

Hydrogen and Its Compounds.

(1) Position of hydrogen in the periodic table

Hydrogen is the first element in the periodic table. Hydrogen is placed in no specific group due to its property of giving electron (When H^- is formed) and also losing electron (When H^+ is formed).

(i) Hydrogen is placed in group I (Alkali metals) as,

(a) It has one electron in its (Outer) Shell- $1s^1$ like other alkali metals which have (inert gas) ns^1 configuration.

(b) It forms monovalent H^+ ion like Li^+ , Na^+ ...

(c) Its valency is also 1.

(d) Its oxide (H_2O) is stable as Li_2O , Na_2O .

(e) It is a good reducing agent (In atomic as well as molecular state) like Na, Li...

(ii) Hydrogen also resembles halogens (Group VIII A) as,

(a) It is also diatomic (H_2) like F_2 , Cl_2 ...

(b) It also forms anion H^- like F^- , Cl^- ... by gain of one electron.

(c) H^- has stable inert gas (He) configuration as CH_4 , C_2H_6 like halogens CCl_4 , SF_2Cl_2 etc.

(d) H is one electron short of duplet (Stable configuration) like F , Cl , ... which are also one electron deficient than octet, $F - 2s^2 2p^5$; $Cl - 3s^2 3p^5$.

(e) (IE) of H (1312 kJ mol^{-1}) is of the same order as that of halogens.

(iii) (IE) of H is very high in comparison with alkali metals. Also size of H^+ is very small compared to that of alkali metal ion. H forms stable hydride only with strongly electropositive metals due to smaller value of its electron affinity (72.8 kJ mol^{-1}).

(iv) In view of the anomalous behavior of hydrogen, it is difficult to assign any definite position to it in the periodic table. Hence it is customary to place it in group I (Along with alkali metals) as well as in group VII (Along with halogens).

(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,

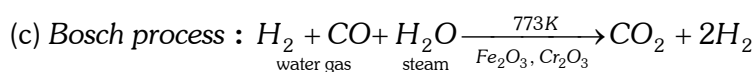
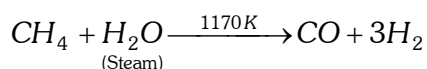
(i) **Laboratory method** : In the laboratory, dihydrogen can be prepared by the action of dil. H_2SO_4 on granulated Zinc, $Zn + H_2SO_4 \text{ (dil.)} \rightarrow ZnSO_4 + H_2$

(ii) **Industrial method**

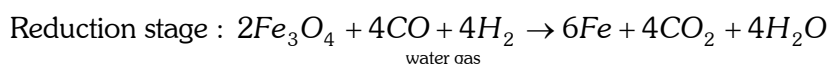
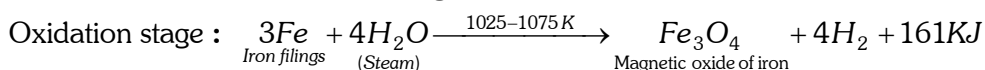
(a) **By the electrolysis of water** : The hydrogen prepared by this method is highly pure. Dihydrogen is collected at cathode. $2H_2O(l) \xrightarrow{\text{Electrolysis}} 2H_{2(g)} + O_{2(g)}$

(b) **Hydrocarbon steam process** : H_2 is prepared by the action of steam on hydrocarbon. e.g.

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(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,



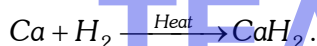
(4) Physical properties of dihydrogen : It is a colourless, tasteless and odourless gas. It is slightly soluble in water. It is highly combustible. The Physical constants of atomic hydrogen are,

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.

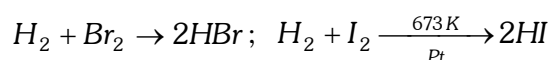
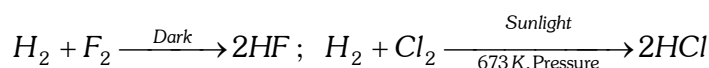
(5) Chemical properties of dihydrogen : Dihydrogen is quite stable and dissociates into hydrogen atoms only when heated above 2000 K, $H_2 \xrightarrow{2000K} H + H$. Its bond dissociation energy is very high, $H_2 \rightarrow H + H$; $\Delta H = 435.9 kJ mol^{-1}$. Due to its high bond dissociation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

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



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.

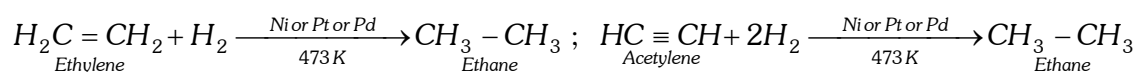
(ii) **Reaction with Non-metals** : $2H_2 + O_2 \xrightarrow{970K} 2H_2O$; $N_2 + 3H_2 \xrightarrow[750K, Pressure]{Fe, Mo} 2NH_3$



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**. The vegetable oils such as groundnut oil or cotton-seed oil are unsaturated in nature because they contain at least one double bond

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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°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.

Isotopes of Hydrogen

Isotopes are the different forms of the same element which have the same atomic number but different mass numbers.

Isotopes of hydrogen

| Name | Symbol | Atomic number | Mass number | Relative abundance | Nature radioactive or non-radioactive |
|---------------------|-----------------------|---------------|-------------|--------------------|---------------------------------------|
| Protium or 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 |

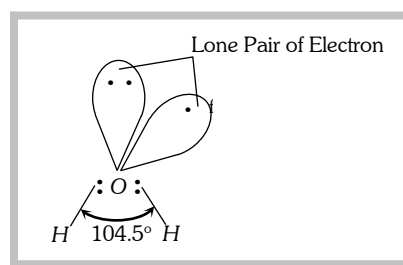
Physical constants of H_2 , D_2 and T_2

| 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 is the oxide of hydrogen. It is an important component of animal and vegetable matter. Water constitutes about 65% of our body. It is the principal constituent of earth's surface.

