s-Block Elements

are called s-block ele nts.

As the s-orbital can accommodate only two electrons, two groups 1 and 2 belong to the s-block.

Flame Test

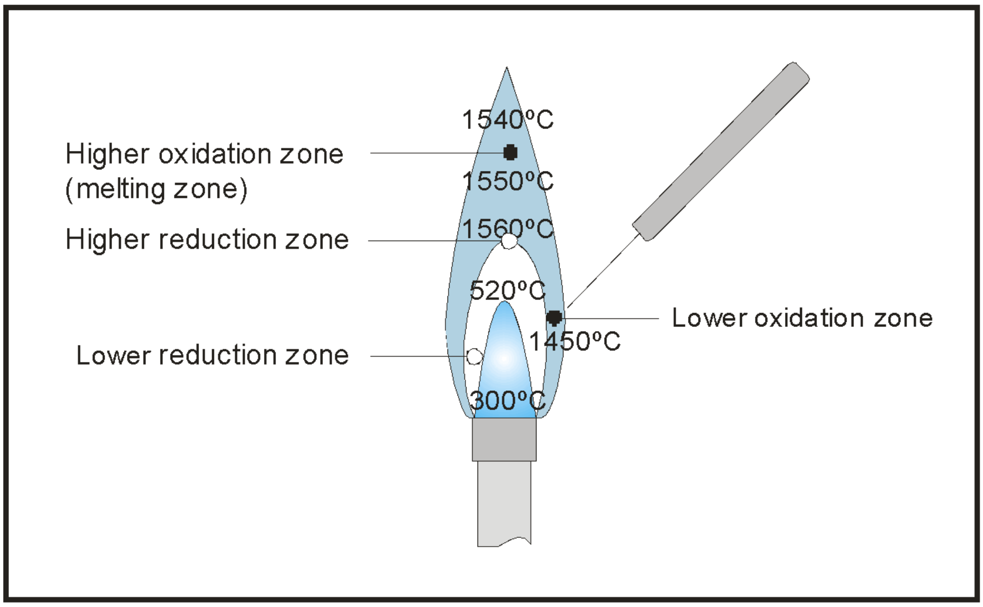
The alkali metals and alkaline earth metals and their salts impart characteristic colour to an oxidizing flame.

Reason : This is because the heat from the flame excites the outermost orbital electron to a higher energy level. When they drop back to the ground state, there is emission of radiation in the visible region.

The electrons in beryllium and magnesium are too strongly bound (due to small size) to get excited by flame. Hence, these elements do not impart any colour to the flame.

Metal	Li	Na	K	Rb	Cs
Colour	Crimson red	Yellow	Violet / Lilac	Red violet	Blue

Metal	Be	Mg	Ca	Sr	Ba
Colour	No colour	No colour	Brick red	Crimson red	Apple green



Section (A) & (B) : Atomic and Physical Properties of Alkali metals and Alkaline earth metal

Group – 1st(IA) Elements : (Alkali Metals)

Atomic and Physical properties of the Alkali metals

Property	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Caesium Cs	Francium Fr
Atomic number	3	11	19	37	55	87
Atomic mass (g mol^{-1})	6.94	22.99	39.10	85.47	132.91	(223)
Electronic configuration	[He] $2s^1$	[Ne] $3s^1$	[Ar] $4s^1$	[Kr] $5s^1$	[Xe] $6s^1$	[Rn] $7s^1$
Ionization enthalpy / kJ mol^{-1}	520	496	419	403	376	~375
Hydration enthalpy/kJ mol^{-1}	–506	–406	–330	–310	–276	–
Metallic radius / pm	152	186	227	248	265	–
Ionic radius M^+ / pm	76	102	138	152	167	(180)
m.p. / K	454	371	336	312	302	–
b.p / K	1615	1156	1032	961	944	–
Density / g cm^{-3}	0.53	0.97	0.86	1.53	1.90	–
Standard potentials $E^{\ominus}$ / V for (M^+ / M)	–3.04	–2.714	–2.925	–2.930	–2.927	–
Occurrence in lithosphere†	18*	2.27**	1.84**	78-12*	2-6*	~ 10^{-18} *

*ppm (part per million), ** Percentage by weight

Group IIA Elements (Alkaline Earth Metals)

Property	Beryllium Be	Magnesium Mg	Calcium Ca	Strontium Sr	Barium Ba	Radium Ra
Atomic number	4	12	20	38	56	88
Atomic mass (g mol^{-1})	9.01	24.31	40.08	87.62	137.33	226.03
Electron configuration	[He] $2s^2$	[Ne] $3s^2$	[Ar] $4s^2$	[Kr] $5s^2$	[Xe] $6s^2$	[Rn] $7s^2$
Ionization enthalpy (I) / kJ mol^{-1}	899	737	590	549	503	509
Ionization enthalpy (II) /kJ mol^{-1}	1757	1450	1145	1064	965	979
Hydration enthalpy (kJ/mol)	– 2494	– 1921	–1577	– 1443	– 1305	–
Metallic radius / pm	112	160	197	215	222	–
Ionic radius M^{2+}/ pm	31	72	100	118	135	148
m.p. / K	1560	924	1124	1062	1002	973
b.p / K	2745	1363	1767	1655	2078	(1973)
Density / g cm^{-3}	1.84	1.74	1.55	2.63	3.59	(5.5)
Standard potential $E^{\ominus}$ / V for (M^{2+}/ M)	–1.97	–2.36	–2.84	–2.89	– 2.92	–2.92
Occurrence in lithosphere	2*	2.76**	4.6**	384*	390*	10^{-6}*

Properties of Alkali and Alkaline earth metals

S.No.	Atomic Properties	Alkali metal	Alkaline earth metals

1.	Outer Electronic configuration	ns^1	ns^2
2.	Oxidation number and valency	(i)These elements easily form univalent +ve ion by losing loosely solitary ns^1 electron due to low IP value.	The IP_1 of these metals are much lower than IP_2 and thus it appears that these metals should form univalent ion rather than divalent ions but in actual practice, all these give bivalent ion.
3.	Atomic and Ionic radii	Increase down the group, because value of n (principal quantum number) increases. Order = Li < Na < K < Rb < Cs.	The atomic and ionic radii of the alkali earth metal are smaller than corresponding alkali metals. Reason higher nuclear charge (Zeff) On moving down the group size increase, as value of n increases. Be < Mg < Ca < Sr < Ba
4.	Ionisation Energy	As size increases, I.E. decreases down the group (so Cs have lowest I.P.) Order = Li > Na > K > Rb > Cs	Down the group IE decreases due to increase in size. Be > Mg > Ca > Sr > Ba IE_1 of Alkali metal < IE_1 of Alkaline earth metal IE_2 of Alkali metal > IE_2 of Alkaline earth metal Reason IE_1 of Alkaline earth metal is large due to increased nuclear charge in Alkaline earth metal as compared to Alkali metal but IE_2 of Alkali metal is large because second electron in Alkali metal is to be removed from cation which has already acquired noble gas configuration
5.	Electropositive character or metallic character	Alkali metals are strongly electropositive and metallic. Down the group electropositive nature increase so metallic nature also increases. i.e. $M \rightarrow M^+ + e^-$ Metallic Nature : Electropositive character 1 /I.P. Order = Li < Na < K < Rb < Cs.	Due to low IE they are strong electropositive but not as strong as Alkali metal because of comparatively high IE. The electropositive character increase down the group. Order = Be < Mg < Ca < Sr < Ba
6.	Hydration of ions	**(i)** Hydration represents for the dissolution of a substance in water to get absorb water molecule by weak valency forces Hydration of ions in the process when ions on dissolution in water get hydrated. **(ii)** Hydration energy ∝ charge density on ion Degree of hydration ∝ 1/Cation size ∝ charge ∝ 1/ionic mobility ∝ 1/conductivity Hydration energy = $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ **(iii)** Li^+ being smallest in size has maximum degree of hydration and that is why lithium salts are mostly hydrated and moves very slowly under the influence of electric field. e.g : $LiCl.2H_2O$.	Hydration energy = $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$
7.	Photoelectric effect	The phenomenon of emission of electrons when electromagnetic rays strikes against them is called photoelectric effect; Alkali metal have low I.P. so show photoelectric effect. Cs and K are used in Photoelectric cells.	
8.	Electronegativity	**(i)**These metals are highly electopositive and there by possess low values of electro negativities. **(ii)**Electronegativity of alkali metals decreases down the group. Order = Li > Na > K > Rb > Cs	**(i)** Their electronegativities are also small but are higher than that of alkali metals **(ii)** Electronegativity decrease from Be to Ba

