YOGANAND H C , P.G.T CHEMISTRY J.N.V BIJAPUR ,KARNATAKA 586201 HYDROGEN

Hydrogen is the first element in the periodic table & is the lightest element known. It exist as diatomic molecule H_2 and is called <u>Dihydrogen</u>.

It was discovered by <u>Henry Cavendish in 1766</u> but the name Hydrogen was proposed by <u>Lavosier</u>, because it "<u>produces water on burning with oxygen</u>".

In Greek: "hydro" means "water", "gen" means "producing".

Unique position of Hydrogen in the periodic table:

Hydrogen is the **<u>first element</u>** in the periodic table.

Its atomic number is 1.

It has one proton & one electron.

Its electronic configuration is $1s^1$.

It resembles both alkali metals and halogens and, therefore, its position is anomalous.

Resemblances with alkali metals Group I:

<u>Hydrogen</u> resembles <u>alkali metals</u> such as lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs) and Francium of group I of the periodic table in the following respects;

1) Electronic configuration:

Hydrogen like alkali metals has one electron in its valence shell.

$$H(Z=1) = 1s^{1}$$

Li (Z=3) = [He] $2s^1$

Na (Z=11) =[Ne] 3s¹

 $K(Z=19) = [Ar] 4s^1$

2) Electropositive character:

Hydrogen like alkali metals is electropositive because it can lose one electron readily to form hydrogen ion (H^+) as

H $H^+ + e^-$

Na Na⁺ + e^{-}

3) Oxidation state:

Like alkali metals, hydrogen also shows an oxidation state of +1 in its compounds.

- H⁺Cl Hydrogen chloride
- Na⁺Cl Sodium chloride
- K⁺Cl Potassium chloride

4) Combination with electronegative elements:

Like alkali metals, hydrogen forms binary compounds with electronegative elements such as halogen, oxygen & sulphur.

Halides: HCl	NaCl, KCl
Sulphides: H ₂ S	Na_2S, K_2S
Oxides: H ₂ O	Na ₂ O, K ₂ O

Resemblance with halogens:

1. Electronic configuration:

Like halogens, hydrogen has only one electron less than the nearest noble gas configuration.

$H(Z=1)=1s^{1}$	$He(Z=2)=1s^2$
$F(Z=9)=1s^2 2s^2 2p^5$	Ne (Z=8)= $1s^2 2s^2 2p^6$
$Cl(Z=17)= 1s^2, 2s^2, 2p^6, 3s^23p^5$	$Ar(z=18)=1s^2, 2s^2, 2p^6, 3s^23p^6$

2. Non-metallic character: like halogens, hydrogen is non-metallic in nature.

3. Atomicity(Diatomic nature): Hydrogen molecule is diatomic (H_2) like halogen molecules (F_2, I_2, Cl_2, Br_2) .

4. Electronegative character:

Hydrogen like halogens has tendency to accept electron to form monovalent anion. By accepting an electron hydrogen as well as halogens acquire noble gas configuration.

H + 1e H^- (He gas configuration)F + 1e F^- (Ne gas configuration)Cl + 1e Cl^- (Ar gas configuration)

5. Oxidation state: Like halogens, hydrogen exhibits oxidation state of -1in its compounds.

Na⁺H⁻

Na⁺Cl⁻

Sodium hydride

Sodium chloride

6. Formation of similar types of compounds: Like halogens, hydrogen combines with non metals such as carbon, silicon, germanium etc to form covalent compounds.

- i. Halides: CCl₄, SiCl₄, GeCl₄
- ii. Hydrides: CH₄, SiH₄, GeH₄

In spite of the fact that hydrogen resembles with alkali and halogens to certain extent, it differ from them as well.

Difference from alkali metals:-

1) Ionization enthalpy:

The ionization enthalpy of hydrogen is very high in comparison to alkali metals.

2) Non- metallic character:

Alkali metals are typical metals while hydrogen is non-metal.

3) Atomicity:

Hydrogen is diatomic, while alkali metals are monoatomic.

4) Nature of compounds:

The compounds of hydrogen are predominantly covalent while those of alkali metals are ionic. For example: HCl is covalent, while NaCl is ionic. The oxides of alkali metals are basic ,while hydrogen oxide is neutral.

Difference from halogens:-

1) Less tendency for hydride formation:

Hydrogen has less tendency to take up electron to form hydride ion (H^-) as compared to the halogens which form halide ions (X^-) very easily.

2) Absence of unshared pairs of electrons:

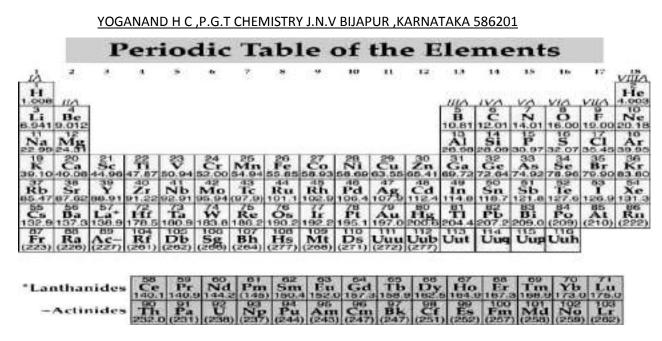
The hydrogen & halogens are diatomic in nature in which the atoms are held by covalent bonds.

