# FOCUS

Class XI

# NEET/JEE 2019

Focus more 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.

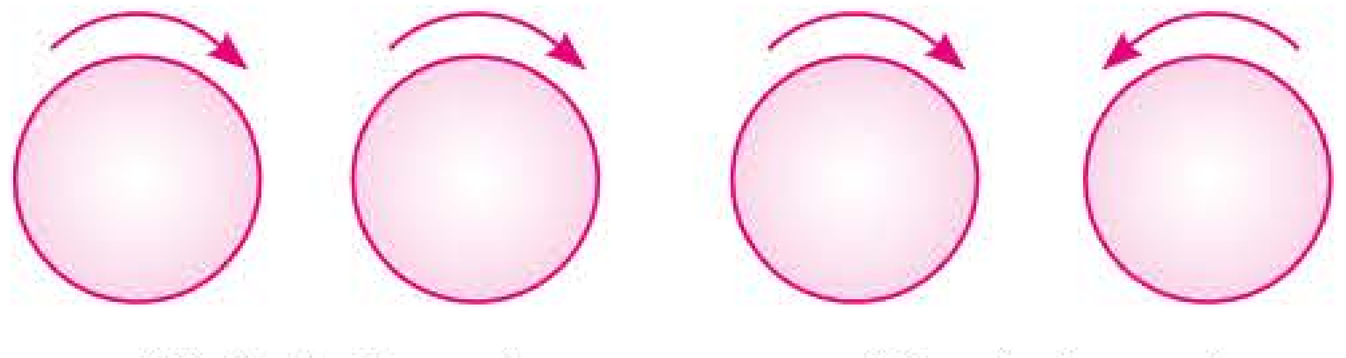
## UNIT - 5 : Hydrogen | The *s*-Block Elements

## HYDROGEN

- Hydrogen is the lightest element. It has the simplest electronic configuration, $1s^1$.
- Hydrogen resembles both alkali metals (loses one electron to form unipositive ion, form oxides, halides and sulphides) and halogens (forms diatomic molecule, hydrides and large number of covalent compounds).

### ALLOTROPES OF HYDROGEN

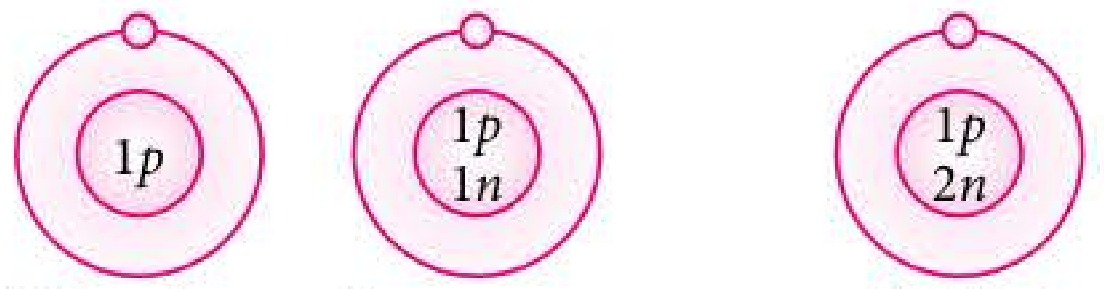
- Two allotropes of hydrogen are *Ortho* hydrogen and *para* hydrogen.



(*Ortho* hydrogen) (*Para* hydrogen)

- At room temperature, ordinary hydrogen contains 75% *ortho*-hydrogen and 25% *para* hydrogen. As the temperature decreases, the percentage of *ortho* hydrogen in the mixture decreases. Pure *para* hydrogen can be prepared by cooling nearly to absolute zero but pure *ortho* hydrogen cannot be prepared.
- **Stability :** *Ortho* hydrogen > *Para* hydrogen
- Differences in physical properties of both is because of differences in internal energy of both. Internal energy of *ortho* $H_2$ > *para* $H_2$.

### ISOTOPES OF HYDROGEN

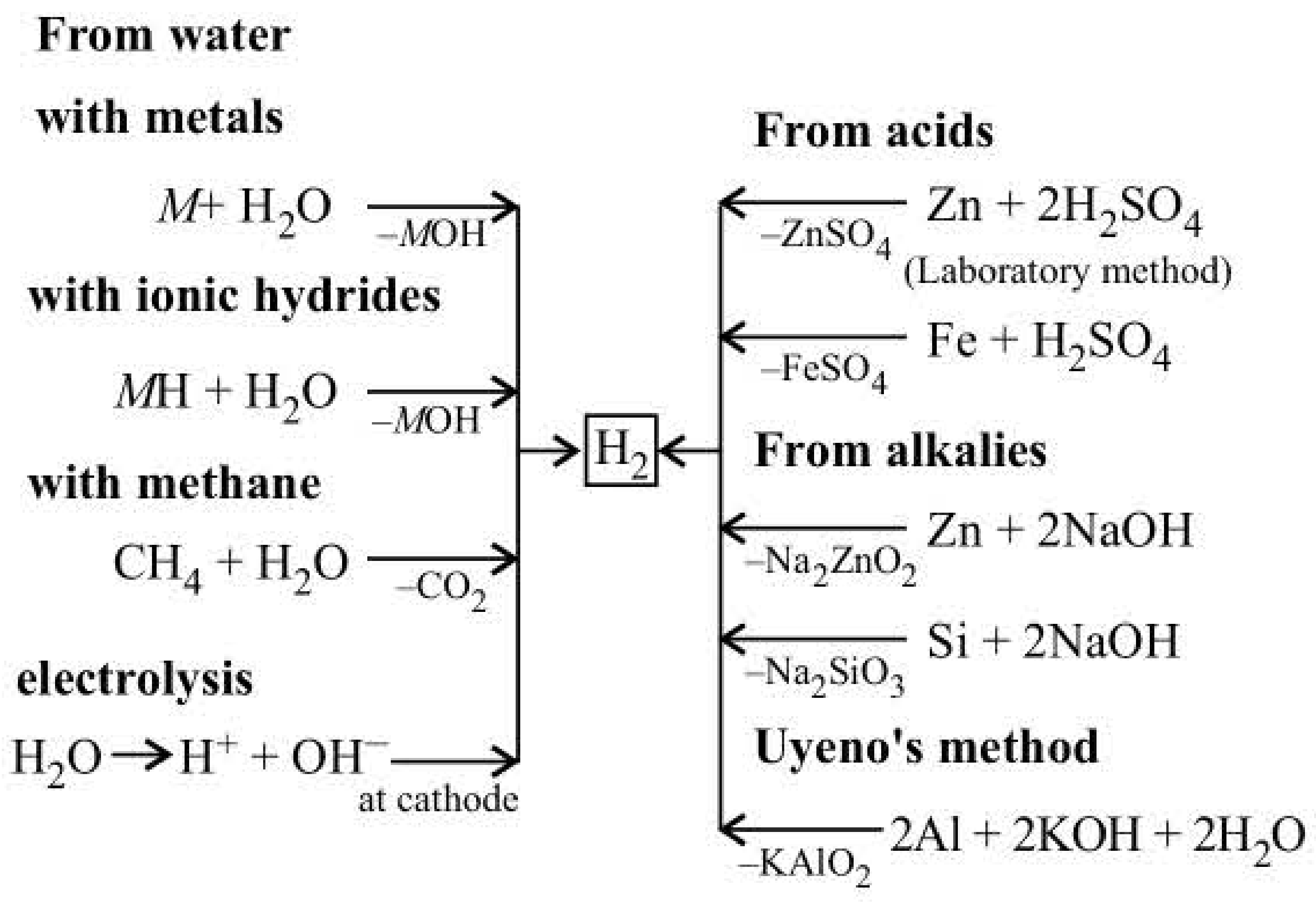


$^1_1H$ Protium (Hydrogen) $^2_1H$ Deuterium (Heavy hydrogen) $^3_1H$ Tritium (Radioactive hydrogen)

