HYDROGEN PEROXIDE (H_2O_2)

Preparation

(i) Hydrogen peroxide can be prepared in the laboratory by the action of cold dilute sulphuric acid on hydrated barium peroxide.

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

(ii) Hydrogen peroxide can also be prepared by the hydrolysis of peroxodisulphuric acid ($H_2S_2O_8$) which is obtained by the electrolytic oxidation of acidified sulphate solution.

$$2HSO_4^-(aq) \xrightarrow{electrolysis} H_2S_2O_8(aq)$$

$$H_2S_2O_8(aq) + 2H_2O \longrightarrow 2H_2SO_4(aq) + H_2O_2(aq)$$

(iii) On an industrial scale, H_2O_2 is prepared by the auto–oxidation of 2–ethyl anthraquinol.

$$2\text{–}ethyl\ anthraquinol \underset{}{\overset{O_2\,(air)}{\rightleftharpoons}} H_2O_2 + oxidised\ product$$

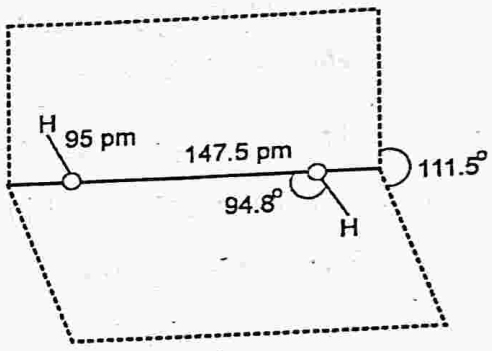
Solution of H_2O_2 is concentrated by distillation under reduced pressure.

H_2O_2 is marketed as 30% solution under the name '100 volume H_2O_2'. This means that one mL of this sample will give 100 mL of oxygen at STP. Commercial H_2O_2 contains 3% H_2O_2 (10 volume). 10 volume H_2O_2 implies that 1 mL of this solution will give 10 mL oxygen at STP.

PROPERTIES OF HYDROGEN PEROXIDE

Physical properties: Pure hydrogen peroxide is a pale blue liquid with a boiling point of 423K. It is denser than water and is completely miscible with water.

***Structure*:** Hydrogen peroxide molecule has a non–planar structure in which the two $O-H$ bonds are in different planes. In the gas phase, the dihedral angle between the two planes is 111.5° while in the solid phase, the dihedral angle reduces to 90.2° due to hydrogen bonding. The two oxygen atoms are linked to each other by a single bond known as peroxide bond.



Structure of H_2O_2

Chemical properties of hydrogen peroxide

(i) Decomposition

H_2O_2 decomposes slowly into water and oxygen on heating or on exposure to light.

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$$

The decomposition reaction is also catalysed by metal surfaces, metal powders, traces of alkali, the rough surface of glass, alkali oxides present in glass etc. Hence **H_2O_2 is stored in wax-lined glass or plastic vessels in dark.** Urea or acetanilide is generally added as stabiliser to check the decomposition.

(ii) Acidic nature

Pure H_2O_2 is a weak acid.

(iii) Oxidising and reducing character

Hydrogen peroxide acts as an oxidising agent as well as reducing agent in both acidic and alkaline media. The following reactions illustrate the *oxidising action* of hydrogen peroxide.

(a) *In acid medium*: It oxidises ferrous salts into ferric salts and lead sulphide to lead sulphate.

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

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$

Traces of hydrogen sulphide in the atmosphere blacken the lead paintings due to the formation of black *PbS*. To restore the colour of old lead paintings, it is dipped in aqueous H_2O_2 solution when the black lead sulphide is oxidised to white lead sulphate.

(c) *In alkaline medium*: H_2O_2 oxidises manganese sulphate to manganese dioxide.

(i.e., Mn^{2+} is oxidised to Mn^{4+})

$$Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$$

The following examples illustrate the *reducing action* of hydrogen peroxide.

(a) *In acidic medium:* H_2O_2 reduces acidified $KMnO_4$ to colourless salts.

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

$$\text{or } 2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

It reduces hypochlorous acid

$$HOCl + H_2O_2 \longrightarrow Cl^- + H_3O^+ + O_2$$

(b) *In basic medium*: H_2O_2 reduces iodine in presence of alkali to iodide ions.

$$I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$$

(iv) Bleaching action

Hydrogen peroxide is a good bleaching agent for ivory, wood, silk, wood and paper pulp. The bleaching action is due to oxidation.

Uses

(i) As a bleaching agent for textiles, wood and paper pulp.

(ii) In the manufacture of chemicals such as sodium perborate, percarbonate etc.

(iii) A dilute solution of H_2O_2 is used as a disinfectant.

(iv) It is used as an antiseptic for wounds, teeth and ears under the name *perhydrol*.

(v) It is used in pollution control treatment of domestic and industrial effluents.

Questions and Answers (Evaluation Pattern)

1. Hydrogen is regarded as the first element in the periodic table. Yet, it does not have a permanemt position in the periodic table.
   Justify the statement by narrating similarities of hydrogen with alkali metals and halogens.

Ans: See text

2. The relative percentage abundance of the isotopes of hydrogen as analysed by a mass spectrograph is as follows:

Isotope I	Isotope 2	Isotope 3
0.0156	99.985	10^{-15}

   (i) Name the isotopes of hydrogen based on their relative abundance. Give their symbols.

   (ii) Which of these isotopes is the major component of naturally occuring hydrogen? Outline its structure.

   (iii) Which is the radioactive isotope of hydrogen?

Ans: (i) Isotope 2 - Protium or ordinary hydrogen ($^{1}_{1}H$); Isotope 1 - Deuterium ($^{2}_{1}H$) and Isotope 3- Tritium ($^{3}_{1}H$)

(ii) Protium – Atomic number 1, mass number 1 – one proton in its nucleus and one electron in its s orbital. (no neutrons)

(iii) Tritium

3. Hydrogen can be prepared from water, acids, alkalies and hydrocarbons.

(i) Name a metal that can liberate hydrogen from aqueous *NaOH*. Write equation for the reaction.

(ii) How is very pure H_2 prepared?

(iii) What is syn gas? How is it prepared from hydrocarbons?

Ans: (i) *Zn*. $Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$

(ii) Very pure H_2 is prepared by electrolysing warm aqueous barium hydroxide solution between nickel electrodes.

(iii) Syngas or synthesis gas is a mixture of CO and H_2. It is formed by passing a mixture of hydrocarbon and steam over nickel catalyst heated to about 1270 K

$$CH_4 + H_2O \xrightarrow[Ni]{1270\,K} CO + 3H_2$$

4. Hydrogen has a common oxidation state of +1. However in certain compounds hydrogen shows -1 oxidation state.

(i) Name the compounds in which hydrogen shows –1 oxidation state

(ii) Classify the following hydrides into different types.
NH_3, NaH, ScH_2, AsH_3, LaH_2, KH, SiH_4, NiH

(iii) How does NaH react with water?

Ans:

(i) Ionic or saline hydrides such as NaH, CaH_2, etc.

(ii) NaH, KH (ionic) ; NH_3, AsH_3, SiH_4 (covalent); LaH_2, NiH, ScH_2 (interstitial)

(iii) $NaH + H_2O \longrightarrow NaOH + H_2$

5. