# s-Block Elements

The elements in which the last electron enters the outermost s-orbital are called s-block elements. As the s-orbital can accommodate only two electrons, two groups 1 and 2 belong to the s-block.

## Flame Test

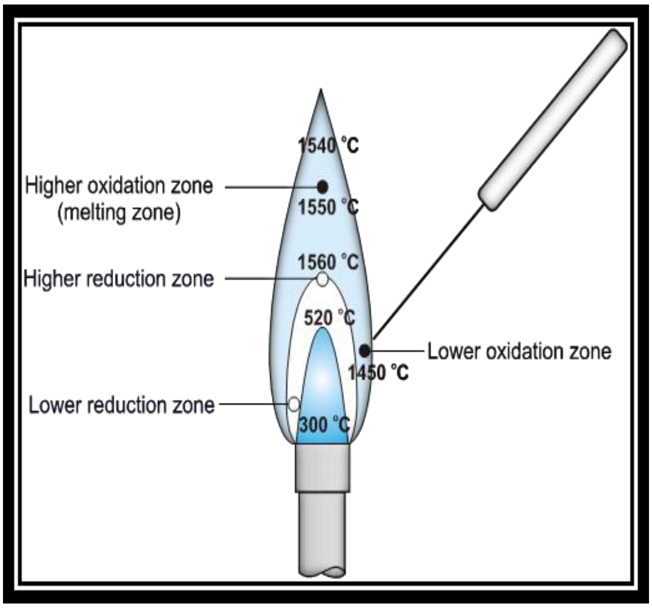
The alkali metals and alkaline earth metals and their salts impart characteristic colour to an oxidizing flame.

**Reason :** This is because the heat from the flame excites the outermost orbital electron to a higher energy level. When they drop back to the ground state, there is emission of radiation in the visible region.

The electrons in beryllium and magnesium are too strongly bound (due to small size) to get excited by flame. Hence, these elements do not impart any colour to the flame.

| Metal | Li | Na | K | Rb | Cs |
|---|---|---|---|---|---|
| Colour | Crimson red | Yellow | Violet / Lilac | Red violet | Blue |

| Metal | Be | Mg | Ca | Sr | Ba |
|---|---|---|---|---|---|
| Colour | No colour | No colour | Brick red | Crimson red | Apple green |



## Group – 1st(IA) Elements : (Alkali Metals)

### Atomic and Physical properties of the Alkali metals

| **Property** | **Lithium Li** | **Sodium Na** | **Potassium K** | **Rubidium Rb** | **Caesium Cs** | **Francium Fr** |
|---|---|---|---|---|---|---|
| Atomic number | 3 | 11 | 19 | 37 | 55 | 87 |
| Atomic mass (g $mol^{-1}$) | 6.94 | 22.99 | 39.10 | 85.47 | 132.91 | (223) |
| Electronic configuration | [He] $2s^1$ | [Ne] $3s^1$ | [Ar] $4s^1$ | [Kr] $5s^1$ | [Xe] $6s^1$ | [Rn] $7s^1$ |
| Ionization enthalpy / kJ $mol^{-1}$ | 520 | 496 | 419 | 403 | 376 | ~375 |
| Hydration enthalpy/kJ $mol^{-1}$ | –506 | –406 | –330 | –310 | –276 | – |
| Metallic radius / pm | 152 | 186 | 227 | 248 | 265 | – |
| Ionic radius $M^+$ / pm | 76 | 102 | 138 | 152 | 167 | (180) |
| m.p. / K | 454 | 371 | 336 | 312 | 302 | – |
| b.p / K | 1615 | 1156 | 1032 | 961 | 944 | – |
| Density / g $cm^{-3}$ | 0.53 | 0.97 | 0.86 | 1.53 | 1.90 | – |
| Standard potentials $E^{\ominus}$ / V for ($M^+$ / M) | –3.04 | –2.714 | –2.925 | –2.930 | –2.927 | – |
| Occurrence in lithosphere† | 18* | 2.27** | 1.84** | 78-12* | 2-6* | ~ $10^{-18}$ * |

*ppm (part per million), ** Percentage by weight

## Group IIA Elements (Alkaline Earth Metals)

| **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 |
| Electron 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 | 112 | 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) |

## Properties of Alkali and Alkaline earth metals

| S.No. | Atomic Properties | Alkali metal | Alkaline earth metals |
|---|---|---|---|
| 1. | Outer Electronic configuration | $ns^1$ | $ns^2$ |
| 2. | Oxidation number and valency | (i)These elements easily form univalent +ve ion by losing loosely solitary $ns^1$ electron due to low IP value. | The $IP_1$ of these metals are much lower than $IP_2$ and thus it appears that<br>these metals should form univalent ion rather than divalent ions but in actual practice, all these give bivalent ion. |
| 3. | Atomic and Ionic radii | Increase down the group, because value of n (principal quantum number) increases. Order = Li < Na < K < Rb < Cs. | The atomic and ionic radii of the alkali earth metal are smaller than corresponding alkali metals.<br>Reason<br>higher nuclear charge (Zeff)<br>On moving down the group size increase, as value of n increases.<br>Be < Mg < Ca < Sr < Ba |
| 4. | Ionisation Energy | As size increases, I.E. decreases down the group (so Cs have lowest I.P.)<br>Order = Li > Na > K > Rb > Cs | Down the group IE decreases due to increase in size. Be > Mg > Ca > Sr > Ba<br>$IE_1$ of Alkali metal < $IE_1$ of Alkaline earth metal<br>$IE_2$ of Alkali metal > $IE_2$ of Alkaline earth metal<br>Reason<br>$IE_1$ of Alkaline earth metal is large due to increased nuclear charge in Alkaline earth metal as compared to Alkali metal but $IE_2$ of Alkali metal is large because second electron in Alkali metal is to be removed from cation which has already acquired noble gas configuration |
| 5. | Electropositive character or metallic character | Alkali metals are strongly electropositive and metallic. Down the group electropositive nature increase so metallic nature also increases.<br>i.e. $M \rightarrow M^+ + e^-$<br>Metallic Nature : Electropositive character $\propto 1/I.P.$<br>Order = Li < Na < K < Rb < Cs. | Due to low IE they are strong electropositive but not as strong as Alkali metal because of comparatively high IE. The electropositive character increase down the group.<br>Order = Be < Mg < Ca < Sr < Ba |
| 6. | Hydration of ions | **(i)** Hydration represents for the dissolution of a substance in water to get absorb water molecule by weak valency forces Hydration of ions in the process when ions on dissolution in water get hydrated.<br>**(ii)** Hydration energy $\propto$ charge density on ion<br>Degree of hydration $\propto$ 1/Cation size $\propto$ charge $\propto$ 1/ionic mobility $\propto$ 1/conductivity<br>Hydration energy = $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$<br>**(iii)** $Li^+$ being smallest in size has maximum degree of hydration and that is why lithium salts are mostly hydrated and moves very slowly under the influence of electric field. e.g : $LiCl.2H_2O$. | Hydration energy = $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ |
| 7. | Photoelectric effect | The phenomenon of emission of electrons when electromagnetic rays strikes<br>against them is called photoelectric effect; Alkali metal have low I.P. so show<br>photoelectric effect. Cs and K are used in Photoelectric cells. | **(i)** Their electronegativities are also small but are higher than that of alkali metals<br>**(ii)** Electronegativity decrease from Be to Ba |
| 8. | Electronegativity | **(i)**These metals are highly electopositive and there by possess low values of electro negativities.<br>**(ii)**Electronegativity of alkali metals decreases down the group.<br>Order = Li > Na > K > Rb > Cs | |

| S.No. | Physical Property | Alkali metal | Alkaline earth metals |
|---|---|---|---|
| 1. | Density | (i)All are light metals.<br>(ii) Density increase down the group but K is lighter than Na.<br>**Order** = Li < K < Na < Rb < Cs | **(i)** Heavier than alkali metals.<br>**(ii)** Density decrease slightly up to Ca after which it increases.<br>**(iii)** Density of Mg is greater than Ca. |
| 2. | Hardness<br><br>The cutting of sodium metal | (i) All are silvery white metals.<br>(ii) Light soft, malleable and ductile metals with metallic luster.<br>(iii) Diamagnetic and colour less in form of ions.<br>(iv) These metals are very soft and can be cut with a knife. Lithium is harder than any other alkali metal. The hardness depends upon cohensive energy.<br>Cohensive energy $\propto$ Force of attraction between atoms. | Relatively soft but harder than Alkali metals. |
| 3. | Melting points/ Boiling points | (i) Lattice energy decreases from Li to Cs and thus Melting points and Boiling points also decrease from Li to Cs.<br>M.P. = Li > Na > K > Rb > Cs<br>B.P. = Li > Na > K > Rb > Cs | They have low Melting points and Boiling points but are higher than corresponding value of group I.<br>Reason<br>They have two valence electrons which may participate in metallic bonding compared with only one electron in Alkali metal. Consequently group II elements are harder and have higher cohesive energy and so, have much higher Melting points / Boiling points than Alkali metal .<br>M.P. = Be > Ca > Sr >Ba > Mg ,B.P. = Be > Ba > Ca > Sr > Mg |
| 4. | Specific heat | It decreases from Li to Cs. Li > Na > K > Rb > Cs ***(*need not to memorise)*** | values are lesser than that of alkali metals, decreases down the group.<br>**need not memorise.* |