S.No.	Physical Property	Alkali metal	Alkaline earth metals
1.	Density	(i)All are light metals. (ii) Density increase down the group but K is lighter than Na. **Order** = Li < K < Na < Rb < Cs	**(i)** Heavier than alkali metals. **(ii)** Density decrease slightly up to Ca after which it increases. **(iii)** Density of Mg is greater than Ca.
2.	Hardness  The cutting of sodium metal	(i) All are silvery white metals. (ii) Light soft, malleable and ductile metals with metallic luster. (iii) Diamagnetic and colour less in form of ions. (iv) These metals are very soft and can be cut with a knife. Lithium is harder than any other alkali metal. The hardness depends upon cohesive energy. Cohensive energy Force of attraction between atoms.	Relatively soft but harder than Alkali metals.
3.	Melting points/ Boiling points	(i) Lattice energy decreases from Li to Cs and thus Melting points and Boiling points also decrease from Li to Cs. M.P. = Li > Na > K > Rb > Cs B.P. = Li > Na > K > Rb > Cs	They have low Melting points and Boiling points but are higher than corresponding value of group I. Reason They have two valence electrons which may participate in metallic bonding compared with only one electron in Alkali metal. Consequently group II elements are harder and have higher cohesive energy and so, have much higher Melting points / Boiling points than Alkali metal . M.P. = Be > Ca > Sr >Ba > Mg ,B.P. = Be > Ba > Ca > Sr > Mg
4.	Specific heat	It decreases from Li to Cs. Li > Na > K > Rb > Cs ***(*need not to memorise)***	values are lesser than that of alkali metals, decreases down the group. **need not memorise.*

Section (C) & (D) : Chemical properties of Alkali & Alkaline earth metals

<table>
<tr><th>S.No.</th><th>Chemical Property</th><th>Alkali metals</th><th>Alkaline earth metals</th></tr>
<tr><td>1.</td><td>Action with O_2 and N_2</td><td>
(i) They generally form oxides and peroxides.

$M+O_2 \longrightarrow M_2O$ (Oxide) $\xrightarrow{O_2}$ M_2O_2 (Peroxide)

The alkali metals tarnish in dry air due to the formation of their oxides on their surface.

$4M + O_2 \longrightarrow 2M_2O$

They react vigorously in oxygen forming following oxides.

$4\,Li + O_2 \longrightarrow 2\,Li_2O$ (Monoxide)

$2\,Na + O_2 \longrightarrow Na_2O_2$ (Peroxide)

$M + O_2 \longrightarrow MO_2$ (Superoxide) where M = K, Rb, Cs

<table>
<tr><th colspan="4">Principal Combustion Product (Minor Product)</th></tr>
<tr><th>Metal</th><th>Oxide</th><th>Peroxide</th><th>Superoxide</th></tr>
<tr><td>Li</td><td>Li_2O</td><td>(Li_2O_2)</td><td></td></tr>
<tr><td>Na</td><td>(Na_2O)</td><td>Na_2O_2</td><td></td></tr>
<tr><td>K</td><td></td><td></td><td>KO_2(Orange/Yellow Crystalline)</td></tr>
<tr><td>Rb</td><td></td><td></td><td>RbO_2 (Orange/Yellow Crystalline)</td></tr>
<tr><td>Cs</td><td></td><td></td><td>CsO_2 (Orange/Yellow Crystalline)</td></tr>
</table>

The oxides and peroxides are colourless when pure.

(ii) All super oxide are paramagnetic and peroxides are diamagnetic in nature.
</td><td>
(i) Be and Mg are kinetically inert towards oxygen becasue of formation of a film of oxide on their surface. However powdered Be burn brilliantly.

$2Be + O_2$ (air) $\xrightarrow{\Lambda}$ 2BeO(amphoteric) ;

$3Be + N_2$ (air) $\xrightarrow{\Lambda}$ Be_3N_2

(ii) Mg is more electropositive and burns with dazzling brilliance in air give MgO and Mg_3N_2.

$Mg + O_2$(air) $\xrightarrow{\Lambda}$ MgO ;

$Mg + N_2$(air) $\xrightarrow{\Lambda}$ Mg_3N_2

Peroxides are coloured due to lattice defect.

(Similar property with Li because both shows diagonal relation.)

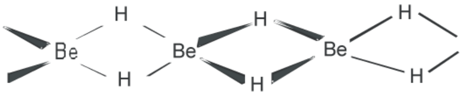
(iii) Ba gives BaO_2 not BaO.

(iv) Calcium, strontium and barium are readily attacked by air to form the oxide and nitride. They also react water with increasing vigour even in cold to form hydroxides.

(v) BeO, MgO are used as refractory, because they have high M.P.

(vi) Other metals (Ba or Sr form peroxide)

$M + O_2 \xrightarrow{\Lambda} MO_2$
</td></tr>
</table>

<table>
<tr><td></td><td></td><td>(iii) The increasing stability of the peroxide or superoxide as the size of the metal ion increases is due to the stabilisation of large anions by larger cations through lattice energy effect.
(iv) Since all the alkali metals are highly reactive towards air ; they are kept in kerosene oil. Reactivity increases from Li to Cs.
(v) Only Lithium reacts with N_2 (at room temperature) to form ionic lithium nitride Li_3N because Li being strongest reducing agent converts N_2 into N^{3-}.
$3Li + 1/2N_2 \longrightarrow Li_3N$</td><td></td></tr>
<tr><td>2.</td><td>Action with water</td><td>(i) Alkali metals decompose water to form the hydroxides having the formula MOH and dihydrogen.
$2M + 2H_2O \longrightarrow 2MOH\ (aq.) + H_2(g)$ (M = An alkali metal).
(ii) Li decompose water slowly, sodium reacts with water quickly K, Rb and Cs react with water vigorously.
(iii) It may be noted that although lithium has most negative $E^{\ominus}$ value (In below table), its reaction with water is less vigorous than that of sodium which has the least negative $E^{\ominus}$ value among the alkali metals. This behaviour of lithium is attributed to its small size and very high hydration energy. It's explanation lies in Kinetics, released energy in case of K, Rb, Cs is sufficient to melt or even vapourise and so more surface area is exposed to the water and kinetically reaction is faster than lithium. Other metals of the group react explosively with water.
<table>
<tr><th rowspan="2">Property</th><th colspan="6">Alkali metals</th></tr>
<tr><th>Li</th><th>Na</th><th>K</th><th>Rb</th><th>Cs</th><th>Fr</th></tr>
<tr><td>Standard potentials $E^{\ominus}$/V for (M^+/M)</td><td>–3.04</td><td>–2.714</td><td>–2.925</td><td>–2.930</td><td>–2.927</td><td>–</td></tr>
</table>
(iv) They also react with proton donors such as alcohol, gaseous ammonia and terminal alkynes evolution of hydrogen.
$\underset{\text{Ethyl alcohol}}{2M + 2C_2H_5OH} \longrightarrow \underset{\text{Metal ethoxide}}{2C_2H_5OM + H_2}$</td><td>(i) Ca , Sr , Ba and Ra decompose cold water readily with evolution of hydrogen.
$M + 2H_2O \longrightarrow M(OH)_2 + H_2$
(ii) Magnesium decomposes boiling water but beryllium is not attacked by water even at high temperatures as its oxidation potential is lower than the other members</td></tr>
<tr><td>3.</td><td>Hydrides</td><td>(i)They react with H_2 forming metal hydride with formula MH which are of ionic nature. Stability of hydride decreases down the group. since the electropositive character decreases from Cs to Li.
$2M + H_2 \longrightarrow 2M^{\oplus}H^{\ominus}$
(iii)The metal hydrides react with water to give MOH and H_2. (act as reducing agent)
$MH + H_2O \longrightarrow MOH + H_2$</td><td>(i) Except Be, all alkaline earth metals form hydrides (MH_2) on heating directly with H_2.
(ii)The stability of hydrides decreases from Be to Ra.
(iii) BeH_2 is prepared by the action of $LiAlH_4$ on $BeCl_2$.
$BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3$
BeH_2 & MgH_2 is covalent and polymeric but other are ionic.

