POSITION OF HYDROGEN IN THE PERIODIC TABLE

Group 1 and Group 17 Yes Yes and No No , Thus,
it is unique in behaviour and is, therefore, best placed separately in the periodic table.

DIHYDROGEN, H_2

- **Occurrence**

70% of the total mass of the universe ; 0.15% by mass in the earth's atmosphere ; in the combined form it constitutes 15.4% of the earth's crust and the oceans.

- **Isotopes of Hydrogen**

Hydrogen has three isotopes: **protium**, H, **deuterium**, $^{2}_{1}H$ or D and **tritium**, $^{3}_{1}H$ or T. These isotopes differ from one another in respect of the presence of neutrons. Ordinary hydrogen, protium, has no neutrons, deuterium (also known as heavy hydrogen) has one and tritium has two neutrons in the nucleus.

The predominant form is protium. Terrestrial hydrogen contains 0.0156% of deuterium mostly in the form of HD. The tritium concentration is about one atom per 1018 atoms of protium. Of these isotopes, only tritium is radioactive and emits low energy β^- particles.

Atomic and Physical Properties of Hydrogen

Property	Hydrogen	Deuterium	Tritium
Relative abundace (%)	99.985	0.0156	10^{-15}
Relative atomic mass (g mol^{-1})	1.008	2.014	3.016
Melting point / K	13.96	18.73	20.62
Boiling point /K	20.39	23.67	25.0
Density / gL^{-1}	0.09	0.18	0.27
Enthalpy of fusion/KJ mol^{-1}	0.117	0.197	–
Enthalpy of vaporization/kJ mol^{-1}	0.904	1.226	–
Enthalpy of bond dissociation/kJ mol^{-1} at 298.2K	435.88	443.35	–
Internuclear distance/pm	74.14	74.14	–
Ionization enthalpy/kJ mol^{-1}	1312	–	–
Electron gain enthalpy/kJ mol^{-1}	–73	–	–
Covalent radius/pm	37	–	–
Ionic radius(H^-)/pm	208		

isotopes same electronic configuration, same chemical properties. The only difference is in their rates of reactions, mainly due to their different enthalpy of bond dissociation. However, in physical properties these isotopes differ considerably due to their large mass differences.

- **Different forms of Hydrogen :**

(a) Based on oxidation Number.

There are three types of hydrogen

	H^+ Proton	H^- Hydride	H Atomic hydrogen
Number of electron	0	2	1
Oxidation number	+1	–1	0
Formation	$H \rightarrow H^+ + e^-$	$H + e^- \rightarrow H^-$	$H_2 \xrightarrow{\Delta} 2H$

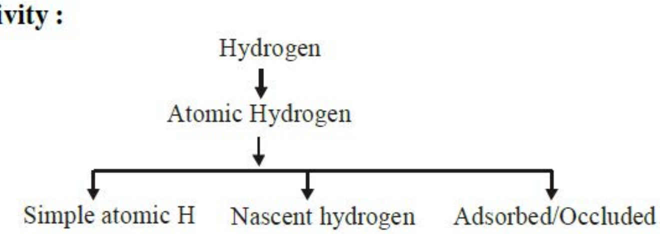
Note : In the aqueous state proton (H^+) exist as $H^+(H_2O)_n$

Where n is a large number.

If $n = 1 \longrightarrow H_3O^+$

$n = 2 \longrightarrow H^+(H_2O)_2$

(b) Based on reactivity :



- **Atomic hydrogen :**

(i) Simple atomic hydrogen – It is formed by simple dissociation of hydrogen.

$$H_2 \underset{}{\overset{3000\text{-}5000}{\rightleftharpoons}} 2H$$

Favourable condition – Favourable condition are high temp & low pressure.

(ii) Nascent hydrogen – Hydrogen at the moment of its birth it called nascent hydrogen means which forms at the instant is known as Nascent hydrogen.

It is formed only by some specific chemical reaction.

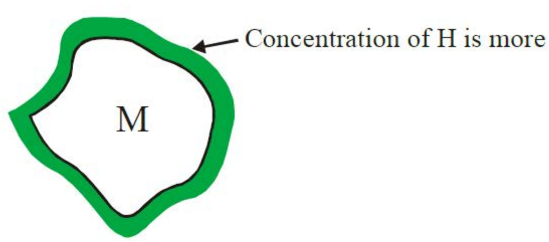
(a) Acid + Metals $\quad Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$

(b) Base + amphoteric metal (Be, Zn, Al, Ga, Pb, Sn) $\quad 2NaOH + Be \longrightarrow Na_2BeO_2 + 2H$

(c) C_2H_5OH + Alkali metal

$$C_2H_5OH + Na \longrightarrow C_2H_5ONa + H$$

(iii) Adsorbed/Occluded hydrogens



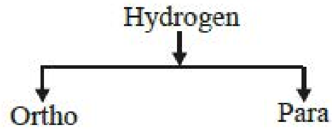
Adsorbed H is hydrogen present at the outer surface of metal.

- **Occlusion :** The property of metal to adsorb any gas is called occlusion.

Reactivity order

Atomic hydrogen > Nascent hydrogen > Molecular hydrogen

(iii) Based on Nuclear spin (Nuclear isomers)



(a) **Ortho hydrogen :** The molecular form of hydrogen having same spin of nucleus is called ortho hydrogen.

(b) **Para hydrogen :** The molecular form of hydrogen having opposite spin of nucleus is called para hydrgen.

In ortho hydrogen spin of nucleus is same, so they will repel each other & because of this repulsion, internal energy of ortho hydrogen increases. So ortho hydrogen has more internal energy.

