

The s-Block Elements

Alkali Metals

- Group 1 elements: lithium, sodium, potassium, rubidium, caesium, and francium
- Called alkali metals because their hydroxides are alkaline in nature

Electronic Configuration

- General outer electronic configuration is ns^1 .
- The electronic configurations of the alkali metals are given in the following table.

Element	Electronic configuration
Lithium (Li)	$1s^2 2s^1$
Sodium (Na)	$1s^2 2s^2 2p^6 3s^1$
Potassium (K)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Rubidium (Rb)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$
Caesium (Cs)	$[\text{Xe}] 6s^1$
Francium (Fr)	$[\text{Rn}] 7s^1$

Atomic and Ionic Radii

- Increase with increase in atomic number (i.e. on moving down the group)

Ionization Enthalpy

- Low
- Decreases on moving down the group, which is because of the following reasons:
 - Increase in size
 - Increase in screening of outermost electrons from the nuclear charge

Hydration Enthalpy

- Decreases on moving down the group

Physical Properties

- Silvery white, soft, and light metals
- Density increases down the group. (exception: Na is denser than K)
- Low melting and boiling points – Reason: weak metallic bond due to the presence of only one electron in the outermost shell
- They and their salts impart characteristic colour to an oxidising flame. Reason: after getting heat from the flame, the valence electrons get excited to higher energy level.

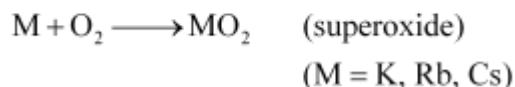
Then they come back to ground state by emitting radiation in the visible region.

- Crimson red – Lithium (Li)
- Golden yellow – Sodium (Na)
- Pale violet – Potassium (K)

Chemical Properties

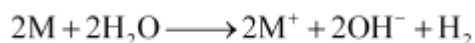
- **Highly reactive because of**
 - large size
 - low ionization enthalpy
 - Reactivity increases down the group
- **Reaction with air:**
 - Tarnish in dry air
 - Reason: formation of oxides and then hydroxides with moisture

- Burns vigorously in air



- Kept in kerosene oil – Reason: highly reactive towards air and water
- Li reacts directly with nitrogen of air to form lithium nitride (Li_3N).

- **Reaction with water:**



(M = alkali metal)

- **Reaction with acids:**

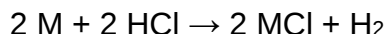
- Reacts vigorously with even dil. acids to give out hydrogen gas.



- **Reaction with dihydrogen:**



- Alkali metal hydrides are ionic solids with high melting point.
- Reaction with acids: React violently with dilute acids



- **Reaction with halogen:**

- Reacts vigorously to form halides which are ionic in nature (exception: LiX is somewhat covalent – Reason: High polarizing capability of Li^+ ion)
- LiI is the most covalent.

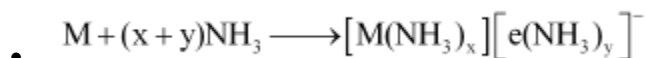
- **Reducing nature**

- Strong reducing agent

- Form unipositive ions easily, $M(g) \rightarrow M^+(g) + e^-$
- Li is the strongest and Na is the weakest.

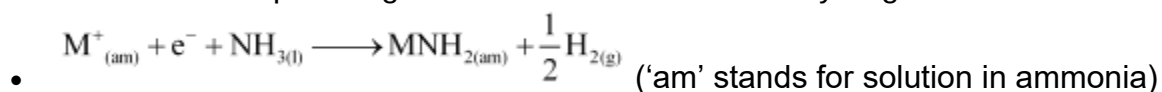
- **Solutions in liquid ammonia**

- Dissolve in liquid ammonia to give conducting deep blue solution



- Reason for blue colour – The ammoniated electron absorbs energy in the visible region of light.

- The solution is paramagnetic in nature and liberates hydrogen to form amide.