(iv) The ionic hydrides of Ca, Sr, Ba liberate H_2 at anode and metal at cathode.</td></tr>
<tr><td>4.</td><td>Halides</td><td>(i)The alkali metals react vigorously with halogens to form ionic halides M^+X^- .
$2M + X_2 \longrightarrow 2M^+X^-$
(ii) Alkali metals halides (Cl_2, Br_2, I_2) formation is increases form Li to Cs due to increase in electropositive character.
Order of reactivity towards F_2
Li > Na > K > Rb > Cs
(iii) LiX have more covalent character (It is because of the high polarisation capability of Lithium ion (fajan's rules)).
(iv)Halides having ionic nature have high melting point and are good conductor of current in fused state. These are readily soluble in water.</td><td>(i)The alkaline earth metals directly combine with halogens on heating to give metal halides MX_2 (X=F,Cl,Br,I)
(ii) Thermal decomposition of $(NH_4)_2BeF_4$ is the best route for the preparation of BeF_2, and $BeCl_2$ is conveniently made from the oxide.
$BeO + C + Cl \xrightarrow{600\text{-}800\ K} BeCl_2 + CO$
Anhydrous beryllium halide can not be obtained from materials made in aqueous solution because the hydrated ions $[Be(H_2O)_4]^{2+}$ is formed. i.e. $[Be(H_2O)_4]Cl_2$
On dehydration, hydrolysis takes place.
$[Be(H_2O)_4]Cl_2 \xrightarrow{\text{heat}} Be(OH)_2 + 2HCl$</td></tr>
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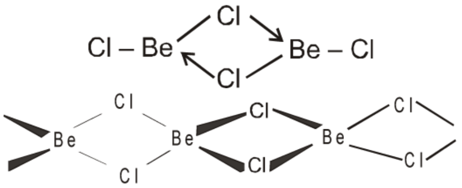
<td>(v) Halides of potassium, rubidium and ceasium have property of combining with extra halogen atoms forming polyhalides.
$KI + I_2 \longrightarrow KI_3$</td>
<td>(iii) Except for beryllium halides, all other halides of alkaline earth metals are ionic in nature. Beryllium halides are essentially covalent and soluble in organic solvents. Beryllium chloride has a chain structure in the solid state as shown below :
Cl–Be–Cl

In the vapour phase $BeCl_2$ tends to form a chloro-bridged dimer which dissociates into the linear monomer at high temperatures of the order of 1200 K.
(iv)The ionic character of halides increases from Be to Ra.
(v)Beryllium halides have covalent character due to small size and high effective nuclear charge and thus do not conduct electricity in molten state.
(vi) The fluorides are relatively less soluble than the chlorides owing to their high lattice energies.
(vii)The decreases in solubility of halides down the group is due to decrease in hydration energy because of increasing size of metal cation .
(viii) The tendency to form halide hydrates gradually decreases (for example, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$) down the group. The dehydration of hydrated chlorides, bromides and iodides of Ca, Sr and Ba can be achieved on heating; however, the corresponding hydrated halides of Be and Mg on heating suffer hydrolysis.
(ix) $CaCl_2$ has strong affinity with water and is used as dehydrating agent.</td>
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<tr>
<td>5.</td>
<td>Reducing nature
(*need not to memorise)</td>
<td>
<table>
<tr><td>Property</td><td colspan="6">Alkali metals</td></tr>
<tr><td></td><td>Li</td><td>Na</td><td>K</td><td>Rb</td><td>Cs</td><td>Fr</td></tr>
<tr><td>Standard potentials $E^{\ominus}/V$ for (M^+/M)</td><td>–3.04</td><td>–2.714</td><td>–2.925</td><td>–2.930</td><td>–2.927</td><td>–</td></tr>
</table>
(i) Reducing agent is electron donor. The alkali metals are strong reducing agents, lithium being the most and sodium the least powerful (above table). The standard electrode potential ($E^{\ominus}$) which measures the reducing power represents the overall change :
$M(s) \longrightarrow M(g)$ Sublimation enthalpy
$M(g) \longrightarrow M^+(g) + e^-$ Ionization enthalpy
$M^+(g) + H_2O \longrightarrow M^+(aq)$ Hydration enthalpy
(ii) Lithium is expected to be least reducing agent due to it's very high I.E. However, lithium has the highest hydration enthalpy which accounts for its high negative $E^{\ominus}$ value and its high reducing power.
Reducing Nature in gas phase
= Li < Na < K < Rb < Cs.
Reducing Nature in aqueous condition
= Li > Cs > Rb > K > Na.</td>
<td>The alkaline earth metals are strong reducing agents. This is indicated by large negative values of their reduction potentials (below table). However their reducing power is less than those of their corresponding alkali metals. Beryllium has less negative value compared to other alkaline earth metals.
However, its reducing nature is due to large hydration energy associated with the small size of Be^{2+} ion and relatively large value of the atomization enthalpy of the metal.
<table>
<tr><td>Property</td><td colspan="6">Alkaline earth metals</td></tr>
<tr><td></td><td>Be</td><td>Mg</td><td>Ca</td><td>Sr</td><td>Ba</td><td>Ra</td></tr>
<tr><td>Standard potentials $E^{\ominus}/V$ for (M^+/M)</td><td>–1.97</td><td>–2.36</td><td>–2.84</td><td>–2.89</td><td>–2.92</td><td>–2.92</td></tr>
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</td>
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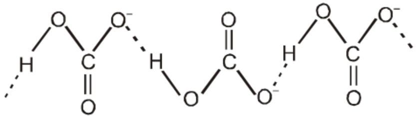
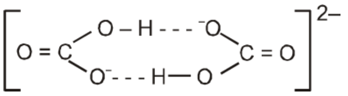
6.	Basic nature of hydroxide	(i) These oxides are easily hydrolysed by water to form the hydroxides. Thus M_2O (oxide) + $H_2O \longrightarrow M^{\oplus}OH^{\ominus}$ M_2O_2 (peroxide) + $H_2O \longrightarrow 2M^{\oplus}OH^{\ominus} + H_2O_2$ MO_2 (superoxide) + $H_2O \longrightarrow 2M^{\oplus}OH^{\ominus} + H_2O_2 + O_2$ (ii) The Hydroxide which are obtained by the reaction of the oxide. With water all are white crystalline solids. The alkali metal hydroxides are the strongest of all bases and dissolve freely in water with evolution of much heat an account of intense hydration. Basic nature/Solubility in water/Thermal stability = LiOH < NaOH < KOH < RbOH < CsOH	Basic/thermal stability = $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$
7.	Carbonates and bicarbonates	(i) The carbonates (M_2CO_3) and bicarbonates ($MHCO_3$) are highly stable to heat, where M as alkali metals. (ii) Group 1 metals are so strongly basic, they (except lithium) also form solid bicarbonates. No other metals form solid bicarbonates. Lithium carbonate is not so stable to heat. Its hydrogencarbonate does not exist as a solid. Although NH_4HCO_3 also exists as a solid. (iii) The stability of these salts increases with the increasing electropositive character from Li to Cs. It is therefore Li_2CO_3 decompose on heating. Thermal stability/Solubility in water. $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$ $LiHCO_3$ does not exist in solid form due to high polarizing power of Li^+ and uncomparable size of Li^+ cation and HCO_3^- anion. $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$ (iv) Bicarbonates are decomposed at relatively low temperature. $2MHCO_3 \xrightarrow{300^0C} M_2CO_3 + H_2O + CO_2$ (v) Hydrolysis of carbonate $Na_2CO_3 + 2H_2O \longrightarrow 2NaOH + H_2CO_3$ $Li_2CO_3 + 2H_2O \longrightarrow$ sparingly soluble (vi) The crystal structures of $NaHCO_3$ and $KHCO_3$ both show hydrogen bonding, but are different. (a) In $NaHCO_3$, the HCO_3^- ions are linked into an infinite chain. (b) in $KHCO_3$, $RbHCO_3$, $CsHCO_3$, HCO_3^- forms a dimeric anion. Solubility in water $NaHCO_3 < KHCO_3 < RbHCO_3 < CsHCO_3$ (a)  (b) 	(i) All these metal carbonates MCO_3 are insoluble in neutral medium but soluble in acids and decompose on red heating. (ii) The stability of carbonates increases with increase in electropositive character of metal. $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$ (iii) Bicarbonates of alkaline earth metals do not exist in solid state but are known in solution only on heating their solution bicarbonates decomposed to liberate CO_2 . $M(HCO_3)_2 \xrightarrow{\Delta} MCO_3 + CO_2 + H_2O$ (Solution) (iv)Solubility of carbonates decrease on moving down the group. $BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$
8.	Complex ion formation	(i) A metal shows complex formation only when it has following characteristics. (a) Small size, (b) High nuclear charge, (c) Presence of empty orbitals in order to accept electron pair from ligand (electron pair donor species). (ii) Due to small size only Lithium in alkali metals, forms a few complex ions. Rest all alkali metals do not possess the tendency to form complex ion.	Be^{2+} on account of smaller size forms many complexes such as $[Be F_3]^-$, $[BeF_4]^{2-}$ Chlorophyll contains Mg^{2+} [Photosynthetic pigment in plants] (C.No.= 4) $[Be(H_2O)_4]^{2+} + H_2O \longrightarrow [Be(H_2O)_3OH]^+ + H_3O^+$
9.	Reaction with acids	Reacts vigorously with acids $2M + H_2SO_4 \longrightarrow M_2SO_4 + H_2$	The alkaline earth metals readily react with acids liberated dihydrogen. $M + 2HCl \longrightarrow MCl_2 + H_2$
10.	Formation of amalgams	(i) Alkali metals get dissolved in mercury to form amalgams with evolution of heat and the amalgamation is highly exothermic.	Alkaline earth metals get dissolved in mercury to form amalgams with evolution of heat and the amalgamation is highly exothermic.

