

HYDROGEN

Hydrogen and Its Compounds

(1) Position of hydrogen in the periodic table

(2) Discovery and occurrence :

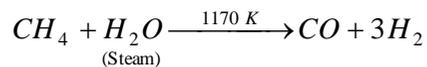
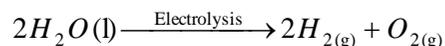
It was discovered by *Henry Cavendish* in 1766. Its name hydrogen was proposed by *Lavoisier*. Hydrogen is the 9th most abundant element in the earth's crust.

(3) Preparation of Dihydrogen : Dihydrogen can be prepared by the following methods,

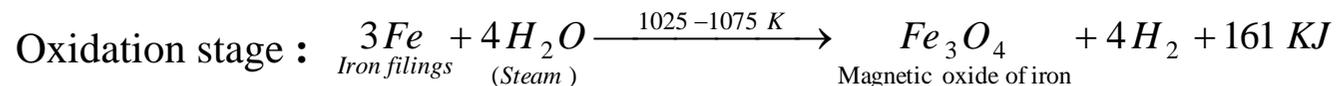
(i) Laboratory method :

granulated Zinc, $Zn + H_2SO_4 \text{ (dil.)} \rightarrow ZnSO_4 + H_2$

(ii) Industrial method



(d) Lane's process : H_2 is prepared by passing alternate currents of steam and water gas over red hot iron. The method consists of two stages,



(4) Physical properties of dihydrogen :

It is a colourless, tasteless and odourless gas.

It is slightly soluble in water. It is highly combustible.

The Physical constants of atomic hydrogen are,

Atomic radius (pm) – 37 ; Ionic radius of H^- ion (pm) – 210; Ionisation energy ($kJ\ mol^{-1}$) – 1312;

Electron affinity ($kJ\ mol^{-1}$) – 72.8; Electronegativity – 2.1.

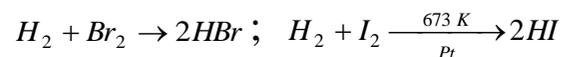
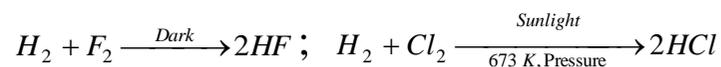
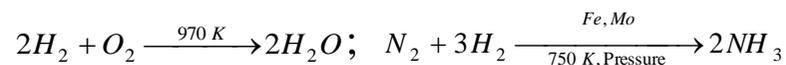
(5) Chemical properties of dihydrogen :

Dihydrogen is quite stable and dissociates into hydrogen atoms only when heated above 2000 K, $H_2 \xrightarrow{2000\text{ K}} H + H$. Its bond dissociation energy is very high, $H_2 \rightarrow H + H$; $\Delta H = 435.9\text{ kJ}\ mol^{-1}$. Due to its high bond dissociation energy, it is not very reactive. However, it combines with many elements or compounds.

(i) **Action with metals** : To forms corresponding hydrides. $2Na + H_2 \xrightarrow{\text{Heat}} 2NaH$; $Ca + H_2 \xrightarrow{\text{Heat}} CaH_2$.

With transition metals (elements of *d* – block) such as *Pd*, *Ni*, *Pt* etc. dihydrogen forms interstitial hydrides in which the small molecules of dihydrogen occupy the interstitial sites in the crystal lattices of these hydrides. As a result of formation of interstitial hydrides, these metals adsorb large volume of hydrogen on their surface. This property of adsorption of a gas by a metal is called **occlusion**. The occluded hydrogen can be liberated from the metals by strong heating.

(ii) **Reaction with Non-metals** :

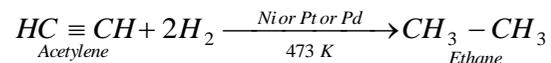
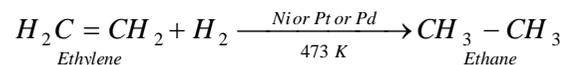


The reactivity of halogen towards dihydrogen decreases as, $F_2 > Cl_2 > Br_2 > I_2$

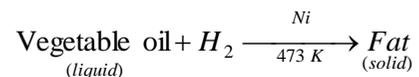
As a result, F_2 reacts in dark, Cl_2 in the presence of sunlight, Br_2 reacts only upon heating while the reaction with I_2 occurs in the presence of a catalyst.

(iii) **Reaction with unsaturated hydrocarbons** :

H_2 reacts with unsaturated hydrocarbons such as ethylene and acetylene to give saturated hydrocarbons.



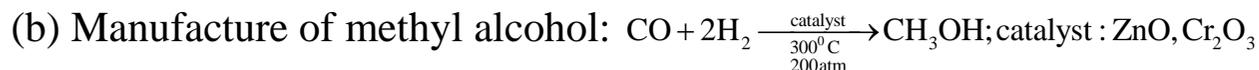
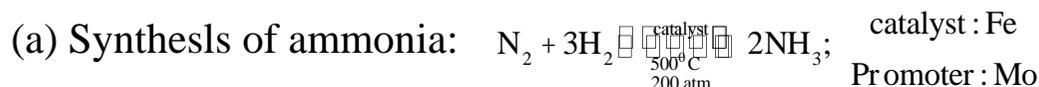
This reaction is used in the **hydrogenation or hardening of oils**.



(6) Uses of Dihydrogen

(i) As a reducing agent, (ii) In the hydrogenation of vegetable oils, (iii) As a rocket fuel in the form of liquid H_2 (iv) In the manufacture of synthetic petrol, (v) In the preparation of many compounds such as NH_3 , CH_3OH , Urea etc, (vi) It is used in the oxy-hydrogen torch for welding if temperature around $2500^\circ C$ is required. It is also used in atomic hydrogen torch for welding purposes in which temperature of the order of $4000^\circ C$ is required.

(7) Applications of Dihydrogen



(d) Hydrogenation of oils: Hydrogen is chiefly used in catalytic hydrogenation of unsaturated (liquid) oils into solid fats for the production of vegetable ghee

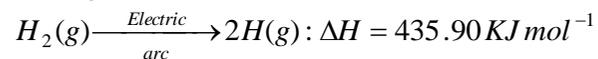
- (e) Synthetic petrol: Petrol substitutes are obtained by subjecting a paste of powdered coal in crude oil to the action of hydrogen under pressure and in presence of catalyst
- (f) Oxy-hydrogen flame. Oxy-hydrogen flame produces a temperature of 2800°C while oxy-atomic hydrogen flame produced a temperature of 4000°C . The heat generated is used for melting substances having very high melting points such as quartz, platinum etc, and also for welding purposes.
- (g) Hydrogen is used for creating a reducing atmosphere in processes like annealing and deoxidizing
- (h) With Helium, it is used for filling balloons employed for atmospheric study.

Different forms of hydrogen

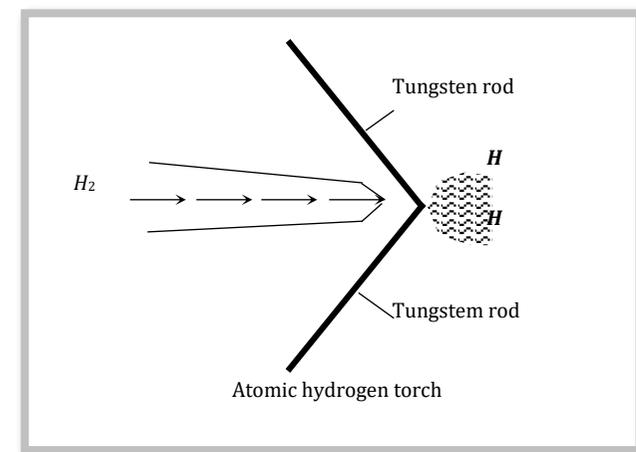
(1) Atomic hydrogen :

It is obtained by the dissociation of hydrogen molecules. The atomic hydrogen is stable only for a fraction of a second and is extremely reactive. It is obtained by passing dihydrogen gas at atmospheric pressure through an electric arc struck between two tungsten rods.

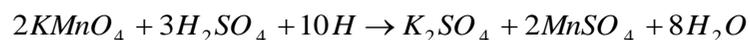
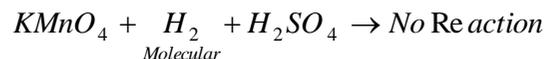
The electric arc maintains a temperature around $4000 - 4500^{\circ}\text{C}$. As the molecules of dihydrogen gas pass through the electric arc, these absorb energy and get dissociated into atoms as



This arrangement is also called atomic hydrogen torch.



(2) **Nascent hydrogen** : The hydrogen gas prepared in the reaction mixture in contact with the substance with which it has to react, is called nascent hydrogen. It is also called newly born hydrogen. It is more reactive than ordinary hydrogen. For example, if ordinary hydrogen is passed through acidified $KMnO_4$ (pink in colour), its colour is not discharged. On the other hand, if zinc pieces are added to the same solution, bubbles of hydrogen rise through the solution and the colour is discharged due to the reduction on $KMnO_4$ by nascent hydrogen.



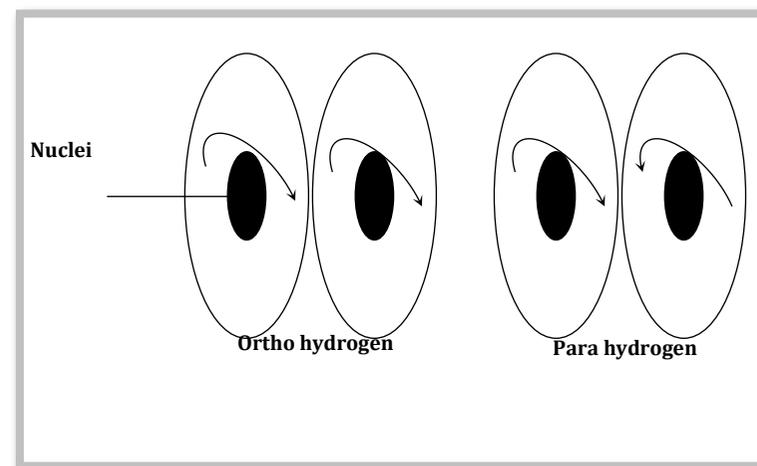
(3) **Ortho and para hydrogen** : Depending upon the direction of the spin of the nuclei, the hydrogen is of two types,

(i) Molecules of hydrogen in which the spins of both the nuclei are in the same directions, called ortho hydrogen.

(ii) Molecules of hydrogen in which the spins of both the nuclei are in the opposite directions, called para hydrogen.

Ordinary dihydrogen is an equilibrium mixture of ortho and para hydrogen. Ortho hydrogen \rightleftharpoons Para hydrogen. The amount of ortho and para hydrogen varies with temperature as,

(a) At $0^\circ K$, hydrogen contains mainly para hydrogen which is more stable.

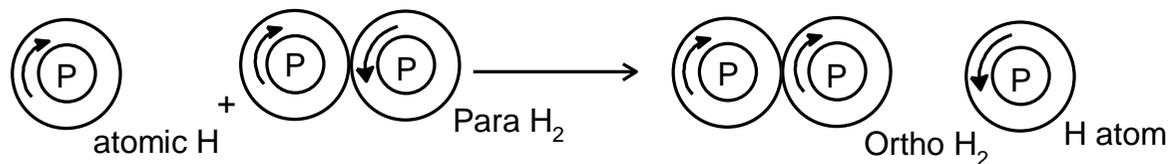


- (b) At the temperature of liquefaction of air, the ratio of ortho and para hydrogen is 1:1.
 - (c) At the room temperature, the ratio of ortho to para hydrogen is 3:1.
 - (d) Even at very high temperatures, the ratio of ortho to para hydrogen can never be more than 3:1.
- Thus, it has been possible to get pure para hydrogen by cooling ordinary hydrogen gas to a very low temperature (close to 20 K) but it is never possible to get a sample of hydrogen containing more than 75% of ortho hydrogen. i.e., Pure ortho hydrogen can not be obtained.

Preparation of Ortho form:

Ortho form is more stable than para and para always tends to revert in ortho form still ortho has not been isolated in the pure form. The conversion of para hydrogen into ortho may be accelerated:

- (a) By heating to 800°C or more
- (b) By the presence of catalysts like Pt or Fe
- (c) By mixing paramagnetic molecules like O_2
- (d) By passing an electric discharge
- (e) By mixing with atomic H_2



Difference in Para and Ortho form: The two forms differ in their physical properties but their chemical properties are same

- (a) Ortho is more stable than para
- (b) Vapour pressure of ortho is more than para
- (c) Sp. Heat of ortho is more than para
- (d) Conductivity of ortho is less than para
- (e) Magnetic moment of para is zero while ortho has twice that of proton

Isotopes of hydrogen

Name	Sym b o l	Atomic numbe r	Mass numbe r	Relative abundance	Nature radioactive or
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					non-radioactive
Protium / Hydrogen	${}^1_1\text{H}$ or H	1	1	99.985%	Non-radioactive
Deuterium	${}^2_1\text{H}$ or D	1	2	0.015%	Non-radioactive
Tritium	${}^3_1\text{H}$ or T	1	3	10^{-15} %	Radioactive

Physical constants of H_2 , D_2 and T_2

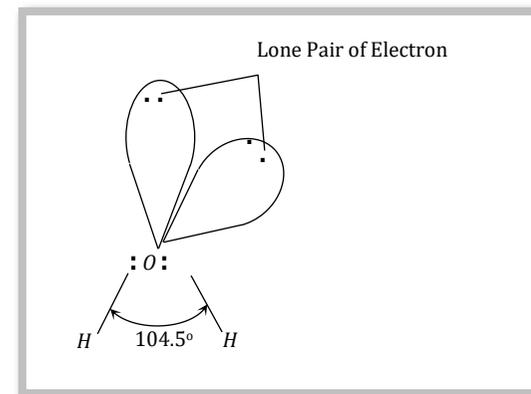
Property	H_2	D_2	T_2
Molecular mass	2.016	4.028	6.03
Melting point (K)	13.8	18.7	20.63
Boiling point (K)	20.4	23.9	25.0
Heat of fusion (kJ mol^{-1})	0.117	0.197	0.250
Heat of vaporisation (kJ mol^{-1})	0.994	1.126	1.393
Bond energy (kJ mol^{-1})	435.9	443.4	446.9

Water

Water constitutes about 65% of our body.