- Its concentrated solution is bronze in colour and diamagnetic in nature.
- The metals also react with alcohol, gaseous ammonia, and alkynes

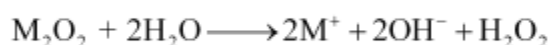
Uses

- In making useful alloys. For example, it is used with lead in making 'white metal' bearings for motor engines
- Li is used in making electrochemical cells.
- Na is used in making Na/Pb alloy, which are used to make organolead compounds – $PbEt_4$ and $PbMe_4$. These compounds were earlier used as anti-knock additives to petrol.
- Liquid Na is used as a coolant in fast breeder nuclear reactors.
- K plays an important role in biological systems
- KCl – used as a fertilizer
- KOH – in the manufacture of soft soap and as an absorbent of CO_2
- Cs is used in devising photoelectric cells.

Oxides and Hydroxides of Alkali Metals

- Alkali metals form oxides on combustion.

- Li – Lithium oxide (Li_2O) (and some lithium peroxide Li_2O_2)
- Na – Sodium peroxide (Na_2O_2) (and some sodium superoxide NaO_2)
- K, Rb, Cs – Superoxides, MO_2
- The stability of peroxides or superoxides increases on moving down the group (i.e., with increase in size).
- Reasons – Larger the cations, more is the stabilization of large anions through lattice energy.
- Oxides are hydrolysed by water to form hydroxides.



- Oxides and peroxides – Colourless when pure

Superoxides – Yellow or orange

- Na_2O_2 – Oxidizing agent in inorganic chemistry
- Superoxide O_2^- is paramagnetic.
- Reason – Presence of one unpaired electron in π^*2p molecular orbital
- Hydroxides obtained by reaction of oxides with water – White crystalline solids
- Hydroxides of alkali metals are the strongest of all the bases.
- Hydroxides dissolve freely in water with evolution of heat.

Halides

- Preparation:

By the reaction of aqueous hydrohalic acid (HX) with appropriate oxide, hydroxide or carbonate

- Physical properties:

- Colourless crystalline solids
- Have high melting points
- Trend in melting and boiling point:

Fluoride > Chloride > Bromide > Iodide

- Soluble in water
- LiF is less soluble.

Reason: High lattice enthalpy

- CsI is less soluble.

Reason: Low hydration enthalpy of the ions

- High negative enthalpies of formation ($\Delta_f H^\ominus$)
- Trend:

For fluorides – $\Delta_f H^\ominus$ is less negative down the group.

For chlorides, bromides, and iodides – $\Delta_f H^\ominus$ is more negative down the group.

For a given metal –

Fluoride → Chloride → Bromide → Iodide

$\xrightarrow{\Delta_f H^\ominus \text{ becomes less negative}}$

Salts of oxo-acids

- An oxo-acid is an acid which
- contains oxygen
- has at least one hydrogen atom attached to oxygen
- contains at least one other atom
- has the hydroxyl group and the oxo group attached to the same atom

Examples: Carbonic acid (H_2CO_3), sulphuric acid (H_2SO_4), nitric acid (HNO_3), phosphoric acid (H_3PO_4)

- Preparation:

By the reaction of alkali metals with oxo-acids

- Physical properties
- Soluble in water
- Thermally stable: Carbonates M_2CO_3 ; and in most cases, hydrogen carbonates (MHCO_3) are highly thermally stable

Exception (I) – Li_2CO_3 is less stable to heat.

Reason: Small size of Li – polarization of large CO_3^{2-} ion – formation of more stable Li_2O and CO_2

Exception (II) – LiHCO_3 does not exist as solid.

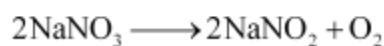
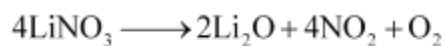
- Stability of carbonates and hydrogen carbonates increases down the group.

Reason: The electropositive character increases down the group.

Anomalous Properties of Lithium

- Reasons for anomalous behaviour of lithium:
- The Li atom and ion are exceptionally small in size.
- Li has high polarizing power. [charge to radius ratio (charge/ radius)]
- Lithium compounds are soluble in organic solvents due to covalent character of lithium compounds because of the above reasons.
- **Points of difference between lithium and alkali metals**
- Li is harder and has high melting and boiling points.

