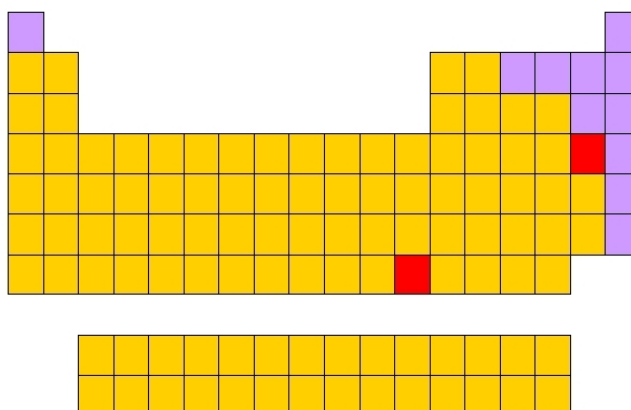




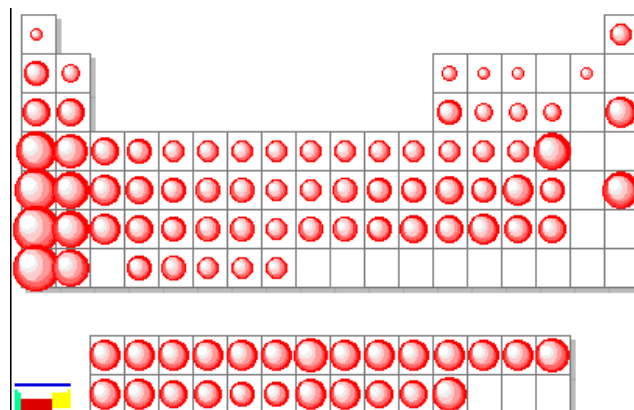
## Physical state

All are greyish-white, light, malleable and ductile metals with metallic lustre. Their hardness progressively decrease with increase in atomic number. Although these are fairly soft but relatively harder than alkali metals.



## Atomic and ionic radii

- (i) The atomic and ionic radii of alkaline earth metals also increase down the group due to progressive addition of new energy shells like alkali metals.



	Be	Mg	Ca	Sr	Ba	Ra
Atomic radius (pm)	112	160	197	215	222	-
Ionic radius of $M^{2+}$ ion (pm)	31	65	99	113	135	140

- (ii) The atomic radii of alkaline earth metals are however smaller than their corresponding alkali metal of the same period. This is due to the fact that alkaline earth metals possess a higher nuclear charge than alkali metals which more effectively pulls the orbit electrons towards the nucleus causing a decrease in size.

## Density

- (i) Density decreases slightly upto Ca after which it increases. The decrease in density from Be to Ca might be due to less packing of atoms in solid lattice of Mg and Ca.

Be	Mg	Ca	Sr	Ba	Ra
1.84	1.74	1.55	2.54	3.75	6.00

(ii) The alkaline earth metals are more denser, heavier and harder than alkali metal. The higher density of alkaline earth metals is due to their smaller atomic size and strong intermetallic bonds which provide a more close packing in crystal lattice as compared to alkali metals.

### Melting point and Boiling point

(i) Melting points and boiling points of alkaline earth metals do not show any regular trend.

	Be	Mg	Ca	Sr	Ba	Ra
m.pt. (K)	1560	920	1112	1041	1000	973
b.pt (K)	2770	1378	1767	1654	1413	-

(ii) The values are, however, more than alkali metals. This might due to close packing of atoms in crystal lattice in alkaline earth metals.

### Ionization energy and electropositive or metallic character

(i) Since the atomic size decreases along the period and the nuclear charge increases and thus the electrons are more tightly held towards nucleus. It is therefore alkaline earth metals have higher ionization energy in comparison to alkali metals but lower ionization energies in comparison to p-block elements.

(ii) The ionization energy of alkaline earth metals decreases from Be to Ba.

	Be	Mg	Ca	Sr	Ba	Ra
First ionization energy (kJ mol <sup>-1</sup> )	899	737	590	549	503	509
Second ionization energy (kJ mol <sup>-1</sup> )	1757	1450	1146	1064	965	979

(iii) The higher values of second ionization energy is due to the fact that removal of one electron from the valence shell, the remaining electrons are more tightly held in which nucleus of cation and thus more energy is required to pull one more electron from monovalent cation.

(iv) No doubt first ionization energy of alkaline earth metals are higher than alkali metals but a closer look on 2nd ionization energy of alkali metals and alkaline earth metals reveals that 2nd ionization energy of alkali metals are more

Li      Be

1st ionization energy (kJ mol<sup>-1</sup>)                      520    899

2nd ionization energy (kJ mol<sup>-1</sup>)                    7296 1757

This may be explained as,  $\text{Li} : 1s^2, 2s^1 \xrightarrow[\text{electron}]{\text{removal of } 2s} \text{Li}^+ : 1s^2 \xrightarrow[\text{electron}]{\text{removal of } 1s} \text{Li}^{2+} : 1s^1$

$\text{Be} : 1s^2, 2s^2 \xrightarrow[\text{electron}]{\text{removal of } 2s} \text{Be}^+ : 1s^2, 2s^1 \xrightarrow[\text{electron}]{\text{removal of } 2s} \text{Be}^{2+} : 1s^2$

The removal of 2<sup>nd</sup> electron from alkali metals takes place from 1s sub shell which are more closer to nucleus and exert more nuclear charge to hold up 1 s electron core, whereas removal of 2<sup>nd</sup> electron from alkaline earth metals takes from 2s sub shell. More closer are shells to the nucleus, more tightly are held electrons with nucleus and thus more energy is required to remove the electron.

(v) All these possess strong electropositive character which increases from Be to Ba.

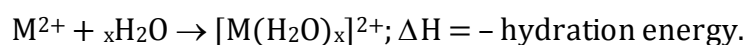
(vi) These have less electropositive character than alkali metals as the later have low values of ionization energy.