(1) **Structure** : The resultant dipole moment of water molecule is 1.84D.

In ice, each oxygen atom is tetrahedrally surrounded by four hydrogen atoms; **two by covalent bonds and two by hydrogen bonds**. The resulting structure of ice is open structure having a number of vacant spaces. Therefore, the density of ice is less than that of water and ice floats over water. It may be noted that water has maximum density (1 g cm^{-3}) at 4°C .



(2) **Heavy water** : Chemically heavy water is deuterium oxide (D_2O). It was discovered by **Urey**.

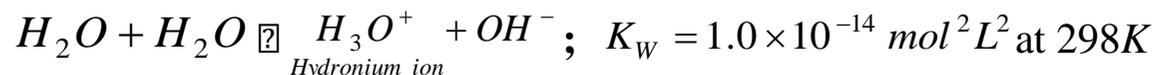
It has been finding use in nuclear reactors as a moderator because it slows down the fast moving neutrons and therefore, helps in controlling the nuclear fission process.

(3) **Physical properties** : Water is colourless, odourless and tasteless liquid at ordinary temperature.

Some physical constants of H₂O and D₂O at 298 K

Constant	Ordinary water H ₂ O	Heavy water D ₂ O
Molecular mass	18.015	20.028
Maximum density (g cm ⁻³)	1.000	1.106
Melting point (K)	273.2	276.8
Boiling point (K)	373.2	374.4
Heat of fusion (kJ mol ⁻¹) at 273K	6.01	6.28
Heat of vaporisation (kJ mol ⁻¹) at 373K	40.66	41.61
Heat of formation (kJ mol ⁻¹)	- 285.9	- 294.6
Ionisation constant	1.008 × 10 ⁻¹⁴	1.95 × 10 ⁻¹⁵

(4) Chemical properties :



(ii) **Amphoteric nature** : Water can act both as an acid and a base and is said to be amphoteric. However, water is neutral towards litmus and its pH is 7.

(iii) **Oxidising and reducing nature** : Water can act both as an oxidising and a reducing agent in its chemical reactions. e.g. $2Na + \underset{\text{Oxidising agent}}{2H_2O} \rightarrow 2NaOH + H_2$; $2F_2 + \underset{\text{Reducing agent}}{2H_2O} \rightarrow 4HF + O_2$

(5) Hard and Soft water

Water which produces lather with soap solution readily is called *soft water*. e.g. distilled water, rain water and demineralised water.

Water which does not produce lather with soap solution readily is called *hard water*. e.g. sea water, river water, well water and tap water.

(i) *Cause of hardness of water :*

The hardness of water is due to the presence of bicarbonates, chlorides and sulphates of calcium and magnesium.

Hard water does not produce lather because the cations (Ca^{+2} and Mg^{+2}) present in hard water react with soap to form insoluble precipitates,

$$M^{+2} + 2C_{17}H_{35}COONa \rightarrow (C_{17}H_{35}COO)_2M + 2Na^+$$

From hard water Sodium stearate (soap) Metal stearate (Ppt.)

Where $M = Ca$ or Mg

Therefore, no lather is produced until all the calcium and magnesium ions are precipitated. This also results into wastage of lot of soap.

(ii) **Type of hardness of water** : The hardness of water is of two types,

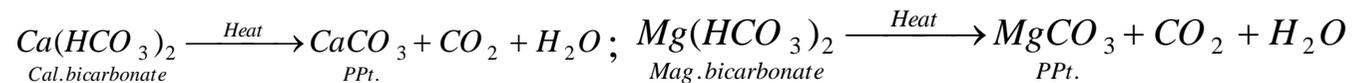
(a) **Temporary hardness** : This is due to the presence of bicarbonates of calcium and magnesium. It is also called carbonate hardness.

(b) **Permanent hardness** : This is due to the presence of chlorides and sulphates of calcium and magnesium. It is also called non-carbonate hardness.

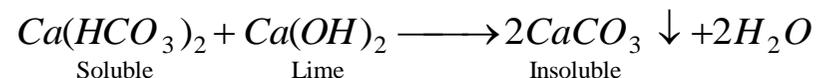
(iii) **Softening of water** : The process of the removal of hardness from water is called softening of water.

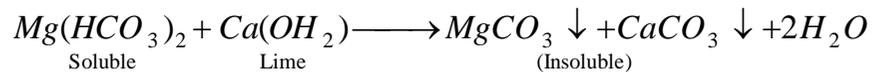
(a) **Removal of temporary hardness** : It can be removed by the following methods,

(i) **By boiling** : During boiling, the bicarbonates of *Ca* and *Mg* decompose into insoluble carbonates and give CO_2 . The insoluble carbonates can be removed by filtration.



(ii) **Clark's method** : This process is used on a commercial scale. In this process, calculated amount of lime [$Ca(OH)_2$] is added to temporary hard water.





(b) *Removal of permanent hardness :*

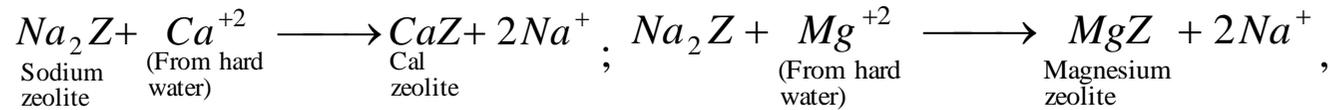
(i) By washing soda method :



(ii) Permutit method :

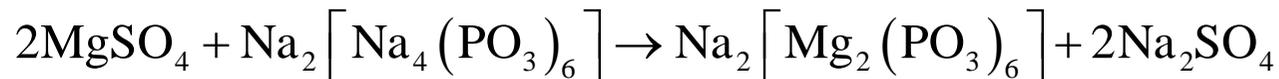
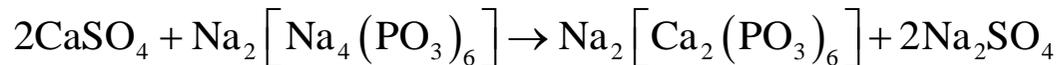
This is a modern method employed for the softening of hard water. hydrated sodium aluminium silicate ($\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$) is called permutit. These complex salts are also known as zeolites.

The permutit is loosely packed in a big tank over a layer of coarse sand. Hard water is introduced into the tank from the top. Water reaches the bottom of the tank and then slowly rises through the permutit layer in the tank. The cations present in hard water are exchanged for sodium ions. Therefore this method is also called ion exchange method.



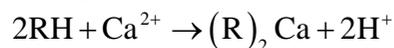
where $Z = \text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$

(iii) Calgon: The complex salt of meta phosphoric acid, sodium hexa meta phosphate $(\text{NaPO}_3)_6$, is known as calgon i.e. $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$. Calcium and magnesium salts present in hard water react with calgon to give complex salts.



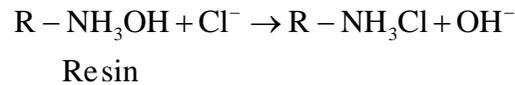
This method is especially used in softening water for boiler use

(iv) Ion exchange resins: Ion exchange resins are the most popular water softeners these days. These resins are synthetic substances. The cation exchanger consists of granular insoluble organic acid resin having giant molecules with $-\text{SO}_3\text{H}$ or $-\text{COOH}$ groups while the anion exchanger contains giant organic molecules with basic groups derived from amines. Ion exchange resins remove all soluble minerals from water. The hard water is first passed through a bed of cation exchanger, which removes the cations like Na^+ , Mg^{+2} , Ca^{+2} and others by exchanging with H^+ ions.



Resin

The water coming from cation exchanger is acidic on account of free H^+ ions. This water is then passed through another bed containing anion exchanger. This exchanger removes anions like Cl^- , SO_4^{2-} , NO_3^- by exchanging with OH^- ions



The OH^- ions neutralize the H^+ ions



Degree of hardness of water: The degree of hardness of water is expressed in terms of ppm (part per million) of $CaCO_3$ i.e.

$$\text{Degree of hardness} = \frac{\text{weight of } CaCO_3}{\text{weight of of } H_2O} \times 10^6$$

(6) Test of water

- (i) Water when added to anhydrous copper sulphate, changes its colour from white to blue
- (ii) Water reacts with CaC_2 to evolve acetylene which burns with bright flame

Hydrogen peroxide

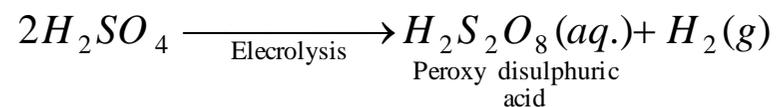
Hydrogen peroxide (H_2O_2) was discovered by French chemist *Thenard*.

(1) **Preparation** : It is prepared by

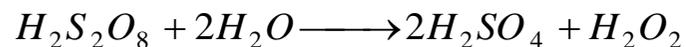
(i) **Laboratory method** :



(ii) **Industrial method** :



This is drawn off from the cell and hydrolysed with water to give H_2O_2 .



(2) Physical properties :

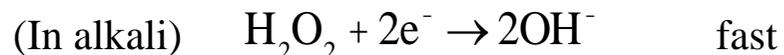
1. Anhydrous H_2O_2 is colourless, viscous liquid soluble in ether, alcohol and water. It gives blue tinge in thick layers
 2. It causes blisters on skin and bitter in taste
 3. Pure H_2O_2 is weak acidic in nature and exist as associated liquid due to hydrogen bonding
 4. Its specific gravity is 1.45 g/ml at 0.C
 5. It is diamagnetic in nature
 6. It boils at 152°C and freezes at 0.89°C . It begins to decompose at b.pt. and thus distilled under reduced pressure
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7. In pure state, its dielectric constant is 93.7 which increases with dilution. Due to high dielectric constant, H_2O_2 and its aqueous solution are good solvent.

(3) Chemical properties

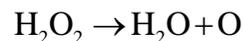
(i) **Decomposition** : Pure H_2O_2 is an unstable liquid and decomposes into water and O_2 either upon standing or upon heating, $2H_2O_2 \longrightarrow 2H_2O + O_2$; $\Delta H = -196.0 kJ$

(ii) **Oxidising nature** : H_2O_2 is a powerful oxidant in acidic as well as in alkaline medium

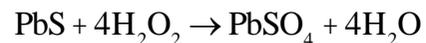


Thus H_2O_2 is more powerful oxidant in alkaline medium.