<table>
<tr><th>S.No.</th><th>Chemical Property</th><th>Alkali metals</th><th>Alkaline earth metals</th></tr>
<tr><td>1.</td><td>Action with $O_2$ and $N_2$</td><td>
<b>(i)</b> They generally form oxides and peroxides.<br>
$M + O_2 \longrightarrow M_2O$ (Oxide) $\xrightarrow{O_2}$ $M_2O_2$ (Peroxide)<br>
The alkali metals tarnish in dry air due to the formation of their oxides on their surface.<br>
$4M + O_2 \longrightarrow 2M_2O$<br>
They react vigorously in oxygen forming following oxides.<br>
$4\,Li + O_2 \longrightarrow 2\,Li_2O$ (Monoxide)<br>
$2\,Na + O_2 \longrightarrow Na_2O_2$ (Peroxide)<br>
$M + O_2 \longrightarrow MO_2$ ( Superoxide) where M = K, Rb, Cs<br>
<table>
<tr><th colspan="4">Principal Combustion Product (Minor Product)</th></tr>
<tr><th>Metal</th><th>Oxide</th><th>Peroxide</th><th>Superoxide</th></tr>
<tr><td>Li</td><td>$Li_2O$</td><td>($Li_2O_2$)</td><td></td></tr>
<tr><td>Na</td><td>($Na_2O$)</td><td>$Na_2O_2$</td><td></td></tr>
<tr><td>K</td><td></td><td></td><td>$KO_2$(Orange/Yellow Crystalline)</td></tr>
<tr><td>Rb</td><td></td><td></td><td>$RbO_2$ (Orange/Yellow Crystalline)</td></tr>
<tr><td>Cs</td><td></td><td></td><td>$CsO_2$ (Orange/Yellow Crystalline)</td></tr>
</table>
The oxides and peroxides are colourless when pure.<br>
(ii) All super oxide are paramagnetic and peroxides are diamagnetic in nature.<br>
(iii) The increasing stability of the peroxide or superoxide as the size of the metal ion increases is due to the stabilisation of large anions by larger cations through lattice energy effect.<br>
(iv) Since all the alkali metals are highly reactive towards air ; they are kept in kerosene oil. Reactivity increases from Li to Cs.<br>
(v) <b>Only Lithium</b> reacts with $N_2$ (at room temperature) to form ionic lithium nitride $Li_3N$ because Li being strongest reducing agent converts $N_2$ into $N^{3-}$.<br>
$3Li + 1/2N_2 \longrightarrow Li_3N$
</td><td>
(i) Be and Mg are kinetically inert towards oxygen becasue of formation of a film of oxide on their surface. However powdered Be burn brilliantly.<br>
$2Be + O_2$ (air) $\xrightarrow{\Delta}$ 2BeO(amphoteric) ; $3Be + N_2$ (air) $\xrightarrow{\Delta}$ $Be_3N_2$<br>
(ii) Mg is more electropositive and burns with dazzling brilliance in air give MgO and $Mg_3N_2$.<br>
$Mg + O_2$ (air) $\xrightarrow{\Delta}$ MgO ; $Mg + N_2$(air) $\xrightarrow{\Delta}$ $Mg_3N_2$<br>
Peroxides are coloured due to lattice defect.<br>
(Similar property with Li because both shows diagonal relation.)<br>
(iii) Ba gives $BaO_2$ not BaO.<br>
(iv) Calcium, strontium and barium are readily attacked by air to form the oxide and nitride. They also react water with increasing vigour even in cold to form hydroxides.<br>
(v) BeO, MgO are used as refractory, because they have high M.P.<br>
(vi) Other metals (Ba or Sr form peroxide)<br>
$M + O_2 \xrightarrow{\Delta} MO_2$
</td></tr>
<tr><td>2.</td><td>Action with</td><td>(i) Alkali metals decompose water to form the</td><td>(i) Ca , Sr , Ba and Ra decompose cold water readily</td></tr>
</table>

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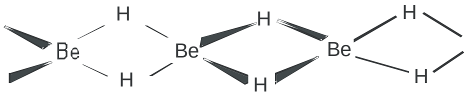
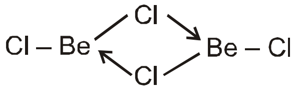
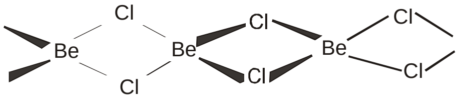
<tr><td></td><td>water</td><td>hydroxides having the formula MOH and dihydrogen.<br>$2M + 2H_2O \longrightarrow 2MOH\ (aq.) + H_2\ (g)$ (M = An alkali metal).<br>(ii) Li decompose water slowly, sodium reacts with water quickly K, Rb and Cs react with water vigorously.<br>(iii) It may be noted that although lithium has most negative $E^\ominus$ value (In below table), its reaction with water is less vigorous than that of sodium which has the least negative $E^\ominus$ value among the alkali metals. This behaviour of lithium is attributed to its small size and very high hydration energy. It's explanation lies in Kinetics, released energy in case of K, Rb, Cs is sufficient to melt or even vapourise and so more surface area is exposed to the water and kinetically reaction is faster than lithium. Other metals of the group react explosively with water.<br>
<table>
<tr><td>Property</td><td colspan="6">Alkali metals</td></tr>
<tr><td></td><td>Li</td><td>Na</td><td>K</td><td>Rb</td><td>Cs</td><td>Fr</td></tr>
<tr><td>Standard potentials $E^\ominus/V$ for $(M^+/M)$</td><td>– 3.04</td><td>– 2.714</td><td>– 2.925</td><td>– 2.930</td><td>– 2.927</td><td>–</td></tr>
</table>
(iv) They also react with proton donors such as alcohol, gaseous ammonia and terminal alkynes evolution of hydrogen.<br>$2M + 2C_2H_5OH \longrightarrow 2C_2H_5OM + H_2$<br>Ethyl alcohol Metal ethoxide</td><td>with evolution of hydrogen.<br>$M + 2H_2O \longrightarrow M(OH)_2 + H_2$<br>(ii) Magnesium decomposes boiling water but beryllium is not attacked by water even at high temperatures as its oxidation potential is lower than the other members</td></tr>
<tr><td>3.</td><td>Hydrides</td><td>(i)They react with $H_2$ forming metal hydride with formula MH which are of ionic nature. Stability of hydride decreases down the group. since the electropositive character decreases from Cs to Li.<br>$2M + H_2 \longrightarrow 2M^\oplus H^\ominus$<br>(iii)The metal hydrides react with water to give MOH and $H_2$. (act as reducing agent)<br>$MH + H_2O \longrightarrow MOH + H_2$</td><td>**(i)** Except Be, all alkaline earth metals form hydrides ($MH_2$) on heating directly with $H_2$.<br>**(ii)**The stability of hydrides decreases from Be to Ra.<br>**(iii)** $BeH_2$ is prepared by the action of $LiAlH_4$ on $BeCl_2$.<br>$BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3$<br>$BeH_2$ & $MgH_2$ is covalent and polymeric but other are ionic.<br><br>**(iv)** The ionic hydrides of Ca, Sr, Ba liberate $H_2$ at anode and metal at cathode.</td></tr>
<tr><td>4.</td><td>Halides</td><td>(i)The alkali metals react vigorously with halogens to form ionic halides $M^+X^-$ .<br>$2M + X_2 \longrightarrow 2\ M^+X^-$<br>(ii) Alkali metals halides ($Cl_2$, $Br_2$, $I_2$) formation is increases form Li to Cs due to increase in electropositive character.<br>Order of reactivity towards $F_2$<br>Li > Na > K > Rb > Cs<br>(iii) LiX have more covalent character (It is because of the high polarisation capability of Lithium ion (fajan's rules)).<br>(iv)Halides having ionic nature have high melting point and are good conductor of current in fused state. These are readily soluble in water.<br>(v) Halides of potassium, rubidium and ceasium have property of combining with extra halogen atoms forming polyhalides.<br>$KI + I_2 \longrightarrow KI_3$</td><td>(i)The alkaline earth metals directly combine with halogens on heating to give metal halides $MX_2$ (X=F,Cl,Br,I)<br>(ii) 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.<br>$BeO + C + Cl \xrightleftharpoons{600-800\ K} BeCl_2 + CO$<br>Anhydrous beryllium halide can not be obtained from materials made in aqueous solution because the hydrated ions $[Be(H_2O)_4]^{2+}$ is formed. i.e. $[Be(H_2O)_4]Cl_2$<br>On dehydration, hydrolysis takes place.<br>$[Be(H_2O)_4]Cl_2 \xrightarrow{heat} Be(OH)_2 + 2HCl$<br>(iii) Except for 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 as shown below:<br>Cl–Be–Cl<br><br><br>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.<br>(iv)The ionic character of halides increases from Be to</td></tr>
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<tr><td></td><td></td><td></td><td>Ra.<br>(v)Beryllium halides have covalent character due to small size and high effective nuclear charge and thus do not conduct electricity in molten state.<br>(vi) The fluorides are relatively less soluble than the chlorides owing to their high lattice energies.<br>(vii)The decreases in solubility of halides down the group is due to decrease in hydration energy because of increasing size of metal cation .<br>(viii) The tendency to form halide hydrates gradually decreases (for example, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$ 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.<br>(ix) CaCl2 has strong affinity with water and is used as dehydrating agent.</td></tr>
<tr><td>5.</td><td>Reducing nature <b><i>(*need not to memorise)</i></b></td><td>
<table>
<tr><td rowspan="2">Property</td><td colspan="6">Alkali metals</td></tr>
<tr><td>Li</td><td>Na</td><td>K</td><td>Rb</td><td>Cs</td><td>Fr</td></tr>
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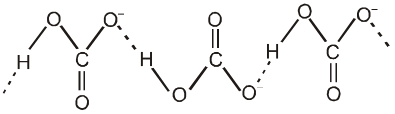
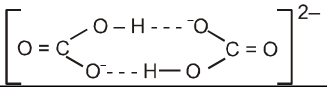
</table>
(i) Reducing agent is electron donor. The alkali metals are strong reducing agents, lithium being the most and sodium the least powerful (above table). The standard electrode potential ($E^{\ominus}$) which measures the reducing power represents the overall change :<br>$M(s) \longrightarrow M(g)$ Sublimation enthalpy<br>$M(g) \longrightarrow M^+(g) + e^-$ Ionization enthalpy<br>$M^+(g) + H_2O \longrightarrow M^+(aq)$ Hydration enthalpy<br><br>(ii) Lithium is expected to be least reducing agent due to it's very high I.E. However, lithium has the highest hydration enthalpy which accounts for its high negative $E^{\ominus}$ value and its high reducing power.<br>Reducing Nature in gas phase<br>= Li < Na < K < Rb < Cs.<br>Reducing Nature in aqueous condition<br>= Li > Cs > Rb > K > Na.</td><td>The alkaline earth metals are strong reducing agents. This is indicated by large negative values of their reduction potentials (below table). However their reducing power is less than those of their corresponding alkali metals. Beryllium has less negative value compared to other alkaline earth metals.<br>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.
<table>
<tr><td rowspan="2">Property</td><td colspan="6">Alkaline earth metals</td></tr>
<tr><td>Be</td><td>Mg</td><td>Ca</td><td>Sr</td><td>Ba</td><td>Ra</td></tr>
<tr><td>Standard potentials $E^{\ominus}$/V for ($M^+$/M)</td><td>– 1.97</td><td>– 2.36</td><td>– 2.84</td><td>– 2.89</td><td>– 2.92</td><td>– 2.92</td></tr>
</table>
</td></tr>
<tr><td>6.</td><td>Basic nature of hydroxide</td><td>(i) These oxides are easily hydrolysed by water to form the hydroxides.<br>Thus $M_2O$ (oxide) + $H_2O \longrightarrow M^{\oplus}OH^{\ominus}$<br>$M_2O_2$ (peroxide) + $H_2O \longrightarrow 2M^{\oplus}OH^{\ominus} + H_2O_2$<br>$MO_2$ (superoxide) + $H_2O \longrightarrow 2M^{\oplus}OH^{\ominus} + H_2O_2 + O_2$<br>(ii) The Hydroxide which are obtained by the reaction of the oxide. With water all are white crystalline solids. The alkali metal hydroxides are the strongest of all bases and dissolve freely in water with evolution of much heat an account of intense hydration.<br>Basic nature/Solubility in water/Thermal stability<br>= LiOH < NaOH < KOH < RbOH < CsOH</td><td>Basic/thermal stability<br>= $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$</td></tr>
<tr><td>7.</td><td>Carbonates and bicarbonates</td><td><b>(i)</b> The carbonates ($M_2CO_3$) and bicarbonates ($MHCO_3$) are highly stable to heat, where M as alkali metals.<br>(ii) Group 1 metals are so strongly basic, they (except lithium) also form solid bicarbonates. No other metals form solid bicarbonates. Lithium carbonate is not so stable to heat. Its hydrogencarbonate does not exist as a solid. Although $NH_4HCO_3$ also exists as a solid.<br>(iii) The stability of these salts increases with the increasing electropositive character from Li to Cs. It is therefore $Li_2CO_3$ decompose on heating.<br>Thermal stability/Solubility in water.<br>$Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$<br>$LiHCO_3$ does not exist in solid form due to high polarizing power of $Li^+$ and uncomparable size of $Li^+$ cation and $HCO_3^-$ anion.</td><td>(i) All these metal carbonates $MCO_3$ are insoluble in neutral medium but soluble in acids and decompose on red heating.<br>(ii) The stability of carbonates increases with increase in electropositive character of metal.<br>$BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$<br>(iii) Bicarbonates of alkaline earth metals do not exist in solid state but are known in solution only on heating their solution bicarbonates decomposed to liberate $CO_2$ .<br>$M(HCO_3)_2 \xrightarrow{\Delta} MCO_3 + CO_2 + H_2O$<br>(Solution)<br>(iv)Solubility of carbonates decrease on moving down the group.<br>$BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$</td></tr>
</table>

