CLASS-XI

for

NEET/JEE 2021

BRUSH UP

Brush up your concepts to get high rank in NEET/JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

Unit 5

Hydrogen | The *s*-Block Elements

Hydrogen

INTRODUCTION

Hydrogen is the first and lightest element in the periodic table. It was discovered by Henry Cavendish in 1766. He prepared the gas by treating iron with dil. H_2SO_4. Name 'hydrogen' was proposed by Lavoisier because it produces water on burning with oxygen (in Greek : hydra means water, gene means producing).

H Hydrogen

Symbol : H

Atomic Number : 1

Electronic configuration : $1s^1$

Molecular forms : H_2, D_2, T_2, HD

Isotopes : Protium, ${}^1_1H$; Deuterium, ${}^2_1H$ or D; Tritium, ${}^3_1H$ or T

Ionic forms : H^-, H^+, H_2^+, H_3^+

Position of Hydrogen in Periodic Table

Resemblance with alkali metals due to

1. Electronic configuration (ns^1): $1s^1$
2. Electropositive character, (M^+) : H^+
3. Oxidation state (+1) : $\overset{+1}{H}\overset{-1}{Cl}$, $\overset{+1}{Na}\overset{-1}{Cl}$

Resemblance with halogens due to

1. Electronic configuration : One e^- less than the nearest inert gas configuration.
2. Electronegative character : Both have tendency to accept one e^- to form anions.
3. Ionisation energy : Comparable with halogens.

Differences from alkali metals and halogens

1. Less electropositive than alkali metals and less electronegative than halogens.
2. Nature of oxides : Oxide of hydrogen is neutral *i.e.* H_2O while alkali metals form basic and halogens form acidic oxides.
3. Size of ions : H^+ is much smaller than alkali metal ions and H^- is much larger than halide ions.

Dihydrogen

Preparation

	Preparation	Properties	Uses
H Y D R O G E N	$2Na + 2H_2O \longrightarrow 2NaOH + H_2$ $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$ $2Al + 2KOH + 2H_2O \longrightarrow 2KAlO_2 + 3H_2$ (Uyeno's method) $\underbrace{CO + H_2}_{\text{Water gas}} + \underset{\text{(Steam)}}{H_2O} \xrightarrow[773\text{ K}]{Fe_2O_3 + Cr_2O_3} CO_2 + 2H_2$ (Bosch process) $3Fe + \underset{\text{(Steam)}}{4H_2O} \xrightarrow{1023\text{-}1073\text{ K}} Fe_3O_4 + 4H_2$ (Lane's process)	$2Na + H_2 \xrightarrow{573\text{ K}} 2NaH$ $3H_2 + N_2 \xrightarrow[673\text{ K, 200 atm}]{Fe/Mo} 2NH_3$ $H_2 + \underset{\text{(molten)}}{S} \longrightarrow H_2S$ $C + 2H_2 \xrightarrow{1275\text{ K}} CH_4$ $H_2 + Cl_2 \xrightarrow[\text{light}]{\text{Diffused}} 2HCl$ $CuO + H_2 \longrightarrow Cu + H_2O$ $Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$ $\text{Vegetable oil} + H_2 \xrightarrow[450\text{ K, 8-10 atm}]{\text{Finely divided Ni}} \text{Solid fat}$	• As a reducing agent. • In hydrogenation of vegetable oils. • In atomic hydrogen torch for welding. • As a rocket fuel in space research. • In the manufacture of synthetic petrol. • In the preparation of water gas, ammonia, nitric acid, metal hydrides, hydrogen chloride, methanol and nitrogenous fertilizers.

Hydrides

Hydrogen form binary hydrides with elements of *s*, *p*, (except noble gases), *d* and *f*-block.

