

## 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.

(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 luster which quickly tarnishes due to surface oxidation.

(ii) These form diamagnetic colorless ions since these ions do not have unpaired electrons, (i.e.  $M^+$  has  $ns^0$  configuration). That is why alkali metal salts are colorless 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

Li	Na	K	Rb	Cs	Fr					
Atomic radius (pm)				152	186	227	248	265	375	
Ionic radius of $M^+$ ions (pm)	60	95	133	148	169	–				

## (3) Density

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

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

(iv) In solid state, they have body centered 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.

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

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

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

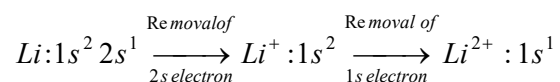
#### (5) Ionization energy & electropositive or metallic character

(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 ionization energy.(I.E.)

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

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

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



Removal of 1s electrons from Li<sup>+</sup> and that too from completely filled configuration requires much more energy and a jump in 2nd ionization is noticed

(iii) Lower are ionization energy values, greater is the tendency to lose  $ns^1$  electron to change in  $M^+$  ion (i.e.  $M \rightarrow M^+ + e$ ) 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 ionization 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 ionization 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 colored which have colored anions e.g.  $K_2Cr_2O_7$  is orange because of orange colored  $Cr_2O_7^{2-}$  ion,  $KMnO_4$  is violet because of violet colored  $MnO_4^{1-}$  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  $M_{(g)}^+ + Aq \rightarrow M_{(aq)}^+ ; \Delta H = -energy$ .

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

(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 current among alkali metals 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.

Li	Na	K	Rb	Cs	Fr		
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.

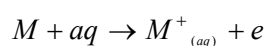
Li	Na	K	Rb	Cs	Fr
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Specific heat (Cal/g)	0.941	0.293	0.17	0.08	0.049
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(10) **Conduction power:** All are good conductors of heat & electricity, because of loosely held valence electrons.

(11) **Standard oxidation potential and reducing properties**

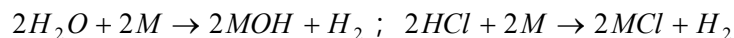
(i) Since alkali metals easily lose  $ns^1$  electron and thus they have high values of oxidation potential i.e.



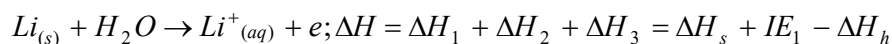
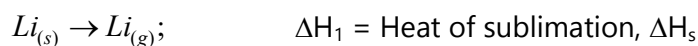
(ii) The standard oxidation potentials of a alkali metals (in volts) are listed below,

Li	Na	K	Rb	Cs
+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 ionization energy for alkali metals reveals that Li should have the minimum tendency to lose electron and thus its reducing nature should be minimum. The greatest reducing nature of Li in aq. medium is accounted due to the maximum hydration energy of  $Li^+$  ion. For Lithium



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

$\Delta H_h$  for Li  $>$   $\Delta H_h$  for Na. Therefore, large negative  $\Delta H$  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 colors:** The alkali metals and their salts give characteristic color to Bunsen flame. The flame energy causes an excitation of the outermost electron which on reverting back to its initial position gives out the absorbed energy as visible light. These colors differ from each other: Li – crimson, Na – Golden yellow, K – Pale violet, Rb and Cs – violet. These different colors are due to different ionization energies of alkali metals. The energy released is minimum in the case of  $\text{Li}^+$  and increases in the order.

