

HYDROGEN and s-BLOCK ELEMENTS

1. HYDROGEN

1.1 Atomic and Molecular Properties of Hydrogen

Atomic Properties		Molecular Properties	
Ionization enthalpy, (kJ mol ⁻¹)	1312	Melting point, (K)	13.8
Electron gain enthalpy (earlier electron affinity), (kJ mol ⁻¹)	-72.8	Boiling point, (K)	20.4
Electronegativity	2.1	Density, (g/cm ³)	0.0899
Atomic radius, (pm)	37	Bond length, (pm)	74.2
Ionic radius (H ⁻), (pm) H ⁺ , pm $\approx 1.5 \times 10^{-3}$	210	Bond enthalpy, (kJ mol ⁻¹)	435.9

Hydrogen in the gaseous state exists as a diatomic species H₂. The diatomic H₂ molecule is also termed as dihydrogen to distinguish it from the hydrogen atom.

1.2 Resemblance with Alkali Metals

Hydrogen resembles alkali metals in the following respects.

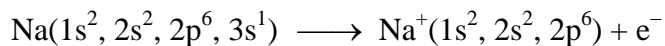
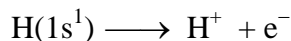
Electronic configuration

The hydrogen atom has one electron in the outermost shell like the alkali metals.

Element	H	Li	Na
Atomic number	1	3	11
Electronic configuration	1s ¹	1s ² , 2s ¹	1s ² , 2s ² , 2p ⁶ , 3s ¹

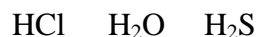
Cation formation

Hydrogen like alkali metals forms singly charged cation by losing the outermost electron.



Affinity for non-metals

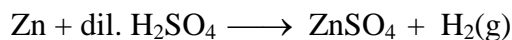
Both hydrogen and alkali metals combine with halogens to form halides, with oxygen to give oxides and with sulphur to give sulphides. For example,



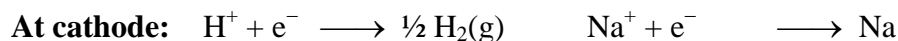
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Electropositive nature

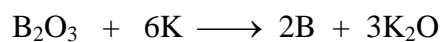
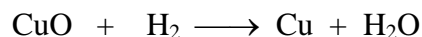
Hydrogen is displaced from acids by metals. In this reaction hydrogen behaves as an electropositive element. For example,



It is further supported by the fact that when an aqueous solution of hydrogen chloride or a molten alkali metal halide is electrolyzed, both hydrogen and alkali metals are liberated at the cathode.



Reducing character



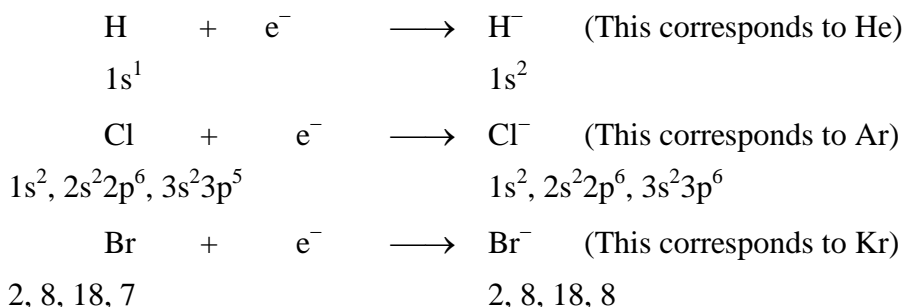
potassium
(an alkali metal)

1.3 Resemblance with Halogens

Hydrogen resembles halogens in the following respects

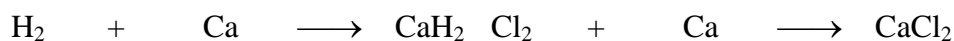
Electronic configuration

Both hydrogen and halogens are one electron short of saturation in their outermost shell. After gaining one electron they acquire stable configuration of the nearest noble gas. Thus, both behave as univalent non-metals as shown below.

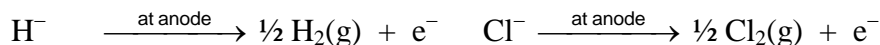


Hydrides and halides

Hydrogen combines with alkali and alkaline earth metals to form hydrides similar to halides.



The fused hydrides on electrolysis produce hydrogen at anode, like chlorine from fused chlorides.



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Ionization enthalpy

The ionization enthalpy of hydrogen is closer to halogens and much different from alkali metals.

	Hydrogen	Alkali metals					Halogens			
Element	H	Li	Na	K	Rb	Cs	F	Cl	Br	I
Ionization enthalpy (kJ mol ⁻¹)	1301	520	496	419	408	375	1680	1256	1142	1008

Formation of covalent compounds

Like halogens, hydrogen readily combines with non-metals such as carbon, silicon, nitrogen etc. to form covalent compounds.

With hydrogen:	CH ₄ Methane	SiH ₄ Silane	NH ₃ Ammonia
With halogens:	CCl ₄ Carbon tetrachloride	SiCl ₄ Silicon tetrachloride	NCl ₃ Nitrogen trichloride

1.4 Properties of Hydrogen in Which it Differs From Alkali Metals As Well As Halogens Both

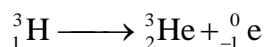
Hydrogen has some properties which neither resemble with alkali metals nor with halogens. For example,

- The oxide of hydrogen, H₂O is neutral, while the oxides of halogens, e.g., Cl₂O, ClO₂, Cl₂O₇ etc. are acidic and the oxides of alkali metals, e.g. Na₂O, K₂O etc are basic.
- Hydrogen atom has no inner electrons and no unshared electrons.

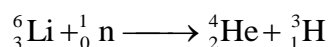
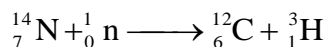
1.5 Isotopes of Hydrogen

Hydrogen has three isotopes. The most abundant and stable isotope is that of protium (¹H).

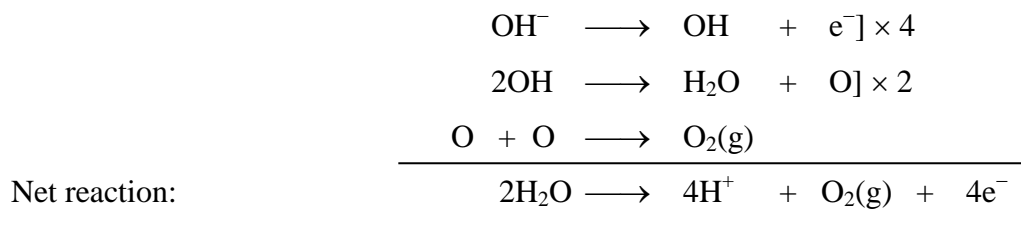
The stable isotope deuterium (²H or D) is also called heavy hydrogen. The third isotope called tritium (³H or T) is radioactive. (t_{1/2} = 12.33 year). It emits low energy β-particles but no γ-radiations.



It is prepared artificially by the bombardment of nitrogen or an isotope of lithium with neutron.



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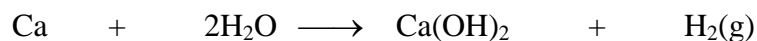
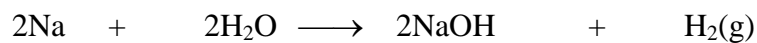


By the action of metals on water

Metals occurring above hydrogen in the electrochemical series displace hydrogen from water under the conditions depending upon their reactivity.

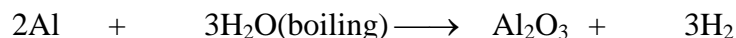
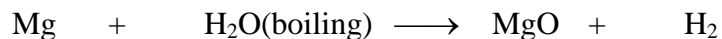
(a) Action of metals on cold water:

Elements like sodium, potassium, calcium etc., displace hydrogen from water at room temperature. With alkali metals the reaction is explosive.



(b) Action of metals on boiling water:

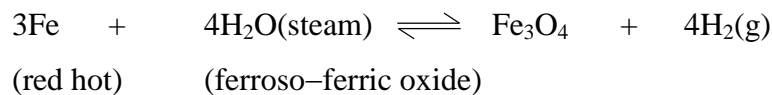
Metals like magnesium and aluminium in powder form decompose boiling water, giving hydrogen gas.



(c) By passing steam over heated metals:

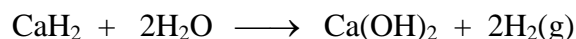
When steam is passed over some heated metals, such as, zinc, magnesium and iron, hydrogen gas is obtained.

The apparatus consists of a long silica tube containing iron filings heated to redness. Steam is passed over heated iron, hydrogen so evolved is collected over water.



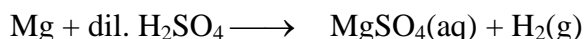
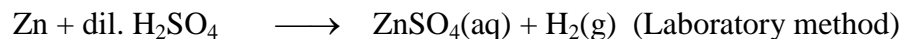
By the action of water on metal hydrides

Hydrides of alkali and alkaline earth metals react readily with water producing hydrogen.



From acids

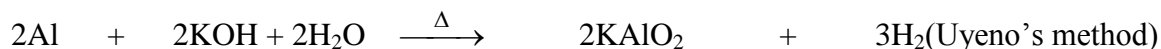
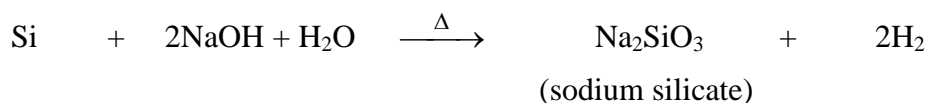
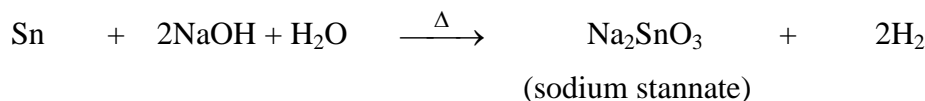
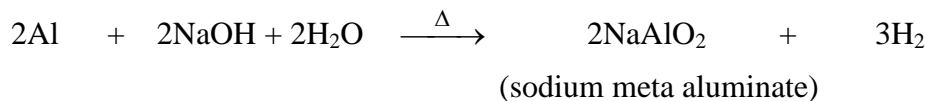
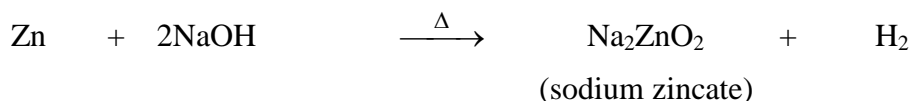
Acids contain replaceable hydrogen. Electropositive metals, such as, zinc, iron, aluminium, magnesium etc., which appear above hydrogen in electrochemical series displace hydrogen from acids. For example,



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From Alkalies

Hydrogen can be prepared by the action of boiling caustic soda or caustic potash solutions on metals like zinc, aluminium, tin etc., or on a non-metal like silicon.

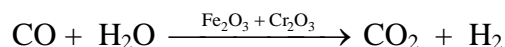


1.7 Commercial Preparation of Hydrogen

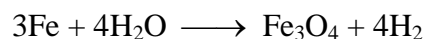
Water is one of the most abundant and cheaper source of hydrogen (or dihydrogen). Hydrogen is commercially obtained from water using different methods.

Bosch process

Water gas is mixed with excess of steam and passed over a heated catalyst, ferric oxide and little chromium oxide at 450°C. Carbon monoxide is oxidized to CO₂.

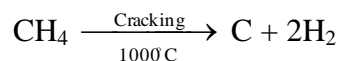
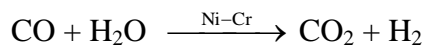
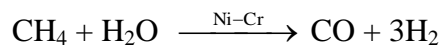


Lane's process



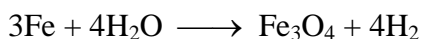
From Natural gas

Natural gas mainly consists of CH₄. Hydrogen gas is obtained from natural gas by either partial oxidation or cracking.



By electrolysis of water

Used where electricity supply is cheap and easily available.



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1.8 Physical Properties of Hydrogen (Or Dihydrogen)

- (i) Hydrogen (dihydrogen) is a colourless, tasteless and odourless gas. It is the lightest element known. Hydrogen has a density of 0.098 g/L.
- (ii) Hydrogen (dihydrogen) is slightly soluble in water, 21.5 mL/L at NTP. Many metals like platinum black or palladium adsorb considerable quantities of hydrogen. Palladium showing the highest capacity ≈ 93.5 volumes; hydrogen is given off when palladium is heated in vacuum. The phenomenon of adsorption of hydrogen on metal surface is known as occlusion.

1.9 Chemical Properties of Hydrogen (Or Dihydrogen)

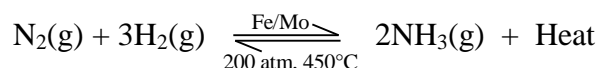
Hydrogen is quite reactive and can form compounds by losing, or by sharing the single electron in its outermost shell. It also reacts via gaining a single electron to achieve the helium (noble gas) configuration in hydride formation. It is highly combustible gas and burns in air or dioxygen with a pale blue flame to form water. However, it is not a supporter of combustion.

Because of its high bond dissociation enthalpy (436 kJ mol^{-1}), dihydrogen is not particularly reactive. At elevated temperatures or in the presence of catalysts, it combines with many non-metals to form covalent hydrides. With reactive metals (e.g., alkali metals) it forms salt-like hydrides, in which its oxidation state is -1 .

In addition to covalent and salt like hydrides, hydrogen (dihydrogen) forms interstitial hydrides with metals such as platinum, palladium and nickel. In the interstitial hydrides, hydrogen atoms because of their small size occupy the interstitial sites in the metallic crystal. Some typical chemical reactions of hydrogen (dihydrogen) are described below.

