

15. s - BLOCK ELEMENTS

HYDROGEN

1. INTRODUCTION

The most abundant element of universe ($\approx 76\%$), the fifteenth most abundant in the earth, and the tenth most abundant in earth crust Hydrogen is the lightest, smallest and first element of periodic table with atomic number one.

In nature, hydrogen is found in the free as well as in the combined state.

In the atmosphere, the presence of hydrogen is found to very minute (only one part in a million by volume) owing to its high chemical reactivity. Low abundance in the atmosphere is also due to the earth's gravitational field which is too small to hold on to so light an element.

Hydrogen

Symbol: H

At. No.: 1

Placed with alkali metals as well as Halogens

At. Wt.: 1.008

Electronic configuration - $1s^1$

2. POSITION OF HYDROGEN IN PERIODIC TABLE

Hydrogen is a unique element, it has only one electron in the $1s$ -orbital and no electrons in the other shell. It may donate one electron forming H^+ (like alkali metals) or may accept one electron forming H^- (like halogens). It ranges in character from being a strong Lewis base (H^-) to being a strong Lewis acid (H^+). It is this nature which makes it difficult for us to assign hydrogen its proper place in the periodic table because of its resemblance with halogens as well as with alkali metals.

2.1 Resemblance with Alkali Metals

Hydrogen resembles alkali metals in the following respects:

- (a) **Electronic Configuration** - Like alkali metals, hydrogen also has one valence electron.
- (b) **Electropositive Character** - Like other alkali metals, Hydrogen readily forms the Hydronium ion, which is very stable.

(c) **Reaction with Non-Metals** - Forms sulphides, oxides and halides same as alkali metals.

(d) **Reducing action** - Like alkali metals, hydrogen also acts as strong reducing agent.



2.2 Resemblance with Halogens

(a) **Electronic configuration:** Like halogens, hydrogen is short of one electron for stability in the outer orbit as explained below-

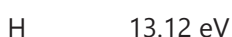


(b) **Atomicity:** All halogens exist as diatomic covalent molecules F_2 , Cl_2 , etc. In a similar way hydrogen is a diatomic covalent molecule.



(c) **Physical state:** Hydrogen is a gas like F_2 and Cl_2 .

(d) **Ionization potential:** I.P of hydrogen is very high, same as in the case of halogens.



(e) **Reaction with non-metals:** Both, halogens and hydrogen combine with other non-metals by forming single bonds to give compounds like CCl_4 , CH_4 , and $SiCl_4$.

3. SPECIAL FORMS OF HYDROGEN

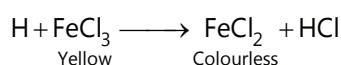
3.1 Nascent Hydrogen

(a) Nascent H is hydrogen at the moment of its generation, i.e., when it is just set free in a chemical reaction.

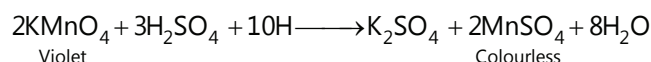


(b) This hydrogen is more reactive and a more powerful reducing agent than ordinary H_2 . It reduces the following:

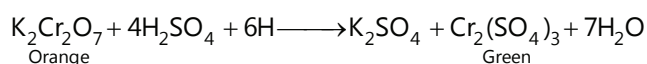
(i) Decolourizes yellow colour of $FeCl_{3(aq)}$.



(ii) Decolourizes violet colour of $KMnO_4$.



(iii) Turns $K_2Cr_2O_7$ solution to green.



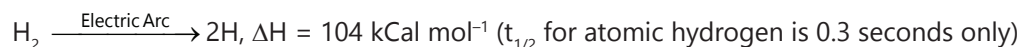
No such change in colour is produced when H_2 is bubbled through the solution of $FeCl_3$, $KMnO_4$ or $K_2Cr_2O_7$.

3.2 Adsorbed Hydrogen (Occluded Hydrogen)

H_2 on bubbling at the surface of platinum black, is adsorbed there and becomes capable of bringing out many chemical changes such as reduction and hydrogenation. This type of hydrogen is named as adsorbed H_2 . Similarly H_2 , occluded or adsorbed on Palladium is a very strong reducing agent and combines with halogens even in the dark, precipitates Hg from $HgCl_2$.

3.3 Atomic Hydrogen

In 1922, Langmuir showed that H_2 placed in contact with a tungsten wire, heated by an electric arc at low pressure dissociates into atoms with an absorption of 104.0 kcal of heat per mol.



3.4 Ortho and Para Hydrogen

When the spins of both the protons (nucleus) in the hydrogen molecule are in the same direction then this form is known as ortho hydrogen. The molecule of hydrogen in which both the protons are spinning in opposite directions known as para hydrogen. These are nuclear isomers.



Figure 15.1: Spins for Ortho and Para Hydrogen

At normal temperature the ratio of ortho and para hydrogen is 3: 1, but as the temperature is lowered, the proportion of para hydrogen increases (at 20°C).

MASTERJEE CONCEPTS

- Difference between Nascent and Atomic Hydrogen - Scientifically, nascent refers to the substance at the point at which it forms. Such as Zinc reacts with sulphuric acid, individual hydrogen atom forms but very quickly reacts with other hydrogen atom forming H_2 molecule. This is the only common situation at which atomic hydrogen exists even very fleetingly.
- Since ortho is more stable than para form at room temperature. Para readily gets converted into ortho by following reaction:

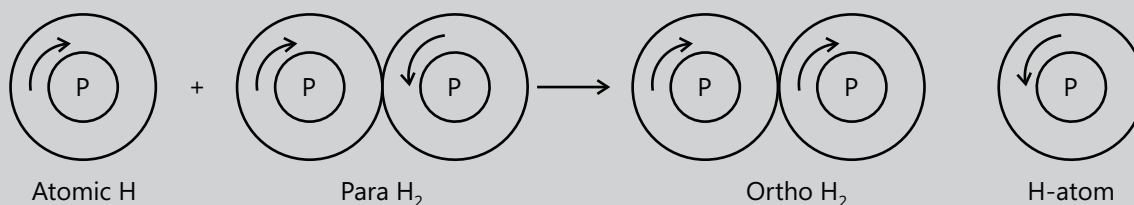


Figure 15.2: Conversion of para H_2 to ortho H_2

- Adsorbed H_2 is more reactive than normal dihydrogen.

Vaibhav Krishnan (JEE 2009, AIR 22)

4. DIHYDROGEN OR DIPROTIIUM

4.1 Methods of Preparation of Dihydrogen

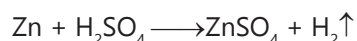
4.1.1 From Water

The cheapest and most widely available source of hydrogen is water. H_2 can be obtained from water using any one of the processes given below:

- (a) By action of water on metals
- (b) By action of water on hydrides
- (c) By action of water on methane
- (d) By electrolysis of water

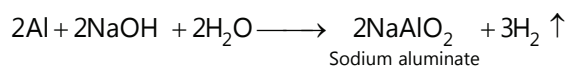
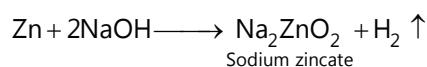
4.1.2 From Acids

Metals which lie above hydrogen in electro-chemical series i.e. metals with positive E°_{OP} do not displace H_2 from dilute mineral acid like HCl or H_2SO_4 . Metals having negative E°_{OP} (i.e. metals lying below hydrogen in ECS) displace H_2 from acids, e.g., Zn , Mg , Fe etc. displace H_2 from acids.



4.1.3 From Alkali

Certain metals like Zn , Sn , Al , Pb , Si etc. (amphoteric metals) react with boiling $NaOH$ to liberate H_2 .

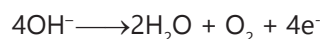


4.2 Manufacture of H_2 on Commercial Scale

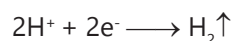
4.2.1 By Electrolysis of Water

The water containing a small amount of an acid or alkali (about 15-20%) is electrolysed in an electrolytic cell. The anode and cathode are separated by an asbestos diaphragm. The cathode is usually made up of iron and anode usually of nickel.

At anode: OH^- ions are discharged and oxygen is evolved.

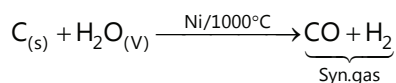


At cathode: H^+ ions are discharged and hydrogen is evolved.



4.2.2 Bosch Process

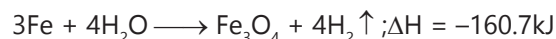
This process is most common, and in this process, first steam is passed over hot coke at $1000^\circ C$ to obtain water gas or Synthesis gas or Syn gas.



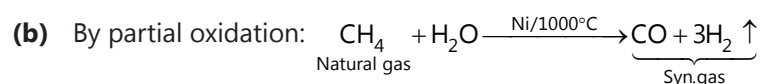
This process of obtaining 'Synthesis gas' from coal or coke is called "Coal gasification"

4.2.3 Lane's Process

This process involves the decomposition of steam by heated Fe (550 - 800°C). The reaction is known as “**gassing reaction**”.



4.2.4 From Hydrocarbons



4.3 Physical Properties of Dihydrogen

- (a) Colourless, odourless, tasteless gas
- (b) Sparingly soluble in water due to non-polar nature
- (c) Density is 0.09 gm/lit
- (d) B.P is 20.4 K
- (e) Pd metal can adsorb H_2 gas

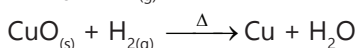
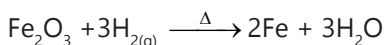
4.4 Chemical Properties of Dihydrogen

- (a) **Nature:** H_2 is neutral and so it does not affect litmus.
- (b) **Combustion:** H_2 is highly combustible and in presence of air, it burns with pale blue flame. It does not support combustion.

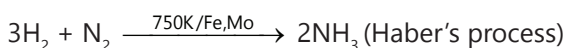


Reaction is highly exothermic and its calorific value is higher than other fuels.

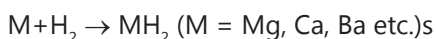
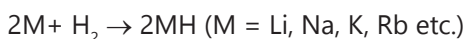
- (c) **Reducing action:** Dihydrogen reduces oxides of certain less electropositive metals (generally less electropositive than Zn and placed above H in ECS) like Fe, Pb, Cu etc. The product is metal, e.g.,



- (d) **Reaction with non-metals:** With non-metals, hydrogen forms covalent hydrides, e.g., $\text{H}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}_2\text{O}$



- (e) **Reaction with Metals:** Under suitable conditions, H_2 reacts with metals to form hydrides which are chiefly ionic. Alkali metals and alkaline earth metals (except Be) react with H_2 directly.



MASTERJEE CONCEPTS

Hydrogen is a diatomic gas having H—H bond. H—H bond is strongest known single bond (Bond energy = $435.9 \text{ kJ mol}^{-1}$) between two atoms of any element.

H_2 is not very reactive at normal temperature and pressure. This lack of reactivity is due to thermodynamics, not kinetics as it is related to bond strength. Since the H—H bond energy is very high it reacts at high temperature only and in the presence of catalysts which further lower the activation energy.

Nikhil Khandelwal (JEE 2009, AIR 94)

5. HEAVY HYDROGEN OR DEUTERIUM

5.1 Preparation of Deuterium

D_2 can be absorbed from H_2 by distillation, diffusion and other chemical properties. One notable method is adsorption of H_2 on charcoal leaving out D_2 .

5.2 Physical Properties

- (a) It is colourless, odourless, tasteless, water insoluble, diatomic gas.
- (b) Its physical constants like b.pt., m.pt., triple point etc. are higher than H_2 .
- (c) Being heavier than H_2 , it diffuses at less speed than H_2 .

5.3 Chemical Properties

D_2 resembles with H_2 , in its chemical properties, but reacts at a slower rate than H_2 , because its bond strength is greater than that of H_2 . There is marked isotope effect as mol. wt. of D_2 is twice to H_2 . Also, its adsorption on the surface of metals is also slower than H_2 .

6. WATER

6.1 Structure of Water

Molecule of water is V-shaped and its structure is given below: In water, the central oxygen atom is sp^3 hybridised. Out of four sp^3 hybrid orbitals, two form σ bond with s-orbital of H-atom while rest two are occupied by lone pairs of electrons. Due to lp-bp repulsion, the H—O—H bond angle is contracted to 104.5° . O—H bond length is 95.7 pm . Due to its V-shaped structure, H_2O is a polar molecule ($\mu = 1.84 \text{ D}$).

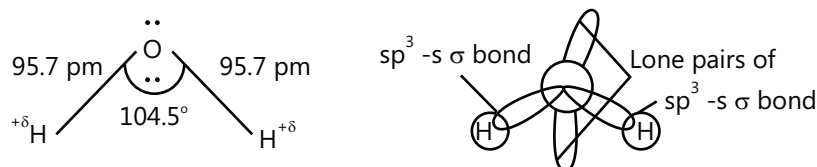


Figure 15.4: Water Molecule

6.2 Structure of Ice

In ice, each oxygen atom is bonded to 4 other oxygen atoms by hydrogen bonds as shown in Fig. This gives ice, an open framework. When ice melts, some hydrogen bonds are broken. The 'bridges' and the open framework collapse, causing water molecules to fall into the empty spaces.

This close packing of molecules allows the liquid to occupy a smaller volume than the ice, and the density increases.

6.3 Physical Properties of Water

Pure water is a colourless, odourless and tasteless liquid. It gives a bluish tinge in thick layers. Water has an abnormally high freezing point, boiling point, heat of vaporization, heat of fusion. Water has a high specific heat, surface tension and thermal conductivity than most other liquids. These properties are responsible for water to play a vital role in life processes. These unique properties of water are due to the presence of hydrogen bonding.

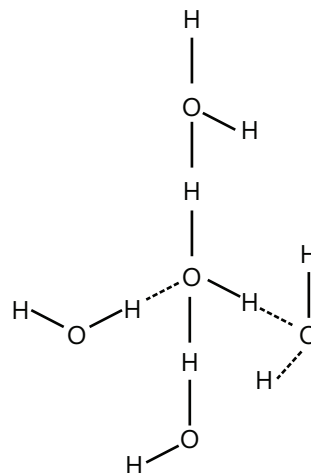
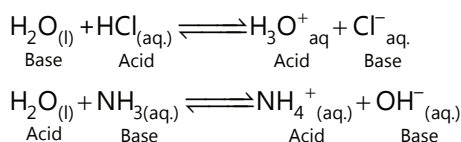


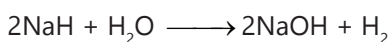
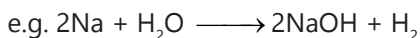
Figure 15.3: Structure of Ice

6.4 Chemical Properties of Water

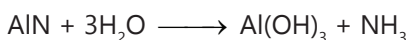
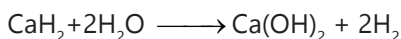
(a) **Acid-Base Nature:** Water acts as both an acid and a base, and is said to be amphoteric. Water acts as a base towards acids stronger than itself and as an acid in the presence of a base stronger than itself, as shown below:



(b) **Oxidation and Reduction:** Water acts both as an oxidizing as well as a reducing agent.