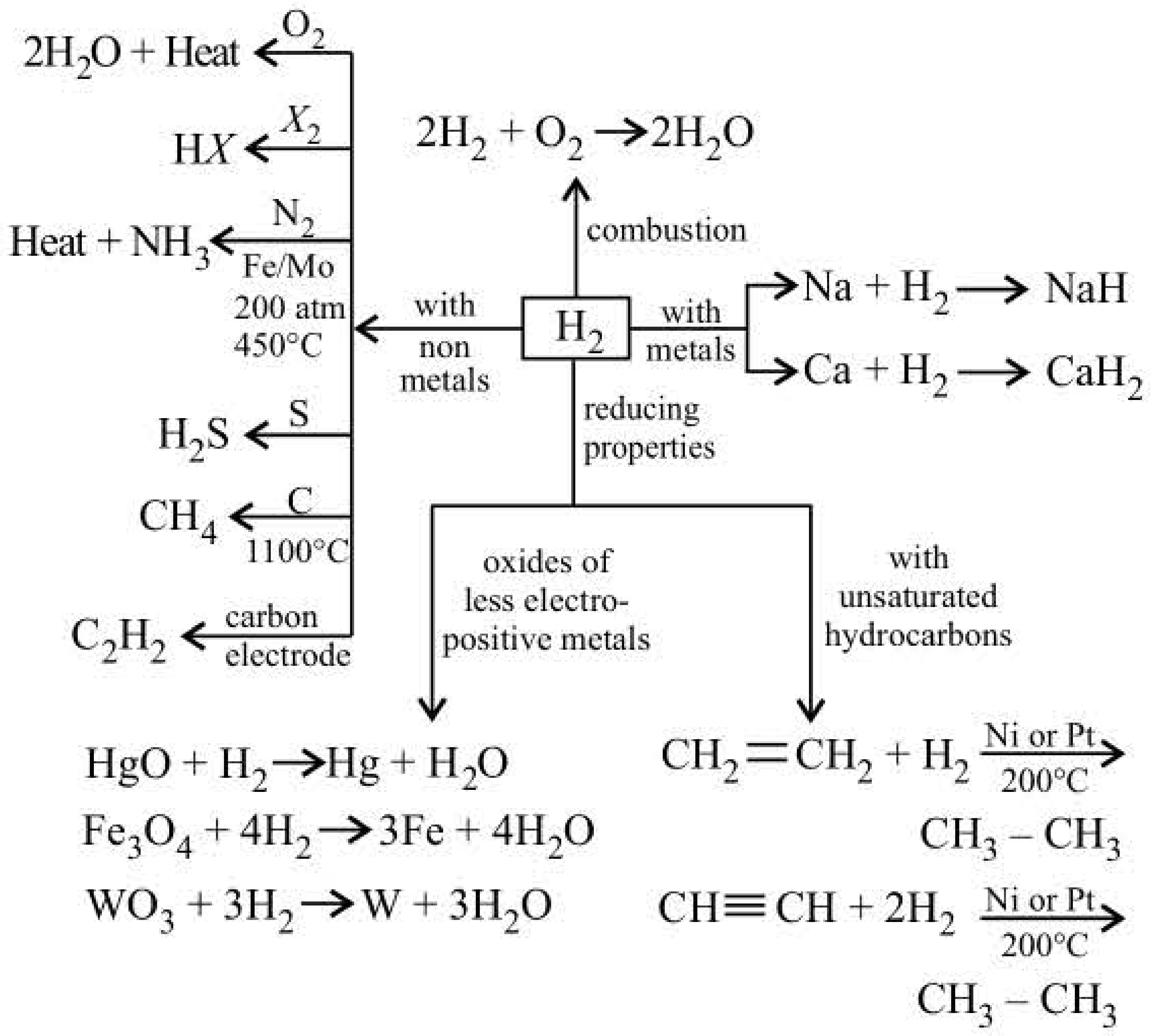
- **Molecular forms :** $^1H_2$ (dihydrogen) $^2H_2$ or $D_2$ (dideuterium) ; $^3H_2$ or $T_2$ (ditritium) alongwith HD, HT, DT, etc.

| Name | Symbol | Atomic mass | *p* | *n* | Abundance % | Nuclear stability | Nuclear spin quantum number | Relative atomic mass |
|---|---|---|---|---|---|---|---|---|
| Protium | $^1_1H$(H) | 1 | 1 | 0 | 99.986 | Stable | 1/2 | 1.007825 |
| Deuterium | $^2_1H$(D) | 2 | 1 | 1 | 0.014 | Stable | 1 | 2.014102 |
| Tritium | $^3_1H$ (T) | 3 | 1 | 2 | $7 \times 10^{-16}$ | Radioactive | 1/2 | 3.106049 |

## PREPARATION OF HYDROGEN



## CHEMICAL PROPERTIES OF HYDROGEN



## HYDRIDES

Hydrogen forms 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. except Be and Mg. $BeH_2$, $MgH_2$ have slightly covalent polymeric structure.
- They are powerful reducing agents, especially at high temperatures.
- LiH and NaH have been used in synthesis of other useful hydrides.
  $8LiH + Al_2Cl_6 \xrightarrow[ether]{Dry} 2LiAlH_4 + 6LiCl$ ; $2NaH + B_2H_6 \xrightarrow[ether]{Dry} 2NaBH_4$

### 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.

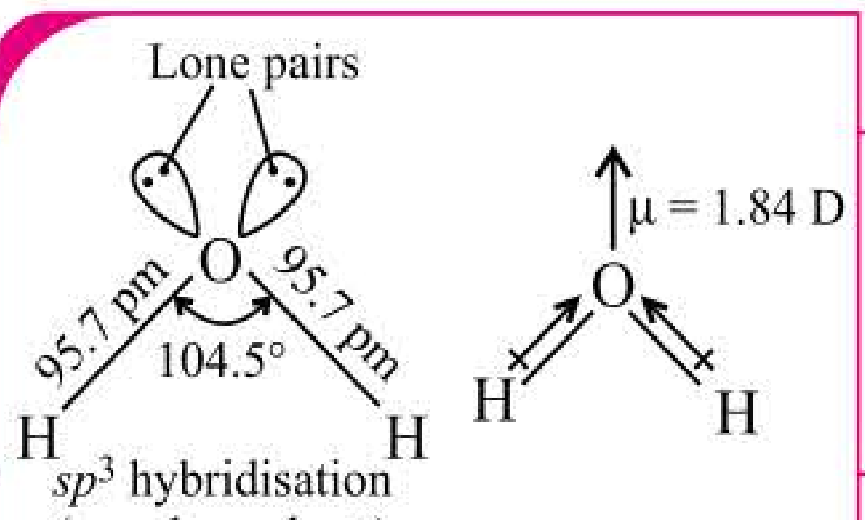
### Covalent or Molecular Hydrides

- *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.

## WATER, $H_2O$

Colourless, odourless and tasteless liquid, gives bluish tinge in thick layers.

Plays a key role in the biosphere due to its high specific heat, thermal conductivity, surface tension, dipole moment and dielectric constant, etc.



$sp^3$ hybridisation (angular or bent)

Extensive hydrogen bonding leads to high freezing point, high boiling point, high heat of vaporisation and high heat of fusion in comparison to $H_2S$ and $H_2Se$.

Water has maximum density at 277 K as above this temperature, the increase in volume due to expansion of liquid water is much more than the decrease in volume due to breaking of H-bonds.

### Chemical Properties

| W | **Amphoteric nature** |
|---|---|
| A | $\underset{\text{Acid}}{H_2O} + \underset{\text{Base}}{NH_3} \rightleftharpoons OH^- + NH_4^+$<br>$\underset{\text{Base}}{H_2O} + \underset{\text{Acid}}{H_2S} \rightleftharpoons H_3O^+ + HS^-$<br>However, water is neutral towards litmus and its pH is 7. |
| | **Redox reactions** |
| T | $2Na + 2H_2O \longrightarrow 2NaOH + H_2$<br>$6CO_2 + 12H_2O \longrightarrow C_6H_{12}O_6 + 6H_2O + 6O_2$<br>$2F_2 + 2H_2O \longrightarrow 4H^+ + 4F^- + O_2$ |
| | **Hydrolysis reactions** |
| E | $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$<br>$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$<br>$N^{3-} + 3H_2O \longrightarrow NH_3 + 3OH^-$ |
| | **Hydrate formation** |
| R | Coordinated water : $[Cr(H_2O)_6]^{3+}3Cl^-$<br>Interstitial water : $BaCl_2 \cdot 2H_2O$<br>Hydrogen-bonded water : $[Cu(H_2O)_4]^{2+}SO_4^{2-} \cdot H_2O$ in $CuSO_4 \cdot 5H_2O$<br>(Only one $H_2O$ which is outside the coordination sphere is hydrogen bonded, other four are coordinated.) |

### Hard and Soft Water

Depending upon its behaviour towards soap solution water may be classified as soft water and hard water.