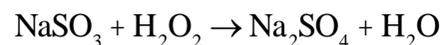
The simple interpretation of H_2O_2 as oxidant can be shown by the equation



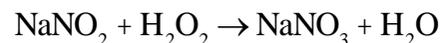
(a). H_2O_2 oxidises black lead sulphide (PbS) to white lead sulphate (PbSO_4)



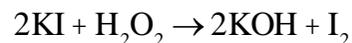
(b). H_2O_2 oxidizes sulphites into sulphates



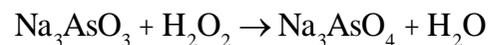
(c). H_2O_2 oxidizes nitrites to nitrates



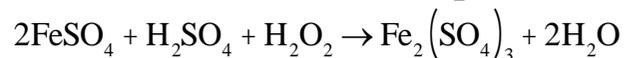
(d). H_2O_2 liberates iodine from potassium iodide



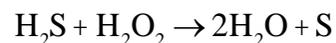
(e). H_2O_2 oxidizes arsenites into arsenates



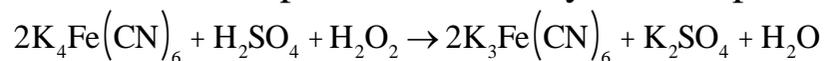
(f). H_2O_2 oxidizes acidified ferrous sulphate to ferric sulphate



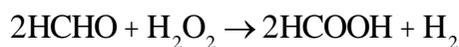
(g). H_2O_2 oxidizes H_2S into sulphur



(h). H_2O_2 oxidizes acidified potassium ferrocyanide to potassium ferricyanide



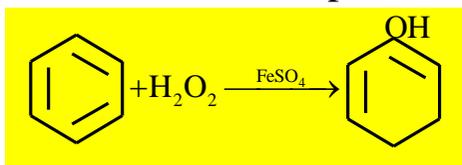
(i). H_2O_2 oxidizes formaldehyde to formic acid in presence of pyrogallol and in alkaline medium



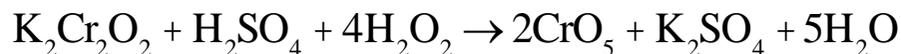
(j). H_2O_2 dissolves the chromic hydroxide precipitate present in NaOH solution forming a yellow solution of sodium chromate



(k). H_2O_2 oxidizes Benzene in presence of ferrous sulphate to phenol



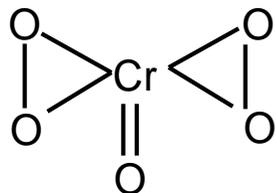
(l). A solution of chromic acid in sulphuric acid or acidified potassium dichromate is oxidized to blue peroxide of chromium (CrO_5) which is unstable, however, it is soluble in ether and produced blue coloured solution



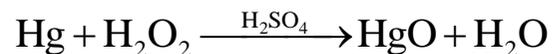
Peroxide of chromium decomposes to form chromic sulphate & oxygen



Peroxide of chromium is represented as



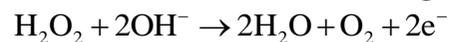
(m) H_2O_2 oxidizes mercury to mercuric oxide in acid solution



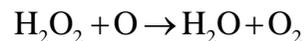
(iii) **Reducing nature** : It can also act as a reducing agent towards powerful oxidising agents



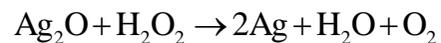
In alkaline solution, however, its reducing action is more effective



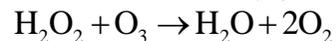
The simple equation when H_2O_2 acts as a reducing agent can be expressed as,



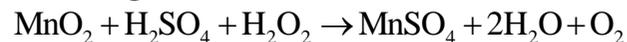
(a) It reduces Ag_2O to silver



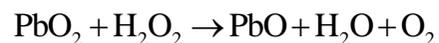
(b) It reduces ozone to oxygen



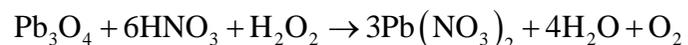
(c) It reduces manganese dioxide in acidic medium to manganese sulphate



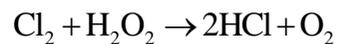
(d) It reduces lead dioxide to lead monoxide



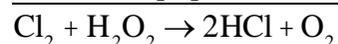
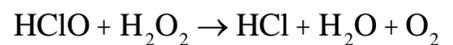
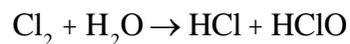
(e) It reduces red lead in presence of HNO_3 to plumbous salt



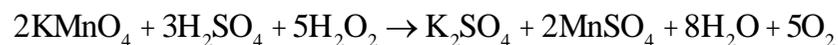
(f) Chlorine and bromine are reduced to corresponding hydric acids



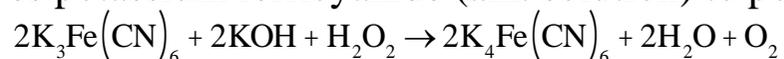
The reaction can be shown in following steps



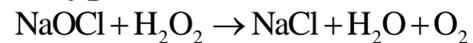
(g) It reduces acidified KMnO_4 solution i.e. acidified KMnO_4 is decolourised by H_2O_2



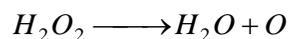
(h) It reduces potassium ferricyanide (alk. solution) to potassium ferrocyanide



(i) It reduces hypohalites to halides



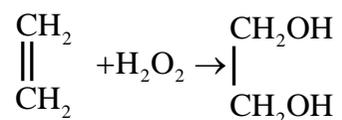
(iv) **Bleaching action** : H_2O_2 acts as a bleaching agent due to the release of nascent oxygen.



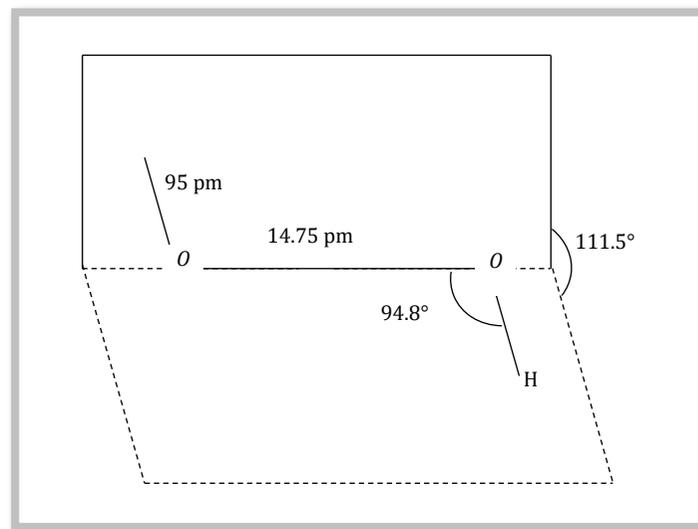
Thus, the bleaching action of H_2O_2 is due to oxidation. It oxidises the colouring matter to a colourless product,
 Colouring matter + $O \rightarrow$ Colour less matter

H_2O_2 is used to bleach delicate materials like ivory, silk, wool, cotton, hair, leather etc.

(v) **Addition reactions**: It shows addition reactions on ethylenic bond



(3) **Structure of H_2O_2** : H_2O_2 has non-planar structure in which two H -atoms are arranged in two directions almost perpendicular to each other and to the axis joining the two oxygen atoms. The $O - O$ linkage is called peroxide linkage.



(5) **Strength of H_2O_2** : The strength of H_2O_2 is expressed in terms of weight or volume,

(i) **As weight percentage** : The weight percentage of H_2O_2 gives the weight of H_2O_2 in 100 g of solution. For example, a 40% solution by *wt.* means 40 g of H_2O_2 are present in 100 g of solution.

(ii) **As volume** : The strength of H_2O_2 is commonly expressed as volume. This refers to the volume of oxygen which a solution of H_2O_2 will give. For example, a “20 volume” of H_2O_2 means that 1 litre of this solution will give 20 litres of oxygen at NTP.

(6) **Uses of H_2O_2**

(i) As germicide and antiseptic for wounds, teeth and ears

(ii) As bleaching agent for wood, hair and other soft materials

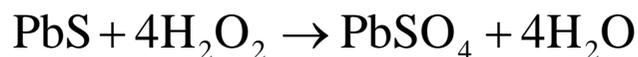
(iii) As preservative for milk and wine

(iv) As fuel for rocket, submarine and torpedo

(v) In refreshing old oil paintings due to the formation of black PbS . H_2O_2 converts it into white $PbSO_4$

white

black

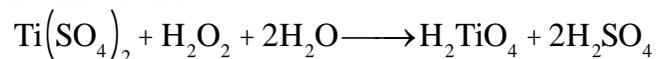


(white)

- (vi) In the detection of Ti^{+4} , V^{+5} and Cr^{+3} ions
- (vii) As antichlor to remove traces of chlorine and hypochlorite

(6) Test of H_2O_2

(i) An acidified solution of titanium salt when treated with H_2O_2 , a yellow or orange colour is developed due to formation of pertitanic acid



(ii) It liberates iodine from KI solution which gives blue colour with starch solution

(iii) It decolourizes acidified $KMnO_4$ solution

(iv) H_2O_2 on shaking with acidified $K_2Cr_2O_7$ with little ether, blue colour is produced (due to formation of peroxide of chromium)

(v) A filter paper with a black stain of PbS on bringing in contact with H_2O_2 solution turns white

S -BLOCK

Alkali Metals and Their Compounds

Element s	Discovery	Electronic configuration (ns^1)
${}_3\text{Li}$	Arfwedson (1817)	$1s^2 2s^1$ or $[\text{He}]^2 2s^1$
${}_{11}\text{Na}$	Davy (1807)	$1s^2 2s^2 2p^6 3s^1$ or $[\text{Ne}]^{10} 3s^1$
${}_{19}\text{K}$	Davy (1807)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ or $[\text{Ar}]^{18} 4s^1$

$_{37}\text{Rb}$	Bunsen (1861)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ or $[\text{Kr}]^{36} 5s^1$
$_{55}\text{Cs}$	Bunsen (1860)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ or $[\text{Xe}]^{54} 6s^1$
$_{87}\text{Fr}$	Percy (1939)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^1$ OR $[\text{Rn}]^{86} 7s^1$

Note : \square Francium is radioactive with longest lived isotope ^{223}Fr with half life period of only 21 minute.

Physical properties

(1) Physical state

- (i) All are silvery white, soft and light solids. These can be cut with the help of knife. When freshly cut, they have bright lustre which quickly tarnishes due to surface oxidation.
- (ii) These form diamagnetic colourless ions since these ions do not have unpaired electrons, (i.e. M^+ has ns^0 configuration). That is why alkali metal salts are colourless and diamagnetic.

(2) Atomic and ionic radii

Li Na K Rb Cs Fr

Atomic radius (pm)	152	186	227	248	265	375
Ionic radius of M^+ ions (pm)	60	95	133	148	169	–

(3) Density

(i) All are light metals, *Li*, *Na* and *K* have density less than water.

The density increases gradually from *Li* to *Cs*, *Li* is lightest known metal among all.

Li = 0.534, *Na* = 0.972, *K* = 0.86, *Rb* = 1.53 and *Cs* = 1.87 g/ml at 20°C.

(iii) *K* is lighter than *Na* because of its unusually large atomic size.

(iv) In solid state, they have body centred cubic lattice.

(4) Melting point and Boiling point

(i) All these elements possess low m.pt and b.pt in comparison to other group members.

	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>	<i>Fr</i>
m.pt (K)	453.5	370.8	336.2	312.0	301.5	–
b.pt (K)	1620	1154.4	1038.5	961.0	978.0	–

(ii) The lattice energy of these atoms in metallic crystal lattice relatively low due to larger atomic size and thus possess low m.pt and b.pt. On moving down the group, the atomic size increases and binding energy of their atoms in crystal lattice decreases which results lowering of m.pt.

(iii) Lattice energy decreases from *Li* to *Cs* and thus m.pt and b.pt also decrease from *Li* to *Cs*.

(5) Ionisation energy & electropositive or metallic character

Ionisation energy	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>	<i>Fr</i>
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IE_1	520	495	418	403	376	–
IE_2	7296	4563	3069	2650	2420	–

Electropositive character increases from *Li* to *Cs*.

Due to their strong electropositive character, they emit electrons even when exposed to light showing **photoelectric effect**. This property is responsible for the use of *Cs* and *K* in photoelectric cell.

(6) Oxidation number and valency

- (i) These elements easily form univalent +ve ion by losing solitary ns^1 electron due to low ionisation energy values.
- (ii) Alkali metals are univalent in nature and form ionic compounds. Lithium salts are, however, covalent.

(7) Hydration of Ions

The energy released when 1 mole of an ion in the gaseous state is dissolved in water to get it hydrated is called hydration energy $M_{(g)}^+ + Aq \rightarrow M_{(aq)}^+ ; \Delta H = -energy$.

Smaller the cation, greater is the degree of hydration.

Hydration energy, $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

Relative ionic radii



Relative hydrated ionic radii



Relative conducting power



(8) Electronegativities

	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>	<i>Fr</i>
Electronegativity	0.98	0.93	0.82	0.82	0.79	

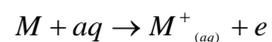
(9) Specific heat :

	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>	<i>Fr</i>
Specific heat (Cal/g)	0.941	0.293	0.17	0.08	0.049	—

(10) **Conduction power** : All are good conductors of heat & electricity, because of loosely held valence electrons.

(11) Standard oxidation potential and reducing properties

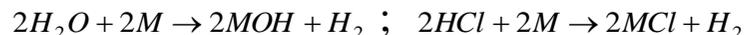
(i) Since alkali metals easily lose ns^1 electron and thus they have high values of oxidation potential i.e.,



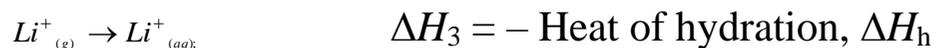
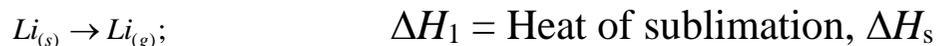
(ii) The standard oxidation potentials of alkali metals (in volts) are listed below,

<i>Li</i>	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>	
+3.05	+2.71		+2.93	+2.99	+2.99

(iii) More is oxidation potential, more is the tendency to get oxidized and thus more powerful is reducing nature in aqueous medium. That is why alkali metals liberate H_2 from H_2O and HCl .



(iv) However, an examination of ionisation energy for alkali metals reveals that Li should have the minimum tendency to lose electron and thus its reducing nature should be minimum. The greatest reducing nature of Li in aq. medium is accounted due to the maximum hydration energy of Li^+ ion. For Lithium



Similarly, for sodium, $Na_{(s)} + H_2O \rightarrow Na^+_{(aq)} + e; \Delta H = \Delta H_s + IE_1 - \Delta H_h$

ΔH_h for $Li > \Delta H_h$ for Na . Therefore, large negative ΔH values are observed in case of Li and this explains for more possibility of Li to get itself oxidized or have reducing nature.

(12) **Characteristic flame colours** : The alkali metals and their salts give characteristic colour to Bunsen flame. The flame energy causes and excitation of the outermost electron which on reverting back to its initial position gives out the absorbed energy as visible light. These colour differ from each other

Li –crimson, Na –Golden yellow, K – Pale violet , Rb and Cs –violet.