With nitrogen

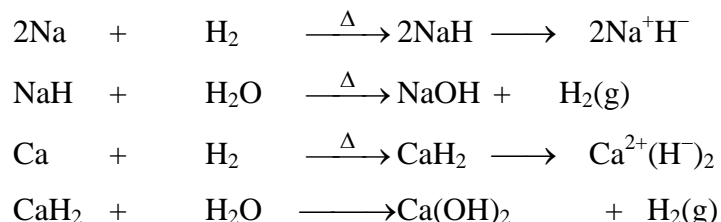
Hydrogen reacts with nitrogen at about $450 - 500^\circ\text{C}$ and under high pressure (200 – 900 atm) in the presence of a catalyst to give ammonia.



This reaction forms the basis of Haber's process for the manufacture of ammonia from nitrogen and hydrogen.

With Metals

Highly electropositive metals such as sodium, lithium and calcium react at high temperatures with hydrogen to form hydrides. In such compounds each hydrogen atom accepts one electron to become a negative hydride ion, H^- . These hydrides are ionic compounds and very unstable to water. These react with water giving hydroxide of the metal and hydrogen gas.

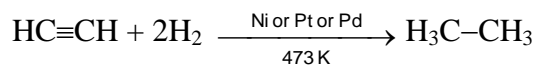
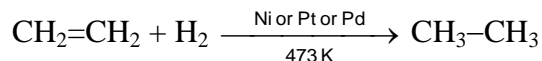


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Metals like iron, nickel, palladium etc., take up hydrogen and form interstitial or metallic hydrides.

Hydrogenation of unsaturated hydrocarbons

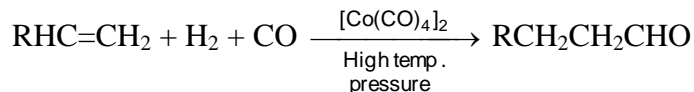
Unsaturated hydrocarbons such as alkenes and alkynes add dihydrogen in presence of a catalyst to form saturated hydrocarbons.



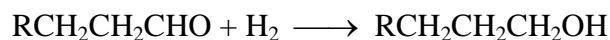
Hydrogenation of unsaturated organic compounds in presence of heterogeneous and homogeneous catalysis is used in many industrial processes.

Hydroformylation of olefins

Olefins react with carbon monoxide and dihydrogen in presence of octacarbonyl dicobalt as catalyst under high temperature and pressure to form aldehydes.



This reaction is called hydroformylation or the oxo process. The aldehydes thus obtained on subsequent catalytic reduction give alcohols.

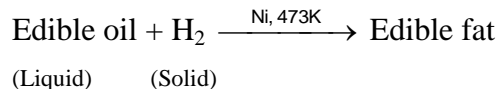


Aldehyde Alcohol

Hydrogenation of oils

The vegetable oils such as soyabean oil, cotton seed oil, ground nut oils are called polyunsaturated oils since they contain many C=C bonds. When these oils are exposed to air for prolonged periods, the double bonds present in them undergo oxidation and the oil becomes rancid i.e. develop unpleasant taste. To avoid this, double bonds are reduced.

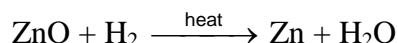
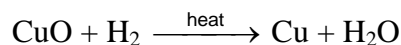
For this purpose, dihydrogen is bubbled through edible oil in presence of finely divided nickel at 473 K when the oils are converted into solid fats.



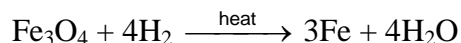
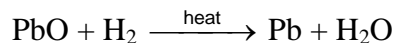
This process is called hydrogenation or hardening of oils and is used in the manufacture of vegetable ghee like Dalda, Gagan, Rath etc. from vegetable oils.

Reduction of metal oxides and ions

Dihydrogen acts as a reducing agent and hence reduces oxides of certain less electropositive metals such as those of Cu, Zn, Pb, Fe etc. to the corresponding metals. For example,

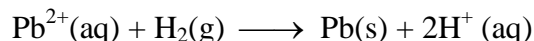


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The oxides of strongly electropositive metals such as those of alkali and alkaline earth metals are not reduced by this method.

Dihydrogen also reduces some metal ions in aqueous solution. For example,

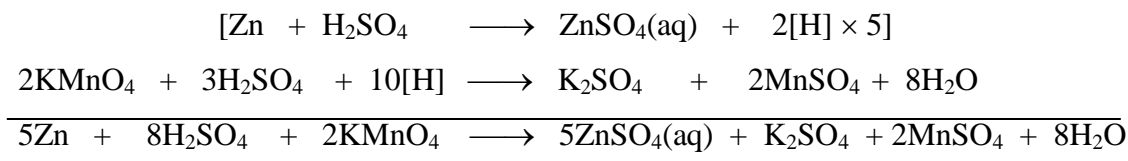


1.10 Nascent and Atomic Hydrogen

Nascent hydrogen

An element is said to be in nascent state (In Latin nascent means = to be born or new born) when it is just liberated as a result of chemical reaction, i.e. at the point of formation.

If hydrogen gas is bubbled through a solution of acidified KMnO_4 , it does not get decolourised, but when a little amount of zinc powder and dilute sulphuric acid are added to a dilute solution of KMnO_4 , it gets decolorised. This is because the hydrogen produced is used up in the reaction immediately. This simple experiment shows that the nascent hydrogen is more reactive than the molecular hydrogen.

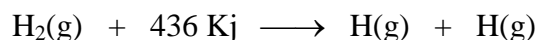


The nascent hydrogen may be prepared in any reacting system by using any of the following systems.



Atomic hydrogen

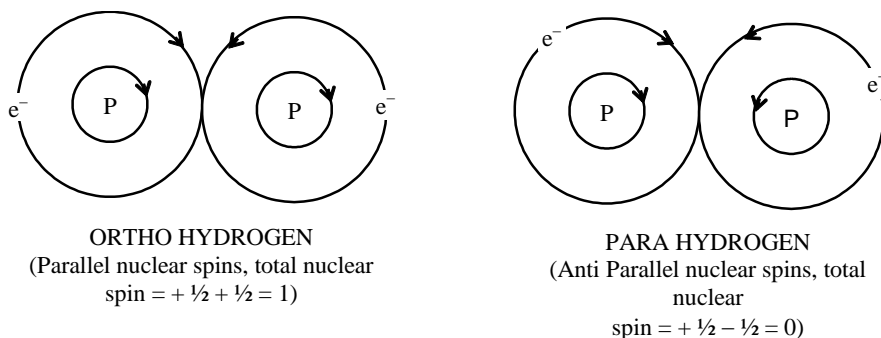
Langmuir in 1915 obtained atomic hydrogen by dissociating molecular hydrogen on a hot filament of tungsten or platinum. The dissociation of molecular hydrogen is an endothermic reaction.



1.11 Ortho and Para Hydrogens

On the basis of quantum mechanics, Heisenberg in 1927 predicted the existence of these two forms of the molecular hydrogen. The nucleus of a hydrogen atom spins like a top. When two atoms of hydrogen combine to form a molecule, their nuclear spins may be either in the same direction or in the opposite directions. The former variety is known as ortho hydrogen and the latter as para hydrogen as depicted in figure.

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At room temperature, ordinary hydrogen consists of about 75% of ortho and 25% of para forms. At 25 K, a sample of ordinary hydrogen contains 99% para and 1% of ortho form. Ortho hydrogen is more stable. The, ortho \longrightarrow para, conversion is accelerated by,

- (a) heating to 800°C
- (b) mixing with paramagnetic molecules, e.g. O₂, NO₂ etc.
- (c) by passing electric discharge.

The physical properties of the dihydrogen are not effected by nuclear spin isomerism. However, some of the notable differences are

- (i) Thermal conductivity of para hydrogen is 50% greater than that of ortho hydrogen.
- (ii) The melting point of para hydrogen is 0.15 K lower than that of hydrogen.

1.12 Ionic Hydrides

- (i) All salt-like (or saline) hydrides are crystalline solids with high melting and boiling points
- (ii) These hydrides are denser than the corresponding metals.
- (iii) In molten state, these hydrides are electrically conducting.

(iv) Thermal stability

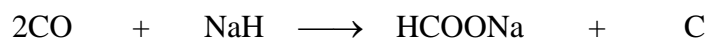
Except LiH (m.p 691°C), all other ionic hydrides decompose before melting. The thermal stability of hydrides follows the order,



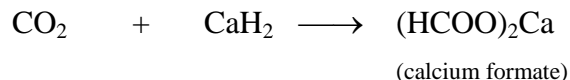
Chemical properties of ionic hydrides

(a) Reducing action:

All hydrides of group 1 and 2 elements are strong reducing agents particularly at higher temperatures.

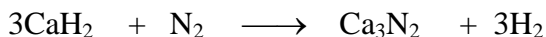


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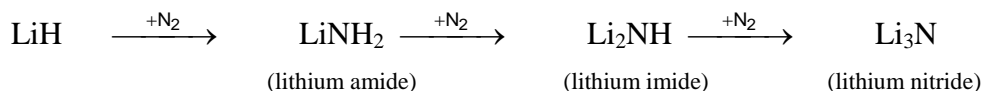


(b) Reaction with nitrogen:

Alkaline earth metal hydrides react with nitrogen to form nitrides

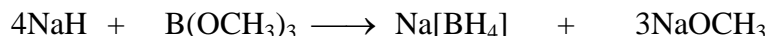
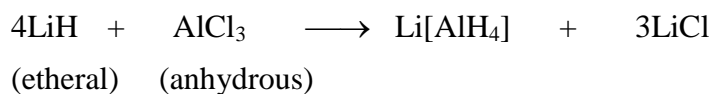


LiH forms nitride through many steps



(c) Reaction with AlCl_3 and $\text{B}(\text{OCH}_3)_3$:

LiH reacts with AlCl_3 (anhydrous) to form lithium aluminium hydride.



Both $\text{Li}[\text{AlH}_4]$ and $\text{Na}[\text{BH}_4]$ are used as reducing agent in organic and inorganic synthesis.

1.13 Covalent (or Molecular) Hydrides

Covalent (or molecular) hydrides are given by p-block elements (except Tl) and s-block elements (Be and Mg). This is because the difference between the electronegativity of these elements and hydrogen is very small.

The elements Sn, Pb, Sb, Bi, Te, Po and halogens give only mononuclear hydrides.

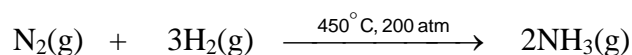
The elements B, Al, Ga, In, C, Si, N, O and S give both mononuclear as well as polynuclear (or polymeric) hydrides.

Preparation of covalent hydrides

Some methods of preparation of covalent hydrides are given below.

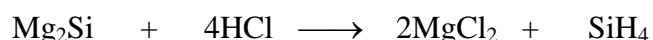
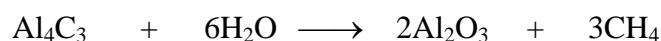
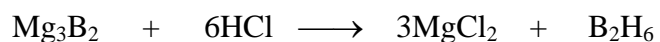
(i) By direct reaction between hydrogen and the element:

The p-block elements (except Tl and At) form covalent hydrides by direct reaction, at higher temperatures.

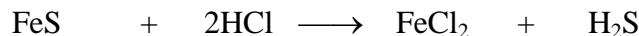


(ii) By hydrolysis of borides, carbides and silicides

The compounds like borides, silicides, nitrides on hydrolysis with water alone or dilute acid solutions give hydrides.

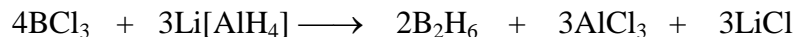


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(iii) By reacting the halide with $\text{Li}[\text{AlH}_4]$ in dry ether:

Anhydrous chlorides of certain p-group elements on reduction with $\text{Li}[\text{AlH}_4]$ in dry ether gives the corresponding hydride.



1.14 Metallic or Interstitial Hydrides

d-block elements of groups 3, 4, 5 (Sc, Ti, V, Y, Zr etc.) 10, 11, 12 (Pd, Cu, Zn etc.) and f-block elements on heating with H_2 under pressure form hydrides. In group 6, Cr alone forms the hydride, CrH . The metals of group 7, 8 and 9 do not form hydrides. In fact, the region of the periodic table from group 7–9 which do not form hydrides is referred to as the hydride gap. These hydrides have properties similar to those of the parent metals and hence are called metallic hydrides. In these hydrides, hydrogen atoms being small in size, occupy space in the metallic lattice that is why these hydrides are also called interstitial hydrides. However, it is not certain whether the hydrogen is present in the interstitial sites as hydrogen atoms or H^+ ions with delocalized electrons.

Properties of Ionic Hydride

- (i) They are hard, have a metallic cluster, conduct electricity and have magnetic properties.
- (ii) The density of these hydrides is lower than those of metals from which they are formed. Since the crystal lattice expands due to inclusion of H_2 .
- (iii) These hydrides are often non-stoichiometric (ZrH_x where $x = 1.30 - 1.75$, TiH_x where $x = 1.8 - 2.0$ etc). Further the ratio of H-atoms to the metal atoms is not fixed but varies with temperature and pressure.

1.15 Polarity of Water Molecule

Oxygen is more electronegative, than hydrogen. Because of its high electronegativity, oxygen atom in a water molecule pulls the shared pairs of electrons more towards itself. As a result, the O–H bond acquires polarity. Since the two O–H bonds in water are inclined at an angle, hence the net dipole moment of water molecule is not zero. The actual dipole moment of water molecule is 1.84 Debye. Debye (denoted as D) is the unit of dipole moment.

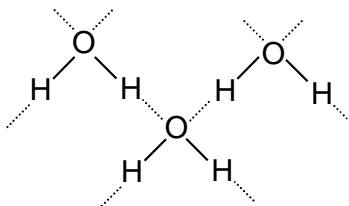
Structure of water molecule in the liquid state

In liquid water, water molecules are held together by intermolecular hydrogen bonds. Each oxygen can form two hydrogen bonds utilising both the lone pairs on it. Experimental studies suggest that liquid water consists of aggregates of varying number of water molecules held together by hydrogen bonds and ‘free’ water molecules in a dynamic equilibrium. The aggregates continually forming, collapsing and reforming. Thus, in liquid water, the equilibrium $n\text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{O})_n$ exists. Hydrogen bonding has very profound effect on the properties of water.

HYDROGEN and s-BLOCK ELEMENTS

Structure of water in solid state (in ice)

Ice, the solid form of water can exist in different crystalline forms depending on the conditions for freezing the water. In the 'normal' hexagonal ice, each oxygen atom is tetrahedrally surrounded by four other oxygen atoms. One hydrogen atom lies in between each pair of oxygen as shown in figure. Thus, each hydrogen is covalently bonded to one oxygen atom and linked to another oxygen atom by a hydrogen bond. Such an arrangement leads to a packing with large open spaces. The density of ice is, therefore, less than that of liquid water. When ice melts some of the hydrogen bonds are broken and the water molecules become more closely packed. As a result, there is an increase in the density of water above its melting points (273 K). The density of water attains a maximum value of 1 g/mL at 277 K (4°C). Above 277 K, the density decreases due to the normal temperature effects.

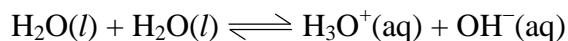


Chemical properties of water

Water shows a versatile chemical behaviour. It acts as an acid, a base, an oxidizing agent, a reducing agent and as a ligand to metal ions. Some typical chemical properties of water are described below:

(i) Self-ionization of water:

A water molecule can act as an acid and a base. So, water shows self-ionization in accordance with the equilibrium.



This reaction is also called autoprotolysis of water.

This reaction is characterised by an equilibrium constant called ionic product constant (K_w) defined as,

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$\text{At } 298 \text{ K, } K_w = 1.0 \times 10^{-14} \text{ mol}^2\text{L}^{-2}$$

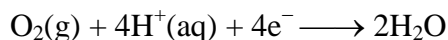
The autoprotolysis of water is thus of great importance in acid-base chemistry.

(ii) Oxidizing and reducing nature of water:

Water can act both as an oxidizing as well as a reducing agent. With active (more electropositive) elements, water acts as an oxidizing agent and in turn gets reduced to give H_2 gas. The reduction potential for the reduction of water at $[\text{OH}^-] = 10^{-7} \text{ mol/L}$ is -0.41 V , viz,



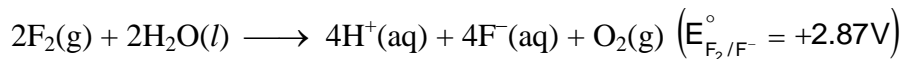
The potential for the reaction,



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$E = +0.82$ for $[H^+] = 10^{-7} \text{ mol L}^{-1}$. So, any element having E° value greater than $+0.82 \text{ V}$ will oxidize water to oxygen.

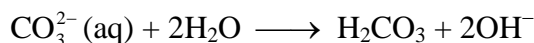
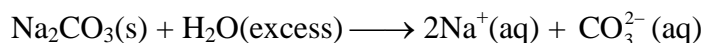
Oxidation of water by fluorine is represented by the equation:



(iii) Hydrolysis reactions:

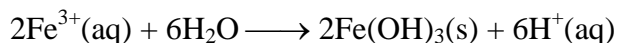
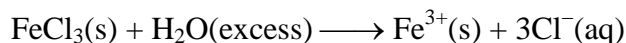
Water can hydrolyze salts of weak acids with strong bases and of weak bases with strong acids. In this H^+ and OH^- of water interact with anions and cations of the compound respectively, leading to the formation of an acid or base or both. For example,

(a) Hydrolysis of Na_2CO_3 :



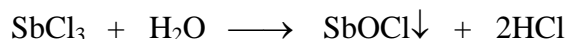
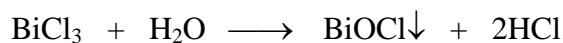
The resulting solution is basic due to the presence of OH^- ions.

(b) Hydrolysis of $FeCl_3$:

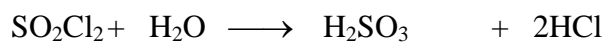
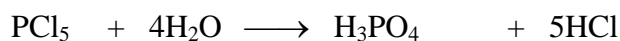
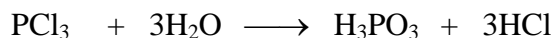


The resulting solution is acidic due to the presence of H^+ ions.

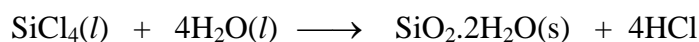
(c) In some cases basic salts are formed.



(d) Halides of non-metals are hydrolysed by water to give the corresponding acid.



(e) In some cases, hydrolysis of a salt may lead to the formation of a compound, which precipitates out of the solution. For example, silicon tetrachloride on hydrolysis gives SiO_2 .



(iv) Hydrate Formation:

Water reacts with certain metal salts to form hydrates. These are of three types.

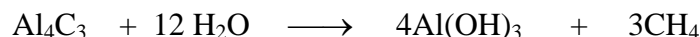
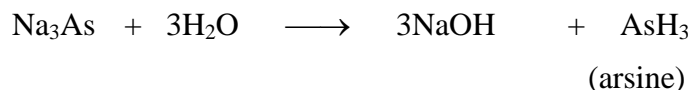
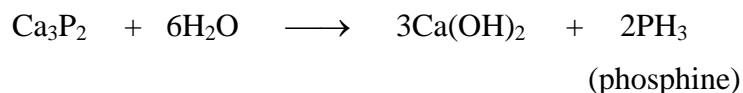
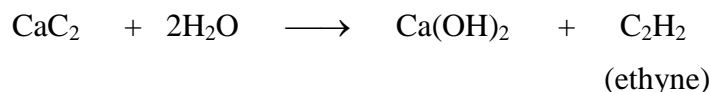
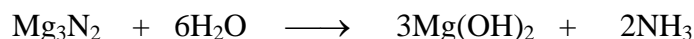
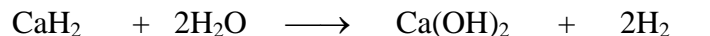
(i) Water molecules form complex, ions by combining with metal ions through Coordinate bond e.g. in $[Ni(H_2O)_6]^{2+}$

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- (ii) Water molecules are coordinated by hydrogen bonding to oxoanions. For example $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ where four water molecules are coordinated to the central Cu^{2+} ion while the fifth water molecule is hydrogen bonded to sulphate.
- (iii) Water is present as lattice. For example, in some alkali metal fluorides and chlorides ($\text{KF} \cdot 2\text{H}_2\text{O}$, $\text{NaCl} \cdot 2\text{H}_2\text{O}$) water molecules occupy interstitial sites in the crystal lattice.

(v) Reaction with hydrides, nitrides, carbides, phosphides and arsenides:

Water reacts with hydrides, nitrides, carbides, phosphides and arsenides at ordinary temperature liberating hydrogen, ammonia, ethyne, phosphine and arsine respectively.

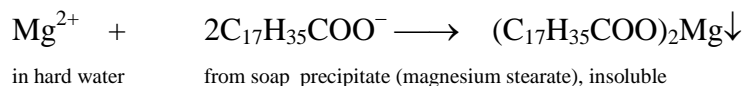
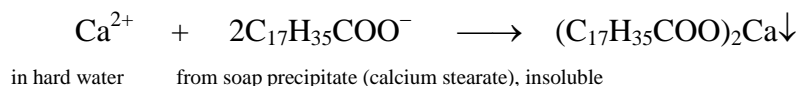


1.16 Hard and Soft Water

Water is described as being hard if it does not lather readily with soap. Soft water, on the other hand, is described as the one which lathers readily with soap.

Behaviour of hard water towards soap:

Soap is the sodium salt of long chain fatty acid ($\text{C}_{17}\text{H}_{35}\text{COO}^-\text{Na}^+$, sodium stearate). When soap is added to hard water, it reacts with the calcium and magnesium ions present in hard water to form insoluble calcium or magnesium stearate (white and curdy precipitate).



As a result, soap will not produce lather with water until all the calcium and magnesium ions have precipitated. Thus, a part of the soap is wasted and washing becomes wasteful. This is also the reason why hard water is not fit for washing (laundry) purposes.

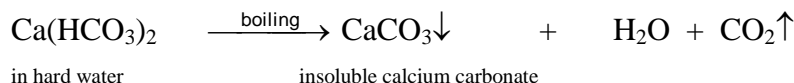
HYDROGEN and s-BLOCK ELEMENTS

Behaviour of soft water towards soap:

Soap is the sodium salt of long chain fatty acid, e.g., sodium stearate ($\text{C}_{17}\text{H}_{35}\text{COONa}$). Sodium salt of stearic acid is soluble in water, whereas calcium and magnesium salts are insoluble. So, when soap (sodium salt) is added to soft water (in the absence of Ca^{2+} and Mg^{2+} ions), it dissolves and forms lather readily. No soap, therefore, is wasted while using soft water.

Hard water is not fit for industrial use:

In industry, if hard water is used in boilers (for steam generation), calcium bicarbonate present in it decomposes to form insoluble calcium carbonate.



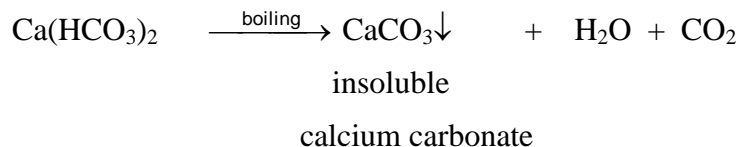
Calcium carbonate precipitates in the boiler tubes as a very hard (stone-like) layer. If the hard water contains calcium sulphate, it leaves a deposit of calcium sulphate on the walls of the boiler tubes. These deposits of calcium carbonate or calcium sulphate in the boiler tubes are bad conductors of heat. Therefore, a lot of fuel is wasted during steam generation.

Moreover, when such solid layers (deposits) crack, the hot water comes in contact with red hot boiler surface and gets vapourised. This generates a large amount of steam and the pressure inside the boiler increases suddenly. This may sometimes lead to the bursting of the boiler.

Methods to remove temporary hardness

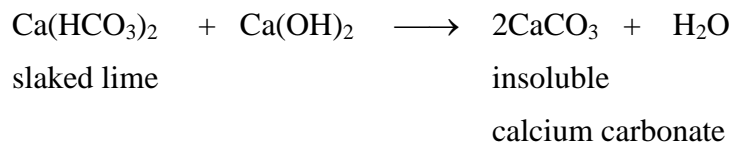
1. By boiling the hard water:

Temporary hardness in water can be easily removed by boiling. On boiling, calcium/magnesium bicarbonate decomposes to give calcium/magnesium carbonate, which is insoluble in water. Therefore, it precipitates out.



2. By the addition of slaked lime (Clark's process):

In Clark's process, slaked lime, $\text{Ca}(\text{OH})_2$ is added to the temporary hard water. Insoluble calcium carbonate precipitates out and no longer produce hardness.

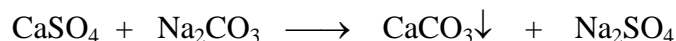


Methods to remove permanent hardness

1. By the addition of washing soda (sodium carbonate):

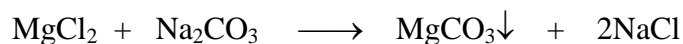
Calcium and magnesium ions present in hard water react with sodium carbonate to produce insoluble carbonates. The water now contains soluble and harmless sodium salts.

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cause of insoluble

permanent hardness

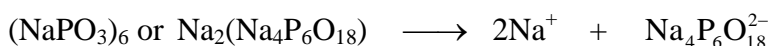


cause of insoluble

permanent hardness

2. Calgon process:

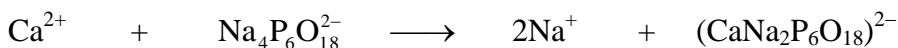
Calgon is a trade name of a complex salt, sodium hexametaphosphate $(\text{NaPO}_3)_6$. It is used for softening hard water. Calgon ionises to give a complex anion, $\text{Na}_4\text{P}_6\text{O}_{18}^{2-}$.



calgon

complex anion

When Calgon is added to hard water, calcium and magnesium ions from hard water displace sodium ions from the anion of the calgon.



from hard water

anion of calgon

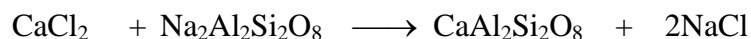
goes into solution

As a result, calcium and magnesium ions from hard water are removed in the form of a complex with calgon, thus softening the water. The released sodium ions go into the water.

3. By the ion-exchange process:

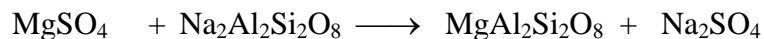
(a) Inorganic exchangers using zeolite (Permutit process):

Permutit is a complex chemical compound called sodium aluminium silicate, which is insoluble in water. Zeolites are naturally-occurring minerals containing sodium aluminium silicates. Permutit or zeolites are packed in a suitable container and a slow stream of hard water is passed through this material. As a result, calcium and magnesium ions present in hard water are exchanged with sodium ions in the permutit ($\text{Na}^+ \text{Al-Silicate}^-$).



in hard water

permutit



in hard water

permutit

The outgoing water contains sodium salts, which do not cause hardness.

(b) Organic exchangers:

Ion exchange resins are giant organic molecules high molecular masses and are essentially of two types:

(i) Cation exchange resins:

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These resins consist of giant hydrocarbon frame work attached to acidic groups such as -COOH (Carboxyl) or $\text{-SO}_2\text{OH}$ (sulphonic acid) groups. They may be represented by the general formula R-COOH or $\text{R-SO}_2\text{OH}$ where R represents the giant hydrocarbon frame work.

Since these resins can exchange H^+ ions with cations such as Ca^{2+} and Mg^{2+} ions present in hard water, they are called cation exchange resins or simply cation exchangers.

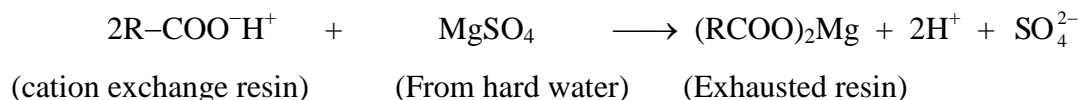
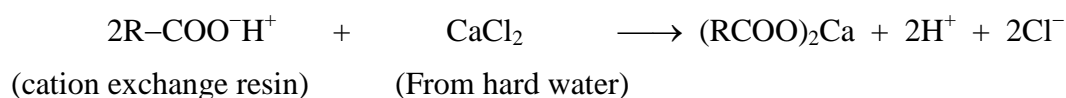
(ii) Anion exchange resins:

These resin consists of giant hydrocarbon frame work attached to basic groups such as OH^- (hydroxide) ions usually in this form or substituted ammonium hydroxides and may be represented by the general formula, $\text{R-NH}_3^+\text{OH}^-$ where R denotes the giant hydrocarbon frame work. Since these resins can exchange OH^- ions with anions such as Cl^- and SO_4^{2-} ions present in hard water, they are called anion exchange resin or simply anion exchangers.

The whole process can be categorized into two steps:

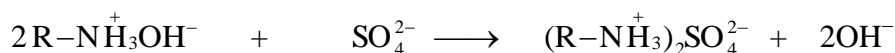
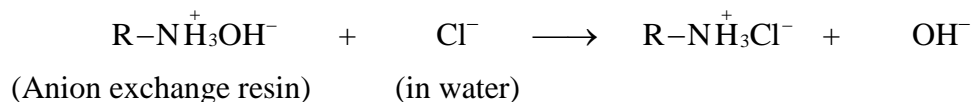
(a) Cationic exchanger:

Hard water is passed through a tank packed with cation exchange resins supported over gravel. All the cations present in hard water are exchanged with H^+ ions furnished by the resins.

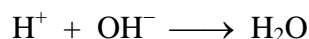


(b) Anionic exchanger:

The water, which comes out from the bottom of the first tank is richer in H^+ ions. This water is then passed through a second tank packed with the anion exchange resin. Here the Cl^- and SO_4^{2-} ions present in hard water are exchanged with OH^- ions of the resin.

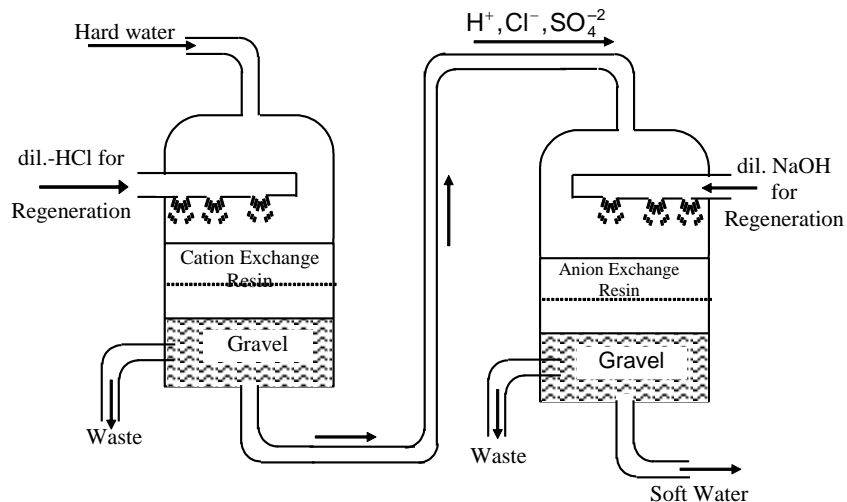


Simultaneously, the H^+ ions coming from the first tank combine with OH^- ions liberated in the second tank to form water.



Thus, the water obtained by this method is free from all types of cations as well as anions.

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REMOVAL OF HARNESS BY THE ORGANIC ION EXCHANGE

1.17 Hydrogen Peroxide, (H_2O_2)

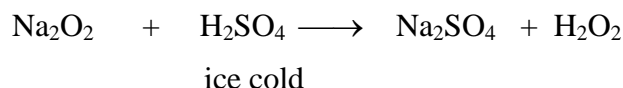
Traces of hydrogen peroxide are found in the atmosphere and water. It is also present in the juice of certain plants.

Preparation of Hydrogen Peroxide

In laboratory, hydrogen peroxide may be prepared from sodium peroxide or barium peroxide.

(i) From sodium peroxide (Merck's method):

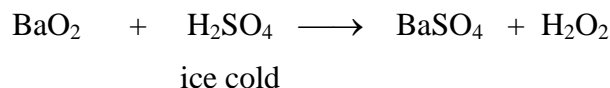
In this method, sodium peroxide is added in small amounts at a time to an ice cold dilute solution (20 percent) of sulphuric acid.



Sodium sulphate is removed by crystallization and a dilute solution of H_2O_2 is obtained.

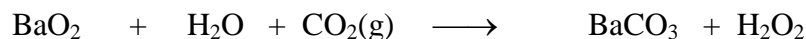
(ii) From barium peroxide (BaO_2):

In this case, a paste of $BaO_2 \cdot 8H_2O$ is prepared and added gradually to an ice-cold dilute sulphuric acid. The solution is kept well-stirred throughout.



Barium sulphate precipitates out, leaving behind a dilute solution of hydrogen peroxide. Phosphoric acid can also be used in place of sulphuric acid.

Alternatively, a current of carbon dioxide is passed through a suspension of barium peroxide in cold water.



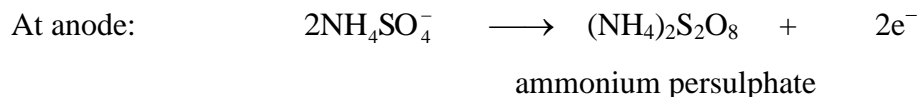
The precipitated barium carbonate is removed by filtration.

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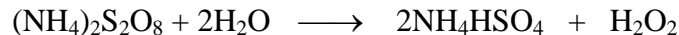
Manufacture of Hydrogen Peroxide

1. By the electrolysis of ammonium hydrogen sulphate:

Hydrogen peroxide can be prepared on a large scale by the electrolysis of ammonium hydrogen sulphate dissolved in excess of sulphuric acid using platinum electrodes and a high current density. In this process, ammonium persulphate is produced by oxidation at the anode while hydrogen is liberated at the cathode.



The solution containing ammonium persulphate is heated at 43 mm pressure when it hydrolyses yielding hydrogen peroxide.



Hydrogen peroxide along with water distils over. The aqueous solution (30–40% H_2O_2) is concentrated to 85–90 percent by fractional distillation under reduced pressure. Water, being more volatile, passes over first.

Ammonium bisulphate recovered as above is used again.

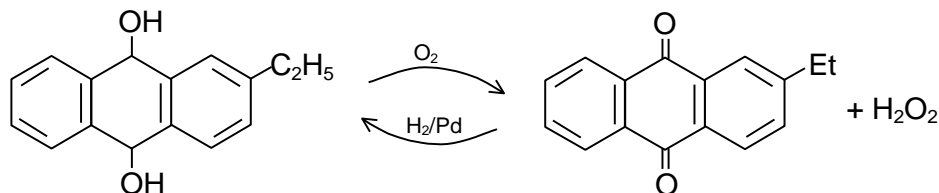
In order to have high current density; (i.e. current strength per unit area of the electrode) at the anode, the area of the anode is kept small.

2. By autoxidation of 2-ethylanthraquinol:

The modern process for the manufacture of H_2O_2 is based on the autoxidation of 2-ethylanthraquinol. In this process, air is passed through 10 percent solution of this compound in a mixture of benzene and an alcohol containing 7–11 carbon atoms.

The resulting 2-ethylanthraquinone is then reduced by passing hydrogen under a pressure of 1 to 3 atmospheres at 4°C . This gives back 2-ethylanthraquinol. This method, thus involves alternate oxidation and reduction steps.

Hydrogen peroxide formed in this reaction is extracted with water and the dilute solution of H_2O_2 is concentrated to obtain H_2O_2 of the required strength.



Physical Properties of Hydrogen Peroxide

(i) Pure hydrogen peroxide is a pale-blue syrupy liquid with a bitter taste.

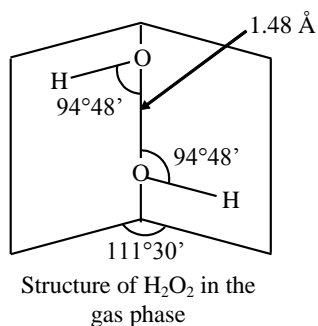
(ii) It is soluble both in water and alcohol.

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- (iii) Pure H_2O_2 is weakly acidic and exists as associated liquid due to hydrogen bonding.
- (iv) Its density is 1.469 g/mL. High specific gravity of H_2O_2 as compared to water is due to strong association of molecules due to hydrogen bonding.
- (iv) It melts at 272.4 K (-0.7°C) and boils under 1 atm pressure at 423.2 K (150°C) with violent decomposition. However, it can be distilled under reduced pressure (≈ 26 torr) at 69.2°C .
- (v) It is diamagnetic.
- (vi) Due to its high dielectric constant, (93.7 for pure H_2O_2) it behaves as an excellent solvent for electrolytes.

Structure of Hydrogen Peroxide

Hydrogen peroxide molecule in the gas phase has a non-planar structure. The bond lengths are, O–O bond length 147.5 pm, O–H bond length 95 pm. Each H–O–O bond angle is about 94.8° , while the angle between the planes containing the hydrogen atoms is 111.5° .



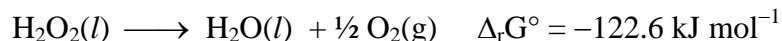
In the crystal, the angle between the planes containing hydrogen atoms gets reduced from 111.5° to 90.2° on account of hydrogen bonding. The two oxygen atoms are joined by a single electron-pair bond.

Chemical Properties of Hydrogen peroxide

Hydrogen peroxide has an interesting chemistry because of its ability to function as an oxidant as well as a reductant in both acid and alkaline solutions. The oxidation state of oxygen in hydrogen peroxide is -1 . It can, therefore, be oxidized to O_2 (zero oxidation state) or reduced to H_2O or OH^- (-2 oxidation state for oxygen). On the whole, hydrogen peroxide is a very powerful oxidising agent and a poor reducing agent.

(i) Stability

Thermodynamically, hydrogen peroxide is unstable as shown by the following equation



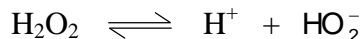
As the reaction from left to right is accompanied by a decrease of free energy, it is a spontaneous process. However, its decomposition at 25°C in the absence of catalysts is slow. The catalysts which accelerate decomposition are platinum, silver, cobalt, iron, copper, manganese dioxide, etc. and light. Concentrated H_2O_2 solution can result into uncontrolled decompositions leading to explosion. H_2O_2 is thus, stored in coloured wax-lined bottles (as

HYDROGEN and s-BLOCK ELEMENTS

rough glass surfaces also causes its decomposition). A few stabilizers such as acids, acetanilide, pyrophosphates and stannates are added to slow down the decomposition of H_2O_2 .

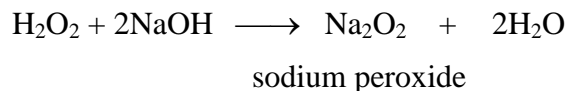
(ii) Acidic nature

Hydrogen peroxide is a weak acid. Its dissociation constant for the equilibrium,



is 1.5×10^{-12} at 20°C .

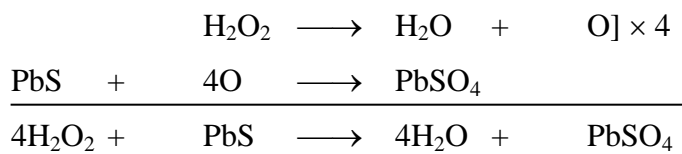
With alkalis, it gives corresponding peroxides.



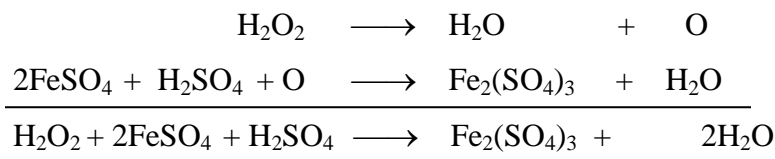
(iii) Oxidizing properties

Hydrogen peroxide provides an atom of oxygen (nascent oxygen) readily. Therefore, it acts as a strong oxidizing agent in acidic as well as alkaline solutions. Some typical oxidation reactions given by H_2O_2 are:

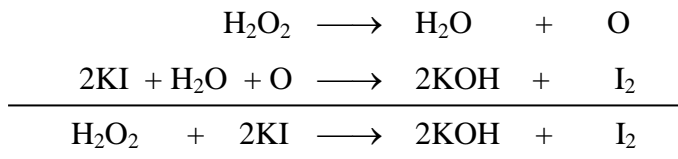
(a) It oxidizes lead sulphide to lead sulphate (in neutral solution)



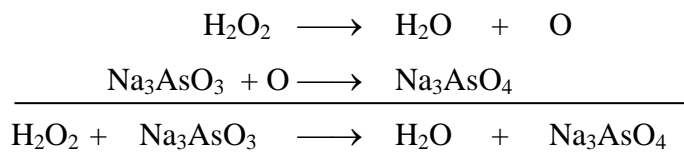
(b) It oxidizes acidified ferrous sulphate to ferric sulphate, (in acidic medium)



(c) It oxidizes potassium iodide to iodine, (in neutral solution)

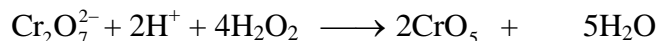


(d) It oxidizes sodium arsenite to sodium arsenate.



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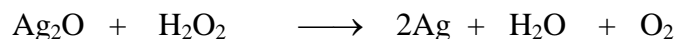
(e) With acidified potassium dichromate, it gives a deep blue solution containing CrO_5 , which is fairly stable in ethereal solution.