- **Soft Water :** Water that produces lather with soap readily is called soft water. *e.g.*, rain water, distilled water.
- **Hard Water :** Water which does not produce lather with soap readily is called hard water. *e.g.*, sea water, river water.

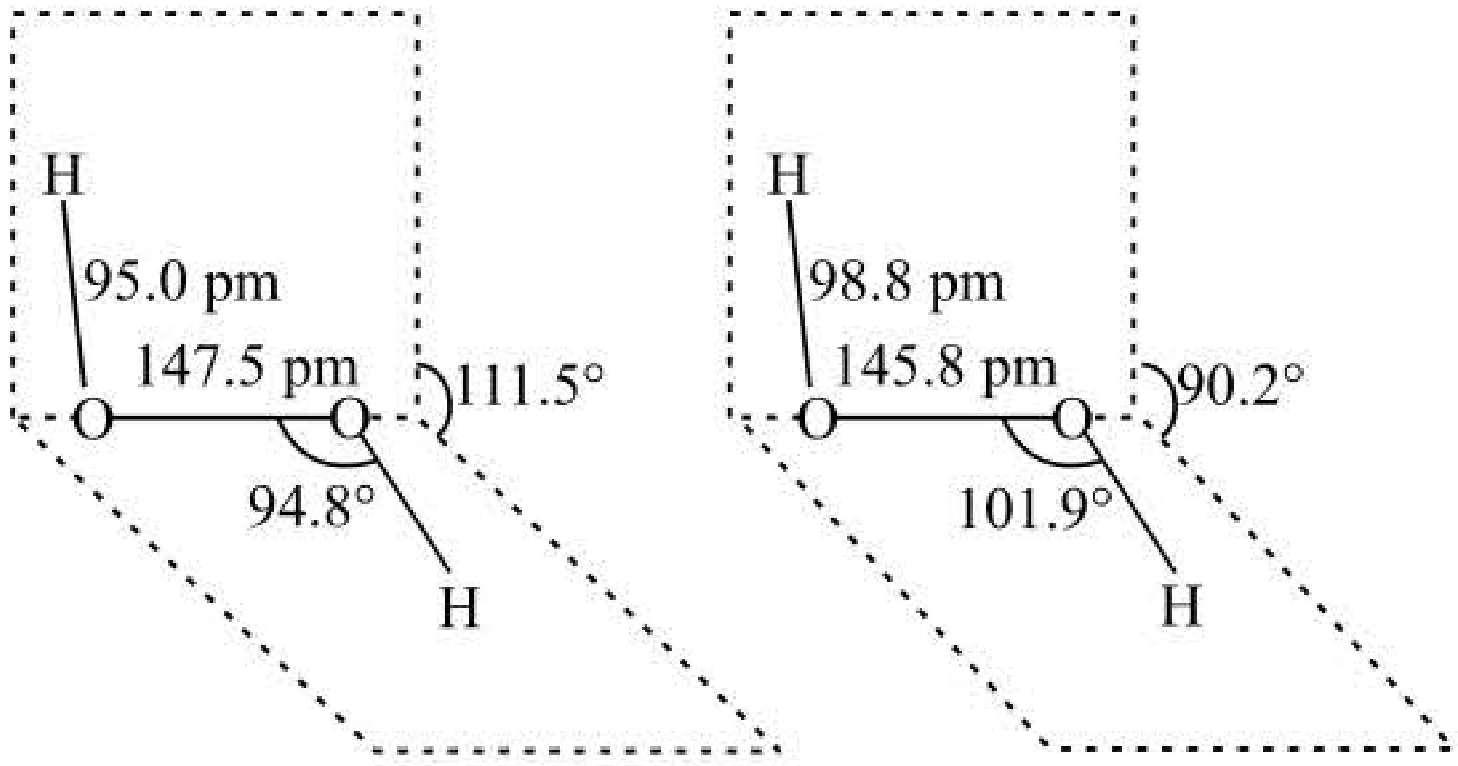
### Hardness of Water

| Temporary hardness | Permanent hardness |
|---|---|
| It is due to the presence of bicarbonates of calcium and magnesium. | It is due to the presence of soluble chlorides and sulphates of calcium and magnesium. |
| It can be easily removed by boiling or by Clark's process (using quick lime). | It can be removed by special methods like washing soda method, ion-exchange method and Calgon's process. |

## HYDROGEN PEROXIDE, $H_2O_2$

- Pure $H_2O_2$ is an almost colourless, odourless, bitter taste liquid but gives a bluish tinge in thick layers.
- $H_2O_2$ is miscible in water in all proportions and forms a hydrate $H_2O_2.H_2O$.
- The dipole moment of $H_2O_2$ is little more (2.1 D) than that of $H_2O$ (1.84 D).