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## Oxidation number and valency

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(i) The IE<sub>1</sub> of the these metals are much lower than IE<sub>1</sub> and thus it appears that these metals should form univalent ion rather than divalent ions but in actual practice, all these give bivalent ions. This is due to the fact that M<sup>2+</sup> ion possesses a higher degree of hydration or M<sup>2+</sup> ions are extensively hydrated to form [M(H<sub>2</sub>O)<sub>x</sub>]<sup>2+</sup>, a hydrated ion. This involves a large amount of energy evolution which counter balances the higher value of second ionization energy.



(ii) The tendency of these metals to exist as divalent cation can thus be accounted as,

(a) Divalent cation of these metals possess noble gas or stable configuration.

(b) The formation of divalent cation lattice leads to evolution of energy due to strong lattice structure of divalent cation which easily compensates for the higher values of second ionization energy of these metals.

(c) The higher heats of hydration of divalent cation which accounts for the existence of the divalent ions of these metals in solution state.

## Hydration of ions

(i) The hydration energies of alkaline earth metals divalent cation are much more than the hydration energy of monovalent cation.

	Mg <sup>+</sup>	Mg <sup>2+</sup>
Hydration energy or Heat of hydration (kJ mol <sup>-1</sup> )	353	1906

The abnormally higher values of heat of hydration for divalent cations of alkaline earth metals are responsible for their divalent nature. MgCl<sub>2</sub> formation occurs with more amount of heat evolution and thus MgCl<sub>2</sub> is more stable.

(ii) The hydration energies of M<sup>2+</sup> ion decreases with increase in ionic radii.

	Be <sup>2+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>
Heat of hydration kJ mol <sup>-1</sup>	2382	1906	1651	1484	1275

(iii) Heat of hydration are larger than alkali metals ions and thus alkaline earth metals compounds are more extensively hydrated than those of alkali metals e.g MgCl<sub>2</sub> and CaCl<sub>2</sub> exists as Mg Cl<sub>2</sub> .6H<sub>2</sub>O and CaCl<sub>2</sub>. 6H<sub>2</sub>O which NaCl and KCl do not form such hydrates.

(iv) The ionic mobility, therefore, increases from Ba<sup>2+</sup> to Ba<sup>2+</sup>, as the size of hydrated ion decreases.

## Electronegativities

(i) The electronegativities of alkaline earth metals are also small but are higher than alkali metals.

(ii) Electronegativity decreases from Be to Ba as shown below,

	Be	Mg	Ca	Sr	Ba
Electronegativity	1.57	1.31	1.00	0.95	0.89

## Conduction power:

Good conductor of heat and electricity.

## Standard oxidation potential and reducing properties

(i) The standard oxidation potential (in volts) are,

Be	Mg	Ca	Sr	Ba
1.69	2.35	2.87	2.89	2.90

(ii) All these metals possess tendency to lose two electrons to give  $M^{2+}$  ion and are used as reducing agent.

(iii) The reducing character increases from Be to Ba, however, these are less powerful reducing agent than alkali metals.

(iv) Beryllium having relatively lower oxidation potential and thus does not liberate  $H_2$  from acids.

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## Characteristic flame colours

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(i) *The characteristic flame colour shown are* : Ca-brick red; Sr –crimson ; Ba-apple green and Ra- crimson.

(ii) Alkaline earth metals except Be and Mg produce characteristic colour to flame due to easy excitation of electrons to higher energy levels.

(iii) Be and Mg atoms due to their small size, bind their electrons more strongly (because of higher effective nuclear charge) Hence these requires high excitation energy and are not excited by the energy of flame with the result that no flame colour is shown by them.

## Chemical properties

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### Occurrence

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These are found mainly in combined state such as oxides, carbonates and sulphates Mg and Ca are found in abundance in nature. Be is not very abundant, Sr and Ba are less abundant. Ra is rare element. Some important ores of alkaline earth metals are given below,

(i) **Beryllium**: Beryl ( $3BeO \cdot Al_2O_3 \cdot 6SiO_2$ ); Phenacite ( $Be_2SiO_4$ )

(ii) **Magnesium**: Magnesite ( $MgCO_3$ ); Dolomite ( $CaCO_3 \cdot MgCO_3$ ); Epsomite ( $MgSO_4 \cdot 7H_2O$ ); Carnallite ( $MgCl_2 \cdot KCl \cdot 6H_2O$ ); Asbestos [ $CaMg_3(SiO_3)_4$ ]

(iii) **Calcium**: Limestone ( $CaCO_3$ ); Gypsum : ( $CaSO_4 \cdot 2H_2O$ ), Anhydrite ( $CaSO_4$ ); Fluorapatite [ $(3Ca_3(PO_4)_2 \cdot CaF_2)$ ] Phosphorite rock [ $Ca_3(PO_4)_2$ ]

(iv) **Barium**: Barytes ( $BaSO_4$ ) ; witherite ( $BaCO_3$ )

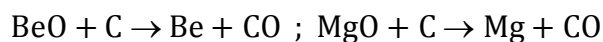
(v) **Radium**: Pitch blende ( $U_3O_8$ ); (Ra in traces); other radium rich minerals are carnotite [ $K_2UO_2$ ] ( $VO_4$ ) $_2 \cdot 8H_2O$  and antamite [ $Ca(UO_2)_2$ ]

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### Extraction of alkaline earth metals

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(i) Be and Mg are obtained by reducing their oxides carbon,



(ii) The extraction of alkaline earth metals can also be made by the reduction of their oxides by alkali metals or by electrolysis of their fused salts.

## Alloy formation

These dissolve in mercury and form amalgams.

## Formation of oxides and hydroxides

(i) The elements (except Ba and Ra) when burnt in air give oxides of ionic nature  $\text{M}^{2+}\text{O}^{2-}$  which are crystalline in nature. Ba and Ra however give peroxide. The tendency to form higher oxides increases from Be to Ra.

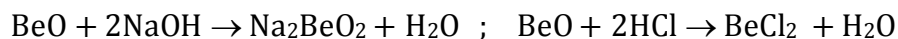


(ii) Their less reactivity than the alkali metals is evident by the fact that they are slowly oxidized on exposure to air; however the reactivity of these metals towards oxygen increases on moving down the group.