(c) **Hydrolytic Reaction:** Compounds like calcium hydride, aluminium nitride, calcium phosphide, calcium carbide, silicon halide etc. undergo hydrolysis with water.



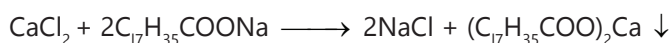
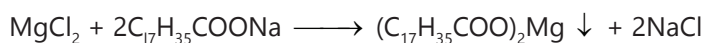
(d) **Hydrate Formation:** Water reacts with certain metal salts to form hydrates. In hydrated salts water may remain in 5 types:

(i) Co-ordinated water, (ii) Hydrogen bonded water, (iii) Lattice water, (iv) Zeolitic water, (v) Clathrate water.

6.5 Soft and Hard Water

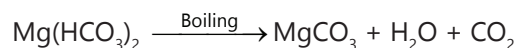
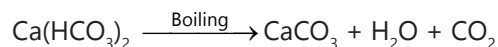
A sample of water which easily produces lather with soap is known as "Soft Water" while "hard water" doesn't produce lather with soap easily.

The soluble Ca^{+2} , Mg^{+2} or Fe^{+2} ions react with soap to give Ca or Mg soap which being insoluble in water get precipitated.

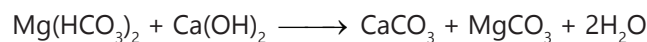
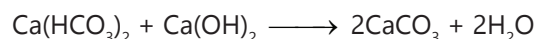


Hardness of Water and Removal

(a) Temporary hardness: It is due to the dissolution of bicarbonates of Ca and Mg in water. It can be removed by boiling.



It can also be done by adding lime

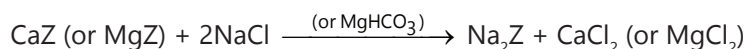
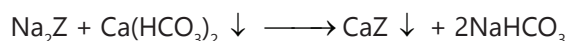


(b) Permanent Hardness and its Removal: Permanent hardness happens due to the dissolution of chloride and sulphates of Ca, Mg, Fe. It cannot be removed by boiling of water.

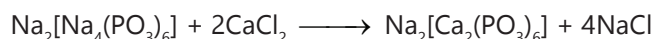
It can be removed by following

(i) Adding washing soda: $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{NaCl}$

(ii) Permutit Method: Permutit is an artificial zeolite. It is sodium aluminosilicates i.e. $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$. The hardness causing ions are retained by the bed and Na^+ ions from bed, form soluble salt like NaHCO_3 . To recharge the bed after complete exhaustion, it is treated with NaCl solution which regenerates the zeolite bed. This process removes both types of temporary and permanent hardness.



(iii) Calgon Process: Calgon which is also known as Graham's salt is the trade name of sodium hexametaphosphate $(\text{NaPO}_3)_6$. The Ca^{+2} and Mg^{+2} ions dissolved in hard water react with calgon to produce complex anions, which are very inactive and don't produce a ppt. with soap.



(iv) By Ion Exchange Resin: Resins are giant organic molecules attached with acidic or basic groups. Cation exchange resin contain $-\text{COOH}$ or $-\text{SO}_3\text{H}$ groups. These remove cations like Na^+ , Ca^{+2} , Mg^{+2} , Fe^{+2} etc by exchange with H^+ . Anion exchange resins contain $-\text{NH}_2$ group they are represented by $\text{RNH}_3^+ \text{OH}^-$. These resins remove negative ions such as Cl^- , SO_4^{-2} , NO_3^- etc.

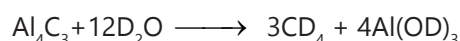
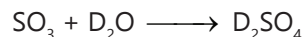
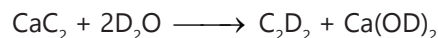
(c) Degree of Hardness: Degree of hardness is usually expressed in parts per million (ppm) and thus may be defined as the number of parts by weight of CaCO_3 (equivalent to calcium and magnesium salt) present in a million (10^6) parts by weight of water.

1 ppm = 1 part of CaCO_3 in 10^6 parts of water.

6.6 Heavy Water

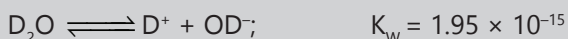
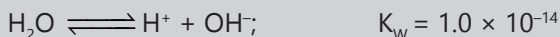
Heavy water is extensively used as a moderator in nuclear reactors and in exchange reactions for the study of reaction mechanisms. It can be prepared by exhaustive electrolysis of water or as a by-product in some fertilizer industries.

It is used for the preparation of other deuterium compounds, for example:



MASTERJEE CONCEPTS

The dissociation constant of D_2O is less than H_2O because O-D bond is stronger than O-H bond so it takes more energy to break O-D bond owing to more atomic mass of D than H which stabilises the bond by reducing the vibration of bonds.



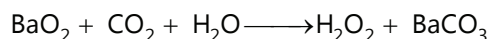
Use of Organic resins for softening the hard water is the best method because purification can be easily done so it is used commercially.

Saurabh Gupta (JEE 2010, AIR 443)

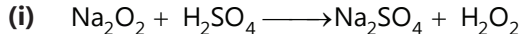
7. HYDROGEN PEROXIDE

7.1 Preparation of H_2O_2

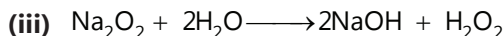
- (a) **Lab method of preparation of H_2O_2** – H_2O_2 obtained by passing a current of CO_2 through a cold pasty solution of BaO_2 in water.



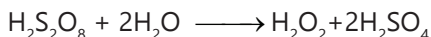
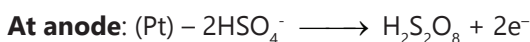
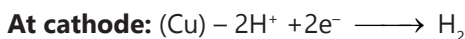
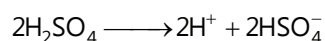
- (b) **Treating Na_2O_2 with $H_2SO_4^{-2}$**



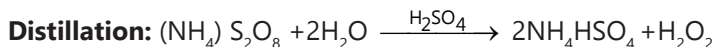
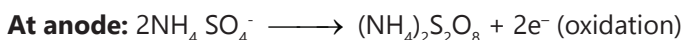
(ii) Also, by small amount of Na_2O_2 added to ice cold water.



- (c) **Industrial process:** By electrolysis of 50% H_2SO_4 at $0^\circ C$ using Pt electrode.

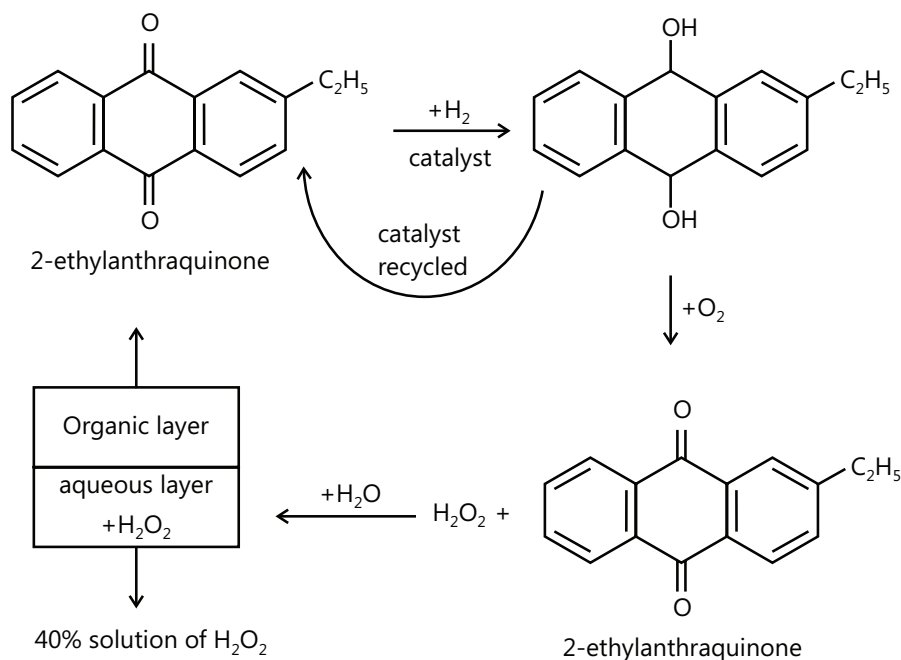


- (d) **Electrolysis of ammonium hydrogen sulphate:** In the electrolysis of ammonium hydrogen sulphate, ammonium per sulphate is formed. It is separated and distilled with dil. H_2SO_4 to give 30 - 40% H_2O_2 (aqueous solution)



- (e) **Auto - oxidation of 2-ethyl anthraquinone:** This is the most modern method and needs H_2 , atmospheric oxygen and water as the major raw materials.

First and foremost, 2-ethyl anthraquinone is catalytically reduced to 2-ethyl anthraquinol in organic solvent by H_2 and Pd (catalyst). Secondly, 2-ethyl anthraquinol is oxidised by air to 2-ethyl anthraquinone. H_2O_2 obtained in the process is extracted with water to give 20% H_2O_2 solution. 2-ethyl anthraquinone is thus reused. The process is repeated, thus it is a cyclic process.



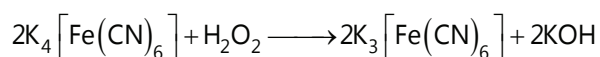
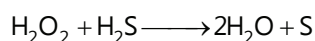
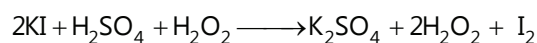
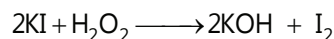
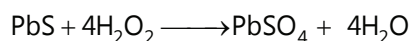
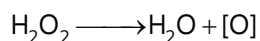
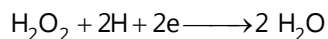
7.2 Physical Properties of H_2O_2

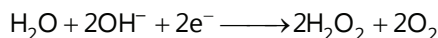
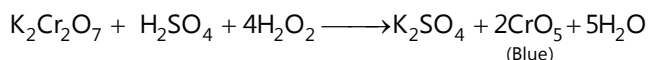
- (a) Pure H_2O_2 is weakly acidic in nature and exists as an associated liquid due to hydrogen bonding.
- (b) Smell of H_2O_2 resembles like nitric acid.
- (c) It causes blisters on skin.
- (d) Stored in plastic containers after addition of stabilizers.
- (e) A dilute solution of H_2O_2 is concentrated by vacuum distillation or by distillation under pressure.

7.3 Chemical Properties

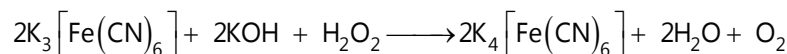
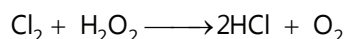
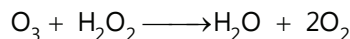
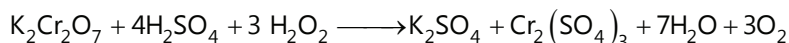
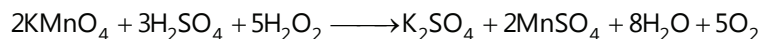
(a) Decomposition $2\text{H}_2\text{O}_2 \xrightarrow{\Delta} 2\text{H}_2\text{O} + \text{O}_2$; $\Delta H = -196\text{kJ}$

(b) Oxidising and reducing nature : H_2O_2 acts as a strong oxidising agent under acidic and alkaline conditions. Oxidation in the acidic medium is slow while rapid in an alkaline solution as H_2O_2 itself is a weak acid.



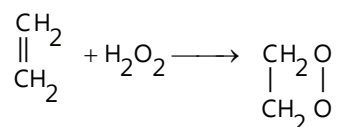


Reducing nature



- (c) **Bleaching action:** H_2O_2 acts as a bleaching agent due to its oxidising nature e.g., bleached human hair (black to golden brown), ivory, silk, wool, feather etc. $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + [\text{O}]$

(d) Addition properties



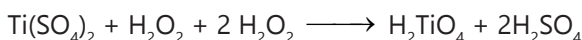
7.4 Uses of H_2O_2

Its wide scale use has led to the tremendous increase in the industrial production of H_2O_2 . Some of the uses are listed below:

- (a) In daily life, it is used as a hair bleach and as a mild disinfectant. As an antiseptic, it is sold in the market as perhydrol.
- (b) It is used to manufacture chemicals like sodium perborate and per-carbonate, which are used in high quality detergents.
- (c) It is used in the synthesis of hydroquinone, tartaric acid and certain food products and pharmaceuticals (cephalosporin) etc.
- (d) It is employed in the industries as a bleaching agent for textiles, paper pulp, leather, oils, fats, etc.
- (e) Nowadays, it is also used in Environmental (Green) Chemistry. For example, in pollution control treatment of domestic and industrial effluents, oxidation of cyanides, restoration of aerobic conditions to sewage wastes, etc.

7.5 Tests for H_2O_2

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



- (b) It liberates iodine from KI solution which gives a blue colour with starch solution
- (c) H_2O_2 on shaking with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ with little ether, blue colour is produced.

7.6 Structure of H_2O_2

All four atoms in H_2O_2 are non-planar. Structure of H_2O_2 has an open book structure having two leaves at 90° , the H-atoms are placed one on each core, the H—O making an angle of 101.5° with O—O bond.

Bond Angle: Dipole moment value of H_2O_2 suggests that all the four atoms in H_2O_2 do not lie in a plane, and the structure can be compared with a book open at angle 94° .

The H—O—O bond angle is 97° .

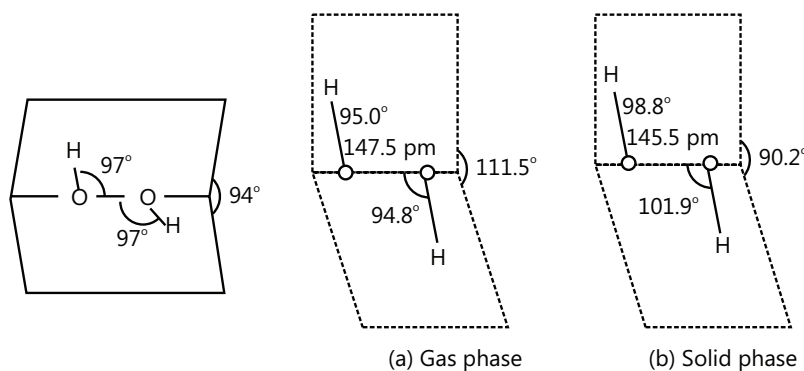


Figure 15.5: Structure of H_2O_2

7.7 Strength of H_2O_2

(a) **As percentage:** The strength of H_2O_2 is sometimes reported in percentage. Bottles containing H_2O_2 are labelled as 40%, 60%... etc. This means that 100 ml solution of H_2O_2 contains 40 g H_2O_2 .