Energy released : $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

λ released : $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

Frequency released : $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

Chemical properties

(1) **Occurrence** : Alkali metals are very reactive and thus found in combined state Some important ores of alkali metals are given ahead.

(i) **Lithium** : Triphylite, Petalite, lepidolite, Spodumene [$LiAl(SiO_3)_3$], Amblygonite [$Li(Al F)PO_4$]

(ii) **Sodium** : Chile salt petre ($NaNO_3$), Sodium chloride ($NaCl$), Sodium sulphate (Na_2SO_4), Borax ($Na_2B_4O_7 \cdot 10H_2O$), Glauber salt ($Na_2SO_4 \cdot 10H_2O$)

(iii) **Potassium** : Sylime (KCl), carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) and Felspar ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$)

(iv) **Rubidium** : Lithium ores Lepidolite, triphylite contains 0.7 to 3% Rb_2O

(v) **Caesium** : Lepidolite, Pollucite contains 0.2 to 7% Cs_2O

(2) Extraction of alkali metals :

Fused NaCl : $NaCl \xrightarrow{\text{fusion}} Na^+ + Cl^-$ Electrolysis : Anode : $2Cl^- \rightarrow Cl_2 + 2e^-$
of fused salt : Cathode : $2Na^+ + 2e^- \rightarrow 2Na$

(3) Alloys Formation

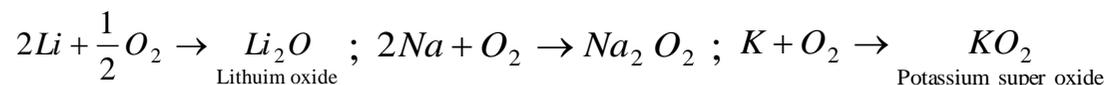
- (i) The alkali metals form alloys among themselves as well as with other metals.
- (ii) Alkali metals also get dissolved in mercury to form amalgam with evolution of heat and the amalgamation is highly exothermic.

(4) Formation of oxides and hydroxides

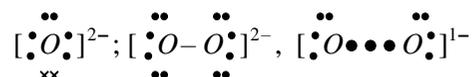
(i) These are most reactive metals and have strong affinity for O_2 quickly tranish in air due to the formation of a film of their oxides on the surface. These are, therefore, kept under kerosene or paraffin oil to protect them from air,



(ii) When burnt air (O_2), lithium forms lithium oxide (Li_2O) sodium forms sodium peroxide (Na_2O_2) and other alkali metals form super oxide (MO_2 i.e. KO_2, RbO_2 or CsO_2)

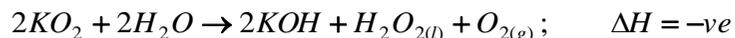
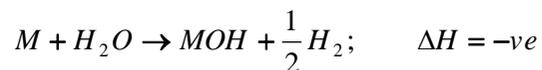


The monoxide, peroxides and superoxides have O^{2-} and o_2^{2-}, o_2^{1-} ions respectively. The structures of each are,



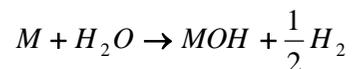
The O_2^{-1} ion has a three electron covalent bond and has one electron unpaired. It is therefore superoxides are paramagnetic and coloured KO_2 is light yellow and paramagnetic substance.

(iii) The oxides of alkali metals and metal itself give strongly alkaline solution in water with evolution of heat



The peroxides and superoxides act as strong oxidising agents due to formation of H_2O_2

(iv) The reactivity of alkali metals towards air and water increases from Li to Cs that is why lithium decomposes H_2O very slowly at $25^\circ C$ whereas Na does so vigorously, K reacts producing a flame and Rb, Cs do so explosively.



(v) The basic character of oxides and hydroxides of alkali metals increases from Li to Cs. This is due to the increase in ionic character of alkali metal hydroxides down the group which leads to complete dissociation and leads to increase in concentration of OH^- ions.

(5) Hydrides



(iii) The metal hydrides react with water to give MOH & H_2 ; $MH + H_2O \rightarrow MOH + H_2$

(iv) The ionic nature of hydrides increases from Li to Cs

Alkali metals also form hydrides like $NaBH_4$, $LiAlH_4$ which are good reducing agent.

(6) Carbonates and Bicarbonates

(i) The carbonates (M_2CO_3) & bicarbonates ($MHCO_3$) are highly stable to heat, where M stands for alkali metals.

(ii) The stability of these salts increases with the increasing electropositive character from Li to Cs. It is therefore Li_2CO_3 decompose on heating, $Li_2CO_3 \rightarrow Li_2O + CO_2$

(iii) Bicarbonates are decomposed at relatively low temperature,



(iv) Both carbonates and bicarbonates are soluble in water to give alkaline solution due to hydrolysis of carbonate ions or bicarbonate ions.

(7) Halides

(i) Alkali metals combine directly with halogens to form ionic halide M^+X^- .

(ii) The ease with which the alkali metals form halides increases from Li to Cs due to increasing electropositive character from Li to Cs.

(iii) covalent character in lithium halides is, $LiI > LiBr > LiCl > LiF$

(iv) These are readily soluble in water. However, lithium fluoride is sparingly soluble. The low solubility of LiF is due to higher forces of attractions among smaller Li^+ and smaller F^- ions (high lattice energy).

(v) Halides having ionic nature have high m.pt. and good conductor of current. The melting points of halides shows the order, $NaF > NaCl > NaBr > NaI$

(vi) Halides of potassium, rubidium and caesium have a property of combining with extra halogen atoms forming polyhalides.

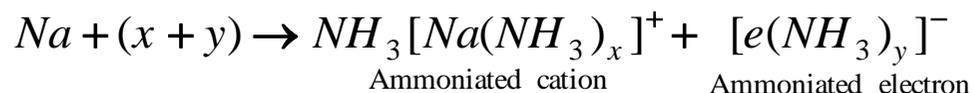
$KI + I_2 \rightarrow KI_3$; In $KI_{3(aq)}$ the ions K^+ and I_3^- are present

(8) Solubility in liquid NH_3

(i) These metals dissolve in liquid NH_3 to produce blue coloured solution, which conducts electricity to an appreciable degree.

(iii) With increasing concentration of ammonia, blue colour starts changing to that of metallic copper after which dissolution of alkali metals in NH_3 ceases.

(iii) The metal atom is converted into ammoniated metal in i.e. $M^+(NH_3)$ and the electron set free combines with NH_3 molecule to produce ammonia solvated electron.

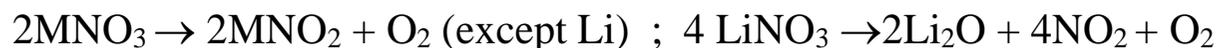


(iv) It is the ammoniated electron which is responsible for blue colour, paramagnetic nature and reducing power of alkali metals in ammonia solution. However, the increased conductance nature of these metals in ammonia is due to presence of ammoniated cation and ammonia solvated electron.

(v) The stability of metal-ammonia solution decreases from Li to Cs.

- (vi) The blue solution on standing or on heating slowly liberates hydrogen, $2M + 2NH_3 \rightarrow 2MNH_2 + H_2$.
Sodamide ($NaNH_2$) is a waxy solid, used in preparation of number of sodium compounds.

(9) **Nitrates:** Nitrates of alkali metals (MNO_3) are soluble in water and decompose on heating. $LiNO_3$ decomposes to give NO_2 and O_2 and rest all give nitrites and oxygen.



(10) Sulphates

(i) Alkali metals' sulphate have the formula M_2SO_4 .

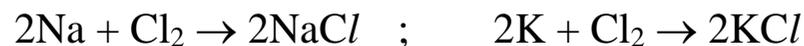
(ii) Except Li_2SO_4 , rest all are soluble water.

(iii) These sulphates on fusing with carbon form sulphides, $M_2SO_4 + 4C \rightarrow M_2S + 4CO$

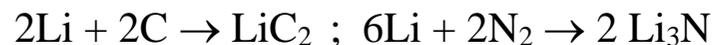
(iv) The sulphates of alkali metals (except Li) form double salts with the sulphate of the trivalent metals like Fe, Al, Cr etc. The double sulphates crystallize with large number of water molecules as alum. e.g. $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24 H_2O$.

(11) Reaction with non-metals

(i) These have high affinity for non-metals. Except carbon and nitrogen, they directly react with hydrogen, halogens, sulphur, phosphorus etc. to form corresponding compounds on heating.

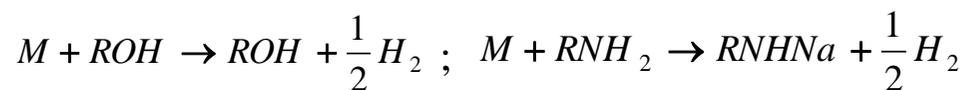
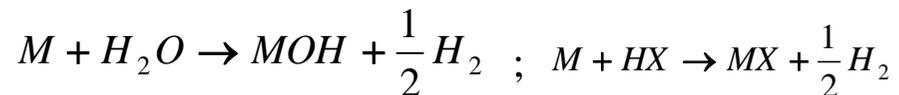


(ii) *Li* reacts, however directly with carbon and nitrogen to form carbides and nitrides.



(iii) The nitrides of these metals on reaction with water give NH_3 . $\text{M}_3\text{N} + 3\text{H}_2\text{O} \rightarrow 3\text{MOH} + \text{NH}_3$

(12) **Reaction with acidic hydrogen** : Alkali metals react with acids and other compounds containing acidic hydrogen (i.e, H atom attached on F, O, N and triply bonded carbon atom, for example, HF, H_2O , ROH, RNH_2 , $\text{CH}\equiv\text{CH}$) to liberate H_2 .



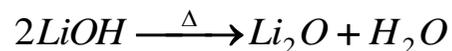
Anomalous behaviour of Lithium

- (1) It is comparatively harder than other alkali metals.
 - (2) It can be melted in dry air without losing its brilliance.
 - (3) Unlike other alkali metals, lithium is reactive among all. It can be noticed by the following properties,
 - (i) It is not affected by air.
 - (ii) It decomposes water very slowly to liberate H_2 .
 - (iii) It hardly reacts with bromine while other alkali metals react violently.
 - (3) Lithium is the only alkali metal which directly reacts with N_2 .
 - (4) Lithium when heated in NH_3 forms imide, $Li_2 NH$ while other metals form amides, MNH_2 .
-

(6) When burnt in air,, lithium form Li_2O sodium form Na_2O and Na_2O_2 other alkali metals form monoxide, peroxide and superoxide.

(7) Li_2O is less basic and less soluble in water than other alkali metals.

(8) LiOH is weaker base than NaOH or KOH and decomposes on heating.



(9) LiHCO_3 is liquid while other metal bicarbonates are solid.

(10) Only Li_2CO_3 decomposes on heating $\text{Li}_2\text{CO}_3 \xrightarrow{\text{heat}} \text{Li}_2\text{O} + \text{CO}_2$. Na_2CO_3 , K_2CO_3 etc. do not decompose on heating.

(11) LiNO_3 and other alkali metal nitrates give different products on heating



(12) LiCl and LiNO_3 are soluble in alcohol and other organic solvents. These salts of other alkali metals are, however, insoluble in organic solvents.

(13) LiCl is deliquescent while NaCl , KBr etc. are not. Lithium chloride crystals contain two molecules of water of crystallisation ($\text{LiCl} \cdot 2\text{H}_2\text{O}$). Crystals of NaCl KBr , KI etc do not contain water of crystallisation.

(14) Li_2SO_4 does not form alums like other alkali metals.

- (15) Li reacts with water slowly at room temperature Na reacts vigorously Reaction with K. Rb and Cs is violent.
- (16) Li reacts with Br₂ slowly. Reaction of other alkali metals with Br₂ is fast.
- (17) Li₂ CO₃ Li₂C₂O₄, LiF, Li₃PO₄ are the only alkali metal salts which are insoluble or sparingly soluble in water.

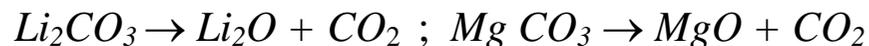
Diagonal Relationship of Li with Mg

Period	Group I	Group II
2	Li	Be
3	Na	Mg



- (1) Both Li and Mg are harder and higher m.pt than the other metals of their groups.
- (2) Due to covalent nature, chlorides of both Li and Mg are deliquescent and soluble in alcohol and pyridine while chlorides of other alkali metals are not so.
- (3) Fluorides, phosphates of li and Mg are sparingly soluble in water whereas those of other alkali metals are soluble in water.

(4) Carbonates of Li and Mg decompose on heating and liberate CO_2 . Carbonates of other alkali metals are stable towards heat and decomposed only on fusion.



(5) Hydroxides and nitrates of both Li and Mg decompose on heating to give oxide. Hydroxides of both Li and Mg are weak alkali.



Hydroxides of other alkali metals are stable towards heat while their nitrates give O_2 and nitrite.