(iii) The oxides of these metals are very stable due to high lattice energy.

(iv) The oxides of the metal (except BeO and MgO) dissolve in water to form basic hydroxides and evolve a large amount of heat. BeO and MgO possess high lattice energy and thus insoluble in water.

(v) BeO dissolves both in acid and alkalis to give salts i.e. BeO possesses amphoteric nature.



Sod. beryllate

Beryllium chloride

(vi) The basic nature of oxides of alkaline earth metals increases from Be to Ra as the electropositive character increases from Be to Ra.

(vii) The tendency of these metal to react with water increases with increase in electropositive character i.e. Be to Ra.

(viii) Reaction of Be with water is not certain, magnesium reacts only with hot water, while other metals react with cold water but slowly and less energetically than alkali metals.

(ix) The inertness of Be and Mg towards water is due to the formation of protective, thin layer of hydroxide on the surface of the metals.

(x) The basic nature of hydroxides increase from Be to Ra. It is because of increase in ionic radius down the group which results in a decrease in strength of M-O bond in M-(OH)<sub>2</sub> to show more dissociation of hydroxides and greater basic character.

(xi) The solubility of hydroxides of alkaline earth metals is relatively less than their corresponding alkali metal hydroxides. Furthermore, the solubility of hydroxides of alkaline earth metals increases from Be to Ba. Be(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> are almost insoluble, Ca(OH)<sub>2</sub> (often called lime water) is sparingly soluble whereas Sr(OH)<sub>2</sub> and Ba(OH)<sub>2</sub> (often called baryta water) are more soluble.

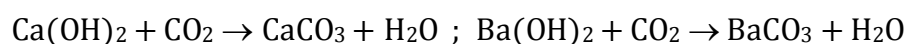
The trend of the solubility of these hydroxides depends on the values of lattice energy and hydration energy of these hydroxides. The magnitude of hydration energy remains almost same whereas lattice energy decreases appreciably down the group leading to more -ve values for  $\Delta H_{\text{solution}}$  down the group.

$$\Delta H_{\text{solution}} = \Delta H_{\text{lattice energy}} + \Delta H_{\text{hydration energy}}$$

More negative is  $\Delta H_{\text{solution}}$  more is solubility of compounds.

(xii) The basic character of oxides and hydroxides of alkaline earth metals is lesser than their corresponding alkali metal oxides and hydroxides.

(xiii) Aqueous solution of lime water [Ca(OH)<sub>2</sub>] or baryta water [Ba(OH)<sub>2</sub>] are used to qualitative identification and quantitative estimation of carbon dioxide, as both of them gives white precipitate with CO<sub>2</sub> due to formation of insoluble CaCO<sub>3</sub> or BaCO<sub>3</sub>



(white ppt)

(white ppt)

Note: SO<sub>2</sub> also give white ppt of CaSO<sub>3</sub> and BaSO<sub>3</sub> on passing through lime water or baryta water. However on passing CO<sub>2</sub> in excess, the white turbidity of insoluble carbonates dissolve to give a clear solution again due to the formation of soluble bicarbonates,




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## Hydrides

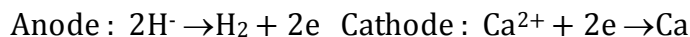
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(i) Except Be, all alkaline earth metals form hydrides (MH<sub>2</sub>) on heating directly with H<sub>2</sub>.  $\text{M} + \text{H}_2 \rightarrow \text{MH}_2$ .

(ii)  $\text{BeH}_2$  is prepared by the action of  $\text{LiAlH}_4$  on  $\text{BeCl}_2$  ;  $2\text{BeCl}_2 + \text{LiAlH}_4 \rightarrow 2\text{BeH}_2 + \text{LiCl} + \text{AlCl}_3$ .

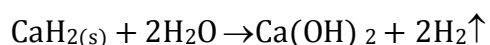
(iii)  $\text{BeH}_2$  and  $\text{MgH}_2$  are covalent while other hydrides are ionic.

(iv) The ionic hydrides of Ca, Sr, Ba liberate  $\text{H}_2$  at anode and metal at cathode.



(v) The stability of hydrides decreases from Be to Ba.

(vi) The hydrides having higher reactivity for water, dissolve readily and produce hydrogen gas.

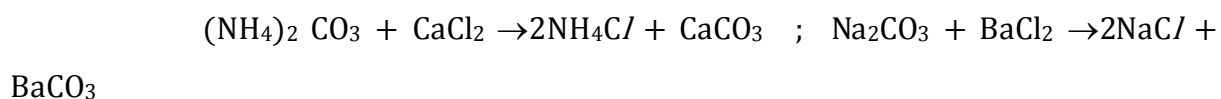



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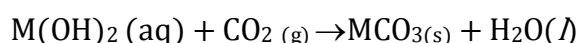
## Carbonates and Bicarbonates

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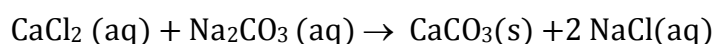
(i) All these metal carbonates ( $\text{MCO}_3$ ) are insoluble in neutral medium but soluble in acid medium. These are precipitated by the addition of alkali metal or ammonium carbonate solution to the solution of these metals.



(ii) Alkaline earth metal carbonates are obtained as white precipitates when a calculated amount of carbon dioxide is passed through the solution of the alkaline metal hydroxides.

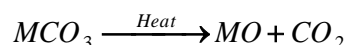


and sodium or ammonium carbonate is added to the solution of the alkaline earth metal salt such as  $\text{CaCl}_2$ .



(iii) Solubility of carbonates of these metals also decreases downward in the group due to the decrease of hydration energy as the lattice energy remains almost unchanged as in case of sulphates.

(vi) The carbonates of these metals decompose on heating to give the oxides, the temperature of decomposition increasing from Be to Ba. Beryllium carbonate is unstable.