| | | | |
|---|---|---|---|
| | | $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$<br>(iv) Bicarbonates are decomposed at relatively low temperature.<br>$2MHCO_3 \xrightarrow{300^0C} M_2CO_3 + H_2O + CO_2$<br>(v) Hydrolysis of carbonate<br>$Na_2CO_3 + 2H_2O \longrightarrow 2NaOH + H_2CO_3$<br>$Li_2CO_3 + 2H_2O \longrightarrow$ sparingly soluble<br>(vi) The crystal structures of $NaHCO_3$ and $KHCO_3$ both show hydrogen bonding, but are different.<br>(a) In $NaHCO_3$, the $HCO_3^-$ ions are linked into an infinite chain.<br>(b) in $KHCO_3$, $RbHCO_3$, $CsHCO_3$, $HCO_3^-$ forms a dimeric anion.<br>Solubility in water $NaHCO_3 < KHCO_3 < RbHCO_3 < CsHCO_3$<br>(a) <br>(b)  | |
| 8. | Complex ion formation | (i) A metal shows complex formation only when it has following characteristics.<br>(a) Small size, (b) High nuclear charge, (c) Presence of empty orbitals in order to accept electron pair from ligand (electron pair donor species).<br>(ii) Due to small size only Lithium in alkali metals, forms a few complex ions. Rest all alkali metals do not possess the tendency to form complex ion. | $Be^{2+}$ on account of smaller size forms many complexes such as $[Be F_3]^-$, $[BeF_4]^{2-}$<br>Chlorophyll contains $Mg^{2+}$ [Photosynthetic pigment in plants] (C.No.= 4)<br>$[Be(H_2O)_4]^{2+} + H_2O \longrightarrow [Be(H_2O)_3OH]^+ + H_3O^+$ |
| 9. | Reaction with acids | Reacts vigorously with acids<br>$2M + H_2SO_4 \longrightarrow M_2SO_4 + H_2$ | The alkaline earth metals readily react with acids liberated dihydrogen.<br>$M + 2HCl \longrightarrow MCl_2 + H_2$ |
| 10. | Formation of amalgams | (i) Alkali metals get dissolved in mercury to form amalgams with evolution of heat and the amalgamation is highly exothermic.<br>(ii) Alkali metals form alloys themselves as well as with other metals. | Alkaline earth metals get dissolved in mercury to form amalgams with evolution of heat and the amalgamation is highly exothermic. |
| 11. | Sulphates | (i) All these form sulphates of type $M_2SO_4$.<br>(ii) Except $Li_2SO_4$ rest all are soluble in water.<br>Thermal stability /solubility in water<br>$Li_2SO_4 < Na_2SO_4 < K_2SO_4 < Rb_2SO_4 < Cs_2SO_4$<br>(iii)These sulphates on fusing with carbon form sulphides.<br>$M_2SO_4 + 4C \longrightarrow M_2S + 4CO$ | (i) $MSO_4$ type sulphates are formed<br>(ii)The solubility of sulphates decreases on moving down the group. The sulphates of the alkaline earth metals are all white solids and stable to heat. $BeSO_4$, 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.<br>Thermal stability<br>$BeSO_4 < MgSO_4 < CaSO_4 < SrSO_4 < BaSO_4$<br>Solubility in water<br>$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$<br>(iii) $MSO_4 + 2C \longrightarrow MS + 2CO_2$ |
| 12. | Sulphides | All metals react with S forming sulphides such as Na2S and Na2Sn (n = 2, 3, 4, 5 or 6). The polysulphide ions are made from zig-zag chains of sulphur atoms. | $M^{2+} + S^{2-} \longrightarrow MS$ |
| 13. | Nitrates | (i) Nitrates of both are soluble in water and decompose on heating.<br>(ii) $LiNO_3$ decomposes to give $NO_2$ and $O_2$ and rest all give nitrites and oxygen.<br>$2MNO_3 \longrightarrow 2MNO_2 + O_2$ (except Li)<br>$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$<br>$2NaNO_3 \xrightarrow[500^oC]{\Delta} 2NaNO_2 + O_2$<br>$2NaNO_3 \xrightarrow[800^oC]{\Delta} Na_2O + N_2 + N_2 + O_2$ | On heating they decompose into their corresponding oxides with evolution of a mixture of nitrogen dioxide and oxygen.<br>$M(NO_3)_2 \longrightarrow MO + 2NO_2 + \frac{1}{2}O_2$<br>(M = Be, Mg , Cr, Sr, Ba) |

| | | | |
|---|---|---|---|
| | | $2NaNO_3 \xrightarrow{Na} Na_2O + N_2 + O_2$ | |
| 14. | Nitride | $Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3\uparrow$ | $Be_3N_2 + 6H_2O \longrightarrow 3Be(OH)_2 + 2NH_3\uparrow$<br>$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3\uparrow$ |
| 15. | Carbide | When Li is heated with carbon, an ionic carbide $Li_2C_2$ is formed.<br>$2Li + 2C \longrightarrow Li_2C_2$<br>Other metals do not react with carbon directly but form carbides when heated with ethyne, or when ethyne is passed through a solution of metal in liquid ammonia.<br>$Na + C_2H_2 \longrightarrow NaH + C_2 \longrightarrow Na_2C_2$<br>$[C\equiv C\text{–}H]^{-}$ $[C\equiv C]^{2-}$<br>$Na_2C_2 + 2H_2O \longrightarrow NaOH + C_2H_2$ | The binary compounds of carbon with other elements (less electronegative or of similar electronegativity) are called carbides. They are classified into following 3 categories :<br>(i) Ionic (ii) Covalent (iii) Interstitial (or metallic)<br>**(i) Ionic carbides (or salt like carbides) :** Generally formed by the most electropositive elements such as alkali and alkaline earth metals and aluminium (Boron is exception). Based on the product obtained on hydrolysis, they are further sub-classified into three types.<br>**(a) Methanides :** These give $CH_4$ on reaction with $H_2O$.<br>$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$ ;<br>$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$<br>These carbides contain $C^{4-}$ ions in their constitution.<br>**(b) Acetylides :** These give $C_2H_2$ on reaction with $H_2O$.<br>$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C2H_2$<br>$Al_2(C_2)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3C2H_2$<br>$SrC_2 + 2H_2O \longrightarrow Sr(OH)_2 + C_2H_2$<br>Such compounds contain C22– ions.<br>**(c) Allylides :** These give 1-propyne on reaction with $H_2O$.<br>$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3\text{–}C\equiv CH$<br>Such compounds contain $C_3^{4-}$ $[:\ddot{\underset{..}{C}}-C\equiv C:]^{4-}$ ions.<br>**Covalent carbides**<br>Molecules like SiC and $B_4C$ are also examples of covalent carbides.<br>**Interstitial or metallic carbides**<br>Such carbides are formed by transition metals and some of the lanthanides and actinides. Interstitial carbides retain many of the properties of metals. They conduct electricity by metallic conduction and have properties of metals (a lusture like a metal). In these compounds carbon atoms occupy octahedral holes in the closed packed metal lattice. These are generally very hard and have very high melting point (e.g. WC). Carbides of Cr, Mn, Fe, Co and Ni are hydrolysed by water or dilute acids. |

**Lattice Energy:** Energy change when one mole of crystalline lattice is formed from gaseous ions

eg. $2Al^{3+} + 3O^{2-} \longrightarrow Al_2O_3 + L.E.$

**Hydration Energy:** It is the energy change when gaseous ions for aqueous ions.

eg. $Na^{+} + aq. \longrightarrow Na^{+} + H.E.\ of\ Na^{+}$

$SO_4^{2-} + aq. \longrightarrow SO_4^{2-} + H.E.\ of\ SO_4^{2-}$

**Solutions in liquid $NH_3$**

Alkali metals dissolve in liquid ammonia (high conc. 3 M) and give blue solution which is conducting, reducing and paramagnetic in nature.

**Reason**

On dissolving Metal in $NH_3$

$M(s) + NH_{3(\ell)} \longrightarrow M^+_{(NH_3)} + e^-_{(NH_3)}$

$M^+ + x\,(NH_3) \longrightarrow [M\,(NH_3)_X]^+$ ⟶ Ammoniated cation

$e^- + y\,(NH_3) \longrightarrow [e(NH_3)_y]^-$ ⟶ Ammoniated electron

The blue colour is due to ⟶ Ammoniated electron

The paramagnetic nature is due to ⟶ Ammoniated electron

The conducting nature is due to ⟶ Ammoniated $M^+$ + Ammoniated electron

On standing the colour fades due to formation of amide After liberating hydrogen.

$$M^+ + e^- + NH_3 \longrightarrow MNH_{2\,(amide)} + H_{2\,(g)}$$

In the absence of impurities like. Fe, Pt, Zn etc, the solutions are stable.

In concentrated solution, the blue colour changes to bronze colour and diamagnetic due to the formation of metal clusters and ammoniated electrons also associate to form electron pairs

$$2\,e^-\,(NH_3)y \longrightarrow [\,e^-\,(NH_3)_y]_2$$

Solutions are of much lower density than the pure solvent, i.e., they occupy for greater volume than that expected from the sum of the volumes of metal and solvent

Peroxide and superoxides of Na & K are widely used as Oxidising agent and air purifiers in space capsules, submarines and breathing mask.

## Alkaline metal in liq. $NH_3$

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

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

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

### Uses of alkali metal

**(1)** Lithium metal is used to make useful alloys,
- with lead to make 'white metal' bearings for motor engines.
- with aluminium to make aircraft parts.
- with magnesium to make armour plates.

**(2)** It is used in thermonuclear reactions.

**(3)** Lithium is also used to make electrochemical cells.

**(4)** Sodium is used to make a Na/Pb alloy needed to make $PbEt_4$ and $PbMe_4$. These organolead compounds were earlier used as anti-knock additives to petrol, but nowadays vehicles use lead-free petrol.

**(5)** Liquid sodium metal is used as a coolant in fast breeder nuclear reactors.

**(6)** Potassium chloride is used as a fertilizer.

**(7)** Potassium hydroxide is used in the manufacture of soft soap. It is also used as an excellent absorbent of carbon dioxide.

**(8)** Caesium is used in devising photoelectric cells.

## Uses of alkaline metal

**(1)** Beryllium is used in the manufacture of alloys.
**(2)** Copper-beryllium alloys are used in the preparation of high strength springs.
**(3)** Metallic beryllium is used for making windows of X-ray tubes.
**(4)** Magnesium forms alloys with aluminium, zinc, manganese and tin. Magnesium-aluminium alloys being light in mass are used in air-craft construction.
**(5)** Magnesium (powder and ribbon) is used in flash powders and bulbs, incendiary bombs and signals.
**(6)** A suspension of magnesium hydroxide in water (called *milk of magnesia*) is used as antacid in medicine.
**(7)** Magnesium carbonate is an ingredient of toothpaste.
**(8)** Calcium is used in the extraction of metals from oxides which are difficult to reduce with carbon.
**(9)** 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.
**(10)** Radium salts are used in radiotherapy, for example, in the treatment of cancer.

## Biological Importance Of Sodium And Potassium:

- Sodium ions are found primarily on the outside of cells, being located in blood plasma and in the interstitial fluid which surrounds the cells. These ions participiate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the tranasport of sugars and amino acids into cells. Sodium and potassium, although so similar chemically, differ quantitatively in their ability to penetrate cell membranes, in their transport mechanisms and in their efficiency to activate enzymes. Thus, potassium ions are the most aundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals

  A typical 70 kg man contains about 90 g of Na and 170 g of K compared with only 5 g of iron and 0.06 g of copper.

## Biological Importance of Magnesium and Calcium :

- 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.
- 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. 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.

  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.

## ANOMALOUS PROPERTIES OF LITHIUM

The anomalous behavior of lithium is due to the :
(i) Exceptionally small size of its atom and ion,
(ii) High polarising power (i.e., charge/ radius ratio ).
As a result, there is increased covalent character of lithium compound which is responsible for their solubility in organic solvent. Further, lithium shows diagonal relationship to magnesium.

| S.No. | Property | Li |
|---|---|---|
| 1. | Hardness | Li is much harder. |
| 2. | M.P and B.P | Higher M.P and B.P |
| 3. | Reactivity | Less reactive |
| 4. | Reducing agent | Strong |
| 5. | Combustion in air | Li form monoxide ($Li_2O$) and nitride ($Li_3N$) ; not for other. |
| 6. | Hydration of ion | Favored for $Li^{\oplus}$ ; not for other.<br>$Li^{\oplus}$ has maximum degree of hydration for this reason. Lithium salts are mostly hydrated. E.g $LiCl.2H_2O$. |
| 7. | Hydrogen Carbonate | Li is not obtained in the solid form while all other elements form solid hydrogen carbonates. |

| | | |
|---|---|---|
| 8. | Ethynide | Favored for $Li^{\oplus}$ ; not for other. |
| 9. | Lithium nitrate | $4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$<br>Lithium Oxide<br>Where as other alkali metal nitrates decompose to give the corresponding nitrite.<br>$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$<br>Sodium nitrite |
| 10. | LiF and $Li_2O$ | These are much less soluble in water. Solubility in water is less than the corresponding compounds of other alkali metal. |
| 11. | Carbide | Li reacts directly with carbon to form anionic carbide. |
| 12. | Hydroxide | Lithium hydroxide is less basic $Li_2CO_3$ , $LiNO_3$ and LiOH all form the oxides an gentle heating. |
| 13. | Carbonate | Less stable. |
| 14. | Nitrite | Less stable. |
| 15. | Bicarbonate | Lithium forms a bicarbonates in solution it does not form a solid bicarbonate.<br>Where as the other all forms stable solid Carbonates. |
| 16. | Complex ion formation | Lithium has a great tendency to form. Complexes not for other. Due to small size of Lithium. |
| 17. | Reaction with $NH_3$ | Li when heated in $NH_3$ imide ($Li_2NH$) while other alkali metals form amides ($MNH_2$) |

**Points of Similarities between Lithium and Magnesium**

The similarity between lithium and magnesium is particularly striking and arises because of their similar size: atomic radii, Li = 152 pm, Mg = 160 pm; ionic radii : $Li^+$ = 76 pm, $Mg^{2+}$ = 72 pm. The main points of similarity are :

| S.No. | Properties | Li and Mg |
|---|---|---|
| 1. | Hardness | Li and Mg are much harder. |
| 2. | Density | These are lighter than other elements in the respective group. |
| 3. | Reaction with water | Both react slowly with water. |
| 4. | Solubility of hydroxide and oxide | Less soluble and their hydroxides decompose in acid on heating. |
| 5. | Reaction with $N_2$ | By direct combination with nitrogen both form a nitride $Li_3N$ and $Mg_3N_2$. |
| 6. | Oxides | The oxides $Li_2O$ and MgO donot combine with excess oxygen to give any superoxide. |
| 7. | Carbonates | Carbonates of both decompose easily on heating to form the oxides and $CO_2$. Solid hydrogen carbonates are not formed by Li and Mg. |
| 8. | Solubility of halides in ethanol | Both LiCl and $MgCl_2$ are soluble. |
| 9. | Hydration of ion | Both LiCl and $MgCl_2$ are deliquescent and crystallise from aqueous solution as hydrates, $LiCl.H_2O$ and $MgCl_2.6H_2O$. |

**Anamolous Behaviour of Beryllium**

The properties of beryllium the first member of the alkaline earth metal, differ from the rest of the member. Its is mainly because of

(i) Its small size and high polarizing power.

(ii) Relatively high electro negativity and ionization energy as compared to other members.

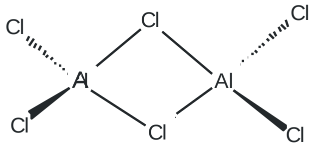
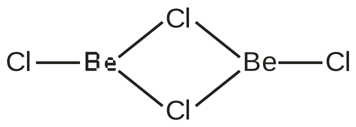
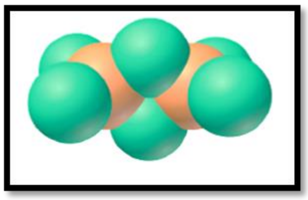
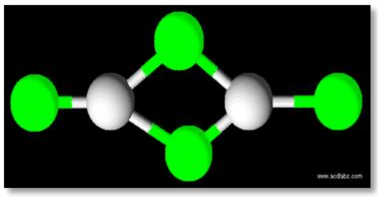
(iii) Absence of vacant d–orbitals in its valence shell.

Some important points of difference between beryllium and other members (especially magnesium) are given below.

| S.No. | Properties | |
|---|---|---|
| 1. | Hardness | Be is harder than other members of its group |
| 2. | Density | Be is lighter than Mg |
| 3. | M.P. and B.P. | Higher then other members of its group. |
| 4. | Reaction with water | Be does not react with water while Mg reacts with boiling water. |
| 5. | Nature of oxides | BeO is amphoteric while MgO is weakly basic. |
| 6. | Nature of compounds | Be forms covalent compounds whereas other members form ionic compounds. |
| 7. | Carbide | Beryllium carbide reacts with water to give methane whereas carbides of other alkaline earth metals gives acetylene gas.<br>$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$<br>$MgC_2 + 2H_2O \rightarrow Mg(OH)_2 + C_2H_2$<br>$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$ |
| 8. | Hydride | The beryllium hydride is electron deficient and polymeric, with muti center bonding like aluminium hydride. |
| 9. | Co-ordination number | Beryllium does not exhibit coordination number more than four as it has four orbitals in the valence shell. The other members of this group has coordination number 6. |
| 10. | Reaction with Alkali | Be dissolves in alkalies with evolution of hydrogen<br>$Be + 2NaOH + 2H_2O \rightarrow \underset{\text{(sodium beryllate}}{Na_2BeO_2.2H_2O} + H_2$<br>Other alkaline earth metals don't react with alkalies. |

**Resemblance of Beryllium with Aluminium (Diagonal relationship)**

The following points illustrate the anomalous behaviour of Be and its resemblance with Al.

| S.No. | Properties | Be and Al |
|---|---|---|
| 1. | Nature of compounds | Unlike groups-2 elements but like aluminium, beryllium forms covalent compounds. |
| 2. | Nature of hydroxide | The hydroxides of Be, [$Be(OH)_2$] and aluminium [$Al(OH)_3$] are amphoteric in nature, whereas those of other elements of group – 2 are basic in nature. |
| 3. | Nature of oxide | The oxides of both Be and Al i.e. BeO and $Al_2O_3$ are high melting insoluble solids. |
| 4. | Polymeric structure | $BeCl_2$ and $AlCl_3$ have bridged chloride polymeric structure.<br> <br> <br><br> |
| 5. | Salts | The salts of beryllium as well as aluminium are extensively hydrolysed. |
| 6. | Carbides | Carbides of both the metal reacts with water liberating methane gas.<br>$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$<br>$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$ |
| 7. | Oxides and hydroxides | The oxides and hydroxides of both Be and Al are amphoteric and dissolve in sodium hydroxide as well as in hydrochloric acid.<br>$BeO + 2HCl \rightarrow BeCl_2 + H_2O$<br>$BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$<br>$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + H_2O$<br>$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$ |
| 8. | Reaction with acids | Like Al, Be is not readily attacked by acids because of the presence of an oxide film. |

# GROUP -I & II OXIDES

## 1. Sodium Oxide ($Na_2O$)

**Preparation:**

| Name of compound | Name and Brief about the process | Related chemical reaction |
|---|---|---|
| Sodium Oxide ($Na_2O$) | (1) By burning sodium at 180°C in a limited supply of air or oxygen and distilling off the excess of sodium in vacuum. | $2Na + \frac{1}{2} O_2 \xrightarrow{180^0} Na_2O$ |
| | (2) By heating sodium peroxide, nitrate or nitrite with sodium. | $Na_2O_2 + 2Na \longrightarrow 2Na_2O$<br>$2NaNO_3 + 10Na \longrightarrow 6Na_2O + N_2$<br>$2NaNO_2 + 6Na \longrightarrow 4Na_2O + N_2$ |
| | (3) Sodium oxide is formed when the mixture of sodium azide and sodium nitrite is heated. | $3NaN_3 + NaNO_2 \longrightarrow 2Na_2O + 5N_2$ |

**Chemical Properties:**

(1) It is white amorphous substance.

(2) It dissolve violently in water, yielding caustic soda (NaOH) and evolving a large amount of heat.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

**Uses :** It is used as dehydrating and polymerising agent in organic chemistry.

## 2. Sodium Peroxide ($Na_2O_2$)

**Preparation**

| Name of compound | Name and Brief about the process | Related chemical reaction |
|---|---|---|
| Sodium Peroxides ($Na_2O_2$) | (1) By heating the metal in excess of air or oxygen at 300°, which is free from moisture and $CO_2$. | $2Na + O_2 \text{ (excess)} \xrightarrow{300^0 C} Na_2O_2$ |
| | (2) **Industrial method :** It is a two stage reaction in the presence of excess air. | $2Na + O_2 \longrightarrow Na_2O$<br>$Na_2O + O_2 \longrightarrow Na_2O_2$ |

**Properties:**

(1) It is a pale yellow solid (when impure), becoming white in air from the formation of a film of NaOH and $Na_2CO_3$.

(2) In cold water (~0°C) produces $H_2O_2$ but at room temperature produces $O_2$. In ice-cold mineral acids also produces $H_2O_2$.

$$Na_2O_2 + 2H_2O \xrightarrow{\sim 0°C} 2NaOH + H_2O_2$$
$$2Na_2O_2 + 2H_2O \xrightarrow{25°C} 4NaOH + O_2$$
$$Na_2O_2 + H_2SO_4 \xrightarrow{\sim 0°C} Na_2SO_4 + H_2O_2$$
$$2Na_2O_2 + H_2SO_4 \xrightarrow{25°C} 2Na_2SO_4 + 2H_2O + O_2$$

(3) It reacts with $CO_2$, giving sodium carbonate and oxygen and hence its use for purifying air in a confined space e.g. submarine, ill-ventilated room.

$$2Na_2O_2 + 2CO_2 \longrightarrow 2Na_2CO_3 + O_2$$
$$Na_2O_2 + CO \longrightarrow Na_2CO_3$$

(4) It is an oxidising agent and oxidises charcoal, CO, $NH_3$, $SO_2$.

$$3Na_2O_2 + 2C \longrightarrow 2Na_2CO_3 + 2Na \text{ [deposition of metallic Na]}$$
$$CO + Na_2O_2 \longrightarrow Na_2CO_3$$
$$SO_2 + Na_2O_2 \longrightarrow Na_2SO_4$$
$$2NH_3 + 3Na_2O_2 \longrightarrow 6NaOH + N_2$$

(5) Sulphides are oxidised to corresponding sulphates

$$Na_2O_2 \longrightarrow Na_2O + [O] \quad ; \quad Na_2S + 4[O] \longrightarrow Na_2SO_4$$

(6) $Na_2O_2 \longrightarrow Na_2O + [O]$ ; $2Al + 3[O] \longrightarrow Al_2O_3$ ; $Al_2O_3 + Na_2O \rightarrow 2NaAlO_2$.

**Uses :**

(1) For preparing $H_2O_2$, $O_2$ .

(2) Oxygenating the air in submarines.

(3) Oxidising agent in the laboratory.

| Oxides of Potassium | $K_2O$ | $K_2O_2$ | $K_2O_3$* | $KO_2$ | $KO_3$ |
|---|---|---|---|---|---|
| Colours | White | White | Red | Bright Yellow | Orange Red Solid |

**3. Potassium sesquioxide (need not memorize).**

**Preparation:**

| Name of compound | Name and Brief about the process | Related chemical reaction |
|---|---|---|
| $K_2O$<br>(Potassium oxide) | By heating potassium nitrate with potassium. | $2KNO_3 + 10K \xrightarrow{\text{heating}} 6K_2O + N_2$<br>$\underset{\text{(White)}}{K_2O} \xrightarrow{\text{heating}} \underset{\text{(Yellow)}}{K_2O}$<br>$K_2O + H_2O \longrightarrow 2KOH$ |

**Properties of Potassium superoxide ($KO_2$)**

It is a orange coloured (chrome yellow) powder and reacts with water according to following reaction.

$$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$$

It reacts directly with CO and $CO_2$.

$$2KO_2 + CO \longrightarrow K_2CO_3 + O_2 \ ; \ 2KO_2 + CO_2 \longrightarrow K_2CO_3 + O_2$$

If more $CO_2$, in presence of moisture is present; then

$$4KO_2 + 4CO_2 + 2H_2O \longrightarrow 4KHCO_3 + 3O_2$$

On heating with sulphur, it forms potassium sulphate

$$2KO_2 + S \longrightarrow K_2SO_4$$

**Uses :** It is used as an oxidising agent and air purifier in space capsules, submarine and breathing mask as it produces $O_2$ and removes $CO_2$.

**4. Magnesium Oxide (MgO):**

| Name of compound | Name and Brief about the process | Related chemical reaction |
|---|---|---|
| Magnesium Oxide (MgO) | It is also called magnesia and obtained by heating natural magnesite. | $MgCO_3 \longrightarrow MgO + CO_2$ |

**Properties :**

(1) It is white powder.

(2) It's m.p. is 2850°C. Hence used in manufacture of refractory bricks for furances. And it is acts as basic flux and facilitates the removal of acidic impurities of Si, P and S from steel through slag formation.

(3) It is very slightly soluble in water imparting alkaline reaction.

**5. Calcium Oxide (CaO):**

**Preparation**

| Name of compound | Name and Brief about the process | Related chemical reaction |
|---|---|---|
| Calcium Oxide (CaO) | It is commonly called as quick lime or lime and made by decomposing lime stone at a high temperature about 1000°C. | $CaCO_3 \overset{\Delta}{\rightleftharpoons} CaO + CO_2$ |

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

**Chemical Properties :**

(1) It is white amorphous powder of m.p. 2570°C. On exposure to atmosphere; it absorbs moisture and carbondioxide.

$$CaO + H_2O \longrightarrow Ca(OH)_2 \quad ; \quad CaO + \underset{\text{acidic oxide}}{CO_2} \longrightarrow CaCO_3$$

(2) It emits intense light (lime light), when heated in oxygen-hydrogen flame.

(3) It combines with limited amount of water to produce slaked lime. This process is called slaking of lime. Quick lime slaked with soda gives solid sodalime (CaO). Being a basic oxide.

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

(4) Soda lime (basic oxide) combines with some acidic oxides at high temperature.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

$$6CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2$$

**Uses :**

(i) It is an important primary material for manufacturing cement and is the cheapest form of alkali.

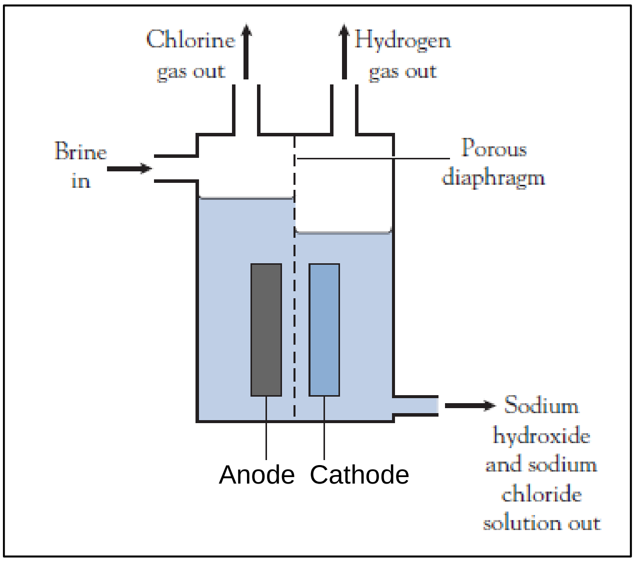
(ii) It is used in the manufacture of sodium carbonate from caustic soda.

(iii) It is employed in the purification of sugar and in the manufacture of dye stuffs.

## HYDROXIDES

### 1. Sodium Hydroxides(Caustic Soda) NaOH:

**Preparation :**

| **Name of compound** | **Name and Brief about the process** | **Related chemical reaction** |
|---|---|---|
| Sodium Hydroxides (NaOH) | **(1) Electrolysis of Brine :**<br>Sodium hydroxide is generally prepared commercially by the electrolysis of sodium chloride in Castner-Kellner cell. A brine solution is electrolysed using a mercury cathode and a carbon anode. Sodium metal discharged at the cathode combines with mercury to form sodium amalgam. Chlorine gas is evolved at the anode.<br>The amalgam is treated with water to give sodium hydroxide and hydrogen gas. | Cathode: $Na^+ + e^- \xrightarrow{Hg} Na\text{-amalgam}$<br>Anode : $Cl^- \longrightarrow \frac{1}{2} Cl_2 + e^-$<br> <br>$2Na\text{-amalgam} + 2H_2O \longrightarrow 2NaOH + 2Hg + H_2$ |
|  | (2) Caustication of $Na_2CO_3$<br>**(Gossage's method)** | $Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + \underset{\text{(suspension)}}{CaCO_3\downarrow}$<br>Since the $K_{sp}$ $(CaCO_3) < K_{sp}(Ca(OH)_2)$, the reaction shifts towards right. |

**Properties:**

(1) Sodium hydroxide is a white, translucent solid. It melts at 591 K. It is readily soluble in water to give a strong alkaline solution. Crystals of sodium hydroxide are deliquescent. The sodium hydroxide solution at the surface reacts with the $CO_2$ in the atmosphere to form $Na_2CO_3$.
(2) It is white crystalline, deliquescent, highly corrosive solid.
(3) It is stable towards heat.
(4) It's aqueous solution alkaline in nature and soapy in touch.
(5)

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_3\uparrow + H_2O$$

$$FeCl_3 + 3NaOH \longrightarrow \underset{\text{Brown ppt}}{Fe(OH)_3\downarrow} + 3NaCl$$

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2\downarrow + 2NaCl$$

$$Zn(OH)_2\downarrow + 2NaOH \longrightarrow \underset{\text{soluble}}{Na_2ZnO_2} + 2H_2O \text{ [Same with } AlCl_3, SnCl_2, PbCl_2]$$

(6) Acidic and amphoteric oxides gets dissolved easily e.g.

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

(7) Aluminium and Zn metal gives $H_2$ from NaOH.

$$2Al + 2NaOH + 2H_2O \longrightarrow 3H_2 + 2NaAlO_2$$

(8) Several non metals such as P, S, Cl etc. yield a hydride instead of hydrogen.e.g.

$$4P + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2 \text{ (Disproportionation reaction)}$$

(9) NaOH is stable towards heat but reduced to metal when heated with carbon.

$$2NaOH + C \longrightarrow 2Na + 2CO + H_2$$

(10). NaOH + Metal Oxide (M)

$$\xrightarrow{+2} Na_2MO_2$$

$$\xrightarrow{+3} Na_3MO_3$$

$$\xrightarrow{+4} Na_2MO_3$$

Above are general reactions of NaOH with metal oxides having metal's Oxidation number +2, +3 & +4 respectively.

**Uses :** It is used in

(i) The manufacture of soap, paper, artificial silk and a number of chemicals.
(ii) In petroleum refining.
(iii) In the purification of bauxite.
(iv) In the textile industries for mercerising cotton fabrics.
(v) For the preparation of pure fats and oils .
(vi) As a laboratory reagent.

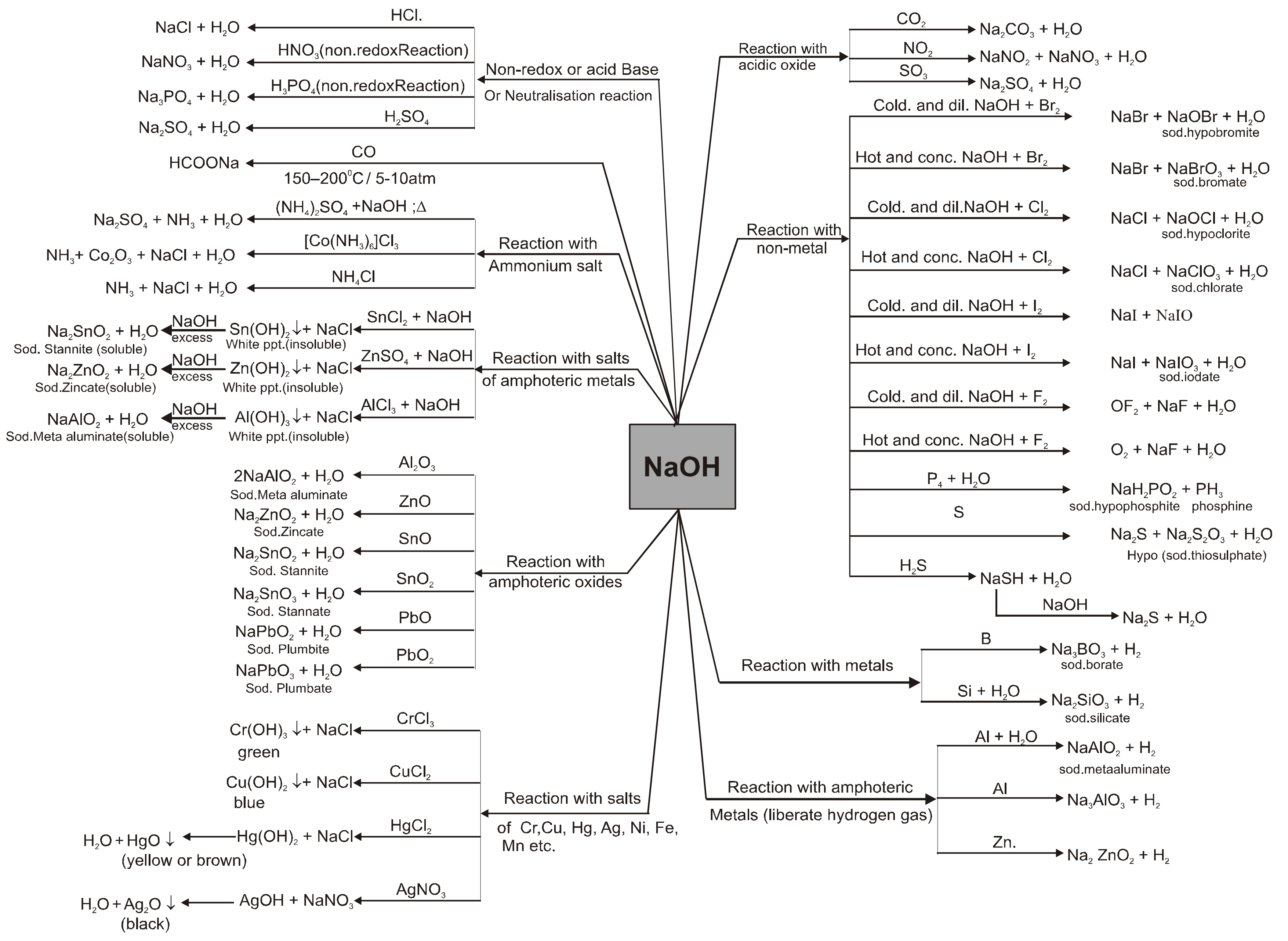
### 2. Potassium Hydroxide (KOH):

**Preparation:**

(1) It is prepared by electrolysis of KCl solution.
(2) KOH resembles NaOH in all its reactions. However KOH is much more soluble in alcohol. This accounts for the use of alcoholic KOH in organic chemistry.
(3) It is used for the absorption of gases like $CO_2$, $SO_2$, etc. It is used for making soft soaps.

**Properties**:Same as NaOH

(1) It is stronger base compared to NaOH.
(2) Solubility in water is more compared to NaOH.
(3) In alcohol, NaOH is sparingly soluble but KOH is highly soluble.
(4) As a reagent KOH is less frequently used but in absorption of $CO_2$, KOH is preferably used compared to NaOH. Because $KHCO_3$ formed is soluble whereas $NaHCO_3$ is insoluble and may therefore choke the tubes of apparatus used.


NaOH
Non-redox or acid Base
Or Neutralisation reaction
HCl. → $NaCl + H_2O$
$HNO_3$(non.redoxReaction) → $NaNO_3 + H_2O$
$H_3PO_4$(non.redoxReaction) → $Na_3PO_4 + H_2O$
$H_2SO_4$ → $Na_2SO_4 + H_2O$
CO, 150–200°C / 5-10atm → HCOONa
Reaction with Ammonium salt
$(NH_4)_2SO_4$ +NaOH ;Δ → $Na_2SO_4 + NH_3 + H_2O$
$[Co(NH_3)_6]Cl_3$ → $NH_3 + Co_2O_3 + NaCl + H_2O$
$NH_4Cl$ → $NH_3 + NaCl + H_2O$
Reaction with salts of amphoteric metals
$SnCl_2$ + NaOH → $Sn(OH)_2\downarrow + NaCl$ White ppt.(insoluble) $\xrightarrow[\text{excess}]{NaOH}$ $Na_2SnO_2 + H_2O$ Sod. Stannite (soluble)
$ZnSO_4$ + NaOH → $Zn(OH)_2\downarrow + NaCl$ White ppt.(insoluble) $\xrightarrow[\text{excess}]{NaOH}$ $Na_2ZnO_2 + H_2O$ Sod.Zincate(soluble)
$AlCl_3$ + NaOH → $Al(OH)_3\downarrow + NaCl$ White ppt.(insoluble) $\xrightarrow[\text{excess}]{NaOH}$ $NaAlO_2 + H_2O$ Sod.Meta aluminate(soluble)
Reaction with amphoteric oxides
$Al_2O_3$ → $2NaAlO_2 + H_2O$ Sod.Meta aluminate
ZnO → $Na_2ZnO_2 + H_2O$ Sod.Zincate
SnO → $Na_2SnO_2 + H_2O$ Sod. Stannite
$SnO_2$ → $Na_2SnO_3 + H_2O$ Sod. Stannate
PbO → $NaPbO_2 + H_2O$ Sod. Plumbite
$PbO_2$ → $NaPbO_3 + H_2O$ Sod. Plumbate
Reaction with salts of Cr,Cu, Hg, Ag, Ni, Fe, Mn etc.
$CrCl_3$ → $Cr(OH)_3\downarrow + NaCl$ green
$CuCl_2$ → $Cu(OH)_2\downarrow + NaCl$ blue
$HgCl_2$ → $Hg(OH)_2 + NaCl$ → $H_2O + HgO\downarrow$ (yellow or brown)
$AgNO_3$ → $AgOH + NaNO_3$ → $H_2O + Ag_2O\downarrow$ (black)
Reaction with acidic oxide
$CO_2$ → $Na_2CO_3 + H_2O$
$NO_2$ → $NaNO_2 + NaNO_3 + H_2O$
$SO_3$ → $Na_2SO_4 + H_2O$
Reaction with non-metal
Cold. and dil. NaOH + $Br_2$ → $NaBr + NaOBr + H_2O$ sod.hypobromite
Hot and conc. NaOH + $Br_2$ → $NaBr + NaBrO_3 + H_2O$ sod.bromate
Cold. and dil.NaOH + $Cl_2$ → $NaCl + NaOCl + H_2O$ sod.hypoclorite
Hot and conc. NaOH + $Cl_2$ → $NaCl + NaClO_3 + H_2O$ sod.chlorate
Cold. and dil. NaOH + $I_2$ → NaI + NaIO
Hot and conc. NaOH + $I_2$ → $NaI + NaIO_3 + H_2O$ sod.iodate
Cold. and dil. NaOH + $F_2$ → $OF_2 + NaF + H_2O$
Hot and conc. NaOH + $F_2$ → $O_2 + NaF + H_2O$
$P_4 + H_2O$ → $NaH_2PO_2 + PH_3$ sod.hypophosphite phosphine
S → $Na_2S + Na_2S_2O_3 + H_2O$ Hypo (sod.thiosulphate)
$H_2S$ → $NaSH + H_2O$ $\xrightarrow{NaOH}$ $Na_2S + H_2O$
Reaction with metals
B → $Na_3BO_3 + H_2$ sod.borate
$Si + H_2O$ → $Na_2SiO_3 + H_2$ sod.silicate
Reaction with amphoteric Metals (liberate hydrogen gas)
$Al + H_2O$ → $NaAlO_2 + H_2$ sod.metaaluminate
Al → $Na_3AlO_3 + H_2$
Zn. → $Na_2 ZnO_2 + H_2$

### 3. Magnesium Hydroxide ($Mg(OH)_2$):

It occurs in nature as the mineral brucite.

**Preparation:**

| Name of compound | Name and Brief about the process | Related chemical reaction |
|---|---|---|
| Magnesium Hydroxide ($Mg(OH)_2$) | It can be prepared by adding caustic soda solution to a solution of Magnesium sulphate or chloride solution. | $MgSO_4 + 2NaOH \longrightarrow Mg(OH)_2 + Na_2SO_4$<br>$MgCl_2 + 2NaOH \longrightarrow Mg(OH)_2 + 2NaCl$<br>$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCl_2$<br>$MgO + H_2O \longrightarrow Mg(OH)_2$ |

**Chemical Properties:**

(1) It can be dried at temperature upto 100°C only otherwise it breaks into its oxide at higher temperature.

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

(2) It is slightly soluble in water imparting alkalinity.

(3) It dissolves in $NH_4Cl$ solution.

$$Mg(OH)_2 + 2NH_4Cl \longrightarrow MgCl_2 + 2NH_3.H_2O$$

Thus, $Mg(OH)_2$ is not therefore precipitated from a solution of $Mg^{2+}$ ions by $NH_3.H_2O$. in presence of excess of $NH_4Cl$.