(b) **As number volume:** The strength of hydrogen peroxide is often expressed in terms of the volume of oxygen evolved on heating. Bottles containing hydrogen peroxide are labelled as '10 Volume',

'20 Volume', '100 Volume' etc. This means that one volume of hydrogen peroxide solution gives so many volumes to oxygen (after complete decomposition) at N.T.P.

Thus 1 mL of '10 Volume' solution produces 10 mL of oxygen at N.T.P, 1,000 mL of a '10 Volume' solution produce 10,000 mL of oxygen at N.T.P, 1000 mL of a '20 Volume' solution produce 20,000 mL of oxygen at N.T.P. etc.

MASTERJEE CONCEPTS

- % strength = $\frac{17}{56} \times \text{volume strength}$
- Volume strength = $5.6 \times \text{normality}$
- Volume strength = $11.2 \times \text{molarity}$

H_2O_2 is a very unstable compound which can easily decompose in the presence of metallic impurities sometimes leading to explosions. To avoid this, stabilizers such as H_3PO_4 or glycerol are used to maintain the equilibrium backward.

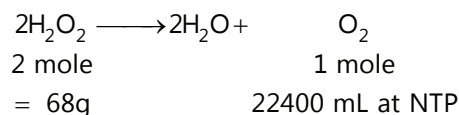
Neeraj Toshniwal (JEE 2009, AIR 21)

Illustration 1: (i) Convert 20 vol. H_2O_2 into % strength.

(ii) Convert 6.8% strength H_2O_2 into volume strength.

(JEE MAIN)

Sol: (i) 20 vol. H_2O_2 means 1 mL of H_2O_2 solution gives 20 mL O_2



\therefore 22400 mL O_2 is obtained by 68 g H_2O_2

\therefore 20 mL O_2 is obtained by $\frac{68 \times 20}{22400} = 0.0607$ g H_2O_2

or 1 mL H_2O_2 solution = 0.0607g H_2O_2

\therefore 100 mL H_2O_2 solution = 0.0607×100 g H_2O_2 = 6.07%

(ii) 6.8% strength H_2O_2 solution means 6.8 g H_2O_2 is present in 100 mL H_2O_2

\therefore 68 g H_2O_2 gives 22400 mL O_2 at NTP

\therefore 6.8g H_2O_2 gives $\frac{22400 \times 6.8}{68} = 2240$ mL O_2

\therefore Volume strength of H_2O_2 gives = $\frac{2240}{100} = 22.4$ Volume

8. HYDRIDES

Binary compounds of hydrogen with other elements, are generally called hydrides, but strictly speaking, this term should be applied to compounds of hydrogen with elements, which are less electronegative than hydrogen. They may be of MH_n or M_mH_n type.

8.1 Ionic Hydrides

- (a) They are hydrides of elements having low electronegativity (ranging between 0.9 to 1.2 usually). They are formed by alkali metals, alkaline earth metals (except Be and Mg) and some lanthanides.
- (b) In these hydrides, hydrogen accepts electrons from combining elements and exists as H^-
- (c) These hydrides can be prepared by heating ($\approx 1000 - 1100$ K) metals with hydrogen directly.

E.g. $2\text{Na} + \text{H}_2 \rightarrow 2\text{NaH}$

Some Important Chemical Properties

- (a) **Stability:** Ionic hydrides have quite high heats of formation and consequently high stability. On moving down in the group, the stability decreases which may be attributed to a poor overlap between the relatively smaller 1s orbital of hydrogen and larger s-orbital of heavier metals. $\text{LiH} > \text{NaH} > \text{KH} > \text{RbH} > \text{CsH}$
- (b) Gets hydrolyzed by giving alkali and H_2 gas.
- (c) At high temperatures, act as strong reducing agents.

8.2 Covalent Hydrides

- (a) These hydrides are formed mainly by p-block elements (except noble gases) and by some s-block elements like Be and Mg.
- (b) These hydrides usually consist of discrete covalent molecules held together by weak 'Vander Waals' forces and so these hydrides are usually volatile. The melting points and boiling points of covalent hydrides are low. Some of them are liquids or even solids in a few cases.
- (c) They do not conduct electricity and their general formula may be MHX (for s-block metals) or $\text{MH}(8-n)$ (for p-block elements), here n is the number of valence electrons. This generalization is not valid for the boron family.

Covalent hydrides can be electron deficient also such as DIBORANE B_2H_6 and other such bridge bond hydrides. They can be electron precise as well as electron rich such as CH_4 and NH_3 respectively.

8.3 Metallic / Interstitial Hydrides

(a) These hydrides are formed by d- and f-block metals, with electronegativity ranging from 1.2 to 1.4.

(b) These hydrides are usually non-stoichiometric (e.g. $TiH_{1.73}$, $LaH_{2.8}$ etc.) and these hydrides have properties similar to those of parent metals i.e. why they are called metallic hydrides.

In these hydrides, hydrogen occupies some interstitial sites in the metallic lattice i.e. why they are called interstitial hydrides. However it is not certain whether the interstitial hydrogen is present as H or H^+ with delocalised electrons.

8.4 Polymeric Hydrides and Complex Hydrides

(a) Polymeric hydrides are formed by elements having electro- negativity in the range 1.4 to 2.0. e.g., $(BeH_2)_n$, $(AlH_3)_n$, $(InH_3)_n$, $(SiH_4)_n$ etc.

(b) In complex hydrides H^- acts as a ligand and is attached to the central metal atom, e.g. $LiAlH_4$, $LiBH_4$, $NaBH_4$ etc.

8.5 Hydrogen Economy - Use of Hydrogen as a Fuel

Advantage: (i) H_2 is an environmentally clean fuel because it gives water on combustion. However, a small amount of nitrogen oxides may be formed due to high temperatures.

(ii) H_2 has the highest calorific value and it is a better fuel than any other fuel.

8.6 Fuel Cell

In a fuel cell, H_2 and O_2 combines with each other, where, H_2 is oxidised at anode, while, O_2 is reduced at cathode. The fuels (H_2 and O_2), do not react directly.

A fuel cell is represented in the fig.

The cell contains porous carbon electrodes impregnated with metal catalysts and an electrolyte consisting of hot aqueous KOH or molten Na_2CO_3 . The fuel (gaseous H_2) and the oxidising agent (gaseous O_2) do not react directly, but instead flow into separate cell compartments where H_2 is oxidised at the anode and O_2 is reduced at the cathode. The overall cell reaction is simply the conversion of hydrogen and oxygen to water.

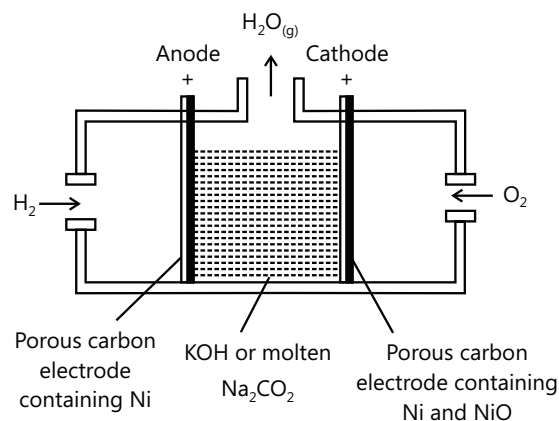
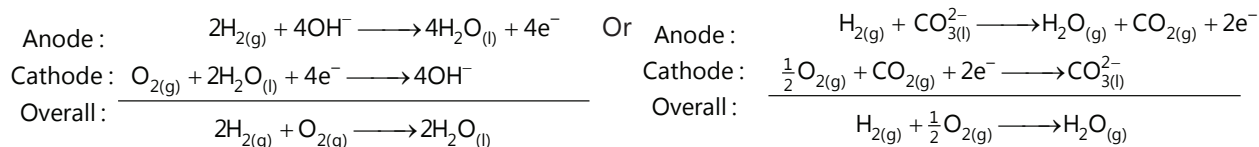


Figure 15.6: Fuel Cell



Fuel cells are very efficient and about 75% of bond energy is converted into electricity.

Disadvantages: No doubt, H_2 is the best alternative to fossil fuels, but the use of hydrogen as a fuel is very dangerous and needs attention. The storage of the mixture of H_2 and O_2 is very risky. In 1986, the space shuttle Challenger, an explosion occurred in the fuel tank containing H_2 and O_2 .

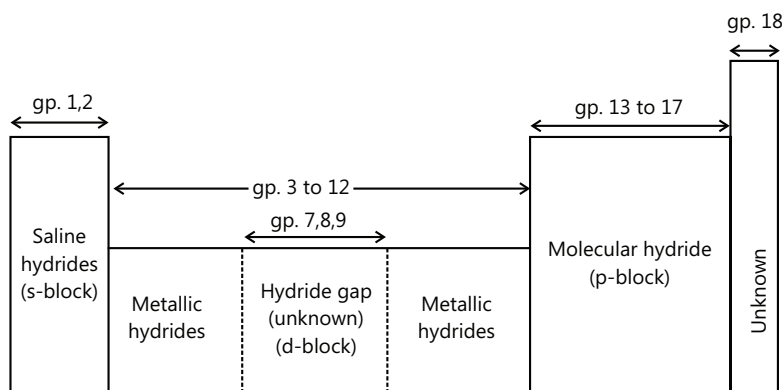


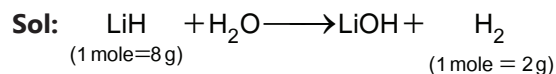
Figure 15.7: General classification of hydrides and some elements

MASTERJEE CONCEPTS

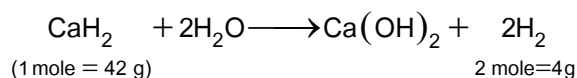
- The above table shows a general classification of hydrides and some elements form intermediate hydrides while hydrides of some others are unknown or unstable.
- The hydrolysis of hydrides with H_2O is highly exothermic and may be explosive as H_2 catches fire. This fire can't be extinguished by CO_2 as it gets reduced by a hot metal hydride. Here only sand must be used.

Aman Gour (JEE 2012, AIR 230)

Illustration 2: On reaction of equal masses of LiH and CaH_2 with water, which will give more H_2 ? **(JEE MAIN)**



8g LiH gives 2g H_2



$$\frac{42}{2} = 21 \text{ g CaH}_2 \text{ gives } 2 \text{ g H}_2$$

8g CaH_2 gives $\frac{2}{21} \times 8 = 0.762 \text{ g H}_2$

s-block elements

1. INTRODUCTION

The elements in which the last electron enters the outermost s-orbital, belong to the s-block of elements. As the s-orbital can accommodate only two electrons, two groups (1 & 2) belong to the s-block of the periodic table.

	I	II	<div>d-Block</div>										III	IV	V	VI	VII	VIII/0							
I	H																								
II	Li	Be																							
III	Na	Mg																							
IV	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr							
V	Rb	Sr	V	Zr	Nb	Mo	Tc	Ru	Th	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe							
VI	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Ti	Pb	Bi	Po	At	Rn							
VII	Fr	Ra	Ac	Unq	Unp	Unh	Uns	Uno	Une	Uun			<div>p-block</div>												
<div>s-block</div>																									

Figure 15.8: Position of s-block elements in the periodic table

Properties of s-block: Table Group 1 of the periodic table consists of the elements: lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr). Collectively known as the alkali metals, because they form hydroxides on reaction with water, which are strongly alkaline in nature. The elements of Group 2 include beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra). These elements with the exception of beryllium are commonly known as the alkaline earth metals. These are so called because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the earth's crust. The general electronic configuration of s- block elements is [noble gas] ns^1 for alkali metals and [noble gas] ns^2 for alkaline earth metals.

2. TRENDS IN PHYSICAL AND CHEMICAL PROPERTIES

2.1 Electronic Configuration

All alkali metals have one valence electron, ns^1 outside the noble gas core. The single valence electron is at a long distance from the nucleus and is held weakly. Hence, the loosely held s electrons in the outermost valence shell of these elements make them the most electropositive metals. They readily lose electrons to give monovalent M^+ ions. Hence, they are never found in the free state in nature. Alkaline earth metals have two electrons in the s-orbital of valence shell. The compounds of these elements are also predominantly ionic.

Table 15.1 : Electronic configuration of s-block elements

Element	Symbol	Electronic configuration
Lithium	Li	$1s^2 2s^2$
Sodium	Na	$1s^2 2s^2 2p^6 3s^1$
Potassium	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Rubidium	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$

Element	Symbol	Electronic configuration
Caesium	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$ $4p^6 4d^{10} 5s^2 5p^6 6s^1$ or [Xe] $6s^1$
Francium	Fr	[Rn] $7s^1$
Beryllium	Be	$1s^2 2s^2$
Magnesium	Mg	$1s^2 2s^2 2p^6 3s^2$
Calcium	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Strontium	Sr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$
Barium	Ba	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$ $4p^6 4d^{10} 5s^2 5p^6 6s^2$ or [Xe] $6s^2$
Radium	Ra	[Rn] $7s^2$

2.2 Atomic and Ionic Radii

The alkali metal atoms have the largest size in a particular period of the periodic table. The atomic and ionic radii of alkali metals increase down the group i.e., they increase in size while going from Li to Cs. Due to the increased nuclear charge in these elements, the atomic and ionic radii of the alkaline earth metals are smaller than those of the corresponding alkali metals in the same periods. Within the group, the atomic and ionic radii increase with the increase in atomic number due to the increase in number of atomic shells.

2.3 Ionization Enthalpy

The ionization enthalpies of the alkali metals are considerably low and decrease down the group from Li to Cs. This is because the effect of increasing size outweighs the increasing nuclear charge and the outermost electron is very well screened from the nuclear charge. The second ionization energy is extremely high because of the removal of the 2nd electron from a stable noble gas electron configuration of the monovalent metal cation. The alkaline earth metals have low ionization enthalpies due to the fairly large size of the atoms. Since the atomic size increases down the group, their ionization enthalpy decreases. Due to their small size as compared to the corresponding alkali metals, the first ionization enthalpy of the alkaline earth metals is higher than those of the corresponding Group 1 metals for the same period. The second ionization enthalpies of the alkaline earth metals are smaller than those of the corresponding alkali metals because for the alkali metals, the second electron is to be removed from an inert gas configuration.