- Strongest reducing agent, forms Li_2O and Li_3N by reacting with air
- LiCl is deliquescent and crystallises as a hydrate, $\text{LiCl} \cdot 2\text{H}_2\text{O}$.
- LiHCO_3 does not exist as solid.
- Does not form ethynide with ethyne
- On heating, lithium nitrate decomposes to oxide while nitrates of other alkali metals decompose to nitrites.

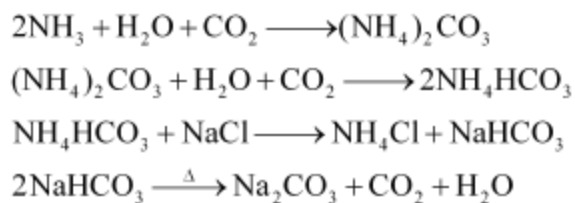


- Fluoride and oxide are less soluble in water.
- Li shows diagonal relationship to Mg.
- **Points of similarities between Li and Mg**
- Both are harder and lighter than the other elements in the respective groups.
- Both react slowly with water; oxides of both are less soluble in water; hydroxides of both decompose on heating.
- Both form nitrides (Li_3N and Mg_3N_2) by directly reacting with nitrogen.
- Both do not form superoxide.
- On heating, carbonates of both give oxides and CO_2 ; hydrogen carbonates of both do not exist as solid.
- Chlorides of both (LiCl , MgCl_2) are soluble in ethanol, deliquescent, and crystallize as hydrates ($\text{LiCl} \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$).
- Reason for similarities between Li and Mg – Similar size

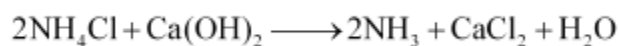
Some Important Compounds of Sodium

Washing Soda or Sodium Carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$)

- **Preparation**
- Solvay process



Recovering of NH_3

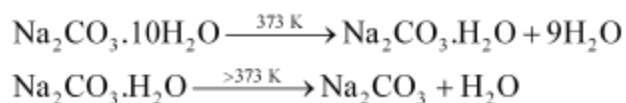


Solvay process is not applied to manufacture K_2CO_3 .

Reason – KHCO_3 is soluble in water and hence, cannot be precipitated.

- **Properties**

- White crystalline solid
- Easily soluble in water
- Loses water of crystallization on heating



- Carbonate part is hydrolysed by water, resulting in alkaline solution.

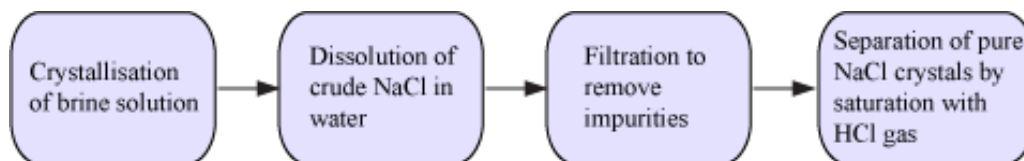


- **Uses**

- In water softening
- In the manufacture of glass, soap, borax, and caustic soda
- In industries in the manufacture of paper, paints, and textile
- In laboratory as a reagent

Sodium Chloride (NaCl)

- **Preparation**



Impurities – Sodium sulphate, calcium sulphate, calcium chloride, magnesium chloride

- **Physical Properties**

- Melts at 1081 K
- Solubility is 36 g in 100 g of water at 273 K.
- With the increase in temperature, solubility does not increase.

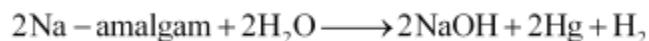
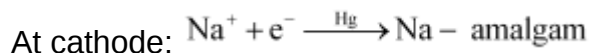
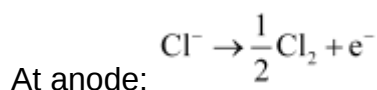
- **Uses**

- For domestic purpose as common salt or table salt
- In the preparation of Na_2O_2 , NaOH , and Na_2CO_3

Caustic Soda or Sodium Hydroxide (NaOH)

- **Preparation**

- By electrolysis of NaCl in Castner – Kellner cell



- **Properties**

- White translucent solid
- Gives alkaline solution by dissolving in water
- Crystals are deliquescent.

- At the surface of NaOH solution, Na_2CO_3 is formed by the reaction with CO_2 in the atmosphere.

- **Uses**

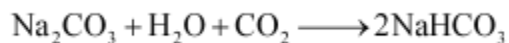
- In petroleum refining process
- In the manufacture of soap paper, artificial silk, and a number of chemicals
- In the process of purifying bauxite
- In textile industries to mercerise cotton fabrics
- In the preparation of pure fats and oils
- As a reagent in laboratory

Baking Soda or Sodium Hydrogen Carbonates (NaHCO_3)

- **Called Baking Soda**

Reason – It decomposes, producing bubbles of CO_2 on heating. This is the reason why holes are formed in cakes or pastries and as a result, they are light and fluffy.

- **Preparation**



Uses

- As an antiseptic for skin infection
- For extinguishing fire

Biological Importance of Na and K

- Sodium ions take part
- in the transmission of nerve signals
- in regulating the water flow across cell membranes
- in the transportation of sugars and amino acids into cells

- Potassium ions participate in
- activating enzymes in cell fluids
- the oxidation of glucose to produce ATP
- the transmission of nerve signals

Alkaline Earth Metals

- Group 2 elements: Beryllium, magnesium, calcium, strontium, barium and radium.
- They are called alkaline earth metals because their oxides and hydroxides are alkaline in nature, and their oxides are found in earth's crust.

Electronic Configuration

- General outer electronic configuration is ns^2
- The electronic configurations of the alkaline earth metals are given in the following table:

Element	Electronic Configuration
Beryllium (Be)	$1s^2 2s^2$
Magnesium (Mg)	$1s^2 2s^2 2p^6 3s^2$
Calcium (Ca)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Strontium (Sr)	$[\text{Kr}] 5s^2$
Barium (Ba)	$[\text{Xe}] 6s^2$

Radium (Ra)	[Rn] 7s ²
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Atomic and ionic radii

- Smaller than the corresponding alkali metals

Reason: Greater nuclear charge

- Increase with the increase in atomic number (i.e., on moving down the group)

Ionisation Enthalpy

- Low
- Decreases on moving down the group. This is because of:
 - Increase in size
 - Increase in the screening of valence electrons from the nuclear charge
- Higher first ionisation enthalpy than that of the corresponding alkali metals. This is due to smaller size and higher nuclear charge as compared to the corresponding group 1 alkali metals.
- Second ionisation enthalpy is lower than that of the corresponding alkali metals

Hydration enthalpy

- Decreases on moving down the group (i.e. with increase in ionic size)
- Larger hydration enthalpy than that of the corresponding alkali metal ions. This is why compounds of alkaline earth metals are more extensively hydrated than those of alkali metals.
- Example: NaCl is not hydrated whereas MgCl₂ exists as MgCl₂·6H₂O. KCl does not form hydrate whereas CaCl₂ exists as CaCl₂·6H₂O.

Physical properties

- Silvery white, lustrous and soft (harder than alkali metals) (Exception – Beryllium and Magnesium are greyish)

- Melting and boiling points of these metals are higher than those of the corresponding alkali metals.

Reason: Smaller size than alkali metals

- Strongly electropositive in nature. Reason: Low ionisation enthalpies
- Flame test:
 - Calcium – Brick red
 - Strontium – Crimson
 - Barium – Apple green
 - Mg and Be do not impart colour because the electrons are too strongly bound to be excited.
- Good conductors of heat and electricity

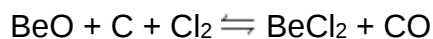
Chemical Properties

- Less reactive than alkali metals
- Reactivity increases down the group
- Reaction with air and water:
 - Be and Mg are kinetically inert to oxygen and water. Reason – formation of oxide film on their surface
 - However, when Mg and powdered Be burn, they give MgO and Mg₃N₂, and BeO and Be₃N₂ respectively.
 - Ca, Sr and Ba react readily with air to form oxides and nitrides; also react with water (even cold), to form hydroxides
- Reaction with halogens:
 - At high temperature



(X = F, Cl, Br, I)

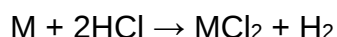
- BeF₂ is prepared by the thermal decomposition of (NH₄)₂BeF₄
- BeCl₂ is prepared from BeO by heating it with carbon and chlorine to about 600-900 K



- Reaction with hydrogen:
- React with hydrogen to form hydrides (Exception – Beryllium)
- Preparation of BeH_2 from BeCl_2 and LiAlH_4 –



- Reaction with acids:



(M = Alkali earth metal)

- Reducing nature:
- Strong reducing agent (weaker than corresponding alkali metals)
- Be is a weaker reducing agent than other alkaline earth metals.
- Solutions in liquid ammonia:

Dissolve in liquid ammonia to give deep, blue-black solution



Uses

- **Beryllium:**
 - For making alloys such as Cu–Be alloys which are used for making high strength springs
 - Metallic Be, for making windows of X-ray tubes
- **Magnesium:**
 - For making alloys with Al, Zn, Mn and Sn
 - Mg–Al alloys are used in the construction of aircraft
 - Magnesium is used in flash powders and bulbs, incendiary bombs and signals
 - Milk of magnesia (suspension of $(\text{MgOH})_2$ in water) is used as an antacid
 - MgCO_3 is a component in toothpaste

- **Calcium:**
- In the process of extraction of metals from oxides which are difficult to reduce with carbon
- For removing air from vacuum tubes. Reason – reacts with oxygen and nitrogen at high temperature
- **Barium:**
- For removing air from vacuum tubes. Reason – reacts with oxygen and nitrogen at high temperature
- **Radium:**
- In radiotherapy (e.g., in the treatment of cancer)

General characteristics of compounds of the alkaline earth metals

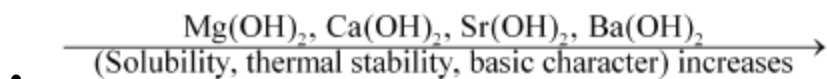
- Compounds of alkaline earth metals are ionic in nature (but less ionic than compounds of corresponding alkali metals).
- Reason – Greater nuclear charge, smaller size
- Compounds of lighter elements (Be, Mg) are more covalent than those of heavier and large elements (Ca, Sr, Ba).

Oxides and hydroxides

- **Oxides**
- Burn in oxygen forming metal monoxide (MO)
- MO has rock salt structure. (Exception – BeO)
- Thermally stable – Reason: High enthalpies of formation
- Ionic in nature (Exception – BeO is amphoteric)
- React with water to form hydroxides, which are sparingly soluble

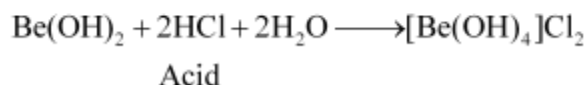
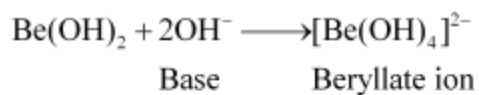


- **Hydroxide**



- Basic in nature (less basic than alkali metal hydroxide)

Exception – Be(OH)_2 is amphoteric.



- Less stable than alkali metal hydroxide

Halides

- Ionic in nature (Exception – BeX_2 is covalent and soluble in organic solvents)
- Structure of BeCl_2 in solid state (chain structure) is



- In vapour phase, BeCl_2 forms chloro-bridged dimer. At high temperature (1200 K), this dimer undergoes dissociation to form linear monomer.
- Tendency to form halide hydrates decreases down the group.

Example – $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

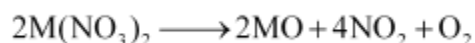
Salts of oxo-acids

- Carbonates
- Insoluble in water
- Precipitated by adding sodium or ammonium carbonate
- Solubility decreases down the group.
- When heated, decompose to given oxide and CO_2

- Thermal stability increases down the group.
- BeCO_3 is unstable and hence, kept in the atmosphere of CO_2 .
- Sulphate
- White solids
- Thermally stable
- Solubility decreases down the group.
- BeSO_4 and MgSO_4 are readily soluble in water. Reason – High hydration enthalpy of Be^{2+} and Mg^{2+}
- Nitrates
- Preparation: By dissolving carbonates in dilute nitric acid
- Tendency to form hydrates decreases down the group. Reason – Increase in size, decrease in hydration enthalpy

Example – $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$

- When heated, decompose to give oxide



Anomalous Properties of Beryllium

- Exceptionally small size of the atom and the cation
- Forms covalent compounds (due to small size and high ionisation enthalpy)
- Highest coordination number is four while other members exhibit six.
- Reason: Be has four orbitals in its valence shell while other members can use *d*-orbitals
- Unlike other elements, the oxides and hydroxides of Be are amphoteric in nature.

Diagonal Relationship Between Be and Al

- Reason: Same charge/radius ratio

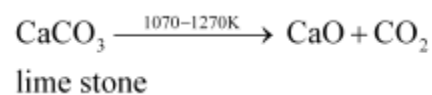
- Similarities:
- Like Al, it is not readily attacked by acids; (Reason – presence of an oxide film on the surface of the metal)
- Both dissolve in excess of alkali, giving beryllate ion $[\text{Be}(\text{OH})_4]^{2-}$ and aluminate ion $[\text{Al}(\text{OH})_4]^-$.
- Like Al_2Cl_6 , BeCl_2 has a Cl^- bridged polymeric structure. Both these compounds are Lewis acids, and are soluble in organic solvents.
- Both form fluoro complex ions, $[\text{BeF}_4]^{2-}$, $[\text{AlF}_6]^{3-}$

Some Important Compounds of Calcium

Quick Lime or Calcium Oxide (CaO)

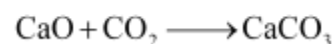
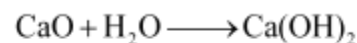
- **Preparation:**

In rotary kiln,

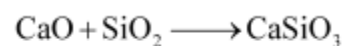


For the completion of the reaction, CO_2 is removed as soon as it is produced.

- **Properties:**
- White amorphous solid
- Melts at 2870 K
- Absorbs moisture and CO_2 when exposed to atmosphere



- Basic oxide – combines with acidic oxides on heating

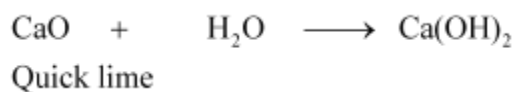


- Slaking of lime – the process of breaking lump of lime by adding a limited amount of water
- When slaked with soda, it gives solid soda lime
- **Uses:**
- For manufacturing cement
- For manufacturing sodium carbonate from caustic soda
- For manufacturing dye stuffs
- For purifying sugar
- It is the cheapest form of alkali

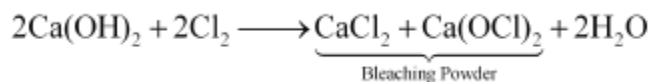
Slaked Lime or Calcium Hydroxide [Ca(OH)₂]

- **Preparation:**

By adding water to quick lime



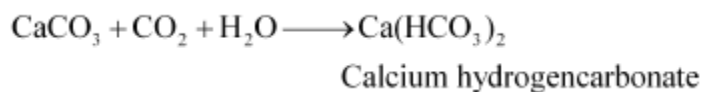
- **Properties:**
- White amorphous powder
- Sparingly soluble in water
- Lime water – clear aqueous solution of Ca(OH)₂
- Milk of lime – suspension of slaked lime in water
- With chlorine, slaked lime gives bleaching powder



- On passing carbon dioxide through lime water, it turns milky due to the formation of calcium carbonate (CaCO₃)



- On passing excess of CO_2 , calcium carbonate (CaCO_3) dissolves, forming calcium hydrogen carbonate

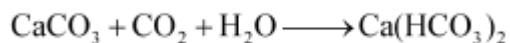


- **Uses:**
- For the preparation of mortar, a building material
- Disinfectant in nature, and hence, used in white washing
- For the manufacture of glass
- For the preparation bleaching powder
- For purifying sugar
- In the tanning industry

Calcium Carbonate (CaCO_3)

- **Naturally Occurs As Limestone, Chalk, Marble**
- **Preparation:**
- By passing CO_2 through slaked lime

On passing excess of CO_2 , CaCO_3 dissolves to form water-soluble calcium hydrogen carbonate.