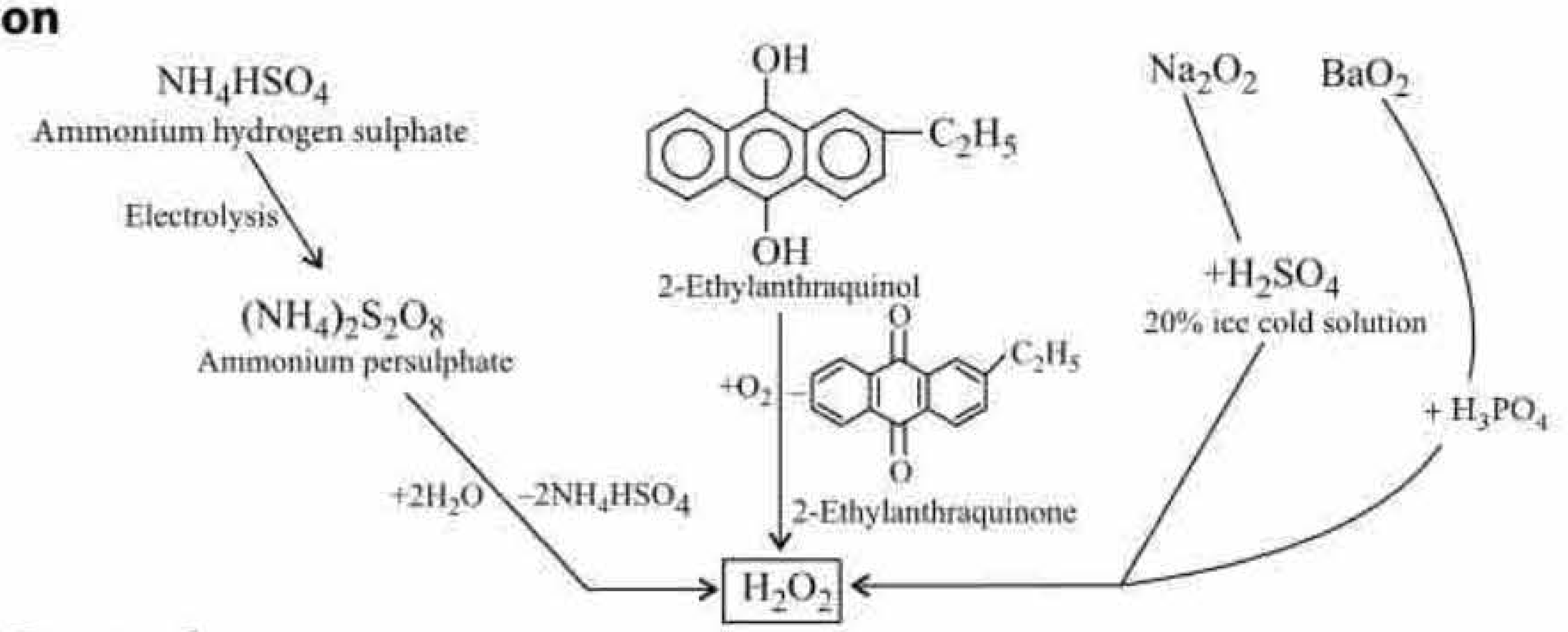
### Structure of $H_2O_2$



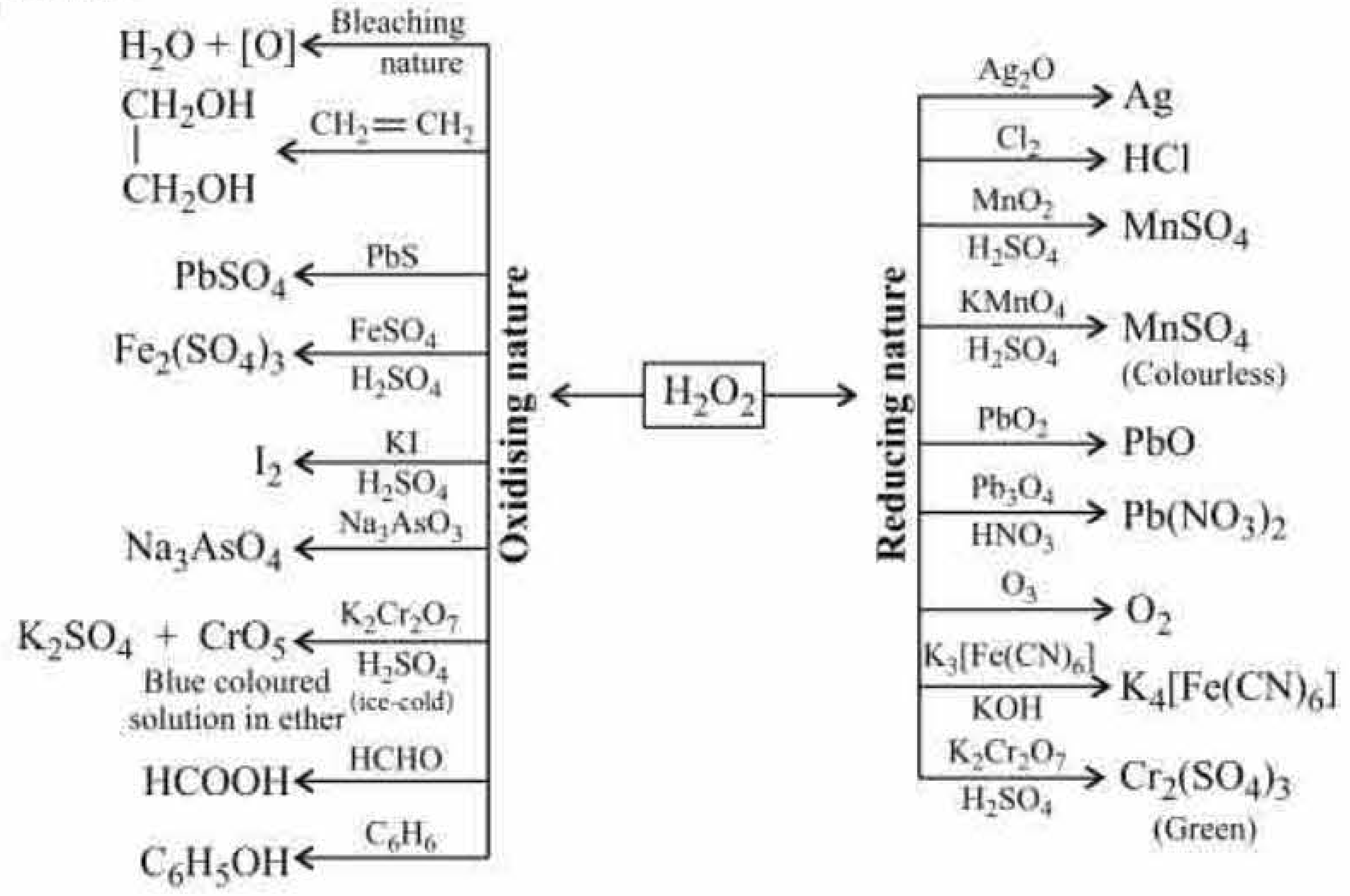
Gas phase

Solid phase

## Preparation



## Chemical Properties



## Strength of $H_2O_2$ Solution

- Volume strength = 5.6 × Normality

$$= 5.6 \times \frac{\text{Percentage strength}}{\text{Eq.wt of } H_2O_2 (i.e., 17)} \times 10$$

$$= 5.6 \times \frac{\text{Strength in gL}^{-1}}{\text{Eq.wt of } H_2O_2 (i.e., 17)}$$

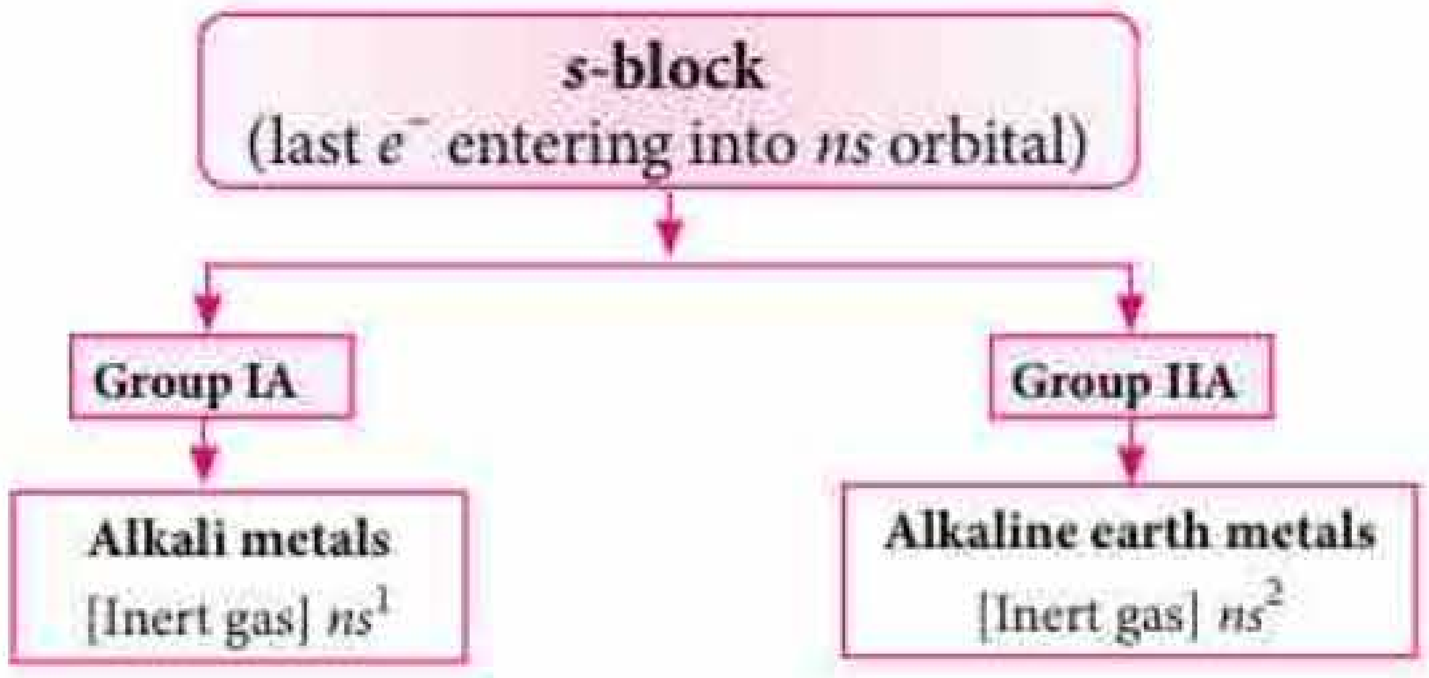
- Volume strength = 11.2 × Molarity

$$= 11.2 \times \frac{\text{Percentage strength}}{\text{Mol.wt of } H_2O_2 (i.e., 34)} \times 10$$

$$= 5.6 \times \frac{\text{Strength in gL}^{-1}}{\text{Eq.wt of } H_2O_2 (i.e., 17)}$$