However, <u>hydrogen do not possess any unshared pair of electrons</u> where as there are <u>three unshared electron pairs on each halogen atom in its molecule</u>.

H−H :Ċi—Ċi:

3) Nature of oxides: The oxides of halogens are acidic, while hydrogen oxide is neutral.

Thus hydrogen is unique in its behaviour & is therefore, best placed separately in the periodic table.



DIHYDROGEN: [H₂]

Occurrence of Hydrogen:

Hydrogen, the <u>most abundant element in the universe</u> (70% of the total mass of the universe) and the third most abundant on the surface of the globe (earth), is being visualised as the major <u>future source of energy</u>.

Isotopes of hydrogen:

Hydrogen has three isotopes namely;

- 1) Protium $-(_1H^1)$
- 2) Deuterium $(_1H^2)$ or D
- 3) Tritium $(_1H^3)$ or T

S.N.	Property	Protium	Deuterium	Tritium
1	Relative abudance	99.985 %	0.015 %	10 ⁻¹⁵ %
2	Relative atomic mass	1.007825	2.014102	3.016
3	Radioactive stability	Non- radioactive	Non- radioactive	Radioactive $t_{1/2} = 12.334$ yrs

PREPARATION OF DIHYDROGEN:

I) Laboratory preparation of dihydrogen:

a) It is usually prepared by the reaction of granulated zinc with dilute hydrochloric acid.



b) It can also be prepared by the reaction of zinc with aqueous alkali like NaOH.

$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$

II)Commercial Production of Dihydrogen:

a) Electrolysis of water:

Dihydrogen of high purity is usually prepared by the electrolysis of water using platinum electrodes in the presence of small amount of acid. A small quantity of acid is added to increase the conductivity of water.

$$2 H_2 O(l) \longrightarrow 2 H_2(g) + O_2(g)$$

During electrolysis, dihydrogen is collected at cathode & dioxygen is liberated at anode.

b) By the electrolysis of brine solution:

Hydrogen gas is obtained as byproduct in the manufacture of sodium hydroxide. When the aqueous brine is electrolysed NaOH,Cl2 &H₂ are produced.

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Brine →sodium hydroxide + chlorine + hydrogen

2\operatorname{NaCl}_{(aq)}+2\operatorname{H}_2\operatorname{O}_{(L)} \rightarrow 2\operatorname{NaOH}_{(aq)} + \operatorname{Cl}_{2(g)} + \operatorname{H}_{2(g)}

⊕ Anode: 2\operatorname{Cl}^{-}(aq) \longrightarrow \operatorname{Cl}_2(g) + 2e^{-}

⊖ Cathode: \operatorname{H}_2\operatorname{O}(I) \longrightarrow \operatorname{H}^+(aq) + \operatorname{OH}^-(aq)

\stackrel{\checkmark}{\xrightarrow{}} \operatorname{H}^+(aq) + 2e^{-} \longrightarrow \operatorname{H}_2(g)
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c) By the reaction of steam on hydrocarbons or coke :-

The reaction of steam with hydrocarbon like methane at very high temperature in the presence of catalyst like nickel results in the formation of water gas (mixture of CO & H_2).

CH₄ + H₂O = CO + 3 H₂ methane water carbon hydrogen monoxide

As this mixture of gas (mixture of CO & H_2) is used for the synthesis of methanol & number of other hydrocarbons. <u>Water gas nowadays is called **syngas**</u>.

 $CO + 2H_2 \longrightarrow CH_3OH$

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Nowadays, syngas is produced by using coal & that process is called "coal gasification".

 $C + H_2O \longleftrightarrow CO + H_2$ (Gasification with Steam)

The production of dihydrogen gas is increased by treating carbon monoxide with steam at 1270 K in the presence of iron chromate catalyst. This reaction is called water gas shift reaction.

 $CO + H_2O \longleftrightarrow H_2 + CO_2$ (Water-Gas Shift Reaction)

PROPERTIES OF DIHYDROGEN:

Physical properties of dihydrogen:

- 1) It is slightly soluble in water (about 2 %).
- 2) It is highly combustible and therefore should be handled carefully.
- 3) It lightest substance. The weight of one litre hydrogen at NTP is only 0.0899 g.

Chemical properties of dihydrogen:

Dihydrogen is **not very reactive due to high bond dissociation** energy (435.88 kJ mol⁻¹ at 298.2 K).

1) Reaction of dihydrogen with halogen:

Dihydrogen reacts with halogens in the presence of light to give hydrogen halides.

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$$

 $H_2 + Cl_2 \xrightarrow{dark} No reaction$

This reaction of hydrogen with fluorine occurs even in the dark, with iodine it requires a catalyst.

