HYDROGEN AND IT'S COMPOUNDS

4.0 INTRODUCTION

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

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 > Earth

The planets 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 atmosphere & 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.

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 atmosphere in atomic form.

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

4.1 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 change occurs in physical properties like melting point, boiling point, bond energy, while minimum changes occurs in chemical properties like state of chemical reaction etc.

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

Ex. 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.

4.2 METHOD OF-PREPARATION :

(a) From acids :

The metal which are placed above H_2 in electrochemical series react with dil acids to liberate H_2.

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

$Cu + H_2SO_4 \longrightarrow$ (No reaction)

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

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

Ex. Why we use impure Zn.

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

(b) By alkalies :

Only (Be, Zn, Al, Sn, Pb, Si) (Amphoteric metal) react with boiling NaOH or KOH to evolve H_2.

$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2\uparrow$
(sodium zincate)

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

$Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2\uparrow$
(sodium stannate)

$Ph + 2NaOH + H_2O \longrightarrow Na_2PbO_3 + 2H_2\uparrow$
(sodium plumbate)

$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2\uparrow$
(sodium silicate)

$Be + 2NaOH \longrightarrow Na_2BeO_2 + H_2$
(sodium beryllate)

(c) With water :

(i) With cold water (7°C-25°C) : Li, K, Ba, Ca, Na, Sr
(ii) With hot water (25°C-90°C) : Mg, Al, Cr, Mn, Zn
(iii) With steam (greater then 100°C) : Fe, Cd, Ni, Sn, Pb

(d) Commercial or industrial method to prepare H_2 :

The commonly used processes are outlined below:
(i) Electrolysis of acidified water using platinumelectrodes gives hydrogen.

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

(ii) High purity (>99.95%) dihydrogenis obtained by electrolysing warm aqueous barium hydroxide solution between nickel electrodes.
(iii) It is obtained as a by product in the manufacture of sodium hydroxide and chlorine by the electrolysis of brine solution. During electrolysis, the reactions that take place are:
at anode: $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$
cathode: $2H_2O(I) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
overall reaction: $2Na^+(aq) + 2Cl^-(aq) + 2H_2O(I) \longrightarrow Cl_2(g) + H_2(g) + 2Na^+(aq) + 2OH^-(aq)$
(iv) From hydrocarbons : Reaction of steam on hydrocarbons or coke at high temperatures in the presence of Catalyst yields hydrogen.

$$C_nH_{2n+2} + nH_2O \xrightarrow[\text{Ni}]{1270K} nCO + (3n + 1)\,H_2$$

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

The mixture of CO and H2 is called ·water gas. As this rnpcture 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',
(v) Bosch process :

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

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

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

This is called water-gas shift r~ction.
(vi) **Lane's process :**

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

steam

4.3 PHYSICAL PROPERTIES OF HYDROGEN :

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

(ii) Its m.p. (–259.20°C) and b.p. (–252°C) are very low indicating less intermolecular attraction. Due to low m.p. liquid hyqrogen 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.

4.4 USES OF HYDROGEN:

1. Hydrogenation of vegetable oil to form solid fats i.e. vanqspati 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 $\rightarrow$ NH_3, (Haber process) alkane, alcohol and other hydrocarbons