Energy released :  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$

$\lambda$  Released :  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$

Frequency released :  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$

### Chemical properties

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

(i) **Lithium:** Triphylite, Petalite, lepidolite, Spodumene [ $\text{LiAl}(\text{SiO}_3)_3$ ], Amblygonite [ $\text{Li}(\text{Al F})\text{PO}_4$ ]

(ii) **Sodium:** Chile salt petre ( $\text{NaNO}_3$ ), Sodium chloride ( $\text{NaCl}$ ), Sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), Borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), Glauber salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ )

(iii) **Potassium:** Sylite ( $\text{KCl}$ ), carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) and Felspar ( $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ )

(iv) **Rubidium:** Lithium ores Lepidolite, triphylite contains 0.7 to 3%  $\text{Rb}_2\text{O}$

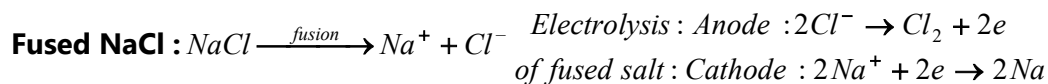
(v) **Caesium:** Lepidolite, Pollucite contains 0.2 to 7%  $\text{Cs}_2\text{O}$

(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.

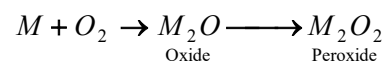


### (3) Alloys Formation

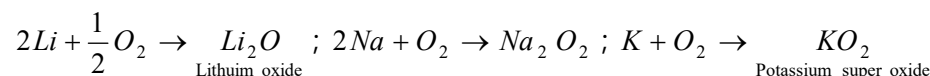
- (i) The alkali metals form alloys among themselves as well as with other metals.
- (ii) Alkali metals also get dissolved in mercury to form amalgam with evolution of heat and the amalgamation is highly exothermic.

### (4) Formation of oxides and hydroxides

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



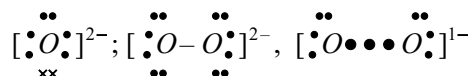
(ii) When burnt air ( $O_2$ ), lithium forms lithium oxide ( $Li_2O$ ) sodium forms sodium peroxide ( $Na_2O_2$ ) and other alkali metals form super oxide ( $MO_2$  i.e.  $KO_2, RbO_2$  or  $CsO_2$ )



The 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.

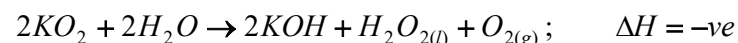
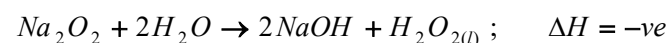
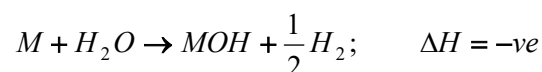


The monoxide, peroxides and superoxides have  $O^{2-}$  and  $O_2^{2-}$ ,  $O_2^{1-}$  ions respectively. The structures of each are,



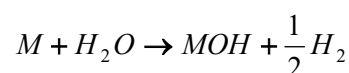
The  $O_2^{1-}$  ion has a three electron covalent bond and has one electron unpaired. It is therefore superoxides are paramagnetic and colored  $KO_2$  is light yellow and paramagnetic substance.

(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 oxidizing agents due to formation of  $H_2O_2$

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



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

## (5) Hydrides

(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 &  $H_2$ ;  $MH + H_2O \rightarrow MOH + H_2$

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

(v) The electrolysis of fused hydrides give  $H_2$  at anode.  $NaH_{fused}$  Contains  $Na^+$  and  $H^-$  i.e.,

At cathode:  $Na^+ + e \rightarrow Na$  ; At anode:  $H^- \rightarrow \frac{1}{2}H_2 + e$

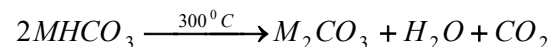
(vi) Alkali metals also form hydrides like  $NaBH_4$ ,  $LiAlH_4$  which are good reducing agent.

### (6) Carbonates and Bicarbonates

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

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

(iii) Bicarbonates are decomposed at relatively low temperature,



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

### (7) Halides

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

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

(iii) 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.

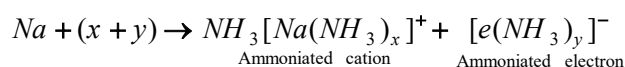
$KI + I_2 \rightarrow KI_3$ ; In  $KI_{3(aq)}$  the ions  $K^+$  and  $I_3^-$  are present

### (8) Solubility in liquid $NH_3$

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

(ii) With increasing concentration of ammonia, blue color 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 color, paramagnetic nature and reducing power of alkali metals in ammonia solution. However, the increased conductance nature of these metals in ammonia is due to presence of ammoniated cation and ammonia solvated electron.