2) Reaction of dihydrogen with dioxygen:

Dihydrogen reacts with dioxygen to form water. This reaction is **highly exothermic**. $H = -285.9 \text{kJ mol}^{-1}$

<u>YOGANAND H C , P.G.T CHEMISTRY J.N.V BIJAPUR , KARNATAKA 586201</u> 3)Reaction with diniotrogen:(manufacture of ammonia)

Dihydrogen reacts with dinitrogen in the presence of iron(as catalyst) & molybdenum (as promoter) at 673 K under 200atm pressure forms ammonia.

$$N_2 + 3H_2 \xrightarrow{673 \text{ K/200 atm}} 2\text{NH}_3(g); \Delta H^\circ = -92.6 \text{ kJ mol}^{-1}$$

4) Reaction with metals:

Reactive metals like Na, K, Ca, Li reacts with hydrogen at a high temperature (500 K -550 K) to form **hydrides.**

$$2Na + H_2 \xrightarrow{\Delta} 2NaH$$

$$Ca + H_2 \xrightarrow{\Delta} CaH_2 (Hydrolith)$$

5) Reactions with metal oxides & metal ions:

Dihydrogen acts as a strong reducing agent and therefore, <u>it reduces</u> <u>metal oxides (less reactive than iron) to metals.</u>

$$CuO + H_2 \xrightarrow{\Delta} Cu + H_2O$$

In general,

$$yH_2(g) + M_xO_y(s) \longrightarrow xM(s) + yH_2O(l)$$

Dihydrogen reduces few metal ions like Pd^{2+} , Cu^{2+} in aqueous solution respective metals.

$$H_2(g) + Pd^{2+}(aq) \longrightarrow Pd(s) + 2H^+(aq)$$

6) Reactions with organic compounds:

Dihydrogen reacts with many organic compounds in the presence of catalysts to give useful hydrogenated products of commercial importance.

i) Hydrogenation of oils:-

Vegetable oils are polyunsaturated in nature. The C=C bonds in oils can easily undergo oxidation and the oil becomes rancid i.e., unpleasant in taste & smell. <u>Hydrogenation</u> reduces the number of double bonds and there by reduces the rancidity.



Hydrogenation of vegetable oils using nickel as catalyst gives edible fats (margarine & vanaspati ghee).

Veg. oil + H₂
$$\xrightarrow{\text{Ni/400K}}$$
 Veg. ghee

ii) Hydroformylation of olefins to aldehydes:

Olefins are the group of unsaturated open chain hydrocarbons possessing one or more double bonds, the simplest of which is ethylene.

Olefins react with <u>carbon monoxide and dihydrogen</u> in the presence of **octacarbonyl dicobalt** $[Co(CO)_4]_2$ as catalyst under high temperature & pressure to form aldehydes. This reaction is called hydroformylation or oxo process.

$$R - CH = CH_2 + H_2 + CO \xrightarrow{[Co(CO)_4]_2} RCH_2CH_2CHO$$

The aldehyde ,thus formed is further reduced to <u>alcohol by nickel</u>.

$$RCH_2CH_2CHO + H_2 \xrightarrow{Ni} RCH_2CH_2CH_2OH$$

Uses of Dihydrogen:

1) The largest single use of H_2 is in the synthesis of NH_3 which is used in the manufacture of HNO_3 and nitrogenous fertilizers.

2) Dihydrogen is used in the manufacture of vanaspati fat by the hydrogenation of polyunsaturated vegetable oils like soyabean, cotton seeds etc.

3) Dihydrogen is used in the manufacture of bulk organic chemicals such as methanol.

$$\operatorname{CO}(g) + 2\operatorname{H}_2(g) \xrightarrow{\operatorname{Co}} \operatorname{CH}_3\operatorname{OH}(l)$$

4) Dihydrogen is used in the manufacture of metal hydrides, hydrogen chloride etc

5) Dihydrogen is used as rocket fuel in space research.

6) Atomic hydrogen & oxy-hydrogen torches are used in cutting & welding purposes.

Dihydrogen is dissociated with the help of an electric arc & the hydrogen atoms thus produced are allowed to recombine on the surface to be welded to generate high temperature of 4000K.

7) Dihydrogen is used in fuel cells for generating electrical energy. It produces large energy per unit mass of fuel in comparison to other fuels.

HYDRIDES:

The compounds of hydrogen with metals and non-metals are called hydrides.

Under certain conditions H_2 combines with almost all the elements, except noble gases to form binary compounds called hydrides.

Types of hydrides:

There are *three types of hydrides*, they are

- (i) Ionic or saline hydrides or salt like hydrides.
- (ii) Covalent or molecular hydrides.

(iii) Metallic or non-stoichiometric hydrides.

Ionic or saline hydrides or saltlike hydrides:

Ionic or saline hydrides are the <u>compounds of H_2 formed with most of the s-block</u> <u>elements</u>, which are <u>highly electro positive in nature</u>.

These are <u>formed by elements of group I & II (except Be and Mg because they form covalent hydrides) by heating them in hydrogen.</u> These are white colourless solids (crystalline) having high MP and BP.

