HYDROGEN

1. INTRODUCTION :

Hydrogen is the lightest element and also the lightest gas in the periodic table.

It is the lightest non-metal. It is the simplest element in periodic table having only 1e^-, 1p & no neutron.

Electronic configuration of H is $1s^1$

Number of e^- = 1 Number of orbital = 1

Number of shells = 1 Number of subshell =1

It is discovered by Henry Cavendish & it was called inflammable element.

The name hydrogen was given by Lavoisier

Hydrogen

Hydro (Water) Gene (Producer) or generator

means according to Lavoisier the gas which produce water on burning with oxygen.

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

Order of Abundance of H :

Hydrogen is the most abundant element in the universe (70% of the total mass of the universe.)

Order of abundance of H :

Universe > Sun atm > Earth

The planet Jupiter & Saturn consist mainly of H_2. Similarly about half the mass of the sun & some other stars is made up of hydrogen.

In Sun's atomsphere & in universe, It is found in atomic form. While in earth it is generally found in molecular form. At Sun, the stratosphere is made up of H (atomic hydrogen) & they undergoes fusion & converted into He nuclei & this reaction is exothermic so lot of amount of energy is liberated.

It is the ninth element on earth in order of abundance.

Earth does not posses enough gravitational force to retain live hydrogen molecule i.e. why it is not found in earth atomosphere in atomic form.

Hydrogen is the most reactive elements in atomic form but it is less reactive in molecular form because of very high bond dissociation energy due to 1s -1s overlapping.

2. POSITION OF H_2 IN PERIODIC TABLE :

Hydrogen is the first element of Periodic table but still it could not be assigned a proper position either in Mendeleef periodic table or in Modern periodic table because of following reasons.

It may kept in 1st/IA or 17th/VIIA group due to following reason.

Resembeles with 1st/IA Alkali metals.

(i) Electronic configuration : Like alkali metals hydrogen also has only one electron in outer most shell.

⇒ H = $1s^1$ K = $4s^1$

⇒ Li = $2s^1$ Rb = $5s^1$ — ns^1

⇒ Na = $3s^1$

(ii) Electropositive characters : Like alkali metals hydrogen also have the tendency to loose one electron to form cation.

e.g. $Na \rightarrow Na^+ + e^-$

$H \rightarrow H^+ + e^-$

(Proton)

(iii) **Oxidation numbers** : Like alkali metals hydrogen can also exhibit the oxidation number of +1 in most of its compound.

e.g. Na^+Cl^- K^+Cl

$H^+ Cl^-$ = +1

(iv) **Reaction with electronegative elements (non-metals)** : Like alkali metals H also reacts with Oxygen, Sulphur, Halogens to form oxides, sulphides and halides respectively.

$O \xrightarrow{\text{gives}} H_2O$, like Na_2O, K_2O

$S \xrightarrow{\text{gives}} H_2S$, like Na_2S, K_2S

with halogen $\xrightarrow{\text{gives}}$ HX, like NaX, KX

(v) **Liberation at Cathode :**

$2Na^+ Cl \xrightarrow{\text{electrolysis}} 2Na + Cl_2$

(liberated at cathode) (liberated at anode)

$2H^+ Cl^- \xrightarrow{\text{electrolysis}} (H_2 + Cl_2)$

like alkali metals H also get liberated at cathode on electrolysis.

(vi) **Reducing nature** : Like alkali metals H_2 also have reducing nature.

$CuO + H_2 \longrightarrow Cu + H_2O$

Due to resembling of these properties with alkali metals H can be placed in IA/group /alkali metals group.

Resembles with halogen/ VIIA/17th

(i) **Electronic configuration :**

Electronic configuration of halogen $H \longrightarrow 1s^1$

$\longrightarrow ns^2np^5$

both these requires one electron to attain the stable configuration of their nearest inert gas.

$H \longrightarrow 1s^1 \xrightarrow{1e^- \text{ less than}} He\ (1s^2)$

$F \longrightarrow 2p^5 \xrightarrow{1e^- \text{ less than}} Ne\ (2p^6)$

$Cl \longrightarrow 3p^5 \xrightarrow{1e^- \text{ less than}} Ar\ (3p^6)$

(ii) **Electronegative character** : Both halogen & Hydrogen has the tendency to gain one e^-.

$F + e^- \longrightarrow F^-$

$H + e^- \longrightarrow H^-$

i.e. why both will act as electronegative species.

(iii) **Ionization potential** : Ionization potential of hydrogen is almost similar to halogen.

(iv) **Oxidation number** : Both halogen & hydrogen can exahibit –1 oxidation number. Hydrogen in metal hydride shows –1 oxidation state.

$NaH \longrightarrow Na^+ + H^-$

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

(v) **Diatomic molecule** : Both halogen & hydrogen have the tendency to exist as diatomic molecule. eg. F_2, Cl_2 Br_2, I_2 & H_2.

(vi) **Liberation at anode** : Whenever Alkali metals halides & hydrides undergoes electrolysis, both halogen and hydrogen will liberate at anode.

$2Na^+ Cl^- \longrightarrow 2Na + Cl_2$ (anode)

$2Na^+ H^- \longrightarrow 2Na + H_2$ (anode)

(vii) Reaction with highly electropositive metals : Hydrogen reacts with highly electropositive element (i.e. s-block elements) & forms their hydrides like their halides.

$2Na + H_2 \longrightarrow 2NaH$

$2Na + Cl_2 \longrightarrow 2NaCl$

This reaction shows oxidising character of hydrogen.

(viii) Formation of covalent compound : Both Hydrogen & halogen on reaction with non metals to form covalent compounds like.

CH_4, NH_3, H_2O

CCl_4, NCl_3, Cl_2O

Conclusion : The position of hydrogen is still in controversy & no proper position is assigned to H in periodic table i.e. why it is also called notorious or rogue elements.

3. ISOTOPES OF HYDROGEN :

There are 3 isotopes of H_2

	Protium or ordinary hydrogen	Deuterium/ Heavy hydrogen	Tritium
Symbol	${}_1H^1$ H_2	${}_1H^2/{}_1D^2$ D_2	${}_1H^3/{}_1T^3$ T_2

Property	Protium or ordinary hydrogen	Deuterium or heavy hydrogen	Tritium
Atomic number	1	1	1
Mass number	1	2	3
Exact atomic mass	1.008123	2.0142	3.0170
Symbol	${}^{1}_{1}H$	${}^{2}_{1}H$ or ${}^{2}_{1}D$	${}^{3}_{1}H$ or ${}^{3}_{1}T$
Molecular formula	H_2	D_2	T_2
No. of protons in the nucleus	1	1	1
No. of neutrons in the nucelus	Nil	1	2
No. of electron	1	1	1
Electronic configu.	$1s^1$	$1s^1$	$1s^1$
Relative abundance	99.984%	0.016%	10^{-15} %
Stability	Stable	Stable	Unstable(Radioactive)

Properties	H_2	D_2	T_2
M.P.	-259^0C	-254.3^0C	-252.4^0C
B.P.	-252.6^0C	-249.3^0C	-248.0^0C
Bond length (H– H)	74 pm	74 pm	74 pm
Bond energy (H—H)	436.0 KJ mol^{-1}	443.3 KJ mol^{-1}	446.9 KJ mol^{-1}
Heat of fusion & vaporisation	Minimum	$H < D < T$	Maximum

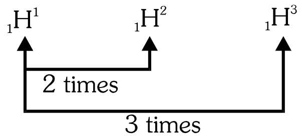
4. ISOTOPIC EFFECT :

The effect which can change the physical & chemical properties of isotopes is called isotopic effect.

It is because of difference in mass.

In isotopic effect maximum changes occurs in physical properties like melting point, boiling point, bond energy, while minimum changes occurs in chemical properties like state of chemical reaction etc.

Imp. Isotopic effect is found only in hydrogen isotopes. Because there is large difference in mass.



While in other isotopes like $_7N^{14}$ $_7N^{15}$ only a fractional mass is increased.

$_6C^{14}$ $_6C^{13}$ $_6C^{12}$ $\longrightarrow$ Here also only a fraction is increased

But in case of hydrogen mass increased to 2 to 3 times in their isotopes.

Q. Isotopic effect is found in :

(1) H (2) N (3) C (4) All

Ans. (1)

Q. Which of the following reaction is fast & why ?

(i) $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$

(ii) $CD_4 + Cl_2 \longrightarrow CD_3Cl + DCl$

Ans. (i) because C–H bond energy is less in comparison to C–D bond energy.

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^+

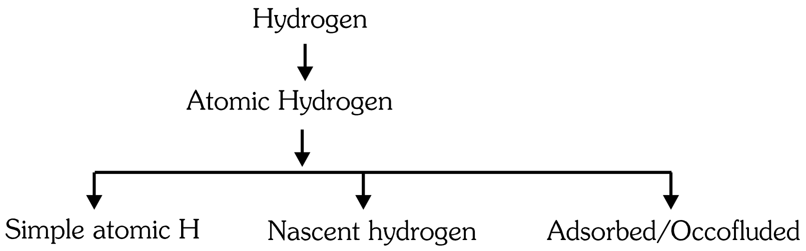
n = 2 $\longrightarrow$ $H^+(H_2O)_2$

Q. In the equeous solution hydrogen ion exist as

(1) H_3O^+ (2) $H^+(H_2O)_2$ (3) $H^+(H_2O)_n$ (4) All

Ans. (4)

(b) Based on reactivity :



Atomic hydrogen :

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

$$H_2 \xrightleftharpoons{3000\text{-}5000} 2H$$

Favourable comdition – 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

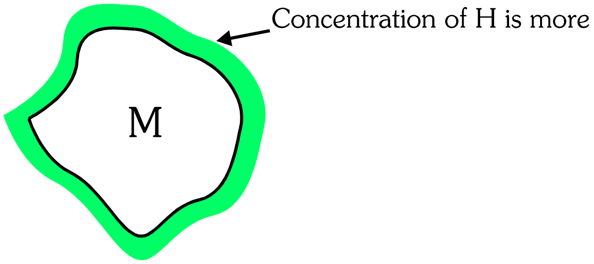
$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$$

(b) Base + element $2NaOH + Be \longrightarrow Na_2BeO_2 + 2H$

(c) C_2H_5OH + Alkali metal

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

(iii) **Adsorbed/Occluded hydrogens**



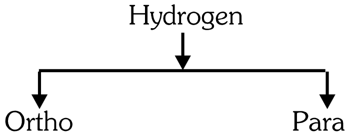
Adsorbed H is hydrogen present at the outer surface of metal.

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 proton is called ortho hydrogen.

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

In ortho hydrogen spin of proton 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 25 C	75%	25%
At –253 C/20K	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.

Method of preparation :

(A) From acids : The metal which are placed about H_2 in electrochemical series react with dil acids they liberate H_2.

e.g. $\underset{(dil)}{Fe + H_2SO_4} \rightarrow FeSO_4 + H_2$

$Cu + H_2SO_4 \rightarrow$ (No reaction)

Lab preparation : When impure Zn reacts with dil H_2SO_4 it forms H_2

$\underset{(impure)}{Zn} + \underset{(dil)}{H_2SO_4} \rightarrow ZnSO_4 + H_2$

Q. Why we use impure Zn.

Ans. Because the rate of reaction with pure Zn is very slow.

2. **By alkalies :** Only (Be, Zn, Al, Sn, Pb, Si) (Amphoteric metal) react with boiling NaOH or KOH they evolve H_2.

$Zn + 2NaOH \rightarrow \underset{\text{(sodium zincate)}}{Na_2ZnO_2} + H_2\uparrow$

$2Al + 2NaOH + 2H_2O \longrightarrow \underset{\text{(sodium meta aluminate)}}{NaAlO_2} + 3H_2\uparrow$

$Sn + 2NaOH + H_2O \longrightarrow \underset{\text{(sodium stannate)}}{Na_2SnO_3} + 2H_2\uparrow$

$Pb + 2NaOH + H_2O \longrightarrow \underset{\text{(sodium plumbate)}}{Na_2PbO_3} + 2H_2\uparrow$

$Si + 2NaOH + H_2O \longrightarrow \underset{\text{(sodium silicate)}}{Na_2SiO_3} + 2H_2\uparrow$

$Be + 2NaOH \longrightarrow \underset{\text{(sodium beryliate)}}{Na_2BeO_2} + H_2$

3. **From water :**

All the metals which are placed above than H_2 when react with water the evolve H_2.

$Zn + H_2O \longrightarrow ZnO + H_2\uparrow$

Three type of water is used

(i) Cold water : The temperature of cold water is 7 to 25 C this water is used for highly reactive metals. Such as Li, K, Ba, Sr, Ca, Na, means alkali metals of alkalic earth metals.

The reaction with alkali metals are vigorous to minimum the rate of reaction these metals are used in the form of amalgam.

$2Na(Hg) + H_2O \longrightarrow 2NaOH + H_2\uparrow$

(ii) Hot water : The temperature of hot water is 25 C to 90 C. This water is used for reactive metals, such as Mg, Al, Mn, Zn, Cr.

(iii) Steam : The temperature of steam is more than 100 C. This form of water is used for very less reactive metals like Fe, Cd, Co, Ni, Sn, Pb.

Condition for best yield of H_2.

(i) Cold water ⟶ With highly reactive metals.

(ii) Hot water ⟶ With reactive metals

(iii) Steam ⟶ With less reactive metals.

4. **On Ionic hydride :**

Whenever ionic hydride reacts with water then form H_2.

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

(Hydrolith)

$NaBH_4 + H_2O \longrightarrow NaBO_2 + 4H_2$

Method to prepare pure hydrogen :

1. **Electrolysis of water** : To prepare pure hydrogen we use impure water (i.e. having 15-20% solution of alkali or acid)

$4H_2O \rightleftharpoons 4H^+ + 4OH^-$

at cathode $4H^+ + 4e^- \longrightarrow 2H_2$

at anode $4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

The SO_4^{-2} or K^+ ion present in acid or alkali does not move towards anode or cathode as their discharge potential is higher than of OH^- ions or H^+ ions rescpectively.

2. **By reaction of Magnesium with dil. H_2SO_4 :**

$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$

3. **B reaction of NaH with water :**

$NaH + H_2O \longrightarrow NaOH + H_2$

4. **Uyeno method** : This method is used for military purpose

$2Al + 2KOH + 2H_2O \longrightarrow 2KAlO_2 + 3H_2\uparrow$

(Potassium meta aluminate)

Because by this reaction we can prepare H_2 in a rapid nanner.

Commercial or industrial method to prepare H_2 :

(i) **Lane process** : Steam is passes over hot iron it converts into Fe_3O_4 & H_2.

$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2\uparrow$

Iron is regenrated by reducing Fe_3O_4 into Fe by water gas ($CO + H_2$)

$2Fe_3O_4 + 4CO + 4H_2 \longrightarrow 6Fe + 4CO_2 + 4H_2O$

$Fe_3O_4 + 2CO + 2H_2 \longrightarrow 3Fe + 2CO_2 + 2H_2O$

This process is a continuous process.

(ii) **Bosch Process** : In this process initially steam is passed over red hot coke then water gas is formed.

$C + H_2O \longrightarrow CO + H_2$

Then water gas is mixed with more stem in presence of Fe_2O_3/Cr_2O_3 then CO will convert into O_2 & we can obtain more H_2.

$CO + H_2 + H_2O \longrightarrow CO_2 + 2H_2$

(iii) **From Natural gas :**

$C_nH_{2n+2} + nH_2O \longrightarrow nCO + (2n + 1)H_2$

5. **PHYSICAL PROPERTIES OF HYDROGEN :**

(i) Hydrogen is a lightest, colourless, odourless and tasteless gas. It is sparingly soluble in water. It is inflammable and less reactive gas.

(ii) Its f.p. ($-$ 259.2^{0}C) and b.p. ($-$252^{0}C) are very low indicating less intermolecular attraction. Due to low f.p. liquid hydrogen is used as a **cryogenic fluid** (to produce low temperature).

(iii) H—H bond energy [104 Kcal mol^{-1}] and 436 KJ/m

(iv) H – H bond length [74 pm] so H_2 is less reactive and require high temp for reaction.

Chemical properties of H_2 :

(i) H_2 is neutral in nature i.e. why it does not react with acids & bases.

(ii) **Less reactive** : Hydrogen is very less reactive in nature because of very high bond dissociation energy.

(iii) **Combustible nature** : H_2 is highly combustible in nature & it burns with oxygen or air with pale blue flame to give water.

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

(iv) **Reaction with highly electropositive metals :**

IA & IIA group elements are called highly electrpositive metal. Whenever H reacts with these metals they form ionic hydrides.

$$2Na + H_2 \longrightarrow 2NaH$$
$$CO + H_2 \longrightarrow CaH_2$$

(v) **Reaction with non-metal :**

(a) **Reaction with halogen**

$$\underset{\underset{[F_2,\ Cl_2,\ Br_2,\ I_2]}{\downarrow}}{H_2 + X_2} \longrightarrow 2HX$$

order of reactivity of halogen with hydrogen

$$F_2 > Cl_2 > Br_2 > I_2$$

(b) **Reaction with sulphur**

$$H_2 + S \longrightarrow H_2S$$

(c) **With nitrogen – (Haber process)**

$$N_2 + 3H_2 \xrightarrow[\text{Fe, Mo, 200atm}]{\text{683K}} 2NH3$$

(vi) **Reducing nature :**

$$CuO + H_2 \longrightarrow Cu + H_2O$$

(vii) **Reaction with carbon mono oxide :**

$$2H_2 + CO \xrightarrow[373K]{ZnO / Cr_2O_3} CH_3OH \text{ (Methanol)}$$

(viii) **Hydrogenation of unsaturated hydrocarbon :**

$$C_2H_2 + 2H_2 \longrightarrow C_2H_6$$

$$C_2H_4 + H_2 \xrightarrow[473K]{Ni / Pb / Pt} C_2H_6$$

When unsaturated hydrocarbon having C = C or C ≡ C reacts with hydrogens in the presence of Ni/Pd/Pt forms saturated hydrocarbons.

Imp. Hydrogenation of vegetable oil.

Vegetable oils are also called polyunsaturated oils because they contain many C = C bond. When these oil are exposed to air for a long time then double bond will get oxidized and the oil becomes. Rancid (having fowl. smell or unpleasant test) in nature. So to avoid this vegetable oil are converted into edible fats (Vanaspati Ghee)

$$\underset{\text{(liquid)}}{\text{Vegetable oils}} + H_2 \xrightarrow{Ni} \text{edible fats solid}$$

This whole process is known as hydrogenation or hardening of oil.

6. USES OF HYDROGEN :

1. Hydrogenation of vegetable oil to form solid fats i.e. vanaspati ghee.
2. In liquid form as a rocket fuel. (Liquid H_2 + Liquid O_2)
3. In a air ship of balloons as a mixture of Hydrogen & Helium [15% H_2 + 85% He]
4. Formation of different compounds.

   Like → NH_3, (Haber process) alkane, alcohol and other hydrocarbon

Hydrides : The compounds of hydrogen with different elements are called hydrides.

These are of three types :

(1) Ionic/Salt like/Saline hydrides :

Compounds of hydrogen with s-block elements except berylium & magnesium are called ionic hydrides.

LiH, NaH, KH, RbH, CsH, CaH_2, SrH_2, BaH_2

BeH_2, MgH_2 are covalent polymeric hydride.

u Structure of these hydrides are similar to rock salt, so they are also called salt like/saline hydrides.

u Down the group size↑ Lattice energy↓ stability↓ Melting point↓ Boiling point↓

u On electrolysis of these hydrides, hydrogen is liberated at anode.

u On reaction with water these hydrides will form hydrogen

$$NaH + H_2O \longrightarrow NaOH + H_2$$

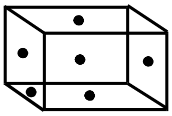
u These hydrides forms complex hydrides which are very good reducing agents.

$$4LiH + AlCl_3 \longrightarrow LiAlH_4 + 3LiCl$$

$NaBH_4 \longrightarrow$ Sodium borohydride

$LiAlH_4 \longrightarrow$ Lithium aluminium hydride.

(2) Mettalic / Interstitial hydrides :



They are the compounds of d & f-block elements.

In these hydrides hydrogen occupies interstitial sites present in metallic lattice, so they are called interstitial hydrides.

u Properties of these hydrides are similar to parent metals, so they are also known as metallic hydrides.

u These hydrides are non. stochiometric in nature (i.e. having variable composition)

$ZrHx$ ($x = 1.3 - 1.75$)

$TiHx$ ($x = 1.8 - 2$)

u Metals of group 7,8,9 donot form any hydrides so this particular part of periodic table is known as hydride gap.

(3) Covalent/Molecules hydrides

u They are the compounds of hydrogen with p-block elements CH_4, NH_3, H_2O, HF, etc.

u These hydrides exist as molecules, so they are also known as molecular hydrides. There hydrides are non-conductor of electricity.

Nomenclature – element + Suffix (ane)

$PH_3 \longrightarrow$ Phosphane

$NH_3 \longrightarrow$ Azane

$H_2O \longrightarrow$ Oxidane

These hydrides are again divides into 3 categories.

(a) Electron deficient hydrides :

u They are the hydrides of group 13 elements.

BH_3, AlH_3, GaH_3 – In these hydrides central element does not have complete octet. i.e. why they are called electron deficient compounds.

(b) Electron precise hydrides – They are the hydrides of group 14 element.

e.g. CH_4, SiH_4, GeH_4

In these type of hydrides central elements has $8e^-$ in their outer most shell.

(c) Electron rich hydrides : These are the hydrides of group 15, 16, 17

e.g. $\ddot{N}H_3$, $H_2\ddot{O}$, $H\underset{..}{\ddot{F}}:$ etc.

In these hydrides lone pair are present on central dement which can be given to others. So they are called electron rich hydrides.

Water (H_2O)

Properties of pure water :

(a) Physical properties :

(i) Pure water is colourless, tasteless and odourless. It gives bluish tinge in thick layers. (ii) It freezes at 0 C and boils at 100 C. (iii) Its maximum density is 1.00 at 4 C. (iv) It is a polar molecule and has V-shaped structure. The bond angle is 104.5 . (v) It has a high dielectric constant. The polar character of water makes it an excellent solvent for polar and ionic substances. (vi) It is a poor conductor of electricity. (vii) It has the tendency to associate. It exists in the liquid state not as a single H_2O molecule but as associated molecules through hydrogen bonding. The existence of hydrogen bonding is responsible for high values of specific heat, the latent heat of fusion and latent heat of vaporisation.

(b) Chemical properties :

(i) Water is neutral in nature. pH of the pure water is 7. It is a weak electrolyte and feebly ionises into H^+ and OH^- ions.

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

In pure water $[H^+] = [OH^-] = 10^{-7}$ at 25 C.

(ii) **With metals** : it reacts with active metals and evolves hydrogen. The reaction is exothermic in the case of alkali and alkaline earth metals.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

(iii) **Reaction with non metals :**

Chlorine decomposes cold water forming HCl and HClO.

$$Cl_2 + H_2O \longrightarrow HCl + \underset{\text{(Hypochlorous acid)}}{HClO}$$

When steam is passed over red hot coke (1000 C), water gas is formed.

$$C + H_2O \rightarrow \underbrace{CO + H_2}_{\text{Water gas}}$$

(iv) **Action on nonmetalic oxides** : Acidic oxides combine with water to form acids.

$CO_2 + H_2O \rightleftharpoons H_2CO_3$ (Carbonic acid)

$SO_2 + H_2O \longrightarrow H_2SO_3$ (Sulphurous acid)

$SO_3 + H_2O \longrightarrow H_2SO_4$ (Sulphuric acid)

$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$ (Orthophosphoric acid)

$N_2O_5 + H_2O \longrightarrow 2HNO_3$ (Nitric acid)

$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$ (Perchloric acid)

(v) **Action on metallic oxides** : basic oxides combine with water to form alkalies.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

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

(vi) **Action on hydrides, carbides, nitrides, phosphides** : Water decomposes these compounds with liberation of hydrogen, acetylene (or methane), ammonia, phosphine respectively.

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

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

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

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

(vii) **Hydrolysis** : Many salts specially the salts of strong bases with weak acids,weak bases with strong acids and weak bases with weak acids undergo hydrolysis with water.

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

$$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

Halides of nonmetals are decomposed by water.

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

Hard and soft water

A water is said to be a soft water if it produces sufficient lather with the soap and water is described as being hard if it forms an insoluble scum before it forms a lather with soap. The hardness of natural water is generally caused by presence of bicarbonates, chlorides and sulphates of calcium and magnesium but infact soluble salts that form a scum with soap cause hardness.

$$Ca^{2+}(aq) + 2C_{17}H_{35}COO^{-}\ (aq) \longrightarrow (C_{17}H_{35}COO)_2Ca$$

$$Mg^{2+}(aq) + \underset{\text{Anion of soap}}{2C_{17}H_{35}COO^{-}(aq)} \longrightarrow \underset{\text{Insoluble precipitates}}{C_{17}H_{35}COO)_2Mg}$$

Soap will not produce lather with water until all the calcium and magnesium ions have been precipitated. Hard water thus wastes soap. Hardness of water is of two types :

(a) Temporary hardness

(b) Permanent hardness

(a) **Temporary hardness** : This is due to the presence of bicarbonates of calcium and magnesium.

Temporary hardness in water is easily removed by boiling, as the bicarbonates decompose readily and the insoluble carbonates are precipitated.

$$Ca(HCO_3)_2 \xrightarrow{\text{Boil}} \underset{\text{(Insoluble)}}{CaCO_3} + H_2O + CO_2$$

$$Mg(HCO_3)_2 \xrightarrow{\text{Boil}} \underset{\text{(Insoluble)}}{MgCO_3} + H_2O + CO_2$$

Temporary hardness can also be removed by Clark's process which involves the addition of slaked lime [$Ca(OH)_2$].

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow \underset{\text{(Insoluble)}}{2CaCO} + 2H_2O$$

It is essential to add only the calculated amount of $Ca(OH)_2$ because excess will cause artificial hardness.

(b) **Permanent hardness** : Permanent hardness is introduced when water passes over rocks containing the sulphates or chlorides of both of calcium and magnesium. This type of hardness cannot be removed by boiling or by the addition of slaked lime.

The various water softeners are :

(i) **Washing soda :** It removes both the temporary and permanent hardness by converting soluble calcium and magnesium compounds into insoluble carbonates.

$$CaCl_2 + NaCO_3 = CaCO_3 + 2NaCl$$

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

$$Ca(HCO_3)_2 + Na_2CO_3 = \underset{\text{(Insoluble)}}{CaCO} + \underset{\text{(Soluble)}}{2NaHCO_3}$$

In place of sodium carbonate, caustic soda or sodium phosphate can also be used.

$$MgCl_2 + 2NaOH \longrightarrow \underset{\text{(Insoluble)}}{Mg(OH)_2} + 2NaCl$$

$$3MgSO_4 + 2Na_3PO_4 \longrightarrow \underset{\text{(Insoluble)}}{Mg_3(PO_4)_2} + 3Na_2SO_4$$

(ii) **Calgon :** The complex salt of metaphosphoric acid, sodium hexametaphosphate $(NaPO_3)_6$, is known as **calgon.** It is represented as $Na_2[Na_4(PO_3)_6]$. Calcium and magnesium salts present in hard water react with calgon to give complex salts.

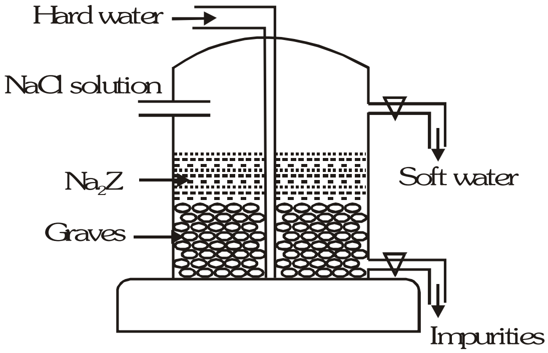
$$2CaSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6] + 2Na_2SO_4$$

$$2MgSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Mg_2(PO_3)_6] + 2Na_2SO_4$$

(iii) **Permutit process :** Permutit is hydrated sodium alumino silicate

$[Na_2Al_2Si_2O_8.\ xH_2O]$

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



Permutit also known as sodium zeolite (Na_2Z). means Zeolite is $Al_2Si_2O_8.xH_2O$.

In this process when hard water is poured into chamber, it may contain organic impurities like plant. This impurities can be removed by gravel.

On moving upwards hard water will react with Na_2Z during this reaction Na^+ ions of Na_2Z will replace Mg^{+2} & Ca^{+2} of impurities.

$$Na_2Z + CaCl_2 \longrightarrow 2NaCl + CaZ$$

NaCl is dissolved in water & water becomes soft.

This soft water is fit for washing purpose but not fit for drinking purpose.

After some time when Na_2Z is completely converted into CaZ. Process is stopped and for regeneration of Na_2Z. We use NaCl solution.

$$2NaCl + CaZ \longrightarrow CaCl_2 + Na_2Z$$

(iv) **Ion exchange resin :** By this process we can remove both cation & anion of hardness.

This process contain two chamber.

(a) Cation exchange resin : This resin contains granular insoluble organic acid having giant molecules with –COOH group.

