s-Block Elements

Alkali Metals; Group -1 Elements

- The group 1 elements have ns^1 electronic configuration and are highly reactive metals.

Elements	Symbols	Atomic Number	Electronic Configuration
Lithium	Li	3	$[He]2s^1$
Sodium	Na	11	$[Ne]3s^1$
Potassium	K	19	$[Ar]4s^1$
Rubidium	Rb	37	$[Kr]5s^1$
Caesium	Cs	55	$[Xe]6s^1$
Francium	Fr	87	$[Rn]7s^1$

Physical Properties of Alkali Metals :

1. Atomic Size

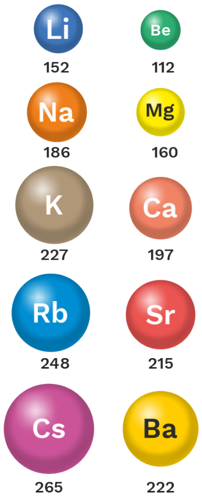
Largest in their respective period (except noble gas element)

Size increases from Li to Cs due to addition of an extra shell

$Li < Na < K < Rb < Cs$

$Cs > Rb > K > Ba > Sr > Ca > Na > Mg > Li > Be$

Comparision of atomic size of Group 1 and 2



Concept Ladder

Francium occurs only in trances as a radioactive decay product because its half life period is very small (half-life 21 minutes).

Previous Year's Questions

Alkali metals lose electrons in **[AIPMT]**

(1) s-orbitals (2) p-orbitals

(3) d-orbitals (4) f-orbitals

2. Oxidation State

The group 1 elements exhibit +1 oxidation state

3. Ionization Energy

- The value of first ionization energies for the atoms in this group are lower than those for any other group in the whole periodic table. (Li > Na > K > Rb > Cs)
- Second ionization energy of alkali metals is very high because by loosing one electron they achieve inert gas configuration.
- Li > Na > K > Rb > Cs (Ionization energy)

4. Density

Alkali metals have large size which accounts for their low density.

$$\text{Density} = \frac{\text{Atomic Mass (M)}}{\text{Atomic Volume (V)}}$$

Atomic mass increases from Li to Cs in the group and volume also increases but increase in atomic weight is more than increase in volume. Therefore density increases from Li to Cs.

Li < K < Na < Rb < Cs

5. Melting and Boiling point

M.P. and B.P. of alkali metals are low due to weak interatomic bonds because of their large atomic radii and presence of only 1 valence electron. (Li > Na > K > Rb > Cs)

6. Electropositive Character

$$\text{Electropositivity} \propto \frac{1}{\text{Ionization Energy}}$$

Alkali metals have the tendency to lose the electron.

$$M_{(g)} \xrightarrow{\quad} M^{+}_{(g)} + e^{-}$$

7. Conductivity

Due to the presence of loosely held valence electrons which are free to move in a metal structure, these elements are good conductor of heat and electricity.

Rack your Brain

Why second ionization enthalpy values of alkali metals are very high?

Concept Ladder

Alkali metals have largest size and lowest ionization energies in their respective periods.

Rack your Brain

Why density of K is less than Na?

Concept Ladder

Densities of alkali metals increase from Li to Cs **Exception :** K is lighter than Na.

8. Nature of Bonds

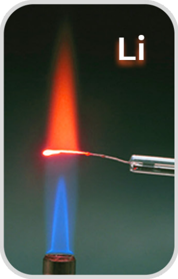
The electronegativity values being low, they combine with other elements to form ionic bond.

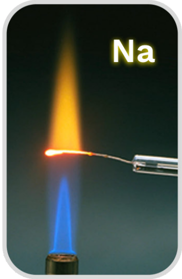
9. Flame Test

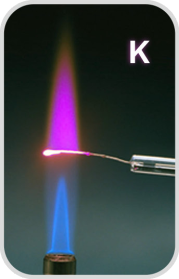
First group elements and their salts gives characteristic color to Bunsen flame. By flame energy electron of outer most shell get excited, which on returning back to its ground state releases absorbed flame energy as a visible light.

The energy released is min. in the case of Li^+ and increases in order Li^+, Na^+, K^+, Rb^+, Cs^+.

Elements	Colour
Li	Crimson red
Na	Golden Yellow
K	Violet
Rb	Red Violet
Cs	Blue







Concept Ladder

Alkali metals are soft with low melting and boiling points. This is due to weak metallic bond.

Concept Ladder

Solution of alkali metals in liquid ammonia is highly conductive and deep blue in colour. This is due to presence of ammoniated electrons.

10. Electronegativity

The tendency to attract elements is low as the alkali metals are electropositive. The electronetativity, thus decreases from Li to Cs as the electropositive character increases.

11. Specific Heat

The specific heat values decrease from Li to Cs.

12. Heat of Atomisation

Heat of atomisation decreases from Li to Cs.

13. Hydration of Ions

The ions are heavily hydrated. The smaller the size of the ion, the greater is the degree of hydration. Thus the degree of hydration decreases down the group from Li^+ to Cs^+. Thus with the increase in hydration electrical conductivity decreases.

14. Lattice Energy

Salts of alkali metals are ionic solids. Lattice energy of salts of alkali metals having common anion decreases on descending down the group.

15. Photoelectric Effect

K, Rb and Cs have quite large atomic size, so their ionization energy is very low.

Due to very low ionization energy their valence shell electrons gets excited even by absorbing visible light.

That's why Cs is used in photoelectric cells.

16. Reducing Character

Alkali metals are strong reducing agents. Reducing character increases down the group.

Concept Ladder

Hydrated radii are in the order :

$Li^+_{(aq)} > Na^+_{(aq)} > K^+_{(aq)} > Rb^+_{(aq)} > Cs^+_{(aq)}$

Ionic mobility :

$Li^+_{(aq)} < Na^+_{(aq)} < K^+_{(aq)} < Rb^+_{(aq)} < Cs^+_{(aq)}$

Rack your Brain

Why, $LiHCO_3$ exists in solution?

Previous Year's Questions

The sequence of ionic mobility in aqueous solution is

[AIPMT-2008]

(1) $Rb^+ > K^+ > Cs^+ > Na^+$
(2) $Na^+ > K^+ > Rb^+ > Cs^+$
(3) $K^+ > Na^+ > Rb^+ > Cs^+$
(4) $Cs^+ > Rb^+ > K^+ > Na^+$

PROPERTIES OF ALKALI METALS

3 **Li** Lithium

11 **Na** Sodium

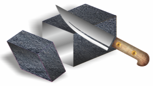
19 **K** Potassium

37 **Rb** Rubidium

55 **Cs** Caesium

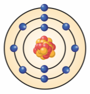
87 **Fr** Francium

VERY SOFT



- Alkali metals can be easily cut with a knife
- Among all alkali metals lithium is hardest.

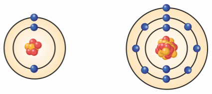
ELECTRONIC CONFIGURATION



ns^1

- They have one valence shell electron.
- Electronic configuration ns^1

ATOMIC SIZE



- Size increases down the group due to added extra orbit.

ELECTROPOSITIVE

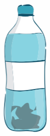
- It is the ability to remove an electron

Cs

- Electropositivity increases down the group
- Caesium has the highest Electropositivity character.

STORED IN KEROSENE

- Alkali metals react with air easily to form oxide layer therefore they are stored in kerosene



REACTS WITH WATER

H_2O

- They reacts violently with water and form hydroxides.
- Don't even dare to go near when caesium reacts with water

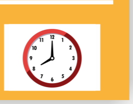
USES

- **LITHIUM**
  Anti depressants
  Batteries

- **SODIUM**
  Street lamps
  Salt

- **POTASSIUM**
  Fertilizers

- **CAESIUM**
  Atomic Clocks



REACTS WITH AMMONIA

On dissolving NH_3 forms ammoniated cation and electron. solution turns blue

$$M^+ + x\,NH_3 \longrightarrow [M(NH_3)X]^+$$

$$e^- + y\,NH_3 \longrightarrow [e(NH_3)y]^-$$

Q.1 Alkali metals are paramagnetic but their salt are diamagnetic. Why?

A.1 In metals, the outermost energy shell is singly occupied but in cations, all the orbitals are doubly occupied (inert gas contiguration).

Chemical Properties

Reaction	Comment
$2M + 2H_2O \rightarrow 2MOH + H_2$	Hydroxides are strongest base known
$4Li + O_2 \rightarrow 2Li_2O$	Monoxide formed by Li and to a small extent by Na
$2Na + O_2 \rightarrow Na_2O_2$	Na and small extent by Li form their peroxide ion.
$K + O_2 \rightarrow KO_2$	Superoxide formed by K, Rb, Cs.
$2M + H_2 \rightarrow 2MH$	Ionic salt like hydrides
$6Li + N_2 \rightarrow 2Li_3N$	Nitride formed only by Li
$2M + S \rightarrow M_2S$	All metals form sulphides
$2M + X_2 \rightarrow 2MX$	All the metals form halides
$2M + 2NH_3 \rightarrow 2MNH_2 + H_2$	All the metals form amides

Reactivity

These elements are very reactive, so do not found in free state in nature.

$$\text{Reactivity} \propto \frac{1}{\text{Ionization Potential}}$$

Order of reactivity – Li < Na < K < Rb < Cs

- They have low values of ionisation energies and readily lose their valence electron to form M^+ ion.

Rack your Brain

Why $NaHCO_3$ and NaOH can't exist together?

Concept Ladder

Alkali metals (except Lithium) show photoelectric effect. This tendency is maximum for caesium.

Rack your Brain

Why Li can't be store in Kerosene?

Previous Year's Questions

Which one of the alkali metals, forms only the normal oxide, M_2O on heating in air

[AIPMT-2012]

(1) Rb (2) K

(3) Li (4) Na

- They have low heat of atomisation and easily come into vaporised form.
- They have higher heats of hydration.

Reactivity towards air

Alkali metals gets tarnish in air due to the formation of oxide at their surface hence they are kept in kerosene or paraffine wax.

Alkali metals when reacts with moist air form carbonates.

$$4Na + O_2 \longrightarrow 2Na_2O$$

$$\underset{\text{(moist)}}{Na_2O + H_2O} \longrightarrow 2NaOH$$

$$\underset{\text{(in air)}}{2NaOH + CO_2} \longrightarrow Na_2CO_3 + H_2O$$

Concept Ladder

Exception :

Lithium is strongest reducing agent due to its highest hydration energy.