These are easily decomposed by water, CO2_etc

 $CaH_2 + 2H_2O$ $Ca(OH)_2 + 2H_2$

 $CaH_2 + 2CO_2$ (HCOO)₂Ca (calcium formate)

Ionic hydrides are strong reducing agents. Alkali metal hydrides are used for making $LiAlH_4$, $NaBH_4$ etc which are strong reducing agents and for removing last traces of water from organic compounds.

Covalent & Molecular Hydrides:

Covalent or molecular hydrides are the **compounds of hydrogen formed with most of the p-block elements having higher electro negativity than hydrogen**. Common elements are **B**,**C**,**N**,**F**,**P**,**S**,**G**a,**G**e etc

Molecular hydrides are further classified in to <u>three types</u> based on the relative <u>number of</u> <u>electrons in their Lewis structure</u>.

- a) Electron deficient hydrides.
- b) Electron precise hydrides.
- c) Electron rich hydrides.

Electron deficient hydrides:

These are the <u>hydrides</u>, which do not have sufficient number of electrons needed to form <u>normal covalent bonds</u>.

The hydrides of group 13 elements are electron deficient hydrides.

Examples: BH₃ (Borane), B₂H₆ (Diborane), AlH₃ (Aluminium hydride) etc.

Electron precise hydrides:

These are the <u>hydrides</u>, which have exact number of electrons needed to form normal <u>covalent bonds</u>. The hydrides of group 14 elements are electron **precise** hydrides.

Examples: CH_4 , SiH_4 (silane or silicon tetra hydride) etc

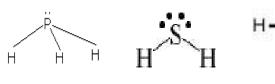
Electron rich hydrides:

These are the <u>hydrides</u>, <u>which have greater/excess number of electrons than required to form</u> <u>normal covalent bonds</u>. The excess electrons in these hydrides are present as lone pairs of electrons.

The hydrides of group 15 to 17 form electron **rich** hydrides.

Examples: NH₃, PH₃, H₂S, HF, HCl, H₂O etc

Metallic or non-stoichiometric hydrides:

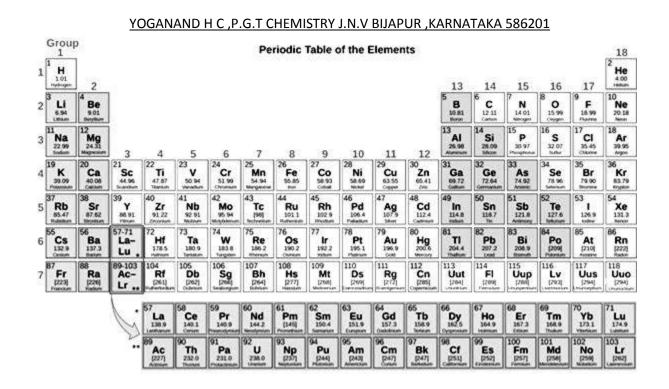


Metallic hydrides are formed by many d-block and f-block elements of the periodic table. The transition metals and rare earth metals combine with hydrogen to from interstitial hydrides.

They exhibit metallic properties and are powerful reducing agents. They are nonstoichiometric hydrides and their composition varies with temperature and pressure. In these hydrides **law constant composition does not hold good**.

Examples: LaH_{2.87}, TiH_{1.73},ZrH_{1.75}

Metals of group 7, 8 and 9 do not form hydrides and this region of the Periodic Table is called hydride gap.



Water:

Water is the most abundant and widely distributed on the earth. It occurs in all the three physical states. Human body has about 65% of water and some plants have as much as 95% water.

Physical Properties of Water:

1. Water is a <u>colourless</u>, <u>odourless</u>, <u>tasteless liquid</u>. It has <u>abnormally high B.P</u>, <u>high F.P &</u> <u>high heat of vaporisation compared to H_2S and H_2Se (Dihydrogen selenide) due to</u> <u>extensive hydrogen bonding</u>.

2. Pure water is not a good conductor, so it is made conductor by adding small amount of acid or alkali.

3. Density of ice (which is mass per unit volume) is lesser than that of water and it floats over water.

4. Water is a highly polar solvent with high dielectric constant 78.39. It interacts with polar or ionic substances effectively with the release of considerable amount of energy due to ion dipole interaction. The dissolution of covalent compounds like urea, glucose and C₂H₅OH, etc is due to the tendency of these molecules to form hydrogen bond with water.

YOGANAND H C , P.G.T CHEMISTRY J.N.V BIJAPUR ,KARNATAKA 586201 STRUCTURE OF WATER:

H₂**O** is a <u>covalent molecule</u> consists of two hydrogen atoms bonded to oxygen atom by covalent bonds.