BEGINNER'S BOX-1

1. Hydrogen does not combine with

(1) Antimony (2) Sodium (3) Bismuth (4) Helium

2. Which of the following produces hydrolith with dihydrogen

(1) Mg (2) Al (3) Cu (4) Ca

3. Hydrogen combines with other elements by

(1) Losing an electron (2) Gaining an electron

(3) Sharing an electron (4) Losing, gaining or sharing electron

4. Hydrogen acts as a reducing agent and thus resembles

(1) Halogen (2) Noble gas

(3) Radioactive elements (4) Alkali metals

5. Hydrogen readily combines with non-metals and thus it shows its

(1) Electronegativity character (2) Bectropositive character

(3) Both (1) and (2) (4) None of these

6. The oxidation states shown by hydrogen are

(1) –1 only (2) Zero only (3) +1, –1, 0 (4) +1 only

7. Hydrogen readily combines with metals and thus shows its

(1) Electropositive character (2) Bectronegative character

(3) Both (1) and (2) (4) None of these

8. In which of the compounds does hydrogen have an oxidation state of –1

(1) CH_4 (2) NH_3 (3) HCl (4) CaH_2

9. Match List I (Fuels) with List II (composition) and select the correct answer using the codes given below the lists.

List I (Fuels)	**List II (Composition)**
A. Water gas	i. A mixture of CO and N_2
B. Producer gas	ii. methane
C. Coal gas	iii. A mixture of CO and H_2
D. Natural gas	iv. A mixture of CO, H_2, CH_4 and CO_2

	A	B	C	D
(1)	iii	i	iv	ii
(2)	iii	i	ii	iv
(3)	i	iii	iv	ii
(4)	iii	ii	iv	i

4.5 HYDRIDES

The binary compounds of hydogen with different ekmients are called hydrides.
These are of three types :

(a) Ionic/Salt like/Saline hydrides :

- Compounds of hydrogen with s-block elements except beryllium & magnesium are called ionic hydrides.
  LiH, NaH, KH, RbH, CsH, CaH_2, SrH_2, BaH_2
  BeH_2, MgH_2 are covalent polymeric hydride.
- Structure of these hydrides are similar to rock salt, so they are also called salt like/saline hydrides.
- Down the group, atomic size↑ Lattice energy, stability↓ Melting point↓ Boillng point↓
- On electrolysis of these hydrides, hydrogen is liberated at anode.
- On reaction with water these hydrides will form hydrogen
  $NaH + H_2O \longrightarrow NaOH + H_2$
- These hydrides form complex hydrides which are very good reducing agents.
  $4LiH + AlCl_3 \longrightarrow NaOH + H_2$
  $LiAlH_4 \longrightarrow$ Lithium alurrinium hydride
  $NaBH_4 \longrightarrow$ Sodium borohydride

(b) Metallic/Interstitial hydrides :

- They are the compounds of d & f-biock elements. In these hydrides hydrogen occupies interstitial sites present in metalliclattice, so they are called interstitial hydrides.
- Properties of these hydrides are similar to parent metals, so they are also known as metallic hydrides.
- These hydrides are non stoichiometric in nature (i.e. having variable composition).
  ZrH_x (x = 1.3 – 1. 75)
  TiH_x (x = 1.8 – 2)
- Metals of group 7,8, 9 don't form any hydrides so this particular part of periodic table is known as hydride gap.
- In group-6 only one hydride CrH is formed.

(c) Covalent/Molecular hydrides

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

- These hydrides exist as molecules, so they are also' known as molecular hydrides. There hydrides are non-conductor of electricity.
- These hydrides are again divides Into 3 categories.

(a) Electron deficient hydrides :

They are the hydrides of group 13 elements.

e.g. BH_3, AlH_3, GaH_3–In these hydrides central eleriient 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 element has $8e^-$ in its outer most shell.

(c) Electron rich hydrides :

These are the hydrides of group 15, 16 and 17

e.g. $\ddot{N}H_3$, $H_2\ddot{O}$, $H\ddot{F}$: –In these hydrides lonepair are present on central element which can be given to others. So they are called electron rich hydrides.

4.6 HARD AND SOFT WATER

Water which produces lather with soap is **soft water** while water which does not produces lather with soap is hard water. The hardness of water is caused by presence of bicarbonates, chlorides and sulphates of calcium and magnesium.

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

$$Mg^{2+}(aq) + 2C_{17}H_{35}COO^-(aq) \longrightarrow (C_{17}H_{35}COO)_2Mg\downarrow$$

Anion of soap — Insoluble precipitates

Hardness of water are 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 compounds are precipitated.