- % strength = Volume strength × 0.3035

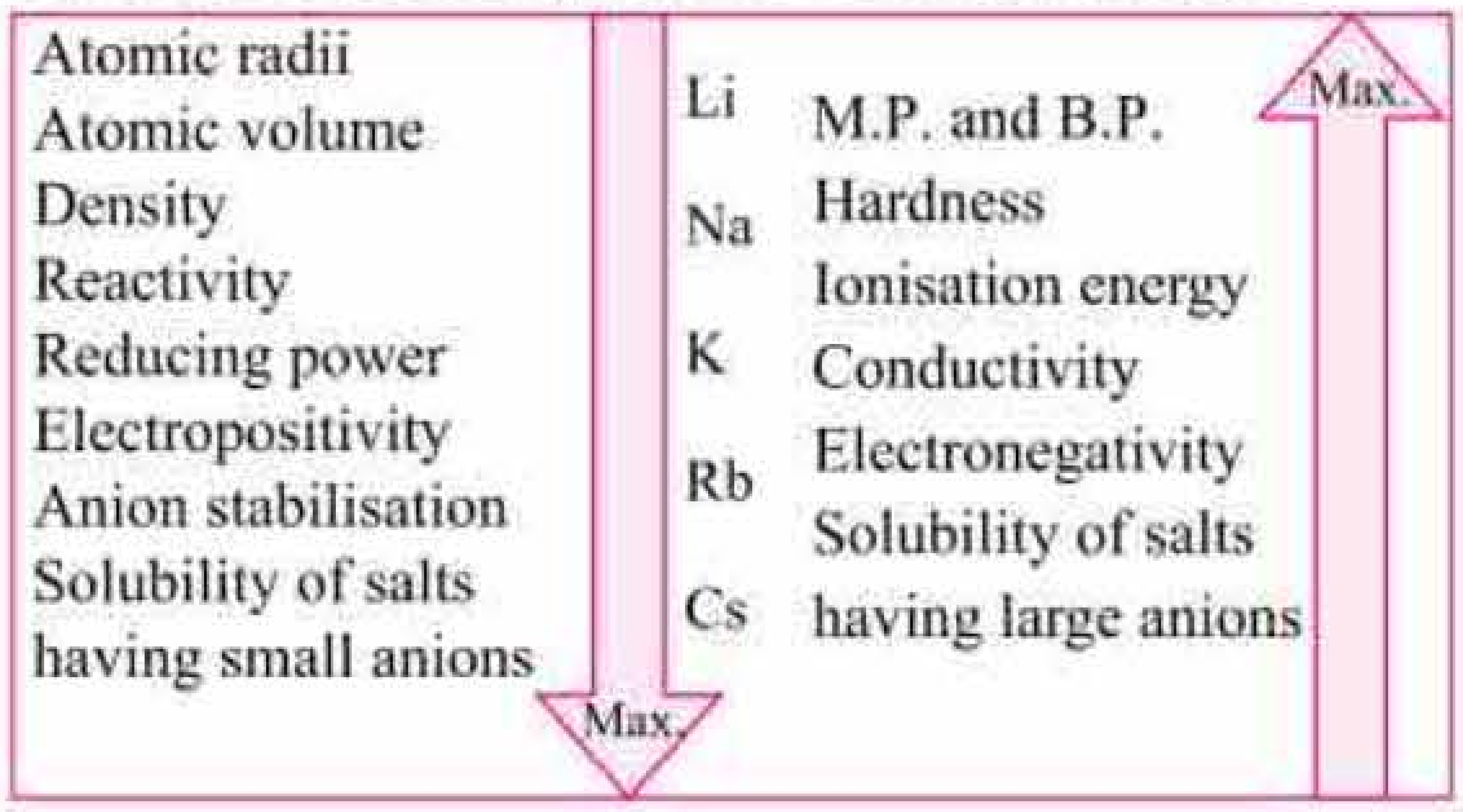
## THE *s*-BLOCK ELEMENTS



### GROUP IA – ALKALI METALS

- The group IA elements are known as alkali metals because hydroxides of these metals are soluble in water and their solution is alkaline in nature. Their valence shell electronic configuration is $ns^1$. Alkali metals are strongly reactive and lose their valence shell electron in order to attain nearest noble gas configuration.

## Gradation in Properties of Alkali Metals



## Chemical Properties

| | |
|---|---|
| **Li** | **Reaction with water**<br>$M + H_2O \longrightarrow MOH + \frac{1}{2}H_2$ |
| **Na** | **Reaction with excess of oxygen**<br>$4Li + O_2 \longrightarrow 2Li_2O$<br>$2Na + O_2 \longrightarrow Na_2O_2$<br>$M + O_2 \longrightarrow MO_2$ ($M$ = K, Rb, Cs) |
| | **Reaction with hydrogen**<br>$2M + H_2 \xrightarrow{673\ K} 2MH$<br>$2Li + H_2 \xrightarrow{1073\ K} 2LiH$ |
| **K** | **Reaction with group 15 elements**<br>$3M + P \longrightarrow M_3P$<br>$3M + As \longrightarrow M_3As$<br>$3M + Sb \longrightarrow M_3Sb$ |
| **Rb** | **Reaction with group 16 elements**<br>$2M + S \longrightarrow M_2S$<br>$2M + Se \longrightarrow M_2Se$<br>$2M + Te \longrightarrow M_2Te$ |
| | **Reaction with halogens**<br>$2M + X_2 \longrightarrow 2MX$<br>($M$ = Li, Na, K, Rb, Cs ; $X$ = F, Cl, Br, I) |
| **Cs** | **Reaction with ammonia**<br>$M + (x + y)\,NH_3 \longrightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$ |
| **Fr** | $M + NH_3 \longrightarrow MNH_2 + \frac{1}{2}H_2$ |

**Trends in alkali metals and their compounds**

- **Electropositive character :** Li < Na < K < Rb < Cs
- **Hydration enthalpy :** $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$
- **Solubility and basic character :** LiOH < NaOH < KOH < RbOH < CsOH
- **Reducing character :** Na < K < Rb < Cs < Li
- **Stability of carbonates :** $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$
- **Stability of bicarbonates :** $NaHCO_3 < KHCO_3 < RbHCO_3 < CsHCO_3$

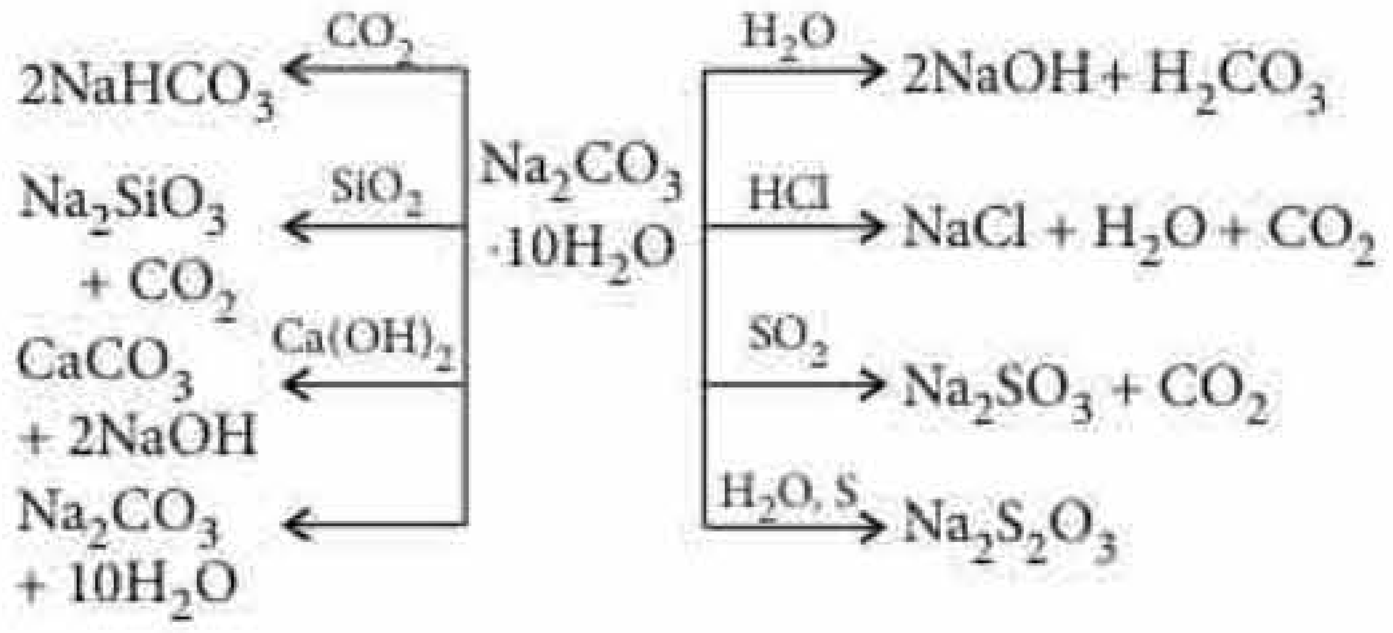
## Anomalous behaviour of Lithium

| All alkali metals | Except |
|---|---|
| Do not react directly with $N_2$ or C. | $Li_3N$ or $Li_2C_2$ |
| Form amide ($MNH_2$) with ammonia. | $Li_2NH$ |
| Nitrates are thermally stable. | $LiNO_3$ |
| Carbonates are thermally stable. | $Li_2CO_3$ |
| Form double salts (alums) from their sulphates. | $Li_2SO_4$ |
| Form acetylides with acetylene. | Li |