		(ii) Alkali metals form alloys themselves as well as with other metals.	
11.	Sulphates	(i) All these form sulphates of type M_2SO_4. (ii) Except Li_2SO_4 rest all are soluble in water. Thermal stability /solubility in water $Li_2SO_4 < Na_2SO_4 < K_2SO_4 < Rb_2SO_4 < Cs_2SO_4$ (iii)These sulphates on fusing with carbon form sulphides. $M_2SO_4 + 4C \longrightarrow M_2S + 4CO$	(i) MSO_4 type sulphates are formed (ii)The solubility of sulphates decreases on moving down the group. The sulphates of the alkaline earth metals are all white solids and stable to heat. $BeSO_4$, and $MgSO_4$ are readily soluble in water; the solubility decreases from $CaSO_4$ to $BaSO_4$. The greater hydration enthalpies of Be^{2+} and Mg^{2+} ions overcome the lattice enthalpy factor and therefore their sulphates are soluble in water. Thermal stability $BeSO_4 < MgSO_4 < CaSO_4 < SrSO_4 < BaSO_4$ Solubility in water $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$ (iii) $MSO_4 + 2C \longrightarrow MS + 2CO_2$
12.	Sulphides	All metals react with S forming sulphides such as Na_2S and Na_2Sn (n = 2, 3, 4, 5 or 6). The polysulphide ions are made from zig-zag chains of sulphur atoms.	$M^{2+} + S^{2-} \longrightarrow MS$
13.	Nitrates	(i) Nitrates of both are soluble in water and decompose on heating. (ii) $LiNO_3$ decomposes to give NO_2 and O_2 and rest all give nitrites and oxygen. $2MNO_3 \longrightarrow 2MNO_2 + O_2$ (except Li) $4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$ $2NaNO_3 \xrightarrow[500^\circ C]{\Delta} 2NaNO_2 + O_2$ $2NaNO_3 \xrightarrow[800^\circ C]{\Delta} Na_2O + N_2 + N_2 + O_2$ $2NaNO_3 \xrightarrow{Na} Na_2O + N_2 + O_2$	On heating they decompose into their corresponding oxides with evolution of a mixture of nitrogen dioxide and oxygen. $M(NO_3)_2 \longrightarrow MO + 2NO_2 + \frac{1}{2}O_2$ (M = Be, Mg , Cr, Sr, Ba)
14.	Nitride	$Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3 \uparrow$	$Be_3N_2 + 6H_2O \longrightarrow 3Be(OH)_2 + 2NH_3 \uparrow$ $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3 \uparrow$
15.	Carbide	When Li is heated with carbon, an ionic carbide Li_2C_2 is formed. $2Li + 2C \longrightarrow Li_2C_2$ Other metals do not react with carbon directly but form carbides when heated with ethyne, or when ethyne is passed through a solution of metal in liquid ammonia. $Na + C_2H_2 \longrightarrow NaH + C_2 \longrightarrow Na_2C_2$ $[C{\equiv}C{-}H]^-$ $[C{\equiv}C]^{2-}$ $Na_2C_2 + 2H_2O \longrightarrow NaOH + C_2H_2$	The binary compounds of carbon with other elements (less electronegative or of similar electronegativity) are called carbides. They are classified into following 3 categories : (i) Ionic (ii) Covalent (iii) Interstitial (or metallic) **(i) Ionic carbides (or salt like carbides) :** Generally formed by the most electropositive elements such as alkali and alkaline earth metals and aluminium (Boron is exception). Based on the product obtained on hydrolysis, they are further sub-classified into three types. **(a) Methanides :** These give CH_4 on reaction with H_2O. $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$; $Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$ These carbides contain C^{4-} ions in their constitution. **(b) Acetylides :** These give C_2H_2 on reaction with H_2O. $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$ $Al_2(C_2)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3C_2H_2$ $SrC_2 + 2H_2O \longrightarrow Sr(OH)_2 + C_2H_2$ Such compounds contain C_2^{2-} ions. **(c) Allylides :** These give 1-propyne on reaction with H_2O. $Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3{-}C{\equiv}CH$ Such compounds contain C_3^{4-} $[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}-C\equiv C:]^{4-}$ ions. **Covalent carbides**

			Molecules like SiC and B_4C are also examples of covalent carbides. **Interstitial or metallic carbides** Such carbides are formed by transition metals and some of the lanthanides and actinides. Interstitial carbides retain many of the properties of metals. They conduct electricity by metallic conduction and have properties of metals (a lusture like a metal). In these compounds carbon atoms occupy octahedral holes in the closed packed metal lattice. These are generally very hard and have very high melting point (e.g. WC). Carbides of Cr, Mn, Fe, Co and Ni are hydrolysed by water or dilute acids.

Lattice Energy: Energy change when one mole of crystalline lattice is formed from gaseous ions

eg. $2Al^{3+} + 3O^{2-} \longrightarrow Al_2O_3 + L.E.$

Hydration Energy: It is the energy change when gaseous ions form aqueous ions.

eg. $Na^{+} + aq. \longrightarrow Na^{+} + H.E.\ of\ Na^{+}$

$SO_4^{2-} + aq. \longrightarrow SO_4^{2-} + H.E.\ of\ SO_4^{2-}$

Solutions in liquid NH_3

Alkali metals dissolve in liquid ammonia (high conc. 3 M) and give blue solution which is conducting, reducing and paramagnetic in nature.

Reason

On dissolving Metal in NH_3

$M(s) + NH_3(\ell) \longrightarrow M^{+}_{(NH3)} + e^{-}_{(NH3)}$

$M+ + x\,(NH_3) \longrightarrow [M\,(NH_3)X\,]+$ –→ Ammoniated cation

$e- + y\,(NH_3) \longrightarrow [e(NH_3)_y]-$ –→ Ammoniated electron

The blue colour is due to –→ Ammoniated electron

The paramagnetic nature is due to –→ Ammoniated electron

The conducting nature is due to –→ Ammoniated M+ + Ammoniated electron

On standing the colour fades due to formation of amide After liberating hydrogen.

$$M+ + e- + NH_3 \longrightarrow MNH_2\ (amide) + H_2\ (g)$$

In the absence of impurities like. Fe, Pt, Zn etc, the solutions are stable.

In concentrated solution, the blue colour changes to bronze colour and diamagnetic due to the formation of metal clusters and ammoniated electrons also associate to form electron pairs

$$2\ e-\ (NH3)y \longrightarrow [\ e-\ (NH3)y]2$$

Solutions are of much lower density than the pure solvent, i.e., they occupy for greater volume than that expected from the sum of the volumes of metal and solvent

Peroxide and superoxides of Na & K are widely used as Oxidising agent and air purifiers in space capsules, submarines and breathing mask.

Alkaline metal in liq. NH_3

Like alkali metals, the alkaline earth metals dissolve in liquid ammonia to give deep blue black solutions forming ammoniated ions

$M + (x + y)NH_3 \longrightarrow [M(NH_3)_x]^{2+} + 2[e(NH_3)_y]^{-}$

From these solutions, the hexa-ammoniates $[M(NH_3)_6]^{2+}$ can be recovered.