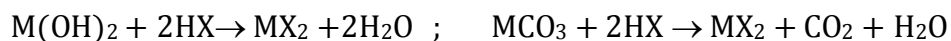



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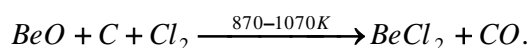
## Halides

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(i) The alkaline earth metals combine directly with halogens at appropriate temperatures forming halides,  $MX_2$ . These halides can also be prepared by the action of halogen acids (HX) on metals, metal oxides, hydroxides and carbonates.



Beryllium chloride is however, conveniently obtained from oxide



(ii)  $BeCl_2$  is essentially covalent, the chlorides  $MgCl_2$ ,  $CaCl_2$ ,  $SrCl_2$  and  $BaCl_2$  are ionic; the ionic character increases as the size of the metal ion increases. The evidence is provided by the following facts,

(a) Beryllium chloride is relatively low melting and volatile whereas  $BaCl_2$  has high melting and stable.

(b) Beryllium chloride is soluble in organic solvents.

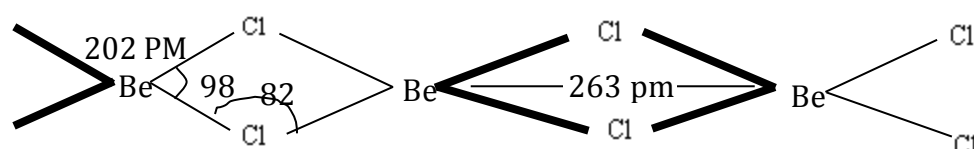
(iii) The halides of the members of this group are soluble in water and produce neutral solutions from which the hydrates such as :  $MgCl_2 \cdot 6H_2O$ ,  $CaCl_2 \cdot 6H_2O$ ,  $BaCl_2 \cdot 2H_2O$  can be crystallised. The tendency to form hydrated halides decreases with increasing size of the metal ions.

(iv)  $BeCl_2$  is readily hydrolysed with water to form acid solution,  $BeCl_2 + 2H_2O \rightarrow Be(OH)_2 + 2HCl$ .

(v) The fluorides are relatively less soluble than the chlorides due to high lattice energies. Except  $BeCl_2$  and  $MgCl_2$  the chlorides of alkaline earth metals impart characteristic colours to flame.

$CaCl_2$	$SrCl_2$	$BaCl_2$
Brick red colour	Crimson colour	Grassy green colour

Structure of  $BeCl_2$  In the solid phase polymeric chain structure with three centre 2 electron bonding with Be-Cl-Be bridged structure is shown below,



In the vapour phase it tends to form a chloro-bridged dimer which dissociates into the linear triatomic monomer at high temperature at nearly 1200 K.

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### Solubility in liquid ammonia:

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Like alkali metals, alkaline earth metals also dissolve in liquid ammonia to form coloured solutions. When such a solution is evaporated, hexammoniate,  $M(\text{NH}_3)_6$  is formed.

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## Nitrides

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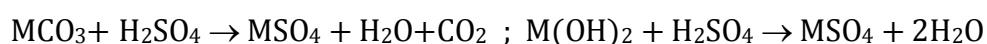
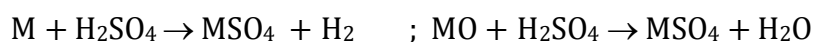
- (i) All the alkaline earth metals directly combine with  $\text{N}_2$  give nitrides,  $\text{M}_3\text{N}_2$ .
- (ii) The ease of formation of nitrides however decreases from Be to Ba.
- (iii) These nitrides are hydrolysed with water to liberate  $\text{NH}_3$ ,  $\text{M}_3\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{M}(\text{OH})_2 + 2\text{NH}_3$

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## Sulphates

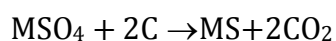
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(i) All these form sulphate of the type  $\text{M SO}_4$  by the action of  $\text{H}_2\text{SO}_4$  on metals, their oxides, carbonates or hydroxides.



(ii) The solubility of sulphates in water decreases on moving down the group.  $\text{BeSO}_4$  and  $\text{MgSO}_4$  are fairly soluble in water while  $\text{BaSO}_4$  is completely insoluble. This is due to increases in lattice energy of sulphates down the group which predominates over hydration energy.

(ii) Sulphates are quite stable to heat however reduced to sulphide on heating with carbon.

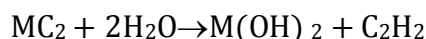



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## Action with carbon:

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Alkaline metals (except Be, Mg) when heated with carbon form carbides of the type  $\text{MC}_2$ . These carbides are also called acetylides as on hydrolysis they evolve acetylene.

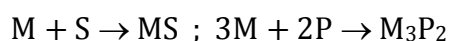



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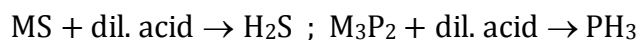
## Action with sulphur and phosphorus:

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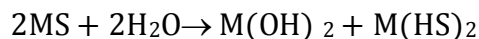
Alkaline earth metals directly combine with sulphur and phosphorus when heated to form sulphides of the type  $\text{MS}$  and phosphides of the type  $\text{M}_3\text{P}_2$  respectively.



Sulphides on hydrolysis liberate  $H_2S$  while phosphides on hydrolysis evolve phosphine.

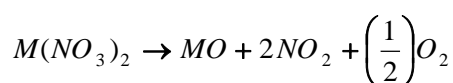


Sulphides are phosphorescent and are decomposed by water



## Nitrates:

Nitrates of these metals are soluble in water. On heating they decompose into their corresponding oxides with evolution of a mixture of nitrogen dioxide and oxygen.



## Formation of complexes

(i) Tendency to show complex ion formation depends upon smaller size, high nuclear charge and vacant orbitals to accept electron. Since alkaline metals too do not possess these characteristics and thus are unable to form complex ion.

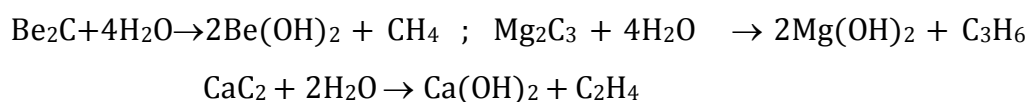
(ii) However,  $Be^{2+}$  on account of smaller size forms many complex such as  $(BeF_3)^{1-}$ ,  $(BeF_4)^{2-}$ .