## Important Compounds of Sodium

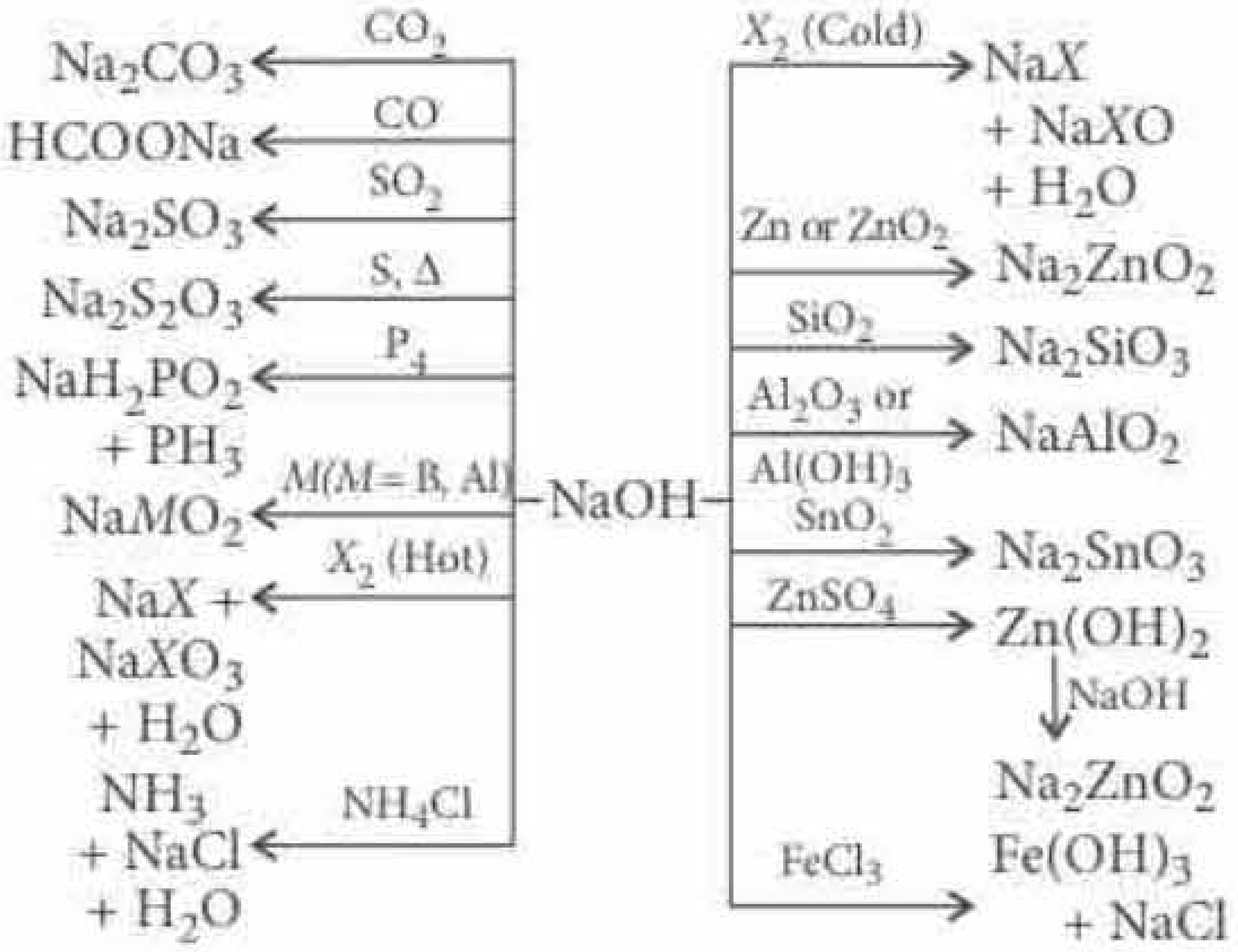
- **Sodium carbonate or Washing soda, $Na_2CO_3 \cdot 10H_2O$**

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

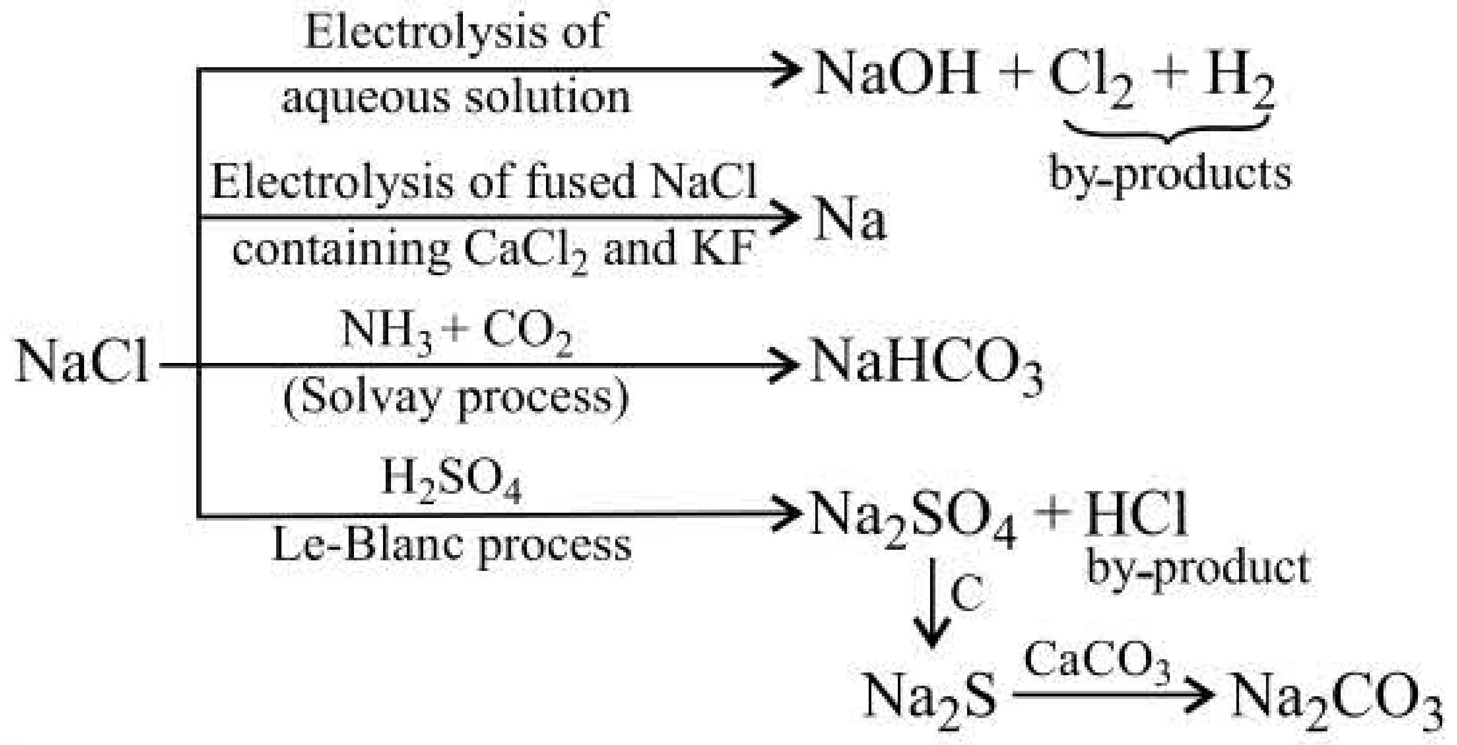


- **Sodium hydroxide or Caustic soda, NaOH**

  Sodium hydroxide is an important compound of chemical industry. This is prepared commercially by the electrolysis of an aqueous solution of sodium chloride using Castner-Kellner cell or Mercury cathode process.