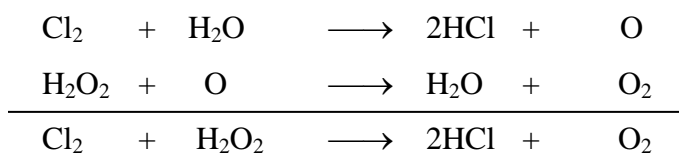
(iv) Reducing properties

Hydrogen peroxide acts as a reducing agent in the presence of other oxidizing agents. This is because it can take up an atom of oxygen to give water and oxygen gas. Some typical reactions showing the reducing property of hydrogen peroxide are given below.

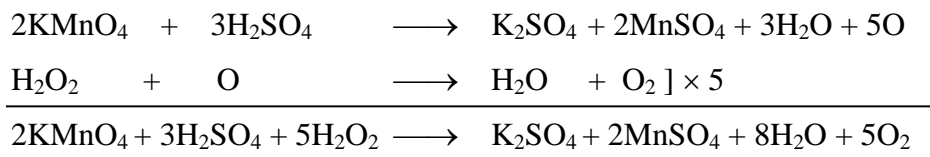
(a) It reduces silver oxide to silver



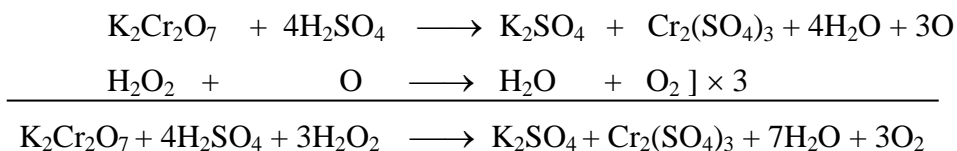
(b) It reduces chlorine to hydrochloric acid



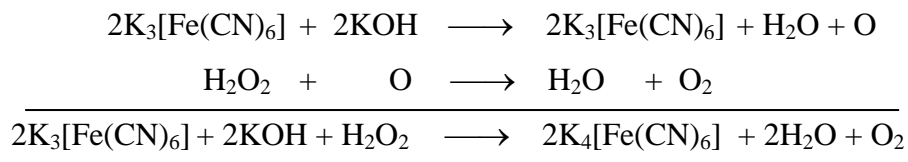
(c) It decolourises pink colour of acidified solution of potassium permanganate.



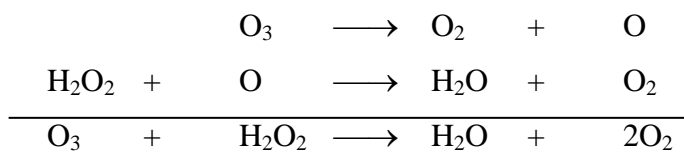
(d) It gives a green colour with acidified potassium dichromate solution.



(e) It reduced alkaline solution of potassium ferricyanide to potassium ferrocyanide.



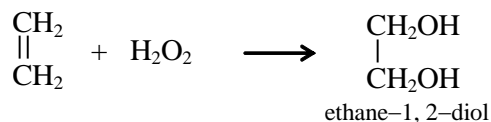
(f) It reduces ozone to oxygen



HYDROGEN and s-BLOCK ELEMENTS

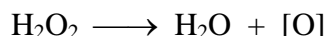
(v) Addition reaction

Hydrogen peroxide is capable of adding itself to double bond.



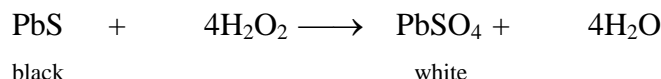
(vi) As a bleaching agent

It acts as a bleaching agent for delicate materials like wool, silk, ivory. It bleaches hair to golden yellow colour. The bleaching action of H_2O_2 is due to its oxidizing character.



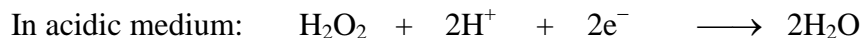
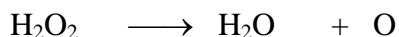
Uses of Hydrogen Peroxide

- (i) It is used as a mild bleaching agent for bleaching delicate articles such as hair, silk, wool, etc.
- (ii) It restores the colour of the old lead paints blackened by the action of H_2S . The lead sulphide (Black) gets oxidized to lead sulphate (white).



Oxidizing property of hydrogen peroxide

Hydrogen peroxide has a tendency to accept electrons in chemical reactions and thus behaves as an oxidizing agent in the acidic and alkaline media.



2. ALKALI METALS

All elements of group 1 are typical metals. These are referred to as alkali metals since they react with water to form highly alkaline substances. Francium is a radioactive element and its longest isotope has a half-life of 21 minutes. So very little is known about this element but in its properties it resembles with Cs and therefore has been placed in group I.

2.1 Physical Properties

We shall confine our discussion to only first five members of the family of alkali metals as very little is known about the last member, namely Francium.

A correlation between atomic and physical properties is discussed. Attempt has been made to explain the physical properties of alkali metals on the basis of two facts:

- (a) Size of the alkali metal atoms and ions.
- (b) Loose binding of electrons.

Melting Point and Boiling Point

All these elements are soft and have low melting point. This is due to the fact that they have only one valence electron per metal atom. Hence, the energy binding the atoms in the crystal lattice of the metal is relatively low. The melting points invariably decrease in moving down the group from Li to Cs. Thus, the melting point decreases with increase in size.

The boiling point also decreases in the same order as the melting point.

Ionization Energy

The first ionization energies for the atoms in this group are appreciably lower than those for any other group in the periodic table. The atoms are very large so the outer electrons are only held weakly by the nucleus hence the amount of energy needed to remove the outer electron is not very large. On descending the group from Li to Cs, the size of the atoms increases, the outermost electrons become less strongly held and so the ionization energy decreases.

The second ionization energy, that is, the energy to remove a second electron from the atoms is extremely high. The second ionization energy is always larger than the first, often by a factor of two, because it involves removing an electron from a smaller positive ion, rather than from a larger neutral atom. The difference between first and second ionization energies is much larger in this case since in addition it corresponds to removing an electron from a closed shell. A second electron is never removed under normal conditions, as the energy required is greater than that needed to ionise the noble gases. The elements commonly form M^+ ions.

Electronegativity

The electronegativity values for the elements in this group are very small, in fact the smallest values of any element. Thus, when these elements react with other elements to form compounds, a large electronegativity difference between the two atoms is probable and ionic bond is formed. However, *these elements also show covalent bonding* in certain cases. For example, the vapour of alkali metals contain diatomic molecules such as Na_2 , Cs_2 , which are covalently bonded. The strength of covalent bond in diatomic molecules decreases down the group.

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Photoelectric Effect and Colouration to the Flame

A result of the low ionization energies is that when these elements are irradiated with light, the light energy absorbed may be sufficient to make an atom lose an electron. Electrons emitted in this way are called photoelectrons and this explains the use of cesium and potassium as cathodes in photoelectric cells.

Electrons may also be quite readily excited to a higher energy level, for example in the flame test. To perform this test, a sample of the metal chloride, or any salt of the metal moistened with concentrated HCl, is heated on a platinum or nichrome wire in a Bunsen burner flame. In general chlorides are more volatile than most of other solids.



When an alkali metal or any of its compounds is heated in burner flame, the e^- s get excited to higher energy levels. When these electrons return to their original (ground level), the excitation energy which had been absorbed by then is released in the form of light, in the visible region of the spectrum. Now for the same excitation energy, the energy level to which the electron in Li rises is lower than that to which the electron in Na rises and this in turn, is lower than the level to which the electron in K rises and so on. These differences are on the account of differences in ionization energy emitted in the bunsen flame will be minimum in the case of Li. It increases in the order from lithium to Cs. Thus, the colour of the flame is crimson red in the case of Li, yellow in the case of Na, violet in the case of K and almost same in the case of Rb and Cs. The colours are specific as they correspond to the definite frequency.

Colour of Compounds

Colour arises because the energy absorbed or emitted in electronic transitions corresponds to a wavelength in the visible region. The group I metal ions all have noble gas configurations in which all the electrons are paired. Thus promoting an electron requires some energy to unpair an electron, some to break a full shell of electrons and some to promote the electron to a higher level. The total energy is large: hence there are no suitable transitions and the compounds are typically white. Any transitions, which do occur, will be of high energy, will appear in the ultraviolet region rather than in the visible region and will be invisible to the human eye. Compounds of Group I metals are typically white except those where the anion is coloured, for example sodium chromate $\text{Na}_2[\text{CrO}_4]$ (yellow), potassium dichromate $\text{K}_2[\text{Cr}_2\text{O}_7]$ (orange) and potassium permanganate $\text{K}[\text{MnO}_4]$ (deep purple). In these cases the colour comes from the anions $[\text{CrO}_4]^-$, $[\text{Cr}_2\text{O}_7]^{2-}$ or $[\text{MnO}_4]^-$ and not from the group I metal ion.

High Luster

This can also be explained due to the presence of highly mobile electrons of the metallic lattice. When the light wave interacts with the electrons of the metal and gets these in oscillatory motion. Like any other moving charged object, these moving electrons radiate electromagnetic energy as light. In other words, the beam of light is reflected from the metal surface.

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TRENDS IN PHYSICAL PROPERTIES OF Gr-IA ELEMENTS

Some physical constants of alkali metals are listed in given table

Property	Element				
	Li	Na	K	Rb	Cs
Atomic (metallic) radius, (pm)	155	190	236	248	267
Covalent radius, (pm)	123	154	203	216	235
Ionic radius, M^+ (pm)	60	95	133	148	169
Melting point, (K)	453.6	370.9	336.8	312.0	301.8
Boiling point, (K)	1603	1165	1033	961	943
Ionization enthalpy, (kJ/mol)	520.3	495.5	418.9	403.0	375.7
Density, (kg/L)	0.534	0.972	0.859	1.525	1.903
Electronegativity	1.0	0.9	0.8	0.8	0.7
E° , (V)	-3.05	-2.71	-2.92	-2.92	-2.92
Flame colour	Crimson red	Golden yellow	Violet	Violet	Violet
Oxidation state	+1	+1	+1	+1	+1
Hydration enthalpy, (kJ mol^{-1})	-520	-405	-321	-300	-277

Lattice Enthalpy of Alkali Metal Compounds

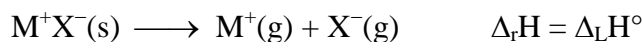
Lattice enthalpies ($\Delta_L H^\circ$) of alkali metal salts are very high. The lattice enthalpy decreases (in magnitude) down the group from Li to Cs.

Salt	Lattice enthalpy (kJ mol^{-1})	Salt	Lattice enthalpy (kJ mol^{-1})
LiCl	840	NaF	914
NaCl	770	NaCl	770
KCl	701	NaBr	728

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RbCl	682	NaI	680
CsCl	630		

The change in enthalpy when one mole of any crystalline solid is completely separated into its constituent units (ions if the solid is ionic and molecule if the solid is molecular) in the gaseous form under standard conditions is called lattice enthalpy ($\Delta_L H^\circ$). For example, the enthalpy change for the reaction,



is called the lattice enthalpy of $M^+X^-(s)$. As per definition lattice enthalpy is a positive quantity.

Compounds of alkali metals are ionic in nature. These compounds consist of cations and anions arranged in space around each other, which are held together by strong columbic forces. Therefore, lattice enthalpies of alkali metal salts are very high.

Lattice enthalpy of any salt depends directly upon the product of the charges on the cation and anion and inversely on the sum of ionic radii ($r_+ + r_-$). So, for a salt of particular type, the lattice enthalpy will be lower for bigger ions. That is why, the magnitude of the lattice enthalpy decreases in going from Li to Cs.

2.2 Chemical Properties

We shall confine our discussion to only first five members of the family of alkali metals as very little is known about the last member, namely Francium.

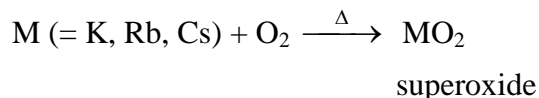
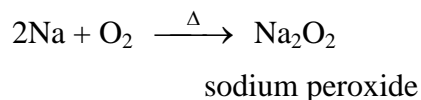
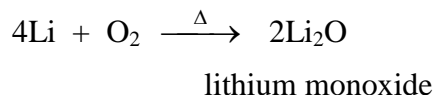
Alkali metals are highly reactive. This is due to,

- (a) their low ionization enthalpies
- (b) their low enthalpy of atomization.

The reactivity of alkali metals increases down the group, i.e. from Li to Cs. Some typical chemical reactions of alkali metals are described below.

Action of Air

Alkali metals react with air or oxygen rapidly and get tarnished due to the formation of oxide layer on the surface. Lithium when burnt in oxygen gives lithium monoxide.

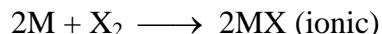


The peroxides (O_2^{2-}) and superoxides (O_2^-) are strong oxidizing agents and react with water to give H_2O_2 and O_2 .

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Reaction with Halogen:

Alkali metals react vigorously with halogens to form metal halides of the general formula MX.

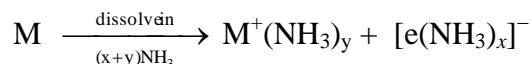


Solution of Metals in Liquid Ammonia

If a small amount of an alkali metal is dissolved in liquefied ammonia, the latter becomes light blue in colour. If more alkali metal is added in the ammonia the later becomes dark blue colour. If more alkali metal is added to the ammonia, a point is reached when a bronze coloured phase separates out and floats on the blue solution. Further addition of alkali metal results in the disappearance of blue solution and its complete conversion to bronze solution. Evaporation of ammonia from the bronze solution allows one to recover unchanged alkali metal. This unusual behaviour has fascinated chemists since its discovery in 1864. The interpretation is as follows:

The blue solutions exhibit the following characteristics:

1. Its colour, which is independent of the metal.
2. Its density, when is similar to that at pure NH_3 .
3. Its conductivity, which is in the same range as those of other electrolytes in NH_3 .
4. Its paramagnetism indicating unpaired electrons.
5. Its reversible nature.
6. Its strong reducing nature. This has been interpreted in terms of ionization of alkali metal to form alkali metal cations and electrons which are solvated by ammonia.