Ionic or Saline Hydrides

- Group-1,2 elements form ionic hydrides, *e.g.*, NaH, CaH_2, CsH, SrH_2 etc.
- BeH_2, MgH_2 have slightly covalent character.
- Used in synthesis of other useful hydrides.
  $8LiH + Al_2Cl_6 \xrightarrow[\text{Ether}]{\text{Dry}} 2LiAlH_4 + 6LiCl$

Metallic or Interstitial Hydrides

- *d* and *f*-block elements form metallic hydrides. These are non-stoichiometric, being deficient in hydrogen, *e.g.*, $LaH_{2.87}$, $YbH_{2.55}$, etc.
- Metals of group-7, 8, 9 do not form hydrides and this region of periodic table is referred as hydride gap.
- Metallic hydrides can be used as hydrogen storage media.

Covalent or Molecular Hydrides

- *p*-Block elements form molecular or covalent hydrides. These are usually volatile compounds with low m.pt. and b.pt. These are of three types :
  - **Electron-deficient hydrides :** Formed by group-13 elements, *e.g.* B_2H_6, $(AlH_3)_n$, etc.
  - **Electron-precise hydrides :** Formed by group-14 elements, *e.g.*, CH_4, SiH_4, etc.
  - **Electron-rich hydrides :** Formed by group-15, 16 and 17 elements, *e.g.*, NH_3, H_2O, HCl, etc.

INFO SHOTS

A new photocatalyst for extraction of hydrogen from seawater !

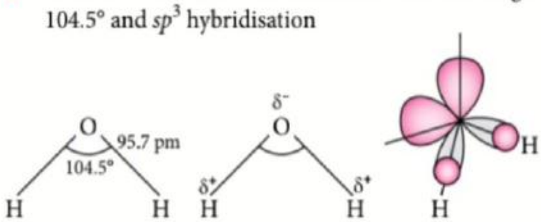
Hydrogen can be produced to power fuel cells by extracting the gas from seawater, but the electricity required to do it makes the process costly. Recently, UCF researchers has come up with a new hybrid nanomaterial that harnesses solar energy and uses it to generate hydrogen from seawater more cheaply and efficiently than current materials. This catalyst not only harvest a much broader spectrum of light than other materials, but also stand up to the harsh conditions found in seawater.

WATER

It is a crucial compound for the survival of all life forms. Human body has about 65% water and some plants have as much as 95% of water. It is a solvent of great importance.

Properties

- **Structure of water :** Bent structure with bond angle 104.5° and sp^3 hybridisation



H_2O molecule

- **Physical Properties :**
  - Pure water is colourless, odourless and tasteless.
  - It freezes at 0 °C and boils at 100 °C.
  - It has maximum density 1 g cm^{-3} at 4 °C.
- **Chemical Properties :**
  - Amphoteric nature

    $$\underset{\text{Acid 1}}{H_2O_{(l)}} + \underset{\text{Base 2}}{H_2O_{(l)}} \longrightarrow \underset{\text{Acid 2}}{H_3\overset{+}{O}_{(aq)}} + \underset{\text{Base 1}}{OH^-_{(aq)}}$$

    This self-ionisation of water is also called auto-protolysis.
  - Hydrolytic reaction

    $$CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)}$$
  - As reducing agent

    $$xCO_2 + yH_2O \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} C_x(H_2O)_y + xO_2$$
  - Hydrate formation : Water combine with ionic salts is called water of crystallisation and such crystals are called hydrated salts.
    - Coordinated water : $[Ni(H_2O)_6]^{2+}$
    - Hydrogen bonded water : $CuSO_4{\cdot}5H_2O$
    - Interstitial water : $BaCl_2{\cdot}2H_2O$

Hard and Soft Water

- Water free from soluble salts of Ca and Mg, and which forms lather with soap readily is called soft water.
- Hard water does not form lather with soap.

Hardness of Water and Methods for Removal

Temporary Hardness

Due to presence of bicarbonates of Ca and Mg.

Boiling

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\downarrow + CO_2\uparrow + H_2O$$
$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 + 2CO_2$$

Clark's process

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$
$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O$$

Synthetic resins method

Cation exchange :

$$2\text{Resin} - H^+ + 2M^+_{(aq)} \longrightarrow M(\text{Resin})_2 + 2H^+$$
(in hard water) (Exhausted resin)

Anion exchange :

$$\text{Resin} - NH_3^+OH^- + Cl^- \rightarrow \text{Resin } NH_3^+Cl^- + OH^-$$
(in hard water) (Exhausted resin)

$[M = Ca^{2+}, Mg^{2+}]$

Permanent Hardness

Due to presence of chlorides and sulphates of Ca and Mg.

