ALLEN CAREER INSTITUTE KOTA (RAJASTHAN)

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PRE-MEDICAL

INORGANIC CHEMISTRY

ENTHUSIAST | LEADER | ACHIEVER

STUDY MATERIAL

Hydrogen & It's Compounds

ENGLISH MEDIUM

Copyright Statement

HYDROGEN AND ITS 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 and Saturn consist mainly of H_2. Similarly about half the mass of the sun and some other stars is made up of hydrogen.

In Sun's atmosphere and 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) and they undergoes fusion and converted into He nuclei and 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 most reactive 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 and 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 a large difference in mass.

Ex. Which of the following reaction is fast and 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 in electrochemical series react with dil acids to liberate H_2.

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

$Cu + \underset{\text{(dil.)}}{H_2SO_4} \rightarrow$ No reaction

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

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

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.

$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2\uparrow$
(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)

$Pb + 2NaOH + H_2O \longrightarrow Na_2PbO_3 + 2H_2\uparrow$
(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 platinum electrodes gives hydrogen.

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

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

(iii) It is obtained as a 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: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

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

overall reaction : $2Na^+(aq) + 2Cl^-(aq) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2Na^+(aq) + 2OH^-(aq)$

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

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

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

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'**. Now days '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 reaction*.

(vi) **Lane's process :**

$$3Fe + \underset{\text{steam}}{H_2O} \longrightarrow Fe_3O_4 + H_2\uparrow$$

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

(iii) H—H bond energy is 104 Kcal mol^{-1} or 436 KJ/mol

(iv) H – H bond length is 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. 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 hydrocarbons

BEGINNER'S BOX-1

1. Which of the following produces hydrolith with dihydrogen ?
(1) Mg (2) Al (3) Cu (4) Ca

2. Hydrogen combines with other elements by :-
(1) Losing an electron (2) Gaining an electron
(3) Sharing an electron (4) Losing, gaining or sharing electron

3. Hydrogen readily combines with non-metals and thus it shows its :-
(1) Electronegativity character (2) Electropositive character
(3) Both (1) and (2) (4) None of these

4. The oxidation states shown by hydrogen are :-
(1) –1 only (2) Zero only (3) +1, –1, 0 (4) +1 only

5. Hydrogen readily combines with metals and thus shows its :-
(1) Electropositive character (2) Electronegative character
(3) Both (1) and (2) (4) None of these

6. In which of the compounds does hydrogen have an oxidation state of –1 :-
(1) CH_4 (2) NH_3 (3) *HCl* (4) CaH_2

7. 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

8. H_2 react with halogen in presence of catalyst to form hydrogen halide HX. X (Halogen) is :-
(1) Cl_2 (2) Br_2 (3) F_2 (4) I_2

9. Which of the following is a method of preparation of H_2 ?
(1) reaction of granulated Zn with dil. HCl (2) reaction of Zn with aqueous Alkali.
(3) by electroysis of Brine solution (4) All of the above

4.5 HYDRIDES

The binary compounds of hydrogen with different elements 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↓ Boiling 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.

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

  $LiAlH_4 \longrightarrow$ Lithium aluminium hydride

  $NaBH_4 \longrightarrow$ Sodium borohydride

(b) Metallic / 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.
- 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 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 element has $8e^-$ in its outer most shell.

(c) Electron rich hydrides :

These are the hydrides of group 15, 16 and 17

e.g. $\ddot{N}H_3$, $H_2\ddot{O}:$, $H\ddot{\underset{\cdot\cdot}{F}}:$ – In these hydrides lone pair 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.

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

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

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.

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

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

(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.

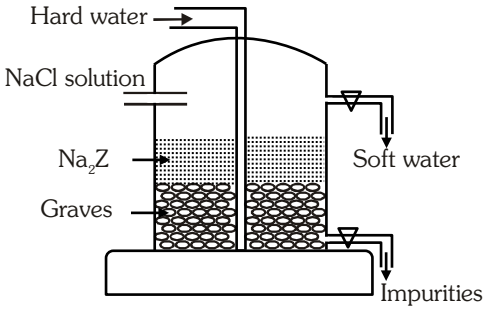
$$2CaSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6] + 2Na_2SO_4$$

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

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

$[Na_2Al_2Si_2O_8.\ xH_2O]$ or $[Na_2O.Al_2O_3.2SiO_2.xH_2O]$

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



In this process when hard water is poured into chamber, it may contain organic impurities like plant. These 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.

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 :** 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.

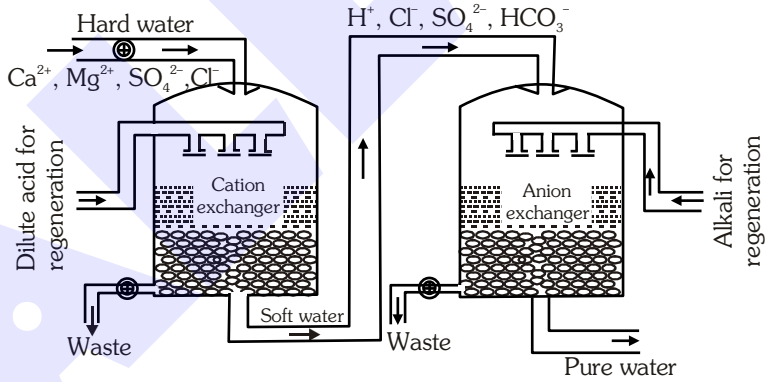
(a) Cation exchange resin : This resin contains granular insoluble organic acid having giant molecules with $RCOO^-H^+$ group.

(b) Anion exchange resin : This resin contain giant organic molecules with basic groups derived from amines with $RNH_3^+OH^-$

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

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

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



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^-.