**Uses :** A suspension of $Mg(OH)_2$ in water is used in medicine as an **antacid** under the name, **milk of magnesia.**

### 4. Calcium Hydroxide ($Ca(OH)_2$):

**Preparation :**

| Name of compound | Name and Brief about the process | Related chemical reaction |
|---|---|---|
| Calcium Hydroxide ($Ca(OH)_2$) | By spraying water on quicklime. | $CaO + H_2O \longrightarrow Ca(OH)_2$ |

**Properties:**

(1) It is a white amorphous powder.

(2) It is sparingly soluble in water.

(3) It's solubility in hot water is less than that of cold water. Hence solubility decreases with increase in temperature.

(4) The aqueous solution is known as lime water and a suspension of slaked lime in water is known as milk of lime.

(5) When carbon dioxide is passed through lime water it turns milky due to the formation of calcium carbonate.

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

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

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

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

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow CaCl_2 + \underset{\text{Bleaching powder}}{Ca(OCl)_2} + H_2O$$

**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.

# CARBONATES

## 1. Sodium Carbonate (Washing soda) $Na_2CO_3.10H_2O$:

**Preparation:**

**1.**

| Name of compound | Name and Brief about the process | Related chemical reaction |
|---|---|---|
| Sodium Carbonate (Washing soda) $Na_2CO_3.10H_2O$ | (1) **Leblanc Process** | $NaCl + H_2SO_4(conc.) \xrightarrow{\text{mild heating}} NaHSO_4 + HCl$<br>$NaCl + NaHSO_4 \xrightarrow[\text{heated}]{\text{Strongly}} Na_2SO_4 + HCl$<br>(Salt Cake)<br>$Na_2SO_4 + 4C \longrightarrow Na_2S + 4CO\uparrow$<br>$Na_2S + CaCO_3 \longrightarrow Na_2CO_3 + CaS$ |
| | **(2) Solvay Process**<br>Step-1 (In ammonia absorber)<br>(i)Saturation of brine with ammonia and $CO_2$<br>(ii) Ammoniated brine is filtered to remove calcium and magnesium impurities as their insoluble carbonates. | $2NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2CO_3$<br>$CaCl_2 + (NH_4)_2CO_3 \longrightarrow CaCO_3\downarrow + 2NH_4Cl$<br>$MgCl_2 + (NH_4)_2CO_3 \longrightarrow MgCO_3\downarrow + 2NH_4Cl$ |
| | Step-2 (In carbonation tower) :<br>(i) Formation of insoluble $NaHCO_3$<br>(ii) Reaction is exothermic and hence there is a cooling arrangement.<br>(iii) $NaHCO_3$ is insoluble in cold brine solution because of the common ion effect. It is separated by filtration and the filtered is used for recovering $NH_3$ & $CO_2$. | $NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$ ;<br>$NH_4HCO_3 + NaCl \xrightarrow{30^oC} NaHCO_3 + NH_4Cl$ |
| | Step-3 (Calcination to get sodium carbonate) : | $2\,NaHCO_3 \xrightarrow{150^oC} Na_2CO_3 + CO_2 + H_2O$ |
| | Step - 4 (In recovery tower) :<br>Recovery of ammonia and carbondioxide.<br>$CaCl_2$ is obtained as by product. | $NH_4\,HCO_3 \xrightarrow{\Delta/\text{Steam}} NH_2 + CO_2 + H_2O$<br>$2NH_4\,Cl + Ca(OH)_2 \xrightarrow{\Delta/\text{Steam}} 2NH_3 + 2H_2O + CaCl_2$ |

* advantage is taken of low solubility of $NaHCO_3$, it gets precipitated in the reaction of $NaCl + NH_4HCO_3$.

**2.** Naturally from trona

$$2(Na_2CO_3.NaHCO_3.2H_2O) \xrightarrow{\text{heat}} 3Na_2CO_3 + CO_2 + 5H_2O$$

**Properties**

(1) Anhydrous $Na_2CO_3$ is called as soda ash, which does not decompose on heating but melts at 852°C.

(2) Sodium carbonate is a white crystalline solid which exists as a decahydrate, $Na_2CO_3{\cdot}10H_2O$. This is also called washing soda. It is readily soluble in water. On heating, the decahydrate loses its water of crystallisation to form monohydrate. Above 373K, the monohydrate becomes completely anhydrous and changes to a white powder called soda ash.

$$Na_2CO_3{\cdot}10H_2O \xrightarrow{375K} Na_2CO_3{\cdot}H_2O + 9H_2O$$

$$Na_2CO_3{\cdot}H_2O \xrightarrow{>373K} \underset{\text{(soda ash)}}{Na_2CO_3} + H_2O$$

Carbonate part of sodium carbonate gets hydrolysed by water to form an alkaline solution.

$$Na_2CO_3 + H_2O \longrightarrow H_2CO_3\,(\text{weak acid}) + NaOH\,(\text{strong})$$

(3) $Na_2CO_3$ absorbs $CO_2$ yielding sparingly soluble sodium bicarbonate which can be calcined at 250° to get pure sodium carbonate.

$$Na_2CO_3 + H_2O + CO_2 \xrightleftharpoons[250°C]{} 2NaHCO_3 \text{ (solid)}$$

(4) It dissolved in acid with effervescence of $CO_2$ and causticised by lime to give caustic soda.

$$Na_2CO_3 + HCl \longrightarrow 2NaCl + H_2O + CO_2$$

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3$$

**Uses:**

(i) It is used in water softening, laundering and cleaning.

(ii) It is used in the manufacture of glass, soap, borax and caustic soda.

(iii) It is used in paper, paints and textile industries.

(iv) It is an important laboratory reagent both in qualitative and quantitative analysis.

### 2. Potassium Carbonate ($K_2CO_3$)

| **Name of compound** | **Name and Brief about the process** | **Related chemical reaction** |
|---|---|---|
| Potassium Carbonate ($K_2CO_3$) | By **leblance process**, it can be prepared but by **solvay process** it **cannot be prepared** because $KHCO_3$ is soluble in water. | $KCl + H_2SO_4 \text{ (conc.)} \xrightarrow{\text{mild heating}} KHSO_4 + HCl$<br>$KCl + KHSO_4 \xrightarrow[\text{heated}]{\text{Strongly}} K_2SO_4 + HCl$<br>$K_2SO_4 + 4C \longrightarrow K_2S + 4CO\uparrow$<br>$K_2S + CaCO_3 \longrightarrow K_2CO_3 + CaS$ |

**Properties:**

It resembles with $Na_2CO_3$, m.p. is 900°C but a mixture of $Na_2CO_3$ and $K_2CO_3$ melts at 712°C.

**Uses** It is used in glass manufacturing.

** need not memories.*

**Note :** Calcium carbonate and Magnesium carbonate found in nature.
Calcium bicarbonate and Magnesium bicarbonate are present in temporary hardness of water.
Unstable and unimportant. Same for $KHCO_3$.

## CHLORIDES

### Sodium Chloride (NaCl) and Potassium Chloride, Calcium Chloride

**Preparation:**

NaCl : Found in nature as rock salt or in sea water.
KCl : Found in nature as sylvine (KCl) or carnallite ($KCl.MgCl_2.6H_2O$)
$CaCl_2$ : Obtained as byproduct in Solvay's process.

**Properties of NaCl :**

(1) It is nonhygroscopic but the presence of $MgCl_2$ in common salt renders it hygroscopic.

(2) It is used to prepare freezing mixture in laboratory [Ice-common salt mixture is called freezing mixture and temperature goes down to –23°C.]

(3) For melting ice and snow on road.

**Uses of NaCl:**

(i) It is used as a common salt or table salt for domestic purpose.

(ii) It is used for the preparation of $Na_2O_2$, NaOH and $Na_2CO_3$.

**Magnesium Chloride ($MgCl_2$)**

It occurs in nature as mineral carnallite, $KCl.MgCl_2.6H_2O$.

**Preparation :** By Dow's Processes (Natural Brine process and Dolomite process).

**Properties:**

(1) It crystallises as hexahydrate. $MgCl_2.\ 6H_2O$

(2) It is deliquescent solid.

(3) This hydrate undergoes hydrolysis as follows:

$$MgCl_2\cdot 6H_2O \longrightarrow Mg(OH)Cl + HCl + 5H_2O$$

$$Mg(OH)Cl \longrightarrow MgO + HCl$$

Hence, Anh. $MgCl_2$ cannot be prepared by heating this hydrate. Because of this formation of HCl. Sea water cannot be used in marine boilers which corrodes the iron body.

(4) Anhydrous $MgCl_2$ can be prepared by heating a double salt like. $MgCl_2.NH_4Cl.6H_2O$ as follows:

$$MgCl_2\ .\ NH_4Cl\ .\ 6H_2O \xrightarrow[\Delta]{-H_2O} MgCl_2.\ NH_4Cl \xrightarrow[\Delta]{\text{strong}} MgCl_2 + NH_3 + HCl$$

(5) It is a colourless crystalline solid, highly deliquescent and highly soluble in water.

(6) Sorel Cement is a mixture of MgO and $MgCl_2$ (paste like) which set to hard mass on standing. This is used in dental filling, flooring etc.

(7) Anh. $CaCl_2$ is used in drying gases and organic compounds but not $NH_3$ or alcohol due to the formation of $CaCl_2\ .\ 8NH_3$ and $CaCl_2\ .\ 4C_2H_5OH$.

## SULPHATES

### 1. Magnesium Sulphate ($MgSO_4$):

It occurs in nature as minerals kiesserite ($MgSO_4.H_2O$), epsom salt ($MgSO_4.7H_2O$)and kainite ($KCl.MgSO_4.3H_2O$).

**Preparation:**

(1) It is obtained by dissolving kieserite. $MgSO_4.H_2O$ in boiling water and then crystallising the solution as a hepta hydrate. i.e. $MgSO_4.7H_2O$. It is called as Epsom salt.

(2) It is also obtained by dissolving magnesite in hot dil. $H_2SO_4$.

$$MgCO_3 + H_2SO_4 \longrightarrow MgSO_4 + H_2O + CO_2$$

(3) By dissolving dolomite ($CaCO_3.MgCO_3$) in hot dil. $H_2SO_4$ and removing the insoluble $CaSO_4$ by filtration.

$$CaCO_3.MgCO_3\ (\text{dolomite}) + 2H_2SO_4 \longrightarrow MgSO_4 + CaSO_4 + 2CO_2 + 2H_2O$$

(4) It is isomorphous with $FeSO_4.7H_2O$, $ZnSO_4.7H_2O$.