Calgon's method

$$Na_6P_6O_{18} \longrightarrow 2Na^+ + Na_4P_6O_{18}^{2-}$$
Sod. hexameta--phosphate

$$M^{2+} + Na_4P_6O_{18}^{2-} \longrightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$$
$(M = Mg, Ca)$

Washing soda

$$MCl_2 + Na_2CO_3 \longrightarrow MCO_3\downarrow + 2NaCl$$
$$MSO_4 + Na_2CO_3 \longrightarrow MCO_3\downarrow + Na_2SO_4$$
$(M = Mg, Ca)$

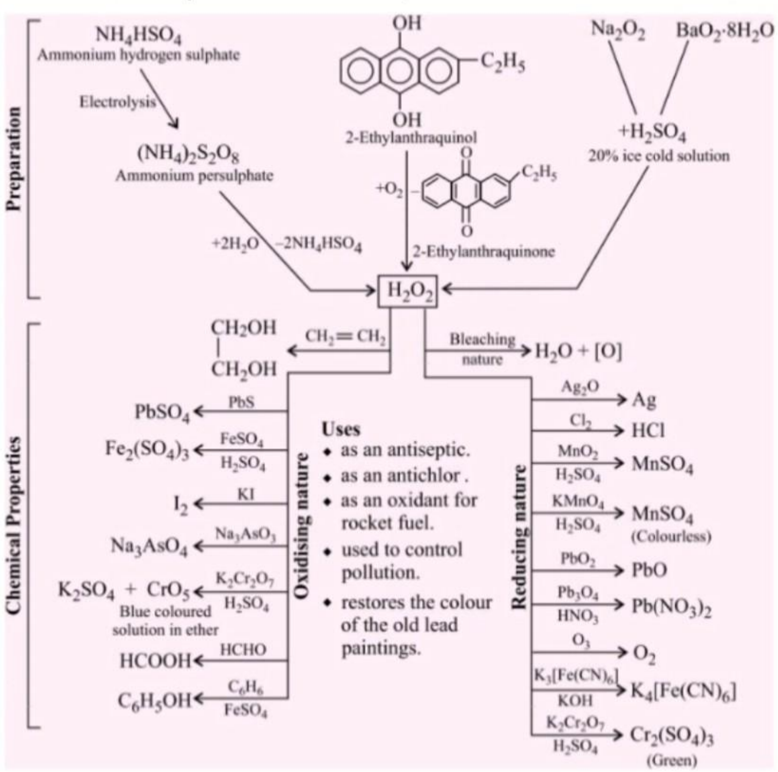
Permutit Process

$$Na_2Z + MCl_2 \longrightarrow MZ + 2NaCl$$
(Sod. zeolite) (From hard water) (Settle down at bottom)

$M = Mg, Ca ; Z = Al_2Si_2O_8 \cdot xH_2O$

HYDROGEN PEROXIDE

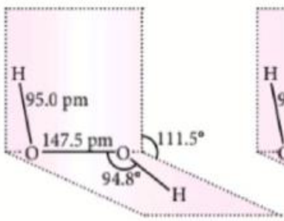
Hydrogen peroxide was discovered by the French chemist J.L. Thenard in 1818. Its molecular formulas is H_2O_2.



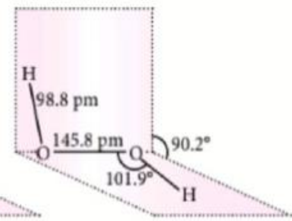
Uses

- As bleaching agent and disinfectant.
- Mixture of H_2O_2 and hydrazine hydrate used as rocket propellent.
- For restoring the colour of old painting.
- As an antiseptic under the name perhydrol.

Structure



(Gas Phase)



(Solid Phase)

Heavy Water (D_2O)

- Prepared by prolonged electrolysis of ordinary water.
- Used to prepare deuterium compounds like
  $CaC_2 + 2D_2O \longrightarrow C_2D_2 + Ca(OD)_2$
  $SO_3 + D_2O \longrightarrow D_2SO_4$
- Used as a moderator in nuclear reactor and in reaction mechanism.