- **Stability of ortho & Para hydrogen**

Stability of ortho & para hydrogen depends upon temperature condition.

At low temp : para hydrogen is more stable than ortho hydrogen while at high temp ortho hydrogen is more stable than para hydrogen.

$$P_{H_2} \underset{T\downarrow}{\overset{T\uparrow}{\rightleftharpoons}} O_{H_2}$$

	Ortho	Para
At high temperature	75%	25%
At absolute zero temp.	0	100%

- **Imp. Note :**

(i) We can obtain 100% pure para hydrogen at low temp but can't ortho because at high temp parahydrogen will dissociate into atomic hydrogen.

(ii) Ortho & Para hydrogen differs only in physical properties but have same chemical properites.

Laboratory Preparation of Dihydrogen

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

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

(ii) It can also be prepared by the reaction of zinc with aqueous alkali.

$$Zn + 2NaOH \rightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2$$

Commercial Production of Dihydrogen

(i) Electrolysis of acidified water using platinum electrodes gives hydrogen.

$$2H_2O(\ell) \xrightarrow[\text{Trances of acid/base}]{\text{Electrolysis}} 2H_2(g) + O_2(g)$$

(ii) High purity (>99.95%) dihydrogen is obtained by electrolysing warm aqueous barium hydroxide solution between nickel electrodes.

(iii) It is obtained as a byproduct in the manufacture of sodium hydroxide and chlorine by the electrolysis of brine solution. During electrolysis, the reactions that take place are: at anode:

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

at cathode: $2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

The overall reaction is

$$2Na^+(aq) + 2Cl^-(aq) + 2H_2O(\ell) \rightarrow Cl_2(g) + H_2(g) + 2Na^+(aq) + 2OH^-(aq)$$

(iv) Reaction of steam on hydrocarbons or coke at high temperatures in the presence of catalyst yields hydrogen.

$$C_nH_{2n-2} + nH_2O \xrightarrow[\text{Ni}]{1270\text{ K}} nCO + (2n-1)\,H_2$$

e.g.,

$$CH_4(g) + H_2O(g) \xrightarrow[\text{Ni}]{1270\text{ K}} CO(g) + 3H_2(g)$$

The mixture of CO and H_2 is called *water gas*. As this mixture of CO and H_2 is used for the synthesis of methanol and a number of hydrocarbons, it is also called *synthesis gas or* **'syngas'**. Nowadays 'syngas' is produced from sewage, saw-dust, scrap wood, newspapers etc. The process of producing 'syngas' from coal is called *'coal gasification'*.

$$C(s) + H_2O(g) \xrightarrow{1270\text{K}} CO(g) + H_2(g)$$

The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst (Fe_2O_3 and Cr_2O_3).

$$CO(g) + H_2O(g) \xrightarrow[\text{catalyst}]{673\text{K}} CO_2(g) + H_2(g)$$

This is called water-gas shift reaction /**Bosch process**. Carbon dioxide is removed by scrubbing with sodium arsenite solution. Presently ~77% of the industrial dihydrogen is produced from petro-chemicals, 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

❑ PROPERTIES OF DIHYDROGEN

◆ Physical Properties

Dihydrogen is a colourless, odourless, tasteless, combustible gas. It is lighter than air and insoluble in water.

- **Chemical Properties**

determined, to a large extent, by bond dissociation enthalpy. The H–H bond dissociation enthalpy is the highest for a single bond between two atoms of any element because the dissociation of dihydrogen into its atoms is only ~0.081% around 2000K which increases to 95.5% at 5000K. Also, it is relatively inert at room temperature due to the high H–H bond enthalpy. Thus, the atomic hydrogen is produced at a high temperature in an electric arc or under ultraviolet radiations. Since its orbital is incomplete with $1s^1$ electronic configuration, it does combine with almost all the elements. It accomplishes reactions by (i) loss of the only electron to give H^+, (ii) gain of an electron to form H^-, and (iii) sharing electrons to form a single covalent bond.

- ***Reaction with halogens :*** It reacts with halogens, X_2 to give hydrogen halides HX,

$$H_2(g) + X_2(g) \rightarrow 2HX(g)\ (X = F, Cl, Br, I)$$

While the reaction with fluorine occurs even in the dark, with iodine it requires a catalyst.

- ***Reaction with dioxygen:*** It reacts with dioxygen to form water. The reaction is highly exothermic.

$$2H_2(g) + O_2(g) \xrightarrow{\text{catalyst or heating}} 2H_2O(\ell);\ \Delta H^\ominus = -285.9\ \text{kJ mol}^{-1}$$

- ***Reaction with dinitrogen:*** With dinitrogen it forms ammonia.

$$3H_2(g) + N_2(g) \xrightarrow[\text{Fe}]{673K/200atm} 2NH_3(g)\ ;\ \Delta H^\ominus = -92.6\ \text{kJ mol}^{-1}$$

This is the method for the manufacture of ammonia by the Haber process.

- ***Reactions with metals :*** With many metals it combines at a high temperature to yield the corresponding hydrides.

$$H_2(g) + 2M(g) \rightarrow 2MH(s)\ ;$$

where M is an alkali metal

- ***Reactions with metal ions and metal oxides:*** It reduces some metal ions in aqueous solution and oxides of metals (less active than iron) into corresponding metals.