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

$$Mg(HCO_3)_2 \xrightarrow{\text{Boiling}} \underset{\text{(Insoluble)}}{Mg(OH)_2} + 2CO_2$$

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

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow \underset{\text{(Insoluble)}}{2CaCO_3} + 2H_2O$$

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

(b) Permanent Hardness : This is due to the presence of 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 compounds.

$$CaCl_2 + Na_2CO_3 \longrightarrow \underset{\text{(Insoluble)}}{CaCO_3} + 2NaCl$$

$$CaSO_4 + Na_2CO_3 \longrightarrow \underset{\text{(Insoluble)}}{CaCO_3} + Na_2SO_4$$

$$Ca(HCO_3)_2 + Na_2CO_3 \longrightarrow \underset{\text{(Insoluble)}}{CaCO_3} + \underset{\text{(Soluble)}}{2NaHCO_3}$$

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

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

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

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

$$2CaSO_4 + Na_2[Na_4PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6] + 2Na_2SO_4$$

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

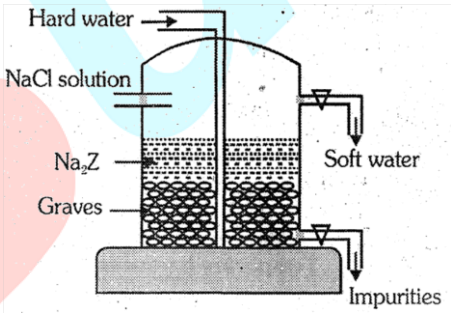
(iii) Pennutit process : Permutit is hydrated sodium alumino silicate

$[Na_2Al_2Si_2O_8.\ xH_2O]$ or $[Na_2OAl_2O_3.2SiO_2.xH_2O]$

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

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

On moving upwards hard water with 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 cbmpletely 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: This process removes both temporary and permanent hardness. Also, by this process we can remove both cation & anion of hardness.

This process contain two chambers.

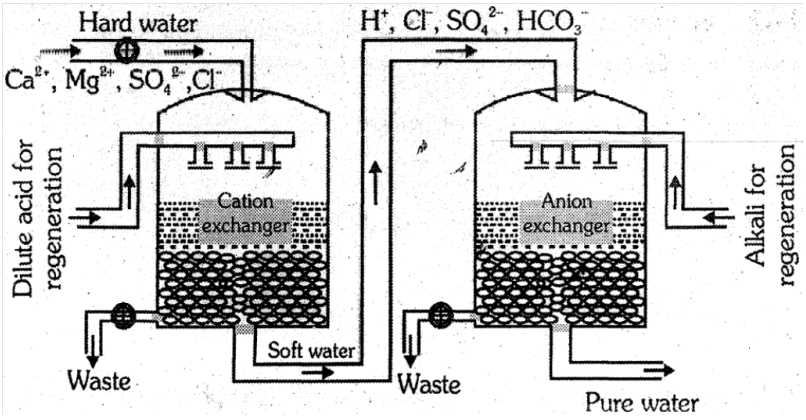
(a) Cation exchange resin : This resin contains granular insoluble orgq,nic acid having giant molecules with $RCOOH^+$ group.

(b) Anion exchange resin : This resin contain giant organic molecules with basic groups derived from amines with RNH_3OH^-

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

$$2RCOOH^+ + CaCl_2 \longrightarrow (RCOO)_2Ca + 2H^+ + 2Cl^-$$

$$2RCOOH^+ + MgSO_4 \longrightarrow (RCOO)_2Mg + 2H^+ + SO_4^{-2}$$



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-}.

$$RNH_3^+ + OH^- + H^+ + Cl^- \longrightarrow RNH_3^+ + H^+OH$$

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

After sometime when both resin gets exhausted process is stopped.