The dissociation into cation and electron accounts for the electrical conductivity. The dilute solutions thus consist of free e^- s (thus showing reducing behaviour); such solutions are metastable and when catalysed give hydrogen and amide.

The bronze solutions show the following characters.

1. Bronze colour with a metallic lustre.
2. Very low densities
3. Conductivities in the range of metals

2.3 Extraction of Sodium

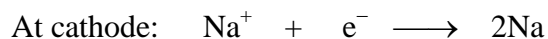
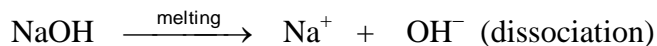
Alkali metals are strong reducing agents and therefore, cannot be extracted by reducing their oxides or other compounds. Sodium and potassium are therefore, obtained by electrolytic reduction of their molten hydroxides or chlorides. The extraction of sodium metal is described below.

Castner's Process

By the electrolysis of fused caustic soda.

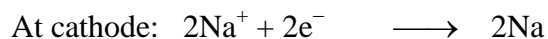
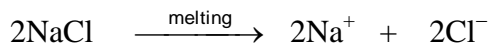
The various reactions taking place during electrolysis are represented below:

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Down's Process

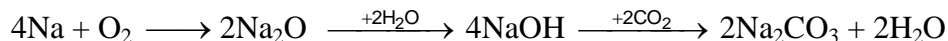
By the electrolysis of fused sodium chloride. Sodium chloride melts at higher temperature (1085 K). To lower the melting temperature of sodium chloride generally a mixture of NaCl (40%) and CaCl₂ (60%) or a mixture containing sodium chloride, potassium chloride and potassium fluoride (NaCl + KCl + KF) is employed. These mixtures melt at about 850–875 K.



2.4 Chemical Properties of Sodium

Action of Air

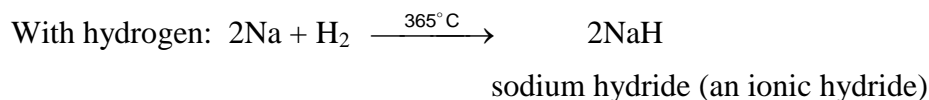
Sodium remains unaffected by dry air but gets readily tarnished in moist air forming a film of oxide, which reacts with moisture giving sodium hydroxide and finally carbonate



Sodium hydroxide is a strong alkali

Action with non-metals

Sodium combines directly with hydrogen, sulphur, halogens and other non-metals on heating.

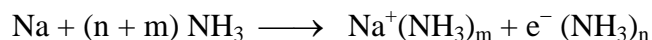


Action with Mercury

With mercury, sodium forms amalgams of varying composition, e.g. NaHg, Na₂Hg, Na₃Hg etc.

Solubility in Liquid Ammonia

Sodium dissolves in liquid ammonia to give conducting, blue-coloured solution. Blue colour of the solution is due to the presence of ammoniated electrons in solutions.

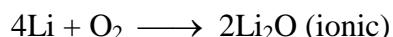


2.3 Compounds of Alkali Elements

Oxides, Peroxides and Superoxides

The nature of the alkali metal plays an important role when they are burnt in O₂.

(i) Li when burnt in air forms mainly lithium monoxide (O²⁻).

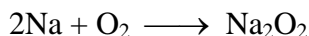


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(Lithiummonoxide)

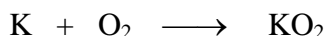
Tiny lithium ion has a strong positive field around it, which on combination with oxide anion restricts the spread of negative charge towards another oxygen atom and thus prevents the formation of higher oxide.

(ii) Na forms peroxide $(\text{O}_2)^{-2}$ on burning in O_2 .



The positive field around Na^+ is too weak to prevent the conversion of the oxide anion (O^{2-}) to a peroxide ion (O_2^{2-}) but is strong enough to prevent further oxidation to a superoxide ion.

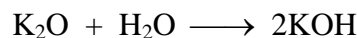
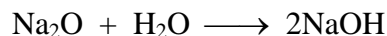
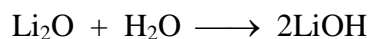
(iii) Other alkali metals react with O_2 to form superoxides of the type $\text{MO}_2(\text{O}_2^-)$



Potassium superoxide

The weak field around larger unipositive ions of potassium, rubidium and cesium allow the superoxide ion O_2^- to be formed.

The superoxides have the tetrahedral lattice of calcium carbide in which anion containing $3e^-$ bonds makes it paramagnetic and coloured. These oxides are usually basic.



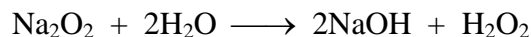
Two factors are, for the responsible of hydroxide ion formation.

(a) Polarity of bond:

Greater the polarity of bond, greater is the ease of ionization. The alkali metal hydroxides $\text{M}-\text{OH}$ don't greatly differ in polarity. This factor is not of much significance here.

(b) The internuclear distance between the oxygen of the hydroxide and metal ion:

Since the cation size increases from Li to Cs, hence internuclear distance increases with increasing atomic number of the metal. This results in greater separation of hydroxide ion from the metal ion. The strength of the bases increases from LiOH to $\text{Cs}-\text{OH}$.



Superoxides are even stronger oxidizing agents than peroxides and give both H_2O_2 and O_2 with either water or acids.

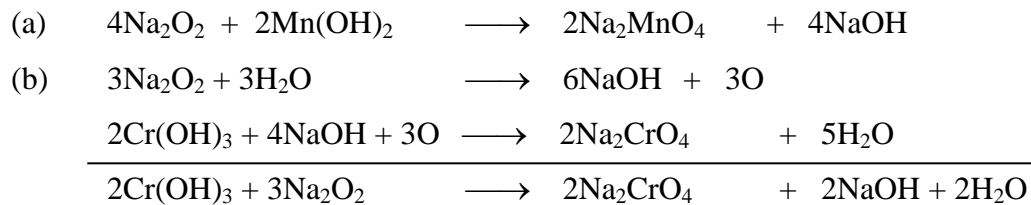


KO_2 is used in space capsules, submarines and breathing masks, because both of it produces oxygen and removes carbon dioxide. Both functions are important in life support systems.

Oxidizing Nature of Peroxides:

Sodium peroxide is a very powerful oxidizing agent. It oxidizes SO_2 to SO_3 , manganese(II) salts to manganates, chromium(III) salts to chromates etc.

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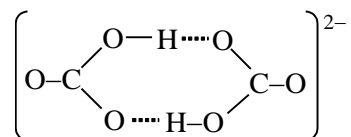


Sodium peroxide is a very strong oxidizing agent. It reacts with organic compounds violently. Sodium peroxide is widely used as a bleaching agent for wool, silk, hair, bones etc.

Oxosalts – Carbonates, Bicarbonates

Group I metals are highly electropositive and thus have quite stable and basic oxosalts. The carbonates are remarkably stable and will melt before they eventually decompose into oxides at temperatures above 1000°C . Li_2CO_3 is considerably less stable and decomposes more readily.

Because group I metals are so strongly basic, they also form solid bicarbonates (also called hydrogen carbonates). No other metals form solid bicarbonates, though NH_4HCO_3 also exists as a solid. Bicarbonates evolve carbon dioxide and turn into carbonates on gentle warming. This is one test for bicarbonates in qualitative analysis. The crystal structures of NaHCO_3 and KHCO_3 both show hydrogen bonding, but are different. In NaHCO_3 the HCO_3^- ions are linked into an infinite chain, whilst in KHCO_3 a dimeric anion is formed.



Lithium is exceptional in that it does not form a solid bicarbonate, though LiHCO_3 can exist in solution. All the carbonates and bicarbonates are soluble in water.

Halides

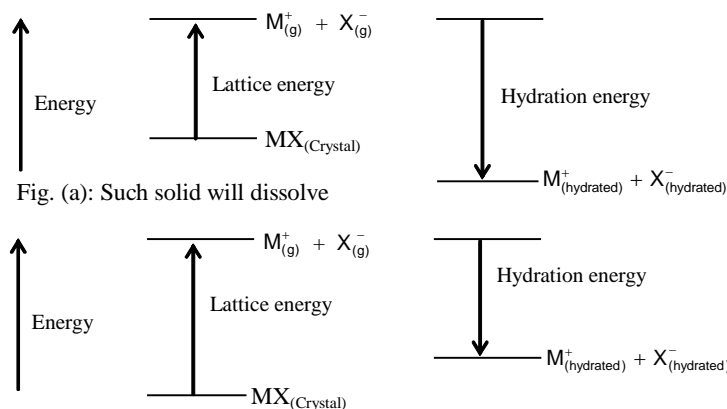
Alkali metals react vigorously with halogens to form metal halides of the general formula MX . Alkali metal halides are ideal ionic compounds i.e. their physical and chemical properties can be interpreted with reasonable accuracy on the assumption that ions are present in solid state. Therefore, the structure and stability of alkali metal halides are determined in part by the lattice energies and radius ratio effects as discussed below:

Solubility of Halides:

LiF is insoluble in water where as other alkali metals are soluble. This is because very small Li^+ is in combination with F^- . This results in high lattice energy of Li-F and thus it does not dissolve in H_2O . The solubility of most of the salts of Group I elements in water decreases on descending the group. For a substance to dissolve the energy evolved when the ions are hydrated (hydration energy) must be larger than the energy required to break the crystal lattice (lattice energy). Conversely, if the solid is insoluble, the hydration energy is less than the lattice energy. Strictly in the two cycles shown in given figure we should use Gibbs free energy ΔG values. In particular, the lattice energy is an enthalpy ΔH° term and we should use ΔG° the standard free energy for converting the crystalline salt into gaseous ions an infinite distance apart. However, the two terms differ only by a small term for the entropy of vaporization of the ions. It should in

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principle be possible to predict solubilities from lattice energies and hydration energies. In practice there are difficulties in predicting solubilities because the values for the data are not known very accurately and the result depends on a small difference between two large values.



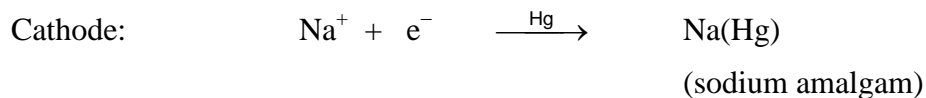
The reason why the solubility of most group I metals decreases on descending the group is that the lattice energy only changes slightly, but the free energy of hydration changes rather more. For example, the difference in lattice energy between NaCl and KCl is 67 kJ mol^{-1} and yet the difference in $\Delta G_{(hydration)}$ for Na^+ and K^+ is 76 kJ mol^{-1} . Thus KCl is less soluble than NaCl.

The group I fluorides and carbonates are exceptional in that their solubilities increase rapidly on descending the group. The reason for this is that their lattice energies change more than the hydration energies on descending the group. The lattice energy depends on electrostatic attraction between ions and is proportional to the distance between the ions, that is proportional to $1/(r^+ + r^-)$. It follows that the lattice energy will vary most when r^- is small, that is with F^- and will vary least when r^+ is large (with I^-). The weight of solute dissolving does not provide a very useful comparison of the solubilities, because the molecular weights differ. The easiest way to compare the number of ions is to compare the solubilities as molar quantities.

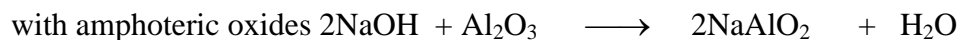
Sodium Hydroxide, (NaOH)

Sodium hydroxide is commonly called caustic soda because of its corrosive action on animal and vegetable tissues. Large quantity of sodium hydroxide is now a days prepared by electrolytic process. There are two electrolytic methods commonly used for preparing sodium hydroxide.

Castner–Kellner Cell:



Some typical chemical reactions given by sodium hydroxide are given below:



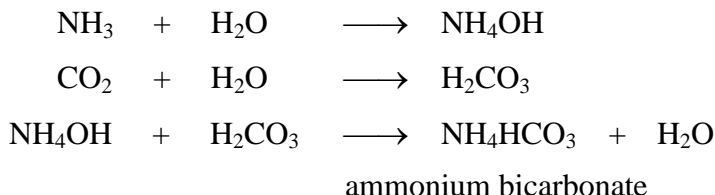
HYDROGEN and s-BLOCK ELEMENTS

Sodium Carbonate

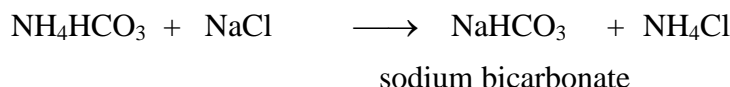
Sodium carbonate exists as anhydrous salt (Na_2CO_3) and also as a hydrated salt. The decahydrate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) is known as washing soda. The anhydrous salt is called soda ash.

Manufacture of sodium carbonate by the Solvay or Ammonia-soda process:

When carbon dioxide is passed into a concentrated solution of brine saturated with ammonia, ammonium bicarbonate is produced,



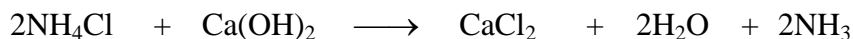
The ammonium bicarbonate then reacts with common salt forming sodium bicarbonate,



Sodium bicarbonate being only slightly soluble (in presence of sodium ions) gets precipitated. The precipitated sodium bicarbonate is removed by filtration and changed into sodium carbonate by heating.

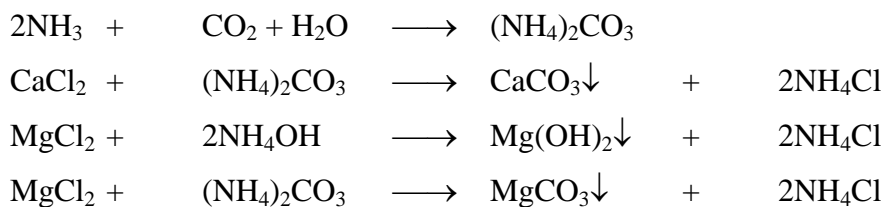


The mother liquor remaining after the precipitation of sodium bicarbonate contains ammonium chloride. This is then heated by steam with milk of lime to regenerate ammonia, which can be used as one of the raw materials.