Uses of alkali metal

(1) Lithium metal is used to make useful alloys,

- with lead to make 'white metal' bearings for motor engines.
- with aluminium to make aircraft parts.
- with magnesium to make armour plates.

(2) It is used in thermonuclear reactions.

(3) Lithium is also used to make electrochemical cells.

(4) Sodium is used to make a Na/Pb alloy needed to make $PbEt_4$ and $PbMe_4$. These organolead compounds were earlier used as anti-knock additives to petrol, but nowadays vehicles use lead-free petrol.

(5) Liquid sodium metal is used as a coolant in fast breeder nuclear reactors.

(6) Potassium chloride is used as a fertilizer.

(7) Potassium hydroxide is used in the manufacture of soft soap. It is also used as an excellent absorbent of carbon dioxide.

(8) Caesium is used in devising photoelectric cells.

Uses of alkaline metal

(1) Beryllium is used in the manufacture of alloys.

(2) Copper-beryllium alloys are used in the preparation of high strength springs.

(3) Metallic beryllium is used for making windows of X-ray tubes.

(4) Magnesium forms alloys with aluminium, zinc, manganese and tin. Magnesium-aluminium alloys being light in mass are used in air-craft construction.

(5) Magnesium (powder and ribbon) is used in flash powders and bulbs, incendiary bombs and signals.

(6) A suspension of magnesium hydroxide in water (called *milk of magnesia*) is used as antacid in medicine.

(7) Magnesium carbonate is an ingredient of toothpaste.

(8) Calcium is used in the extraction of metals from oxides which are difficult to reduce with carbon.

(9) Calcium and barium metals, owing to their reactivity with oxygen and nitrogen at elevated temperatures, have often been used to remove air from vacuum tubes.

(10) Radium salts are used in radiotherapy, for example, in the treatment of cancer.

Biological Importance Of Sodium And Potassium:

- Sodium ions are found primarily on the outside of cells, being located in blood plasma and in the interstitial fluid which surrounds the cells. These ions participiate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the tranasport of sugars and amino acids into cells. Sodium and potassium, although so similar chemically, differ quantitatively in their ability to penetrate cell membranes, in their transport mechanisms and in their efficiency to activate enzymes. Thus, potassium ions are the most aundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals

A typical 70 kg man contains about 90 g of Na and 170 g of K compared with only 5 g of iron and 0.06 g of copper.

Biological Importance of Magnesium and Calcium :

- Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in **biological fluids**. These ions perform important **biological functions** such as maintenance of ion balance and nerve impulse conduction.
- All enzymes that utilise ATP in phosphate transfer require magnesium as the cofactor. The main pigment for the absorption of light in plants is chlorophyll which contains magnesium. About 99 % of body calcium is present in bones and teeth. It also plays important roles in neuromuscular function, interneuronal transmission, cell membrane integrity and blood coagulation.
- The calcium concentration in plasma is regulated at about 100 mgL^{-1}. It is maintained by two hormones : calcitonin and parathyroid hormone. Do you know that bone is not an inert and unchanging substance but is continuously being solubilised and redeposited to the extent of 400 mg per day in man? All this calcium passes through the plasma.

An adult body contains about 25 g of Mg and 1200 g of Ca compared with only 5 g of iron and 0.06 g of copper. The daily requirement in the human body has been estimated to be 200–300 mg.

ANOMALOUS PROPERTIES OF LITHIUM

The anomalous behavior of lithium is due to the :

(i) Exceptionally small size of its atom and ion,

(ii) High polarising power (i.e., charge/ radius ratio).

As a result, there is increased covalent character of lithium compound which is responsible for their solubility in organic solvent. Further, lithium shows diagonal relationship to magnesium.

S.No.	Property	Li
1.	Hardness	Li is much harder.
2.	M.P and B.P	Higher M.P and B.P
3.	Reactivity	Less reactive
4.	Reducing agent	Strong
5.	Combustion in air	Li form monoxide (Li_2O) and nitride (Li_3N) ; not for other.
6.	Hydration of ion	Favored for $Li^{\oplus}$; not for other. $Li^{\oplus}$ has maximum degree of hydration for this reason. Lithium salts are mostly hydrated. E.g $LiCl.2H_2O$.
7.	Hydrogen Carbonate	Li is not obtained in the solid form while all other elements form solid hydrogen carbonates.
8.	Ethynide	Favored for $Li^{\oplus}$; not for other.
9.	Lithium nitrate	$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$ Lithium Oxide Where as other alkali metal nitrates decompose to give the corresponding nitrite. $2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$ Sodium nitrite
10.	LiF and Li_2O	These are much less soluble in water. Solubility in water is less than the corresponding compounds of other alkali metal.
11.	Carbide	Li reacts directly with carbon to form anionic carbide.
12.	Hydroxide	Lithium hydroxide is less basic Li_2CO_3 , $LiNO_3$ and LiOH all form the oxides on gentle heating.
13.	Carbonate	Less stable.
14.	Nitrite	Less stable.
15.	Bicarbonate	Lithium forms a bicarbonates in solution it does not form a solid bicarbonate. Where as the other all forms stable solid Carbonates.
16.	Complex ion formation	Lithium has a great tendency to form. Complexes not for other. Due to small size of Lithium.
17.	Reaction with NH_3	Li when heated in NH_3 form imide (Li_2NH) while other alkali metals form amides (MNH_2)

Points of Similarities between Lithium and Magnesium

The similarity between lithium and magnesium is particularly striking and arises because of their similar size: atomic radii, Li = 152 pm, Mg = 160 pm; ionic radii : Li^+ = 76 pm, Mg^{2+} = 72 pm. The main points of similarity are :

S.No.	Properties	Li and Mg
1.	Hardness	Li and Mg are much harder.
2.	Density	These are lighter than other elements in the respective group.
3.	Reaction with water	Both react slowly with water.

4.	Solubility of hydroxide and oxide	Less soluble and their hydroxides decompose in acid on heating.
5.	Reaction with N_2	By direct combination with nitrogen both form a nitride Li_3N and Mg_3N_2.
6.	Oxides	The oxides Li_2O and MgO donot combine with excess oxygen to give any superoxide.
7.	Carbonates	Carbonates of both decompose easily on heating to form the oxides and CO_2. Solid hydrogen carbonates are not formed by Li and Mg.
8.	Solubility of halides in ethanol	Both LiCl and $MgCl_2$ are soluble.
9.	Hydration of ion	Both LiCl and $MgCl_2$ are deliquescent and crystallise from aqueous solution as hydrates, $LiCl.H_2O$ and $MgCl_2.6H_2O$.

Anamolous Behaviour of Beryllium

The properties of beryllium the first member of the alkaline earth metal, differ from the rest of the member. Its is mainly because of

(i) Its small size and high polarizing power.

(ii) Relatively high electro negativity and ionization energy as compared to other members.

(iii) Absence of vacant d–orbitals in its valence shell.

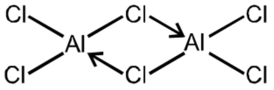
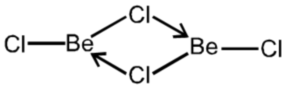
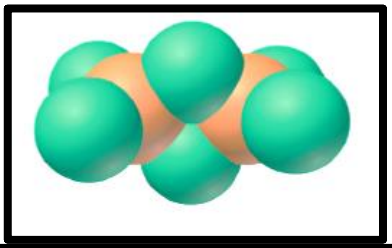
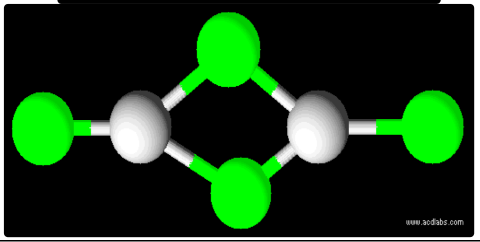
Some important points of difference between beryllium and other members (especially magnesium) are given below.