- **Sodium chloride or Table salt, NaCl**
  Sodium chloride is found in abundance in sea water with an average concentration of 3%. NaCl obtained from sea water may have the impurities of $CaSO_4$, $Na_2SO_4$, $CaCl_2$, $MgCl_2$, etc.



- **Sodium hydrogen carbonate or Baking soda, $NaHCO_3$**
  $NaHCO_3$ on heating decomposes to produce bubbles of $CO_2$ which make the cakes and pastries fluffy.

  $2NaHCO_3 \xrightarrow[100°C]{\Delta} Na_2CO_3 + H_2O + CO_2$

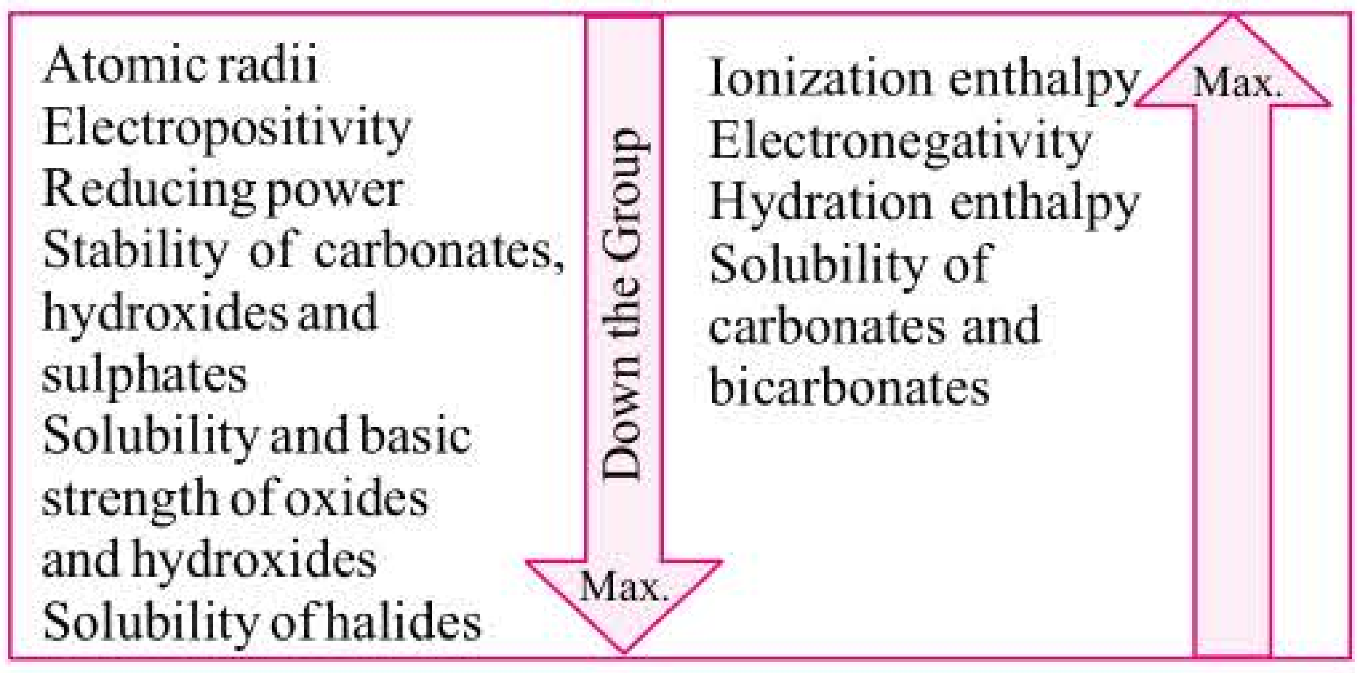
  It is amphiprotic *i.e.*, it can act as $H^+$ donor as well as $H^+$ acceptor.

  $HCO_3^- + H^+ \rightleftharpoons H_2CO_3; HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

## GROUP IIA – ALKALINE EARTH METALS

The name 'alkaline earth' is given to group IIA elements because their oxides form alkaline solution with water (except Be).

### Gradation in Properties of Alkaline Earth Metals



### Chemical Properties

| | |
|---|---|
| **Be** | **Reaction with water**<br>$M + 2H_2O \longrightarrow M(OH)_2 + H_2$ ($M$ = Ca, Sr, Ba) |
| **Mg** | **Reaction with $X_2$ or H$X$**<br>$M + X_2 \longrightarrow MX_2$<br>$M + 2HX \longrightarrow MX_2 + H_2$ |
| **Ca** | **Reaction with oxygen**<br>With quantitative amount of oxygen :<br>$2M + O_2 \xrightarrow{\Delta} 2MO$ ($M$ = Be, Mg, Ca)<br>With excess oxygen :<br>$M + O_2 \longrightarrow MO_2$ ($M$ = Ra, Sr, Ba) |
| **Sr** | **Reaction with hydrogen**<br>$M + H_2 \xrightarrow{\Delta} MH_2$ ($M$ = Mg, Ca, Sr, Ba) |
| **Ba** | **Reaction with group 15 elements**<br>$3M + N_2 \xrightarrow{\Delta} M_3N_2$<br>$3M + 2P \longrightarrow M_3P_2$ |
| **Ra** | **Reaction with group 16 elements**<br>$M + S \longrightarrow MS$<br>$M + Se \longrightarrow MSe$<br>$M + Te \longrightarrow MTe$ |
| | **Reaction with $NH_3$**<br>$M + (x + 2y) NH_3 \longrightarrow [M(NH_3)_x]^{2+} + 2[e(NH_3)_y]^-$<br>$M + 2NH_3 \longrightarrow M(NH_2)_2 + H_2$ |

### Trends in alkaline earth metals and their compounds

- **Hydration enthalpy :** $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$
- **Reducing character :** Be < Mg < Ca < Sr < Ba < Ra
- **Solubility, thermal stability and basic character of hydroxides :** $Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$
- **Solubility of carbonates :** $BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$
- **Stability and ionic character of carbonates :** $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$
- **Solubility of sulphates :** $BeSO_4 > MgSO_4 > CaSO_4 > \underbrace{SrSO_4 > BaSO_4}_{\text{Virtually insoluble}}$