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

$$yH_2(g) + M_xO_y(s) \rightarrow xM(s) + yH_2O(\ell)$$

- ***Reactions with organic compounds:*** It reacts with many organic compounds in the presence of catalysts to give useful hydrogenated products of commercial importance. For example :

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

(ii) Hydroformylation of olefins yields aldehydes which further undergo reduction to give alcohols.

$$H_2 + CO + RCH = CH_2 \rightarrow RCH_2CH_2CHO$$

$$H_2 + RCH_2CH_2CHO \rightarrow RCH_2CH_2CH_2OH$$

Uses of Dihydrogen

The largest single use of dihydrogen is in the synthesis of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers.

- Dihydrogen is used in the manufacture of vanaspati fat by the hydrogenation of polyunsaturated vegetable oils like soyabean, cotton seeds etc. . It is used in the manufacture of bulk organic chemicals, particularly methanol.

$$CO(g) + 2H_2(g) \xrightarrow[\text{catalyst}]{\text{cobalt}} CH_3OH(\ell)$$

- It is widely used for the manufacture of metal hydrides.
- It is used for the preparation of hydrogen chloride, a highly useful chemical.
- In metallurgical processes, it is used to reduce heavy metal oxides to metals.
- Atomic hydrogen and oxy-hydrogen torches find use for cutting and welding purposes. Atomic hydrogen atoms (produced by dissociation of dihydrogen with the help of an electric arc) are allowed to recombine on the surface to be welded to generate the temperature of 4000 K.
- It is used as a rocket fuel in space research.
- Dihydrogen is used in fuel cells for generating electrical energy. It has many advantages over the conventional fossil fuels and electric power. It does not produce any pollution and releases greater energy per unit mass of fuel in comparison to gasoline and other fuels.

HYDRIDES

Dihydrogen, under certain reaction conditions, combines with almost all elements, except noble gases, to form binary compounds, called **hydrides**. If 'E' is the symbol of an element then hydride can be expressed as EH_x (e.g., MgH_2) or E_mH_n (e.g., B_2H_6).

The hydrides are classified into three categories :

(i) Ionic or saline or saltlike hydrides

(ii) Covalent or molecular hydrides

(iii) Metallic or non-stoichiometric hydrides

Ionic or Saline Hydrides

These are stoichiometric compounds of dihydrogen formed with most of the *s*-block elements which are highly electropositive in character. However, significant covalent character is found in the lighter metal hydrides such as LiH, BeH_2 and MgH_2. In fact BeH_2 and MgH_2 are polymeric in structure. The ionic hydrides are crystalline, non-volatile and nonconducting in solid state. However, their melts conduct electricity and on electrolysis liberate dihydrogen gas at anode, which confirms the existence of H^- ion.

$$2H^-\text{(melt)} \xrightarrow{\text{anode}} H_2(g) + 2e^-$$

Saline hydrides react violently with water producing dihydrogen gas.

$$NaH(s) + H_2O(aq) \rightarrow NaOH(aq) + H_2(g)$$

Lithium hydride is rather unreactive at moderate temperatures with O_2 or Cl_2. It is, therefore, used in the synthesis of other useful hydrides, e.g.,

$$8LiH + Al_2Cl_6 \rightarrow 2LiAlH_4 + 6LiCl$$

$$2LiH + B_2H_6 \rightarrow 2LiBH_4$$

- **Covalent or Molecular Hydride**

  Dihydrogen forms molecular compounds with most of the *p*-block elements. Most familiar examples are CH_4, NH_3, H_2O and HF. For convenience hydrogen compounds of nonmetals have also been considered as hydrides. Being covalent, they are volatile compounds. Molecular hydrides are further classified according to the relative numbers of electrons and bonds in their Lewis structure into :

  (i) electron-deficient, (ii) electron-precise, and (iii) electron-rich hydrides.

  An electron-deficient hydride, as the name suggests, has too few electrons for writing its conventional Lewis structure. Diborane (B_2H_6) is an example. In fact all elements of group 13 will form electron-deficient compounds. They act as Lewis acids i.e., electron acceptors.

  Electron-precise compounds have the required number of electrons to write their conventional Lewis structures. All elements of group 14 form such compounds (e.g., CH_4) which are tetrahedral in geometry.

  Electron-rich hydrides have excess electrons which are present as lone pairs. Elements of group 15-17 form such compounds. (NH_3 has 1- lone pair, H_2O – 2 and HF –3 lone pairs). They will behave as Lewis bases i.e., electron donors. The presence of lone pairs on highly electronegative atoms like N, O and F in hydrides results in hydrogen bond formation between the molecules. This leads to the association of molecules.

- **Metallic or Non-stoichiometric (or Interstitial) Hydrides**

  These are formed by many *d*-block and *f*-block elements. However, the metals of group 7, 8 and 9 do not form hydride. Even from group 6, only chromium forms CrH. These hydrides conduct heat and electricity though not as efficiently as their parent metals do. Unlike saline hydrides, they are almost always nonstoichiometric, being deficient in hydrogen. For example, $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.5–1.8}$, $ZrH_{1.3–1.75}$, $VH_{0.56}$, $NiH_{0.6–0.7}$, $PdH_{0.6–0.8}$ etc. In such hydrides, the law of constant composition does not hold good.

  Earlier it was thought that in these hydrides, hydrogen occupies interstices in the metal lattice producing distortion without any change in its type. Consequently, they were termed as interstitial hydrides. However, recent studies have shown that except for hydrides of Ni, Pd, Ce and Ac, other hydrides of this class have lattice different from that of the parent metal. The property of absorption of hydrogen on transition metals is widely used in catalytic reduction / hydrogenation reactions for the preparation of large number of compounds. Some of the metals (e.g., Pd, Pt) can accommodate a very large volume of hydrogen and, therefore, can be used as its storage media. This property has high potential for **hydrogen storage** and as a **source of energy**.