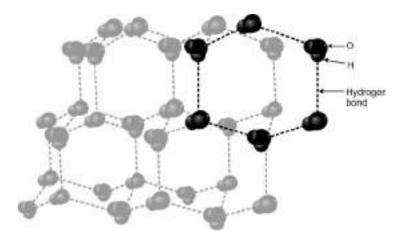
The <u>oxygen in the water</u> molecule is \underline{sp}^3 hybridised. Out of <u>four sp^3 hybrid orbitals</u>, <u>two sp^3 hybrid orbitals</u> form <u>covalent bond with s-orbitals of two hydrogen atoms</u> and <u>remaining two lone pairs of electrons</u>.

Due to the presence of two lone pairs of electrons on the oxygen atom, there is <u>repulsion with two bonded pair of electrons</u>. Due to this repulsion, <u>the tetrahedral</u> structure of water gets distorted & hence the geometry of water appears **bent or angular** with a bond angle 104.5° & O-H bond length is 95.7pm.



Structure of ice:-

Ice has <u>highly ordered three dimensional hydrogen bonded structure</u> as shown below. <u>Each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a</u> <u>distance of 276 pm.</u> <u>Hydrogen bonding gives ice a rather open type structure with wide holes</u>. These holes can hold some other molecules of appropriate size interstitially.



Chemical Properties of Water:

1. Water is amphoteric in nature:

It has the ability to acts as an acid as well as a base i.e., it behaves as an amphoteric substance.

With <u>NH₃ it acts as an acid</u> & with H_2S or HCl, it acts as base.

 $H_{2}O(l) + NH_{3}(aq) \rightleftharpoons NH_{4}^{+}(aq) + OH^{-}(aq)$ acid base acid base $H_{2}O(l) + H_{2}S(aq) \rightarrow H_{3}O^{+}(aq) + HS^{-}(aq)$

 $\begin{array}{c} H_2O(l) + HCl(aq) \rightleftharpoons H_3O^+(aq) + Cl^-(aq) \\ \text{base} & \text{acid} \end{array}$

The auto-protolysis (self ionisation) of water takes place as follows;

 $H_2O(1) + H_2O(aq) \rightarrow H_3O^+(aq) + OH^-(aq)$

2. Redox reactions involving water:

<u>Water can be easily reduced to H_2 by highly electropositive metals.</u>

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

With fluorine also, water is oxidised to oxygen.

 $2\mathbf{F}_2(g) + 2\mathbf{H}_2\mathbf{O}(l) \longrightarrow 4\mathbf{H}^+ + 4\mathbf{F}^- + \mathbf{O}_2(g)$

3. Hydrolysis reaction:

Due to high dielectric constant, it has a very strong hydrating tendency .It dissolves many ionic compounds.

	P ₄ O ₁₀ (s)	+	6H ₂ 0(I)	\rightarrow	4H ₃ PO ₄ (aq)
Tetraphosphorus decaoxidePhospharic acid					
	SiCl ₄ (I)	+	2H ₂ O(I)	\rightarrow	SiO ₂ (s) + 4HCl(aq)

Silicon tetrachloride

4. Hydrates formation:-

From the aqueous solutions, many <u>salts can be crystallized as hydrated salts</u>. It is of different types.

a) Coordinated water: Example; $[Cr(H_2O)_6]^{3+}$ $3Cl^{-}$

b) Interstitial water: Example; BaCl₂.2H₂O

c) Hydrogen bonded water: Example; $[Cu(H_2O)_4]^{2+}$ SO₄²⁻. H₂O in CuSO₄.5 H₂O

Hard & Soft Water:-

The <u>water</u> which <u>contains dissolved salts of bicarbonates</u>, <u>sulphates and chlorides of calcium</u> and <u>magnesium</u> is called **hard water**. Hard water does not produce lather with soap solution. <u>Soft water</u> is free from <u>bicarbonates</u>, <u>sulphates and chlorides of calcium and magnesium</u>. It produces lather with soap solution easily. Examples: distilled water, rain water.

Reaction of soap with hard water:

Soap is sodium or potassium salts of higher fatty acids like stearic acid ($C_{17}H_{35}COOH$), oleic acid ($C_{17}H_{33}COOH$) or palmitic acid($C_{17}H_{31}COOH$).

When soap is added to hard water, anionic part of soap react with Ca^{2+} or Mg^{2+} ions to form white precipitate of calcium and magnesium salts called scum(technically called lime soap), which are insoluble in water.

 $2 C_{17}H_{35}COO^{-}Na^{+} + Ca^{2+}$

 $(C_{17}H_{35}COO)_2Ca + 2 Na^+$

Calcium stearate(scum)

 $2 C_{17}H_{35}COO^{-}Na^{+} + Mg^{2+} (C_{17}H_{35}COO)_{2}Mg + 2 Na^{+}$

Magnesium stearate(scum)

It is <u>unsuitable for the laundry</u>. It is also <u>harmful for boilers</u> because of <u>deposition of salts</u> in the form of scale, which in turn <u>reduces the efficiency of boilers</u>.

Types of hardness:-

The hardness of water is of two types

(i)Temporary hardness:

Due to presence of soluble **bicarbonates** of calcium and magnesium. Temporary hardness can be removed by **simple boiling**.