(i) Saturating the ammoniating tank

In this tank, ammonia gas mixed with a little carbon dioxide gas (from ammonia recovery tower) is bubbled through a 20% sodium chloride solution (brine). Impurities of calcium and magnesium salts present in brine are precipitated as carbonates or hydroxides.



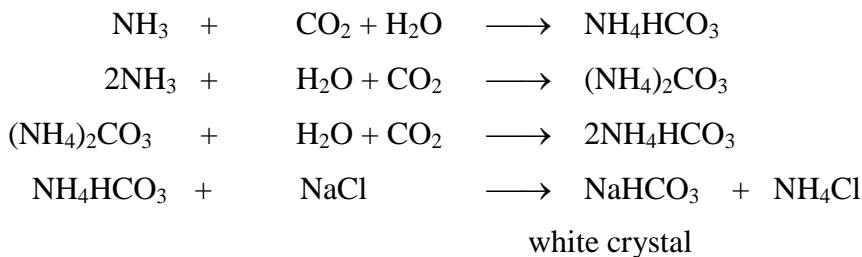
The ammonia that escapes absorption in the saturating tank is absorbed by ammonia absorption tower fitted at the top of the saturating tank.

(ii) Carbonating tower

In this tower carbonation of ammoniacal brine is carried out on the principle of counter-current. The clear ammoniacal brine solution is pumped to the top of the tower which flows downward and meets a current of carbon dioxide (obtained from a lime kiln) introduced from the bottom of

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the tower at a pressure of 1–2 atmosphere. As a result of reaction shown below, ammonium chloride and crystals of sodium bicarbonate are formed.



These crystals remain suspended in the mother liquor giving rise to thick milky liquid.

3. ALKALINE EARTH METALS

The elements are known as alkaline earth metals because:

- (i) Their oxides are similar to those of alkali metal oxides, i.e. their oxides react with water to give hydroxides, which are alkalies.
- (ii) The name “earth” was given by chemists to substance like alumina, which remained unchanged even on heating. Calcium and barium oxides could stand very high temperatures and hence they were also called “earths”. Thus, the metal Ca, Ba and Sr come to be known as alkaline earth metals. The name is now applied to all elements of group II A.

The oxides and hydroxides are less basic than those of group I, hence their oxosalts (carbonates, sulphates, nitrates) are less stable to heat.

Loose binding of ‘s’ electrons are responsible for the following properties:

- (i) Formation of bipoisitive ions
- (ii) Reducing agents
- (iii) Colouration to the flame.

3.1 Reducing Agents

The high negative value of standard electrode potential indicate that in aqueous solution these elements are good reducing agents quite comparable to alkali metals and this is due to their great hydration energies. The high negative E° values of these elements mean that all react vigorously with water also.

There is a gradual increase in the E° values of these elements indicating stronger tendency to act as reducing agents as we move down the group.

3.2 Coloration to the Flame Except Be and Mg

The chlorides of these elements produce characteristic flames due to easy excitation of electrons to higher energy levels.

In case of Be and Mg, the excitation energy is very high (because of their high I.E) and their salts don’t impart any colour to the flame. The flame spectra of alkaline earth metals are more

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complex than those of the alkali metals because their atoms have two 's' electrons, which are "excitable" at flame temperatures whereas alkali metals have only single 's' electron which is "excitable" at flame temperature.

3.3 Conductors of Heat and Electricity

In the metallic state, the two 's' electrons resonate and thus form covalent bonds between each atom and its nearest neighbour (roughly 12 in number) in the crystal lattice. These electrons can move through the crystal lattice under the influence of electrical potential. Consequently, elements are good conductors of heat and electricity.

3.4 Size of Atoms and Ions

Group II atoms are large, but are smaller than the corresponding group I elements as the extra charge on the nucleus draws the orbital electrons in. Similarly the ions are large, but are smaller than those of group I, especially because the removal of two orbital electrons increases the effective nuclear charge even further. Thus, these elements have higher densities than group I, metals.

Group II metals are silvery white in colour. They have two valency electrons that may participate in metallic bonding, compared with one electron for Group I metals. Consequently Group II metals are harder, have higher cohesive energy and have much higher melting points and boiling points than Group I elements, but the metal are relatively soft. The melting points do not vary regularly, mainly because the metals adopt different crystal structures.

The metal bond strength (as is evident from heat of atomisation) diminishes with increasing atomic number in the group as the size of the atoms increases.

Property	Element					
	Be	Mg	Ca	Sr	Ba	Ra
Covalent radius, (pm)	90	136	174	191	198	–
Melting point, (K)	1550	923	1111	1036	987	973
Boiling point (K)	1773	1380	1713	1653	1810	–
Ionization enthalpy $\Delta_I H_1$, (kJ mol ⁻¹) $\Delta_I H_2$	899.5 1757.1	737.7 1450.7	590.2 1145.4	547.5 1064.3	502.9 965.2	509.4 979.1
Density, (kg L ⁻¹)	1.84	1.74	1.55	2.54	3.75	6.00
Electronegativity	1.5	1.2	1.0	1.0	0.9	0.9

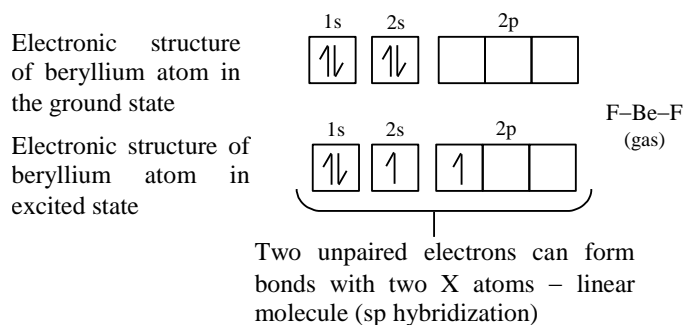
3.5 Anomalous Behaviour of Beryllium

Be differs from the rest of the group for three reasons.

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1. It is extremely small and Fajan's rules state that small highly charged ions tend to form covalent compounds.
2. Be has a comparatively high electronegativity. Thus when beryllium reacts with another atom, the difference in electronegativity is seldom large, which again favours the formation of covalent compounds. Even BeF_2 (electronegativity difference 2.5) and BeO (electronegativity difference 2.0) show evidence of covalent character.
3. Be is in the second row of the periodic table and the outer shell can hold a maximum of eight electrons. (The orbitals available for bonding are one 2s and three 2p orbitals. Thus Be can form a maximum of four conventional electron pair bonds and in many compounds the maximum coordination number of Be is 4. The later elements can have more than eight outer electrons and may attain a coordination number of 6 using one 's', three 'p' and two 'd' orbitals for bonding. Exceptions occur if multi-centre bonding occurs, as for example in basic beryllium acetate, when higher coordination numbers are obtained.

Thus, we should expect Be to form mainly covalent compounds and commonly have a coordination number of 4. Anhydrous compounds of Be are predominantly two-covalent and BeX_2 molecules should be linear.

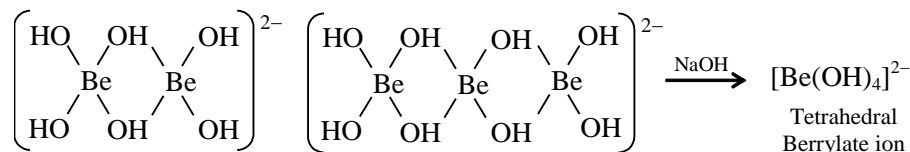


In fact linear molecules exist only in the gas phase, as this electronic arrangement has not filled the outer shell of electrons. In the solid state four fold coordination is always achieved. There are several ways by which this can be achieved.

- (i) Two ligands that have a lone pair of electrons may form coordinate bonds using the two unfilled orbitals in the valence shell of Be. Thus two F^- ions might coordinate to BeF_2 , forming $[\text{BeF}_4]^{2-}$. Similarly diethyl ether can coordinate to $\text{Be}(\text{II})$ in BeCl_2 , forming $[\text{BeCl}_2(\text{OEt})_2]$.
- (ii) The BeX_2 molecules may polymerise to form chains, containing bridging halogen groups, for example $(\text{BeF}_2)_n$, $(\text{BeCl}_2)_n$. Each halogen forms one normal covalent bond and uses a lone pair to form a coordinate bond.
- (iii) $(\text{BeMe}_2)_n$ has essentially the same structure as $(\text{BeCl}_2)_n$, but the bonding in the methyl compound is best regarded as three-centre two electron bonds covering one Me and two Be atoms.
- (iv) A covalent lattice may be formed with a zinc blende or wurtzite structure (coordination number 4), for example by BeO and BeS .

In water beryllium salts are extensively hydrolysed to give a series of hydroxo complexes of unknown structure. They may be polymeric and of the type:

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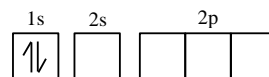


If alkali is added to these solutions, the polymers break down to give the simple mononuclear beryllate ion $[\text{Be}(\text{OH})_4]^{2-}$, which is tetrahedral. Many beryllium salts contain the hydrated ion $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$, which is tetrahedral. Many beryllium salts contain the hydrated ion $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ rather than Be^{2+} and the hydrated ion too is a tetrahedral complex ion. Note that the coordination number is 4. Forming a hydrated complex increases the effective size of the beryllium ion, thus spreading the charge over a larger area. Stable ionic salts such as $[\text{Be}(\text{H}_2\text{O})_4]\text{SO}_4$, $[\text{Be}(\text{H}_2\text{O})_4](\text{NO}_3)_2$ and $[\text{Be}(\text{H}_2\text{O})_4]\text{Cl}_2$ are known.

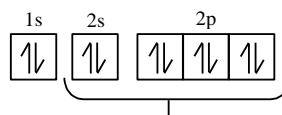
Electronic structure of beryllium atom in the ground state



Electronic structure of Be^{2+} ion

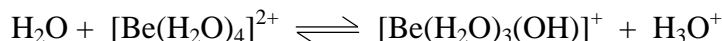


Electronic structure of Be^{2+} ion having gained four electron pairs from four oxygen atoms in water molecules



Four electron pairs tetrahedral (sp^3 hybridization)

Beryllium salts are acidic when dissolved in pure water because the hydrated ion hydrolyses producing H_3O^+ . This happens because the Be–O bond is very strong and so in the hydrated ion this weakens the O–H bonds and hence there is a tendency to lose protons. The initial reaction is



but this may be followed by further polymerization, involving hydroxobridged structures.

In alkaline solutions $[\text{Be}(\text{OH})_4]^{2-}$ is formed. The other group II salts do not interact so strongly with water and do not hydrolyse appreciably.

Beryllium salts rarely have more than four molecules of water of crystallization associated with the metal ion, because there are only four orbitals available in the second shell of electrons, whereas magnesium can have a coordination number of 6 by using some 3d orbitals as well as 3s and 3p orbitals.

3.6 Solubility and Lattice Energy

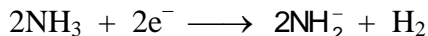
The solubility of most salts decreases with increased atomic weight, though the usual trend is reversed with the fluorides and hydroxides in this group. Solubility depends on the lattice energy of the solid and the hydration energy of the ions. With most compounds, on descending the group, the hydration energy decreases more rapidly than the lattice energy; hence the compounds become less soluble as the metal gets larger. However, with fluorides and hydroxides the lattice

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energy decreases more rapidly than the hydration energy and so their solubility increases on descending the group.

3.7 Solutions of the Metals in Liquid Ammonia

These metals, all dissolve in liquid ammonia as do the group I metals. Dilute solutions are bright blue in colour due to the spectrum from the solvated electron. These solutions decompose very slowly, forming amides and evolving hydrogen, but the reaction is accelerated by many transition metals and their compounds.



Evaporation of the ammonia from solutions of group I metals yields the metal, but with group II metals evaporation of ammonia gives hexammoniates of the metals. These slowly decompose to give amides.



Concentrated solutions of the metals in ammonia are bronze coloured, due to the formation of metal clusters.

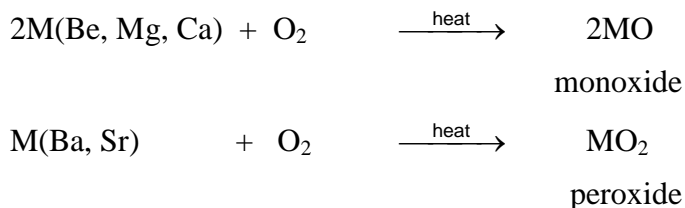
3.8 Compounds of Alkaline Earth Metals

Oxides and Peroxides

All the elements in this group burn in O_2 to form oxides MO . Be metal is relatively unreactive in the massive form and does not react below 600°C , but the powder is much more reactive and burns brilliantly. The elements also burn in air, forming a mixture of oxide and nitride.

Action of oxygen/air:

All the metals of this group (except Be and Mg) are easily oxidized by the atmospheric oxygen. Barium readily inflames in air. All alkaline earth metals have affinity towards oxygen.



Nature of oxides:

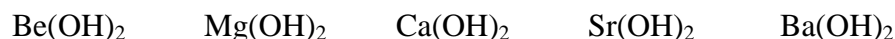
BeO is amphoteric, MgO is weakly basic, CaO is more basic while SrO and BaO are extremely basic.

Solubility:

BeO and MgO are insoluble in water, while the other oxides react with water to give corresponding hydroxides of the type $\text{M}(\text{OH})_2$, viz,



BeO and MgO are insoluble in water due to their large lattice enthalpies.