S.No.	Properties	Be
1.	Hardness	Be is harder than other members of its group
2.	Density	Be is lighter than Mg
3.	M.P. and B.P.	Higher then other members of its group.
4.	Reaction with water	Be does not react with water while Mg reacts with boiling water.
5.	Nature of oxides	BeO is amphoteric while MgO is weakly basic.
6.	Nature of compounds	Be forms covalent compounds whereas other members form ionic compounds.
7.	Carbide	Beryllium carbide reacts with water to give methane whereas carbides of other alkaline earth metals gives acetylene gas. $Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$ $Mg_2C_2 + 2H_2O \rightarrow Mg(OH)_2 + C_2H_2$ $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$
8.	Hydride	The beryllium hydride is electron deficient and polymeric, with muti center bonding like aluminium hydride.
9.	Co-ordination number	Beryllium does not exhibit coordination number more than four as it has four orbitals in the valence shell. The other members of this group has coordination number 6.
10.	Reaction with Alkali	Be dissolves in alkalies with evolution of hydrogen $Be + 2NaOH + 2H_2O \rightarrow \underset{\text{(sodium beryllate)}}{Na_2BeO_2.2H_2O} + H_2$ Other alkaline earth metals don't react with alkalies.

Resemblance of Beryllium with Aluminium (Diagonal relationship)

The following points illustrate the anomalous behaviour of Be and its resemblance with Al.

S.No.	Properties	Be and Al
1.	Nature of compounds	Unlike groups-2 elements but like aluminium, beryllium forms covalent compounds.
2.	Nature of hydroxide	The hydroxides of Be, [$Be(OH)_2$] and aluminium [$Al(OH)_3$] are amphoteric in nature, whereas those of other elements of group – 2 are basic in nature.
3.	Nature of oxide	The oxides of both Be and Al i.e. BeO and Al_2O_3 are high melting insoluble solids.

4.	Polymeric structure	$BeCl_2$ and $AlCl_3$ have bridged chloride polymeric structure.    
5.	Salts	The salts of beryllium as well as aluminium are extensively hydrolysed.
6.	Carbides	Carbides of both the metal reacts with water liberating methane gas. $Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$ $Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$
7.	Oxides and hydroxides	The oxides and hydroxides of both Be and Al are amphoteric and dissolve in sodium hydroxide as well as in hydrochloric acid. $BeO + 2HCl \rightarrow BeCl_2 + H_2O$ $BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$ $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + H_2O$ $Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$
8.	Reaction with acids	Like Al, Be is not readily attacked by acids because of the presence of an oxide film.

Section (E) : Compounds of Alkali metals

- **SODIUM OXIDE (Na_2O) :**

PREPARATION :

○ By heating sodium in limited supply of air at 180ºC :

$$Na + O_2 \longrightarrow Na_2O$$

PROPERTIES :

○ It is a white amorphous substance. It reacts with water violently forming sodium hydroxide and evolving a large amount of heat energy

$$Na_2O + H_2O \longrightarrow 2NaOH$$

○ On heating at 400°C, it disproportionates forming sodium peroxide and metallic sodium vapour.

$$2Na_2O \xrightarrow{400^\circ C} Na_2O_2 + 2Na$$ Referance as

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

- **SODIUM PEROXIDE (Na_2O_2)** :

PREPARATION :

○ It is formed by heating sodium in excess of air free from moisture and carbon dioxide or in excess of pure oxygen.

$$2Na + O_2(\text{excess}) \xrightarrow{350^\circ C} Na_2O_2$$

❍ Industrial method : It is a two stage reaction in the presence of excess air.

$$2Na + \frac{1}{2}O_2 \longrightarrow Na_2O \quad ; \quad Na_2O + \frac{1}{2}O_2 \longrightarrow Na_2O_2$$

PROPERTIES :

❍ It is a pale yellow (when impure)hygroscopic powder stable towards heat in dry air. On exposure to moist air, it becomes white as it reacts with moisture and carbon dioxide.

$$2Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2 \quad ; \quad 2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

❍ **Action of water :**

$$Na_2O_2 + 2H_2O \xrightarrow{\text{cold}} 2NaOH + H_2O_2 \; ; \quad 2Na_2O_2 + 2H_2O \xrightarrow{\text{warm}} 4NaOH + O_2$$

❍ **Reaction with CO and CO_2 :**

$$Na_2O_2 + CO \longrightarrow Na_2CO_3 \; ; \quad 2Na_2O_2 + 2CO_2 \longrightarrow 2Na_2CO_3 + O_2$$

So, it is used to purify the air in sub-marine and confined spaces as it removes both CO and CO_2 and gives oxygen.

❍ **As an oxidising agent :** It is a powerful oxidant and many of its reactions are dangerously violent, particularly with the reducing agents, such as Al powder, charcoal, sulphur and many organic liquids.

(a) Chromic compounds are oxidised to chromates

$$2Cr(OH)_3 + 3O_2^{2-} \longrightarrow 2CrO_4^{2-} + 2OH^- + 2H_2O$$

(b) Manganous salt is oxidised to sodium manganate.

$$Mn(OH)_2 + 2O_2^{2-} \longrightarrow MnO_4^{2-} + 2OH^-$$

USE :

❍ Used for the production of oxygen under the name oxone.

❍ It is used as bleaching agent for bleaching wood pulp, paper and fabrics such as cotton and linen.

● **SODIUM HYDROXIDE OR CAUSTIC SODA (NaOH) :**

PREPARATION : It is most conveniently manufactured by one of the following processes.

(a) Methods involving sodium carbonate as a starting material :

❍ **Gossage process (causticising process) :**

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons CaCO_3 + 2NaOH$$

The most suitable concentration of sodium carbonate taken in this process is 15 – 20%. The caustic soda produced by this method is not pure and contains some calcium carbonate, sodium carbonate and calcium hydroxide as impurities.

❍ **Methods involving sodium chloride as starting material :**

Electrolysis of sodium chloride solution occurs according to following principle.

$$NaCl \rightleftharpoons Na^+ + Cl^- \; ; \; H_2O \rightleftharpoons H^+ + OH^-$$

On passing electricity, Na^+ and H^+ ions move towards cathode and Cl^- and OH^- ions move towards anode. The discharge potential of H^+ ions is less than Na^+ ions, thus hydrogen ions get discharged easily and hydrogen is liberated. Similarly, at anode Cl^- ions are easily discharged as their discharge potential is less than that of OH^- ions. Cl_2 gas is, therefore, liberated at anode.

It is necessary that chlorine should not come in contact with sodium hydroxide during electrolysis, otherwise following reaction take place.

$$2NaOH + Cl_2 \longrightarrow NaCl + NaClO + H_2O$$

To overcome this problem, the anode is separated from the cathode in the electrolytic cell either by using a porous diaphragm or by using a mercury cathode.

❍ **(Hg-Cathode Process)**

The mercury cathode cell (Castner-Kellner cell) :

In this cell mercury flows along the bottom of the cell and is made cathode (as shown in figure (a)). The brine solution flows in the same direction and anode consists of a number of graphite blocks. The brine electrolyzes and since, hydrogen has a high overvoltage at mercury cathode, sodium is preferentially discharged forming amalgam with mercury.

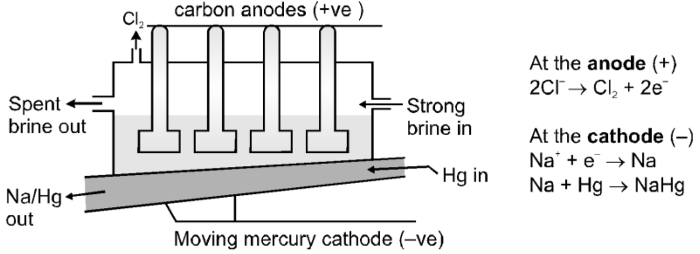


Figure (a) The Castner-Kellner Cell

The sodium amalgam flows out and is reacted with water to give NaOH

$$2NaHg + 2H_2O \rightarrow 2NaOH + 2Hg + H_2$$

The mercury is re-circulated to the cell. Hydrogen and chlorine are the two important by-products.

PROPERTIES :

(i) It is a white crystalline solid and has soapy touch.

(ii) It is highly soluble in water and is bitter in taste, and is corrosive in nature.