Temporary hardness of water is also called carbonate hardness.

(ii)Permanent hardness

Due to presence of **chlorides and sulphates** of calcium and magnesium. Permanent hardness of water can be removed by **special treatments**.

Permanent hardness is also called non-carbonate hardness.

Softening of water:-

The process of removal of Ca^{2+} and Mg^{2+} ions from hard water is called **softening of** water.

<u>YOGANAND H C , P.G.T CHEMISTRY J.N.V BIJAPUR , KARNATAKA 586201</u> <u>I Removal of Temporary Hardness of water:</u>

<u>Temporary hardness</u> of water is due to the presence of <u>magnesium and calcium bi</u> <u>carbonates.</u> It can be removed by the following processes;

(a) By boiling:

During boiling, the soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ is changed to <u>insoluble CaCO_3</u>. Thus soluble bicarbonates of Ca & Mg are converted into Ca & Mg insoluble carbonates. These precipitates can be removed by filtration. The filtrate thus obtained is soft water.

 $\begin{array}{ccc} \text{Ca} (\text{HCO}_3)_2 & \xrightarrow{\text{Heat}} & \text{Ca} \text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2\\ \text{Insoluble} \\ \\ \text{Mg} (\text{HCO}_3)_2 & \xrightarrow{\text{Heat}} & \text{Mg}(\text{OH})_2 + 2\text{CO}_2\\ \text{Insoluble} \end{array}$

(b) By Clark's method: or calcium hydroxide method

In this method, <u>calculated amount of lime $[Ca(OH)_2]$ is added to hard water</u>. It precipitates out calcium carbonate and magnesium hydroxide which can be filtered off.

$Ca(HCO_3)_2 + Ca(OH)_2$	$2CaCO_3$	$+ 2H_2O$
(Soluble)	(Insoluble)	
$Mg(HCO_3)_2 + 2Ca(OH)_2$	2CaCO ₃	+ $Mg(OH)_2$ + $2H_2$
(Soluble)	(Insoluble)	(Insoluble)

II.Removal of Permanent Hardness of water:

Permanent hardness of water is <u>due to the presence of chlorides and sulphates of</u> <u>magnesium and calcium.</u> Permanent hardness of water <u>cannot be removed by boiling</u> but can be removed by special methods as shown below;

1) By washing soda (Na₂CO₃.10H₂O) treatment:

In this method, water is treated with a <u>calculated amount of washing soda(Na_2CO_3)</u>, which converts the <u>chloride & sulphates of calcium and magnesium</u> into their respective insoluble <u>carbonates</u>.

$CaCl_2$	+ Na_2CO_3	$2CaCO_3 + 2NaCl$
		(Insoluble)
MgSO ₄	+ Na_2CO_3	$MgCO_3 + Na_2SO_4$
		(Insoluble)

2) By Calgon's process(Sequestration):

This is the <u>most modern method of the softening of water</u>. In this method, <u>the Ca²⁺ and</u> Mg^{2+} ions present in the hard water are sequestered (rendered ineffective) in the form of soluble complexes by adding sodium poly metaphosphate(commercially called **Calgon**-meaning **calcium gone**).

Commonly used calgon is sodium hexametaphosphate $Na_6P_6O_{18}$ or $Na_2[Na_4(PO_3)_6]$, which combines with calcium and magnesium ions to form complex ions ,which are soluble in water .

 $Na_{2}[Na_{4}(PO_{3})_{6}] + 2 Ca^{2+} Na_{2}[Ca_{2}(PO_{3})_{6}] + 4 Na^{+}$

 $Na_2[Na_4(PO_3)_6] + 2 Mg^{2+}$ $Na_2[Mg_2(PO_3)_6] + 4 Na^+$

The complex <u>calcium and magnesium ions do not form any precipitate with soap</u> and therefore water can easily form lather with soap.

3) Ion- exchange method:(permutit method or Zeolite method)

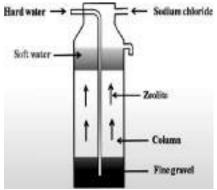
(Inorganic cation exchanger)

In this method, <u>the ions responsible for the hardness of water are exchanged by certain</u> <u>less damaging ions</u> present in some chemical compounds called **ion exchangers like zeolites**.

Zeolites are the <u>hydrated sodiumaluminium silicates</u> ($Na_2Al_2Si_2O_8.X H_2O$) which have <u>interesting property of</u> exchanging cations such as Ca^{2+} and Mg^{2+} ions present in the hard water with Na^+ ions.

Zeolites are **naturally occurring**, where as artificial zeolites which are artificially synthesised is called <u>**Permutit.**</u>

$\begin{array}{rl}Na_{2}Al_{2}Si_{2}O_{8}\ +\ CaCl_{2}\\Zeolite\end{array}$	$Ca(Al_2Si_2O_8)_2 + 2NaCl$ Settles at bottom
$\begin{array}{rl} Na_2Al_2Si_2O_8 \ + \ MgCl_2 \\ Zeolite \end{array}$	$Mg(Al_2Si_2O_8)_2 + 2NaCl$ Settles at bottom





The <u>zeolite can be regenerated by treatment with sodium chloride</u> <u>solution</u>.