Dihydrogen as a fuel

- Hydrogen economy is the transportation and storage of energy in the form of liquid or gaseous dihydrogen.
- Pollutants in combustion of dihydrogen will be less than petrol.

The *s*-Block Elements

Introduction

Elements of periodic table in which the last electron enters the outermost *s*-orbital, are called *s*-block elements. They are classified in two groups :

Group	1 (alkali metals)	2 (alkaline earth metals)
Electronic configuration	ns^1	ns^2

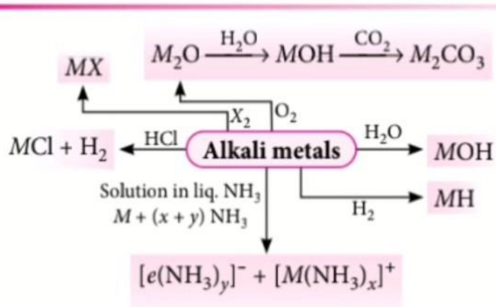
Electronic Configurations of *s*-Block Elements

Alkali metals			Alkaline earth metals		
Elements	Atomic Number	Electronic configuration	Elements	Atomic Number	Electronic configuration
Lithium (Li)	3	[He] $2s^1$	Beryllium (Be)	4	[He] $2s^2$
Sodium (Na)	11	[Ne] $3s^1$	Magnesium (Mg)	12	[Ne] $3s^2$
Potassium (K)	19	[Ar] $4s^1$	Calcium (Ca)	20	[Ar] $4s^2$
Rubidium (Rb)	37	[Kr] $5s^1$	Strontium (Sr)	38	[Kr] $5s^2$
Caesium (Cs)	55	[Xe] $6s^1$	Barium (Ba)	56	[Xe] $6s^2$
Francium (Fr)	87	[Rn] $7s^1$	Radium (Ra)	88	[Rn] $7s^2$

General Properties of s-Block Elements

Alkali metals	Alkaline earth metals
Atomic/ionic radii	
• Increase on moving down from Li to Cs.	• Smaller than group-1 elements and increase from Be to Ra.
Ionization enthalpy	
• Decreases down the group as the size increases.	• 1st *I.E.* of group-2 is higher than group-1 due to small size. In general, on moving down the group *I.E.* decreases.
Hydration enthalpy	
• Decreases with increase in size. $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$	• Decreases with increase in size. $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$
Physical appearance	
• Silvery white due to presence of mobile electron.	• Silver white lustre but harder than alkali metals.
Melting and boiling point	
• Decreases with increase in atomic number.	• Higher than group-1 and there is no regular trend in their m.pt. and b.pt.

Chemical Properties of Alkali metals



Trends in Alkali Metals

- **Strength of hydroxide (basicity) :** $CsOH > RbOH > KOH > NaOH > LiOH$
- **Stability of carbonates :** $Cs_2CO_3 > Rb_2CO_3 > K_2CO_3 > Na_2CO_3 > Li_2CO_3$
- **Reactivity towards H_2/X :** $Li > Na > K > Rb > Cs$
- **M.pt. and b.pt. of halides :** $MF > MCl > MBr > MI$

Uses of Alkali Metals

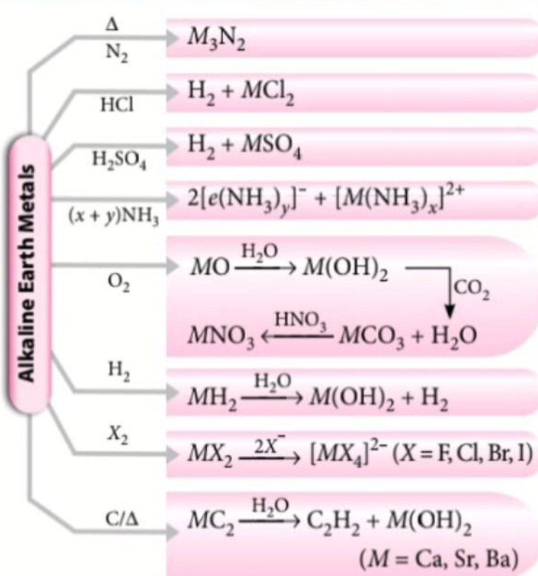
Li
- In alloy formation.
- Used in armour plate and aircraft parts.
- In refining of Cu and Ni to treat rheumatism.