(1) **Structure** : Due to the presence of lone pairs, the geometry of water is distorted and the $\text{H}-\text{O}-\text{H}$ bond angle is 104.5° , which is less than the normal tetrahedral angle (109.5°). The geometry of the molecule is regarded as angular or bent. In water, each $\text{O}-\text{H}$ bond is polar because of the high electronegativity of oxygen (3.5) in comparison to that of hydrogen (2.1). 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

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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 (1g 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.

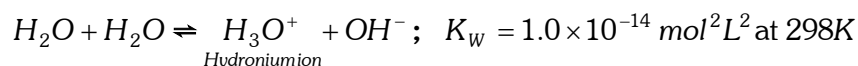
(3) **Physical properties** : Water is colourless, odourless and tasteless liquid at ordinary temperature.

Some physical constants of H_2O and D_2O at 298 K

| Constant | Ordinary water H_2O | Heavy water D_2O |
|---|-------------------------------------|----------------------------------|
| 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** : Water shows a versatile chemical behaviour. It behaves as an acid, a base, an oxidant, a reductant and as ligand to metals.

(i) **Dissociation of water** : Water is quite stable and does not dissociate into its elements even at high temperatures. Pure water has a small but measurable electrical conductivity and it dissociates as,



(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. $2\text{Na} + \underset{\text{Oxidising agent}}{2\text{H}_2\text{O}} \rightarrow 2\text{NaOH} + \text{H}_2$; $2\text{F}_2 + \underset{\text{Reducing agent}}{2\text{H}_2\text{O}} \rightarrow 4\text{HF} + \text{O}_2$

(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.

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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,

$$\underset{\text{From hard water}}{M^{+2}} + 2\underset{\text{Sodium stearate (soap)}}{C_{17}H_{35}COONa} \rightarrow \underset{\text{Metal stearate (PPT.)}}{(C_{17}H_{35}COO)_2M} + 2Na^+, \text{Where}$$

$M = \text{Ca or Mg}$

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,

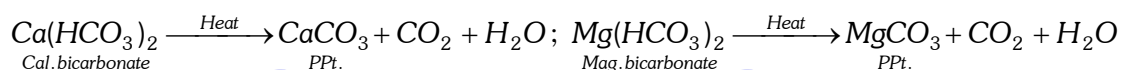
(a) *Temporary hardness* : This is due to the presence of bicarbonates of calcium and magnesium. It is also called carbonate hardness.

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

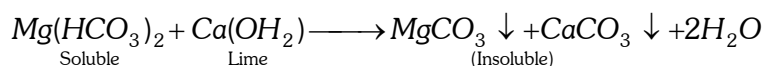
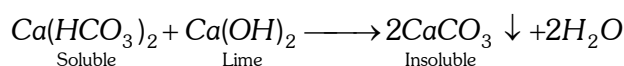
(iii) **Softening of water** : The process of the removal of hardness from water is called softening of water.

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

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.

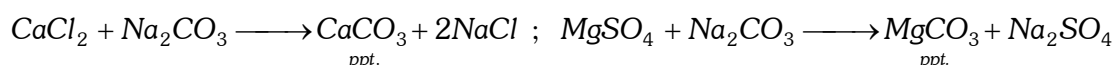


Clark's method : This process is used on a commercial scale. In this process, calculated amount of lime [Ca(OH)_2] is added to temporary hard water.



(b) *Removal of permanent hardness* : Permanent hardness can be removed by the following methods,

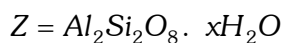
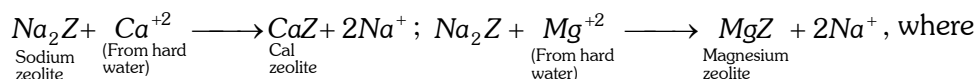
By *washing soda method* : In this method, water is treated with a calculated amount of washing soda (Na_2CO_3) which converts the chlorides and sulphates of Ca and Mg into their respective carbonates which get precipitated.



Permutit method : This is a modern method employed for the softening of hard water. hydrated sodium aluminium silicate ($\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot xH_2O$) 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.

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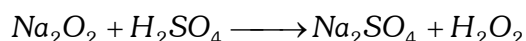


Hydrogen peroxide

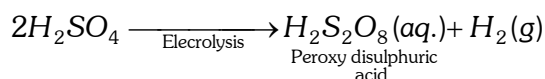
Hydrogen peroxide (H_2O_2) was discovered by French chemist **Thenard**.

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

(i) **Laboratory method** : In laboratory, H_2O_2 is prepared by Merck's process. It is prepared by adding calculated amounts of sodium peroxide to ice cold dilute (20%) solution of H_2SO_4 .



(ii) **Industrial method** : On a commercial scale, H_2O_2 can be prepared by the electrolysis of 50% H_2SO_4 solution. In a cell, peroxy disulphuric acid is formed at the anode.



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

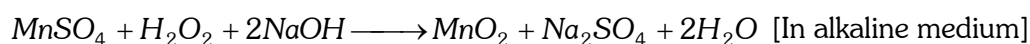
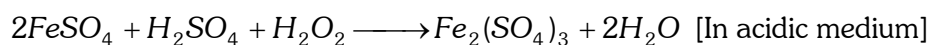
$\text{H}_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} \longrightarrow 2\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ The resulting solution is distilled under reduced pressure when H_2O_2 gets distilled while H_2SO_4 with high boiling point, remains undistilled.