Physical Properties: All alkali metals are silvery white, soft and light metals. This is due to having only one valence electron which participates in bonding. These elements have a low density which increases down the group from Li to Cs, because of their larger size. However, potassium is lighter than sodium because of its larger atomic volume. The melting and boiling points of the alkali metals are low, which indicate weak metallic bonding, due to the presence of only a single valence electron in them. The strength of the metallic bond decreases down the group, and the m.p. decreases accordingly. The m.p. of lithium is nearly twice as high as that of sodium because of the stronger metallic bonding on account of its smaller size. However, the m.p. of all the others are close together. The alkali metals and their salts impart a characteristic colour to oxidizing flames. This is because the heat from the flame excites the outermost orbital electron to a higher energy level. When the excited electrons come back to the ground state, there is an emission of radiation in the visible region as given below:

Table 15.2 (a) : Characteristic flame color of group 1 elements

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

When these elements are irradiated with light, the light energy absorbed may be sufficient to make an atom lose an electron. This property makes caesium and potassium useful as electrodes in photoelectric cells. The alkaline earth metals, in general, are silvery white, lustrous and relatively soft, but are however, harder than the alkali metals. Beryllium and magnesium appear to be somewhat greyish. The melting and boiling point of these metals are higher than alkali metals due to their smaller size and two valence electrons. Due to their low ionization enthalpies, they are strongly electropositive in nature. The electropositive character increases down the group from Be to Ba. Calcium, strontium and barium, all impart a characteristic colour to the flame.

Table 15.2 (b): characteristic flame color of group 2 elements

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

The electrons in beryllium and magnesium are too strongly bound to get excited by the flame. Hence, these elements do not impart any colour to the flame. Like alkali metals, the electrical and thermal conductivity of alkaline earth metals are high.

MASTERJEE CONCEPTS

Softness increases from Li to Cs due to weakening of interatomic attractions

Note: Trends of Melting and Boiling Points:

In case of Alkali Metals – $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs} > \text{Fr}$

In Case of alkaline earth metals – $\text{Be} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$

Note-Trends in case of heat of atomization:

In case of alkali metals – $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs} > \text{Fr}$

Not – In Case of density, following trend is observed:

The reason for this type of trend is:

Explanation: On moving down, both atomic mass and atomic volume increase, but increase in atomic volume can't compensate for the increase in atomic mass. An exceptionable is the lower density of K as compared to Na, which is due to the abnormal increase in the size of K.

Note: Trends of density in case of alkaline earth metals:

All are light metals, since the densities of alkaline earth metals decrease slightly from Be to Ca after which there is an increase.

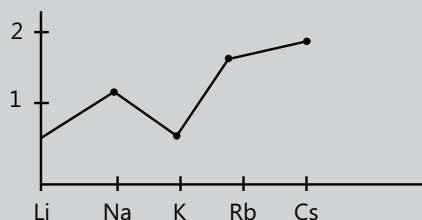


Figure 15.9: Density plot

Saurabh Gupta (JEE 2010, AIR 443)

2.4 Hydration Enthalpy

Hydration represents the dissolution of a substance in water by adsorbing a water molecule by weak valency forces.

Note: The hydration is an exothermic process, i.e., energy is released during hydration

MASTERJEE CONCEPTS

Smaller the cation, greater is the degree of hydration energy

$\text{Li}^{\oplus} > \text{Na}^{\oplus} > \text{K}^{\oplus} > \text{Rb}^{\oplus} > \text{Cs}^{\oplus}$

Saurabh Gupta (JEE 2010, AIR 443)

The hydration enthalpies of alkali metal ions, decrease with the increase in ionic sizes. Li^+ has a maximum degree of hydration and for these reasons lithium salts are mostly hydrated e.g., $\text{LiCl} \cdot 2\text{H}_2\text{O}$. Like alkali metal ions, hydration enthalpies of alkaline earth metal ions decrease with the increase in ionic size down the group.

The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Thus compounds of alkaline earth are more extensively hydrated than those of alkali metals, e.g., MgCl_2 and CaCl_2 exist as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ while NaCl and KCl do not form such hydrates.

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$$\text{Relative conducting power} \propto \frac{1}{\text{Relative hydrated}}$$

Neeraj Toshniwal (JEE 2009, AIR 21)

Therefore, the Trend of Relative Conducting Power in case of Alkali Metals Would be:



Note: The Trend in Case of Relative ionic radii is:



Reverses in Case of Relative Hydrated radii:



2.5 Standard Oxidation Potential and Reducing Properties in case of Alkali metals

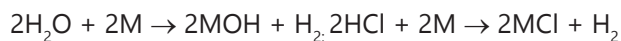
(a) Since alkali metals easily lose electrons, they have high values of oxidation potential accounting for the good reducing nature.

(b) Standard oxidation potentials are listed below:

	Li	Na	K	Rb	Cs
E°_{OP}	+3.05	+2.71	+2.93	+2.99	+2.99

(c) More the oxidation potential, more is the tendency, to get oxidized and thus more powerful is the reducing nature in an aqueous medium.

(d) Alkali metals liberate H_2 from H_2O and HCl



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From the ionization energy trend, we expect Li to have the lowest oxidation potential. But that is not so. The greatest reducing nature of Li in an aqueous medium is accounted for, due to the maximum hydration energy of the Li^{\oplus} ion.

Aman Gour (JEE 2012, AIR 230)

In case of Alkaline Earth Metals,

- (a) Standard oxidation potential $Ra > Ba > Sr > Ca > Mg > Be$
- (b) The reducing character increases from Be to Ba, due to the increasing order of the oxidation potential.

3. CHEMICAL PROPERTIES

Alkali metals are highly reactive due to their larger size and low ionization enthalpy. The reactivity of these metals increases down the group. The alkaline earth metals are less reactive than the alkali metals. The reactivity of these elements increases on going down the group.

Reasons for High Reactivity of Alkali Metals-

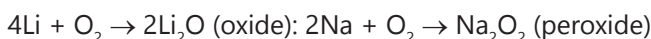
Alkali metals exhibit very high chemical reactivity, and the reasons for their high reactivity are:

- (a) Low IE,
- (b) Low heat of atomization
- (c) High heats of hydration

3.1 Reactivity towards Air and Water

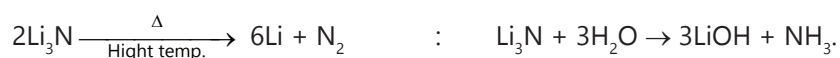
Alkali metals tarnish in dry air due to the formation of their oxides which in turn react with moisture to form hydroxides. They burn vigorously in oxygen, forming oxides.

Lithium forms a monoxide, sodium forms a peroxide, and the other metals form a superoxide. The superoxide O_2^- ion is stable only in the presence of larger cations such as K, Rb, Cs,

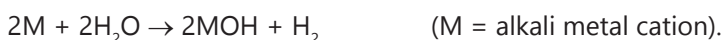


All five metals can be induced to form the normal oxides, peroxides or superoxides by dissolving the metal in liquid ammonia and bubbling in the appropriate amount of oxygen. Lithium shows exceptional behaviour in a reaction directly with nitrogen of air to form the nitride, Li_3N . Li_3N is ionic

($3Li^+$ and N^{3-}), and is ruby red.



The alkali metals react with water to form hydroxides and dihydrogen. The reaction becomes increasingly violent on descending the group. Although lithium has the most negative electrode potential (E^\ominus) value, its reaction with water is less vigorous than that of sodium which has the least negative electrode potential (E^\ominus) value among the alkali metals. This behaviour of lithium is attributed to its small size and very high hydration energy. Other metals of the group react explosively with water.



They also react with proton donors such as alcohol, gaseous ammonia and alkynes. This is because of their high reactivity towards air and water, the alkali metals are normally kept in kerosene oil. Beryllium and magnesium are inert to oxygen and water because of the formation of an oxide film on their surface. However, powdered beryllium burns brilliantly on ignition in air to give BeO and Be_3N_2 .

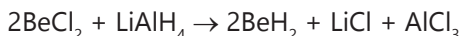
Magnesium is more electropositive and burns with a dazzling brilliance in air to give MgO and Mg_3N_2 .

Calcium, strontium and barium are readily attacked by air to form the oxide and nitride. They also react with water with increasing its reactivity.

3.2 Reactivity towards Dihydrogen

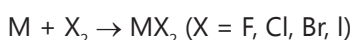
The alkali metals react with dihydrogen at about 673 K (lithium at 1073 K) to form hydrides. All the metal hydrides are ionic solids with high melting points.

All alkaline earth metals except beryllium combine with hydrogen upon heating to form their hydrides, MH_2 , which are also high melting solids. BeH_2 however, can be prepared by the reaction of $BeCl_2$ with $LiAlH_4$.



3.3 Reactivity towards Halogens

Reactivity towards halogens: The alkali metals readily react vigorously with halogens to form ionic halides, MX . However, lithium halides are somewhat covalent. This is because of the high polarization capability of the lithium ion. The Li^+ ion is very small in size and has a high tendency to distort electron clouds around the negative halide ion. Since anion with larger sizes can be easily distorted, among halides lithium iodide is the most covalent in nature. All the alkaline earth metals combine with halogens at elevated temperatures forming their halides.



3.4 Reducing Nature

Alkali metals, are strong reducing agents, lithium being the most and sodium the least powerful with the small size of its ion, lithium has the highest hydration enthalpy which accounts for its high negative E° value and its high reducing power. Like alkali metals, the alkaline earth metals are strong reducing agents. This is indicated by the large negative value of their reduction potentials. Beryllium has a less negative value compared to other alkaline earth metals, due to a relatively large value of the atomization enthalpy of the metal. However, its reducing nature is due to a large hydration energy associated with the small size of Be^{2+} ion.

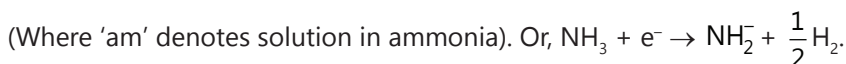
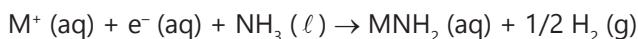
3.5 Solution in Liquid Ammonia

The alkali metals dissolve in liquid ammonia giving deep blue solutions.

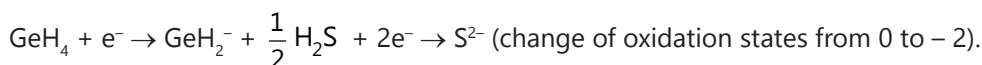


In dilute solutions, the main species are metal ions (M^+) and electrons, which are solvated (i.e. ammoniated). The blue colour, corresponding to a broad absorption band near 1500 nm that falls into the visible range, is attributed to the solvated electron.

The blue solution of alkali metals in liquid ammonia, decompose very slowly with the liberation of hydrogen (i.e., reduction of the solvent).



Decomposition is accelerated by the presence of many transition metal compounds, e.g., by stirring the solution with a rusty iron wire. The solution of metals in liquid ammonia act as powerful reducing agents (it even reduces the aromatic ring).



Like alkali metals, the alkaline earth metals, except beryllium, dissolve in liquid ammonia to give a deep blue-black solution forming ammoniated ions. The colour is due to the spectrum from solvated electrons.



These solution decompose very slowly forming amides but the reaction is accelerated by many transition metals and their compounds. $2\text{NH}_3 + 2\text{e}^- \rightarrow 2\text{NH}_2^- + \text{H}_2$

Evaporation of ammonia from the solution of alkali metals yields the metal, but with alkaline earth metals evaporation of ammonia gives hexammoniates of the metals, $[\text{M}(\text{NH}_3)_6]^{2+}$. These slowly decompose to give amides. $\text{M}(\text{NH}_2)_3 \rightarrow \text{M}(\text{NH}_2)_3 + 4\text{NH}_2 + \text{H}$

Illustration 1: The correct order of size of the ions is:

(JEE MAIN)

- (A) $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$ (B) $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$
(C) $\text{Cs}^+ > \text{Na}^+ > \text{K}^+ > \text{Li}^+$ (D) $\text{Cs}^+ > \text{Li}^+ > \text{Na}^+ > \text{K}^+$

Sol: Down the group, the size of ions increases because of the increase in the number of atomic shells.

The increase in the number of atomic shells over weighs the increase in effective nuclear charge.

Therefore (B) option is correct.

Illustration 2: Which of the following has the highest hydration enthalpy in an aqueous solution?

- (A) Na^+ (B) Be^{2+} (C) Ba^{2+} (D) Cs^+

(JEE MAIN)

Sol: The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions on earth metal ions decrease with increase in ionic size down the group.

$\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$. Therefore (B) option is correct.

Illustration 3: Which one the following metals is most commonly used in photoelectric cells?

- (A) Li (B) Ca (C) Cs (D) Fr

(JEE ADVANCED)

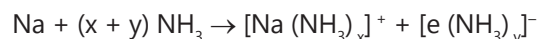
Sol: The ionization enthalpies of the alkali metals are considerably low and decrease down the group from Li to Cs. This is because the effect increasing size outweighs the increasing nuclear charge, and the outermost electrons are very well screened from the nuclear charge. When alkali metals are irradiated with light, the light energy absorbed may be sufficient to make an atom lose an electron. This property make caesium and potassium useful as electrodes in photoelectric cells. Therefore (c) option is correct.

Illustration 4: A blue coloured solution of sodium in liquid ammonia at -33°C behaves as strong reducing agent because of:

(JEE ADVANCED)

- (A) The formation of ammoniated sodium (B) The formation of ammoniated electron
(C) The formation of sodium amide (D) The formation of sodium nitride

Sol: The solution of metals in liquid ammonia act as powerful reducing agents (it even reduces the aromatic ring) because of ammoniated electron,



E.g., $\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^-$; $\text{O}_2 + 2\text{e}^- \rightarrow \text{O}_2^{2-}$ (change of oxidation states from 0 to -1),

$[\text{Ni}(\text{CN})_4]^{2-} + 2\text{e}^- \rightarrow [\text{Ni}(\text{CN})_4]^{4-}$ (change of oxidation states from $+II$ to 0).