Reactivity towards oxygen

$$\begin{tikzcd} \underset{\text{Alkali metals}}{M} \arrow[r, "O_2"] & \underset{\text{Oxide}}{M_2O} \arrow[r, "H_2O"] \arrow[d, "O_2"] & \underset{\text{Hydroxide}}{MOH} \arrow[r, "CO_2"] & \underset{\text{Carbonate}}{M_2CO_3} \\ & \underset{\text{Peroxide}}{M_2O_2} & & \end{tikzcd}$$

O^{2-}
Oxide ion

$[-O-O-]^{2-}$
Peroxide ion

$[:\ddot{O}\cdots\ddot{O}:]^{-}$
Superoxide

Rack your Brain

Why alkali metals are highly reactive in air?

Normal oxides – Monoxide

$$4Na + O_2 \longrightarrow 2Na_2O$$

Peroxides

$$2Na + O_2(\text{excess}) \xrightarrow{300°C} Na_2O_2$$

Superoxides

Superoxides are ionic oxides $M^+O_2^-$

$$M + O_2(\text{excess}) \rightarrow MO_2$$

(M = K, Rb, Cs)

Concept Ladder

Alkali metal superoxides have unpaired electron and hence are paramagnetic whereas oxides and peroxide are diamagnetic and colourless.

Superoxides are stronger oxidizing agents than peroxides.

The stability of these superoxides is in the order :

$$KO_2 < RbO_2 < CsO_2$$

Stability of Oxides : Normal oxide > Peroxide > Superoxide

Reaction with Hydrogen

Alkali metals combine with H_2 forming ionic hydrides

$$2M + H_2 \rightarrow 2MH$$

Hydrides of alkali metals are attacked by water to give back hydrogen

$$MH + H_2O \rightarrow MOH + H_2$$

Thermal stability : LiH > NaH > KH > RbH > CsH

Basic property : CsH > RbH > KH > NaH > LiH

Reaction with Water

Alkali metals react vigorously with H_2O forming hydroxides with the liberation of H_2.

$$2M + 2H_2O \rightarrow 2MOH + H_2$$

Reactivity with water increase form Li to Cs.

Li → least reactive towards water
Na → reacts vigorously
K → reacts producing a flame
Rb, Cs → reacts explosively

Monoxides gives strongly alkaline solution with water

$$M_2O + H_2O \rightarrow 2MOH$$

Reaction with dilute acids

Due to alkaline nature, these metals react rapidly with dilute acids and the rate of reaction increases form Li to Cs because of increase in basic character.

Rack your Brain

What is the reason for the increasing stability of peroxides and superoxides of alkali metals down the group?

Concept Ladder

The electrolysis of the fused hydride (LiH) yields hydrogen at anode.

$$MH + H_2O \rightarrow MOH + H_2 \uparrow$$

Previous Year's Questions

The alkali metals form salt-like hydrides by the direct synthesis at elevated temperature. The thermal stability of these hydrides decreases in which of the following orders

[AIPMT-2008]

(1) NaH > LiH > KH > RbH > CsH
(2) LiH > NaH > KH > RbH > CsH
(3) CsH > RbH > KH > NaH > LiH
(4) KH > NaH > LiH > CsH > RbH

Carbonates and Bicarbonates

(a) Small size and strong polarisation of Li distorts the e^- cloud of the near by oxygen atom of the large CO_3^{2-} to such an extent that the C—O bond gets weakened.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

(b) Replacement of the larger carbonate ion by a smaller ion leads to increased lattice energy and thus favours the decomposition.

$$M_2CO_3 \xrightarrow{\Delta} M_2O + CO_2 \uparrow$$

Halides

All the metals in this group form halides of type MX. Li^+ is the smallest ion among alkali metals, it would be expected to form hydrated salts more readily than other metals.

Properties :

As evident from their following properties, alkali metal halides are ideal ionic compounds.

(i) All alkali halides except lithium fluoride are freely soluble in water (LiF is soluble in non-polar solvents).

(ii) They have high melting and boiling points. For the same alkali metal, the melting and boiling points decrease regularly in the order: Fluoride > chloride > bromide > iodide.

Concept Ladder

Stability and solubility of carbonates, bicarbonates and nitrates increases down for group 1 elements.

Rack your Brain

Amongst LiF and LiI which has more covalent character and Why?

Previous Year's Questions

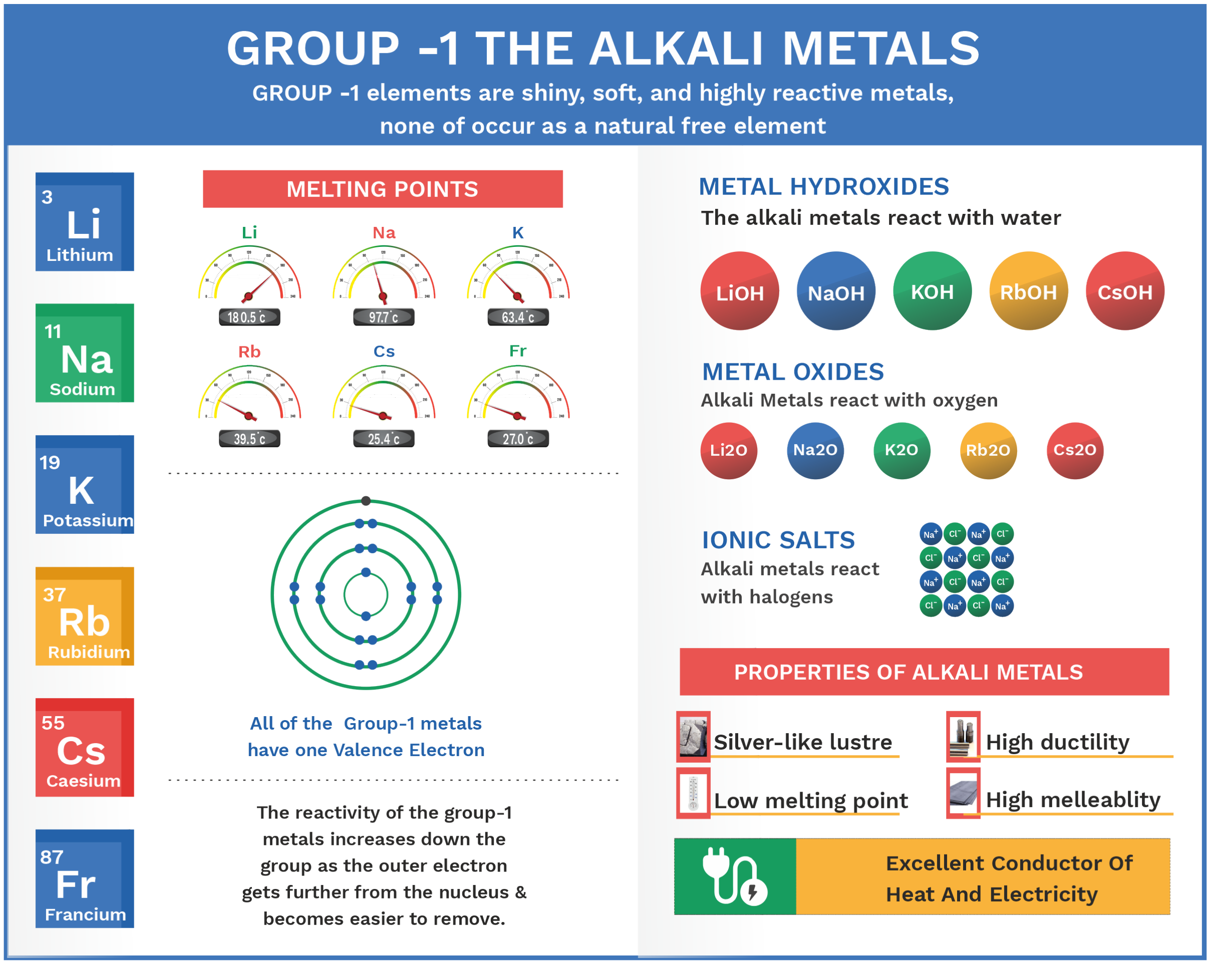
Which compound will show the highest lattice energy?

[AIPMT]

(1) RbF (2) CsF
(3) NaF (4) KF

Q.2 LiBr has lower melting point than LiF. Why?

A.2 Br^- ion, on account of bigger size than F^- ion, is more polarisable than F^- ion, is more polarisable than F^- ion. Hence, LiBr is more covalent than LiF and thus, it has lower melting point.



GROUP -1 THE ALKALI METALS

GROUP -1 elements are shiny, soft, and highly reactive metals, none of occur as a natural free element

MELTING POINTS

Li	Na	K
180.5°c	97.7°c	63.4°c

Rb	Cs	Fr
39.5°c	25.4°c	27.0°c

All of the Group-1 metals have one Valence Electron

The reactivity of the group-1 metals increases down the group as the outer electron gets further from the nucleus & becomes easier to remove.

METAL HYDROXIDES

The alkali metals react with water

LiOH NaOH KOH RbOH CsOH

METAL OXIDES

Alkali Metals react with oxygen

Li2O Na2O K2O Rb2O Cs2O

IONIC SALTS

Alkali metals react with halogens

PROPERTIES OF ALKALI METALS

- Silver-like lustre
- High ductility
- Low melting point
- High melleablity
- Excellent Conductor Of Heat And Electricity

Sodium :

(a) **Ores** : -

- **Chile salt peter** – $NaNO_3$
- **Rock salt** – NaCl
- **Glauber's salt** $Na_2SO_4 . 10H_2O$

Extraction of sodium :

- Na is obtained on large scale by 2 processes.

Castner's process :

- In this process, electrolysis of fused NaOH is carried out at 330°C using iron as cathode and nickel as anode.

$$2NaOH \rightleftharpoons 2Na^+ + 2OH^-$$

Previous Year's Questions

In which of the following processes, fused sodium hydroxide is electrolysed at 330°C temperature for extraction of sodium?

[AIPMT]

(1) Castner's process
(2) Down's process
(3) Cyanide process
(4) Both (2) and (3)

At cathode : $2Na^+ + 2e^- \rightarrow 2Na$

At anode : $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

- During electrolysis, O_2 and H_2O are produced. H_2O formed at the anode gets partly evaporated and is partly broken down and H_2 is discharged at cathode.