(2) **Physical properties** : Pure H_2O_2 is a thick syrupy liquid with pale blue colour. It is more viscous and dense than water. It is completely miscible with water, alcohol and ether in all proportions.

(3) **Chemical properties**

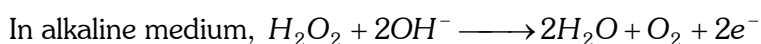
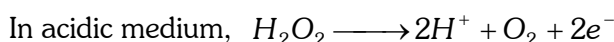
(i) **Decomposition** : Pure H_2O_2 is an unstable liquid and decomposes into water and O_2 either upon standing or upon heating, $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$; $\Delta H = -196.0 \text{ kJ}$

(ii) **Oxidising nature** : It is a powerful oxidising agent. It acts as an oxidising agent in neutral, acidic or in alkaline medium. e.g. $2\text{KI} + \text{H}_2\text{O}_2 \longrightarrow 2\text{KOH} + \text{I}_2$ [In neutral medium]

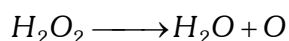


(iii) **Reducing nature** : H_2O_2 has tendency to take up oxygen from strong oxidising agents and thus, acts as a reducing agent, $\text{H}_2\text{O}_2 + \underset{\substack{\text{From oxidising} \\ \text{agent}}}{\text{O}} \longrightarrow \text{H}_2\text{O} + \text{O}_2$. It can act as a reducing agent in acidic, basic or

even neutral medium.



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



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

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

(4) **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.

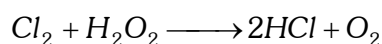
(5) **Strength of H_2O_2** : The strength of H_2O_2 is expressed in terms of weight or volume,

(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) It is used as an antichlor in bleaching because it can reduce chlorine.



(ii) It is used for restoring the colour of lead paintings.

(iii) It is used as an antiseptic for washing wounds, teeth and ears under the name perhydrol.

Alkali Metals and Their Compounds.

The group 1 of the periodic table contains six elements, namely lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr). All these elements are **typical metals**. These are usually referred to as alkali metals since their hydroxides forms strong bases or alkalies.

Electronic configuration

| Elements | 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 : * Francium is radioactive with longest lived isotope ${}^{223}\text{Fr}$ with half life period of only 21 minute.

(1) Because of similarity in electronic configuration, they exhibit similar properties. A regular gradation in their properties with increase in at. no. is observed due to increasing size of atoms/ions and the low binding energy of valency electrons.

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(2) Of all the alkali metals, only sodium and potassium are found in abundance in nature. Francium occurs only in minute quantities as a radioactive decay product.

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

(i) The alkali metals have largest atomic and ionic radii than their successive elements of other groups belonging to same period.

(ii) The atomic and ionic radii of alkali metals, however, increases down the group due to progressive addition of new energy shells.

No doubt the nuclear charge also increases on moving down the group but the influence of addition of energy shell predominates

| | <i>Li</i> | <i>Na</i> | <i>K</i> | <i>Rb</i> | <i>Cs</i> | <i>Fr</i> |
|---------------------------------|-----------|-----------|----------|-----------|-----------|-----------|
| 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. Low values of density are because these metals have high atomic volume due to larger atomic size. On moving down the group the atomic size as well as atomic mass both increase but increase in atomic mass predominates over increase in atomic size or atomic volume and therefore the ratio mass/volume i.e. density gradually increases down the groups

(ii) 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 $20^\circ C$.

(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.

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

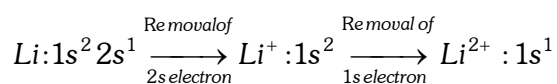
(5) Ionisation energy & electropositive or metallic character

(i) Due to unpaired lone electron in *ns* sub-shell as well as due to their larger size, the outermost electron is far from the nucleus, the removal of electron is easier and these low values of ionisation energy.(*I.E.*)

(ii) Ionisation energy of these metal decreases from *Li* to *Cs*.

| | Ionisation energy | <i>Li</i> | <i>Na</i> | <i>K</i> | <i>Rb</i> | <i>Cs</i> |
|-----------|------------------------|-----------|-----------|----------|-----------|-----------|
| <i>Fr</i> | <i>IE</i> ₁ | 520 | 495 | 418 | 403 | 376 |
| – | <i>IE</i> ₂ | 7296 | 4563 | 3069 | 2650 | 2420 |
| – | | | | | | |

A jump in 2nd ionisation energy (huge difference) can be explained as,



Removal of 1s electrons from *Li*⁺ and that too from completely filled configuration requires much more energy and a jump in 2nd ionisation is noticed

(iii) Lower are ionisation energy values, greater is the tendency to lose *ns*¹ electron to change in *M*⁺ ion (i.e. *M* → *M*⁺ + *e*) and therefore stronger is electropositive character.

(iv) 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.

(iii) Further, the *M*⁺ ion acquires the stable noble gas configuration. It requires very high values of energy to pull out another electron from next to outer shell of *M*⁺ ion and that is why their second ionisation energy is very high. Consequently, under ordinary conditions, it is not possible for these metals to form *M*²⁺ ion and thus they show +1 oxidation state.

(iv) Since the electronic configuration of *M*⁺ ions do not have unpaired electron and thus alkali metal salts are diamagnetic and colourless. Only those alkali metal salts are coloured which have coloured anions e.g. *K*₂*Cr*₂*O*₇ is orange because of orange coloured *Cr*₂*O*₇²⁻ ion, *KMnO*₄ is violet because of violet coloured *MnO*₄¹⁻ ion.

