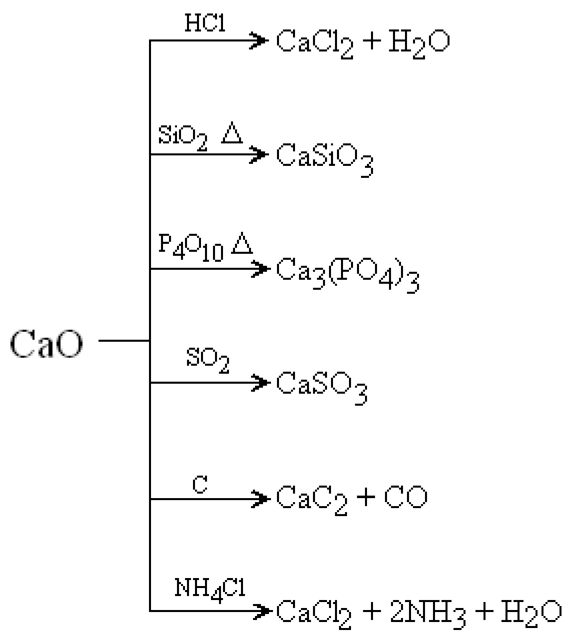
SOME IMPORTANT COMPOUNDS OF ALKALINE EARTH METALS

CALCIUM OXIDE (CaO)
Quick lime (CaO) is prepared by strong heating of lime stone ($CaCO_3$) in lime kiln. Smaller piece of limestone are introduced from the top and heating is done from lower end. Lime stone decomposes at about 1000^{O}C to give calcium oxide
$CaCO_3 (s) \rightarrow CaO (s) + CO_2(g)$ at 1000^{O}C ; $\Delta H = 180$ kJ/mol
The temperature of kiln is not allowed to rise above 1000^{O}C otherwise silica SiO_2 present as impurity in lime stone would react with CaO to form slag $CaSiO_3$

Properties
Calcium oxide is a white amorphous solid. On heating, quick lime CaO glows at high temperature. This glow of white dazzling light is called lime light. Quick lime melts at 2870K or 2597^{O}C
On exposure to the atmosphere, it absorbs moisture and carbon dioxide to finally give calcium carbonate
When water is poured over quicklime, a lot of heat is produced giving out steam with a hissing sound. This is called slaking of lime and is due to the following reaction.
$CaO + H_2O \rightarrow Ca(OH)_2$; $\Delta H = -65$ kJ/mole
Quick lime when slaked with caustic soda gives a solid called sodalime
Uses
For white washing of buildings
For the manufacture of bleaching powder, glass, calcium carbide, soda ash, etc
For tanning of leather.
As a fertilizer for acidic soil
In building and construction industry as an important raw material.

Chemical reactions of calcium oxide

CaO is basic oxide and hence reacts with acids and acidic oxides to form salts



CALCIUM CARBONATE, ($CaCO_3$)

Calcium carbonate occurs abundantly as dolomite, $MgCO_3$. $CaCO_3$, a mixture of calcium and magnesium carbonates. It is the chief constituent of shells of sea animal and also of bones along with tricalcium phosphate.

Preparation

Laboratory preparation

Calcium carbonate is prepared in the laboratory by passing carbon dioxide gas into lime water

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

Calcium carbonate is also obtained by adding the solution of a soluble carbonate to soluble calcium salt

$CaCl_2\ (aq) + Na_2CO_3\ (aq) \rightarrow CaCO_3\ + 2NaCl(aq)$

The resulting precipitate is filtered, washed and dries. The product obtained is known as precipitated chalk.

Excess of carbon dioxide should be avoided since this leads to the formation of calcium hydrogen carbonate

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

Properties

Calcium carbonate is a white fluffy powder. It is almost insoluble in water

Action of heat

When heated to 1200K, it decomposes to give lime and carbon dioxide

With acid

Calcium carbonate reacts with dilute acids to liberated carbon dioxide

Uses

In the manufacture of quick lime

As a building material in form of marble

As a raw material for manufacture of sodium carbonate in Solvay process

In the extraction of metals such as iron (as flux)

As a constituent of tooth paste, an antacid, chewing gum and filler in cosmetics.