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode : $2H^+ + 2e^- \rightarrow 2H \rightarrow H_2$

Down’s process :

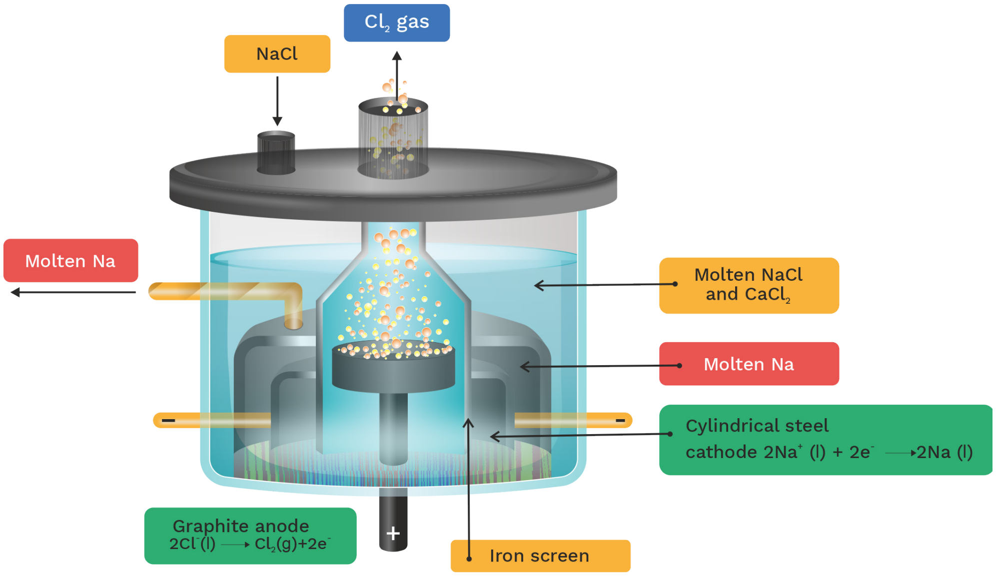
- It involves the electrolysis of fused NaCl containing $CaCl_2$ and KF, using iron as cathode and graphite as anode, at about 600°C.

Concept Ladder

In Down’s process Na is obtained by electrolysis of a mixture of NaCl (40%) and $CaCl_2$ (60%) in fused state.

Rack your Brain

In Down’s process which gas is liberated at cathode side?



Reactions : $NaCl \rightleftharpoons Na^+ + Cl^-$

At cathode : $2Na^+ + 2e^- \rightarrow 2Na$

At anode : $2Cl^- \rightarrow Cl_2 + 2e^-$

Na obtained by this method is 99.5% pure.

(i) The fusion temperature of NaCl is high, i.e., 803°C (1076 K) which is difficult to maintain.

(ii) Sodium is volatile at this temperature and therefore, a part of it vapourises and forms a metallic fog.

(iii) At this temperature, the products of electrolysis, sodium and chlorine are corrosive and may attack the material of the cell.

- To remove the above difficulties, pure sodium chloride is mixed with calcium chloride and potassium fluoride.

Sodium Hydroxide (Caustic Soda)

Methods involving sodium carbonate as a starting material

Causticing process (or **Gossage process**)

$Na_2CO_3+Ca(OH)_2 \rightarrow CaCO_3\downarrow + 2\,NaOH$

Methods involving sodium chloride as a starting material

Electrolytic process : Electrolysis of aq. NaCl

$$2NaCl + 2H_2O \xrightarrow{\text{electricity}} 2NaOH + H_2 + Cl_2$$

Four methods are used in electrolysis of NaCl

(i) Porous diaphragm process (Nelson cell process)

(ii) Castner-Kellner cell

(iii) Solvay-Kellner cell

(iv) Diaphragm cell

Porous diaphragm process (Nelson cell process)

Nelson cell consist of a perforated steel tube lined inside with asbestos. The tube acts as a cathode.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Concept Ladder

In Down's process Na metal obtained is about 99% pure. Cl_2 is by product of this process.

Rack your Brain

Name the two important processes used to extract sodium metal?

Previous Year's Questions

Which of the following is known as fusion mixture?

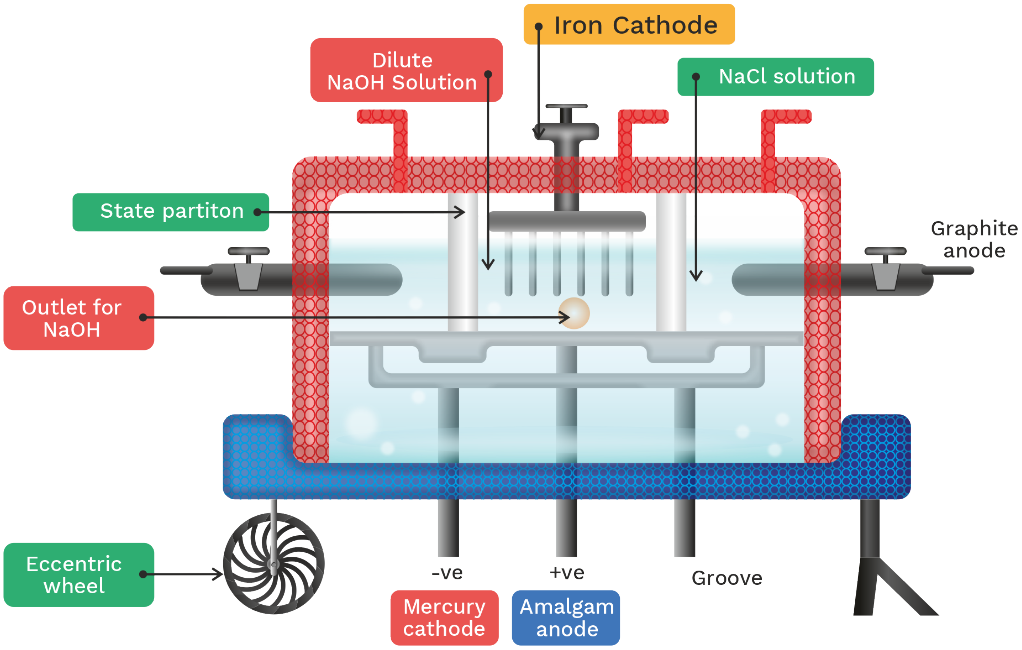
[AIPMT]

(1) Mixture of Na_2CO_3 + $NaHCO_3$

(2) $Na_2CO_3.10H_2O$

(3) Mixture of K_2CO_3 + Na_2CO_3

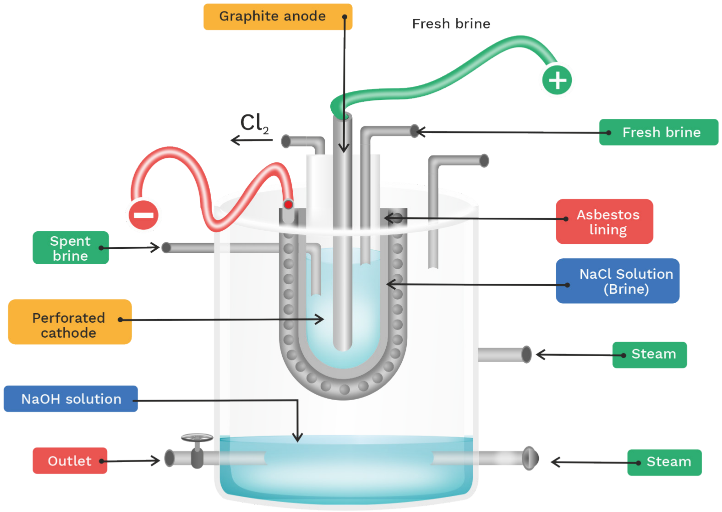
(4) $NaHCO_3$



At cathode : $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$

$Na^+ + OH^- \rightleftharpoons NaOH$

At anode: $2Cl^- \rightleftharpoons Cl_2 + 2e^-$



The sodium containing NaOH and NaCl as impurity is taken out and evaporated to dryness.

Concept Ladder

Nelson cell is used for the industrial production of Cl_2. As well as this cell can be used for the production of Na_2CO_3, for which CO_2 is mixed with steam.

Rack your Brain

Name the element which when heated with NaOH reduces it metal?

Castner-Kellner cell :

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

At anode :

$$2Cl^- \longrightarrow 2Cl + 2e^- \longrightarrow Cl_2$$

At cathode :

$$Na^+ + e^- \longrightarrow Na$$

$$Na + Hg \longrightarrow \text{Amalgam}$$

- The sodium amalgam thus formed comes in the inner compartment due to rocking. Here, the sodium amalgam acts as the anode and ions rods act as cathode.

At anode :

$$\text{Na-amalgam} \longrightarrow Na^+ + Hg + e^-$$

At cathode :

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$$

- The concentrated solution of sodium hydroxide (about 20%) is taken out from inner compartment and evaporated to dryness to get solid NaOH.

Solvay-Kellner cell :

At anode :

$$2Cl^- \longrightarrow Cl_2 + 2e$$

At cathode :

$$2Na + 2Hg + 2e \longrightarrow \underset{\text{Sodium − amalgam}}{2Na\,.\,Hg}$$

- The amalgam flows out in a vessel containing water. Sodium hydroxide is formed with evolution of hydrogen.

$$2Na\text{-}Hg + 2H_2O \longrightarrow 2NaOH + 2Hg + H_2$$

Concept Ladder

In Castner-Kellner cell sodium amalgam is removed from the cell. It is then decomposed in a separate cell by water giving NaOH, hydrogen & Hg. Then Hg is recirculated to the cell.