(7) Hydration of Ions

(i) Hydration represents for the dissolution of a substance in water to get adsorb water molecule by weak valency force. Hydration of ions is the exothermic process when ions on dissolution water get hydration.

(ii) The hydration is an exothermic process i.e energy is released during hydration.

(iii) 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 $M_{(g)}^+ + Aq \rightarrow M_{(aq)}^+ ; \Delta H = - \text{energy}$.

(iv) Smaller the cation, greater is the degree of hydration. Hydration energy, *Li*⁺ > *Na*⁺ > *K*⁺ > *Rb*⁺ > *Cs*⁺

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(v) Li^+ being smallest in size has maximum degree of hydration and that is why lithium salts are mostly hydrated, $LiCl \cdot 2H_2O$. Also lithium ion being heavily hydrated, moves very slowly under the influence of electric field and, therefore, is the poorest conductor of current among alkali metal ions. It may, therefore, be concluded that it is the degree of hydration as well as the size of ion is responsible for the current carried by an ion.

| | |
|-------------------------------|-----------------------------------|
| Relative ionic radii | $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ |
| Relative hydrated ionic radii | $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ |
| Relative conducting power | $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ |

(8) Electronegativities

(i) These metals are highly electropositive and thereby possess low values of electronegativities.

(ii) Electronegativity of alkali metals decreases down the group as the trend of numerical values of electronegativity given below on Pauling scale suggests.

| | | | | | | |
|-------------------|-----------|-----------|----------|-----------|-----------|-----------|
| | <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 | – |

Note : * *Fr* being radioactive elements and thus studies on physical properties of this element are limited.

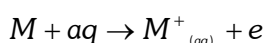
(9) **Specific heat** : It decreases from *Li* to *Cs*.

| | | | | | |
|------------------------------------|-----------|-----------|----------|-----------|-----------|
| | <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

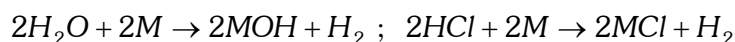
(i) Since alkali metals easily lose ns^1 electron and thus they have high values of oxidation potential i.e.,



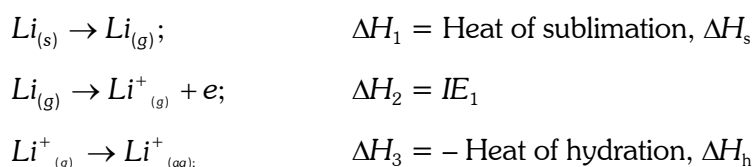
(ii) The standard oxidation potentials of alkali metals (in volts) are listed below,

| | | | | |
|-----------|-----------|----------|-----------|-----------|
| <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 |

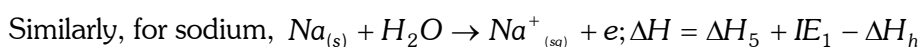
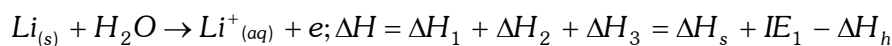
(iii) More is oxidation potential, more is the tendency to get oxidized and thus more powerful is reducing nature in aqueous medium. That is why alkali metals liberate H_2 from H_2O and HCl .



(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

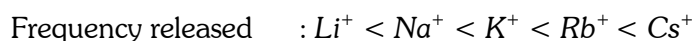
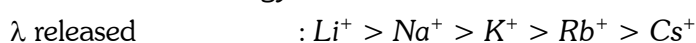
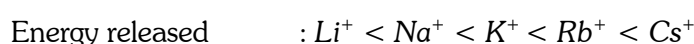


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ΔH_h for $Li > \Delta H_h$ for Na . Therefore, large negative ΔH values are observed in case of Li and this explains for more possibility of Li to get itself oxidized or have reducing nature.

(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. These different colours are due to different ionisation energy of alkali metals. The energy released is minimum in the case of Li^+ and increases in the order.



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 [$Li(AlF)PO_4$]

(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

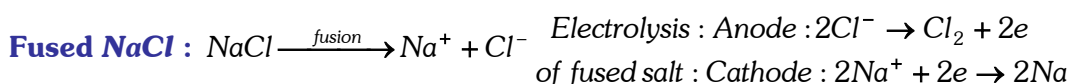
(v) **Caesium :** Lepidolite, Pollucite contains 0.2 to 7% Cs_2O

(2) Extraction of alkali metals : Alkali metals cannot be extracted by the usual methods for the extraction of metals due to following reasons.

(i) Alkali metals are strong reducing agents, hence cannot be extracted by reduction of their oxides or other compounds.

(ii) Being highly electropositive in nature, it is not possible to apply the method of displacing them from their salt solutions by any other element.

(iii) The aqueous solutions of their salts cannot be used for extraction by electrolytic method because hydrogen ion is discharged at cathode instead of an alkali metal ions as the discharge potentials of alkali metals are high. However, by using Hg as cathode, alkali metal can be deposited. The alkali metal readily combines with Hg to form an amalgam from which its recovery difficult. The only successful method, therefore, is the electrolysis of their fused salts, usually chlorides. Generally, another metal chloride is added to lower their fusion temperature.



(3) Alloys Formation

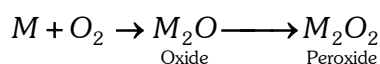
(i) The alkali metals form alloys among themselves as well as with other metals.

(ii) Alkali metals also get dissolved in mercury to form amalgam with evolution of heat and the amalgamation is highly exothermic .