- **Physical Properties of Water**

It is a colourless and tasteless liquid. Its physical properties are given in Table along with the physical properties of heavy water. The unusual properties of water in the condensed phase (liquid and solid states) are due to the presence of extensive hydrogen bonding between water molecules. This leads to high freezing point, high boiling point, high heat of vaporisation and high heat of fusion in comparison to H_2S and H_2Se. In comparison to other liquids, water has a higher specific heat, thermal conductivity, surface tension, dipole moment and dielectric constant, etc. These properties allow water to play a key role in the biosphere.

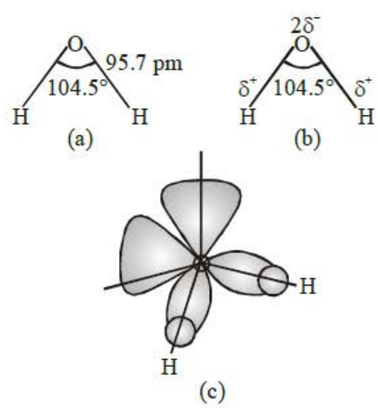
Physical Properties of H_2O and D_2O

Property	H_2O	D_2O
Molecular mass (g mol^{-1})	18.0151	20.0276
Melting point/K	273.0	276.8
Boiling point/K	373.0	374.4
Enthalpy of formation/kJ mol^{-1}	–285.9	–294.6
Enthalpy of vaporisation (373K)/kJmol^{-1}	40.66	41.61
Enthalpy of fusion/kJ mol^{-1}	6.01	-
Temp of max. density/K	276.98	284.2
Density(298K)/g cm^{-3}	1.0000	1.1059
Viscosity/centipoise	0.8903	1.107
Deielectric constant/C^2/N.m^2	78.39	78.06
Electrical conductivity (293K/ohm^{-1} cm^{-1})	5.7×10^{-8}	-

The high heat of vaporisation and heat capacity are responsible for moderation of the climate and body temperature of living beings. It is an excellent solvent for transportation of ions and molecules required for plant and animal metabolism. Due to hydrogen bonding with polar molecules, even covalent compounds like alcohol and carbohydrates dissolve in water.

- **Structure of Water**

In the gas phase water is a bent molecule with a bond angle of 104.5° and O–H bond length of 95.7 pm as shown in Fig (a).



H_2O molecule

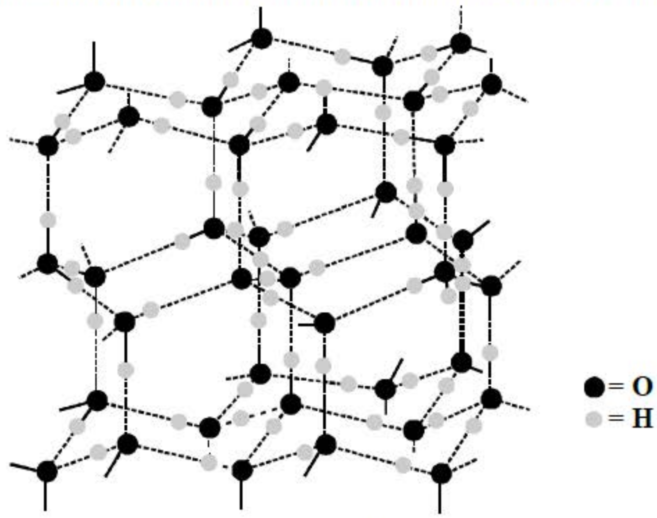
(a) The bent structure of water; (b) the water molecule as a dipole and (c) the orbital overlap picture in water molecule.

It is a highly polar molecule, (Fig (b)). Its orbital overlap picture is shown in Fig. (c). In the liquid phase water molecules are associated together by hydrogen bonds.

The crystalline form of water is ice. At atmospheric pressure ice crystallises in the hexagonal form, but at very low temperatures it condenses to cubic form. Density of ice is less than that of water. Therefore, an ice cube floats on water. In winter season ice formed on the surface of a lake provides thermal insulation which ensures the survival of the aquatic life. This fact is of great ecological significance.

- **Structure of Ice**

  Ice has a highly ordered three dimensional hydrogen bonded structure as shown in Fig. Examination of ice crystals with X-rays shows that each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 276 pm. Hydrogen bonding gives ice a rather open type structure with wide holes. These holes can hold some other molecules of appropriate size interstitially.



The Structure of Ice

- **Chemical Properties of Water**

  Water reacts with a large number of substances. Some of the important reactions are given below.

(1) ***Amphoteric Nature :***

It has the ability to act as an acid as well as a base i.e., it behaves as an amphoteric substance. In the Brönsted sense it acts as an acid with NH_3 and a base with H_2S.

$H_2O(\ell) + NH_3(aq) \rightarrow OH^-(aq) + NH_4^+(aq)$

$H_2O(\ell) + H_2O(aq) \rightarrow H_3O^+(aq) + HS^-(aq)$

The auto-protolysis (self-ionization) of water takes place as follows :

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

acid-1	base-2	acid-2	base-1
(acid)	(base)	(conjugate acid)	(conjugate base)

(2) ***Redox Reactions Involving Water:***

Water can be easily reduced to dihydrogen by highly electropositive metals.

$$2H_2O(\ell) + 2Na(s) \rightarrow 2NaOH(aq) + H_2(g)$$

Thus, it is a great source of dihydrogen.