**Chemical Properties:**

**Heating effect:**

(1) When heated to 150°C, it changes to monohydrate. On further heating, it becomes anhydrous at 200°C. On strong heating, it decomposes into MgO.

$$MgSO_4.7H_2O \xrightarrow{150^\circ C} MgSO_4.H_2O \xrightarrow{200^\circ C} MgSO_4 \xrightarrow[\text{heating}]{\text{strong}} MgO + SO_2 + O_2.$$

(2) Magnesium sulphate when heated with lamp black at 800°C produces $SO_2$ and $CO_2$ gases.

$$2MgSO_4 + C \longrightarrow 2MgO + 2SO_2 + CO_2$$

(3) It forms double salts with alkali metal sulphates, e.g., $K_2SO_4.MgSO_4.6H_2O$.

### 2. Calcium Sulphate (Plaster of paris) $CaSO_4.½\ H_2O$

It occurs as anhydrite $CaSO_4$ , hemihydrate $CaSO_4.½H_2O$ and as the dihydrate ($CaSO_4.2H_2O$) gypsum, alabaster or satin-spar.

**Preparation:**

(1) It is a hemihydrate of calcium sulphate. It is obtained when gypsum, $CaSO_4 \cdot 2H_2O$, is heated to 393 K.

$$2(CaSO_4.2H_2O) \longrightarrow 2(CaSO_4).H_2O + 3H_2O$$

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

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.

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

$$CaCl_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HCl \; ; \quad CaCl_2 + Na_2SO_4 \longrightarrow CaSO_4 + 2NaCl$$

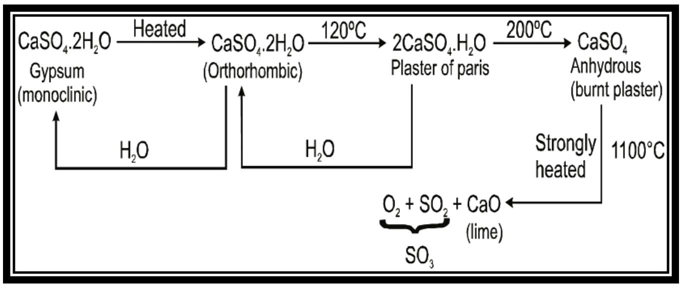
**Properties:**

It is a white crystalline solid. It is sparingly soluble in water and solubility decreases as temperature increases.

It dissolves in dilute acids. It also dissolves in ammonium sulphate due to the formation of double sulphate, $(NH_4)_2SO_4.CaSO_4.H_2O$.

The setting process is **exothermic**. The process of setting takes place in stages. In the first stage, there is conversion of Plaster of Pairs into orthorhombic form of gypsum (setting step) and in the second stage orthorhombic form changes into monoclinic form (hardening step).

The setting of Plaster of Paris may be **catalysed by sodium chloride** while it is retarded by borax or alum. Addition of alum to Plaster of Paris makes the setting very hard. The mixture is known as **Keene's cement**.



**Dead plaster** has no setting property as it takes up water only very slowly.

A suspension of gypsum when saturated with ammonia and carbon dioxide forms ammonium sulphate, a nitrogenous fertilizer.

$$2NH_3 + CaSO_4 + CO_2 + H_2O \longrightarrow (NH_4)_2SO_4 + CaCO_3$$

When strongly heated with carbon, it forms calcium sulphide.

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

**Uses:** For preparing blackboard chalk.

In anhydrous form as drying agent.

## Fertilizer

**1.** **Cynamide:** It is an organic compound with the formula $CN_2H_2$. This white solid is widely used in agriculture and the production of pharmaceuticals and other organic compounds.

Cyanamide is produced by hydrolysis of calcium cyanamide, which in turn is prepared from calcium carbide via the frank-Caro process.

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C \; ; \; \text{frank-Caro process}$$

$$CaCN_2 + H_2O + CO_2 \longrightarrow CaCO_3 + H_2NCN \text{ (Cynamide)}$$

The main reaction exhibited by cyanamide involves additions of compounds containing an acidic proton. Water, hydrogen sulfide, and hydrogen selenide react with cyanmide to give urea, thiourea, and selenourea, respectively :

$$H_2NCN + H_2E \rightarrow H_2NC(E)NH_2 \; ; \; (E = O, S, Se)$$

**2.** **Fluorapatite:** It is a phosphate mineral with the formula $Ca_5(PO_4)_3$.

## Cement

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 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 ($CaSO_4.2H_2O$) 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 ($Ca_3Al_2O_6$) 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.

## Common Names

The names marked with asterisk (*) should be memorized with formulae. Others are given only for reference. You need not memorize them.

| **Metal** | **Ore name** | **Formula** |
|---|---|---|
| **Lithium (Li)** | Spodumene | $LiAl(SiO_3)_2$ |
| | Lepidolite | $KLi_2Al(Al,Si)_3O_{10}(F,OH)_2$ |
| | Petalite | $LiAl(Si_2O_5)_2$ |
| **Sodium (Na)** | *Washing soda | $Na_2CO_3.10H_2O$ |
| | *Baking soda | $NaHCO_3$ |
| | *Sodium carbonate (soda ash/ washing soda) | $Na_2CO_3$ |
| | *Sodium chloride (rock salt or halite) | NaCl |
| | *Sodium nitrate (Chile saltpeter) | $NaNO_3$ |
| | Salt cake | $Na_2SO_4$ |
| | Fusion mixture | $Na_2CO_3$ + $K_2CO_3$ (eq. molar mix.) |
| | Sodium sesquicarbonate (trona) | $Na_2CO_3.NaHCO_3.2H_2O$ ( it is a double salt ) |
| | *Microcosmic salt | $Na(NH_4)HPO_4.4H_2O$ (it is obtained by mixing solutions of sodium phosphate and ammonium phosphate or chloride) |
| | Soda feldspar or sodium feldspar (albite) | $Na_2O.\ Al_2O_3.\ 6SiO_2$ |
| | Potash feldspars or orthoclase or microcline or Potassium feldspars | $K_2O.\ Al_2O_3.6SiO_2$ |
| | *Hypo | $Na_2S_2O_3\ .\ 5H_2O$ |
| | *Sodium aluminium fluoride (cryolite) | $Na_3AlF_6$ |
| | *Borax (Tincal) | $Na_2B_4O_7.10H_2O$ |
| | *Sodium sulphate (glauber's salt) | $Na_2SO_4.10H_2O$<br>(**Sodium sulfate** is the sodium salt of sulfuric acid. When anhydrous, it is a white crystalline solid of formula $Na_2SO_4$ known as the mineral thenardite; the decahydrate $Na_2SO_4{\cdot}10H_2O$ is known as **Glauber's salt**) |
| | Sodium aluminium silicate (Soda Feldspar) | $NaAlSi_3O_8$ |
| **Potassium (K)** | Sylvite | KCl |

| | | |
|---|---|---|
| | Schonite | $K_2SO_4.MgSO_4.6H_2O$ |
| | Kainite | $MgSO_4.KCl.3H_2O$ |
| | *Carnallite | $MgCl_2.KCl.6H_2O$ |
| | *Indian saltpetre (Nitre) | $KNO_3$ (used especially as a fertilizer and explosive) |
| | Pearl ash | $K_2CO_3$ |
| | Schonite | $K_2SO_4.MgSO_4.6H_2O$( it is a double salt) |
| | Langbeinite | $K_2SO_4.2MgSO_4$ |
| | Polyhalite | $K_2SO_4.MgSO_4.2CaSO_4.2H_2O$ |
| | *Potassium Alum | $K_2SO_4.\ Al_2\ (SO_4)_3.\ 24H_2O$ |
| | Alunite or Alumstone | $K_2SO_4.\ Al_2\ (SO_4)_3.\ 4Al(OH)_3$ |
| | Mica | $K_2O.\ 3Al_2O_3.\ 6SiO_2.2H_2O$ |
| | Feldspar | $KAlSi_3O_8(K_2O.Al_2O_3.6SiO_2)$ |
| **Beryllium (Be)** | Beryl | $3BeO.\ Al_2O_3\ 6SiO_2$ |
| | Chrysoberyl | $BeO.Al_2O_3$ |
| | Phenacite | $BeSiO_4$ |
| | Bromalite | $BeO$ |
| | *Baryta | $Ba(OH)_2$ |
| **Magnesium (Mg)** | *Magnesite | $MgCO_3$ |
| | *Dolomite | $MgCO_3.CaCO_3$ |
| | *Epsom salt | $MgSO_4.7H_2O$ |
| | Kieserite | $MgSO_4.H_2O$ |
| | Asbestos | $CaMg_3\ (SiO_3)_4$ |
| | Talc | $Mg(Si_2O_5)_2\ Mg\ (OH)_2$ |
| | Brucite | $Mg(OH)_2$ |
| | *Magnesia | $MgO$ |
| | Artinite | $MgCO_3.Mg(OH)_2\ .3H_2O$ |
| | *Sorel cement (magnesia cement) | $Mg_4Cl_2(OH)_6(H_2O)_8$ |
| **Calcium (Ca)** | *Quick lime | $CaO$ |
| | *Slaked lime | $Ca(OH)_2$ |
| | *Hydrolith | $CaH_2$ |
| | *Calcium cynamide | $CaCN_2$ OR $CaNCN$ |
| | *Limestone (Marble / Whiting) | $CaCO_3$ |
| | Anhydrite | $CaSO_4$ |
| | *Gypsum | $CaSO_4.2H_2O$ |
| | *Fluorspar or Fluorite | $CaF_2$ |
| | Phosphorite | $Ca_3\ (PO_4)_2$ |
| | *Fluorapatite | $3Ca_3\ (PO_4)_2.CaF_2$ OR $Ca_5(PO_4)_3F$ |
| | *Plaster of paris | $CaSO_2.\frac{1}{2}H_2O$ |
| | *Bleaching powder | $CaOCl_2$ |
| | *Rock phosphate | $Ca_3\ (PO_4)\ _2$ |
| | Wollastonite | $CaSiO_2$ |
| | Colmanite | $2CaO.3Ba_2O_3.5H_2O$ |
| **Strontium(Sr)** | Strontianite | $SrCO_3$ |
| | Celestite | $SrSO_4$ |
| | Barytes or Heavy spar | $BaSO_4$ |

## Periodic Properties of s-Block

| **Properties** | **Order** |
|---|---|
| Thermal stability | $LiH > NaH > KH > RbH > CsH$ |
| Basic strength | $BeO < MgO < CaO < SrO$ |
| Basic Strength or Solubility in water or thermal stability | $LiOH < NaOH < KOH < RbOH < CsOH$ |
| Basic Strength and Solubility in water | $Be(OH)_2<Mg(OH)_2<Ca(OH)_2<Ba(OH)_2$ |
| Thermal stability | $Be(OH)_2<Mg(OH)_2<Ca(OH)_2<Sr(OH)_2< Ba(OH)_2$ |
| Solubility in water or thermal stability | $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$ |
| Solubility in water | $BaCO_3 < CaCO_3 < MgCO_3 < BeCO_3$ |
| Thermal stability | $BeCO_3 < MgCO_3 < CaCO_3 < BaCO_3$ |
| Solubility in water | $BaSO_4 < SrSO_4 < CaSO_4 < MgSO_4 < BeSO_4$ |