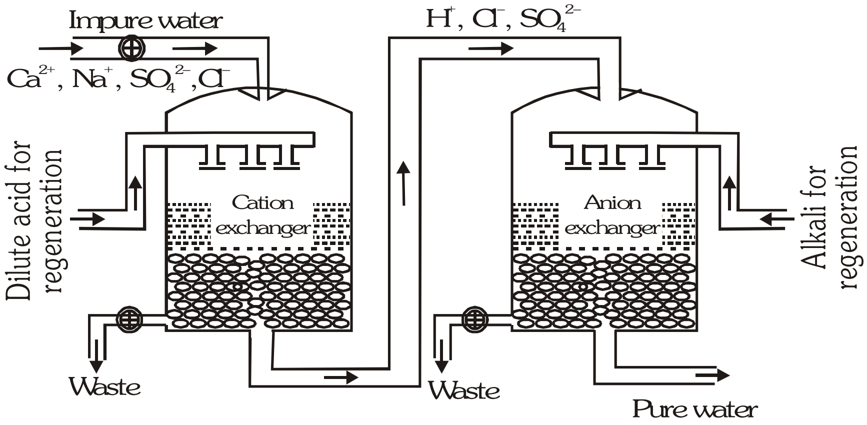
(b) Anion exchange resin : This resin contain giant organic molecules with basic groups derived from amines.

$$R{-}NH_3^+OH^-$$

Process : When hard water is poured into first chamber the cation of hardness (Mg^{+2}. Ca^{+2}) removed by H^+ ions of organic acid.

$$2R\text{–}COO^-H^+ + CaCl_2 \longrightarrow (R\text{–}COO)_2Ca + 2H^+ + 2Cl^-$$

$$+ MgSO_4 \longrightarrow (R\text{–}COO)_2Mg + 2H^+ + SO_4^{-2}$$



This water becomes soften but not used for drinking purpose because this water contain the impurity of acid. To remove anion of hardness this acidic water then passed through another bed containing anion exchanger. This exchanger removes anion like Cl^-, SO_4^{-2} & HCO_3^-.

$$R\text{–}NH_3^+OH^- + H^+ + Cl^- \longrightarrow R\text{–}NH_3^+Cl^- + H^+OH$$

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.

$$2H^+Cl^- + (R\text{–}COO)_2Ca \longrightarrow 2R^-COO^-H^+ + CaCl_2$$

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

$$R\text{–}NH_3^+Cl^- + Na^+OH^- \longrightarrow Na^+Cl^- + R\text{–}NH_3^+OH^-$$

Heavy water (D_2O)

Method of preparation :

Repeated electrolysis of H_2O : On electrolysis of water (impure) H_2O dissociate into H^+ & OH^- while a fractional part of D_2O will dissociate into D^+ & OD^-

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

$$D_2O \rightleftharpoons D^+ + OD^-$$

D^+ & OD^- due to more mass have less mobility i.e. why H^+ & OH^- will move towards cathode & anode respectively while D^+ & OD^- will be in solution.

This process will repeated for six time.

Properties of Heavy water :

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.

Chemical properties : Heavy water is chemically similar to ordinary water. However, D_2O reacts more slowly than H_2O in chemical reactions.

(a) **Action of metals** : D_2O reacts with alkali and alkaline earth metals liberates heavy hydrogen.

$$2D_2O + 2Na \longrightarrow \underset{\text{Sodium deuteroxide}}{2NaOD} + D_2$$

$$2D_2O + Ca \longrightarrow \underset{\text{Calcium deuteroxide}}{Ca(OD)_2} + D_2$$

(b) **Action with metallic oxides** : D_2O reacts slowly with basic oxides to form heavy alkalies.

$$Na_2O + D_2O \longrightarrow 2NaOD$$

$$CaO + D_2O \longrightarrow Ca(OD)_2$$

(c) **Action with nonmetallic oxides** : D_2O reacts slowly with acidic oxides to form deutero acids.

$$N_2O_5 + D_2O \longrightarrow \underset{\text{Deutero nitric acid}}{2DNO_3}$$

$$P_2O_5 + 3D_2O \longrightarrow \underset{\text{Deutero phosphoric acid}}{2D_3PO_4}$$

$$SO_3 + D_2O \longrightarrow \underset{\text{Deutero sulphuric acid}}{D_2SO_4}$$

(d) **Action with metallic carbides, phosphides, nitrides, arsenides, etc.** : Like H_2O heavy water reacts with carbides, phosphide nitrides, arsenides, etc. to form corresponding deutero compounds.

$$CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + \underset{\text{Deutero acetylene}}{C_2D_2}$$

$$Al_4C_3 + 12D_2O \longrightarrow 4Al(OD)_3 + \underset{\text{Deutero methane}}{3CD_4}$$

$$Mg_3N_2 + 6D_2O \longrightarrow 3Mg(OD)_2 + \underset{\text{Deutero ammonia}}{2ND_3}$$

$$AlN + 3D_2O \longrightarrow Al(OD)_3 + \underset{\text{Deutero ammonia}}{ND_3}$$

$$Ca_3P_2 + 6D_2O \longrightarrow 3Ca(OD)_2 + \underset{\text{Deutero phosphine}}{2PD_3}$$

$$Na_3As + 3D_2O \longrightarrow 3NaOD + \underset{\text{Deutero arsine}}{AsD_3}$$

(e) **Electrolysis** : A solution of heavy water containing Na_2CO_3 when electrolysed evolve heavy hydrogen at cathode.

$$2D_2O \xrightarrow{\text{Electrolysis}} \underset{\text{(Cathode)}}{2D_2} + \underset{\text{(Anode)}}{O_2}$$

Uses : 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.

H_2O_2 (Hydrogen Peroxide)

Laboratory method :

In laboratory, H_2O_2 is prepared by adding calculated amounts of sodium peroxide to ice cod dilute (20%) solution of H_2SO_4.

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

By the action of sulphuric acid or phosphoric acid on hydrated barium peroxide $BaO_2.8H_2O$ (Merck process)

(a) $BaO_2.8H_2O + H_2SO_4 \longrightarrow BaSO_4\downarrow + H_2O_2 + 8H_2O$

Anhydrous barium peroxide does not react readity with sulphuric acid (because a coating of insoluble barium sulphate is formed on its surface which stops further action of the acid). Therefore, hydrated barium peroxide, $BaO_2.8H_2O$ must be used.