## Anomalous behavior of Beryllium

Beryllium differs from rest of the alkaline earth metals on account of its small atomic size, high electronegativity  $Be^{2+}$  exerts high polarizing effect on anions and thus produces covalent nature in its compounds. Following are some noteworthy difference of Be from other alkaline earth metals,

- (1) Be is lightest alkaline earth metal.
- (2) Be possesses higher m.pt. and b.pt than other group members.
- (3)  $BeO$  is amphoteric in nature whereas oxides of other group members are strong base.
- (4) It is not easily effected by dry air and does not decompose water at ordinary temperature.
- (5)  $BeSO_4$  is soluble in water.
- (6) Be and Mg carbonates are not precipitated by  $(NH_4)_2CO_3$  in presence of  $NH_4Cl$ .

- (7) Be and Mg salts do not impart colour to flame.
- (8) Be does not form peroxide like other alkaline earth metals.
- (9) It does not evolve hydrogen so readily from acids as other alkaline earth metals do so.
- (10) It has strong tendency to form complex compounds.
- (11)  $\text{Be}_3\text{N}_2$  is volatile whereas nitrides of other alkaline earth metals are non-volatile.
- (12) It's salts can never have more than four molecules of water of crystallization as it has only four available orbitals in its valence shell.
- (13) Beryllium carbide reacts water to give methane whereas magnesium carbide and calcium carbide give propyne and acetylene respectively.




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### Diagonal relationship of *Be* with *Al*

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Due to its small size Be differs from other earth alkaline earth metals but resembles in many of its properties with Al on account of diagonal relationship.

- (1)  $\text{Be}^{2+}$  and  $\text{Al}^{3+}$  have almost same and smaller size and thus favour for covalent bonding.
- (2) Both these form covalent compounds having low m. pt and soluble in organic solvent.
- (3) Both have same value of electronegativity (i.e.1.5).
- (4) The standard O.P of these elements are quite close to each other ;  $\text{Be}^{2+}=1.69$  volts and  $\text{Al}^{3+}= 1.70$  volts.
- (5) Both become passive on treating with conc.  $\text{HNO}_3$  in cold.
- (6) Both form many stable complexes e.g.  $(\text{BeF}_3)^-$ ,  $(\text{AlH}_4)^-$ .
- (7) Like BeO,  $\text{Al}_2\text{O}_3$  is amphoteric in nature. Also both are high m. pt. solids.
- $$\text{Al}_2\text{O}_3 + 2\text{NaOH} \rightarrow 2\text{NaAlO}_2 + \text{H}_2\text{O} ; \text{Al}_2\text{O}_3 + 6\text{HCl} \rightarrow 2\text{AlCl}_3 + 3\text{H}_2\text{O}$$
- (8) Be and Al both react with NaOH to liberate  $\text{H}_2$  forming beryllates and alluminates.
- $$\text{Be} + 2\text{NaOH} \rightarrow \text{Na}_2\text{BeO}_2 + \text{H}_2 ; 2\text{Al} + 6\text{NaOH} \rightarrow 2\text{Na}_3\text{AlO}_3 + 3\text{H}_2$$
- (9)  $\text{Be}_2\text{C}$  and  $\text{Al}_4\text{C}_3$  both give  $\text{CH}_4$  on treating with water.
- $$\text{Be}_2\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + 2\text{BeO} ; \text{Al}_4\text{C}_3 + 6\text{H}_2\text{O} \rightarrow 3\text{CH}_4 + 2\text{Al}_2\text{O}_3$$

(10) Both occur together in nature in beryl ore,  $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ .

(11) Unlike other alkaline earths but like aluminium, beryllium is not easily attacked by air (Also Mg is not attacked by air)

(12) Both Be and Al react very slowly with dil. HCl to liberate  $\text{H}_2$ .

(13) Both Be and Al form polymeric covalent hydrides while hydrides of other alkaline earth are ionic.

(14) Both  $\text{BeCl}_2$  and  $\text{AlCl}_3$  are prepared in similar way.



(15) Both  $\text{BeCl}_2$  and  $\text{AlCl}_3$  are soluble in organic solvents and act as catalyst in Friedel-Crafts reaction.

(16) Both  $\text{Be}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$  are amphoteric whereas hydroxides of other alkaline earths are strong alkali.

(17) The salts of Be and Al are extensively hydrated.

(18)  $\text{BeCl}_2$  and  $\text{AlCl}_3$  both have a bridged polymeric structure.

(19) Be and Al both form fluoro complex ions  $[\text{BeF}_4]^{2-}$  and  $[\text{AlF}_6]^{3-}$  in solution state whereas other members of 2nd group do not form such complexes.

### Difference between alkali metals and alkaline earth metals

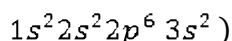
Properties	Alkaline earth metals	Alkali metals
Electronic configuration	Two electrons are present in the valency shell. The configuration is $ns^2$	One electron is present in the valency shell. The configuration is $ns^1$
Valency	Bivalent	Monovalent
Electropositive nature	Less electropositive	More electropositive
Carbonates	Insoluble in water. Decompose on heating	Soluble in water. Do not decompose on heating ( $\text{Li}_2\text{CO}_3$ is an exception).
Hydroxides	Weak bases, less soluble and decompose on heating	Strong bases, highly soluble and stable towards heat.