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

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

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



### (10) Sulphates

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

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

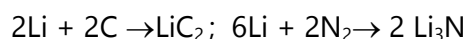
- (iii) These sulphates on fusing with carbon form sulphides,  $M_2SO_4 + 4C \rightarrow M_2S + 4CO$
- (iv) The sulphates of alkali metals (except Li) form double salts with the sulphate of the trivalent metals like Fe, Al, Cr etc. The double sulphates crystallize with large number of water molecules as alum. e.g.  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24 H_2O$ .

**(11) Reaction with non-metals**

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

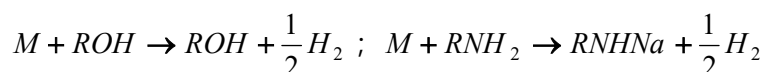
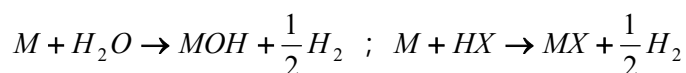


(ii) Li reacts, however directly with carbon and nitrogen to form carbides and nitrides.



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

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



**(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 behavior of Lithium**

Anomalous behavior 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 H<sub>2</sub>. (iii) It hardly reacts with bromine while other alkali metals react violently.

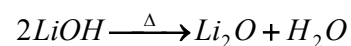
(4) Lithium is the only alkali metal which directly reacts with N<sub>2</sub>.

(5) Lithium when heated in NH<sub>3</sub> forms imide, Li<sub>2</sub>NH while other metals form amides, MNH<sub>2</sub>.

(6) When burnt in air, lithium forms Li<sub>2</sub>O sodium forms Na<sub>2</sub>O and Na<sub>2</sub>O<sub>2</sub> other alkali metals form monoxide, peroxide and superoxide.

(7) Li<sub>2</sub>O is less basic and less soluble in water than other alkali metals.

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



(9) LiHCO<sub>3</sub> is liquid while other metal bicarbonates are solid.

(10) Only Li<sub>2</sub>CO<sub>3</sub> decomposes on heating  $Li_2CO_3 \xrightarrow{heat} Li_2O + CO_2$ . Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> etc. do not decompose on heating.

(11) LiNO<sub>3</sub> and other alkali metal nitrates give different products on heating



(12) LiCl and LiNO<sub>3</sub> are soluble in alcohol and other organic solvents. These salts of other alkali metals are, however, insoluble in organic solvents.

(13) LiCl is deliquescent while NaCl, KBr etc. are not. Lithium chloride crystals contain two molecules of water of crystallization (LiCl · 2H<sub>2</sub>O). Crystals of NaCl, KBr, KI etc do not contain water of crystallization.

(14) Li<sub>2</sub>SO<sub>4</sub> 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.

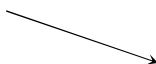
(16) Li reacts with Br<sub>2</sub> slowly. Reaction of other alkali metals with Br<sub>2</sub> is fast.

(17) Li<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, LiF, Li<sub>3</sub>PO<sub>4</sub> 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 CO<sub>2</sub>. 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.

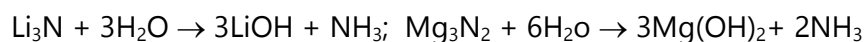




Hydroxides of other alkali metals are stable towards heat while their nitrates give  $\text{O}_2$  and nitrite.