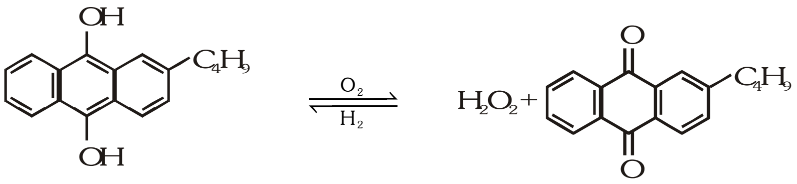
(b) $3BaO_2 + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 3H_2O$

$Ba_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3BaSO_4 + 2H_3PO_4$

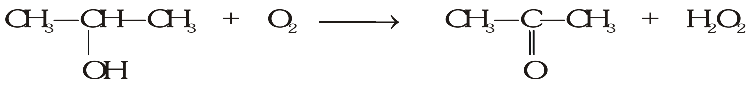
Phosphoric acid is preferred over H_2SO_4 because soluble impurities like barium persulphate ($BaO_2.8H_2O$ –H_2SO_4) tends to decompose H_2O_2 while H_3PO_4 acts as preservative (negative catalyst) for H_2O_2.

Industrial Method

(i) **Auto oxidation of 2 butyl anthraquinol (cyclic process) :**



(ii) **Oxidation of isopropyl alcohol :**



$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 + O_2 \longrightarrow CH_3-\underset{O}{\underset{\|}{C}}-CH_3 + H_2O_2$$

(iii) **Electrolytic Process :** Used 50% H_2SO_4 in electrolytic cell using Pt as anode graphite as cathode.

$2H_2SO_4 \longrightarrow 2H^+ + 2HSO_4^{\ominus}$

At Cathode $2H^+ + 2e^- \longrightarrow H_2\uparrow$

At Anode $2HSO_4^- \longrightarrow H_2S_2O_8 + 2e^{-1}$

Peroxo disulphhuric acid

$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$

$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$

Physical property :

(i) Pure H_2O_2 is colour less, odourless liquid and impure with bluish layer.

(ii) It has more Hydrogen bonding then H_2O, So order of boiling point. $H_2O_2 > D_2O > H_2O$

(iii) It is soluble in H_2O, alcohol and ether

(iv) It has bitter test and harmful for skin

(v) It is a dibasic weak acid

(vi) It has a oxidising as well as reducing property

(vii) H_2O_2 easily decompose in presence of light and temperature, So H_2O_2 always kep in dark bottles and kept at cool places.

(viii) 30% solution of H_2O_2 is called **Perhydrol**.

Chemical property :

1. **Stabily** : It is unstable in nature decompose on standing and heating. It is an example of auto oxidation-reduction Reaction ; $H_2O_2 \rightarrow H_2O + O$

   Note : Nascent oxygen working as colourless agent

   Decomposition of H_2O_2 ; $2H_2O_2 \rightleftharpoons 2H_2O + O_2$

   Note : This is retarded by R–OH, acetenilide, glycerol

2. **Oxidizing nature** : H_2O_2 is a powerful oxidant in acidic as well as in alkaline medium.

   (In acid) $H_2O_2 + 2H^+ + 2e \xrightarrow{\text{Fast}} 2H_2O \qquad E^0_{RP} = 1.77V$

   (In alkali) $H_2O + HO_2^- + 2e \xrightarrow{\text{Slow}} 3HO^- \qquad E^0_{RP} = 0.87V$

   Thuse H_2O_2 is more powerful oxidant in acidic medium. The simple interpretation of H_2O_2 as oxidant can be shown by the equation.

   $$H_2O_2 \longrightarrow H_2O + O$$

   Following are some important examples of oxidant action of H_2O_2 :

   (a) H_2O_2 oxidises black lead sulphide (PbS) to white lead sulphate ($PbSO_4$). This reaction is used in restoring the white colour of old paintings which have blackened due to the formation of lead sulphide by the action of H_2S present in air.

   $$4[H_2O_2 \longrightarrow H_2O + O]$$
   $$PbS + 4O \longrightarrow PbSO_4$$
   $$\overline{PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O}$$

   (b) H_2O_2 oxidises sulphites into sulphates.

   $$H_2O_2 \longrightarrow H_2O + O$$
   $$Na_2SO_3 + O \longrightarrow Na_2SO_4$$
   $$\overline{Na_2SO_3 + H_2O_2 \longrightarrow Na_2SO_4 + H_2O}$$

   (c) H_2O_2 oxidises nitrites to nitrates.

   $$H_2O_2 \longrightarrow H_2O + O$$
   $$Na_2NO_2 + O \longrightarrow NaNO_3$$
   $$\overline{Na_2NO_2 + H_2O_2 \longrightarrow Na_2NO_3 + H_2O}$$

   (d) H_2O_2 oxidises H_2S into sulphur.

   $$H_2O_2 \longrightarrow H_2O + O$$
   $$H_2S + O \longrightarrow H_2O + S$$
   $$\overline{H_2S + H_2O_2 \longrightarrow 2H_2O + S}$$

3. **Reducing nature** : It can also act as a reducing agent towards powerful oxidising agents.

   $$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$$

   (a) It reduces Ag_2O to silver.

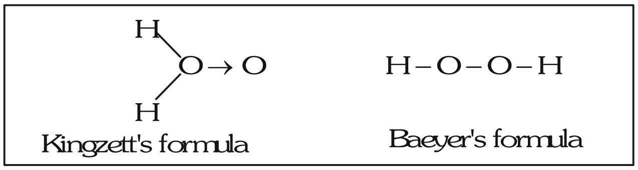
   $$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$$

   (b) It reduces ozone to oxygen.