Bicarbonates	These are not known in free state.	These are known in solid state.
Action of carbon	Exist only in solution Directly combine with carbon and form carbides	Do not directly combine with carbon.
Action of nitrogen	Directly combine with nitrogen and form nitrides	Do not directly combine with nitrogen.
Nitrates	Decompose on heating evolving a mixture of $\text{NO}_2$ and oxygen	Decompose on heating evolving Only oxygen
Hydration of compounds	The compounds are extensively hydrated. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ are hydrated chlorides	The compounds are less hydrated $\text{NaCl}$ , $\text{KCl}$ , $\text{RbCl}$ form non-hydrated chlorides.
Solubility of salts	Sulphates, phosphates, fluorides, chromates, oxalates etc. are insoluble in water	Sulphates, phosphates, fluorides, chromates, oxalates, etc. are soluble in water
Physical properties	Comparatively harder. High melting points. Diamagnetic	Soft. Low melting points, Paramagnetic

## MAGNESIUM

Atomic Number: 12

Atomic Weight: 24



### Ores of magnesium:

Magnesite ( $MgCO_3$ ), Dolomite ( $MgCO_3 \cdot CaCO_3$ ), Epsomite (Epsom salt) ( $MgSO_4 \cdot 7H_2O$ ) Carnalite ( $MgCl_2 \cdot KCl \cdot 6H_2O$ ) Asbestos ( $CaMg_3(SiO_3)_4$ ), Talc ( $Mg_2(Si_2O_5)_2 \cdot Mg(OH)_2$ ).

### Extraction of magnesium:

It is prepared by the electrolysis of fused magnesium chloride which is obtained from Carnalite and Magnesite.

### Compounds of magnesium

(i) **Magnesia ( $MgO$ )**: It is used as magnesia cement. It is a mixture of  $MgO$  and  $MgCl_2$ . It is also called Sorel's cement.

(ii) **Magnesium hydroxide**: Its aqueous suspension is used in Medicine as an antacid. Its medicinal name is milk of magnesia.

(iii) **Magnesium sulphate or Epsom salt** ( $MgSO_4 \cdot 7H_2O$ ): It is isomorphous with  $ZnSO_4 \cdot 7H_2O$ . It is used as a purgative in medicine, as a mordant in dyeing and as a stimulant to increase the secretion of bile.

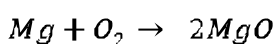
(iv) **Magnesium chloride** ( $MgCl_2 \cdot 6H_2O$ ): It is a deliquescent solid. Hydrated salt on heating in air undergoes partial hydrolysis.

$$MgCl_2 \cdot 6H_2O \xrightarrow{\text{Heat}} Mg(OH)Cl + HCl + 5H_2O$$

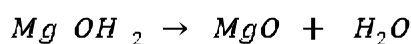
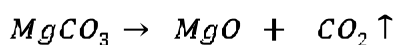
## Magnesium oxide

### Preparation

Mg is burnt in  $O_2$ , burns with a dazzling white light:-



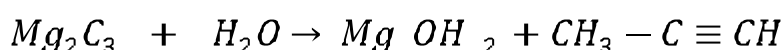
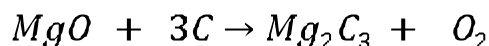
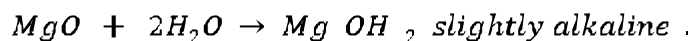
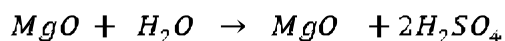
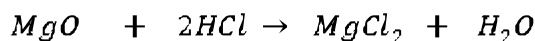
By heating (a) Magnesite (calcined magnesia):-



## Properties

Light white amorphous refractory solid with M.P=2850<sup>o</sup> C of slightly soluble in water.

Basic oxide:-



It dissolve in aq. Solution of  $MgCl_2, MgBr_2$  forming salts as  $MgCl_2 \cdot 6H_2O, Mg(OH)_2 \cdot 5H_2O$ .

## $Mg(OH)_2$ magnesium hydroxide:-

### Preparation

- $MgSO_4 + NaOH \rightarrow Mg(OH)_2 + Na_2SO_4$
- $MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl$
- $MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$

### Properties

- It is white powder, very soluble in water.
- Basic in nature, dissolve in dil. HCl
- It dissolve in  $NH_4Cl$  soln and is therefore not ppted in group III of qualitative analysis.

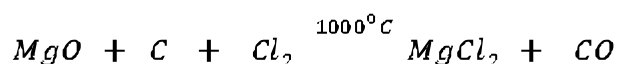
## Magnesium chloride ( $MgCl_2 \cdot 6H_2O$ )

### Preparation

- $MgCO_3 + HCl \rightarrow MgCl_2 + H_2O + CO_2$
- $Mg(OH)_2 + HCl \rightarrow MgCl_2 + H_2O$
- $MgO + 2HCl \rightarrow MgCl_2 + H_2O$

resulting solution is cooled when crystals of hydrated  $MgCl_2$  are sep.

### Anhydrous $MgCl_2$ :-



## Properties

Hydrated  $MgCl_2$  is a white crystalline and deliquescent substance. Extremely soluble in water.

- $2 MgCl_2 \cdot 6H_2O \xrightarrow{180^\circ C} Mg_2OCl_2 + HCl + 11H_2O$
- $MgOCl_2 + O_2 \xrightarrow{600^\circ C} MgO + Cl_2$

## Magnesium sulphate, Epsom salt( $MgSO_4 \cdot 7H_2O$ )

Kieserite:-  $MgSO_4 \cdot H_2O$  kainite :-  $MgSO_4 \cdot KCl \cdot 3H_2O$

## Preparation

- $MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + H_2CO_3$
- $Mg + H_2SO_4 \rightarrow MgSO_4 + H_2 \uparrow$
- $MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$

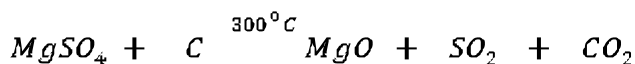
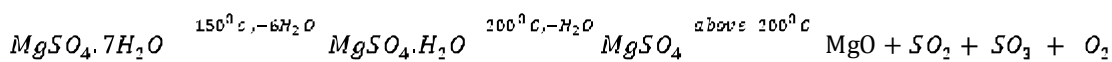
Dolomite :-  $MgCO_3 \cdot CaCO_3 + H_2SO_4 \rightarrow MgSO_4 + CaSO_4 + H_2O + CO_2$

Prom kieserite :-  $MgSO_4 \cdot H_2O + 6H_2O \rightarrow MgSO_4 \cdot 7H_2O$

(Epsom salt)

## Properties

Colourless crystalline solid, isomorphous with( $ZnSO_4 \cdot FeSO_4 \cdot 7H_2O$ ).highly soluble in water.