 $Ca(Al_2Si_2O_8)_2 + 2NaCl \qquad Na_2Al_2Si_2O_8 + CaCl_2$

 $Mg \; (Al_2Si_2O_8)_2 \; + \; 2NaCl \qquad \qquad Na_2Al_2Si_2O_8 \; + \; MgCl_2$

<u>YOGANAND H C, P.G.T CHEMISTRY J.N.V BIJAPUR, KARNATAKA 586201</u> 4) Synthetic resin method or organic ion exchanger (ion exchange resins):-

Synthetic resins are the insoluble polymeric solids having **giant hydrocarbon** network containing reactive acidic or basic groups. These are <u>superior to Zeolite</u>, because <u>they can</u> remove all types of cations as well as anions present in water. This resulting water is known as <u>demineralised or deionised water</u>.

These are two types of resins namely:

a)Cation exchange resins:

They have <u>acidic groups such as COOH (carboxyl group) or SO₃H (sulphonyl group)</u>. They may be represented as **Resin-H⁺**. These are <u>capable of exchanging the H⁺ ions with cations</u> of the hard water (Ca²⁺ and Mg²⁺ ions) and hence are called cation exchange resins or cation exchangers.

 $\begin{array}{rll} Ca^{2+} &+& 2H\text{-}Resin & Ca(Resin)_2 &+& 2H^+ \\ & Cation exchanger & \\ Mg^{2+} &+& 2H\text{-}Resin & Mg(Resin)_2 &+& 2H^+ \\ & Cation exchanger & \end{array}$

Exhausted anion exchange resin beds are regenerated by treatment with dilute acid solutions.

b) Anion exchange resins:

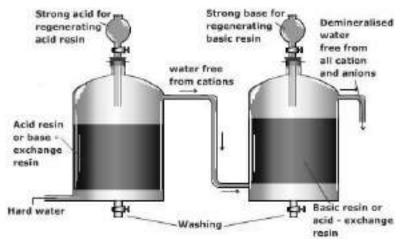
They have <u>basic groups such as $-OH^-$ or $-NH_2$ </u>. They may be represented as **Resin**—OH or **Resin** NH^+OH^-

Resin—NH₃ OH

These are capable of exchanging the OH⁻ with anions of the hard water (SO₄²⁻ and Cl⁻ ions)</sup> and hence are called anion exchange resins or anion exchangers.</sup>

SO_4^{2-}	+ 2HO-Resin	SO_4 (Resin) ₂	+ 20H ⁻
Cl	anion exchanger + HO-Resin anion exchanger	Cl (Resin)	+ OH ⁻

Exhausted anion exchange resin beds are regenerated by treatment with dilute alkali solutions.



<u>YOGANAND H C , P.G.T CHEMISTRY J.N.V BIJAPUR , KARNATAKA 586201</u> <u>**Hydrogen peroxide** $[H_2O_2]$:</u>

Hydrogen peroxide was discovered by French chemist J.L. Thenard in 1818. It is an important chemical used in pollution control treatment of domestic and industrial effluents.

Methods of preparation:

1) From Barium peroxide:-

Hydrogen peroxide was first prepared by J. L. Thenard in 1818 by <u>acidifying barium</u> <u>Peroxide using H_2SO_4 and removal of excess water by evaporation</u> under reduced pressure.

 $BaO_2 \cdot 8H_2O + H_2SO_4 \longrightarrow BaSO_4 + 8H_2O + H_2O_2$

Barium sulphate is filtered off leaving behind H_2O_2 .

2) From sodium peroxide (Merck's process):-

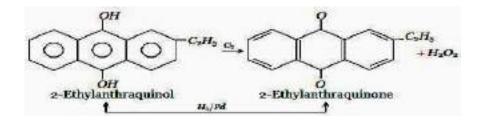
Sodium peroxide on acidification with sulphuric acid to form hydrogen peroxide. This method of preparation of hydrogen peroxide is called Merck's process.

Na_2O_2	+	H_2SO_4	Na_2SO_4	+	H_2O_2

(20% ice cooled solution)

3) By auto oxidation of 2-alkylanthraquinols:-(Ex: 2-ethyl anthraquinol)

Industrially hydrogen per oxide is prepared by the auto oxidation of 2-ethylanthraquinol. This is a <u>reversible reaction</u>, after the removal of hydrogen per oxide, the oxidised product 2-ethylanthraquinone is reduced to 2-ethylantraquinol using hydrogen in the presence of <u>palladium</u> catalyst.



Store of Hydrogen peroxide:-

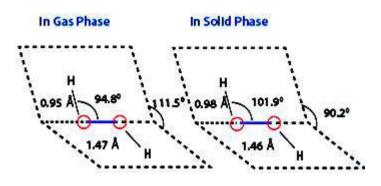
- a) It must be kept in **wax lined coloured bottles** because the **rough glass surface causes its decomposition** $(2H_2O_2 \qquad 2H_2O + O_2)$.
- b) A small amount of phosphoric acid, glycerol or acetanilide is generally added which retard the decomposition of H_2O_2 . These are also called negative catalysts. Sometimes urea is also added as <u>stabiliser</u>.