$RNH_3^+OH^- + H^+ + Cl^- \longrightarrow RNH_3^+Cl^- + H^+\bar{O}H$

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 tasteless 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.

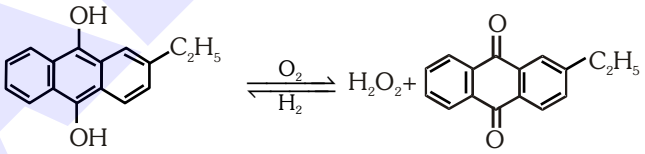
4.8 H_2O_2 (HYDROGEN PEROXIDE)

Method of preparation (According to NCERT)

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

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

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



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

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

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

At Anode $2HSO_4^- \longrightarrow \underset{\text{(Peroxo disulphuric acid)}}{H_2S_2O_8} + 2e^-$:

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

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

Physical properties :

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

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

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

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

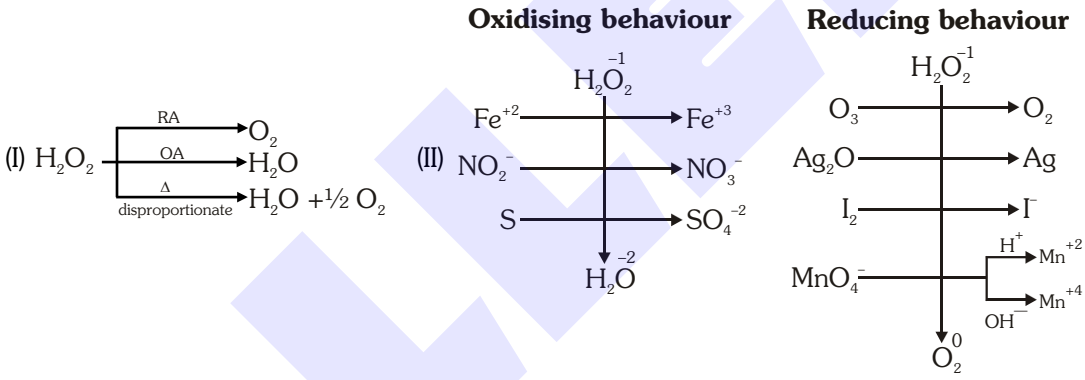
(vii) H_2O_2 easily decompose in presence of light and temperature, so H_2O_2 always kept in dark bottles and kept at cool places and small amount of inhibitor is added like R–OH, glycerol and Acetone.

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

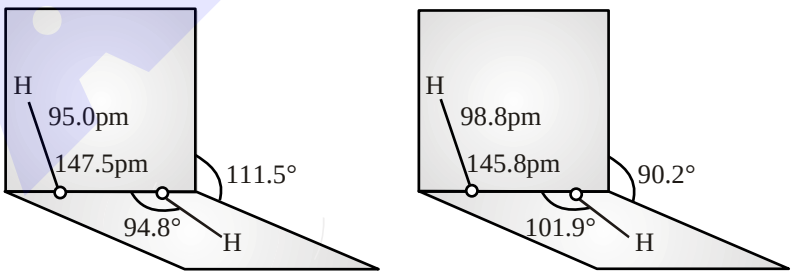
(ix) H_2O_2 decomposes at its boiling point hence its distillation is carried out under reduced pressure.

Chemical properties :

(A) Oxidising and Reducing behaviour of H_2O_2



Structure of hydrogen peroxide



(a) Gas phase (a) Solid phase

Uses

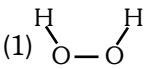
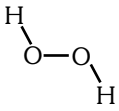
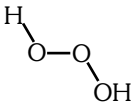
(i) Bleaching agent (ii) Hair dying

(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. The structure of H_2O_2 is

(1)  (2)  (3) H–O–O–H (4) 

2. Temporary hardness may be removed from water by adding

(1) $CaCO_3$ (2) $Ca(OH)_2$ (3) $CaSO_4$ (4) HCl

3. Temporary hardness of water can be removed by

(1) Addition of potassium permanganate (2) Boiling
(3) Filtration (4) Addition of chlorine

4. 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

5. 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

6. 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

7. Impurity of $Mg(HCO_3)_2$ is removed from water on boiling. It removes in the form of

(1) $MgCO_3$ (2) $Mg(OH)_2$ (3) $Mg(HCO_3)_2$ (4) None of these

8. In cation exchange process for permanent hardness, H^+ exchange for Na^+, Mg^{+2}, Ca^{+2} and other cation present in water. This process result in proton release and thus makes the nature of water :-

(1) Acidic (2) Basic (3) Neutral (4) Amphoteric

9. Which of the following option is correct ?
[Statement T for true & F for false]
(a) H_2O_2 is almost colourless (very pale blue) liquid
(b) H_2O_2 is miscible with water in all proportion and forms hydrated $H_2O_2.H_2O$
(c) 1% H_2O_2 is concentrated to 30% by distillation under reduced pressure
(d) 1 ml of 30 % H_2O_2 solution will give 100 ml of oxygen at STP

(1) TTTT (2) FTTT (3) FTFT (4) FFTT

10. In a following chemical reaction

$MnO_4^- + H^+ + H_2O_2 \rightarrow$

The incorrect option is

(1) O_2 is release (2) Mn^{+7} reduced into Mn^{+2}
(3) H_2O_2 acts as an oxidising agent (4) All of these

ANSWER'S KEY

BEGINNER'S BOX-1	**Que.**	1	2	3	4	5	6	7	8	9	
	Ans.	**4**	**4**	**2**	**3**	**2**	**4**	**1**	**4**	**4**	
BEGINNER'S BOX-2	**Que.**	1	2	3	4	5	6	7	8	9	10
	Ans.	**2**	**2**	**2**	**3**	**3**	**2**	**2**	**1**	**1**	**3**