Na
- Used for making antiknocking compounds.
- In sodium vapour lamps.
- Used in many organic compounds formation.
- As a liquid coolant in nuclear powder stations.

K
- As a fertilizer.
- In biological systems.
- In manufacturing of soap.
- As an excellent adsorbent of CO_2.

Cs
- In devising photoelectric cells (solar cells).

Chemical Properties of Alkaline Earth Metals



Trends in Alkaline Earth Metals

- **Basic character/solubility :** $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$
- **Lattice enthalpy :** $Be(OH)_2 > Mg(OH)_2 > Ca(OH)_2 > Sr(OH)_2 > Ba(OH)_2$
- **Thermal stability :** $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$
- **Hydration enthalpy :** $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$
- **Basicity of oxides :** $\underset{\text{Amphoteric}}{BeO} < \underset{\text{Weakly basic}}{MgO} < \underset{\text{Basic}}{CaO} < \underbrace{SrO < BaO}_{\text{Strongly basic}}$
- **Solubility of halides :** $BeX_2 < MgX_2 < CaX_2 < SrX_2 < BaX_2$
- **Reducing nature :** $Be < Mg < Ca < Sr < Ba$

Uses of Alkaline Earth Metals

- **Be**
  - In alloy formation.
  - In windows of X-ray tubes.
  - In high strength spring.
- **Mg**
  - Its alloy used in aircraft construction.
  - In toothpaste.
  - In aluminothermy.
  - In Grignard reagent.
- **Ca**
  - In the extractions of metals.
  - In casting and forging.
  - In cement and mortar.

Anomalous Behaviour

Anomalous behaviours of the first element of a group is due to

- small atomic and ionic radii
- high electronegativity and ionization enthalpy
- high polarising power
- absence of d-electrons in its valence shell.

Diagonal Relationship

Diagonal similarity is known as diagonal relationship, is due to similarity in ionic sizes and/or charge/radius ratio of the elements.

	Group 1	Group 2	Group 3	Group 4
2^{nd} period	Li ↘	Be ↘	B ↘	C
3^{rd} period	Na	Mg	Al	Si

Points of Difference

Li with other alkali metals	Be with other alkaline earth metals
• Much harder	• Harder than magnesium.
• Higher m.pt. and b.pt.	• Higher m.pt. and b.pt.
• Li forms monoxide while others form peroxides (M_2O_2) and superoxides (MO_2).	• Does not react with cold water while other metals (except Mg) do, *e.g.*, $Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$
• Ability to form nitrides.	• Be forms covalent compound while others form ionic.
• LiOH is weak base while others are strong.	• Does not exhibit coordination number more than four.
• Ability to form hydrates $LiCl \cdot 2H_2O$	• Oxide and hydroxide of Be are amphoteric in nature.
• $LiNO_3$ forms the oxide on gentle heating while others form nitrites. $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$ $2NaNO_3 \rightarrow 2NaNO_2 + O_2$	• Be_2C reacts with water, forming methane while others give alkyne. $Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + \underset{\text{Methane}}{CH_4}$ $Mg_2C_3 + 4H_2O \rightarrow 2Mg(OH)_2 + \underset{\text{Propyne}}{C_3H_4}$

The Biological Significance of the Cations Na^+ and K^+

- Sodium and potassium are present in biological fluids. The most remarkable feature of Na^+ and K^+ ions is the development and functional features of nerve cells. In the resting state, a nerve cell shows a potential corresponding to the potassium ion concentration across the membrane. During activation of nerve cells, a chemical, acetyl-choline, is released near its end plate and the membrane potential is discharged. This discharge is transmitted through the length of the nerve cell by an electric pulse. This action illustrates the importance of Na^+ and K^+ ions.