Previous Year's Questions

In Castner-Kellner cell for production of sodium hydroxide

[NEET-2013]

(1) Brine is electrolyzed using graphite electrodes

(2) Molten sodium chloride is electrolyzed

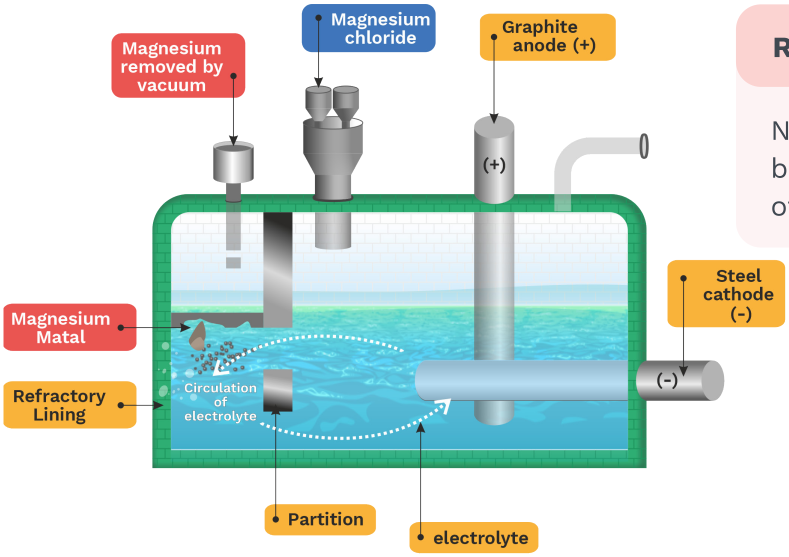
(3) Sodium amalgam is formed at mercury cathode

(4) Brine is electrolyzed with Pt electrodes

Q.3 Name the compound form when CO_2 and H_2O react with Na_2CO_3?

A.3 Sodium Hydrogen Carbonate

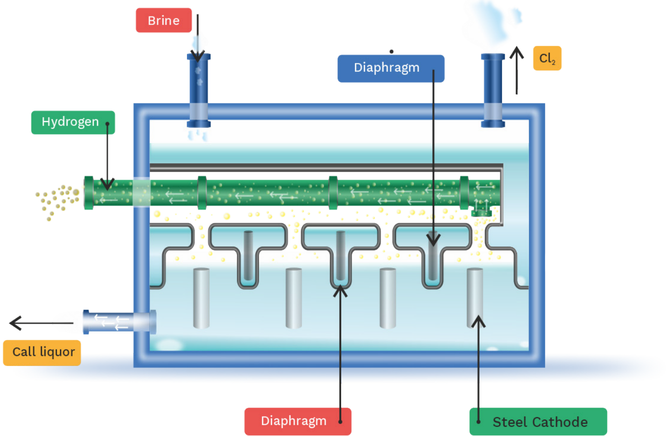
$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$$



Diaphragm cell :

Most modern method for the production of sodium hydroxide from brine (aqueous sodium chloride solution) uses a diaphragm cell, containing steel and titanium electrodes which are separated by porous diaphragms to isolate the products.

$2NaCl + 2H_2O \longrightarrow 2NaOH + Cl_2 + H_2$



Abnormal behaviour of lithium :

- The lithium, being the first member of alkali group, exhibits the characteristic properties of alkali metals but it differs at the same time in many respects from them.

Rack your Brain

Name the component used in baking powder for manufacturing of fire extinguishers?

Concept Ladder

NaOH can be used in manufacturaing of paper, soap and artificial silk. It is also used for petroleum refining, purification of bauxite.

Rack your Brain

Name the compound which will be reduced in diaphragm cell to discharge hydrogen?

Reasons for its abnormal behaviour are mainly due to the following reasons:

(i) **Forms only monoxide while others form per and superoxides also.**

(ii) **Li reacts with N_2 to form Li_3N, other alkali metals do not react with N_2.**

(iii) $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$, other carbonates do not give CO_2.

(iv) **LiOH is weak base** which **decomposes on heating** and other hydroxide are stable.

(v) Salts of Li are insoluble in H_2O but that of other alkali metals are soluble.

(vi) **$LiNO_3$ on heating evolves NO_2 and O_2** while **other nitrates give only O_2**

Diagonal relationship between Li and Mg :

(i) Both hard and ductile metal.

(ii) LiOH and $Mg(OH)_2$ both weak bases.

(iii) Nitrates of both on heating evolve NO_2 and O_2

(iv) $LiHCO_3$ does not exist in solid state.

(v) Both react with N_2 to form nitride (Li_3 and Mg_3N_2).

Concept Ladder

Li shows anomolous property because it has exceptionally small in size and have greater polarizing power in lithium ion.

Concept Ladder

Due to its anomolous property, there is increase in covalent character of lithium compounds which is responsible for their solubility in organic solvents.

Q.4 Alkali metals are paramagnetic but their salts are diamagnetic. Explain :

A.4 In metals, the outermost energy shell is singly occupied, but in cations, all the orbitals are doubly occupied (inert gas configuration).

e.g., Na, $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$, $4s^1$ $\boxed{4s^1}$ paramagnetic

Na^+ $1s^2$, $2s^2$ $2p^6$, $\boxed{3s^2 3p^6}$ Diamagnetic.

Q.5 Which alkali metal ion has the maximum polarising power and why ?

A.5 Li^+ ion has the maximum polarising power among all alkali metal ions. This is due to small size of Li^+ ion.

Q.6 Sodium salts in aqueous solutions are either neutral or alkaline in nature. Explain.

A.6 The anions in sodium salts are either from strong acids or weak acids. When anions are from strong acids, there is no hydrolysis and aqueous solutions are neutral (NaCl, $NaNO_3$, Na_2SO_4 solutions are neutral).
On the other hand, when anions are from weak acids, there is hydrolysis and the solutions are alkaline in nature. For example, in the case of sodium carbonate or bicarbonate, solutions are alkaline.

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

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

Q.7 Why is KO_2 paramagnetic ?

A.7 The superoxide O_2^- is paramagnetic because of one unpaired electron in π^*2p molecular orbital.
KK $\sigma\,(2s)^2\sigma^*\,(2s)^2\ \sigma\,(2p_x)^2\ \pi(2p_x)^2\ (\pi 2p_y)^2\ \pi^*\,(2p_x)^2\ \pi^*\,(2p_y)^1$

Q.8 What happens when following compounds are heated ?
(a) Li_2CO_3 (b) $Na_2CO_3.10H_2O$ (c) $LiNO_3$ (d) $NaNO_3$

A.8 $Li_2CO_3 \longrightarrow Li_2O + CO_2$
$Na_2CO_3.10H_2O \longrightarrow Na_2CO_3 + 10H_2O$
$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$
$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$

Q.9 Why do alkali metals tarnish in air?

A.9 They tarnish because of formation of their oxides.

Alkaline Earth Metals; Group 2 Elements

- The group two elements have ns^2 electronic configuration.

Elements	**Symbols**	**Atomic Number**	**Electronic Configuration**
Beryllium	Be	4	$[He]2s^2$
Magnesium	Mg	12	$[Ne]3s^2$
Calcium	Ca	20	$[Ar]4s^2$
Strontium	Sr	38	$[Kr]5s^2$
Barium	Ba	56	$[Xe]6s^2$
Radium	Ra	88	$[Rn]7s^2$

Physical properties of alkaline earth metal :

(1) Atomic Size :

- Smaller than IA group elements, since extra charge on nucleus attracts the electron cloud.
- Size increases gradually from Be to Ba.
  $Be < Mg < Ca < Sr < Ba$

(2) Oxidation State : The group 2 elements exhibit +2 oxidation state.

(3) Ionisation Energy :

- First ionisation energy is higher than IA group because of smaller atomic size and completely filled s-orbital (stable electronic configuration).

  Decreasing order of ionisation energy :

  $$Be > Mg > Ca > Sr > Ba$$

- Second ionisation energy is lesser than IA group.

Rack your Brain

Why first I.E. of alkaline earth metals is higher than that of corresponding alkali metals?

Concept Ladder

Exception :
Radium and its all isotopes are radioactive. The longest lived isotope being Ra^{226} with half-life 1600 years. This isotope is formed in natural decay series of U^{238}.

(4) Density :

The size of group 2 elements are smaller than those of group 1 thus these elements have higher density than group 1 elements. Density increases from Be to Ra.

(5) Melting and Boiling point :

Since the cohesive force decreases down the group the melting point of elements of group 2 decreases down the group.

Exception :

Mg has the lowest melting point. Boiling points do not show regular trends. They are harder than alkali metals.

(6) Electro-positive Character or Metallic Character :

Their atomic size is smaller than IA group so these are lesser electro-positive than IA group. Electropositivity increases from Be to Ba.

(7) Conductivity :

These are also good conductor of heat and electricity due to presence of two free electrons.

(8) Nature of Bonds :

Be mainly forms covalent compound. The rest of the elements in group 2 forms ionic bond.

(9) Flame Test :

Element	Colour
Ca	Brick red
Sr	Crimson red
Ba	Apple green
Ra	Crimson

Previous Year's Questions

In context with beryllium, which one of the following statements is incorrect **[NEET-2016]**

(1) Its hydride is electron-deficient and polymeric

(2) It is rendered passive by nitric acid

(3) It forms Be_2C

(4) Its salts rarely hydrolyse

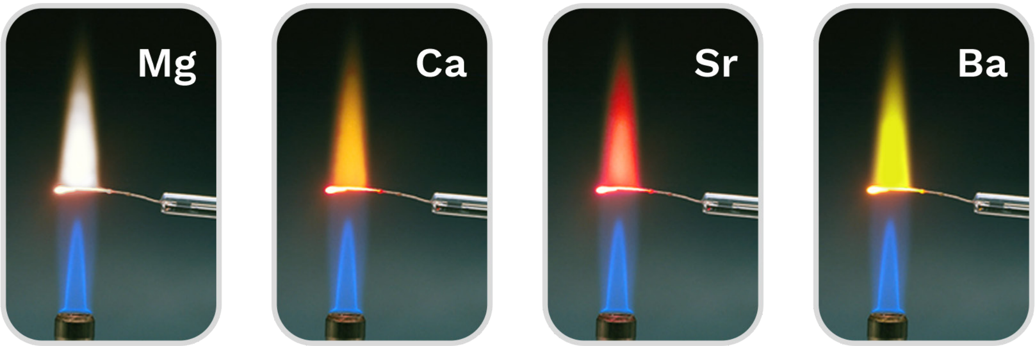
Concept Ladder

Exception :

Magnesium has lowest while beryllium has highest melting point among alkaline earth metals.

Concept Ladder

- Be has smallest size,
- While Cs has largest size.
- Atomic size increases down the group.



(10) Electronegative Values :

The electronegativity values of group 2 are low but are higher than the values of group 1. The value of decreases down the group.

(11) Lattice Energy :

Lattice energy of salts of alkali metals having common anion decreases on descending down the group.