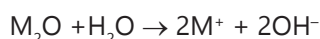
4. GENERAL CHARACTERISTICS OF THE COMPOUNDS OF THE ALKALI METALS AND ALKALINE EARTH METALS

Compounds of the alkali metals are generally ionic in nature. On combustion, in the excess of air, alkali metals form different type of oxides as given in the following table:

Table 15.3: Principal Combustion Product (Minor Product)

Alkali Metal	Oxide	Peroxide	Superoxide
Li	Li_2O	(Li_2O_2)	
Na	(Na_2O)	Na_2O_2	
K			KO_2
Rb			RbO_2
Cs			CsO_2

The increasing stability of the peroxide or superoxide, as the size of the metal ion increases, is due to the stabilization of large anions by larger cations through lattice energy effects, these oxides are easily hydrolyzed by water to form hydroxides according to the following reactions:



The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange in colour. LiO_2 and NaO_2 are yellow. KO_2 and CsO_2 are orange whereas RbO_2 is brown in colour. The superoxides are also paramagnetic. The hydroxides are all white crystalline solids. The alkali metal hydroxides are the strongest of all bases and dissolve freely in water with the evolution of much heat on the account of intense hydration. The melting and boiling points of alkali metal halides always follow the trend: fluoride > chloride > bromide > iodide. All alkali metal halides are generally soluble in water. The low solubility of LiF in water is due to its high lattice enthalpy whereas the low solubility of Cs is due to the smaller hydration enthalpy of its two ions. Other halides of lithium are soluble in ethanol. Acetone and ethyl acetate; LiCl is soluble in pyridine also.

The alkali metals form salts with all the oxo-acids. The thermal stability of oxy-acid salts generally increases down the group with increasing metallic character, i.e. electropositive character. They are generally soluble in water and thermally stable. Their carbonates (M_2CO_3) and in most cases the hydrogencarbonates (MHCO_3) also are highly stable to heat. As the electropositive character increases down the group, the stability of the carbonate and hydrogencarbonates increases.

Group 1 metals are so strongly basic, that they (except lithium) also form solid bicarbonates. No other metals form solid bicarbonates. Lithium carbonate is not so stable to heat. Its hydrogencarbonates do not exist as solids. Although NH_4HCO_3 also exists as a solid. 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 and (b) in KHCO_3 , HCO_3^- forms a dimeric anion.

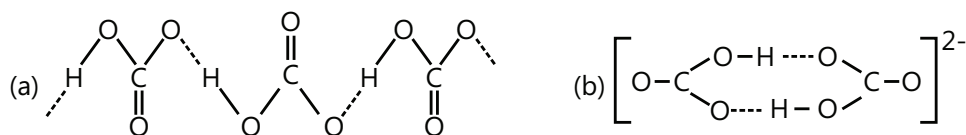
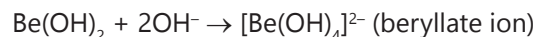


Figure 15.10: Hydrogen Bonding in NaHCO_3 and KHCO_3

The solubility of the alkali metal salts except fluorides, carbonates and hydroxides decreases down the group from Li to Cs . This is because of the fact that down the group with the increasing size of the cation the lattice energy as well as hydration energy also decrease but the change in hydration energy is more as compared to that of lattice

energy. The alkaline earth metals form compounds which are predominantly ionic but less ionic than the alkali earth metals, which forms compounds of alkali metals. This is due to an increased nuclear charge and smaller size. The oxide and other compounds of beryllium and magnesium are more covalent than those formed by the heavier and large sized member (Ca, Sr, Ba). The alkaline earth metals burn in oxygen to form the monoxide, MO which, except for BeO has a rock-salt structure. The BeO is essentially covalent in nature. The enthalpies of formation of these oxides are quite high and consequently they are very stable to heat. BeO is amphoteric while oxides of other elements are ionic in nature. All these oxides except BeO are basic in nature and react with water to form sparingly soluble hydroxides. $\text{MO} + \text{H}_2\text{O} \rightarrow \text{M}(\text{OH})_2$. The solubility, thermal stability and the basic character of these hydroxides increases with the increasing atomic number from $\text{Mg}(\text{OH})_2$ to $\text{Ba}(\text{OH})_2$. The alkaline earth metal hydroxides are however, less basic and less stable than alkali metal hydroxides. Beryllium hydroxide is amphoteric in nature as it reacts with acid and alkali both.



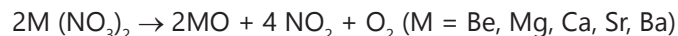
The anhydrous halides of alkaline earth metals are polymeric. Except for beryllium halides, all other halides of alkaline earth metal are ionic in nature. Beryllium halides are essentially covalent and soluble in organic solvents. Beryllium chloride vapours contains BeCl_2 and $(\text{BeCl}_2)_2$ but the solid is polymerized. Beryllium chloride in the solid state has a chain structure as shown below:



Figure 15.11: Beryllium chloride in solid state

In the vapour phase BeCl_2 tends to form a chloro-bridged dimer which dissociates into the linear monomer at a high temperature of the order of 1200 K. The tendency to form halide hydrates gradually decreases (for example, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) 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. The fluorides are relatively less soluble than the chlorides owing to their high lattice energies. Carbonate of alkaline earth metals are insoluble in water and can be precipitated by the addition of a sodium or ammonium carbonate solution to a solution of a soluble salt of these metals. The solubility of carbonates in water decreases as the atomic number of the metal ion increases. All carbonates decompose on heating to give carbon dioxide and the oxide. Beryllium carbonate is unstable and can be kept only in the atmosphere of CO_2 . The thermal stability increases with increasing cationic size. The sulphates of the alkaline earth metals are all white solids and are 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.

The nitrates are made by the dissolution of the carbonate in dilute nitric acid, magnesium nitrate crystallizes with six molecules of water, whereas barium nitrate crystallizes as the anhydrous salt. This again shows a decreasing tendency to form hydrates with increasing size and decreasing hydration enthalpy. All of them decompose on heating to give an oxide like lithium nitrate.



The solubility of the alkaline earth metal salts except hydroxides and fluorides decreases down the group from Be to Ba. This is because of the fact that down the group with the increasing size of the cation, the lattice energy as well as hydration energy also decreases, but the change in hydration energy is more as compare to that of lattice energy. Except BeF_2 all other fluorides are water insoluble. The solubility of beryllium fluoride in water is due to higher solvation energy on account of the higher polarizing power of Be^{2+} . The thermal stability of oxy-acid salts of alkaline earth metals generally increases down the group with increasing metallic character, i.e. electropositive character.

MASTERJEE CONCEPTS

Low thermal stability of Li_2CO_3 can be explained as follows:

The small Li^+ ion exerts a strong polarizing action and distorts the electron cloud of nearby oxygen atom of the large CO_3^{2-} ion. This results in the weakening of C–O bond and strengthening of Li–O bond, favouring the formation of Li_2O and CO_2 . High lattice energy of Li_2O than Li_2CO_3 also favours the decomposition of Li_2CO_3 .

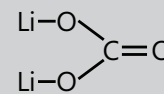


Figure 15.10:
 Li_2CO_3 molecule

B Rajiv Reddy (JEE 2012, AIR 11)

Illustration 5: Select the correct set of statements.

(JEE ADVANCED)

- (i) Solubility of alkali hydroxides is in order, $\text{CsOH} > \text{RbOH} > \text{KOH} > \text{NaOH} > \text{LiOH}$
- (ii) Solubility of alkali carbonates is in order, $\text{Li}_2\text{CO}_3 > \text{Na}_2\text{CO}_3 > \text{K}_2\text{CO}_3 > \text{Rb}_2\text{CO}_3 > \text{Cs}_2\text{CO}_3$
- (iii) Hydrated radii is in order, $\text{Li} < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$
- (iv) Stability of peroxides is in order, $\text{Na}_2\text{O}_2 < \text{K}_2\text{O}_2 < \text{Rb}_2\text{O}_2 < \text{Cs}_2\text{O}_2$

The options are: (A) (i), (iv) (B) (i), (iii) (C) (ii), (iii), (iv) (D) All

Sol: Compare the lattice energy and the hydration energy of the cations.

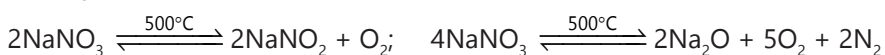
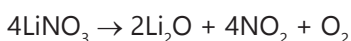
(i) While going from lithium to cesium hydroxide, the decrease in lattice energy is more as compared to that of hydration energy. So, the solubility of hydroxides increases down the group (iv). This is because of fact that the bigger cation stabilizes the bigger anion through crystal lattice energy. Therefore (A) option is correct.

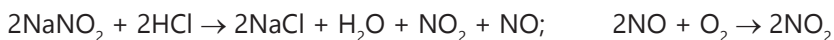
5. ANOMALOUS PROPERTIES OF LITHIUM

The anomalous behaviour of lithium is due to the: (i) exceptionally small size of its atom and ion, and (ii) high polarizing power (i.e., charge/radius ratio). As a result, there is an increased covalent character of lithium compounds, which is responsible for their solubility in an organic solvent. Further, lithium shows a diagonal relationship to magnesium.

Points of difference between lithium and other alkali metals

- (a) Lithium is much harder. Its melting point and boiling point are higher than the other alkali metals.
- (b) Lithium is the least reactive but the strongest reducing agent among all the alkali metals. On combustion in air it forms mainly monoxide, Li_2O and the nitride, Li_3N unlike other alkali metals.
- (c) The lithium ion itself, and also its compounds are more heavily hydrated than those of the rest of the group. LiCl is deliquescent and crystallizes as a hydrate, $\text{LiCl} \cdot 2\text{H}_2\text{O}$ whereas other alkali metal chlorides do not form hydrates.
- (d) Lithium hydrogencarbonates is not obtained in the solid form while all other elements form solid hydrogencarbonates.
- (e) Lithium unlike other alkali metal forms no ethynide on reaction with ethyne.
- (f) Lithium nitrate when heated gives lithium oxide, Li_2O , whereas other alkali metal nitrates decompose to give the corresponding nitrite.





- (g) LiF and Li₂O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.
- (h) Lithium hydroxide is less basic than the other hydroxides in the group and therefore, many of its salts are less stable, Li₂CO₃, LiNO₃ and LiOH all form the oxides on gentle heating; the analogous compounds of the rest of the group are stable. Another example of its less basic nature is that though lithium forms a bicarbonates in solution, it does not form a solid bicarbonate, whereas the other all form stable solid carbonates.
- (i) Lithium reacts directly with carbon to form anionic carbide. None of the other group 1 elements do this, but group 2 elements all react similarly with carbon.
- (j) Lithium has a great tendency to form complexes than have the heavier elements, and ammoniated salts such as [Li(NH₃)₄]⁺ exist as solids.

Illustration 6: Which of the following alkali metal ions has the lowest mobility in aqueous solution?

- (A) Li⁺ (B) Na⁺ (C) K⁺ (D) Cs⁺ **(JEE ADVANCED)**

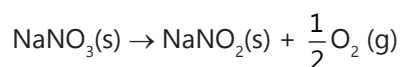
Sol: Mobility depends upon the cationic size and the tendency of the cation to get hydrated. Because Li⁺ has the smallest size, so it is highly hydrated and its effective size becomes larger therefore mobility decreases in aqueous medium.

Therefore (A) option is correct.

Illustration 7: Give the reaction of the thermal decomposition of the nitrate of sodium. Explain the occurrence of the reaction in term of energy factor. What is the pH expected of an aqueous solution of NaNO₃. Why?

(JEE ADVANCED)

Sol: The occurrence of the reaction depends upon the stability of the reactant and the products formed pH depends upon the hydrolysis extent.



Since the size of NO₂⁻ is less than that of NO₃⁻, this results in the formation of a more stable ionic lattice when bonded to a sodium ion. The pH of solution would be about 7 since neither the cation nor the anion undergoes hydrolysis to any appreciable extent.

6. 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, Mg²⁺ = 72 pm. The main points of similarity are:

- (a) Both lithium and magnesium are harder and lighter than other elements in their respective groups.
- (b) Lithium and magnesium react slowly with water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride, Li₃N and Mg₃N₂, by a direct combination with nitrogen.
- (c) The oxides, Li₂O and MgO do not combine with excess oxygen to give any superoxide.
- (d) The carbonates of lithium and magnesium decompose easily on heating to form the oxides and CO₂. Solid hydrogencarbonates are not formed by lithium and magnesium.
- (e) Both LiCl and MgCl₂ are soluble in ethanol.
- (f) Both LiCl and MgCl₂ are deliquescent and crystallize from aqueous solution as hydrates, LiCl.2H₂O and MgCl₂.6H₂O.

Illustration 8: About alkali metal-liquid NH_3 solution which of following statement is not true?

- (A) Blue colour is due to ammoniated electrons. **(JEE ADVANCED)**
 (B) Blue colour changes to bronze on dilution due to formation of metal ion clusters.
 (C) With an increase in concentration of alkali metals paramagnetic nature decreases due to electron-electron combination.
 (D) On heating, the blue colour becomes colourless due to the formation of a metal amide and H_2 gas.

Sol: The change depicts the formation of some complex structures.

Blue colour changes to bronze with increase in concentration of alkali metal due to formation of metal ion clusters. Therefore (B) option is correct.

Illustration 9: (A) Give the three different crystal structures of NaO_2 ?

(JEE ADVANCED)

- (B) Sodium sulphide is readily oxidized by air to form sodium thiosulphate. Write the chemical reaction only.
 (C) Group 1 sulphides hydrolyze appreciably in water, giving strongly alkaline solutions. Explain?

Sol: Sodium, the alkali metal has been discussed over here, which is a highly reactive metal and forms sodium thiosulphate in its sulphide form.

(A) NaO_2 exists in following three different crystal structures at different temperatures.

- (i) Marcasite structure at -50°C ,
 (ii) Pyrite structure between -77°C and -50°C ,
 (iii) Calcium carbide structure at room temperature.

(B) $2\text{Na}_2\text{S} + 2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaOH}$

(C) Na_2S hydrolyses in water according to the following reaction. $2\text{Na}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{NaSH} + \text{NaOH}$

Illustration 10: The properties of Li are similar to those of Mg. This is because.

(JEE ADVANCED)

- (A) Both have nearly the same size (B) The ratio of their charge to size is nearly the same.
 (C) Both have similar electronic configurations. (D) Both are found together in nature

Sol: We discuss about the diagonal relation of the alkali and the alkaline earth metals over here, wherein similarities are pointed out.

They are diagonally related because of same polarizing power, polarizing power = charge on cation / size of cation. Therefore. (B) Option is correct.