- Forms double salts;  $K_2SO_4$ ,  $MgSO_4 \cdot 6H_2O$
- Used in grillos' process for making  $H_2SO_4$  as a cat.
- Magnesium carbonate ( $MgCO_3$ ) (magnesite)

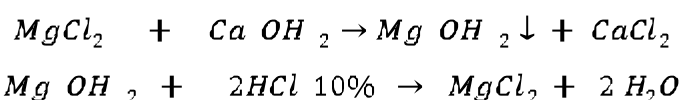
## Mg extraction :-

### Preparation of $MgCl_2$

#### Hydrated $MgCl_2$ :-

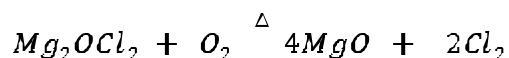
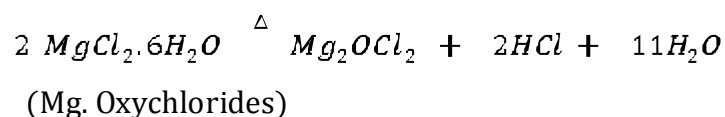
(a) from carnalite:- $KCl, MgCl_2, 6H_2O$  is dissolved in  $H_2O$  & the soln. is conc. By evaporation. The less soluble KCl separated out as crystals on cooling & the more soluble  $MgCl_2$  remains in soln. On conc. & cooling crystals of  $MgCl_2$  sep. Out.

from sea water:-

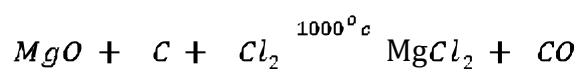


#### Anhydrous $MgCl_2$ :-

- Anhydrous  $MgCl_2$  cannot be prepared from hydrated  $MgCl_2$  by direct heating.



- Hydrated  $MgCl_2$  is heated to  $175^\circ C$  in vacuum in a current of dry HCl gas when anhydrous  $MgCl_2$  is formed.
- Anhydrous  $MgCl_2$  can also be prep. By heating a mixture of  $MgO$  &  $C$  in a current of dry  $Cl_2$  at  $1000^\circ C$ .



## CALCIUM

Atomic Number: 20

Atomic Weight: 40

$Ar4s^2$

#### Ores of calcium:

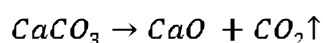
Lime stone or marble or chalk ( $CaCO_3$ ), Gypsum ( $CaSO_4 \cdot 2H_2O$ ), Dolomite ( $CaCO_3 \cdot MgCO_3$ ), Fluorspar ( $CaF_2$ ), phosphorite  $Ca_3(PO_4)_2$ . Calcium phosphate is a constituent of bones and teeth.

**Manufacture:**

It is manufactured by the electrolysis of a molten mixture of calcium chloride containing some calcium fluoride. Calcium chloride in turn is obtained as a by product of the Solvay process.

**Compounds of Calcium:****Calcium Oxide (quick lime)(CaO):-****Preparation:-**

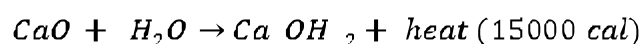
**By thermal decomposition:-** By heating limestone at high temperature.(900°C – 1000°C)



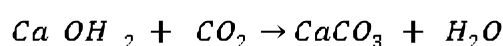
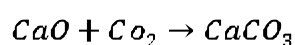
As the reaction is reversible, the produced  $CO_2$  is removed continuously from the system. As a result, the forward reaction is favoured and the reaction proceeds towards completion. Although high temp. Favours the forward reaction and thus to have a greater yield of lime, yet the temp. Is kept between (900°C – 1000°C). The  $SiO_2$  and  $Al_2O_3$  present in limestone reacts with the surface of lime to form a layer of slag on the surface of lime. This layer of slag hinder the slaking of lime.

**Properties:-**

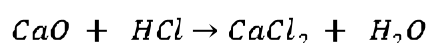
- CaO is white & amorphous powder.
- When it is heated in oxy-hydrogen flame it emits intense white light is called lime light.
- M.P=2750°C
- Calcium oxide absorbs moisture to power and  $CO_2$  from air with evolution of heat and is converted to power. This power is a mixture of  $CaCO_3$  and  $Ca OH_2$ .

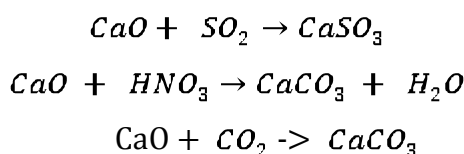


- This reaction proceeds with a hissing sound with the product of lots of heat, slaking of lime.(lime swells up and finally crumbles to white power of slaked lime)

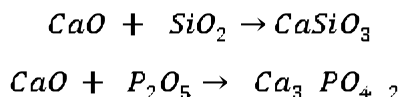


- It is a basic oxide:-

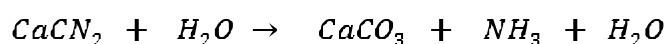
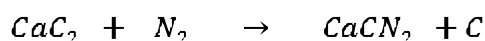
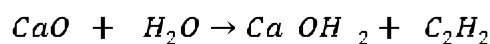
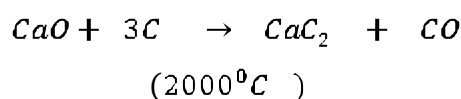
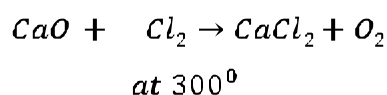
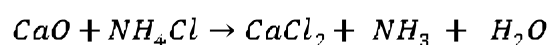




- At high temp:-



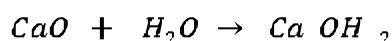
- With ammonium salts it liberates  $NH_3$ :-



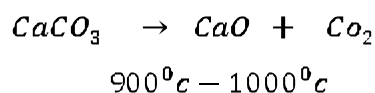
## Calcium hydroxide [ $Ca(OH)_2$ ] *slaked lime*

### Preparation:-

Vigorous reaction, heat + hissing sound, lime swells up and cracks and is converted to a fine powder.