PLASTER OF PARIS, ($CaSO_4 . \frac{1}{2} H_2O$)

Calcium sulphate with half molecule of water per molecule of the salt (hemi-hydrate) is called plaster of paris

Preparation

It is preparation

It is prepared by heating gypsum ($CaSO_4 . 2H_2O$) at 120^OC in in rotary kilns, where it gets partially dehydrated.

$$2(CaSO_4 \cdot H_2O) \xrightarrow{120^O C} 2(CaSO_4) \cdot H_2O + 3H_2O$$

The temperature should be kept below 140^OCotherwise further dehydration will take place resulting in anhydrous $CaSO_4$ which is known as dead burnt plaster because it loses the property of setting with water

Properties

It is a white powder. When mixed with water (1/3 rd of its mass), it evolves heat and quickly sets to a hard porous mass within 5 to 15 minutes. . During setting, a slight expansion (about 1%) in volume occurs so that it fills the mould completely and takes a sharp impression. The process of setting occurs as follows.

$$CaSO_4 \cdot \frac{1}{2} H_2O \xrightarrow{H_2O} CaSO_4 \cdot H_2O \xrightarrow{hardening} CaSO_4 \cdot 2H_2O$$

The first step is called the setting stage and the second, the hardening stage. The setting of plaster is catalyzed by sodium chloride, while it is reduced by borax, or alum

Use

For making casts in density, for surgical instruments, and toys, etc

In surgery for setting broken or fractured bones

In making statues, models and other decorative items

In construction industry

Cement

Cement is grayish, finally powder mixture of calcium silicates and aluminates along with small quantities of gypsum which sets into hard mass when mixed with water

This hardened stone-like mass resembles a natural rock mined on Isle of Portland, a famous building stone of England. Since then the name Portland cement is given to the product.

Composition of cement: The average composition of Portland cement is

Compound	Pecentage
CaO	50 – 60%
SiO_2	20 – 25 %
Al_2O_3	5 – 10%
MgO	1 - 3 %
Fe_2O_3	1 – 2%
SO_3	1 – 2%
Na_2O	1%
K_2O	1%

Raw materials

Raw material for the manufacture of cement are limestone provides lime , clay (provides both silica and alumina) and gypsum ($CaSO_4 . 2H_2O$). Small amount of magnesia (MgO) and iron oxide (Fe_2O_3) are also used for imparting colour to cement.

Setting of cement

Cement absorbs water on mixing to form a gelatinous mass. This sets to hard mass and is very resistant to pressure. This process is called the setting of cement. This process involves a complicated set of reaction of hydration and hydrolysis, leading to the formation of Si-O-Si and Si-O-Al chains

CALCIUM SULPHATE, ($CaSO_4.2H_2O$) – GYPSUM

It is found in nature as anhydride ($CaSO_4$) and gypsum ($CaSO_4.2H_2O$)

Preparation

It can be prepared by reacting any calcium salt with either sulphuric acid or a soluble sulphate

$CaCl_2 + H_2SO_4 \rightarrow CaSO_4 + 2HCl$

$CaCl_2 + Na_2SO_4 \rightarrow CaSO_4 + 2NaCl$

Properties

It is white crystalline solid. It is sparingly soluble in water

It dissolves in dilute acids

When strongly heated with carbon, it forms calcium sulphide

$CaSO_4 + 4C \rightarrow CaS + 4CO$

Gypsum when heated at different temperature gives burnt plaster and finally lime (CaO)

$$\underset{\text{(monoclinic)}}{CaSO_4 \cdot 2H_2O} \xrightarrow{\text{heating}} \underset{\text{(orthorombhic)}}{CaSO_4 \cdot 2H_2O} \xrightarrow{120^{\circ}C} 2CaSO_4 \cdot H_2O$$

$$\xrightarrow{200^{\circ}C} \underset{\text{burnt plaster}}{CaSO_4} \xrightarrow{\text{strong heating}} \underset{\text{lime}}{CaO} + SO_2 + O_2$$

ALKALINE EARTH MATELS IN BIOLOGICAL ACTION

Biological role of Mg^{+} and Ca^{2+}

Mg^{2+} ions are concentrated in animal cells and Ca^{2+} are concentrated in the body fluids outside the cell. Mg^{2+} ion form a complex with ATP. They are also essential for the transition of impulse along nerve fibres. Mg^{2+} is an important constituent of chlorophyll, in the green parts of plants. Ca^{2+} is present in bones and teeth as apatite $Ca_3(PO_4)_2$ and the enamel on teeth as fluoroapatite $[3(Ca_3(PO_4)_2 . CaF_2]$, Ca^{2+} ions are important in blood clotting and are required to trigger the contraction of muscles and to maintain the regular beating of the heart.