Illustration 11: Magnesium burns in air to give:

(JEE ADVANCED)

- (A) MgO (B) Mg_3N_2 (C) MgCO_3 (D) MgO and Mg_3N_2 both

Sol: Magnesium

Mg burns in air to form both MgO and Mg_3N_2

$2\text{Mg} + \text{O}_2 \xrightarrow{\Delta} 2\text{MgO}$; $3\text{Mg} + \text{N}_2 \xrightarrow{\Delta} \text{Mg}_3\text{N}_2$ Therefore, (D) option is correct.

7. ANOMALOUS BEHAVIOUR OF BERYLLIUM

Beryllium, the first member of the Group 2 metals, shows anomalous behaviour as compared to magnesium and rest of the members of the group. Further, it shows a diagonal relationship to aluminium.

- Beryllium has an exceptionally small atomic and ionic size and thus does not compare well with other members of the group. Because of the high ionization enthalpy and small size it forms compound, which is largely covalent and gets easily hydrolyzed.
- Beryllium does not exhibit a coordination number more than four as in its valence shell there are only four orbitals. The remaining members of the group can have a coordination number of six by making use of d-orbitals.
- The oxide and hydroxide of beryllium, unlike the hydroxides of other elements in the group, are amphoteric in nature.
- Beryllium hydride is electron deficient and polymeric, with multi-center bonding like aluminium hydride.
- The most unusual oxygen containing complexes of Be have the formula $\text{Be}_4\text{O}(\text{O}_2\text{CR})_6$ and are formed by refluxing $\text{Be}(\text{OH})_2$ with carboxylic acids. These white crystalline compounds are soluble in non-polar organic solvents, such as alkanes, but are insoluble in water and lower alcohols. In a solution, the compounds are unionized and monomeric.

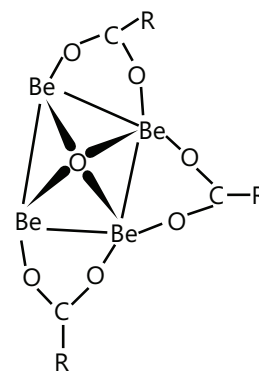


Figure 15.12: Complexes of Be

The central oxygen atom is tetrahedral surrounded by the four Be atoms and each Be atom is tetrahedrally surrounded by four oxygen atoms. The six acetate groups are arranged along the six edges of the tetrahedral ion.

Diagonal relationship between beryllium and aluminium

The ionic radius of Be^{2+} is estimated to be 31 pm; the charge/radius ratio is nearly the same as that of the Al^{3+} ion. Hence beryllium resembles aluminium in some ways. Some of the similarities are:

- Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal, i.e. they are rendered passive by nitric acid.
- Beryllium hydroxide dissolves in excess of alkali to give a beryllate ion, $[\text{Be}(\text{OH})_4]^{2-}$ just as aluminium hydroxide gives the aluminate ion, $[\text{Al}(\text{OH})_4]^-$.
- The chlorides of both beryllium and aluminium have Cl^- bridged chloride structure in the vapour phase.
- Both the chlorides are soluble in organic solvents and are strong Lewis acids. They are used as Friedel Craft catalysts.
- Beryllium and aluminium ions have a strong tendency to form complexes, BeF_4^{2-} and AlF_6^{3-} respectively.

8. COMPOUNDS OF ALKALI METALS

8.1 Sodium Oxide (Na_2O)

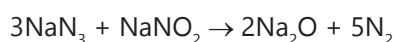
Preparation:

- By reduction of nitrites and nitrates of sodium with metallic sodium:



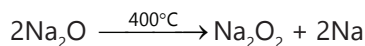
- By heating sodium in limited supply of air at 180°C : $\text{Na} + \text{O}_2 \rightarrow \text{Na}_2\text{O}$

- Pure sodium oxide is formed when the mixture of sodium azide and sodium nitrite is heated



Properties:

- (a) It is a white amorphous substance. It reacts with water violently forming sodium hydroxide and evolving a large amount of heat energy $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$
- (b) On heating at 400°C , it decomposes forming sodium peroxide and metallic sodium vapour.



- (c) Reaction with liquid ammonia; $\text{Na}_2\text{O} + \text{NH}_3 \rightarrow \text{NaNH}_2 + \text{NaOH}$

Use: It is used as a dehydrating and polymerizing agent in organic chemistry.

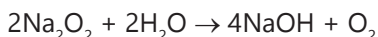
8.1 Sodium Peroxide (Na_2O_2)**Preparation:**

- (a) It is formed by heating sodium in an excess of air, free from moisture and carbon dioxide or in excess of pure oxygen. $2\text{Na} + \text{O}_2 (\text{excess}) \xrightarrow{350^\circ\text{C}} \text{Na}_2\text{O}_2$

- (b) **Industrial method:** It is a two stage reaction in the presence of excess air.

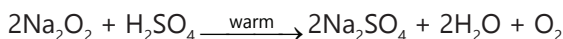
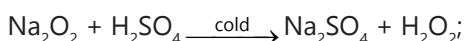
**Properties:**

- (a) 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.



- (b) **Action of water:** $\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{cold}} 2\text{NaOH} + \text{H}_2\text{O}_2$; $2\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{warm}} 4\text{NaOH} + \text{O}_2$

- (c) **Action of acid:**

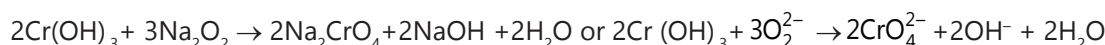


- (d) **Reaction with CO and CO_2 :** $\text{Na}_2\text{O}_2 + \text{CO} \rightarrow \text{Na}_2\text{CO}_3$; $2\text{Na}_2\text{O}_2 + 2\text{CO}_2 \rightarrow 2\text{Na}_2\text{CO}_3 + \text{O}_2$

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

- (e) 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.

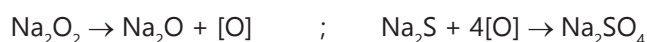
- (i) Chromic compounds are oxidized to chromates



- (ii) Manganous salt is oxidized to sodium manganate.

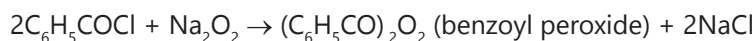


- (iii) Sulphides are oxidized to corresponding sulphates

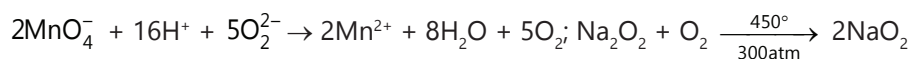


- (iv) $\text{Na}_2\text{O}_2 \rightarrow \text{Na}_2\text{O} + [\text{O}] \quad ; \quad 2\text{Al} + 3[\text{O}] \rightarrow \text{Al}_2\text{O}_3$

(v) Benzoyl peroxide (bleaching agent) is formed when $\text{C}_6\text{H}_5\text{COCl}$ reacts with Na_2O_2 .



(vi) Reduces stronger oxidizing agent such as acidified KMnO_4



Use:

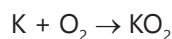
(a) Used for the production of oxygen under the name ozone.

(b) It is used as a bleaching agent for bleaching wood pulp, paper and fabrics such as cotton and linen.

8.3 Potassium Superoxide (KO_2)

Preparation:

(a) It is prepared by burning potassium in the excess of oxygen free from moisture.



Properties:

(a) It is an orange coloured (chrome yellow) powder and reacts with water according to following reaction.
 $2\text{KO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{KOH} + \text{H}_2\text{O}_2 + \text{O}_2$

(b) It reacts directly with CO and CO_2 . $2\text{KO}_2 + \text{CO} \rightarrow \text{K}_2\text{CO}_3 + \text{O}_2$; $2\text{KO}_2 + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3 + \frac{3}{2}\text{O}_2$

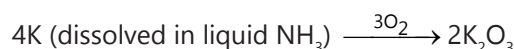
If more CO_2 in presence of moisture is present; then $4\text{KO}_2 + 4\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{KHCO}_3 + 3\text{O}_2$

(c) On heating with sulphur, it forms potassium sulphate; $2\text{KO}_2 + \text{S} \rightarrow \text{K}_2\text{SO}_4$

Use: It is used as an oxidizing agent and air purifier in space capsules, submarine and Breathing mask as it produces O_2 and removes CO_2 .

8.4 Potassium Sesquioxide (K_2O_3)

It is obtained when oxygen is passed through liquid ammonia containing potassium.



8.5 Sodium Hydroxide or Caustic Soda (NaOH)

Preparation: It is most conveniently manufactured by one of the following processes,

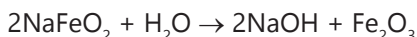
(a) Methods involving sodium carbonate as a starting material:

(i) **Gossage process** (causticising process): $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 \rightleftharpoons \text{CaCO}_3 + 2\text{NaOH}$

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.

(ii) **Lowig's process:** $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3 \xrightarrow{\text{red heat}} 2\text{NaFeO}_2 + \text{CO}_2$

The sodium ferrite is cooled and thrown into hot water, the hydrolysis of sodium ferrite occurs forming NaOH .



(iii) Methods involving sodium chloride as starting material: Electrolysis of sodium chloride solution occurs according to following principle.



On passing electricity, Na^+ and H^+ ions move towards cathode and Cl^- and OH^- ions move towards the 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 the anode. It is necessary that chlorine should not come in contact with sodium hydroxide during electrolysis, otherwise the following reaction will take place. $2\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaCl} + \text{NaClO} + \text{H}_2\text{O}$

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.

- (a) **The mercury cathode cell (Castner-Kellner cell):** In this cell mercury flows along the bottom of the cell and is a made cathode. The brine solution flows in the same direction and the anode consists of a number of graphite blocks. The brine is electrolyzed and since, hydrogen has a high overvoltage at the mercury cathode, sodium is preferentially discharged forming an amalgam with mercury.

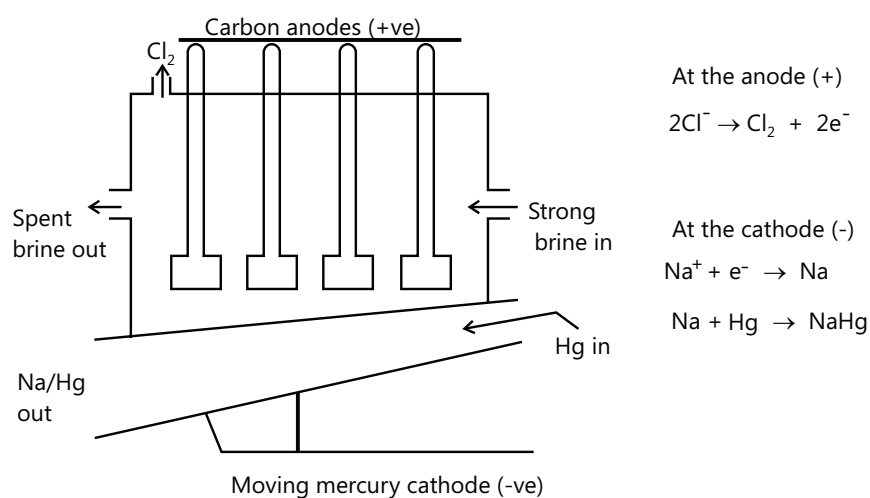


Figure 15.13 (a): Castner-Kellner cell

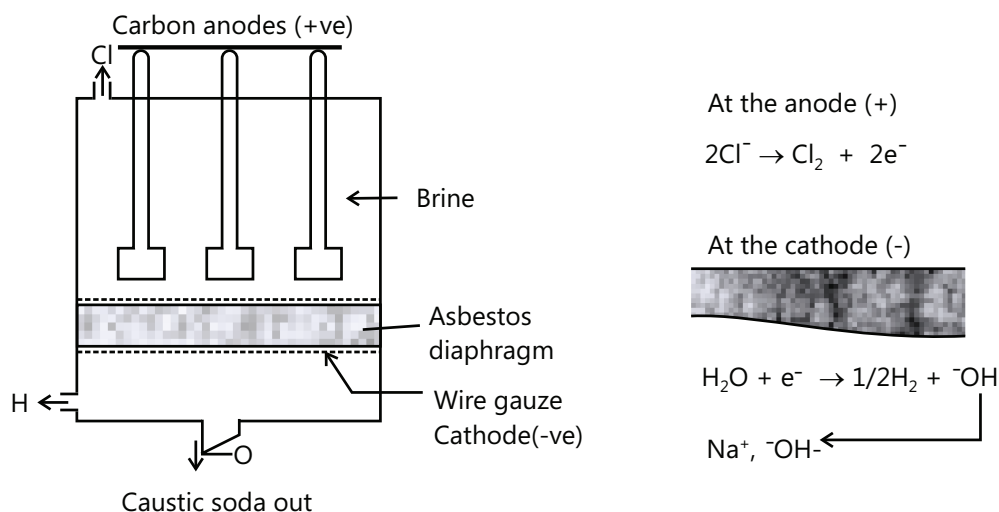
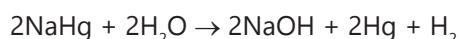


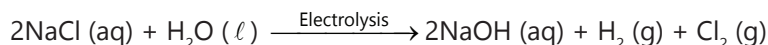
Figure 15.13 (b): Working of Castner-Kellner cell

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



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

- (b) **Diaphragm cell:** In this type of cell alkali and chlorine are kept separate by the use of a diaphragm and on contact with a negative wire gauze, electrolysis begins. Chlorine is liberated at the graphite anode and sodium hydroxide is formed at the outside edges of the cathode.
- (c) **Using Nafion Membrane Cell:** The natural brine (NaCl) is now electrolyzed in a membrane cell in which the anode and the cathode are separated by a NAFION membrane. Nafion is a copolymer of tetrafluoromethylene and pentafluorosulphonyl ethoxyether. The copolymer is supported by a Teflon mesh.



Presently the method makes use of Nafion membrane in place of diaphragm.

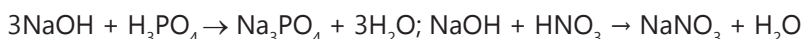
8.5.1 Preparation of Pure Sodium Hydroxide

Commercial sodium hydroxide is purified with the help of an alcohol. Sodium hydroxide dissolves in alcohol, while impurities like NaCl, Na_2CO_3 , Na_2SO_4 etc., remain insoluble. The alcoholic filtrate is distilled. The alcohol distils off while pure solid sodium hydroxide is left behind.

Properties:

- (a) It is a white crystalline solid and has a soapy touch.
- (b) Its density is 2.13 g/mL and melting point is 318.4°C.
- (c) It is highly soluble in water and is bitter in taste, and is corrosive in nature.