Water is oxidised to O_2 during photosynthesis.

$$6CO_2(g) + 12H_2O(\ell) \rightarrow C_6H_{12}O_6(aq) + 6H_2O(\ell) + 6O_2(g)$$

With fluorine also it is oxidised to O_2.

$$2F_2(g) + 2H_2O(\ell) \rightarrow 4H^+ (aq) + 4F^-(aq) + O_2(g)$$

(3) *Hydrolysis Reaction:*

Due to high dielectric constant, it has a very strong hydrating tendency. It dissolves many ionic compounds. However, certain covalent and some ionic compounds are hydrolysed in water.

$P_4O_{10}(s) + 6H_2O(\ell) \rightarrow 4H_3PO_4\ (aq)$

$SiCl_4(\ell) + 2H_2O(\ell) \rightarrow SiO_2(s) + 4HCl(aq)$

$N^{3-}(s) + 3H_2O(\ell) \rightarrow NH_3(g) + 3OH^-(aq)$

(4) *Hydrates Formation:*

From aqueous solutions many salts can be crystallised as hydrated salts. Such an association of water is of different types viz.,

(i) coordinated water e.g.,
$[Cr(H_2O)_6]^{3+}\ 3Cl^-$

(ii) interstitial water e.g., $BaCl_2.2H_2O$

(iii) hydrogen-bonded water e.g.,
$[Cu(H_2O)_4]^{2+}\ SO_4^{2-}.\ H_2O$ in $CuSO_4.5H_2O$.

- **Hard and Soft Water**

Rain water is almost pure (may contain some dissolved gases from the atmosphere). Being a good solvent, when it flows on the surface of the earth, it dissolves many salts. Presence of calcium and magnesium salts in the form of hydrogencarbonate, chloride and sulphate in water makes water **'hard'**. **Hard water** does not give lather with soap. Water free from soluble salts of calcium and magnesium is called **Soft water**. It gives lather with soap easily.

Hard water forms scum/precipitate with soap. Soap containing sodium stearate ($C_{17}H_{35}COONa$) reacts with hard water to precipitate out Ca/Mg stearate.

$2C_{17}H_{35}COONa(aq) + M^{2+}(aq) \rightarrow (C_{17}H_{35}COO)_2M \downarrow + 2Na^+(aq)$; M is Ca/Mg

It is, therefore, unsuitable for laundry. It is harmful for boilers as well, because of deposition of salts in the form of scale. This reduces the efficiency of the boiler. The hardness of water is of two types: (i) temporary hardness, and (ii) permanent hardness.

- **Temporary Hardness :**

Temporary hardness is due to the presence of magnesium and calcium hydrogencarbonates. It can be removed by :

(i) Boiling : During boiling, the soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ is changed to insoluble $CaCO_3$. It is because of high solubility product of $Mg(OH)_2$ as compared to that of $MgCO_3$, that $Mg(OH)_2$ is precipitated. These precipitates can be removed by filtration. Filtrate thus obtained will be soft water.

$$Mg(HCO_3)_2 \xrightarrow{\text{Heating}} Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$

$$Ca(HCO_3)_2 \xrightarrow{\text{Heating}} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

(ii) Clark's method : In this method calculated amount of lime is added to hard water. It precipitates out calcium carbonate and magnesium hydroxide which can be filtered off.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$$

- **Permanent Hardness**

  It is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in water. Permanent hardness is not removed by boiling. It can be removed by the following methods:

  (i) ***Treatment with washing soda (sodium carbonate) :*** Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates.

  $MCl_2 + Na_2CO_3 \rightarrow MCO_3 \downarrow + 2NaCl$ (m + Mg, Ca)

  $MSO_4 + Na_2CO_3 \rightarrow MCO_3 \downarrow + Na_2SO_4$

  (ii) ***Calgon's method :*** Sodium hexametaphosphate ($Na_6P_6O_{18}$), commercially called 'calgon', when added to hard water, the following reactions take place.

  $Na_6P_6O_{18} \rightarrow 2Na^+ + Na_4P_6O_{18}^{2-}$ (M = Mg. Ca)

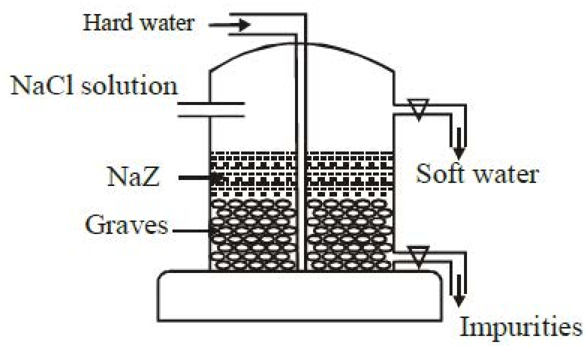
  $M^{2+} + Na_4P_6O_{18}^{2-} \rightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$

  The complex anion keeps the Mg^{2+} and Ca^{2+} ions in solution.

(iii) Ion-exchange method (By Zeolite) : This method is also called zeolite / permutit process.

$[Na_2Al_2Si_2O_8.\ xH_2O]$

$[Na_2O.Al_2O_3.2SiO_2.xH_2O]$



Hydrated sodium aluminium silicate is zeolite/ permutit. For the sake of simplicity, sodium aluminium silicate ($NaAlSiO_4$) can be written as NaZ. When this is added in hard water, exchange reactions take place.

$2NaZ(s) + M^{2+}(aq) \rightarrow MZ_2(s) + 2Na^+(aq)$ (M=Mg, Ca)

Permutit/zeolite is said to be exhausted when all the sodium in it is used up. It is regenerated for further use by treating with an aqueous sodium chloride solution.