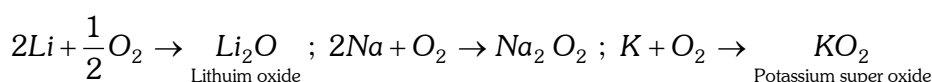
s & p Block Elements part 1

(4) Formation of oxides and hydroxides

(i) These are most reactive metals and have strong affinity for O_2 quickly tarnish 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)



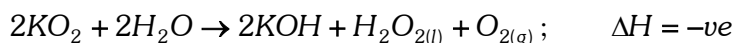
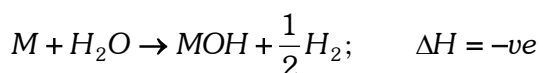
The reactivity of alkali metals towards oxygen to form different oxides is due to strong positive field around each alkali metal cation. Li^+ being smallest, possesses strong positive field and thus combines with small anion O^{2-} to form stable Li_2O compound. The Na^+ and K^+ being relatively larger thus exert less strong positive field around them and thus reacts with larger oxygen anion i.e. O_2^{2-} and O_2^{1-} to form stable oxides.

The monoxide, peroxides and superoxides have O^{2-} and O_2^{2-}, O_2^{1-} ions respectively. The structures of

each are, $[\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:]^{2-}; [\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:]^{2-}, [:\overset{\cdot\cdot}{O}\cdots\overset{\cdot\cdot}{O}:]^{1-}$

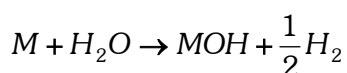
The O_2^{1-} ion has a three electron covalent bond and has one electron unpaired. It is therefore superoxides are paramagnetic and coloured KO_2 is light yellow and paramagnetic substance.

(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.

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(5) Hydrides

(i) These metal combines H to give white crystalline ionic hydrides of the general of the formula MH.

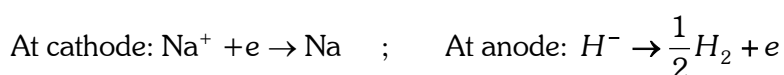
(ii) The tendency to form their hydrides, basic character and stability decreases from Li to Cs since the electropositive character decreases from Cs to Li.



(iii) The metal hydrides react with water to give MOH & H₂ ; $MH + H_2O \rightarrow MOH + H_2$

(iv) The ionic nature of hydrides increases from Li to Cs because of the fact that hydrogen is present in the these hydrides as H⁻ and the smaller cation will produce more polarisation of anion (according to Fajan rule) and will develop more covalent character.

(v) The electrolysis of fused hydrides give H₂ at anode. NaH_{fused} Contains Na⁺ and H⁻ i.e.,



(vi) Alkali metals also form hydrides like NaBH₄, LiAlH₄ which are good reducing agent.

(6) Carbonates and Bicarbonates

(i) The carbonates (M₂CO₃) & bicarbonates (MHCO₃) 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 Li₂CO₃ decompose on heating, $Li_2CO_3 \rightarrow Li_2O + CO_2$

(iii) Bicarbonates are decomposed at relatively low temperature, $2MHCO_3 \xrightarrow{300^\circ C} M_2CO_3 + H_2O + CO_2$

(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) Lithium halides however have more covalent nature. Smaller is the cation, more is deformation of anion and thus more is covalent nature in compound. Also among lithium halides, lithium iodide has maximum covalent nature because of larger anion which is easily deformed by a cation (The Fajan's rule) Thus 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.

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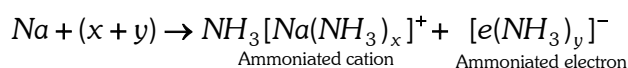
$KI + I_2 \rightarrow KI_3$; In $KI_{3(aq)}$ the ions K^+ and I_3^- are present

(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.

(ii) 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, $M_2SO_4 + 4C \rightarrow M_2S + 4CO$

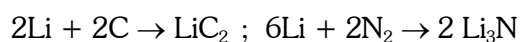
(iv) The sulphates of alkali metals (except Li) form double salts with the sulphate of the trivalent metals like Fe, Al, Cr etc. The double sulphates crystallize with large number of water molecules as alum. e.g. $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.

(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.



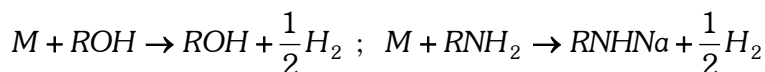
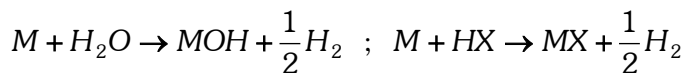
(ii) Li reacts, however directly with carbon and nitrogen to form carbides and nitrides.



(iii) The nitrides of these metals on reaction with water give NH_3 . $M_3N + 3H_2O \rightarrow 3MOH + NH_3$

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(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, H₂O, ROH, RNH₂, CH≡CH) to liberate H₂ .



(13) **Complex ion formation** : A metal shows complex formation only when it possesses the following characteristics, (i) Small size (ii) High nuclear charge (iii) Presence of empty orbitals in order to accept electron pair ligand. Only Lithium in alkali metals due to small size forms a few complex ions Rest all alkali metals do not possess the tendency to form complex ion.