Regeneration of resin :

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

$$2H^+Cl^- + (RCOO)_2Ca \longrightarrow 2RCOO^-H^+ + CaCl_2$$

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

$$RNH_3^+Cl^- + Na^+OH^- \longrightarrow Na^+Cl^- + RNH_3^+OH^-$$

4.7 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 is repeated six times.

Properties of Heavy water :

Physical properties :

(a) Heavy water is a colourless, odourless and t~steless mobile liquid.

(b) Nearly all the physical constants are higher than the corresponding values of ordinary water. (dielectric constant order $H_2O > D_2O$)

Chemical properties :

(a) Heavy water is chemically similar to ordinary water. However, D_2O reacts more slowly than H_2O in chemical reactions.

(b) All chemical properties are same, but reactions are slow.

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.

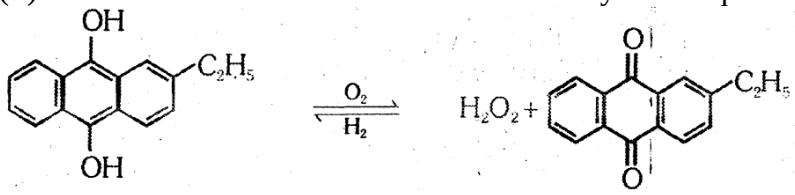
4.8 H_2O_2 (HYDROGEN PEROXIDE)

Method of preparation

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

$$BaO_2.8H_2O(s) + H_2SO_4 \longrightarrow BaSO_4(s) + H_2O_2(aq) + 8H_2O(\lambda)$$

(ii) Industrial Method : Auto oxidation of 2 ethyl anthraqoinol (cyclic process) :



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

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

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

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

(Peroxo disulphuric acid)

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$$ [Peroxo monosulphuric acid (Caro's acid)]

$$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$$

Physical properties :

(i) Pure H_2O_2 is colourless, odourless liquid and impurewith bluish layer.

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

Order of melting point = $\left[\underset{-0.35°C}{H_2O_2} < \underset{0°C}{H_2O} \right]$

(iii) It is soluble in H_2O, alcoholand ether.

(iv) It has bitter taste and harmful for skin.

(v) It is a dibasic weak acid.

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

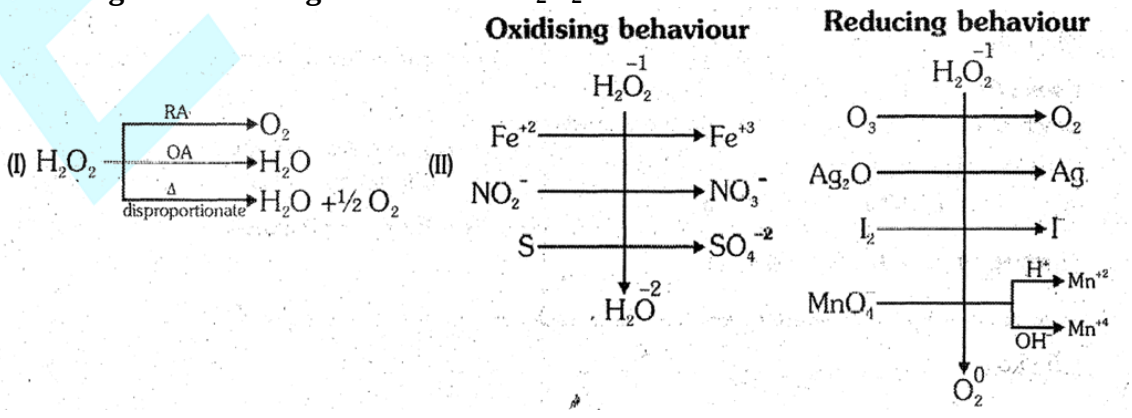
(vii) H_2O_2 easily decompose in presence of lightand temperature, so H_2O_2 always kept in darkbottles and kept at cool places & small amount of inhibitor is added like R–OH, glycerol & Acetone.