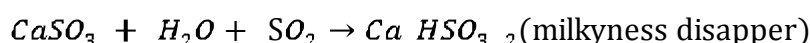
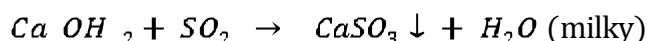
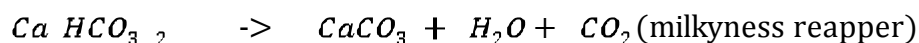
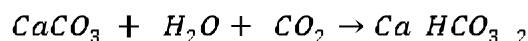
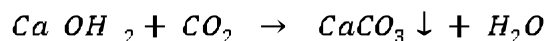
Industrial process:-



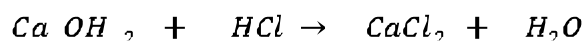
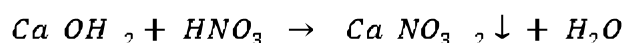
### Properties:

- White amorphous powder.
- Sparingly soluble, solubility decreases with increase of temperature.
- Lime water:- small amount of  $Ca(OH)_2$ , excess of water, some dissolves while the other undissolved part settle down giving a sat. Soln (clear)  $\rightarrow$  lime water.

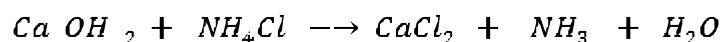
- Milk of lime:- excess  $Ca OH_2$  and little water, some goes into solution & rest remains as suspension. This suspension.
- Lime water turns milky :-



- Basic nature :-

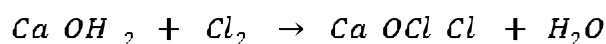


But with dil.  $H_2SO_4$ , at first insoluble  $CaSO_4$  it formed which form a layer on  $Ca OH_2$  & reaction stops.

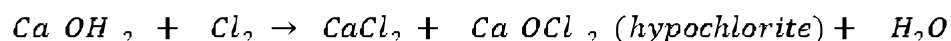


- Action with  $Cl_2$ :-

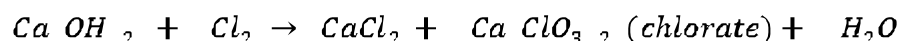
(a) Dry  $Cl_2$  over dry  $Ca OH_2$  at  $40^\circ C$  gives bleaching power.



- When  $Cl_2$  is passed through excess of lime water in cold:-



- In hot milk of lime :-



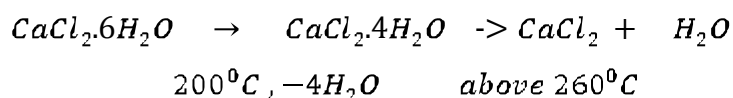
## Calcium chloride( $CaCl_2 \cdot 6H_2O$ ):-

### Preparation:-

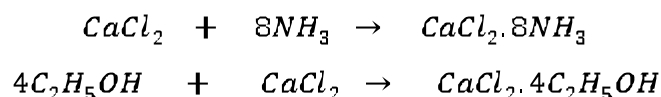
- $CaCO_3 + HCl \rightarrow CaCl_2 + CO_2 + H_2O$
- $CaO + HCl \rightarrow CaCl_2 + H_2O$
- $Ca OH_2 + HCl \rightarrow CaCl_2 + H_2O$

### Properties:-

- Colourless crystalline solid
- Highly soluble
- Action of heat:-



- Highly deliquescent; dissolve in moisture.
- Addition products:-



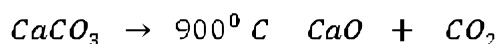
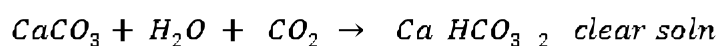
## Calcium carbonate:-

### Preparation:-

- $\text{CaCO}_3 + \text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$
- $\text{CaCl}_2 + \text{NH}_4\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{NH}_4\text{Cl}$
- $\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$

### properties:-

- Exists in 2 crystalline forms (a) calcite (b) aragonite
- Insoluble in water



(bond very stable)

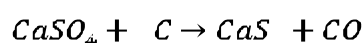
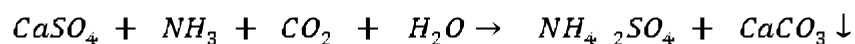
## Calcium sulphate :-

### Preparation:-

- $\text{CaCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{HCl}$
- $\text{CaO} + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O}$
- $\text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{CO}_2 + \text{H}_2\text{O}$

## Properties:-

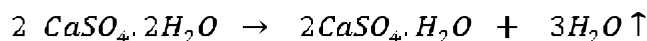
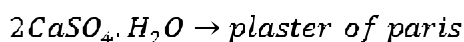
- White crystalline solid, sparingly soluble in cold water, solubility decreases with rise of temperature.
- Soluble in a conc. Soln of  $NH_4_2SO_4$  due to formation of  $CaSO_4 \cdot NH_4_2SO_4$
- Only way to produce  $NH_4_2SO_4$
- Without  $H_2SO_4$  :-



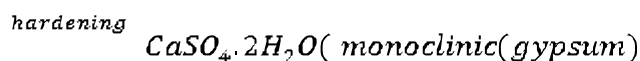
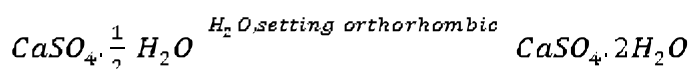
## Plaster of Paris:-

Monoclinic crystals of gypsum when heated, first changes into orthorhombic

From without any loss of water. On further heating to  $120^\circ C$ , it loses  $3/4^{th}$  of its water of crystallisation and forms hemihydrates.



Plaster of paris is a white powder which when mixed with water takes up the water of crystallisation again, thus converted back into the dehydrate with a slight expansion & sets into a hard mass. Setting takes about 10-15 minute, may be catalysed by addition of NaCl or use of alum or borax.



Plaster of paris or gypsum when heated at about  $200^\circ C$ , it loses all its  $H_2O$  of crystallisation with the formation of anhydrous calcium sulphate or dead burnt as it does not set like plaster of paris when moistened with water.