Anomalous behaviour of Lithium

Anomalous behaviour of lithium is due to extremely low size of lithium its cation On account of small size and high nuclear charge, lithium exerts the greatest polarizing effect out of all alkali metals on negative ion. Consequently lithium ion possesses remarkable tendency towards solvation and develops covalent character in its compounds. Li differs from other alkali metals in the following respects,

- (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 H₂. (iii) It hardly reacts with bromine while other alkali metals react violently.
 - (4) Lithium is the only alkali metal which directly reacts with N₂.
 - (5) Lithium when heated in NH₃ forms imide, Li₂ NH while other metals form amides, MNH₂.
 - (6) When burnt in air,, lithium form Li₂O sodium form Na₂O and Na₂O₂ other alkali metals form monoxide, peroxide and superoxide.
 - (7) Li₂O 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.
$$2LiOH \xrightarrow{\Delta} Li_2O + H_2O$$
 - (9) LiHCO₃ is liquid while other metal bicarbonates are solid.
 - (10) Only Li₂CO₃ decomposes on heating $Li_2CO_3 \xrightarrow{heat} Li_2O + CO_2$. Na₂CO₃, K₂CO₃ etc. do not decompose on heating.
 - (11) LiNO₃ and other alkali metal nitrates give different products on heating
$$4LiNO_3 = 2Li_2O + 4NO_2 + O_2 ; 2NaNO_3 = 2NaNO_2 + O_2$$
 - (12) LiCl and LiNO₃ are soluble in alcohol and other organic solvents. These salts of other alkali metals are, however, insoluble in organic solvents.

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(13) LiCl is deliquescent while NaCl, KBr etc. are not. Lithium chloride crystals contain two molecules of water of crystallisation (LiCl. 2H₂O). Crystals of NaCl KBr, KI etc do not contain water of crystallisation.

(14) Li₂SO₄ 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) Li₂CO₃ Li₂C₂O₄, LiF, Li₃PO₄ are the only alkali metal salts which are insoluble or sparingly soluble in water.

Diagonal Relationship of Li with Mg

Due to its small size lithium differs from other alkali metals but resembles with Mg as its size is closer to Mg Its resemblance with Mg is known as diagonal relationship. Generally the periodic properties show either increasing or decreasing trend along the group and vice versa along the period which brought the diagonally situated elements to closer values. Following are the characteristics to be noted.

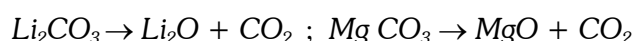
| Period | Group I | Group II |
|--------|---------|----------|
| 2 | Li | Be |
| 3 | Na | Mg |

(1) Both Li and Mg are harder and higher m.p.t than the other metals of their groups.

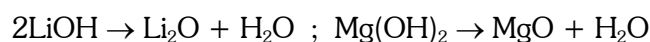
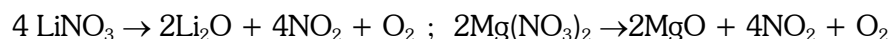
(2) Due to covalent nature, chlorides of both Li and Mg are deliquescent and soluble in alcohol and pyridine while chlorides of other alkali metals are not so.

(3) Fluorides, phosphates of Li and Mg are sparingly soluble in water whereas those of other alkali metals are soluble in water.

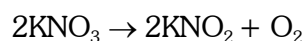
(4) Carbonates of Li and Mg decompose on heating and liberate CO₂ Carbonates of other alkali metals are stable towards heat and decomposed only on fusion.



(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 O₂ and nitrite.



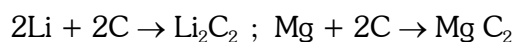
(6) Both Li and Mg combine directly with N₂ to give nitrides Li₃N and Mg₃N₂. Other alkali metals combine at high temperature, 6Li + N₂ → 2Li₃N; 3Mg + N₂ → Mg₃N₂. Both the nitrides are decomposed by water to give NH₃



(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.

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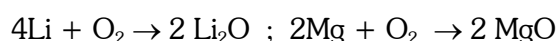


(9) The periodic properties of Li and Mg are quite comparable

| | 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**.



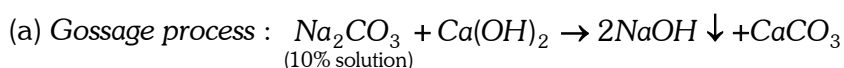
Note : * Sodium cannot be extracted from aqueous NaCl because $E_{\text{H}_2\text{O}/\text{H}_2}^0$ (-0.83V) is more than $E^0 \text{Na}^+ / \text{Na}$ (-2.71V).

* Anode and cathode are separated by means of a wire gauze to prevent the reaction between Na and Cl₂.

(3) **Compound of sodium**

Sodium hydroxide (Caustic soda), NaOH

(i) **Preparation**

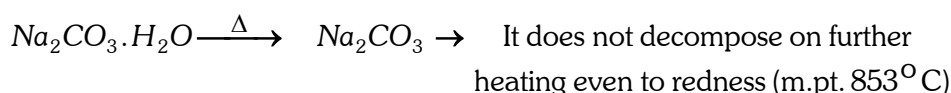


(b) **Electrolytic method** : Caustic soda is manufactured by the electrolysis of a concentrated solution of NaCl.

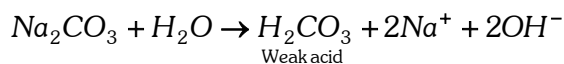


(c) **Castner - Kellener cell** (Mercury cathode process) : NaOH obtained by electrolysis of aq. solution of brine. The cell comprises of rectangular iron tank divided into three compartments.

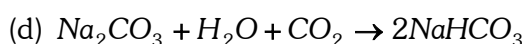
s & p Block Elements part 1



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



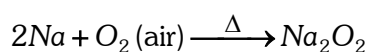
(c) It is readily decomposed by acids with the evolution of CO_2 gas.



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

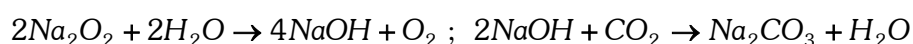
Sodium peroxide (Na_2O_2)

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



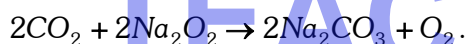
(ii) **Properties** : (a) When pure it is colourless. The faint yellow colour of commercial product is due to presence of small amount of superoxide (NaO_2).