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

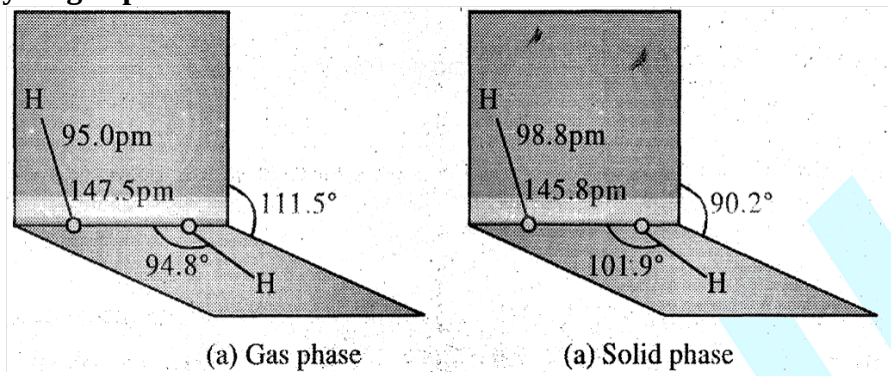
(ix) H_2O_2 decomposes at its boiling point hence its distillation is carried out under reduced pressure.

Chemical properties :

(A) Oxidising and Reducing behaviour of H_2O_2



Structure of hydrogen peroxide



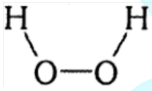
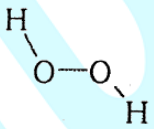
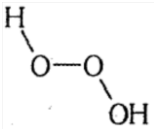
Uses

(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

BEGINNER'S BOX-2

1. Among the following, identify the compqund which cannot act as both oxidising and reducing agents
(1) H_2O_2 (2) H_2 (3) SO_2 (4) HCl

2. In which of the following reaction hydrogen peroxide is a reducing agent
(1) $2FeCl_2 + 2HCl + H_2O_2 \longrightarrow 2FeCl_3 + 2H_2O$
(2) $Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$
(3) $2HI + H_2O_2 \longrightarrow 2H_2O + I_2$
(4) $H_2SO_3 + H_2O_2 \longrightarrow H_2SO_4 + H_2O$

3. The structure of H_2O_2 is
(1)  (2)  (3) H–O–O–H (4) 

4. The oxide that gives hydrogen peroxide on the treatment with a dilute acid is
(1) MnO_2 (2) PbO_2 (3) Na_2O_2 (4)TiO_2

5. Temporary hardness may be removed from water by adding
(1) $CaCO_3$ (2) $Ca(OH)_2$ (3)$CaSO_4$ (4) HCl

6. Temporary hardness of water can be removed by
(1) Addition of potassium pennanganate (2) Boiling
(3) Filtration (4) Addition of chlorine

7. When zeolite (Hydrated sodium aluminium silicate) is treated with hard water the sodium ions are exchanged with
(1) OH^- ions (2) SO_4^{2-} ions (3) Ca^{2+} ions (4) H^+ ions

8. The velocity of neutrons in nuclear reactor is slowed down by

(1) Heavy water (2) Ordinary water (3) Zinc rod (4) Fused caustic soda

9. When temporary hard water containing $Mg(HCO_3)_2$ is boiled the ppt. formed is of
(1) $MgCO_3$ (2) MgO (3) $Mg(OH)_2$ (4) None of these

10. Which of the following can effectively remove all types of hardness of water
(1) Soap (2) Washing soda (3) Slaked lime (4) None of these

ANSWER KEY

BEGINNER'S BOX-1

1.	(4)	**2.**	(4)	**3.**	(4)	**4.**	(4)	**5.**	(2)
6.	(3)	**7.**	(2)	**8.**	(4)	**9.**	(1)		

BEGINNER'S BOX-1

1.	(4)	**2.**	(2)	**3.**	(2)	**4.**	(3)	**5.**	(2)
6.	(2)	**7.**	(3)	**8.**	(1)	**9.**	(3)	**10.**	(2)