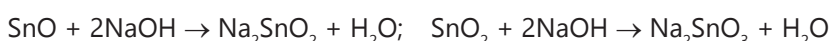
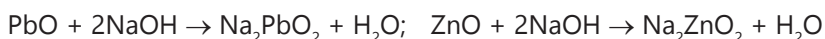
- (d) Neutralization and hydrolysis reactions:



These are non-redox type of reactions.

- (e) Reaction with acidic oxides: $2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$
 $2\text{NaOH} + 2\text{NO}_2 \rightarrow \text{NaNO}_2 + \text{NaNO}_3 + \text{H}_2\text{O}; 2\text{NaOH} + \text{SO}_3 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$

- (f) Reaction with amphoteric oxides:



- (g) Reacts with non-metals:

- (i) Halogens

- With cold & dilute NaOH: $2\text{NaOH} + \text{Br}_2 \rightarrow \text{NaBr} + \text{NaOBr} + \text{H}_2\text{O}$
 - With hot & concentrated NaOH: $6\text{NaOH} + 3\text{Br}_2 \rightarrow 5\text{NaBr} + \text{NaBrO}_3 + 3\text{H}_2\text{O}$
- F_2 with cold & dilute NaOH gives OF_2 and with hot & concentrated NaOH gives O_2

- (ii) With white phosphorus: $3\text{NaOH} + \text{P}_4 \rightarrow 3\text{NaH}_2\text{PO}_2 + \text{PH}_3$

- (iii) With sulphur: $6\text{NaOH} + 4\text{S} \rightarrow 2\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$

- (iv) With boron: $2\text{B} + 6\text{NaOH} \rightarrow 2\text{Na}_3\text{BO}_3 + 3\text{H}_2$

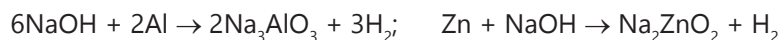
- (v) With silicon: $2\text{NaOH} + \text{Si} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SiO}_3 + 2\text{H}_2$

- (h) Reaction with metals and salts:

- (i) Reaction with amphoteric metals (e.g. Al, Pb, Sn, Zn etc.):

They liberate hydrogen gas.





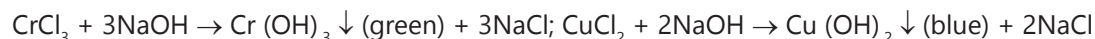
(ii) Reaction with salts of amphoteric metals:

Salts dissolves in sodium hydroxide (excess)

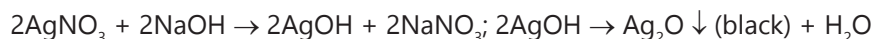
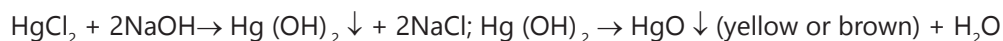


(iii) Reaction with salts of Cr, Ni, Fe, Mn. Cu etc.

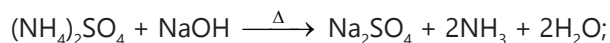
Form insoluble hydroxides



(iv) Reaction with salts of Hg and Ag:



(v) Reaction with ammonium salts: It liberates ammonia from both ammonium salts and coordination complexes where ammonia acts as ligand.



(vi) Reaction with carbon monoxide: $\text{NaOH} + \text{CO} \xrightarrow[5-10\text{atm}]{150-200^\circ\text{C}} \text{HCOONa}$

(vii) Reaction with H_2S : $\text{NaOH} + \text{H}_2\text{S} \rightarrow \text{NaSH} + \text{H}_2\text{O}$; $\text{NaSH} + \text{NaOH} \rightarrow \text{Na}_2\text{S} + \text{H}_2\text{O}$.

It is used to remove mercaptans from petroleum products.

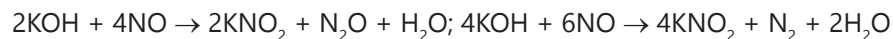
(viii) Reaction with alcohols: $\text{NaOH} + \text{EtOH} \rightarrow \text{NaOEt} + \text{H}_2\text{O}$.

Caustic property: Sodium hydroxide is a powerful cautery and breaks down the proteins of skin to a pasty mass. On account of this property, it is commonly called caustic soda.

8.6 Potassium Hydroxide (KOH)

It is prepared by the electrolysis of KCl solution. KOH resembles NaOH in all its reactions. However KOH is much more soluble in alcohol. This accounts for the use of alcoholic KOH in organic chemistry.

KOH is called caustic potash, because of their corrosive properties (for example on glass or on skin) and its aqueous solution is known as potash lye.



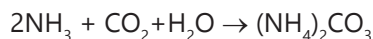
It is used for the absorption of gases like CO_2 , SO_2 , etc. It is used for making soft soaps.

8.7 Sodium Carbonate or Washing Soda (Na_2CO_3)

Preparation:

(a) **By Solvay ammonia soda process:** It involves followings steps.

(i) **Saturation of brine with ammonia and CO_2 (In ammonia absorber):**

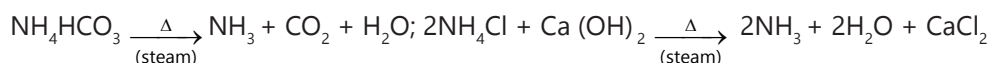


Ammoniated brine is filtered to remove calcium and magnesium impurities as their insoluble carbonates.

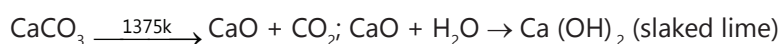
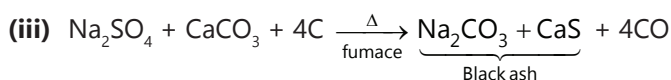
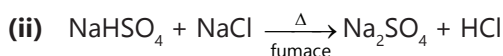
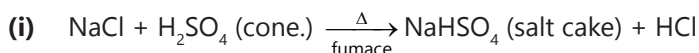
(ii) Formation of insoluble NaHCO_3 (In carbonation tower):

Reaction is exothermic and hence there is a cooling arrangement.

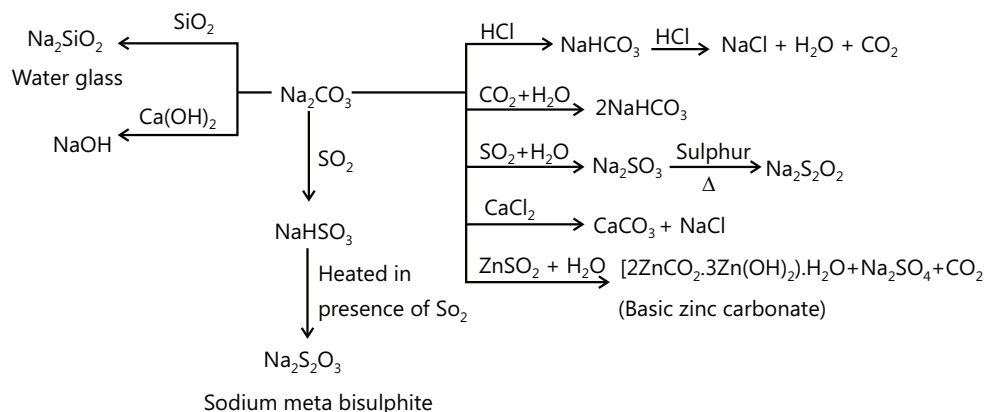
NaHCO_3 is insoluble in cold brine solution because of the common ion effect. It is separated by filtration and the filtered is used for recovering NH_3 & CO_2

(iii) Calcination to get sodium carbonate: $2\text{NaHCO}_3 \xrightarrow{150^\circ\text{C}} \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ **(iv) Recovery of ammonia and carbon dioxide (In recovery tower):**

CaCl_2 is obtained as by product.

(v) Preparation of CO_2 (In lime kiln):**(b) Le-Blanc process:** It involves following steps

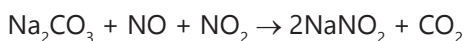
Black ash contains 45% Na_2CO_3 is extracted with water when Na_2CO_3 dissolves leaving behind insoluble as impurities called as alkali sludge or waste.

Properties:

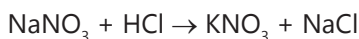
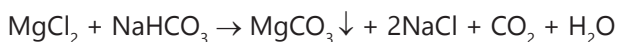
Flowchart 15.1: Chemical properties of sodium carbonate

(a) It is white crystalline solid. It is known in several hydrated forms. The common form is decahydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. This form is called washing soda. The decahydrate form on standing in air effloresces and crumbles to powder. It is the monohydrate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$.

(b) It is soluble in water with the evolution of considerable amount of heat. The solution is alkaline in nature due to hydrolysis. $\text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{NaOH} + \text{H}_2\text{CO}_3$



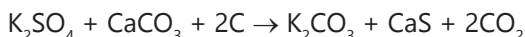
Bicarbonates precipitate normal carbonates while carbonates precipitate basic carbonates from some metal salt solutions.



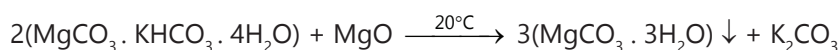
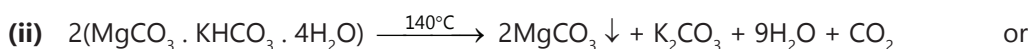
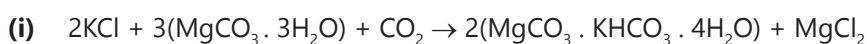
8.8 Potassium Carbonate, Potash or Pearl Ash (K_2CO_3)

Preparation:

(a) By Le-Blanc process:



(b) By Prechts process:



It is a white powder and deliquescent in nature. The mixture of K_2CO_3 and Na_2CO_3 is used as a fusion mixture in the laboratory. $2\text{HNO}_3 + \text{K}_2\text{CO}_3 \rightarrow 2\text{KNO}_3 + \text{CO}_2 + \text{H}_2\text{O}$

The potassium carbonate like sodium carbonate, cannot be prepared by Solvay process because of the intermediate, KHCO_3 formed which is soluble in an appreciable amount in water.

8.9 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. $\text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{NaHCO}_3$ (sparingly soluble)

Properties: It is a white crystalline solid, sparingly soluble in water. The solution is alkaline in nature due to hydrolysis. The solution is weakly basic and gives a yellow colour with methyl orange but no colour with phenolphthalein. $\text{NaHCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{H}_2\text{CO}_3$

On heating, it loses carbon dioxide and water forming sodium carbonate.



Use: It is largely used for making baking powder. Baking powder contains NaHCO_3 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and starch. The $\text{Ca}(\text{H}_2\text{PO}_4)_2$ 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% $\text{NaAl}(\text{SO}_4)_2$ and 10% $\text{Ca}(\text{H}_2\text{PO}_4)_2$. The $\text{NaAl}(\text{SO}_4)_2$ slows the reaction down so the CO_2 is given off more slowly.

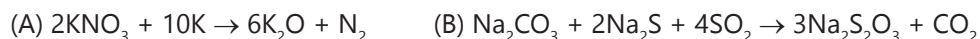
Illustration 12: What happens when-

(JEE ADVANCED)

(A) Anhydrous potassium nitrate is heated with excess of metallic potassium.

(B) Solution containing sodium carbonate and sodium sulphide is treated with sulphur dioxide.

Sol: Self-explanatory



8.10 Sodium Sulphate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$)

It is also known as Glauber's salt.

Preparation:

(a) **By heating NaCl with concentrated. H_2SO_4 :** $2\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$

(b) **By Hargreaves process:** $4\text{NaCl (dry lumps)} + 2\text{SO}_2 (\text{g}) + 2\text{H}_2\text{O (g)} + \text{O}_2 (\text{g}) \rightarrow 2\text{Na}_2\text{SO}_4 + 4\text{HCl}$

Properties:

(a) It is a white crystalline solid and effloresces readily in dry air to form anhydrous sodium sulphate.

(b) It is reduced to sodium sulphide when heated with carbon. $\text{Na}_2\text{SO}_4 + 4\text{C} \rightarrow \text{Na}_2\text{S} + 4\text{CO} \uparrow$

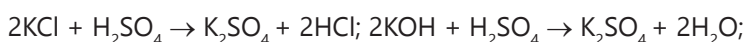
(c) It forms sodium bisulphate when reacted with concentrated H_2SO_4 . $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \rightarrow 2\text{NaHSO}_4$

(d) Reaction with metal salts. $\text{BaCl}_2 + \text{Na}_2\text{SO}_4 \rightarrow \text{BaSO}_4 \downarrow + 2\text{NaCl}$; $\text{Pb}(\text{NO}_3)_2 + \text{Na}_2\text{SO}_4 \rightarrow \text{PbSO}_4 \downarrow + 2\text{NaNO}_3$

8.11 Potassium Sulphate (K_2SO_4)

Preparation:

(a) It is prepared by the reaction of potassium chloride or hydroxide with concentrated. H_2SO_4 .



(b) $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O} + 2\text{KCl} \rightarrow 2\text{K}_3\text{SO}_4 + \text{MgCl}_2 + 6\text{H}_2\text{O}$

Properties: It is a white crystalline solid and soluble in water. It is used as a fertilizer for tobacco and wheat.

Illustration 13: Why is there a white deposit in the glass vessel containing NaOH solution noticed after some time?
(JEE ADVANCED)

Sol: SiO_2 present in glass reacts with NaOH to give insoluble silicate.

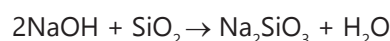
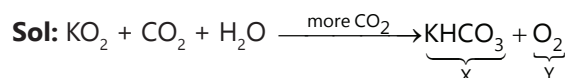


Illustration 14: $\text{KO}_2 + \text{CO}_2 + \text{H}_2\text{O} \xrightarrow{\text{more CO}_2} [\text{X}] + [\text{Y}]$ (JEE ADVANCED)

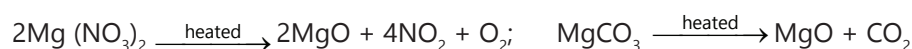
Products [X] and [Y] are respectively: (A) K_2CO_3 , O_2 (B) KHCO_3 , O_2 (C) KOH , K_2CO_3 (D) KHCO_3 , H_2O



9. COMPOUNDS OF ALKALINE EARTH METALS

9.1 Magnesium Oxide or Magnesia (MgO)

Preparation: It can be prepared by following reaction.