(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.



Alkaline Earth Metals and Their Compounds .

The group 2 of the periodic table consists of six metallic elements. These are beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra). These (except Be) are known as alkaline earth metals as their oxides are alkaline and occur in earth crust.

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

s & p Block Elements part 1

(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

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

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

| | 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 |

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

s & p Block Elements part 1

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

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

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

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

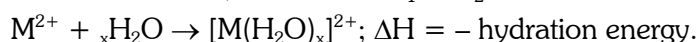
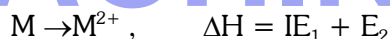
The removal of 2nd electron from alkali metals takes place from 1s sub shell which are more closer to nucleus and exert more nuclear charge to hold up 1 s electron core, whereas removal of 2nd electron from alkaline earth metals takes from 2s sub shell. More closer are shells to the nucleus, more tightly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

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

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

(6) Oxidation number and valency

(i) The IE₁ of the these metals are much lower than IE₁ and thus it appears that these metals should form univalent ion rather than divalent ions but in actual practice, all these give bivalent ions. This is due to the fact that M²⁺ ion possesses a higher degree of hydration or M²⁺ ions are extensively hydrated to form [M(H₂O)_x]²⁺, a hydrated ion. This involves a large amount of energy evolution which counter balances the higher value of second ionisation energy.



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

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

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



s & p Block Elements part 1

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 Be^{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 [$\text{Ca}_3(\text{PO}_4)_2$]

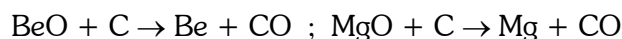
(iv) **Barium** : Barytes (BaSO_4) ; witherite (BaCO_3)

s & p Block Elements part 1

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

(2) Extraction of alkaline earth metals

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

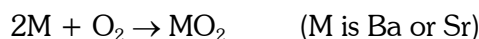


(ii) The extraction of alkaline earth metals can also be made by the reduction of their oxides by alkali metals or by electrolysis of their fused salts.

(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.

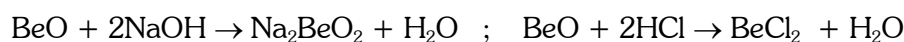


(ii) Their less reactivity than the alkali metals is evident by the fact that they are slowly oxidized on exposure to air. However the reactivity of these metals towards oxygen increases on moving down the group.

(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 alkalis to give salts i.e. BeO possesses amphoteric nature.



Sod. beryllate

Beryllium chloride

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

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

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

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

(x) The basic nature of hydroxides increase from Be to Ra. It is because of increase in ionic radius down the group which results in a decrease in strength of M-O bond in $M-(OH)_2$ 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.

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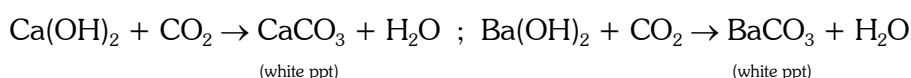
The trend of the solubility of these hydroxides depends on the values of lattice energy and hydration energy of these hydroxides. The magnitude of hydration energy remains almost same whereas lattice energy decreases appreciably down the group leading to more $-Ve$ values for $\Delta H_{\text{solution}}$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

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

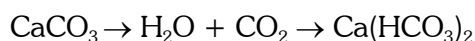
More negative is $\Delta H_{\text{solution}}$ more is solubility of compounds.

(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 $[\text{Ca}(\text{OH})_2]$ or baryta water $[\text{Ba}(\text{OH})_2]$ are used to qualitative identification and quantitative estimation of carbon dioxide, as both of them gives white precipitate with CO_2 due to formation of insoluble CaCO_3 or BaCO_3



Note : * SO_2 also give white ppt of CaSO_3 and BaSO_3 on passing through lime water or baryta water. However on passing CO_2 in excess, the white turbidity of insoluble carbonates dissolve to give a clear solution again due to the formation of soluble bicarbonates,



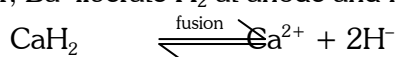
(5) Hydrides

(i) Except Be, all alkaline earth metals form hydrides (MH_2) on heating directly with H_2 . $\text{M} + \text{H}_2 \rightarrow \text{MH}_2$.

(ii) BeH_2 is prepared by the action of LiAlH₄ on BeCl_2 ; $2\text{BeCl}_2 + \text{LiAlH}_4 \rightarrow 2\text{BeH}_2 + \text{LiCl} + \text{AlCl}_3$.

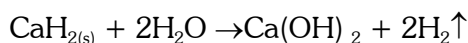
(iii) BeH_2 and MgH_2 are covalent while other hydrides are ionic.

(iv) The ionic hydrides of Ca, Sr, Ba liberate H_2 at anode and metal at cathode.



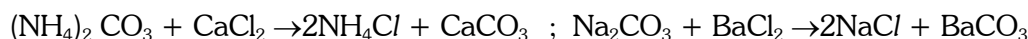
(v) The stability of hydrides decreases from Be to Ba.

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

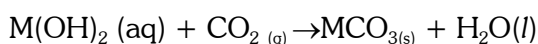


(6) Carbonates and Bicarbonates

(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.

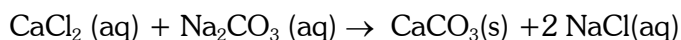


(ii) Alkaline earth metal carbonates are obtained as white precipitates when calculated amount of carbon dioxide is passed through the solution of the alkaline metal hydroxides.