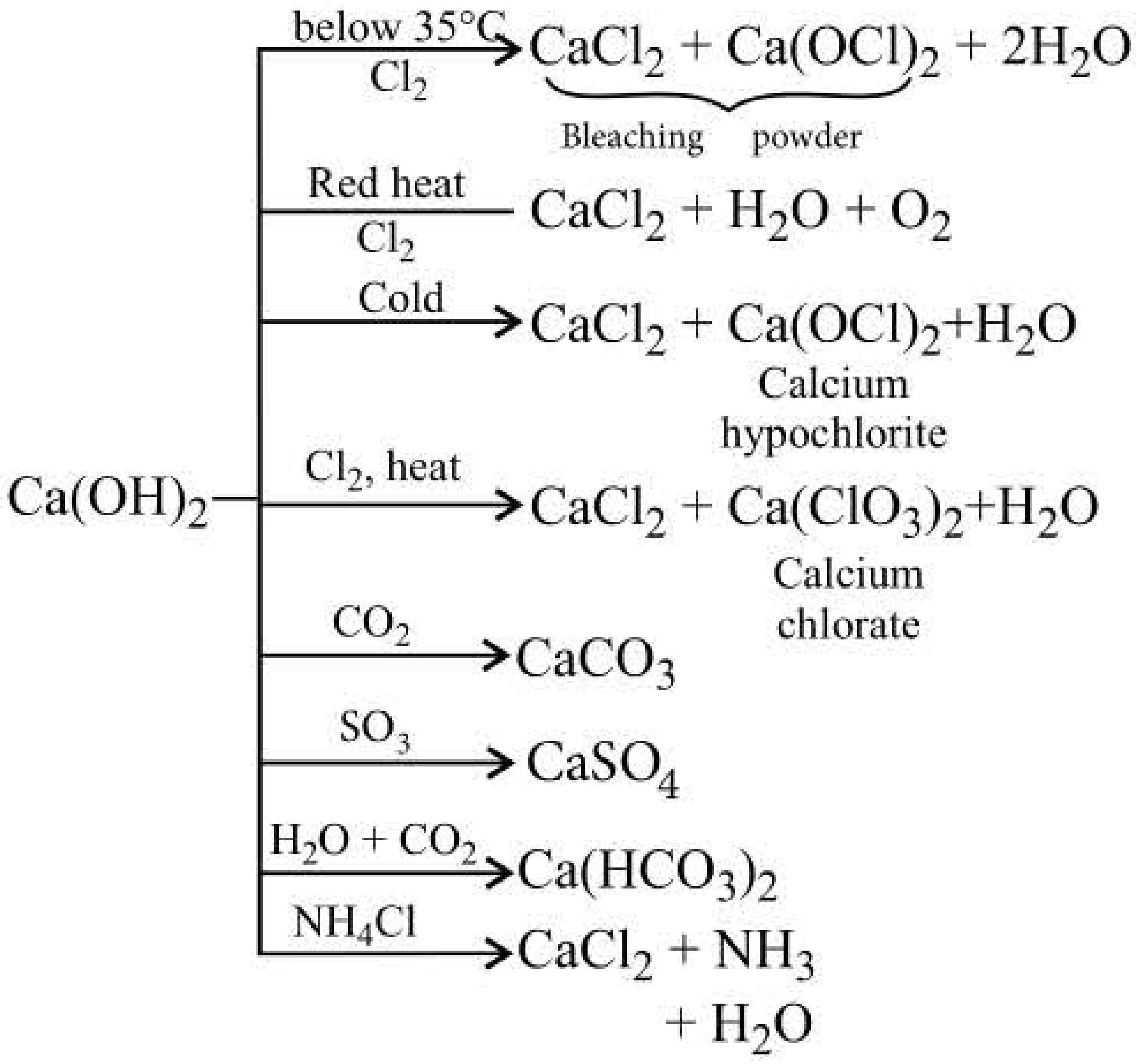
### Anomalous Properties of Beryllium

| Property of Be | Properties of other alkaline earth metals |
|---|---|
| Forms covalent compounds | Form ionic compounds |
| Dissolves in alkalies<br>$Be + 2NaOH + 2H_2O \longrightarrow Na_2BeO_2 \cdot 2H_2O + H_2$ | Does not react with alkalies. |
| Hydroxide of Be is covalent and amphoteric. | Hydroxides are ionic and basic in nature. |

## Important Compounds of Calcium

- **Calcium hydroxide or slaked lime, $Ca(OH)_2$**

  Calcium hydroxide is prepared on a commercial scale by adding water to quick lime. This process is called slaking of lime.



$Ca(OH)_2 \xrightarrow[Cl_2]{below\ 35°C} \underbrace{CaCl_2 + Ca(OCl)_2}_{Bleaching\ powder} + 2H_2O$

$Ca(OH)_2 \xrightarrow[Cl_2]{Red\ heat} CaCl_2 + H_2O + O_2$

$Ca(OH)_2 \xrightarrow{Cold} CaCl_2 + \underset{\text{Calcium hypochlorite}}{Ca(OCl)_2} + H_2O$

$Ca(OH)_2 \xrightarrow{Cl_2,\ heat} CaCl_2 + \underset{\text{Calcium chlorate}}{Ca(ClO_3)_2} + H_2O$

$Ca(OH)_2 \xrightarrow{CO_2} CaCO_3$

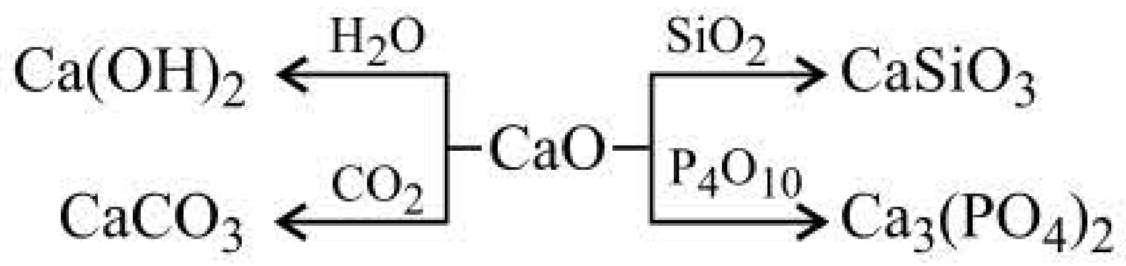
$Ca(OH)_2 \xrightarrow{SO_3} CaSO_4$

$Ca(OH)_2 \xrightarrow{H_2O + CO_2} Ca(HCO_3)_2$

$Ca(OH)_2 \xrightarrow{NH_4Cl} CaCl_2 + NH_3 + H_2O$

- **Calcium oxide or quick lime, CaO**

  Quick lime (CaO) is prepared by strong heating of limestone ($CaCO_3$) in a lime kiln at 1000°C.



$Ca(OH)_2 \xleftarrow{H_2O} CaO \xrightarrow{SiO_2} CaSiO_3$

$CaCO_3 \xleftarrow{CO_2} CaO \xrightarrow{P_4O_{10}} Ca_3(PO_4)_2$

- **Calcium carbonate, $CaCO_3$**

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

  $CaCO_3 \xrightarrow{1200\ K} CaO + CO_2$

  $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$

  $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$

- **Plaster of Paris, $CaSO_4 . 1/2\ H_2O$**

  It is prepared by heating gypsum ($CaSO_4 . 2H_2O$) at 120°C in rotary kilns.

  $2(CaSO_4)\cdot H_2O \xrightarrow[H_2O]{Setting} \underset{\text{Orthorhombic}}{CaSO_4\cdot 2H_2O}$

  $\underset{\text{Monoclinic}}{CaSO_4\cdot 2H_2O} \xleftarrow{Hardening}$

  $2(CaSO_4)\cdot H_2O \xrightarrow[200°C]{\Delta} \underset{\text{Dead plaster}}{CaSO_{4(anhy.)}}$

# SPEED PRACTICE

1. The hydride ion, $H^-$ is a stronger base than hydroxide ion, $OH^-$. Which of the following reactions will occur if sodium hydride (NaH) is dissolved in water?
   (a) $H^-_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)}$
   (b) $H^-_{(aq)} + H_2O_{(l)} \longrightarrow OH^-_{(aq)} + H_{2(g)}$
   (c) $H^- + H_2O \longrightarrow$ No reaction
   (d) None of these

2. Select the incorrect order for given property.
   (a) LiH > NaH > KH > RbH (Thermal stability)
   (b) $Li_2CO_3 > Na_2CO_3 > K_2CO_3$ (Covalent character)
   (c) $BeCO_3 > MgCO_3 > CaCO_3$ (Thermal stability)
   (d) $BeF_2 > MgF_2 > CaF_2 > SrF_2$ (Solubility in water)

3. Hydrogen peroxide oxidises $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ in acidic medium but reduces $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ in alkaline medium. The other products formed are, respectively
   (a) $(H_2O + O_2)$ and $H_2O$
   (b) $(H_2O + O_2)$ and $(H_2O + OH^-)$
   (c) $H_2O$ and $(H_2O + O_2)$
   (d) $H_2O$ and $(H_2O + OH^-)$

4. $NaOH_{(aq)} \xrightarrow{S,\ \Delta} Na_2S +$ Salt (S)

   Salt (S) $\xrightarrow{AgNO_3,\ \Delta} (P) \xrightarrow{H_2O} Q$

   Product (Q) is
   (a) white ppt. (b) black ppt.
   (c) white turbidity (d) clear solution.

5. Select the pair in which both do not give same gas when react with dil. HCl.
   (a) Ca, $CaH_2$ (b) $K_2CO_3$, $KHCO_3$
   (c) $CaCO_3$, $K_2CO_3$ (d) $Ca_3N_2$, $Ca_3P_2$

6. Ionic mobility of which of the following alkali metal ions is lowest when aqueous solution of their salts are put under an electric field?
   (a) K (b) Rb
   (c) Li (d) Na

7. Black ash is
   (a) $CaS + NaHCO_3$ (b) $CaSO_4 + Na_2CO_3$
   (c) $CaSO_4 + NaHCO_3$ (d) $CaS + Na_2CO_3$