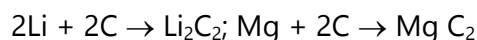


(6) Both Li and Mg combine directly with  $\text{N}_2$  to give nitrides  $\text{Li}_3\text{N}$  and  $\text{Mg}_3\text{N}_2$ . Other alkali metals combine at high temperature,  $6\text{Li} + \text{N}_2 \rightarrow 2\text{Li}_3\text{N}$ ;  $3\text{Mg} + \text{N}_2 \rightarrow \text{Mg}_3\text{N}_2$ .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



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

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

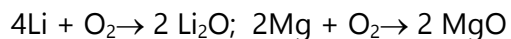


(9) The periodic properties of Li and Mg are quite comparable

	Li	Mg
Electronegativity	1.0	1.2
Atomic radii	1.23	1.36
Ionic radii	0.60( $\text{Li}^+$ )	0.65( $\text{Mg}^{+2}$ )
Atomic volume	12.97 c.c	13.97 c.c

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

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



(12)  $\text{Li}_2\text{SO}_4$  Like  $\text{MgSO}_4$  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  $MgCl_2$  both are deliquescent and separate out from their aqueous solutions as hydrated crystals,  $LiCl \cdot 2H_2O$  and  $MgCl_2 \cdot 2H_2O$ .

## Sodium and its compounds

(1) **Ores of sodium:**  $NaCl$  (common salt),  $NaNO_3$  (chile salt petre),  $Na_2SO_4 \cdot 10H_2O$  (Glauber's salt), borax (sodium tetraborate or sodium borate,  $Na_2B_4O_7 \cdot 10H_2O$ ).

(2) **Extraction of sodium:** It is manufactured by the electrolysis of fused sodium chloride in the presence of  $CaCl_2$  and  $KF$  using graphite anode and iron cathode. This process is called **down process**.



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

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

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

## (3) Compound of sodium

**Sodium hydroxide** (Caustic soda), **NaOH**

### (i) Preparation

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

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

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

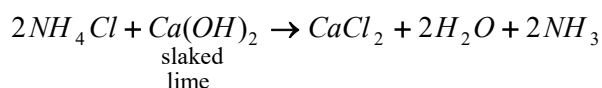
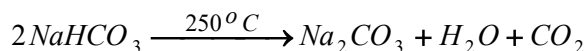
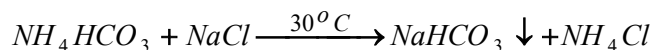
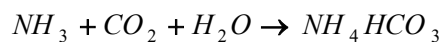
(c) Castner - Kellener cell (Mercury cathode process):  $NaOH$  obtained by electrolysis of aq. solution of brine. The cell comprises of rectangular iron tank divided into three compartments.

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

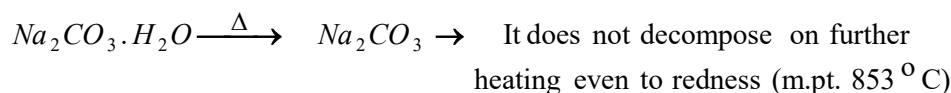
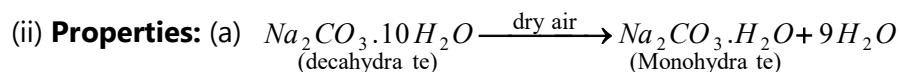




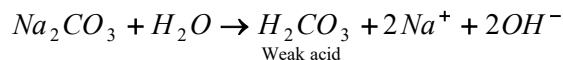
(i) **Preparation:** Solvay process : In this process, brine ( $NaCl$ ),  $NH_3$  and  $CO_2$  are the raw materials.



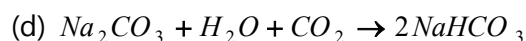
Note:  $CaCl_2$  so formed in the above reaction is a byproduct of solvay process.



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



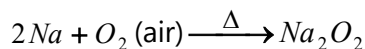
(c) It is readily decomposed by acids with the evolution of  $CO_2$  gas.



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

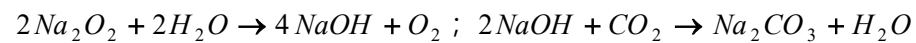
### Sodium peroxide ( $Na_2O_2$ )

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



(ii) **Properties:** (a) When pure it is colorless. The faint yellow color 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 oxidizing agent. It oxidizes *Cr* (III) hydroxide to sodium chromate, *Mn* (II) to sodium manganite and sulphides to sulphates.

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