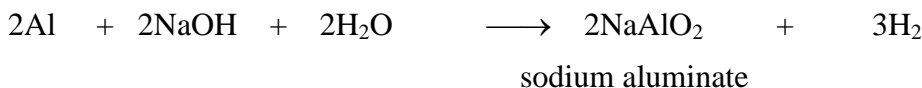
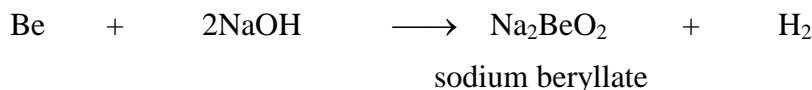
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amphoteric

strongly basic

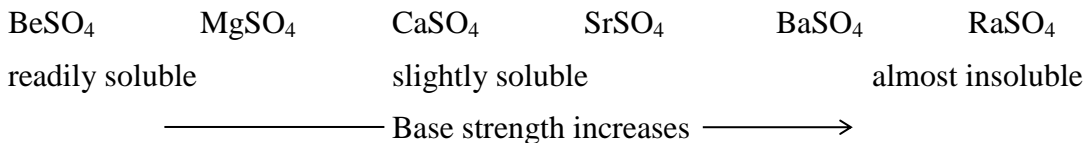
————— Base strength increases —————>

Be and Al dissolve in strong alkalis liberating hydrogen and forming beryllates and aluminates.



Sulphates

The sulphates of alkaline earth metals are less soluble than the sulphate of corresponding alkali metal. The solubility of the sulphates of alkaline earth metals decreases in going down the group. The solubilities of these sulphates in water follow the order,

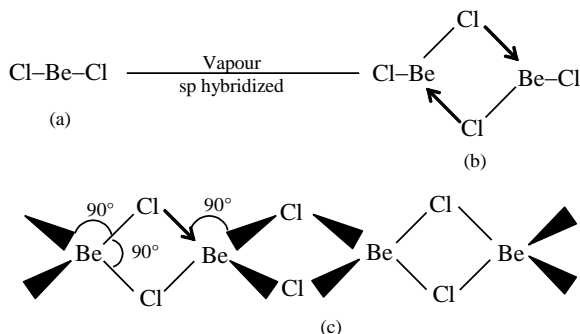


The lattice enthalpies of alkaline earth metal sulphates are higher than those of the alkali metal sulphates. This is why the sulphates of alkaline earth metals are less soluble than those of alkali metals.

On moving down the group, the hydration energy becomes smaller and therefore, the solubility of sulphates of alkaline earth metals decreases down the group.

Halides

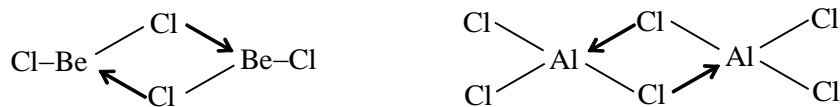
The anhydrous halides are polymeric. Beryllium chloride vapour contains BeCl_2 and $(\text{BeCl}_2)_2$, but the solid is polymerized. Though the structure of the $(\text{BeCl}_2)_n$ polymer is similar to that for $(\text{BeH}_2)_n$, the bonding is different. Both show clustering, but the hydride has three-centre bonding. Whereas the halides have halogen bridges, in which a halogen atom bonded to one beryllium atom uses a lone pair of electrons to form a coordinate bond to another beryllium atom.



Beryllium fluoride is very soluble in water, owing to the high solvation energy of Be in forming $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$. The other fluorides MF_2 are all almost insoluble.

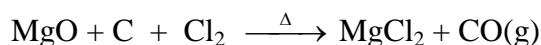
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Both BeCl_2 and Al_2Cl_6 are covalent and have a bridged polymeric structure. Both these chlorides are soluble in organic solvents and act as strong Lewis acid.



BeCl_2 can also polymerize in two dimensional plane an $(\text{BeCl}_2)_n$.

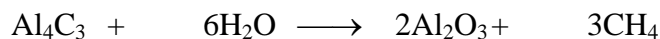
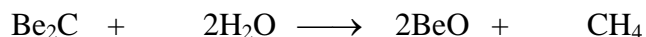
If magnesium chloride hydrate is heated strongly, it hydrolyses to yield magnesium oxide (magnesia) which is a refractory material and not the anhydrous magnesium chloride.



Magnesium chloride upon electrolysis gives magnesium metal at the cathode.

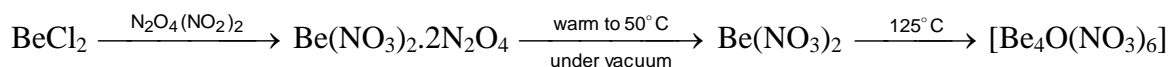
Carbides

The carbides of beryllium (Be) and aluminium (Al) react with water to give

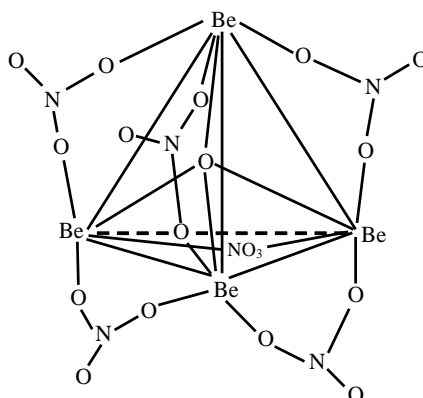


Nitrates

Nitrates of the metals can all be prepared in solution and can be crystallized as hydrated salts by the reaction of HNO_3 with carbonate oxides or hydroxides. Heating the hydrated solids does not give the anhydrous nitrate because the solid decomposes to the oxide. Anhydrous nitrates can be prepared using liquid dinitrogen tetra oxide and ethyl acetate. Beryllium is unusual in that it forms a basic nitrate in addition to the normal salt.



Normal Be nitrate



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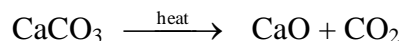
3.9 Some Important Compounds of Calcium

Important compounds of calcium are calcium oxide, calcium hydroxide, calcium sulphate, calcium carbonate and cement. These are industrially important compounds.

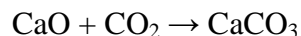
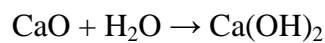
Calcium Oxide or Quick Lime, CaO

Preparation of Quick Lime:

Calcium oxide is prepared on a commercial scale by heating limestone (CaCO_3) in a rotary kiln at 1070-1270 K.

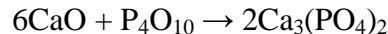
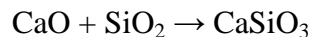


The carbon dioxide is removed as soon as it is produced to enable the reaction to proceed to completion. Calcium oxide is a white amorphous solid. It has a melting point of 2870 K. On exposure to atmosphere, it absorbs moisture and carbon dioxide.



The addition of limited amount of water breaks the lump of lime. This process is called slaking of lime. Quick lime slaked with soda gives solid sodalime.

Being a basic oxide, it combines with acidic oxides at high temperature.



Uses of Quick Lime:

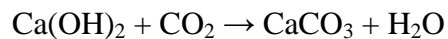
Quick lime is an important primary material for manufacturing cement and is the cheapest form of alkali. It is used in the manufacture of sodium carbonate from caustic soda. It is employed in the purification of sugar and in the manufacture of dye stuffs.

Calcium Hydroxide (Slaked lime), Ca(OH)_2

Preparation of Slaked lime:

Calcium hydroxide is prepared by adding water to quick lime, CaO. It is a white amorphous powder. It is sparingly soluble in water. The aqueous solution is known as lime water and a suspension of slaked lime in water is known as milk of lime.

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



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



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Uses of Slaked Lime:

Slaked lime is used in the preparation of mortar, a building material. It is used in white wash due to its disinfectant nature. It is used in glass making, in tanning industry, for the preparation of bleaching powder and for purification of sugar.

Bleaching Powder, $\text{Ca}(\text{OCl})_2$

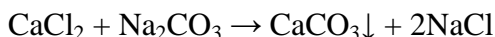
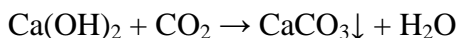
Milk of lime reacts with chlorine to form hypochlorite, a constituent of bleaching powder.



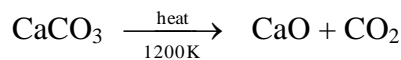
Calcium Carbonate, CaCO_3

Preparation of Calcium Carbonate:

Calcium carbonate occurs in nature in several forms like limestone, chalk, marble etc. It can be prepared by passing carbon dioxide through slaked lime or by the addition of sodium carbonate to calcium chloride. CaCO_3 gets precipitated because it is water insoluble.



Excess of carbon dioxide should be avoided since this leads to the formation of water soluble calcium hydrogencarbonate. Calcium carbonate is a white fluffy powder. It is almost insoluble in water. When heated to 1200 K, it decomposes to evolve carbon dioxide.



It reacts with dilute acid to liberate carbon dioxide gas.



Uses of Calcium Carbonate:

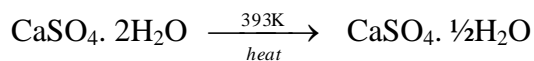
It is used as a building material in the form of marble and in the manufacture of quick lime. Calcium carbonate along with magnesium carbonate is used as a flux in the extraction of metals such as iron. Specially precipitated CaCO_3 is extensively used in the manufacture of high quality paper. It is also used as an antacid, mild abrasive in tooth paste, a constituent of chewing gum, and a filler in cosmetics.

Plaster of Paris [$(2\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O})$]

Calcium sulphate with half a molecule of water per molecule of the salt (hemihydrate) is called plaster of paris.

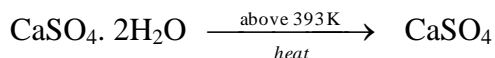
Preparation of Plaster of Paris:

Plaster of Paris is obtained when gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is heated to 393 K.



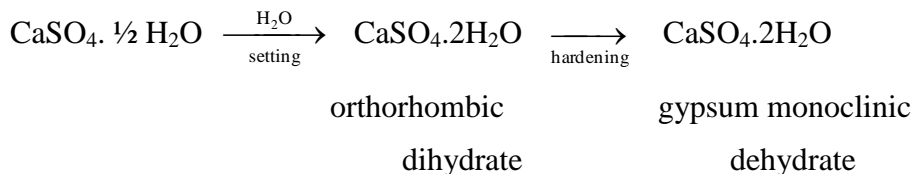
Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate, CaSO_4 is formed. This is known as 'dead burnt plaster'.

HYDROGEN and s-BLOCK ELEMENTS



Setting of Plaster of Paris:

Plaster of Paris has a remarkable property of setting with water. On mixing with an adequate quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes due to change in crystal structure.



Uses of Plaster of Paris:

The largest use of Plaster of Paris is in the building industry as well as plasters. It is used for immobilizing the affected part of organ where there is a bone fracture or sprain. It is also employed in dentistry, in ornamental work and for making casts of statues and busts.

3.10 Cement

Cement is an important building material. It is also called Portland cement because it resembles with the natural limestone quarried in the Isle of Portland, England. Cement is a product obtained by combining a material rich in lime, CaO with other material such as clay which contains silica, SiO₂ along with the oxides of aluminium, iron and magnesium.

Composition of Cement

The average composition of Portland cement is:

CaO (50-60%); SiO₂ (20-25%); Al₂O₃ (5-10%); MgO (23%); Fe₂O₃ (1-2%) and SO₃ (1-2%).

For a good quality cement, the ratio of silica (SiO₂) to alumina (Al₂O₃) should be between 2.5 and 4 and the ratio of lime (CaO) to the total of the oxides of silicon (SiO₂) aluminium (Al₂O₃) and iron (Fe₂O₃) should be as close as possible to 2.

The raw materials for the manufacture of cement are limestone and clay. When clay and lime are strongly heated together they fuse and react to form 'cement clinker'. This clinker is mixed with 2-3% by weight of gypsum (CaSO₄·2H₂O) to form cement. Thus important ingredients present in Portland cement are dicalcium silicate (Ca₂SiO₄) 26%, tricalcium silicate (Ca₃SiO₅) 51% and tricalcium aluminate (Ca₃Al₂O₆) 11%.

Setting of Cement

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

Uses of Cement

HYDROGEN and s-BLOCK ELEMENTS

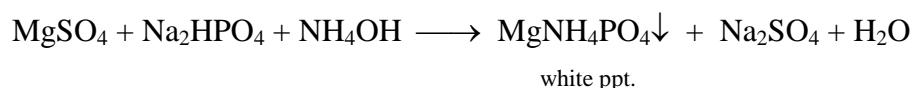
Cement has become a commodity of national necessity for any country next to iron and steel. It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

3.11 Complex Formation

Due to similar charge/radius ratio (i.e. cation) both Be^{2+} and Al^{3+} ions form complexes. For example, beryllium forms tetrahedral complexes, such as BeF_4^{2-} , $[\text{Be}(\text{C}_2\text{O}_4)_2]^{2-}$ and Al forms octahedral complexes such as AlF_6^{3-} and $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$ in solution.

3.12 Test for Mg^{2+} Ion

To a solution of any magnesium salt add ammonium hydroxide until it smells of ammonia. Add disodium hydrogen phosphate and scratch the sides of the test tube with a glass rod. Formation of white crystalline magnesium ammonium phosphate confirms the presence of Mg^{2+} in the given solution.



3.13 Biological Importance of Magnesium and Calcium

An adult body contains about 25 g of Mg and 1200 g of Ca compared with only 5 g of iron and 0.06 g of copper. The daily requirement in the human body has been estimated to be 200 – 300 mg. All enzymes that utilize ATP in phosphate transfer require magnesium as the cofactor. The main pigment for the absorption of light in plants is chlorophyll which contains magnesium. About 99 % of body calcium is present in bones and teeth. It also plays important roles in neuromuscular function, interneuronal transmission, cell membrane integrity and blood coagulation. The calcium concentration in plasma is regulated nearly at 100 mgL^{-1} . It is maintained by two hormones: calcitonin and parathyroid hormone. Bone is not an inert and unchanging substance but is continuously being solubilized and redeposited to the extent of 400 mg per day in man. All this calcium passes through the plasma.