$MZ_2(s) + 2NaCl(aq) \rightarrow 2NaZ(s) + MCl_2(aq)$

(iv) Ion exchange method (By synthetic resins) : Ion exchanges resins are the most popular water softener these days. This resins are synthetic substance. The **cation exchanger** consists of granular insoluble organic acid resins having giant molecules with $-SO_3H$ or $-COOH$ groups (represented as RH) while the **anion exchanger** contains giant organic molecules with basic groups derived from amine (represented as ROH). Ion exchange resins remove all soluble mineral from water.

Reaction at Cation exchanger

$Ca^{2+} + RH \longrightarrow R_2Ca + 2H^{\oplus}$

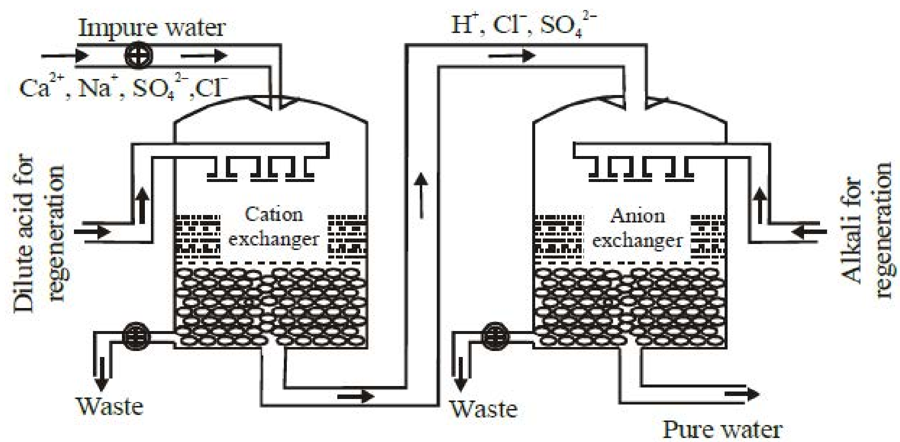
$Mg^{2+} + RH \longrightarrow R_2Mg + 2H^{\oplus}$

Reaction at Anion exchanger

$$ROH + Cl^- \longrightarrow RCl + OH^-$$

$$2ROH + SO_4^{2-} \longrightarrow R_2SO_4 + 2OH^-$$

The water coming from cation exchanger is acidic due to $H^{\oplus}$. This water is then passed through another bed containing anion exchanger. This exchanger removes anion like Cl^-, SO_4^{2-}, NO_3^- by exchanging with OH^- ions.



$$H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$$

This water is free from impurities & can be used for drinking purpose.

After some times when both resin gets exhausted process is stopped.

Regenration of resin :

(i) Cation exchange resin : We use dil acid.

$$2HCl + R_2Ca \longrightarrow RH + CaCl_2$$

(ii) Anion exchange resin : We use dil NaOH solution

$$NaOH + RCl \longrightarrow NaCl + ROH$$

❑ HYDROGEN PEROXIDE (H_2O_2)

Hydrogen peroxide is an important chemical used in pollution control treatment of domestic and industrial effluents.

Preparation

It can be prepared by the following methods.

(i) $Na_2O_2 + H_2O$ (ice cold water) $\longrightarrow 2NaOH + H_2O_2$

(ii) Acidifying barium peroxide and removing excess water by evaporation under reduced pressure gives hydrogen peroxide.

$$BaO_2.8H_2O(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + H_2O_2(aq) + 8H_2O(\ell)$$

Instead of H_2SO_4, H_3PO_4 is added now-a-days because H_2SO_4 catalyses the decomposition of H_2O_2 whereas H_3PO_4 favours to restore it.

$$3BaO_2 + 2H_3PO_4 \rightarrow Ba_3(PO_4)_2 + 3H_2O_2$$

and $Ba_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3BaSO_4 + 2H_3PO_4$ (reused again)

(iii) Peroxodisulphate, obtained by electrolytic oxidation of acidified sulphate solutions at high current density, on hydrolysis yields hydrogen peroxide.

$$2H_2SO_4 \rightleftharpoons 2H^+ + 2HSO_4^-$$

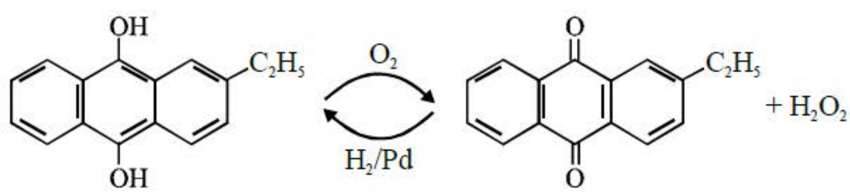
$2HSO_4^- \longrightarrow H_2S_2O_8 + 2e$. [At anode] [At cathode $2H^+ + 2e \rightarrow H_2$]

$$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$$

This method is now used for the laboratory preparation of D_2O_2.

$$K_2S_2O_8(s) + 2D_2O(\ell) \longrightarrow 2KDSO_4(aq) + D_2O_2(\ell)$$

(iii) Industrially it is prepared by the autooxidation of 2-alklylanthraquinols.



2-ethylanthraquinol 2-ethylanthraquinone

In this case 1% H_2O_2 is formed. It is extracted with water and concentrated to ~30% (by mass) by distillation under reduced pressure. It can be further concentrated to ~85% by careful distillation under low pressure. The remaining water can be frozen out to obtain pure H_2O_2.

• Physical Properties

In the pure state H_2O_2 is an almost colourless (very pale blue) liquid. Its important physical properties are given in Table. H_2O_2 is miscible with water in all proportions and forms a hydrate $H_2O_2.H_2O$ (mp 221K). 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 will give 100 mL of oxygen at STP. Commercially marketed sample is 10 V, which means that the sample contains 3% H_2O_2.