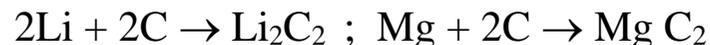


(6) Both Li and Mg combine directly with N_2 to give nitrides Li_3N and Mg_3N_2 . Other alkali metals combine at high temperature, $6\text{Li} + \text{N}_2 \rightarrow 2\text{Li}_3\text{N}$; $3\text{Mg} + \text{N}_2 \rightarrow \text{Mg}_3\text{N}_2$. Both the nitrides are decomposed by water to give NH_3



(7) Bicarbonates of Li and Mg are more soluble in water than carbonates whereas carbonates of alkali metals are more soluble.

(8) Both Li and Mg combine with carbon on heating.



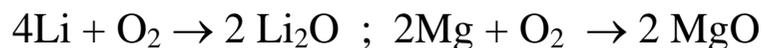
(9) The periodic properties of Li and Mg are quite comparable

	Li	Mg
Electronegativity	1.0	1.2
Atomic radii	1.23	1.36
Ionic radii	0.60(Li^+)	0.65(Mg^{+2})

Atomic volume 12.97 c.c 13.97 c.c

(10) Both have high polarizing power. Polarizing Power = Ionic charge / (ionic radius)².

(11) Lithium and Mg Form only monoxide on heating in oxygen.



(12) Li₂SO₄ Like MgSO₄ does not form alums.

(13) The bicarbonates of Li and Mg do not exist in solid state, they exist in solution only.

(14) Alkyls of Li and Mg (R.Li and R. MgX) are soluble in organic solvent.

(15) Lithium chloride and MgCl₂ both are deliquescent and separate out from their aqueous solutions as hydrated crystals, LiCl. 2H₂O and MgCl₂ . 2H₂O.

Sodium and its compounds

(1) **Ores of sodium** : NaCl (common salt), NaNO₃ (chile salt petre), Na₂SO₄ . 10H₂O (Glauber's salt), borax (sodium tetraborate or sodium borate, Na₂B₄O₇ . 10H₂O).

(2) **Extraction of sodium** : It is manufactured by the electrolysis of fused sodium chloride in the presence of CaCl₂ and KF using graphite anode and iron cathode. This process is called *Down process*.



At cathode : $Na^+ + e^- \rightarrow Na$; At anode : $Cl^- \rightarrow Cl + e^-$; $Cl + Cl \rightarrow Cl_2 \uparrow$

Note : Sodium cannot be extracted from aqueous $NaCl$ because $E_{H_2O/H_2}^0 (-0.83V)$ is more than $E^0 Na^+ / Na (-2.71V)$.

Anode and cathode are separated by means of a wire gauze to prevent the reaction between Na and Cl_2 .

(3) Compound of sodium

Sodium hydroxide (Caustic soda), $NaOH$

(i) Preparation

(a) *Gossage process* : $Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH \downarrow + CaCO_3$
(10% solution)

(b) *Electrolytic method* : Caustic soda is manufactured by the electrolysis of a concentrated solution of $NaCl$.

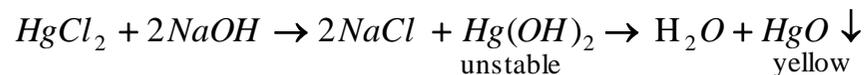
At anode: Cl^- discharged; At cathode: Na^+ discharged

(c) *Castner - Kellener cell* (Mercury cathode process) : $NaOH$ obtained by electrolysis of *aq.* solution of brine. The cell comprises of rectangular iron tank divided into three compartments.

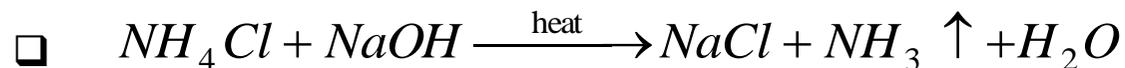
Outer compartment – Brine solution is electrolysed ; Central compartment – 2% $NaOH$ solution and H_2

(ii) *Properties* : White crystalline solid, highly soluble in water, It is only sparingly soluble in alcohol.

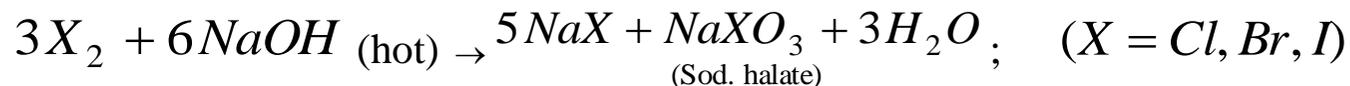
(a) *Reaction with salt* : $FeCl_3 + 3NaOH \rightarrow Fe(OH)_3 \downarrow + 3NaCl$
(Insoluble hydroxide)



Note : □ *Zn, Al, Sb, Pb, Sn* and *As* forms insoluble hydroxide which dissolve in excess of *NaOH* (amphoteric hydroxide).



(b) *Reaction with halogens* : $\text{X}_2 + 2\text{NaOH}$ (cold) $\rightarrow \text{NaX} + \underset{\text{sod. hypohalite}}{\text{NaXO}} + \text{H}_2\text{O}$



(c) *Reaction with metals*: Weakly electropositive metals like *Zn, Al* and *Sn* etc.

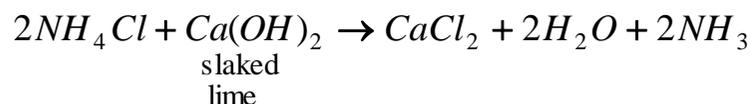
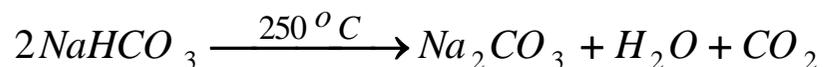
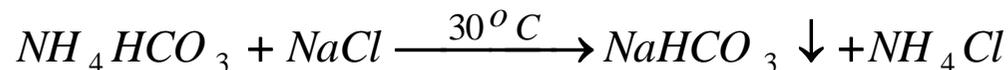


(d) *Reaction with sand, SiO₂* : $2\text{NaOH} + \text{SiO}_2 \rightarrow \underset{\text{Sod. silicate (glass)}}{\text{Na}_2\text{SiO}_3} + \text{H}_2\text{O}$

(e) *Reaction with CO*: $\text{NaOH} + \text{CO} \xrightarrow[5-10 \text{ atm}]{150-200^\circ \text{C}} \underset{\text{Sod. formate}}{\text{HCOONa}}$

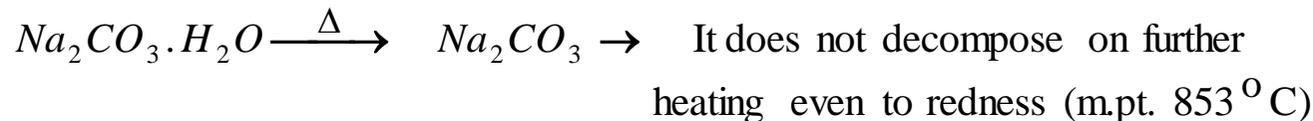
Sodium carbonate or washing soda, Na_2CO_3

(i) **Preparation : Solvay process** : In this process, brine (NaCl), NH_3 and CO_2 are the raw materials.

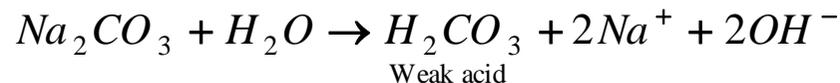


Note : \square CaCl_2 so formed in the above reaction is a by product of solvay process.

(ii) **Properties** : (a) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \xrightarrow{\text{dry air}} \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} + 9\text{H}_2\text{O}$
 (decahydrate) (Monohydrate)



(b) It is soluble in water with considerable evolution of heat.



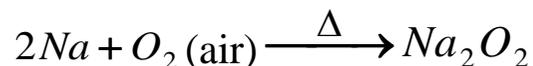
(c) It is readily decomposed by acids with the evolution of CO_2 gas.

(d) $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow 2\text{NaHCO}_3$

(iii) **Uses** : In textile and petroleum refining, Manufacturing of glass, NaOH soap powders etc.

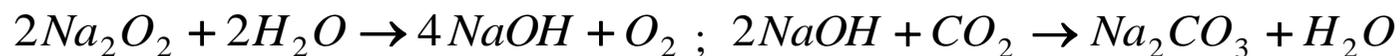
Sodium peroxide (Na_2O_2)

(i) **Preparation** : It is manufactured by heating sodium metal on aluminium trays in air (free from CO_2)



(ii) **Properties** : (a) When pure it is colourless. The faint yellow colour of commercial product is due to presence of small amount of superoxide (NaO_2).

(b) On coming with moist air it become white due to formation of $NaOH$ and Na_2CO_3 .

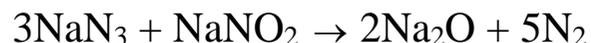
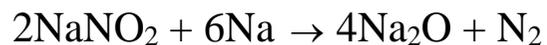


(c) It is powerful oxidising agent. It oxidises Cr (III) hydroxide to sodium chromate, Mn (II) to sodium manganate and sulphides to sulphates.

(iii) **Uses** : As a bleaching agent and it is used for the purification of air in confined spaces such as submarines because it can combine with CO_2 to give Na_2CO_3 and oxygen, $2CO_2 + 2Na_2O_2 \rightarrow 2Na_2CO_3 + O_2$.

Sodium Oxide, Na_2O

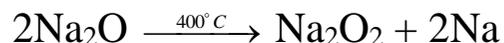
Preparation: By heating sodium nitrite with metallic sodium, or sodium azide (NaN_3) with sodium nitrite.



Properties :

(a) Na_2O is a white amorphous substance. It reacts with water violently forming $NaOH$.

(b) On heating above $400^\circ C$, it disproportionates to give peroxide and metallic sodium.



(c) It reacts with liquid ammonia forming sodamide and $NaOH$.



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

Sodium bicarbonate (Baking soda), NaHCO_3

Preparation :

- (i) It is obtained as the intermediate product in the solvay ammonia soda process.
- (ii) Normal carbonate can be changed to bicarbonate by passing carbon dioxide through its saturated solution.



Sparingly soluble

Properties :

- (1) NaHCO_3 is a white crystalline solid, sparingly soluble in water.
- (2) The solution is alkaline in nature due to hydrolysis.



Its aqueous solution gives yellow colour with methyl orange but no colour with phenolphthalein and thus weak base.

- (3) On heating, it loses carbon dioxide and water forming sodium carbonate.



- (4) The metal salt which forms basic carbonate with sodium carbonate, gives normal carbonate with sodium bicarbonate.



Uses: NaHCO_3 is

- (i) as a medicine (soda bicarb) to neutralise the acidity in the stomach.

- (ii) in making effervescent drinks.
- (iii) for making baking powder. Baking powder is a mixture of potassium hydrogen tartrate and sodium bicarbonate.
- (iv) for production of carbon dioxide.
- (vi) in fire extinguishers.

Sodium chloride (Common salt) or (table salt) or (rock salt), NaCl

Sodium chloride is the most common salt of sodium. It is also called sea salt.

Manufacture from sea water : The sea water is allowed to dry up under summer heat in small tanks or pits. The solid crust of NaCl so formed is collected. Sodium chloride thus obtained contains impurities like magnesium chloride, calcium chloride etc. It is purified by passing hydrogen chloride through a saturated solution of the commercial salt. The precipitation of sodium chloride occurs due to common ion effect.

Properties:

- (a) It is a white crystalline solid soluble in water. It dissolves in water with absorption of heat.
- (b) It is insoluble in alcohol.
- (c) The common salt is the starting material for the preparation of all the other sodium compounds e.g. NaOH, Na₂CO₃, NaHCO₃ etc. and extraction of sodium.

Uses: NaCl is used as (i) an essential constituent of food.

- (ii) a preservative of food articles like fish, meat etc.
- (iii) for making useful sodium compounds.
- (iv) in salting out of soap, and in making freezing mixtures.

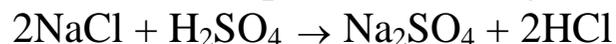
Pure NaCl is not hygroscopic. It shows hygroscopic nature due to impurities.

Sodium Sulphate (Glauber's salt), $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

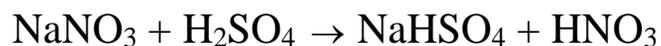
Preparation of Salt cake:

(i) The anhydrous sodium sulphate (salt cake) is obtained as a by-product in the manufacture of hydrochloric acid.

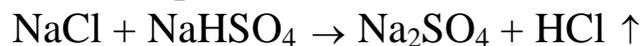
(ii) Salt cake is also produced during the manufacture of sodium carbonate when NaCl is heated with H_2SO_4 .



(iii) Now-a-days, it is manufactured by heating NaCl with sod. bisulphate (nitre cake). Nitre cake is obtained by the action of H_2SO_4 on sodium nitrate (Chile saltpetre).



Chile saltpeter Nitre cake



Nitre cake Salt cake

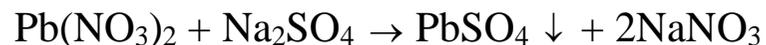
Preparation of Glauber's salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$:

The salt cake (Na_2SO_4) is dissolved in water and the solution is subjected for crystallization. Below 32°C , the decahydrate salt crystallises out from the aqueous solution. Above 32°C the anhydrous salt separates. Saturated solution of the decahydrate, on cooling below 12°C , gives crystals of heptahydrate.

Properties :

(i) The decahydrate effloresces in dry air forming the anhydrous salt. It is a crystalline solid, soluble in water.