Properties:

(a) It is slightly soluble in water and forms magnesium hydroxide. $\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2$

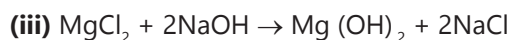
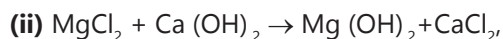
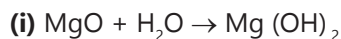
(b) It is basic in nature. It reacts with acids to form corresponding salts. $\text{MgO} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2\text{O}$

(c) It is reduced by carbon at a very high temperature. $\text{MgO} + \text{C} \rightarrow \text{Mg} + \text{CO}$

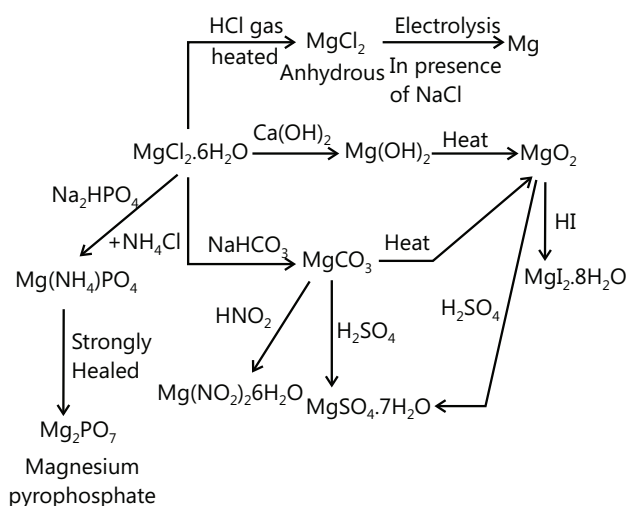
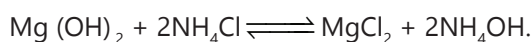
Magnesium oxide when mixed with a saturated solution of magnesium chloride sets to a hard mass like cement known as magnesia cement or Sorel's cement. The composition is $\text{MgCl}_2 \cdot 5\text{MgO} \cdot x\text{H}_2\text{O}$.

9.2 Magnesium Hydroxide [$\text{Mg}(\text{OH})_2$]

Preparation:



Properties: It is a white powder. It is sparingly soluble in water. It is basic in nature and forms a salt with acids. It decomposes on heating. It readily dissolves in ammonium chloride solution and is, therefore, not precipitated in group IIIrd of qualitative analysis.



Flowchart 15.2: Chemical properties of Magnesium Hydroxide

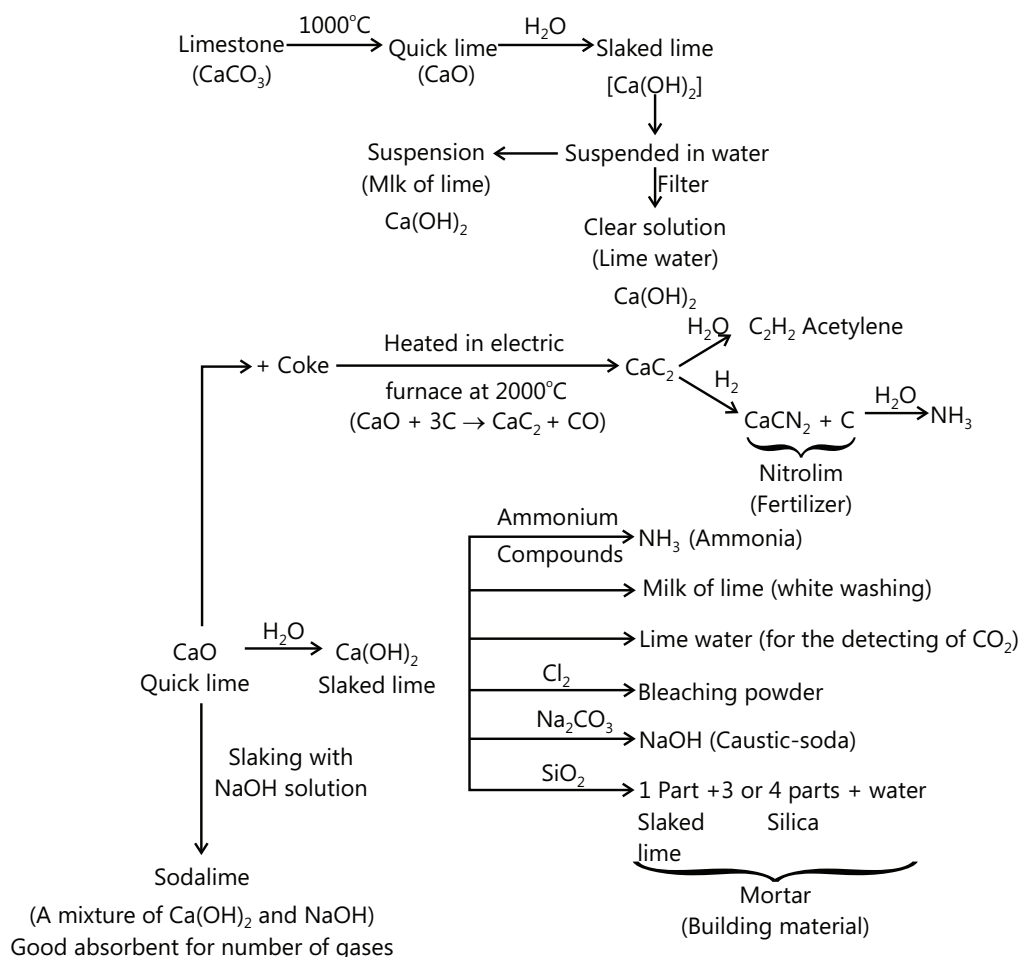
Use: A suspension of $\text{Mg}(\text{OH})_2$ in water is used in medicine as an antacid under the name, milk of magnesia.

9.3 Magnesium Chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)

It occurs in nature as mineral carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

Properties: It is a colourless crystalline solid, highly deliquescent and highly soluble in water.

9.4 Quick Lime, Slaked Lime and Lime Water



Flowchart 15.3: Reactions of Quick lime, slaked lime and lime water

9.5 Magnesium Carbonate (MgCO_3)

Preparation:

- (a) It can be prepared by adding sodium bicarbonate to a hot solution of magnesium salt.



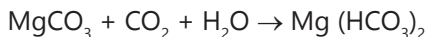
- (b) $2\text{MgSO}_4 + 2\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{MgCO}_3 \cdot \text{Mg(OH)}_2 + 2\text{Na}_2\text{SO}_4 + \text{CO}_2$

When CO_2 gas is passed through the suspension of the basic carbonate of magnesium, magnesium bicarbonate is formed which on heating forms MgCO_3 .



Properties:

- (a) It dissolves readily in water containing an excess of carbon dioxide.



- (b) It dissolves in acids forming salts with evolution of CO_2 .



On heating, it decomposes with the evolution of CO_2 .



(c) It forms double carbonates with alkali metal carbonates.



9.6 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 . $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$; $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaCl}$

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

Properties: It is a white powder insoluble in water. It dissolves in the presence of CO_2 due to the formation of calcium bicarbonate. $\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Ca}(\text{HCO}_3)_2$

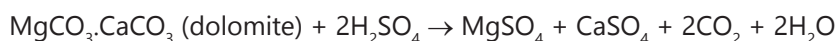
Uses:

- (a) Precipitated chalk is used in tooth pastes and face powders, in medicine for indigestion, in adhesives and in cosmetics.
- (b) Chalk is used in paints and distempers.

9.7 Magnesium Sulphate (MgSO_4)

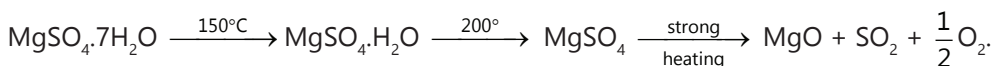
It occurs in nature as minerals kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$).

Preparation: It is prepared by reacting magnesite (MgCO_3) or dolomite with dilute sulphuric acid.

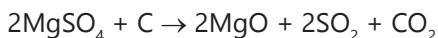


Properties:

(a) **Heating effect:** When heated to 150°C , it changes to monohydrate. On further heating, it becomes anhydrous at 200°C . On strong heating, it decomposes into MgO .



(b) Magnesium sulphate when heated with lamp black at 800°C produces SO_2 and CO_2 gases.



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

9.8 Calcium Sulphate (CaSO_4)

It is found in nature as an anhydride (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)

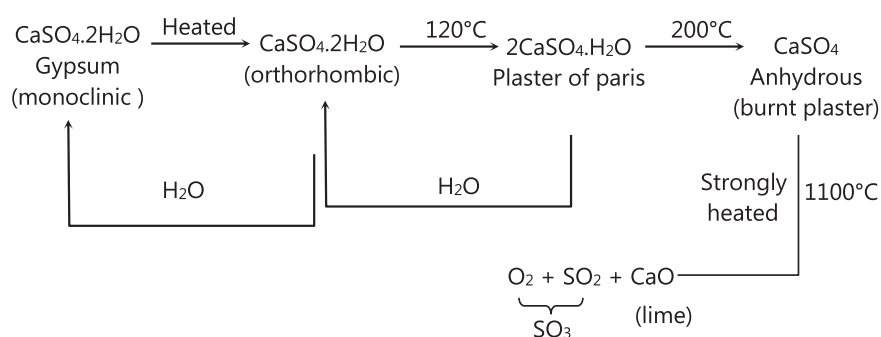
It can be prepared by reacting any calcium salt with either sulphuric acid or a soluble sulphate.



Properties:

- (a) It is a white crystalline solid. It is sparingly soluble in water and solubility decreases as temperature increases.
- (b) It dissolves in dilute acids. It also dissolves in ammonium sulphate due to the formation of double sulphate, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$

- (c) Gypsum when heated first changed from monoclinic form to orthorhombic form without loss of water. At 120°C, it loses three-fourth of its water of crystallization and forms hemihydrate, $(2\text{CaSO}_4 \cdot \text{H}_2\text{O})$ which is commonly known as the Plaster of Paris. At 200°C, it becomes anhydrous. The anhydrous form is known as burnt plaster or dead plaster.



Flowchart 15.4: Chemical Properties of calcium sulphate

- (d) Dead plaster has no setting property as it takes up water only very slowly.
- (e) A suspension of gypsum when saturated with ammonia and carbon dioxide forms ammonium sulphate, a nitrogenous fertilizer $2\text{NH}_3 + \text{CaSO}_4 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{CaCO}_3$
- (f) When strongly heated with carbon, it forms calcium sulphide. $\text{CaSO}_4 + 4\text{C} \rightarrow \text{CaS} + 4\text{CO}$

Use: (a) For preparing blackboard chalk. (b) In anhydrous form as drying agent.

9.9 Plaster of Paris ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$) (Calcium sulphate hemihydrate)

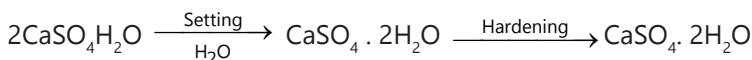
Preparation: It is obtained when gypsum, calcium sulphate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), is heated at 120°C (393K).



Gypsum Plaster of Paris

Properties:

- (a) Plaster of Paris is a white powder.
- (b) It has the property of setting to a hard mass when a paste with water is allowed to stand aside for some time. Slight expansion occurs during the setting as water is absorbed to reform $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum). The setting process is exothermic. The process of setting takes place in stages. In the first stage, there is a conversion of Plaster of Paris into an orthorhombic form of gypsum (setting step) and in the second stage the orthorhombic form changes into a monoclinic form (hardening step).



Plaster of Paris Orthorhombic Monoclinic

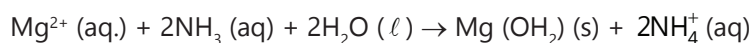
The setting of Plaster of Paris may be catalysed by sodium chloride while it is retarded by borax or alum. Addition of alum to Plaster of Paris makes the setting very hard. The mixture is known as Keene's cement.

Illustration 15: An element X exhibits only the +2 oxidation state in its compounds. The compounds are white and frequently crystallize as hydrates. Its hydroxide used as an antacid is the least soluble one in its family and can be precipitated from solutions containing X^{2+} by NH_3 (g). Identify the element and give the balanced equations.

(JEE MAIN)

- (a) For the effect of heat on its (hexahydrate) chloride.
- (b) For the precipitation of the hydroxide using aq. NH_3 .

Sol: The element is magnesium as its hydroxide known as milk of magnesia is used as an antacid.



PROBLEM SOLVING TACTICS

The correct order of stability of for the following super oxides is:

- (A) $\text{KO}_2 > \text{RbO}_2 > \text{CsO}_2$ (B) $\text{RbO}_2 > \text{CsO}_2 > \text{KO}_2$ (C) $\text{CsO}_2 > \text{RbO}_2 > \text{KO}_2$ (D) $\text{KO}_2 > \text{CsO}_2 > \text{RbO}_2$

Solution: The approach should be as follows

- (i) The stability of super oxides depend on the polarizing power of the cation. Lesser the polarizing power, greater is the stability of the superoxide ion.
- (ii) The polarizing power of cations of the same charge decreases with the increase in the size.
- (iii) Therefore, the stability of super oxides increases with increase in the size of cations.
- (iv) The increasing order of size of ions is: $\text{K}^+ < \text{Rb}^+ < \text{Cs}^+$.
- (v) The correct order of stability is: $\text{CsO}_2 > \text{RbO}_2 > \text{KO}_2$

Which one of the following orders presents the correct sequence of the increasing basic nature of the given oxides?

- (A) $\text{K}_2\text{O} < \text{Na}_2\text{O} < \text{Al}_2\text{O}_3 < \text{MgO}$ (B) $\text{Al}_2\text{O}_3 < \text{MgO} < \text{Na}_2\text{O} < \text{K}_2\text{O}$
 (C) $\text{MgO} < \text{K}_2\text{O} < \text{Al}_2\text{O}_3 < \text{Na}_2\text{O}$ (D) $\text{MgO} < \text{K}_2\text{O} < \text{Na}_2\text{O} < \text{Al}_2\text{O}_3$

Explanation: (i) Basic nature of oxides increases with increase in the size of cation.

(ii) The increasing order of cations is: $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+ < \text{K}^+$

(iii) Therefore the increasing correct order of basic strength is: $\text{Al}_2\text{O}_3 < \text{MgO} < \text{Na}_2\text{O} < \text{K}_2\text{O}$

Conclusion: Correct option is: 'B'.

POINTS TO REMEMBER

Trends in Physical Properties of Alkaline Earth Metals:

Characteristic	Trend
Oxidation state	All elements show +2 oxidation state
Atomic / ionic radii	Be < Mg < Ca < Sr < Ba Size of the alkaline earth metals increases from top to bottom due to increase in the number of shells.
Ionization enthalpy	Be > Mg > Ca > Sr > Ba As the size increases it becomes easier to remove an electron from the outermost shell.