(12) Hydration Energy :

The hydration energies of the alkaline earth metal ions are 4 or 5 time greater than for alkali metal ions due to their smaller size and increased charge. $\Delta H_{hydration}$ decreases down the group as the size of the ions increases.

(13) Photoelectric Effect :

These elements do not show this property as their atomic size is small hence ionisation energy is higher than IA group.

Previous Year's Questions

Which of the following compounds has the lowest melting point **[AIPMT-2011]**

(1) CaF_2 (2) $CaCl_2$
(3) $CaBr_2$ (4) CaI_2

Concept Ladder

M.P. and B.P. are more than that of alkali metals due to smaller size and closed packed structure.

Q.10 Write the trend in hydration enthalpies of alkaline earth metal ions?

A.10 Like group 1 metal ions, the hydration enthalpies of group 2 metal ions decreases with increase in ionic size down the group.
$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

(14) Standard Oxidation Potential :

Standard oxidation potential of alkaline earth metals :

Element	Oxidation Reaction	Standard Oxidation Potential (volt)
Be	Be → $Be^{2+} + 2e^-$	1.85
Mg	Mg → $Mg^{2+} + 2e^-$	2.37
Ca	Ca → $Ca^{2+} + 2e^-$	2.87
Sr	Sr → $Sr^{2+} + 2e^-$	2.89
Ba	Ba → $Ba^{2+} + 2e^-$	2.90

Chemical properties of alkaline earth metal :

Reactivity : Less reactive than alkali metals.

Order of reactivity : Be < Mg < Ca < Sr < Ba

Reactivity towards air :

- Except Be, these metals easily tarnished in air.
- Beryllium in powered form, burns brilliantly on ignition in air.
- In moist air, except Be all the elements convert into carbonates.
- In dry air all elements of II-A give nitride and oxide both.

Reactivity towards oxygen :

- Alkaline earth metals reacts with O_2 to form 'MO' type oxides.
  (M = Be, Mg, Ca, Sr, Ba)
- In II-A only Ca, Sr, Ba form peroxide.
  Ex : CaO_2, SrO_2, BaO_2
- BeO shows amphoteric property.
  MgO → weak basic
  CaO, SrO and BaO → Strong basic
- Basic properties increases from BeO to BaO.

Concept Ladder

(i) Be, Mg and Ca form monoxides while Sr and Ba form peroxides.

(ii) The solubilities of hydroxides of alkaline earth metals increases on moving down the group i.e., $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$.

Rack your Brain

Why Be and Mg don't show any colour?

Previous Year's Questions

In which of the following the hydration energy is higher than the lattice energy **[AIPMT-2007]**

(1) $BaSO_4$ (2) $MgSO_4$

(3) $RaSO_4$ (4) $SrSO_4$

Reactivity towards hydrogen :

- Except Be all the alkaline metals forms MH_2 type hydrides (MgH_2, CaH_2, SrH_2, BaH_2) on heating directly with H_2.
- BeH_2 is prepared by action of $BeCl_2$ with $LiAlH_4$
  $2BeCl_2 + \underset{\text{Reducing agent}}{LiAlH_4} \rightarrow 2BeH_2 + LiCl + AlCl_3$
- BeH_2 and MgH_2 are covalent, other are ionic.

Concept Ladder

$BeCl_2$ — Polymer in solid state
$BeCl_2$ — Dimer in gaseous state

Reactivity towards water :

- Calcium, strontium, barium and radium decompose cold water readily with evolution of hydrogen.
  $M + 2H_2O \longrightarrow M(OH)_2 + H_2$
- Magnesium decomposes boiling water but beryllium does not react with water, even when red hot, its protective oxide film survives even at high temperature as its oxidation potential is lower than the other members.
- Reactivity of alkaline earth metals increases on moving down the group as the oxidation potential increases. However, the reaction of alkaline earth metals is less vigorous than alkali metals.

Rack your Brain

How Be_2H is different from the hydrides of other members of group 2 ?

Reactivity towards halogens :

- All the group 2 elements combine with halogen at elevated temperatures forming their halides.

$$M + X_2 \rightarrow MX_2 \ (X = F, Cl, Br)$$

- 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.

$$BeO + C + Cl_2 \xrightarrow{600\text{–}800\ K} BeCl_2 + CO$$

Concept Ladder

- Alkaline metals reacts with X (Halogen) to form MX_2.
- Order of ionic nature
  $BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$

Reactivity towards acids :

- The alkaline earth meals readily react with acids liberating dihydrogen.
  $M + 2HCl \rightarrow MCl_2 + H_2$

Diagonal relationship – Be and Al :

(i) Both do not impart colour to flame.

(ii) Carbides of both on reaction with H_2O give CH_4.

(iii) Both are rendered passive by conc. HNO_3.

(iv) Oxides and hydroxides of both are amphoteric.

Concept Ladder

The charge/radius ratio of Be^{2+} is nearly the same as that of the Al^{3+} ion. Hence Be resembles Al in some ways.

Magnesium

(a) Ores of Magnesium :

(i) Magnesite $MgCO_3$

(ii) Carnallite $KCl.MgCl.6H_2O$

(iii) Asbestos $Mg_3(Si_2O_5)(OH)_4$

(iv) Epsom salt $MgSO_4.\ 7H_2O$

(b) Extraction of Mg is done by electrolysis of fused $MgCl_2$ which in turn is obtained from carnallite or magnesite.

(i) Carnallite can't be used directly to get anhydrous $MgCl_2$ by heating because all the water of crystallisation cannot be removed by heating. Strong heating may change Carrallite into MgO.

$$MgCl_2 + 2H_2O \xrightarrow{\Delta} MgO + 2HCl + H_2O$$

(ii) Dow's process

$$\underset{\text{From sea water}}{MgCl_2.6H_2O} \xrightarrow{\text{dry HCl}} MgCl_2 \xrightarrow[\text{Electrolysis 700°C}]{\text{Fused with NaCl}} Mg$$

Rack your Brain

Why Mg can't be obtained by electrolysis of carnallite?

(c) Compounds and uses Magnesium :

(i) Sorel's Cement – ($MgO + MgCl_2$) used in dentistry.

(ii) Epsom salt ($MgSO_4.\ 7H_2O$) – used as purgative in medicine and mordant in days.

(iii) Magnesia alba [$3MgCO_3.Mg(OH)_2 3H_2O$] is used in tooth paste and cosmetics.

Concept Ladder

The mixed oxides (CaO.MgO) obtained from calcination of dolomite ($CaCO_3.MgCO_3$) are reduced by ferrosilicon.

Calcium :

(a) Ores

(i) Dolomite - $MgCO_3.CaCO_3$

(ii) Gypsum – $CaSO_4.2H_2O$

(iii) Flusopar – CaF_2

(iv) Phosphorite – $Ca_3(PO_4)_2$

Rack your Brain

Why $Mg(OH)_2$ is called 'milk of magnesia'?

(b) Calcium oxide CaO (Burnt lime or quick lime)

- (i) $CaO + H_2O \xrightarrow{\text{Hissing sound}} Ca(OH)_2 + \text{Heat}$
- (ii) Mortar = CaO + Sand + Water
- (iii) Limelight – When exposed to oxyhydrogen flame, it starts emitting light called limelight.

(c) Gypsum or albastar ($CaSO_4.2H_2O$)

$$\underset{\text{Gypsum}}{CaSO_4.2H_2O} \xrightarrow{390K} \underset{\text{Plaster of Pairs}}{CaSO_4.\frac{1}{2}H_2O} + 1\frac{1}{2}H_2O$$

Plaster of pairs settles and becomes hard or cooling.

(d) Milk of lime : Suspension of $Ca(OH)_2$ in water

Cement :

(i) Cement is chemically – Calcium silicate + Calcium aluminate + 1% gypsum

(ii) Raw material – Limestone (Provides CaO)
Clay (Provides SiO_2,Fe_2O_3, Al_2O_3)

(iii) Approximate composition of cement

CaO	50-60%
SiO_2	20-25%
Al_2O_3	5-10%
MgO	1-3%
Fe_2O_3	1-3%

(iv) If cement has

- Excess of lime cracks appear
- Excess of silica slow setting
- Less of lime weak cement
- Excess of Al_2O_3 fast setting

(v) Cement with Fe is white cement

(vi) Setting of cement is exothermic process.

(vii)Concrete = cement + sand + gravel.

(viii) Mortar = $CaCO_3$ and sands in 1 : 3 ratio.

(ix) Reinforced cement = cement + sand + iron rod

Previous Year's Questions

HCl was passed through a solution of $CaCl_2$, $MgCl_2$ and NaCl. Which of the follwoing compound(s) crystallise(s)?

[NEET-2020]

(1) Both $MgCl_2$ and $CaCl_2$
(2) Only NaCl
(3) Only $MgCl_2$
(4) NaCl, $MgCl_2$ and $CaCl_2$

Rack your Brain

Why $Ca(OH)_2$ is used in white washing?

Concept Ladder

Cement was first introduced in England in 1824 by Joseph Aspdin. It is also called Portland cement.

Group–I and II

Oxides

Sodium Oxide : (Na_2O) :

Preparation :

(i) Na_2O is obtained by burning Na at 180°C in a limited supply of air or O_2 and distilling off the excess of Na in vacuum.

$$2Na + \frac{1}{2}O_2 \xrightarrow{180^\circ} Na_2O$$

(ii) By heating sodium peroxide or nitrate with sodium.

$$Na_2O_2 + 2Na \longrightarrow 2Na_2O$$

$$2NaNO_3 + 10Na \longrightarrow 6Na_2O + N_2$$

$$2NaNO_2 + 6Na \longrightarrow 4Na_2O + N_2$$

Properties :

(i) It is white amorphous mass.

(ii) It decomposes at 400°C into Na_2O_2 and Na.

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

(iii) It dissolve violently in H_2O, yielding NaOH.

$$Na_2O + H_2O \rightarrow 2NaOH$$

Sodium peroxides (Na_2O_2) :

Preparation : Na_2O_2 is formed by heating the metal in excess of air or O_2 at 300°, which is free from moisture and CO_2.

Properties :

(i) Na_2O_2 is a pale yellow solid, becoming white in air from the formation of a film of NaOH and Na_2CO_3.