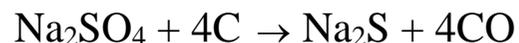
(ii) On treatment with lead, barium or strontium salts, it forms the corresponding insoluble sulphate, e.g.



(iii) When a solution having equivalent quantity of anhydrous Na_2SO_4 and conc. H_2SO_4 is cooled, prismatic crystals of sodium bisulphate (sodium hydrogen sulphate, NaHSO_4) are formed.



(iv) On heating with carbon it is reduced to sod. sulphide.



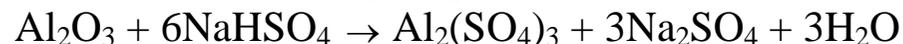
Uses: Sodium sulphate is used :

(i) in the manufacture of craft paper (brown paper for wrapping, etc.) and paper board,

(ii) in the manufacture of window glass,

(iii) as mild laxative (in medicine) and

(iv) in the preparation of Na_2S , $\text{Na}_2\text{S}_2\text{O}_3$ and NaHSO_4 . sod. bisulphate is an acidic salt in solution and can be used in place of sulphuric acid. For example, Al_2O_3 , which is not attacked by H_2SO_4 , may be converted into sulphate when fused with sodium hydrogen sulphate.



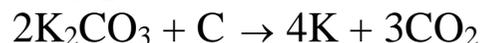
Potassium :

The important minerals of potassium are:

- (1) Carnallite : $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
- (2) Kainite : $\text{KCl} \cdot \text{MgSO}_4 \cdot \text{MgCl}_2 \cdot 3\text{H}_2\text{O}$
- (3) Indian salt peter : KNO_3
- (4) Felspar : $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ or $(\text{KAlSi}_3\text{O}_8)$
- (5) Polyhalite : $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{CaSO}_4 \cdot 6\text{H}_2\text{O}$
- (6) Sylvine : KCl

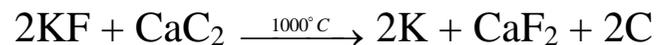
Preparation or Extraction : Metallic potassium is not of much demand because cheaper sodium metal serves almost all the purposes where potassium metal is needed. However it can be prepared by:

(i) heating potassium carbonate with coke.



(ii) electrolysing fused KCl alongwith little KF or CaCl_2 .

(iii) heating potassium fluoride with calcium carbide.



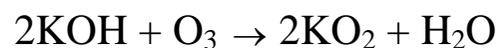
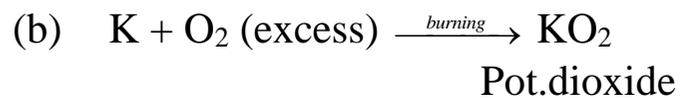
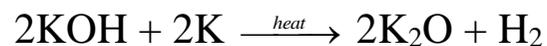
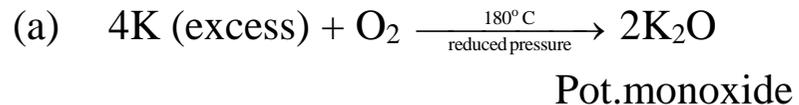
Compounds of Potassium

1. Oxides

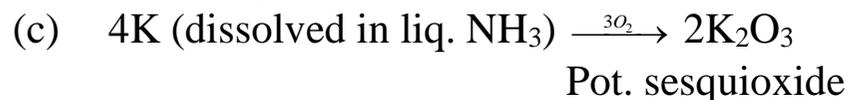
Three oxides of potassium are known:

- (i) potassium monoxide (potassium oxide), K_2O ;
- (ii) potassium dioxide (tetroxide or super oxide), KO_2 or K_2O_4 ; and
- (iii) potassium sesquioxide, K_2O_3 .

Preparation :

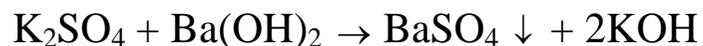


(dry)



2. Potassium Hydroxide (Caustic Potash), KOH

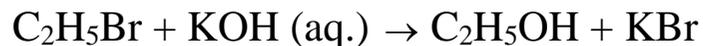
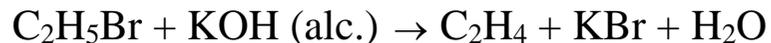
It is manufactured like that of NaOH, i.e. by the electrolysis of KCl solution or by the action of lime on potassium carbonate. It can also be obtained by the action of baryta, Ba(OH)₂ on potassium sulphate.



Properties: KOH has properties similar to those of sodium hydroxide. However, it is a stronger alkali and more soluble in alcohol and is, therefore used in organic reactions instead of caustic soda, as well as it is a better absorber of CO₂ than NaOH because potassium carbonate is more soluble in water. Its aqueous solution is known as potash lye.

Uses: Potassium hydroxide is used:

- (i) for the absorption of CO₂ and SO₂,
 - (ii) in the manufacture of soft soap,
 - (iii) in the form of alcoholic solution (alcoholic caustic potash) in organic chemistry for elimination reagent.
-

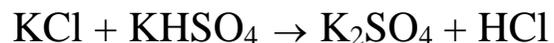
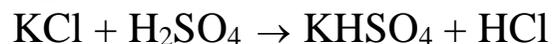


(iv) for drying gases since it is extremely deliquescent.

3. Potassium Carbonate (Potash or Pearl Ash), K_2CO_3

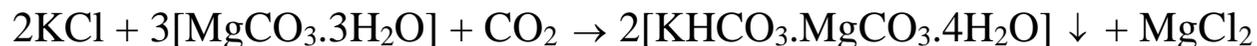
Preparation : It is noted here that unlike sodium carbonate, potassium carbonate cannot be prepared by the solvay method because potassium bicarbonate, being highly soluble in water, would not be precipitated out.

1. Leblanc process. Potassium chloride of carnallite is converted into K_2SO_4 which is then heated with coal and limestone to give K_2CO_3 .



Black ash

2. Precht process (Magnesia process). In this process carbon dioxide is passed into a solution of KCl at 20°C in the presence of hydrated magnesium carbonate to give potassium magnesium hydrogen carbonate.



Potassium magnesium hydrogen carbonate is taken out and decomposed by either of the following methods.

(i) It is heated at 140°C under pressure to give K_2CO_3 .



(ii) It is treated with a suspension of magnesium oxide in water below 20°C.



Hydrated magn. carbonate

Magnesium carbonate, obtained in either of the method, is removed and used again.

Properties: It is a white deliquescent powder readily soluble in water. It forms fusion mixture when mixed with sodium carbonate. It resembles sodium carbonate in most of its reactions. However, it is more alkaline and more soluble in water than sodium carbonate. On heating with steam to redness, it is decomposed to give KOH.



Uses: Potassium carbonate is used:

- (i) as fusion mixture (equimolecular quantities of Na_2CO_3 and K_2CO_3) which fuses at low temperature than either of the constituents.
- (ii) in the manufacture of soft soap (toilet soaps), hard glass and various potassium compounds.
- (iii) in washing wool and
- (iv) as a drying agent in the laboratory.

4. Potassium Bicarbonate, KHCO_3

By passing CO_2 through a cold saturated solution of potassium carbonate, KHCO_3 is obtained.

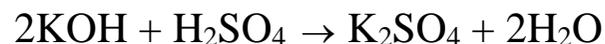
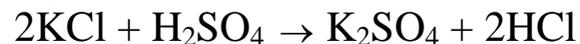


Properties and Uses: It resembles sodium bicarbonate in all properties except that it is more soluble in water. It is used in medicine and in and in baking powders.

5. Potassium Sulphate, K_2SO_4

Preparation :

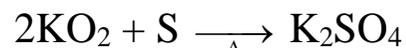
(i) By treating KCl or KOH with H₂SO₄.



(ii) By heating naturally-occurring mineral schonite (K₂SO₄.MgSO₄.6H₂O) with sylvine (KCl).



(iii) By heating dry KO₂ with sulphur



dry

Properties :

(i) It is a white crystalline solid, not very soluble in water.

(ii) Its crystals do not contain water of crystallization.

(iii) When heated with carbon, it is reduced to potassium sulphide.

(vi) It forms a series of double salts with the sulphates of trivalent metals, e.g. potash alum, K₂SO₄.Al₂(SO₄)₃.24H₂O.

Uses:

(i) It is used as a fertiliser for tobacco and wheat.

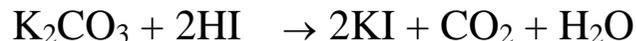
(ii) for the manufacture of potash alum and glass.

(iii) as a purgative I medicine.

6. Potassium iodide, KI**Preparation:**

(i) It is obtained by the action of HI on potassium hydroxide or potassium carbonate.



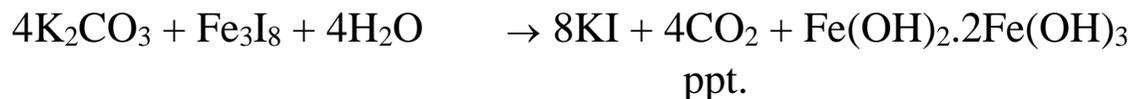


(ii) It may also be prepared by heating iodine with hot and concentrated solution of potassium hydroxide. The resulting liquid (consists of KI and KIO₃) is evaporated to dryness and the solid residue is then ignited with powdered charcoal to convert iodate also into iodide.



The mass is extracted out with water, filtered and the clear solution is evaporated to dryness.

(iii) Potassium iodide is manufactured by the action of ferrous ferric iodide on potassium carbonate. The solution is boiled.



[Fe₃I₈ is formed separately by adding iodine to iron fillings in water]



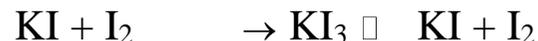
The precipitate is filtered out and the clear filtrate on crystallization gives crystals of potassium iodide.

KBr, potassium bromide can also be obtained similarly.

Properties:

(a) It is a white crystalline solid, highly soluble in water and alcohol.

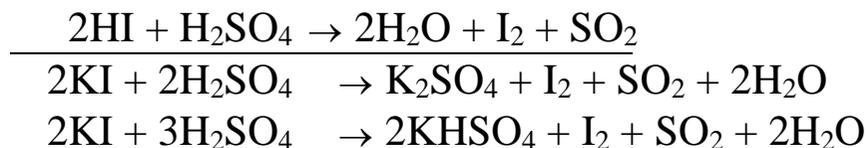
(b) It dissolves free iodine and forms potassium tri iodide and thus solubility of iodide and thus solubility of iodine increases in presence of potassium iodide.



KI₂ is unstable and gives up extra iodine readily.

(c) Sulphuric acid decomposes potassium iodide to I₂.

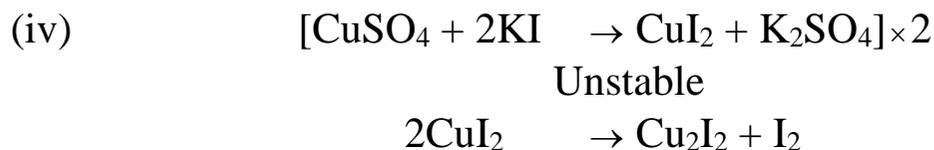
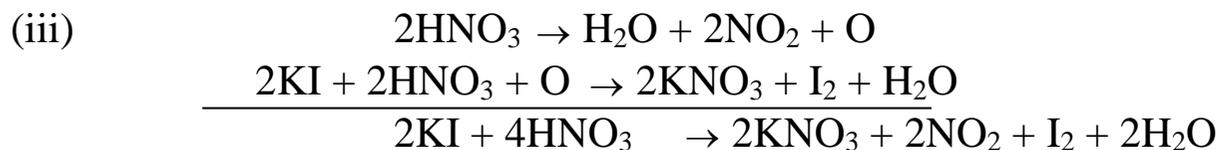
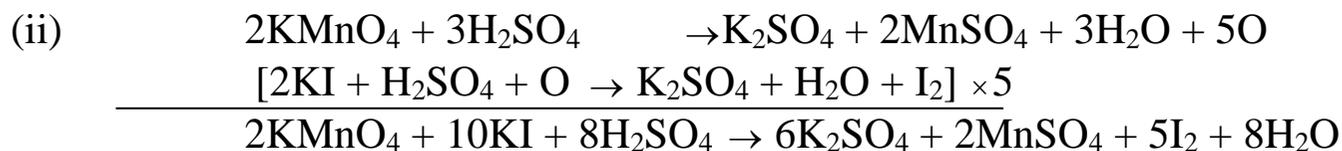
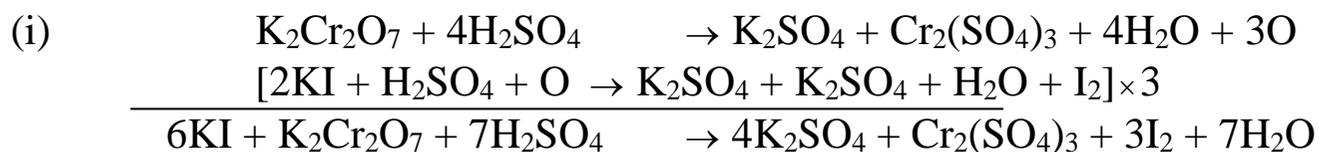


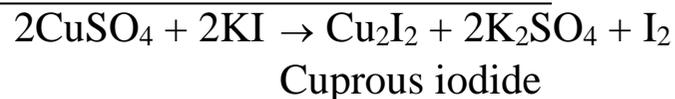


(d) F_2 , Cl_2 , Br_2 liberate iodine from potassium iodide solution.