(iii) Neutralisation and hydrolysis reactions :

$$3NaOH + H_3PO_4 \longrightarrow Na_3PO_4 + 3H_2O \; ; \; NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

(iv) Reaction with acidic oxides :

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

$$2NaOH + SO_3 \longrightarrow Na_2SO_4 + H_2O$$

(v) Reaction with amphoteric oxides :

$$PbO + 2NaOH \longrightarrow Na_2PbO_2 + H_2O \; ; \quad PbO_2 + NaOH \longrightarrow Na_2PbO_3 + H_2O$$

$$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$$

(vi) Reaction with non-metals :

(a) Halogens :

❍ With cold & dilute NaOH :

$$2NaOH + Br_2 \longrightarrow NaBr + NaOBr + H_2O$$

❍ With hot & concentrated NaOH :

$$6NaOH + 3Br_2 \longrightarrow 5NaBr + NaBrO_3 + 3H_2O$$

☞ F_2 with cold & dilute NaOH gives OF_2 and with hot & concentrated NaOH gives O_2

(b) With sulphur : $6NaOH + 4S \longrightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O$

(c) With silicon : $2NaOH + Si + H_2O \longrightarrow Na_2SiO_3 + 2H_2$

(vii) Reaction with metals :

$$4NaOH + 2H_2O + 2Al \longrightarrow 2NaAlO_2 + 3H_2$$

$$6NaOH + 2Al \longrightarrow 2Na_3AlO_3 + 3H_2 \; ; \quad Zn + NaOH \longrightarrow Na_2ZnO_2 + H_2$$

(viii) Reaction with salts :

(a) $SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2\downarrow$ (white) + 2NaCl

$$Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$$

(b) $(NH_4)_2SO_4 + NaOH \xrightarrow{\Delta} Na_2SO_4 + 2NH_3 + 2H_2O$

Uses :

(i) It is used in the manufacture of soap, paper, artificial silk and a number of chemicals.

(ii) It is used in petroleum refining.

(iii) It is used in the purification of bauxite.

(iv) It is used in the textile industries for mercerising cotton fabrics.

(v) It is used for the preparation of pure fats and oils.
(vi) It is used as a laboratory reagent.

- **SODIUM CARBONATE OR WASHING SODA ($Na_2CO_3.10H_2O$) :**
  PREPARATION :

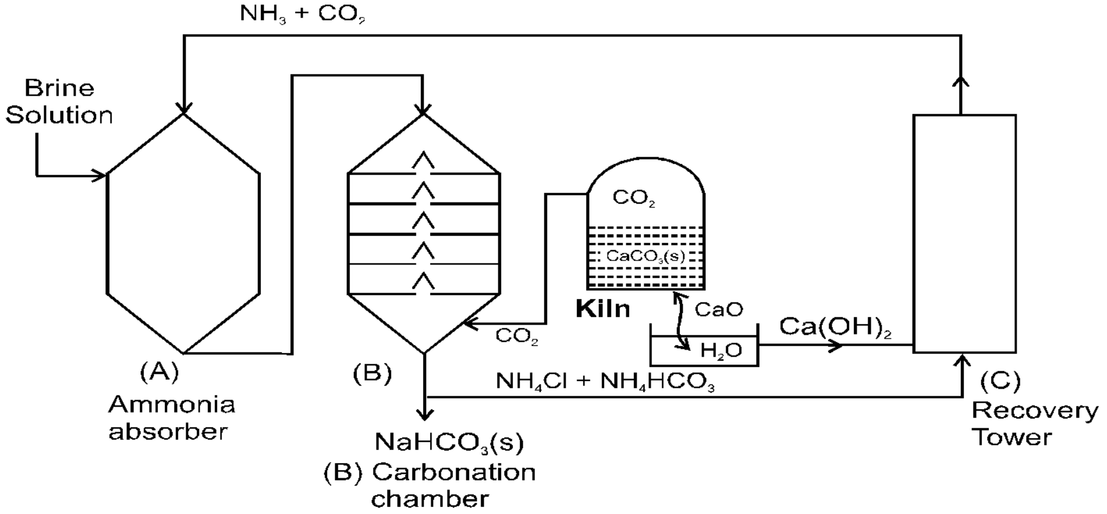
CARBONATES

Sodium Carbonate (Washing soda) $Na_2CO_3.10H_2O$

Preparation :

Name of compound	Name and Brief about the process	Related chemical reaction
Sodium Carbonate (Washing soda) $Na_2CO_3.10H_2O$	(1) **Leblanc Process**	$NaCl + H_2SO_4(conc.) \xrightarrow{\text{mild heating}} NaHSO_4 + HCl$ $NaCl + NaHSO_4 \xrightarrow[\text{heated}]{\text{Strongly}} Na_2SO_4 + HCl$ (Salt Cake) $Na_2SO_4 + 4C \longrightarrow Na_2S + 4CO \uparrow$ $Na_2S + CaCO_3 \longrightarrow Na_2CO_3 + CaS$
	(2) Solvay Process Step-1(In ammonia absorber) (i)Saturation of brine with ammonia and CO_2 (ii) Ammoniated brine is filtered to remove calcium and magnesium impurities as their insoluble carbonates.	$2NH_3 + CO_2 + H_2O \longrightarrow (NH4)_2CO_3$ $CaCl_2 + (NH_4)_2CO_3 \longrightarrow CaCO_3 \downarrow + 2NH_4Cl$ $MgCl_2 + (NH_4)_2CO_3 \longrightarrow MgCO_3 \downarrow + 2NH_4Cl$
	Step-2 (In carbonation tower) : (i) Formation of insoluble NaHCO3 (ii) Reaction is exothermic and hence there is a cooling arrangement. (iii) NaHCO3 is insoluble in cold brine solution because of the common ion effect. It is separated by filtration and the filtered is used for recovering NH3 & CO2.	$NH3 + CO2 + H2O \longrightarrow NH4HCO3$; $NH4HCO3 + NaCl \xrightarrow{30°C} NaHCO3 + NH4Cl$
	Step-3 (Calcination to get sodium carbonate) :	$2\ NaHCO3 \xrightarrow{150°C} Na2CO3 + CO2 + H2O$
	Step - 4 (In recovery tower) : Recovery of ammonia and carbondioxide. CaCl2 is obtained as by product.	$NH4\ HCO3 \xrightarrow{\Delta / \text{Steam}} NH3 + CO2 + H2O$ $2NH4\ Cl + Ca(OH)2 \xrightarrow{\Delta / \text{Steam}} 2NH3 + 2H2O + CaCl2$

* advantage is taken of low solubility of $NaHCO_3$, it gets precipitated in the reaction of $NaCl + NH_4HCO_3$.



Line Diagram of Solvay ammonia soda process

PROPERTIES :

❍ It is white crystalline solid. It is known in several hydrated forms. The common form is decahydrate, $Na_2CO_3.10H_2O$. This form is called **washing soda.** The decahydrate form on heating crumbles to powder. It is the monohydrate, $Na_2CO_3.H_2O$. Above 373 K, the monohydrate becomes completely anhydrous and changes to a while powder called soda ash.

$$Na_2CO_3.10H_2O \xrightarrow{375\ K} Na_2CO_3.H_2O + 9H_2O$$

$$Na_2CO_3.H_2O \xrightarrow{> 373\ K} Na_2CO_3 + H_2O$$

❍ It is soluble in water with evolution of considerable amount of heat. The solution is alkaline in nature due to hydrolysis.

$$CO_3^{2-} + H_2O \rightleftharpoons OH^- + HCO_3^{3-}$$

Note : The potassium carbonate like sodium carbonate, can not be prepared by Solvay process because the intermediate, $KHCO_3$ formed is soluble in appreciable amount in water.

Uses :

(i) It is used in water softening, laundering and cleaning.
(ii) It is used in the manufacture of glass, soap, borax and caustic soda.
(iii) It is used in paper, paints and textile industries.
(iv) It is an important laboratory reagent both in qualitative and quantitative analysis.

- **SODIUM BICARBONATE OR BAKING SODA ($NaHCO_3$) :**

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

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3 \text{ (sparingly soluble)}$$

PROPERTIES :

It is a white crystalline solid, sparingly soluble in water. The solution is alkaline in nature due to hydrolysis. On heating, it loses carbon dioxide and water forming sodium carbonate.

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

USE :

(i) It is largely used for making baking powder. Baking powder contains $NaHCO_3$, $Ca(H_2PO_4)_2$ and starch. The $Ca(H_2PO_4)$ is acidic and when water is added, it reacts with $NaHCO_3$, giving CO_2. The starch is a filler. Improved baking powder contains about 40% starch, 30% $NaHCO_3$, 20% $NaAl(SO_4)_2$ and 10% $Ca(H_2PO_4)_2$. The $NaAl(SO_4)_2$ slows the reaction down so the CO_2 is given off more slowly.
(ii) It is used in fire extinguishers.
(iii) It is used in medicines as antiseptic for skin infections.