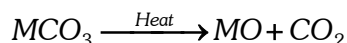
s & p Block Elements part 1

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



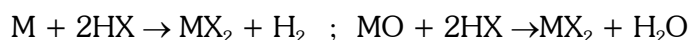
(iii) Solubility of carbonates of these metals also decreases downward in the group due to the decrease of hydration energy as the lattice energy remains almost unchanged as in case of sulphates.

(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.

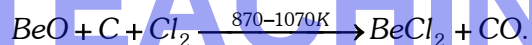


(7) Halides

(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.

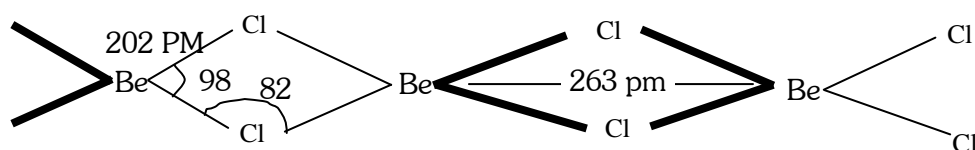
(iii) The halides of the members of this group are soluble in water and produce neutral solutions from which the hydrates such as : $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ can be crystallised. The tendency to form hydrated halides decreases with increasing size of the metal ions.

(iv) BeCl_2 is readily hydrolysed with water to form acid solution, $\text{BeCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Be}(\text{OH})_2 + 2\text{HCl}$.

(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,



s & p Block Elements part 1

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, $M(\text{NH}_3)_6$ is formed.

(9) Nitrides

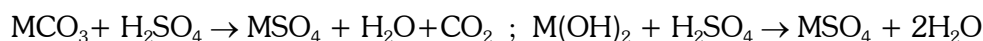
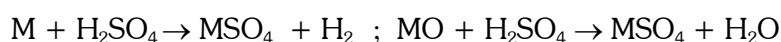
(i) All the alkaline earth metals directly combine with N_2 give nitrides, M_3N_2 .

(ii) The ease of formation of nitrides however decreases from Be to Ba.

(iii) These nitrides are hydrolysed with water to liberate NH_3 , $\text{M}_3\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{M}(\text{OH})_2 + 2\text{NH}_3$

(10) Sulphates

(i) All these form sulphate of the type M SO_4 by the action of H_2SO_4 on metals, their oxides, carbonates or hydroxides.

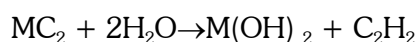


(ii) The solubility of sulphates in water decreases on moving down the group. BeSO_4 and MgSO_4 are fairly soluble in water while BaSO_4 is completely insoluble. This is due to increases in lattice energy of sulphates down the group which predominates over hydration energy.

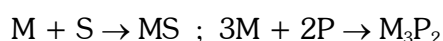
(ii) Sulphates are quite stable to heat however reduced to sulphide on heating with carbon.



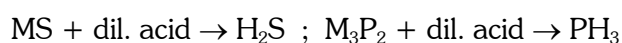
(11) **Action with carbon** : Alkaline metals (except Be, Mg) when heated with carbon form carbides of the type MC_2 . These carbides are also called acetylides as on hydrolysis they evolve acetylene.



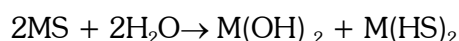
(12) **Action with sulphur and phosphorus** : Alkaline earth metals directly combine with sulphur and phosphorus when heated to form sulphides of the type MS and phosphides of the type M_3P_2 respectively.



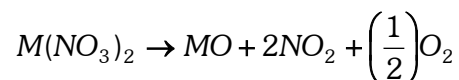
Sulphides on hydrolysis liberate H_2S while phosphides on hydrolysis evolve phosphine.



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 complexes such as $(\text{BeF}_3)^{-1}$, $(\text{BeF}_4)^{-2}$.

Anomalous behaviour of Beryllium

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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,

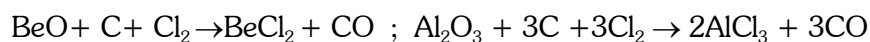
- (1) Be is lightest alkaline earth metal.
- (2) Be possesses higher m.pt. and b.pt than other group members.
- (3) BeO is amphoteric in nature whereas oxides of other group members are strong base.
- (4) It is not easily effected by dry air and does not decompose water at ordinary temperature.
- (5)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



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.

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(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 |

Magnesium and its compounds

(1) **Ores of magnesium** : Magnesite (MgCO_3), Dolomite ($\text{MgCO}_3 \cdot \text{CaCO}_3$), Epsomite (epsom salt) ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) Carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$) Asbestos ($\text{CaMg}_3(\text{SiO}_3)_4$), Talc ($\text{Mg}_2(\text{Si}_2\text{O}_5)_2 \cdot \text{Mg}(\text{OH})_2$).

s & p Block Elements part 1

(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.

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

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

(iv) **Magnesium chloride** ($MgCl_2 \cdot 6H_2O$) : It is a deliquescent solid. Hydrated salt on heating in air undergoes partial hydrolysis. $MgCl_2 \cdot 6H_2O \xrightarrow{\text{Heat}} Mg(OH)Cl + HCl + 5H_2O$.

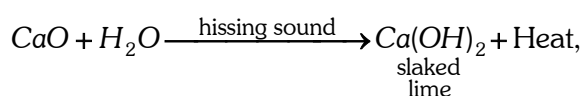
Calcium and its compounds

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

(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)** : Its aqueous suspension is known as slaked lime.



When exposed to oxy-hydrogen flame, it starts emitting light called lime light.

Note : * 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 (CaCO₃)** : $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$.

Note : * It is insoluble in water but dissolves in the presence of CO_2 due to the formation of calcium bicarbonate. $CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$

* It is a constituent of protective shells of marine animals.