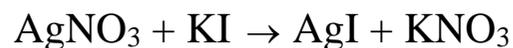


(e) It acts as a reducing agent. Acidified KMnO_4 , acidified $\text{K}_2\text{Cr}_2\text{O}_7$, HNO_3 , H_2O_2 , CuSO_4 etc. (oxidants) liberate iodine from KI.

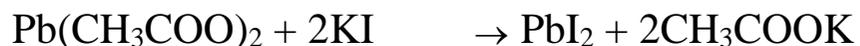




(f) Potassium iodide forms insoluble iodides with AgNO_3 and lead salts.



Yellow



Yellow

(g) It forms a red precipitate with HgCl_2 which dissolves in excess of potassium iodide forming potassium mercuric iodide.



The alkaline solution of K_2HgI_4 is called Nessler's reagent and used for the detection and estimation of NH_4^+ ion.

Uses: It is used

- (a) as a solvent of iodine.
- (b) as a reagent in laboratory.
- (c) in medicine and photography.
- (d) for making Nessler's reagent in the laboratory.

ALKALINE EARTH METAL

Alkaline Earth Metals and Their Compounds

Electronic configuration

Element	Electronic configurations (ns^2)
${}_4\text{Be}$	$1s^2 2s^2$ OR $[\text{He}]2s^2$
${}_{12}\text{Mg}$	$1s^2 2s^2 2p^6 3s^2$ OR $[\text{Ne}]3s^2$
${}_{20}\text{Ca}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ OR $[\text{Ar}]4s^2$
${}_{38}\text{Sr}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$ OR $[\text{Kr}]5s^2$
${}_{56}\text{Ba}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$ OR $[\text{Xe}]6s^2$
${}_{88}\text{Ra}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^2$ OR $[\text{Rn}]7s^2$

Note : ☐ Radium was discovered in the ore pitch blende by madam Curie. It is radioactive in nature.

Physical properties

(1) **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.

(2) **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.

(3) **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.

(4) **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	–

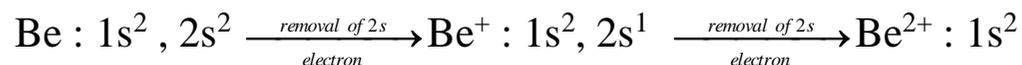
(ii) The values are, however, more than alkali metals. This might due to close packing of atoms in crystal lattice in alkaline earth metals.

(5) **Ionisation energy and electropositive or metallic character**

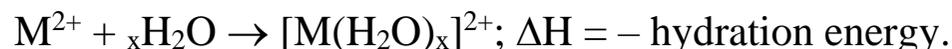
	Be	Mg	Ca	Sr	Ba	Ra
First ionisation energy (kJ mol ⁻¹)	899	737	590	549	503	509
Second ionisation energy (kJ mol ⁻¹)	1757	1450	1146	1064	965	979

	Li	Be
1st ionisation energy (kJ mol ⁻¹)	520	899
2nd ionisation energy (kJ mol ⁻¹)	7296	1757

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



(6) Oxidation number and valency



(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 ionisation 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.

(7) Hydration of ions

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

	Mg ⁺	Mg ²⁺
Hydration energy or Heat of hydration (kJ mol ⁻¹)	353	1906

The abnormally higher values of heat of hydration for divalent cations of alkaline earth metals are responsible for their divalent nature. MgCl₂ formation occurs with more amount of heat evolution and thus MgCl₂ is more stable.

(ii) The hydration energies of M²⁺ ion decreases with increase in ionic radii.



Heat of hydration kJ mol^{-1} 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_2 and CaCl_2 exists as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ which NaCl and KCl do not form such hydrates.

(iv) The ionic mobility, therefore, increases from Ba^{2+} to Ba^{2+} , as the size of hydrated ion decreases.

(8) **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

(9) **Conduction power** : Good conductor of heat and electricity.

(10) **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.

(11) **Characteristic flame colours**

(i) *The characteristic flame colour shown are :*

Ca-brick red; Sr –crimson ; Ba-apple green and Ra-crimson.

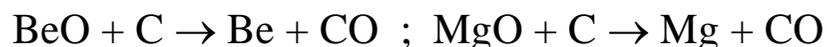
- (ii) Alkaline earth metals except Be and Mg produce characteristic colour to flame due to easy excitation of electrons to higher energy levels.
- (iii) Be and Mg atoms due to their small size, bind their electrons more strongly (because of higher effective nuclear charge) Hence these requires high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

Chemical properties

- (1) **Occurrence** : 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 ($3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$); Phenacite (Be_2SiO_4)
- (ii) **Magnesium** : Magnesite (MgCO_3); Dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$); Epsomite($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$); Carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$); Asbestos [$\text{CaMg}_3(\text{SiO}_3)_4$]
- (iii) **Calcium** : Limestone (CaCO_3); Gypsum : ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), Anhydrite (CaSO_4); Fluorapatite [$(3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2)$] Phosphorite rock [$\text{Ca}_3(\text{PO}_4)_2$]
- (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) $_2$ $8\text{H}_2\text{O}$ and antamite [$\text{Ca}(\text{UO}_2)_2$]

(2) **Extraction of alkaline earth metals**

- (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 electrolysing their fused salts.

(3) **Alloy formation** : These dissolve in mercury and form amalgams.

(4) **Formation of oxides and hydroxides**

(i) The elements (except Ba and Ra) when burnt in air give oxides of ionic nature $M^{2+}O^{2-}$ 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 alkalies 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)₂ 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)₂ and Mg (OH)₂ are almost insoluble, Ca (OH)₂ (often called lime water) is sparingly soluble whereas Sr(OH)₂ and Ba (OH)₂ (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)₂] or baryta water [Ba(OH)₂] are used to qualitative identification and quantitative estimation of carbon dioxide, as both of them gives white precipitate with CO₂ due to formation of insoluble CaCO₃ or BaCO₃



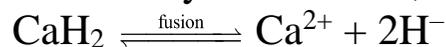
(5) Hydrides

(i) Except Be, all alkaline earth metals form hydrides (MH₂) on heating directly with H₂. $\text{M} + \text{H}_2 \rightarrow \text{MH}_2$.

(ii) BeH_2 is prepared by the action of LiAlH_4 on BeCl_2 ; $2\text{BeCl}_2 + \text{LiAlH}_4 \rightarrow 2\text{BeH}_2 + \text{LiCl} + \text{AlCl}_3$.

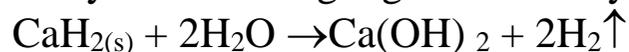
(iii) BeH_2 and MgH_2 are covalent while other hydrides are ionic.

(iv) The ionic hydrides of Ca, Sr, Ba liberate 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.

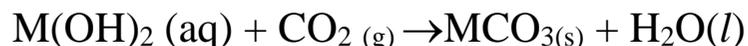


(6) Carbonates and Bicarbonates

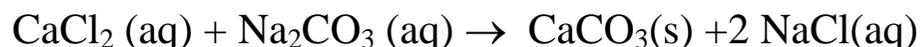
(i) All these metal carbonates (MCO_3) are insoluble in neutral medium but soluble in acid medium. These are precipitated by the addition of alkali metal or ammonium carbonate solution to the solution of these metals.



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

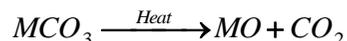


and sodium or ammonium carbonate is added to the solution of the alkaline earth metal salt such as CaCl_2 .



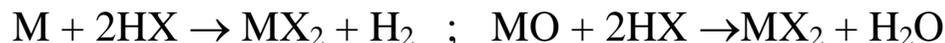
(iii) Solubility of carbonates of these metals also decreases downward in the group due to the decrease of hydration energy as the lattice energy remains almost unchanged as in case of sulphates.

(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.

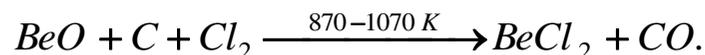


(7) Halides

(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.

$CaCl_2$

$SrCl_2$

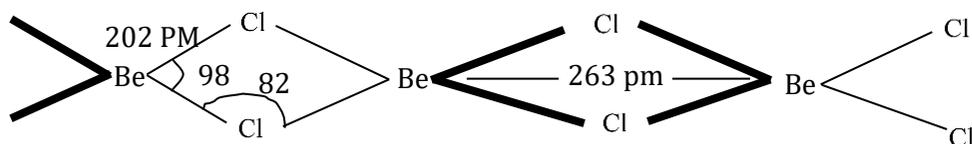
$BaCl_2$

Brick red colour

Crimson colour

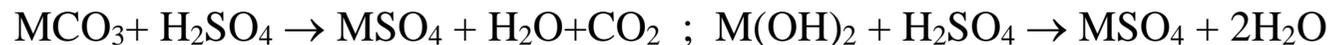
Grassy green colour

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,



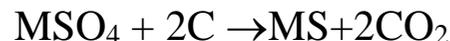
In the vapour phase it tends to form a chloro-bridged dimer which dissociates into the linear triatomic monomer at high temperature at nearly 1200 K.

- (8) **Solubility in liquid ammonia** : Like alkali metals, alkaline earth metals also dissolve in liquid ammonia to form coloured solutions. When such a solution is evaporated, hexammoniate, $M(NH_3)_6$ is formed.
- (9) **Nitrides**
- All the alkaline earth metals directly combine with N_2 give nitrides, M_3N_2 .
 - The ease of formation of nitrides however decreases from Be to Ba.
 - These nitrides are hydrolysed with water to liberate NH_3 , $M_3N_2 + 6H_2O \rightarrow 3M(OH)_2 + 2NH_3$
- (10) **Sulphates**
- All these form sulphate of the type $M SO_4$ by the action of $H_2 SO_4$ on metals, their oxides, carbonates or hydroxides.



(ii) The solubility of sulphates in water decreases on moving down the group $BeSO_4$ and $MgSO_4$ are fairly soluble in water while $BaSO_4$ is completely insoluble. This is due to increases in lattice energy of sulphates down the group which predominates over hydration energy.

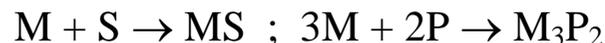
(ii) Sulphate are quite stable to heat however reduced to sulphide on heating with carbon.



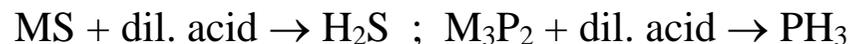
(11) **Action with carbon** : Alkaline metals (except Be, Mg) when heated with carbon form carbides of the type MC_2 . These carbides are also called acetylides as on hydrolysis they evolve acetylene.



(12) **Action with sulphur and phosphorus** : Alkaline earth metals directly combine with sulphur and phosphorus when heated to form sulphides of the type MS and phosphides of the type M_3P_2 respectively.



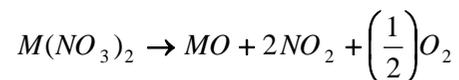
Sulphides on hydrolysis liberate H_2S while phosphides on hydrolysis evolve phosphine.



Sulphides are phosphorescent and are decomposed by water



(13) **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.



(14) Formation of complexes

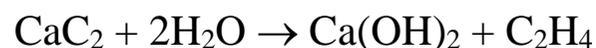
- (i) Tendency to show complex ion formation depends upon smaller size, high nuclear charge and vacant orbitals to accept electron. Since alkaline metals too do not possess these characteristics and thus are unable to form complex ion.
- (ii) However, Be^{2+} on account of smaller size forms many complex such as $(BeF_3)^{1-}$, $(BeF_4)^{2-}$.

Anomalous behaviour 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 $(\text{NH}_4)_2 \text{CO}_3$ in presence of $\text{NH}_4 \text{Cl}$.
- (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) Be_3N_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.



Diagonal relationship of *Be* with *Al*

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) Be^{2+} and 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. HNO_3 in cold.
- (6) Both form many stable complexes e.g. $(\text{BeF}_3)^-$, $(\text{AlH}_4)^-$.
- (7) Like BeO , Al_2O_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 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) Be_2C and Al_4C_3 both give 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 H_2 .
- (13) Both Be and Al form polymeric covalent hydrides while hydrides of other alkaline earth are ionic.
- (14) Both BeCl_2 and AlCl_3 are prepared is similar way.
 $\text{BeO} + \text{C} + \text{Cl}_2 \rightarrow \text{BeCl}_2 + \text{CO}$; $\text{Al}_2\text{O}_3 + 3\text{C} + 3\text{Cl}_2 \rightarrow 2\text{AlCl}_3 + 3\text{CO}$
- (15) Both BeCl_2 and 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) BeCl_2 and 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 (Li_2CO_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.

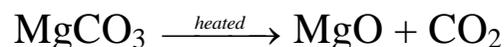
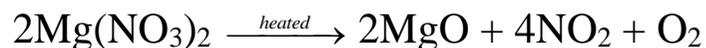
Action of nitrogen	Directly combine with nitrogen and form nitrides	Do not directly combine with nitrogen.
Nitrates	Decompose on heating evolving a mixture of NO_2 and oxygen	Decompose on heating evolving Only oxygen
Hydration of compounds	The compounds are extensively hydrated. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ are hydrated chlorides	The compounds are less hydrated NaCl , KCl , 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

- (1) **Ores of magnesium :** Magnesite ($MgCO_3$), Dolomite ($MgCO_3 \cdot CaCO_3$), Epsomite (epsom salt) ($MgSO_4 \cdot 7H_2O$) Carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$) Asbestos ($CaMg_3(SiO_3)_4$), Talc ($Mg_2(Si_2O_5)_2 \cdot Mg(OH)_2$).
- (2) **Extraction of magnesium :** It is prepared by the electrolysis of fused magnesium chloride which is obtained from carnallite and magnesite.