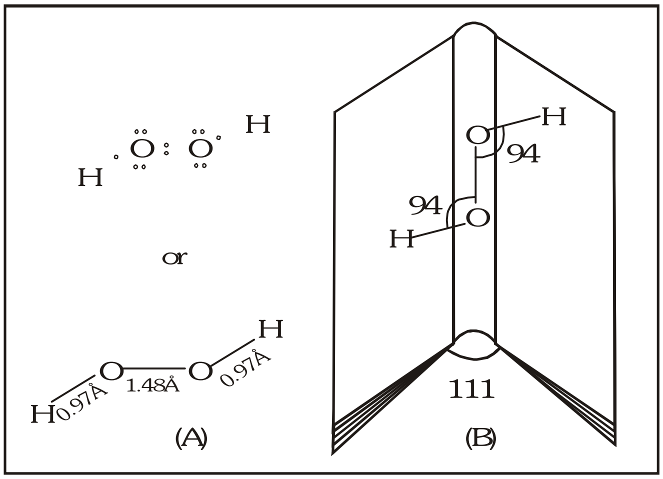
   $$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$

Structure of Hydrogen Peroxide

The vapour density as determined by Victor Meyer method at 90 C is 17. Hence, the molecular mass of H_2O_2 is 34. Two formulae have been suggested for hydrogen peroxide.



The calculated value of the single bond O–O distance is 1.48Å and X-ray measurements shows what in hydrogen peroxide, O–O bond distance is 1.46 + 0.03Å. The value of dipole moment of H_2O_2 is 2.1 D. This suggests that all the four atoms do not lie in the same plane. The molecule can be pictured as lying on the spine of a book open to an angle of 111 . The hydrogen atoms are present one on each cover and H–O bonds making angles of 94 with the O–O bond as shown in fig. The bond distance between O–H is 0.97Å.



Precautions :

(i) H_2O_2 can not be stored in simple glass bottles since rough surface of glass [alkali oxides present in it] excited by light and decomposed H_2O_2.

So the H_2O_2 usually stored in coloured, paraffin wax coated, plastic bottle.

(ii) Always with H_2O_2 add small quantity of inhibitor or negative catalyst to stay decomposition of H_2O_2.

like H_3PO_4, acetanilides etc.

Uses

(i) Bleaching agent
(ii) Hair dying
(iii) $H_2O_2 + N_2H_4$ as Rocket propellent
(iv) H_2O_2 as oxidant and reductant
(v) Antiseptic

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

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 liquid)	LPG	CH_4 gas	Octane (in liquid state)
per mole	286	285	2220	880	5511
per gram	143	142	50	53	47
per litre	12	9968	25590	35	34005

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.

MISCELLANEOUS SOLVED EXAMPLES HYDROGEN

1. H_2O_2 and heavy water was discovered by respectively :-

(1) Thenard, Urey (2) Urey, Rutherford

(3) Aston, Urey (4) Aston, Chadwick

Sol. **(1)**

H_2O_2 was discovered by Thenard where was Urey discovered heavy water.

2. $4D_2O + 3Fe \xrightarrow{\text{red}-\text{hot}} Fe_3O_4$ + gas.

The gas produced in the above reaction is :-

(1) O_2 (2) H_2 (3) D_2 (4) None

Sol. **(3)**

The gas produced in the reaction is deuterium.

3. Which of the following compound affects mercury

(1) D_2O (2) H_2O (3) O_3 (4) dil. HCl

Sol. **(3)**

Ozone wipes out meniscus of mercury due to the formation of Hg_2O as a result of $[O_3 - Hg]$ reaction

4. An inorganic substance liberates oxygen on heating and turns an acidic solution of KI brown and reduces acidified $KMnO_4$ solution. The substance is :-

(1) HgO (2) H_2O_2

(3) KNO_3 (4) $Pb(NO_3)_2$

Sol. **(2)**

$$2H_2O_2 \xrightarrow{\text{Heat}} 2H_2O + O_2 \ ;$$

$$2KI + H_2O_2 \xrightarrow{\text{Acidic}} 2KOH + \underset{\text{Brown}}{I_2} \ ;$$

Acidified $KMnO_4$ acts as an oxidising agent when it is decolourised, $H_2O_2 + O \longrightarrow H_2O + O_2$

5. In which of the following reactions does hydrogen act as an oxidising agent :-

(1) $H_2 + F_2 \longrightarrow$ (2) $H_2 + SiCl_4 \longrightarrow$

(3) $Na + H_2 \longrightarrow$ (4) $CuO + H_2 \longrightarrow$

Sol. **(3)**

The reaction in which hydrogen accepts the electron or its oxidation number changes from 0 to – 1, it acts as an oxidising agent.

$$2Na + H_2 \longrightarrow 2Na^{+}H^{-}$$

6. When H_2O_2 is added to ice cold solution of acidified potassium dichromate in ether and the contents are shaken and allowed to stand :

(1) A blue colour is obtained in ether due to formation of $Cr_2(SO_4)_3$

(2) A blue colour is obtained in ether due to formation of CrO_5

(3) A blue colour is obtained in ether due to formation of CrO_3

(4) Chromyl chloride is formed

Sol. **(2)**

$$Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \rightarrow \underset{\substack{\text{Blue colour}\\ \text{in ether}}}{2CrO_5} + 5H_2O$$

7. When a substance A reacts with water, it produces a combustible gas B and a solution of substance C in water. D reacts with this solution of C and produces the same gas B on warming. D can also produce gas B on reaction with dilute H_2SO_4. A imparts a deep golden yellow colour to smokeless flame. A, B, C and D respectively are :-

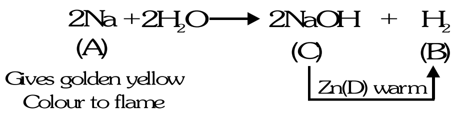
(1) Na, H_2, NaOH, Zn

(2) K, H_2, KOH, Al

(3) Ca, H_2, $Ca(OH)_2$, Sn

(4) CaC_2, C_2H_2, $Ca(OH)_2$, Fe

Sol. **(1)**



$$\underset{\substack{(A)\\ \text{Gives golden yellow}\\ \text{Colour to flame}}}{2Na} + 2H_2O \longrightarrow \underset{(C)}{2NaOH} + \underset{(B)}{H_2}$$

$$\underset{(D)}{Zn} + \underset{\text{Dilute}}{H_2SO_4} \longrightarrow ZnSO_4 + \underset{(B)}{H_2}$$