(ii) In cold water (0°C) it produce H_2O_2 but at room temperature it produce O_2. In ice- cold minerals acids also produces H_2O_2.

$$Na_2O_2 + 2H_2O \xrightarrow{0^\circ C} 2NaOH + H_2O_2$$

$$2Na_2O_2 + 2H_2O \xrightarrow{25^\circ C} 4NaOH + O_2$$

$$Na_2O_2 + H_2SO_4 \xrightarrow{-0^\circ C} Na_2SO_4 + H_2O_2$$

Concept Ladder

Na_2O_2 can also be prepared by heating sodium metal on aluminium trays in air (free from CO_2)

$$2Na + O_2 \longrightarrow Na_2O_2$$

Rack your Brain

Write various uses of sodium oxide?

Concept Ladder

Uses :

- For preparing H_2O_2, O_2.
- Oxygenating the air in submarines.
- Oxidising agent in the laboratory.

Rack your Brain

Name the oxides formed by sodium.

(iii) Na_2O_2 reacts with CO2, giving Na_2CO_3 and O_2 and hence its use for purifying air in a confined space e.g.ill-ventilated room, submarine, etc.

$$2Na_2O_2 + 2CO_2 \longrightarrow 2Na_2CO_3 + O_2$$

(iv) Na_2O_2 is an oxidising agent and oxidises charcoal, CO, NH_3, SO_2.

$$3Na_2O_2 + 2C \longrightarrow 2Na_2CO_3 + 2Na$$

[Deposition of metallic Na]

$$CO + Na_2O_2 \longrightarrow Na_2CO_3$$

$$SO_2 + Na_2O_2 \longrightarrow Na_2SO_4$$

$$2NH_3 + 3Na_2O_2 \longrightarrow 6NaOH + N_2$$

(v) It contains peroxide ion $[—O—O—]^{-2}$

Oxides of Potasssium :

	K_2O	K_2O_2	K_2O_3	KO_2
Colours	White	White	Red	Bright yellow

Preparation :

(i) $2KNO_3 + 10\ K \xrightarrow{\text{Heating}} 6K_2O + N_2$

$$\underset{\text{(White)}}{K_2O} \xrightarrow{\text{Heating}} \underset{\text{(Yellow)}}{K_2O}$$

$$K_2O + H_2O \longrightarrow 2KOH$$

(ii) $2K + O_2 \xrightarrow[\text{Air at 300°C}]{\text{Controlled}} K_2O_2$

(iii) Passage of oxygen through a blue solution of potassium in liquid ammonia yields oxides, KO_2 (deep yellow), K_2O_3 (red) and K_2O_2 (white)

$$NH_3 \xrightarrow{O_2} \underset{\text{White}}{K_2O_2} \longrightarrow \underset{\text{Red}}{K_2O_3} \longrightarrow \underset{\text{Yellow}}{KO_2}$$

- KO_2 reacts with water and produces hydrogen peroxide and oxygen both.

$$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$$

Concept Ladder

K_2O is an unstable substance which easily oxidized to other oxides, peroxides or acid oxide of potassium (KHO).

Rack your Brain

Name the industrial products in which you can find potassium oxides?

Previous Year's Questions

A solid compound 'X' on heating gives CO_2 gas and a residue. The residue mixed with water forms 'Y'. On passing an excess of CO_2 through 'Y' in water, a clear solution, 'Z' is obtained. On boiling 'Z', compound 'X; is reformed. The compound 'X' is : **[AIPMT(Mains)-2010]**

(1) Na_2CO_3 (2) K_2CO_3
(3) $Ca(HCO_3)_2$ (4) $CaCO_3$

KO_3 :

$$\underset{\text{(Dry powdered)}}{KOH} + O_3 \xrightarrow{-10^\circ \text{ to } -15^\circ C} \underset{\text{(Orange solid)}}{KO_3}$$

(Ozonised oxygen)

Magnesium Oxide (MgO) :

- It is obtained by heating natural magnesite and also called magnesia.

$$MgCO_3 \longrightarrow MgO + CO_2$$

Properties :

(i) It is white powder.
(ii) Its melting point is 2850°C, hence used in manufacture of refractory brick for furnaces.
(ii) It is slightly soluble in H_2O imparting alkaline reaction.

Concept Ladder

Uses :

- MgO_2 is used as an antiseptic in tooth paste as a bleaching agent.

Calcium Oxide (CaO) :

- CaO is commonly called as quick lime or lime and made by decomposing lime stone at a high temperature about 1000°C.

$$CaCO_3 \longrightarrow CaO + CO_2 \qquad \Delta H = 42000 \text{ cal}$$

Properties :

(i) It is white amorphous powder of melting point 2570°C.
(ii) It ejects intense light (lime light), when heated in O_2–H_2 flame.
(iii) It combines with some acidic oxide and have properties similar to basic oxide.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$
$$CaO + CO_2 \longrightarrow CaCO_3$$

(iv) It combines with H_2O to produce $Ca(OH)_2$.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Rack your Brain

(i) What is slaking of lime?
(ii) Quick lime combines with which types of oxides?

Magnesium Peroxide (MgO_2) and Calcium Peroxide (CaO_2) :

- MgO_2 and CaO_2 are obtained by passing H_2O_2 in a solution of $Mg(OH)_2$ and $Ca(OH)_2$ respectively.

Concept Ladder

MgO can also be obtained by burning Mg in air, by heating hydroxide, nitrate, sulphate or carbonate. Oxide prepared by heating magnesite ($MgCO_3$) is called Calcined Magnesia.

Hydroxides

Sodium Hydroxides :

Preparation :

(i) Electrolysis of Brine :

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

At anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$

At cathode: $2H^+ + 2e^- \longrightarrow H_2$

(ii) Caustication of Na_2CO_3 (Gossage's method) :

$$Na_2CO_3 + \underset{\text{(Suspension)}}{Ca(OH)_2} \rightleftharpoons 2NaOH + CaCO_3$$

Since the K_{sp} $(CaCO_3)$ < K_{sp} $(Ca(OH)_2$, the reaction shifts towards right.

Properties :

(i) NaOH is highly corrosive solid and white crystalline.

(ii) It has stablized form towards heat.

(iii) It's aqueous solution alkaline in nature and soapy in touch.

(iv) $NH_4Cl + NaOH \longrightarrow NaCl + NH_3 + H_2O$

$FeCl_3 + 3NaOH \longrightarrow \underset{\text{Brown ppt}}{Fe(OH)_3} + 3NaCl$

$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2NaCl$

$Zn(OH)_2 + 2NaOH \xrightarrow{\text{Excess}} \underset{\text{Soluble}}{Na_2ZnO_2} + 2H_2O$

[Same with $AlCl_3$, $SnCl_2$, $PbCl_2$]

(v) Amphoteric and acidic oxides gets dissolved easily e.g.

$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$

$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$

(vi) Al and Zn metal gives hydrogen from NaOH

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

(vii) Several non metals such as P, Cl, S etc. yield a hydride instead of H_2 e.g.

$4P + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$

(Disproportionation reaction)

Concept Ladder

All peroxides of alkaline earth metals are white crystalline ionic solids containing the peroxide ion, O_2^{2-}. Treatment of peroxide with acids librates with hydrogen peroxides.

$MgO_2 + 2HCl \rightarrow MgCl_2 + H_2O_2$

Rack your Brain

Which cell is used for manufacturing of sodium hydroxide?

Previous Year's Questions

Which of the following oxides is not expected to react with sodium hydroxide?

[AIPMT]

(1) CaO (2) SiO_2

(3) BeO (4) B_2O_3

Potassium Hydroxide :

Preparation : By electrolysis of aqueous solution of KCl.

Properties : Same as NaOH.

(a) It has stronger base compared to NaOH.
(b) Solubility in H_2O is more compared to NaOH.
(c) In alcohol, sodium hydroxyde is sparingly soluble but KOH is highly soluble.
(d) As a reagent potassium hydroxide is less frequently used but in absorption of CO_2, potassium hydroxide is preferably used compared to sodium hydroxide, because potassium bicarbonate formed is soluble whereas sodium bicarbonate is insoluble, hence choke the tubes of apparatus used.

Magnesium Hydroxide : It occurs in nature as mineral brucite.

Preparation : $Mg(OH)_2$ can be prepared by adding caustic soda solution to a solution of Mg-sulphate or chloride solution.

$$Mg^{2+} + 2NaOH \longrightarrow 2\,Na^+ + Mg(OH)_2$$

Properties :

(i) (i) It can be dried at temp. upto 100°C only, otherwise at higher temp. it breaks down into its oxide.

$$Mg(OH)_2 \longrightarrow MgO + H_2O$$

(ii) It dissolves in ammonium chloride solution.

$$Mg(OH)_2 + 2NH_4Cl \longrightarrow MgCl_2 + 2NH_4OH$$

- Thus, magnesium hydroxide is not therefore precipitated from a solution of Mg^{2+} ions by NH_4OH in presence of excess of NH_4Cl.

Calcium Hydroxide :

Preparation : By spraying water on quick lime.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Properties :

(i) It is sparingly soluble in water.
(ii) It's solubility in hot H_2O is less than that of cold H_2O. Therefore solubility decreases with increase in temperature.

Concept Ladder

The hydroxides of all alkali metals are white crylstalline solids. They are strongest of all the gases and readily dissolve in water with the evolution of extent heat.

Rack your Brain

Write the increasing order of basic strength in hydroxides of alkaline earth metals?

Previous Year's Questions

The suspension of slaked lime in water is known as **[NEET-2016]**

(1) Aqueous solution of slaked lime
(2) Limewater
(3) Quicklime
(4) Mile of lime

(iii) $Ca(OH)_2$ readily absorbs CO_2 as used as a test for the gas.

(iv) It is used as a mortar, which is a mixture of slaked lime (1 Part) and sand (3 Parts) made into paste with H_2O.