(3) **Compounds of magnesium**

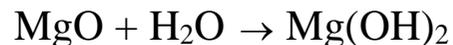
(i) **Magnesia (MgO) :** It is used as magnesia cement. It is a mixture of MgO and $MgCl_2$. It is also called Sorel's cement.

Preparation : MgO can be prepared by the following reactions.

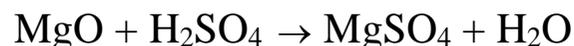


Properties:

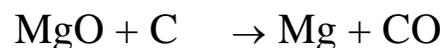
(i) It is a light infusible white powder (m.pt. $2800^\circ C$), slightly soluble in water and forms magnesium hydroxide.



(ii) It is basic in nature and thus reacts with acids to form corresponding salts.



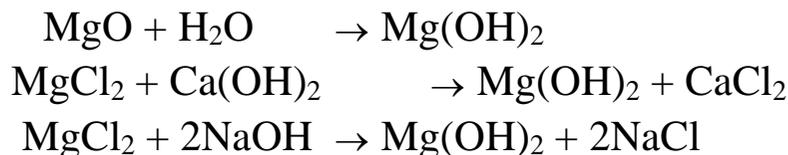
(iii) It is reduced by carbon at very high temperature.



(iv) Magnesium oxide when mixed with a saturated solution of magnesium chloride sets to hard mass like cement known as magnesia cement or sorel's cement. The composition is $MgCl_2 \cdot 5MgO \cdot xH_2O$

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

Preparation : It is obtained by dissolving magnesium oxide in water or by treating magnesium salt with an alkali.



Properties:

- (i) It is white powder, sparingly soluble in water.
- (ii) It is basic in nature and forms salts with acids.
- (iii) It decomposes on heating.
- (iv) It readily dissolves in strong solution of NH_4Cl .

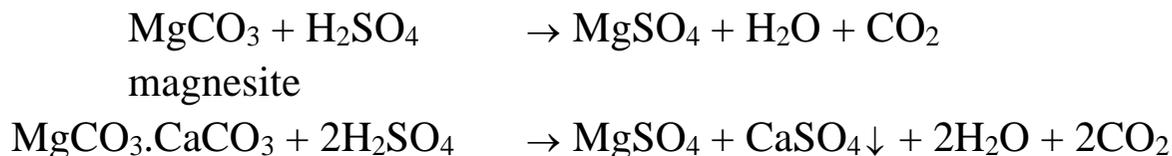


(iii) **Magnesium sulphate or Epsom salt** ($MgSO_4 \cdot 7H_2O$): It is isomorphous with $ZnSO_4 \cdot 7H_2O$. It is used as a purgative in medicine, as a mordant in dyeing and as a stimulant to increase the secretion of bile.

It occurs in nature as kieserite, $MgSO_4 \cdot H_2O$; Epsom salt, $MgSO_4 \cdot 7H_2O$; and kainite, $KCl \cdot MgSO_4 \cdot 3H_2O$.

Preparation:

- (i) From magnesite or dolomite



dolomite

(ii) From Kieserite (Commercial method) : By boiling kieserite in water and cooling the resulting solution when crystals of Epsom salt separate out.



Properties:

(i) It is a colourless, efflorescent crystalline substance with bitter taste and forms a number of hydrates.

(ii) When heated to 150°C, it changes to monohydrate which on further heating changes to anhydrous state at 200°C.



On further heating it decomposes to form MgO.



(iii) It is reduced by lamp black at 300°C.



(iv) It forms double salts with alkali metal sulphates, e.g. $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$

(iv) **Magnesium chloride** ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$): It is a deliquescent solid. Hydrated salt on heating in air undergoes partial hydrolysis. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \xrightarrow{\text{Heat}} \text{Mg}(\text{OH})\text{Cl} + \text{HCl} + 5\text{H}_2\text{O}$.

It occurs in nature as mineral carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and bischofite, $\text{MgCl}_2 \cdot \text{H}_2\text{O}$. It is found in sea water, mineral springs, etc.

Preparation:

(a) The mineral carnallite is fused and cooled to 176°C when whole of KCl is deposited while $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ remains in the fused state.

(b) It can also be obtained by dissolving Mg, MgO, Mg(OH)₂ or MgCO₃ in dilute hydrochloric acid. The preparation of anhydrous magnesium chloride has already been described in the extraction of magnesium.

Properties: It is colourless crystalline solid, highly deliquescent and highly soluble in water. It is the starting material for various magnesium compounds.

(v) Magnesium Carbonate, MgCO₃

It occurs in nature as magnesite (MgCO₃) and dolomite (MgCO₃.CaCO₃).

Preparation: By adding sodium bicarbonate to a hot solution of magnesium salt, MgO₃ is formed.

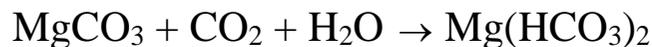


The magnesium carbonate cannot be obtained by the addition of sodium carbonate to the solution of magnesium salt. A white precipitate of a basic carbonate of composition 3MgCO₃.Mg(OH)₂.3H₂O is obtained which is known as magnesia alba. It is suspended in water and CO₂ is passed when magnesium bicarbonate known as fluid magnesia is formed. The solution is boiled when normal magnesium carbonate separates out.



Properties :

(i) It is a white powder insoluble in water. It dissolves readily in water containing excess of carbon dioxide.



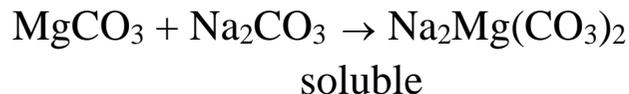
(ii) It dissolves in acids forming salts with evolution of CO₂.



(iii) On heating it decomposes with evolution of CO₂.

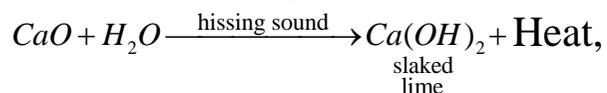


(iv) It forms double carbonates with alkali carbonates.

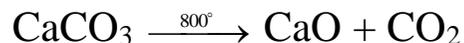


Calcium and its compounds

- (1) **Ores of calcium** : Lime stone or marble or chalk (CaCO_3), Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), Dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$), Fluorspar (CaF_2), phosphorite $\text{Ca}_3(\text{PO}_4)_2$. Calcium phosphate is a constituent of bones and teeth.
- (2) **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.
- (3) **Compounds of calcium**
 - (i) **Calcium oxide or Quick lime or Burnt lime (CaO)** : It's aqueous suspension is known as slaked lime.



Preparation : CaO is formed by the decomposition of CaCO_3 at 800°C .



- (i) The reactions being reversible and thus to assure the complete decomposition of CaCO_3 , carbon dioxide formed must be swept away by a current of air.
- (ii) At high temperature, clay present as impurity in lime stone reacts with lime to form fusible silicates and thus temperature should not be high.

Properties :

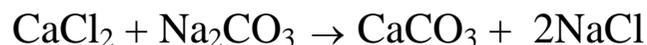
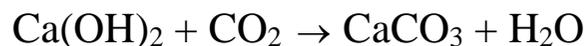
Note : \square CaO is used as basic flux, for removing hardness of water, as a drying agent (for NH_3 gas) for preparing mortar ($CaO + \text{sand} + \text{water}$).

(ii) **Calcium chloride** ($CaCl_2 \cdot 6H_2O$): Fused $CaCl_2$ is a good desiccant (drying agent). It can't be used to dry alcohol or ammonia as it forms additional products with them.

(iii) **Calcium carbonate** ($CaCO_3$) : $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$.

Preparation:

It is obtained by passing carbon dioxide through lime water or by adding sodium carbonate solution to $CaCl_2$.



Properties:

(i) It is a white powder, insoluble in water.

(ii) It dissolves in water in presence of CO_2 due to formation of calcium bicarbonate, otherwise insoluble.

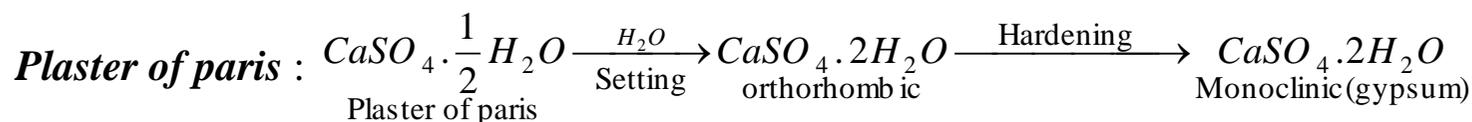
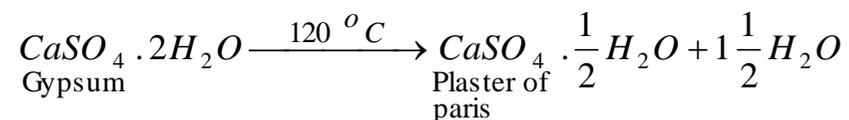


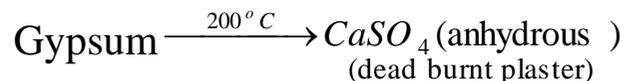
Note : \square It is insoluble in water but dissolves in the presence of CO_2 due to the formation of calcium bicarbonate.



\square It is a constituent of protective shells of marine animals.

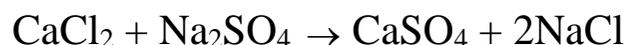
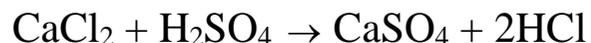
(iv) **Gypsum** ($CaSO_4 \cdot 2H_2O$): On partial dehydration to produce plaster of paris.





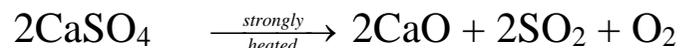
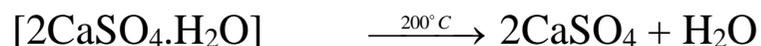
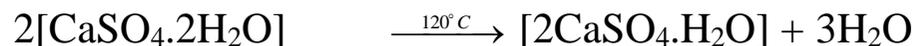
Preparations:

It is prepared by reacting any calcium salt with either sulphuric acid or a soluble sulphate (e.g. Na₂SO₄)



Properties :

- (i) It is a white crystalline solid, sparingly soluble in water and solubility decreases as the temperature increases.
- (ii) It dissolves in dilute acids. It also dissolves in ammonium sulphate due to the formation of double sulphate, (NH₄)₂SO₄.CaSO₄.H₂O.
- (iii) Gypsum on heating first changes from monoclinic form to orthorhombic form without loss of water. At 120°C, it loses three-fourth of its water of crystallisation and forms hemihydrate (2CaSO₄).H₂O or CaSO₄.(1/2)H₂O which is commonly known as plaster of paris. It becomes anhydrous at 200°C. The anhydrous form is known as burnt plaster or dead plaster. On strongly heating, it decomposes to give calcium oxide.



(iv) A suspension of gypsum on saturated with ammonia and carbon dioxide forms ammonium sulphate, a nitrogenous fertilizer.



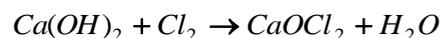
(v) It forms calcium sulphide on heating strongly with carbon. $\text{CaSO}_4 + 4\text{C} \rightarrow \text{CaS} + 4\text{CO}$

Gypsum when heated to about 200°C is converted into anhydrous calcium sulphate. The anhydrous form (anhydrite) is known as dead burnt plaster because it does not set like plaster of paris when moistened with water.

(v) **Calcium Hydroxide** $\text{Ca}(\text{OH})_2$ (slaked lime)



Suspension of $\text{Ca}(\text{OH})_2$ in water is called milk of lime.

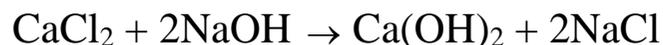


Preparation:

(i) By treating lime (quick lime) with water.



(ii) By the action of caustic alkalies on a soluble calcium salt

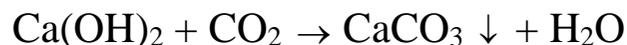


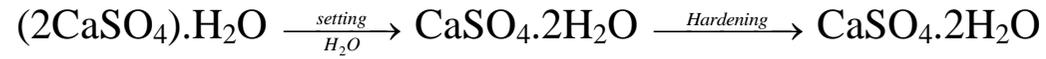
Properties:

(i) It is a white amorphous powder, sparingly soluble in water.

(ii) When dried and heated to redness, it loses a molecule of water and get converted into calcium oxide (lime).

(iii) Action of CO_2 : Lime water [$\text{Lime} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$] is frequently used for the detection of CO_2 and SO_2 gas. These gases turn lime water milky due to formation of CaCO_3 or CaSO_3 .





Plaster of Paris

Orthorhombic

Monoclinic

The setting of plaster of Paris is catalysed by sodium chloride and is retarded by borax or alum.