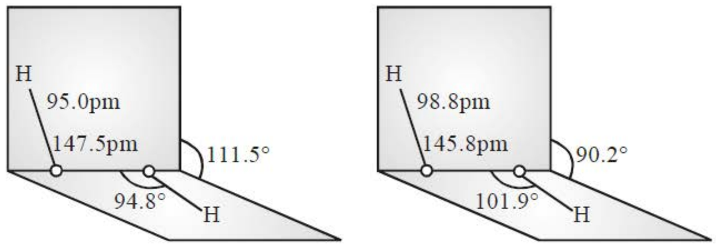
30% (w / v) or "100 V" H_2O_2 solution is called **per hydrol**.

Physical Properties of Hydrogen Peroxide

Melting point/K	272.4	Density (liquid at 298K)/g cm^{-3}	1.44
Boiling point (exrapolated)/K	423	Viscosity (290 K)/centipoise	1.25
Vapour pressure (298K) mmHg	1.9	Dielectric constant (298K)/C^2/N m^2	70.7
Density (solid at 268.5K)/g cm^{-3}	1.64	Electrical conductivity (298K)/Ω^{-1} cm^{-1}	5.1×10^{-8}

Structure

Hydrogen peroxide has a non-planar structure. The molecular dimensions in the gas phase and solid phase are shown in Fig.



(a) Gas phase (a) Solid phase

***Fig.** (a) H_2O_2 structure in gas phase, dihedral angle is 111.5°. (b) H_2O_2 structure in solid phase at 110K, dihedral angle is 90.2°.*

Chemical Properties:

(i) Acidic nature : $H_2O_2 + 2NaOH \longrightarrow Na_2O_2 + H_2O$

$H_2O_2 + Ba(OH)_2 \longrightarrow BaO_2 + 2H_2O$

$H_2O_2 + Na_2CO_3 \longrightarrow Na_2O_2 + CO_2 + H_2O$

(ii) It is oxidant as well as reductant.

$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$ [reaction in acidic medium]

$H_2O_2 + 2e \rightarrow 2OH^-$ [rxn^n in alkali medium]

Oxidising Properties:

(i) $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$ (Used in washing of oil painting)

(ii) $NaNO_2 + H_2O_2 \longrightarrow NaNO_3 + H_2O$

$Na_2SO_3 + H_2O_2 \longrightarrow Na_2SO_4 + H_2O$

$Na_3AsO_3 + H_2O_2 \longrightarrow Na_3AsO_4 + H_2O$

$2KI + H_2O_2 \longrightarrow 2KOH + I_2$

$H_2S + H_2O_2 \longrightarrow S\downarrow + 2H_2O$

[$X_2 + H_2O_2 \longrightarrow 2HX + O_2$ X = Cl, Br.
S.R.P order of $Cl_2 > Br_2 > H_2O_2 > I_2$]

$H_2SO_4 + 2FeSO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$

$2\,K_4[Fe(CN)_6] + H_2O_2 + H_2SO_4 \longrightarrow 2K_3[Fe(CN)_6] + K_2SO_4 + 2H_2O$

$2[Cr(OH)_4]^- + 3H_2O_2 + 2OH^- \longrightarrow 2CrO_4^{2-} + 8H_2O$

$CrO_4^{2-} + 2H^+ + 2H_2O_2 \rightarrow CrO_5\ \text{(Blue)}\downarrow + 3H_2O$

$4CrO_5 + 12H^+ \longrightarrow 4Cr^{+3} + 7O_2 + 6H_2O$

$Mn^{+2} + OH^- + H_2O_2 \longrightarrow MnO_2 + 2H_2O \Rightarrow$ This reaction can be utilised to detect NH_3

Reducing properties:

(a) $Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$

(b) $O_3 + H_2O_2 \longrightarrow H_2O + 2O_2$

(c) $MnO_2 + H_2O_2 + H_2SO_4 \rightarrow MnSO_4 + 2H_2O + O_2$

(d) $PbO_2 + H_2O_2 \rightarrow PbO + H_2O + O_2$

(e) $Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

$PbO_2 + H_2O_2 \longrightarrow PbO + H_2O + O_2$

$PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O$

$Pb_3O_4 + H_2O_2 + 6HNO_3 \longrightarrow 3Pb(NO_3)_2 + 4H_2O + O_2$

(f) $X_2 + H_2O_2 \longrightarrow 2HX + O_2$ [X = Cl, Br]

$2KMnO_4 + 3H_2O_2 \rightarrow 2KOH + 2MnO_2 + 2H_2O + 3O_2$

$2MnO_4^- + 2OH^- \longrightarrow 2MnO_4^{2-} + H_2O + O$

$2MnO_4^{2-} + 2H_2O \longrightarrow 2MnO_2 + 4OH^- + 2O$

$2MnO_4^- + H_2O \longrightarrow 2MnO_2 + 2OH^- + 3O$

(g) $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 5O_2 + 8H_2O$

(h) $2[Fe(CN)_6]^{3-} + 2OH^- + H_2O_2 \longrightarrow 2[Fe(CN)_6]^{4-} + 2H_2O + O_2$

(i) $NaOCl + H_2O_2 \longrightarrow NaCl + H_2O + O_2$

(j) $NaIO_4 + H_2O_2 \longrightarrow NaIO_3 + H_2O + O_2$

It acts as an oxidising as well as reducing agent in both acidic and alkaline media. Simple reactions are described below.