Sodium chloride (NaCl) :

The important source of sodium chloride is sea water which contains about 2.7 to 2.9% of salt. Crude salt obtained by the solar evaporation of sea water contains calcium sulphate, sodium sulphate, calcium chloride and magnesium chloride as impurities. $CaCl_2$ and $MgCl_2$ are undesirable impurities as they are deliquescent (absorb moisture easily from the atmosphere). For the purification, the crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with hydrogen chloride gas. Crystals of pure sodium chloride separate out. Calcium and magnesium chloride, being more soluble than sodium chloride, remain in solution.

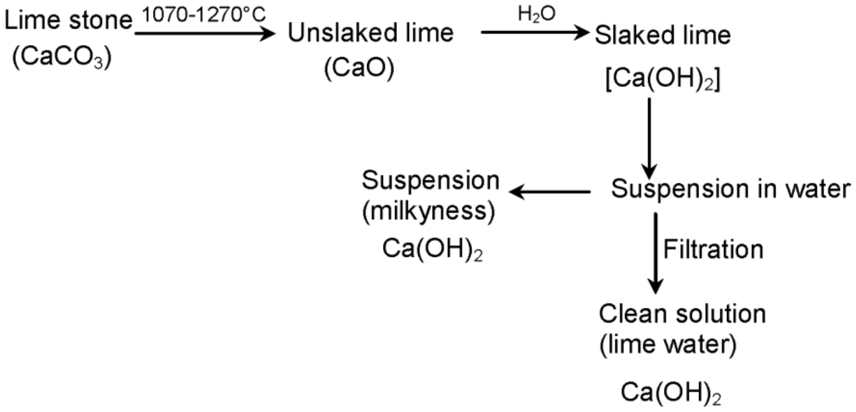
Sodium chloride is a white crystalline solide which melts at 108 K. It has a solubility of 36.0 g in 100 g of water at 273 K. The solubility does not increase appreciably with increase in temperature.

Uses :

(i) It is used as a common salt or table salt for domestic purpose.
(ii) It is used for the preparation of Na_2O_2, NaOH and Na_2CO_3.
(iii) It is used in freezing mixture.
(iv) It is used for the regeneration of exhausted ion exchange resins.

Section (F) : Compounds of Alkaline earth metals

- **Quick Lime, Slaked Lime and Lime Water.**



- **Calcium Oxide or Quick Lime, CaO :**

It is a white amorphous solid having melting point 2870. When it is exposed to atmosphere, it absorbs mosture and carbondioxide.

$$CaO + H_2O \longrightarrow Ca(OH)_2 \qquad CaO + CO_2 \longrightarrow CaCO_3$$

The addition of limited amount of water breaks the lump of lime. This process is called slaking of lime. Quick lime slaked with soda gives solid sodalime. Being a basic oxide, it combines with acidic oxides at high temperature.

$$CaO + SiO_2 \longrightarrow CaSiO_3 \qquad 6CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2$$

Uses :

(i) It is raw material for manufacturing cement.
(ii) It is used as building material.
(iii) It is used in softening of hard water.
(iv) It is used in the manufacture of sodium carbonate from caustic soda.
(v) It is employed in the purification of sugar and in the manufacture of dye stuffs.

- **Calcium Hydroxide (Slaked lime), $Ca(OH)_2$**

It is a white amorphous powder. It is sparingly soluble in water.

When carbon dioxide is passed through lime water it turns milky due to the formation of calcium carbonate.

On passing excess of carbon dioxide, the precipitate dissolves to form calcium hydrogencarbonate.

$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow \text{ (White)} + H_2O$; $CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$.

Milk of lime reacts with chlorine to form hypochlorite, a constituent of bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow CaCl_2 + \underset{\text{Bleaching powder}}{Ca(OCl)_2} + 2H_2O$$

Uses :

(i) It is used in the preparation of mortar, a building material.

(ii) Due to its disinfectant nature it is used in white wash.

(iii) It is used in glass making, in tanning industry, for the preparation of bleaching powder and for purification of sugar.

• Calcium Carbonate ($CaCO_3$)

PREPARATION :

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

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \ ; \quad CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$

The precipitate of $CaCO_3$ thus obtained is known as precipitated chalk.

PROPERTIES :

It is a white fluffy powder, insoluble in water. It dissolves in presence of CO_2 due to formation of calcium bicarbonate.

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

It reacts with dilute acid to liberate carbon dioxide.

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

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

Uses :

(i) Precipitated chalk is used in tooth pastes and face powders, in medicine for indigestion, in adhesives and in cosmetics.

(ii) Chalk is used in paints and distempers.

(iii) Specially precipitated $CaCO_3$ is extensively used in the manufacture of high quality paper.

• Plaster of Paris ($2CaSO_4.H_2O$)

(Calcium sulphate hemihydrate)

PREPARATION :

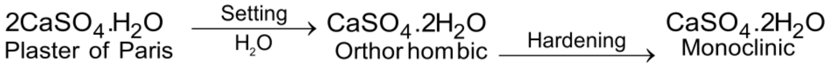
It is obtained when gypsum, calcium sulphate dihydrate ($CaSO_4.2H_2O$), is heated at 120°C (393 K).

$$\underset{\text{Gypsum}}{2[CaSO_4.2H_2O]} \longrightarrow \underset{\text{Plaster of Paris}}{2CaSO_4.H_2O} \text{ (calcium sulphate hemihydrate)} + 3H_2O$$

PROPERTIES :

○ It is hemihydrade of calcium sulphate. Plaster of Paris is a white powder. Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate, $CaSO_4$ is formed. This is known as 'dead burnt plaster'.

❍ It has the property of setting to a hard mass when a paste with water is allowed to stand aside for sometime. Slight expansion occurs during the setting as water is absorbed to reform $CaSO_4.2H_2O$ (gypsum). The setting process is **exothermic**. The process of setting takes place in various stages. In the first stage, there is conversion of Plaster of Pairs into orthorhombic form of gypsum (setting step) and in the second stage orthorhombic form changes into monoclinic form (hardening step).



$$\underset{\text{Plaster of Paris}}{2CaSO_4.H_2O} \xrightarrow[H_2O]{\text{Setting}} \underset{\text{Orthorhombic}}{CaSO_4.2H_2O} \xrightarrow{\text{Hardening}} \underset{\text{Monoclinic}}{CaSO_4.2H_2O}$$

The setting of Plaster of Paris may be **catalysed by sodium chloride** while it is retarded by borax or alum. Addition of alum to Plaster of Paris makes the setting very hard. The mixture is known as

Keene's cement.

Uses :

(i) It is used in building industry as well as plasters.
(ii) It is used for immoblising the affected part of organ when there is a bone fracture of sprain.
(iii) It is also used in dentistry, in ornamental work and for making casts of statues and busts.

- **Cement :**

Cement is mainly used as a building material. It is also called portland cement because it resembles with the natural limestone quarried in the Isle of portland, England.
It is a product obtained by mixing a material rich in lime, CaO with other material such as clay which contains silica, SiO_2 along with the oxides of aluminium, iron and magnesium. The composition of cement is : CaO, 50-60%; SiO_2, 20-25%; Al_2O_3, 5-10%; MgO, 2-3%; Fe2O3, 1-2% and SO_3, 1-2%. For a good quality cement, the ratio of silica (SiO_2) to alumina (Al_2O_3) should be between 2.5 and 4 and the ratio of lime (CaO) to the total of the oxides of silicon (SiO_2) aluminium (Al_2O_3) and iron (Fe_2O_3) should be as close as possible to 2.
The important raw mateirals for the manufacture of cement are lime stone and clay. Clay and lime is mixed and then they are strongly heated, when they fuse to form 'cement clinker'. The clinker is then mixed with 2-3% by weight of gypsum ($CaSO_4.2H_2O$) to form cement. The important ingredients of portland cement are dicalcium silicate (Ca_2SIO_4) 26%, tricalcium silicate (Ca_3SiO_5)51% and tricalcium aluminate ($Ca_3Al_2O_6$) 11%.

- **Setting of Cement :**

When water is added to cement, the setting of cement takes place to give a hard mass. The setting involves the hydration of the molecules of the constituents and their rearrangement. The gypsum is added only to slow down the process of setting of the cement so that it gets sufficiently hardened.

Uses :

(i) It is used in concrete and reinforced concrete.
(ii) It is used in plastering and in the construction of bridges, dams and buildings.