- Na^+ and K^+ are most common cations in biological fluids.
- The ratio of K^+ to Na^+ in red blood cells (RBC's) is 7 : 1 in mammals such as human beings, rabbits, rats and horses, whereas it is 1 : 15 in cats and dogs.

Compounds of Calcium

Calcium Hydroxide (Slaked Lime) ; $Ca(OH)_2$

Preparation :

- $CaO + H_2O \longrightarrow Ca(OH)_2$
- $CaCl_2 + 2NaOH \longrightarrow Ca(OH)_2 + 2NaCl$

Properties :

- White amorphous powder, spraringly soluble in water.
- Its aqueous solution is known as lime water and suspension of it in water is known as milk of lime.
- $Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{(Milkiness)}}{CaCO_3} + H_2O$
- $2Ca(OH)_2 + 2Cl_2 \longrightarrow \underbrace{CaCl_2 + Ca(OCl)_2}_{\text{Bleaching Powder}} + 2H_2O$
- $CaCO_3 + H_2O + CO_2 \longrightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2}$

Uses :

- In the manufacture of bleaching powder.
- For absorbing acidic gases.
- For detection of CO_2.
- As a disinfectant.

Calcium Oxide (Quick Lime) ; CaO

Preparation : $CaCO_3 \xrightleftharpoons{\Delta} CaO + CO_2$

Properties :

- It is a white amorphous solid.
- On heating in oxyhydrogen flame, emits brilliant white light (known as limelight).
- When exposed to atmosphere,
  $CaO + \underset{\text{(Moisture)}}{H_2O} \rightarrow \underset{\text{(Slaked Lime)}}{Ca(OH)_2}$; $CaO + CO_2 \rightarrow \underset{\text{(Limestone)}}{CaCO_3}$
- Being a basic oxide, can combine with acidic impurities.
  $CaO + SiO_2 \xrightarrow{\Delta} CaSiO_3$

Uses :

- Purification of sugar.
- Important constituent of cement, mortar, caustic soda lime (CaO + NaOH) etc.

Calcium Carbonate (Limestone) ; $CaCO_3$

Preparation :

- From slaked lime : $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$
- From calcium chloride :
  $CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$

Properties :

- White fluffy solid and insoluble in water.
- $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$
- Liberates CO_2
  $CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2\uparrow + H_2O$
  $CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2\uparrow + H_2O$

Uses :

- In building material, in the manufacturing of quick lime, Na_2CO_3.
- In the extraction of metals.
- As an antacid, abrasive in toothpaste, filler in cosmetics.

Calcium Sulphate (Plaster of Paris) ; $(CaSO_4)_2 \cdot H_2O$

Plaster of Paris is calcium sulphate hemihydrate $CaSO_4 \cdot \frac{1}{2} H_2O$.

Preparation :

- $\underset{\text{Gypsum}}{2(CaSO_4 \cdot 2H_2O)} \xrightarrow[393\text{ K}]{\Delta} \underset{\text{Plaster of Paris}}{2(CaSO_4) \cdot H_2O} + 3H_2O$
  $2(CaSO_4).H_2O \xrightarrow{473\text{ K}} \underset{\text{(Dead burnt plaster)}}{2CaSO_4 + H_2O}$

Properties :

- It is white powder.
- On mixing with water, it sets into hard mass after sometime.
  $(CaSO_4)_2 \cdot H_2O + 3H_2O \longrightarrow \underset{\text{Gypsum}}{2(CaSO_4 \cdot 2H_2O)}$

Uses :

- For producing moulds for pottery, ceramic etc.
- For making statues, models and other decorative materials.
- In surgical bandages.
- In dentistry.

Cement

It was first introduced in England in 1824 by Joseph Aspdin. It is also called Portland cement because it resembles with the famous building store found near Portland in England. It is a finely ground mixture of calcium silicates and aluminates which set to a hard mass when treated with water.

Composition of Cement

CaO = 50-60%	MgO = 2-3%	SiO_2 = 20-25%
Fe_2O_3 = 1-2%	Al_2O_3 = 5-10%	SO_3 = 1-2%