(i) Oxidising action in acidic medium

(a) $2Fe^{2+}(aq) + 2H^+(aq) + H_2O_2(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O(\ell)$

(b) $PbS(s) + 4H_2O_2(aq) \rightarrow PbSO_4(s) + 4H_2O(\ell)$

(ii) Reducing action in acidic medium

(a) $2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$

(b) $HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$

(c) $CrO_4^{2-} + 2H^+ + 2H_2O_2 \rightarrow CrO_5$ (Blue) $+ 3H_2O$

$4CrO_5 + 12H^+ \longrightarrow 4Cr^{+3} + 7O_2 + 6H_2O$

(iii) Oxidising action in basic medium

(a) $2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^-$

(b) $Mn^{2+} + H_2O_2 \rightarrow Mn^{4+} + 2OH^-$

(iv) Reducing action in basic medium

(a) $I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$

(b) $2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$

- **Storage**

H_2O_2 decomposes slowly on exposure to light.

$2H_2O_2(\ell) \rightarrow 2H_2O(\ell) + O_2(g)$

In the presence of metal surfaces or traces of alkali (present in glass containers), the above reaction is catalysed. It is, therefore, stored in wax-lined glass or plastic vessels in dark. Acetanalide or Glycerol or Urea can be added as a stabiliser. It is kept away from dust because dust can induce explosive decomposition of the compound.

Uses

Its wide scale use has led to tremendous increase in the industrial production of H_2O_2.

Some of the uses are listed below :

(i) In daily life it is used as a hair bleach and as a mild disinfectant. As an antiseptic it is sold in the market as perhydrol.

(ii) It is used to manufacture chemicals like sodium perborate and per-carbonate, which are used in high quality detergents.

(iii) It is used in the synthesis of hydroquinone, tartaric acid and certain food products and pharmaceuticals (cephalosporin) etc.

(iv) It is employed in the industries as a bleaching agent for textiles, paper pulp, leather, oils, fats, etc.

(v) As a rocket propellant:

$NH_2.NH_2 + 2H_2O_2 \longrightarrow N_2 + 4H_2O$ [highly exothermic and large increase in volume]

(vi) In detection of Cr^{+3}, Ti^{+4} etc.

$Ti(SO_4)_2 + H_2O_2 + 2H_2O \longrightarrow \underset{\text{Yellow or orange}}{H_2TiO_4} + 2H_2SO_4$

Pertitanic acid

(vii) Nowadays it is also used in Environmental (Green) Chemistry. For example, in pollution control treatment of domestic and industrial effluents, oxidation of cyanides, restoration of aerobic conditions to sewage wastes, etc.

HEAVY WATER, D_2O :

It can be prepared by exhaustive electrolysis of water or as a by-product in some fertilizer industries.

- **Physical properties :**

(a) Heavy water is a colourles, odourless and tasteless mobile liquid, (b) Nearly all the physical constants are higher than the corresponding values of ordinary water.

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

$CaC_2 + 2D_2O \rightarrow C_2D_2 + Ca(OD)_2$

$SO_3 + D_2O \rightarrow D_2SO_4$

$Al_4C_3 + 12D_2O \rightarrow 3CD_4 + 4Al(OD)_3$

- **Uses :** It is extensively used as a moderator & coolant in nuclear reactors and in exchange reactions for the study of reaction mechanisms. **As a neutron moderator :** Fission in uranium-235 is brought by slow speed neutrons. The substances which are used for slowing down the speed of neutrons are called moderators. Heavy water is used for this purpose in nuclear reactors.

DIHYDROGEN AS A FUEL

Dihydrogen releases large quantities of heat on combustion. The data on energy released by combustion of fuels like dihydrogen, methane, LPG etc. are compared in terms of the same amounts in mole, mass and volume, are shown in Table.

From this table it is clear that on a mass for mass basis dihydrogen can release more energy than petrol (about three times). Moreover, pollutants in combustion of dihydrogen will be less than petrol. The only pollutants will be the oxides of dinitrogen (due to the presence of dinitrogen as impurity with dihydrogen).

This, of course, can be minimised by injecting a small amount of water into the cylinder to lower the temperature so that the reaction between dinitrogen and dioxygen may not take place. However, the mass of the containers in which dihydrogen will be kept must be taken into consideration. A cylinder of compressed dihydrogen weighs about 30 times as much as a tank of petrol containing the same amount of energy. Also, dihydrogen gas is converted into liquid state by cooling to 20K. This would require expensive insulated tanks. Tanks of metal alloy like $NaNi_5$, $Ti–TiH_2$, $Mg–MgH_2$ etc. are in use for storage of dihydrogen in small quantities. These limitations have prompted researchers to search for alternative techniques to use dihydrogen in an efficient way.

In this view Hydrogen Economy is an alternative. The basic principle of hydrogen economy is the transportation and storage of energy in the form of liquid or gaseous dihydrogen. Advantage of hydrogen economy is that energy is transmitted in the form of dihydrogen and not as electric power. It is for the first time in the history of India that a pilot project using dihydrogen as fuel was launched in October 2005 for running automobiles. Initially 5% dihydrogen has been mixed in CNG for use in four-wheeler vehicles. The percentage of dihydrogen would be gradually increased to reach the optimum level.

Nowadays, it is also used in fuel cells for generation of electric power. It is expected that economically viable and safe sources of dihydrogen will be identified in the years to come, for its usage as a common source of energy.

The Energy Released by Combustion of Various Fuels in Moles, Mass and Volume

Energy released on Combustion in kJ state)	Dihydrogen in gaseous state)	Dihydrogen (in liuqid)	LPG	CH_4 gas	Octance (in liuquid state)
per mole	286	285	2220	880	5511
per gram	143	142	50	53	47
per litre	12	9968	25590	35	34005