- By adding aqueous solution of sodium carbonate to calcium chloride

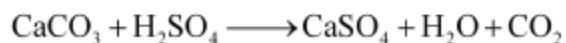
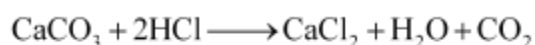


- **Properties:**

- White fluffy powder
- Insoluble in water
- Decomposes to CO₂ on heating



- Reacts with dilute acids to liberate CO₂



- **Uses:**

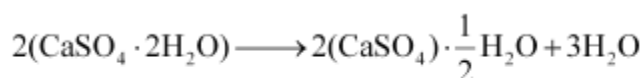
- As a building material in the form of marble
- For manufacturing quick lime
- As a flux with MgCO₃ in the extraction of metals such as iron
- Precipitated CaCO₃ for the manufacture of high quality paper
- As antacid, mild abrasive in toothpaste, in chewing gums, and as filler in cosmetics

Plaster Of Paris or Calcium Sulphate $\left(\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O} \right)$

- **Hemihydrate of Calcium Sulphate**

- **Preparation:**

By heating gypsum to 393 K



Gypsum

Above 393 K, water is liberated to form anhydrous calcium sulphate (CaSO₄), known as 'dead burnt plaster'.

- **Property:**

On mixing with water, it forms a plastic mass which sets into a hard solid in 5 – 15 minutes.

- **Uses:**

- As plaster and as building material
- In surgical bandages, for setting broken and fractured bones
- In dentistry
- For making statues, busts, and in ornamental work

Cement

- Also called Portland cement
- Reason: Resembles the natural limestone extracted in the Isle of Portland, England
- Composition of cement:

$\text{CaO} = 50 - 60\%$

$\text{SiO}_2 = 20 - 25\%$

$\text{Al}_2\text{O}_3 = 5 - 10\%$

$\text{MgO} = 2 - 3\%$

$\text{Fe}_2\text{O}_3 = 1 - 2\%$

$\text{SO}_3 = 1 - 2\%$

- For a good-quality cement:

The ratio of SiO_2 : $\text{Al}_2\text{O}_3 = 2.5$ to 4

The ratio of CaO : $(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) = 2$

- Manufacture of cement:
- Raw materials – limestone and clay

On strong heating, clay and lime fuse and react to form 'Cement clinker'.
↓
'Cement clinker' is mixed with 2 – 3% by weight of gypsum to form cement.



- Important ingredients present in Portland cement:

Dicalcium silicate (Ca_2SiO_4) = 26%

Tricalcium silicate (Ca_3SiO_5) = 51%

Tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$) = 11%

- Setting of cement:

On mixing with water, cement sets to give a hard solid

- Reason – hydration of the molecules of the constituents and their rearrangement
- Reason for adding gypsum – to slow down the process of setting of the cement; this results in sufficient hardening of the cement
- Uses:

As a construction material –

- In concrete and reinforced concrete
- In plastering
- In construction of buildings, bridges and dams

Biological Importance of Magnesium and Calcium

- Amount of Mg in the human body = 25 g (approx)

Amount of Ca in the human body = 1200 g (approx)

- Daily requirement of Ca and Mg in the human body = 200 – 300 mg
- Importance of Mg:
 - Required as cofactor by the enzymes that utilise ATP in phosphate transfer
 - Present in chlorophyll
- Importance of Ca:
 - Bones and teeth contain about 99% body calcium.
 - Plays important roles in – neuromuscular function, inter-neuronal transmission, cell membrane integrity, blood coagulation
 - The calcium concentration in plasma is maintained at 100 mgL^{-1} by two hormones –
 - Calcitonin
 - Parathyroid hormone
 - Bone is not an inert and unchanging substance. It is continuously being solubilised and re-deposited to the extent of 400 mg per day in humans.