^{(30%} solution)

<u>YOGANAND H C , P.G.T CHEMISTRY J.N.V BIJAPUR , KARNATAKA 586201</u> Structure of hydrogen peroxide:

Hydrogen peroxide has a *non planar structure*, in which <u>two H-atoms are arranged in</u> <u>two directions almost perpendicular to each other</u> and <u>to the axis joining the two oxygen</u> <u>atoms.</u>

The <u>O-O linkage</u> is called <u>peroxide linkage</u>. In the soild phase, dihedral angle is reduced to 90.2° from 111.5° in the gas phase.



Physical properties of Hydrogen peroxide:-

1. In the pure state, H_2O_2 is an almost colourless (very pale blue) liquid. 2. H_2O_2 is miscible with water in all proportions and forms a hydrate H_2O_2 . H_2O (MP 221K).

3. A **30% solution of H_2O_2** is marketed as '100 volume' hydrogen peroxide. It means that one millilitre of 30% H_2O_2 solution on decomposition will give 100 V of oxygen at STP. Commercially, H_2O_2 is marketed as **10 V**, which means it contains **3% H_2O_2**.

Chemical properties of Hydrogen peroxide:-

1) Acidic nature:

It is **weakly acidic in nature** and pure hydrogen peroxide <u>turns blue litmus red</u>.

2) Oxidising agent :

It acts as a strong oxidising agent in acidic as well as in basic medium.

i) Oxidising action in acidic medium: H_2O_2 oxidises the ferrous sulphate to ferric sulphate.

 $2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + H_2O$ $2Fe^{2+} + 2H^+ + H_2O_2 \qquad 2 Fe^{3+} + 2H_2O$ $PbS + 4 H_2O_2 \qquad PbSO_4 + 4H_2O$

ii) Oxidising action in basic medium: In basic medium, H_2O_2 oxidises chromium salts to chromates.

 $2Cr^{3+} + 3H_2O_2 + 10OH^- \longrightarrow 2CrO_4^{2-} + 8H_2O_4$

In basic medium, H₂O₂ oxidises manganese sulphate to manganese dioxide.

 $MnSO_4 + H_2O_2 + 2 NaOH \qquad 2MnO_2 + Na_2SO_4 + 2 H_2O$ $Mn^{2*} + H_2O_2 + 2OH^- \longrightarrow MnO_2 + 2H_2O$

2) Reducing agent :

It acts as a strong reducing agent in acidic as well as in basic medium.

i) Reducing action in acidic medium:

H₂O₂ reduces acidified Potassium permanganate solution to colourless manganese sulphate.

 $2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O_4 + 5O_2$ $MnO_4^- + 6H^+ + 5H_2O_2 - 2Mn^{2+} + 8H_2O + 5O_2$

ii) Reducing action in basic medium:

In basic medium, H₂O₂ reduces potassium permanganate to manganese dioxide.

 $2KMnO4 + 3H_2O_2 = 2MnO_2 + 2H_2O + 3O_2 + 2KOH$

 $2 \text{ MnO}_4^- + 3 \text{ H}_2\text{O}_2$ $2 \text{ MnO}_2 + 2 \text{ H}_2\text{O} + 3\text{O}_2^- + \text{OH}^-$

In basic medium, H₂O₂ reduces potassium ferricyanide to potassium ferrocyanide.

 $2K_{3}[Fe(CN)_{6}] + 2KOH + H_{2}O_{2} \longrightarrow$ $2K_{4}[Fe(CN)_{6}] + 2H_{2}O + O_{2}$ $[Fe(CN)_{6}]^{3} + 2OH^{2} + H_{2}O_{2} \qquad [Fe(CN)_{6}]^{4} + 2H_{2}O + O_{2}$

Uses of hydrogen peroxide:

1) Domestically hydrogen peroxide is used as hair bleach and disinfectant.

2) It is used as bleaching agent in industries such as textile, paper, leather etc

3) It is used as antiseptic to wash wound, teeth, ear under the name perhydrol.

4) It is used in the manufacture of sodium perborates & percarbonates, which are the constituents of very high quality detergents.

5) It is used in the manufacture of cephalosporins antibiotics & food products such as tartaric acid.

6) Nowadays, it is used in pollution control treatment of domestic and industrial effluents, oxidation of cyanides & restoration of aerobic conditions.

Heavy Water [D2O]:

Chemically heavy water is deuterium oxide. It was discovered by Urey in 1932.

It can be prepared by exhaustive electrolysis of ordinary water using nickel electrodes.

It is colourless, odourless, tasteless liquid.

Uses of Heavy Water:

It is used

- 1. in nuclear reactors to slow down the speed of neutrons and called moderator.
- 2. as a tracer compound to study the mechanisms of many reactions.