Carbonates

Sodium Carbonate :

Preparation :

(i) Leblanc Process :

$$NaCl + H_2SO_4\ (conc.) \xrightarrow{\text{Mild heating}} NaHSO_4 + HCl$$

$$NaCl + NaHSO_4 \xrightarrow[\text{heated}]{\text{Strongly}} \underset{\text{(Salt Cake)}}{Na_2SO_4} + HCl$$

$$Na_2SO_4 + 4C \longrightarrow Na_2S + 4CO$$

$$Na_2S + CaCO_3 \longrightarrow Na_2CO_3 + CaS$$

(ii) Solvay Process :

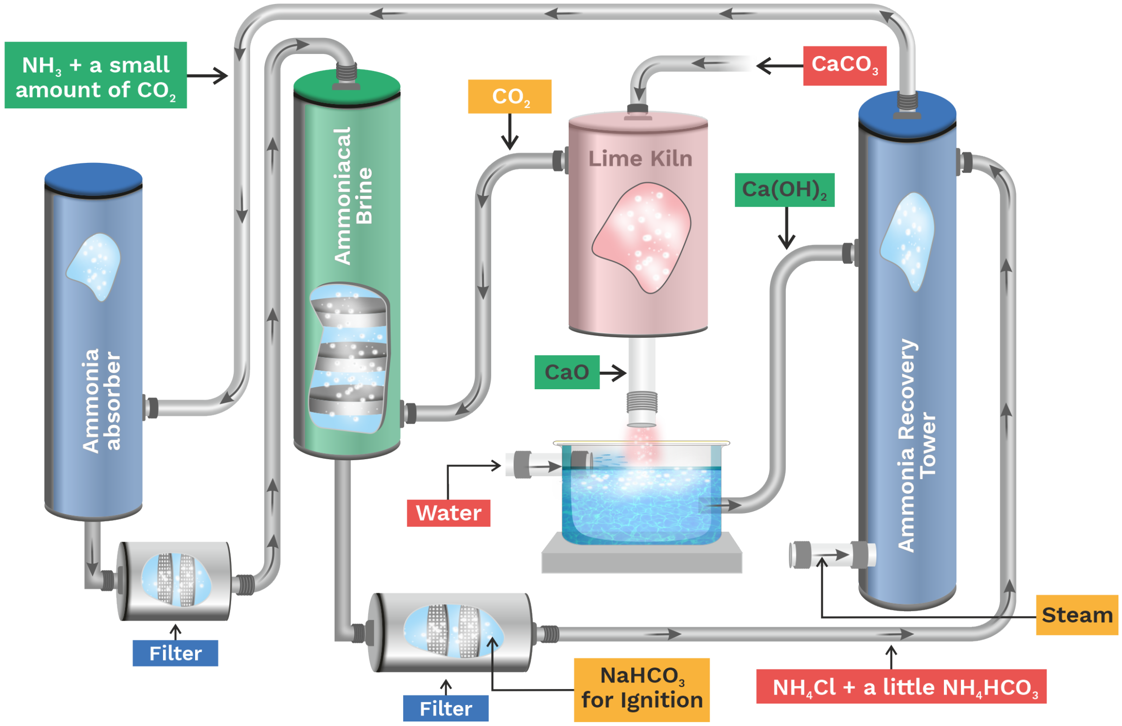
It is used for the preparation of washing soda. ($Na_2CO_2.10H_2O$) soda ($NaHCO_3$)

Concept Ladder

The hydroxides of alkaline earth metals are less basic corresponding alkali metal hydroxides because of higher ionization energies, smaller ionic sizes and greater lattice energies.

Rack your Brain

Arrange alkaline earth metals in increasing order of their solubility in water?



H_2CO_3 can not be prepared from Solvay's process since $KHCO_3$ is water soluble . (no PPT)
Washing soda ($Na_2.CO_3.10H_2O$) also shows efflorescence just like blue vitriol.

$$\begin{array}{c} Na_2CO_3.10H_2O \xrightarrow[(D)]{\sim 375\ K} Na_2CO_3.H_2O + 9H_2O \\ \Big\downarrow {\scriptstyle > 375\ K} \\ Na_2CO_3.10H_2O \\ \text{(Soda ash)} \end{array}$$

Properties :

(i) Anhydrous Na_2CO_3 is called as soda ash, which melts at 852°C but does not decompose on heating.

(ii) It forms number of hydrates.

$Na_2CO_3\ .\ H_2O \longrightarrow$ Crystal carbonate

Na_2CO_3 + Moisture in air $\longrightarrow$ Soda ash
$Na_2CO_3\ .\ 7H_2O \longrightarrow$ Calcined soda

$Na_2CO_3\ .10H_2O \longrightarrow$ Washing soda

(iii) Sodium carbonate absorbs CO_2 yielding sparingly soluble $NaHCO_3$ which can be calcined at 250° to get pure Na_2CO_3.

$$Na_2CO_3 + H_2O + \underset{250°C}{\rightleftharpoons} 2NaHCO_3$$

(iv) It dissolved in acid with effervescence of carbon dioxide and causticized by lime to give NaOH.

$$Na_2CO_3 + HCl \longrightarrow 2NaCl + H_2O + CO_2$$

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

Potassium Carbonate :

- By Leblanc process, it can be prepared but by Solvay process it cannot be prepared because $KHCO_3$ is soluble in water.

Concept Ladder

The Na_2CO_3 exists in various forms, namely anhydrous sodium carbonate Na_2CO_3 (soda-ash); monohydrate $Na_2CO_3.H_2O$ (crystal carbonate); heptahydrate $Na_2CO_3.7H_2O$ and decahydrate $Na_2CO_3.10H_2O$ (washing soda).

Rack your Brain

Write down the raw materials used in Solvay process?

Previous Year's Questions

On heating which of the following releases CO_2 most easily?

[NEET-2015]

(1) Na_2CO_3 (2) $MgCO_3$
(3) $CaCO_3$ (4) K_2CO_3

Properties :

- It resembles with Na_2CO_3, melting point is 900°C but a mixture of Na_2CO_3 and K_2CO_3 melts at 712°C.

Calcium Carbonate :

- It occurs in nature as chalk, calcite, coral, limestone, marble etc. It is prepared by dissolving limestone or marble in HCl and removing Al and Fe present, by precipitating with ammonia and then adding ammonium carbonate to the solution.

$$CaCl_2 + (NH_4)_2CO_3 \longrightarrow CaCO_3 + 2NH_4Cl$$

Properties :

(i) It dissociates above 1000°C as follows :

$$CaCO_3 \longrightarrow CaO + CO_2$$

(ii) $CaCO_3$ dissolves in water containing CO_2 forming $Ca(HCO_3)_2$ but is precipitated from the solution by boiling.

$$CaCO_3 + H_2O + CO_2 \underset{\text{Boiling}}{\rightleftharpoons} Ca(HCO_3)_2$$

Magnesium Carbonate :

- $Mg(CO_3)_2$ occurs in nature as magnesite, isomorphous with calcite. It is obtained as a white ppt by adding $NaHCO_3$ to a solution of a magnesium salt; but only basic carbonate, called magnesia alba, having the approximate composition $MgCO_3 . Mg(OH)_2.3H_2O$ is precipitated.

Properties :

Same as calcium carbonate.

Bicarbonates

Sodium Bicarbonates :

Preparation :

By adsorption of CO_2 in Na_2CO_3 solution.

$$Na_2CO_3 + H_2O + CO_2 \rightleftharpoons \underset{\text{less soluble}}{2NaHCO_3} > 100°C$$

Concept Ladder

All the carbonates of alkaline earth metals are however more soluble in the presence of CO_2 due to the formation of corresponding bicarbonates.

$$CaCO_3(s) + CO_2(g) + H_2O(g) \rightarrow Ca(HCO_3)_2(aq)$$

Rack your Brain

Why potassium carbonate cannot be prepared by Solvay process?

Previous Year's Questions

Which of the following substance is used in the laboratory for fast drying of neutral gases **[AIIMS]**

(1) Sodium phosphate
(2) Phosphorus pentoxide
(3) Sodium sulphate
(4) Anhydrous calcium chloride

Uses : It is used as baking powder and in medicine.

Potassium bicarbonates :

Preparation : Same as $NaHCO_3$

Properties : Same as $NaHCO_3$

But $KHCO_3$ is soluble in H_2O and more alkaline compared to $NaHCO_3$.

Magnesium bicarbonate :

$$MgCO_3 + CO_2 + H_2O \xrightleftharpoons[\text{Boiling}]{} Mg(HCO_3)_2$$

Calcium bicarbonate :

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

Chlorides

Sodium Chloride :

Prepared from brine containing 25% NaCl.

Properties :

(i) It is nonhygroscpic but the presence of magnesium chloride in common salt renders it hygroscopic.

(ii) It is used to prepare freezing mixture in laboratory (Ice-common salt mixture is called freezing mixture and temperature goes down to –23°C).

(iii) For melting ice and snow on road.

Potassium Chloride :

KCl is also occurs in nature as sylvyne (KCl) or carnalite ($2KCl, MgCl_2, 6H_2O$)

Uses : It is used as fertiliser.

Preparation : By dissolving $MgCO_3$ in dil. HCl.

$$MgCO_3 + 2HCl \longrightarrow MgCl_2 + H_2O + CO_2$$

Properties :

(i) It crystallises as hexahydrate, $MgCl_2.6H_2O$.

(ii) It is deliquescent solid.

(iii) This hydrate undergoes hydrolysis as follows.

$$MgCl_2.6H_2O \longrightarrow Mg(OH)Cl + HCl + 5H_2O$$

$$Mg(OH)Cl \longrightarrow MgO + HCl$$

Concept Ladder

The bicarbonates of alkaline earth metals are prepared by passing CO_2 through a suspension of metal carbonates in water.

$$\underset{\text{(insoluble)}}{M_2CO_3} + H_2O + CO_2 \rightarrow \underset{\text{(soluble)}}{M(HCO_3)_2}$$

Rack your Brain

Write some uses of bicarbonates of K, Mg and Ca.

Concept Ladder

All the bicarbonates of alkaline earth metals are stable only in solution and have not been isolated in the pure state.

- Hence, anhydrous magnesium chloride cannot be prepared by heating this hydrate.
- Because of this formation of HCl. Sea water cannot be used in marine boilers which corrodes the iron body.

(iv) Anhydrous $MgCl_2$ can be prepared by heating a double salt like.

$MgCl_2 . NH_4Cl . 6H_2O$ as follows :

$$MgCl_2 . NH_4Cl . 6H_2O \xrightarrow[\Delta]{-H_2O} MgCl_2 . NH_4Cl$$

$$MgCl_2 . NH_4Cl \xrightarrow[\Delta]{\text{Strong}} MgCl_2 + NH_3 + HCl$$

Sorel Cement :

Sorel cement is set to hard mass on standing when MgO and $MgCl_2$ (paste like). This is used in flooring, dental filling etc.

Calcium Chloride :

(i) It is the by-product in Solvay process.

(ii) $CaCl_2$ may also be prepared by dissolving the carbonate in HCl.

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

Properties :

(i) It is deliquescent crystals.

(ii) $CaCl_2$ gets hydrolysed like $MgCl_2$ hence anhydrous $CaCl_2$ cannot be prepared.

$$CaCl_2 + H_2O \rightleftharpoons CaO + 2HCl$$

Hence, anhydrous $CaCl_2$ is prepared by heating $CaCl_2.6H_2O$ in a current of HCl (dry).

(iii) Anhydrous calcium chloride is used in drying gases and organic compounds but not ammonia or alcohol due to the formation of $CaCl_2.8NH_3$ and $CaCl_2.4C_2H_5OH$.

Sulphates

Sodium Sulphate :

Preparation : Na_2SO_4 is formed in the 1st step of Leblanc process by heating common salt with sulphuric acid.

Concept Ladder

Slaked lime reacts with chlorine to form calcium hypo chloride; a constituent of bleaching powder.

$CaCl_2 + Ca(OCl)_2 + 2H_2O$

Rack your Brain

What are A and B for given reaction?

$CaCl_2 + 2NaOH \rightarrow A + B$

Previous Year's Questions

Solubility of the alkaline earth's metal sulphates in water decreases in the sequence? **[AIPMT-2015]**

(1) Ca > Sr > Ba > Mg

(2) Sr > Ca > Mg > Ba

(3) Ba > Mg > Sr > Ca

(4) Mg > Ca > Sr > Ba

Thus the salt cake formed is crystalised out from its aq. solution as $Na_2SO_4.10H_2O$. This termed as Glauber's salt.

- When it is crystalised below 32.4°, then $Na_2SO_4.10H_2O$ is obtained but above 32.4°C, Na_2SO_4 (anhyd.) comes out.

Properties :

Na_2SO_4 is reduced to Na_2S when fused with C.

$$Na_2SO_4 + 4C \longrightarrow Na_2S + 4CO$$

Magnesium Sulphate :

Preparation :

(i) It is obtained by dissolving $MgSO_4.H_2O$ in boiling water and then crystallising the solution as a hepta hydrate. i.e. $MgSO_4.7H_2O$. It is called as Epsom salt.

(ii) It is also obtained by dissolving $MgCO_3$ in hot dil. H_2SO_4.

$$MgCO_3 + H_2SO_4 \longrightarrow MgSO_4 + H_2O + CO_2$$

(iii) By dissolving dolomite ($CaCO_3.MgCO_3$) in hot dil. H_2SO_4 and removing the insoluble $CaSO_4$ by filtration.

(iv) It is isomorphous with $ZnSO_4.7H_2O$, $FeSO_4.7H_2O$.

Calcium Sulphate :

It occurs as anhydrite calcium sulphate and as the dihydrate gypsum, alabaster or satin-spar.

Properties :

(i)

$$\begin{tikzcd}\text{Gypsum}(CaSO_4.2H_2O) \arrow[r, shift left, "120°C"] & 2CaSO_4.H_2O\ \text{(Plaster of Paris)} \arrow[l, shift left, "+H_2O"] \arrow[d, "200°C"] \\ & \text{(anhydrous) } CaSO_4 \\ & \text{Dead burnt plaster}\end{tikzcd}$$

(ii) Solubility of $CaSO_4$ at first increase upto

Concept Ladder

Out of minerals of sodium like

(i) Soda feldspar ($Na_2O.Al_2O_3.6SiO_2$)

(ii) Rock salt (NaCl)

(iii) Chile salt ($NaNO_3$)

(iv) Glauber's salt ($Na_2SO_4.10H_2O$)

(v) Borax ($Na_2B_4O_7.10H_2O$)

Only NaCl has been used economically to extract the sodium metal.

Previous Year's Questions

Crude sodium chloride obtained by crystallisation of brine solution does not contain

[NEET-2019]

(1) $MgCO_4$ (2) Na_2SO_4

(3) $MgCl_2$ (4) $CaSO_4$

a certain point and then decreases with rise of temperature.

(iii) POP is used in mould making due to its porous body.

Q.11 (a) Mg_3N_2 when reacted with water, gives off NH_3 but HCl is not obtained from $MgCl_2$ on reaction with water at room temperature. Why ?

(b) The crystalline salts of alkaline earth metals contain more water of crystallization than corresponding alkali metal salts. Why ?

A.11 (a) Mg_3N_2 is a salt of a strong base and weak acid hence its hydrolysis is possible.

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

$MgCl_2$ is a salt of a strong base, $[Mg(OH)_2]$, and a strong acid, (HCl), and hence its hydrolysis is not possible.

(b) Alkaline earth metal ions have higher tendency of hydration in comparison to alkali metal ions due to its small size and high Z_{eff}. Thus, the salts of alkaline earth metals contain more water of crystallization than the salts of alkali metals.

Q.12 What happens when :

(i) Beryllium carbide reacts with water.

(ii) Magnesium nitrate is heated.

(iii) Quick lime is heated in electric furnace with powdered coke.

A.12 (i) Methane gas is evolved.

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

(ii) Brown coloured gas, NO_2, is evolved.

$$2MgNO_3 \longrightarrow 2MgO + 4NO_2 + O_2$$

(iii) Calcium carbide is formed with evolution of CO gas.

$$CaO + 3C \xrightarrow[\text{Arc}]{\text{Electric}} CaC_2 + CO$$

	Properties	**Alkaline Earth Metals**	**Alkali Metals**
(i)	Electronic configuration	Two electrons are present in the valency shell. The configuration is ns^2.	One electron is present in the valency shell. The configuration is ns^1.
(ii)	Valency	Bivalent	Monovalent.
(iii)	Electropositive nature	Less electropositive.	More electropositive.
(iv)	Hydroxides	Weak bases, less soluble and decompose on heating.	Strong bases, highly soluble and stable towards heat.
(v)	Bicarbonates	These are not known in free state. Exist only in solution.	These are known in solid state.
(vi)	Carbonates	Insoluble in water. Decompose on heating.	Soluble in water. Do not decompose on heating (Li_2CO_3 is an exception).
(ix)	Nitrates	Decompose on heating evolving a mixture of NO_2 and oxygen.	Decompose on heating evolving only oxygen.
(x)	Solubility of salts	Sulphates, phosphates, fluorides, chromates, oxalates, etc., are insoluble in water.	Sulphates, phosphates, fluorides, chromates, oxalates etc, are soluble in water.
(xi)	Physical properties	Are less reactive and comparative harder metals. High melting points. Diamagnetic.	Soft, low melting points. Paramagnetic.
(xii)	Hydration of compounds	The compounds are extensively hydrated. $MgCl_2.6H_2O$, $CaCl_2.6H_2O$ and $BaCl_2.2H_2O$ are hydrated chlorides.	The compounds are less hydrated. NaCl, KCl and RbCl form non-hydrated chlorides.
(xiii)	Reducing power	Weaker, as ionization potential values are high and oxidation potential values are low.	Stronger, as ionization potential values are low and oxidation potential values are high.

Q.13 Why cannot sodium and potassium be prepared by the electrolysis of their aqueous solutions ?

A.13 The electrode potential i.e. reduction potential of Na (–2.71 V) or K (–2.92) is much lower than that of H_2O (–0.83 V), therefore, upon electrolysis, water gets reduced in preference to Na^+ or K^+ ions. In other words, sodium and potassium cannot be obtained by electrolytic reduction of Na^+ or K^+ ions in aqueous solution.

Q.14 Amongst alkali metals, why is lithium regarded as strongest reducing agent in aqueous solutions ?

A.14 Li+ has the smallest size among alkali metals therefore, it has highest hydration energy.
In other words, it has the lowest electrode potential ($E° = -3.04$ V), i.e., it has the maximum tendency to lose electrons and hence is the strongest (most apt) reducing agent amongst alkali metals.

Q.15 Why Be and Mg do not give characteristic colour to the flame whereas other alkaline earth metals do give?

A.15 Be and Mg have high ionization enthalpies and hence their valence electrons are not easily excited.

Q.16 Explain why halides of beryllium fume in moist air but other alkaline earth metal halides do not?

A.16 $BeCl_2$ being a salt of weak base, $Be(OH)_2$ and a strong acid, HCl undergoes hydrolysis by water to form HCl which fumes in air. $BaCl_2$, on the other hand, being a salt of a strong base, $Ba(OH)_2$ and strong acid, HCl does not undergo hydrolysis by water to form HCl and hence does not fume in air.

$$BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl$$

$$BaCl_2 + H_2O \not\longrightarrow Ba(OH)_2 + 2HCl$$

Summary

- General Electronic Configuration ns^1
- General Oxidation State is $+1$
- Atomic Size $Li < Na < K < Rb < Cs$
- Ionisation Energy $Li > Na > K > Rb > Cs$
- Density $Li < K < Na < Rb < Cs$

  Reducing property (i) $Li < Na < K < Rb < Cs$ (Molten)

  (ii) $Li > K \approx Rb > Cs > Na$ (Aqueous)
- Simple ionic radii are in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

  Hydrated radii $Li^+(aq) > Na^+(aq) > K^+(aq) < Rb^+(aq) < Cs^+(aq)$

  Ionic mobility $Li^+(aq) < Na^+(aq) < K^+(aq) < Rb^+(aq) < Cs^+(aq)$
- Li shows resemblance with Mg, an element of group IIA. This resemblance is termed as diagonal relationship.
  - (i) Ionic radii and atomic radii of Li and Mg are not very much different.
  - (ii) Both have high polarising power (Ionic potential).
- General Electronic Configuration ns^2
- General Oxidation State is $+2$
- Atomic Size $Be < Mg < Ca < Sr < Ba$
- Ionisation Energy $Be > Mg > Ca > Sr > Ba$
- Reducing Property $Be^{+2} < Mg^{+2} < Ca^{+2} < Sr^{+2} < Ba^{+2}$

  (in aqueous and gaseous medium)
- $Mg(OH)_2$ is called 'milk of magnesia and is used as antacid. $Ca(OH)_2$ is called 'milk of lime'.
- Be shows diagonal relationship with aluminium, the second element of III A group.
  - (a) The polarising power of Be^{2+} and Al^{3+} ions is high, consequently the compounds are covalent.
  - (b) The electronegativity of both the elements is nearly the same.
  - (c) Be_2C and Al_4C_3 on hydrolysis evolve CH_4.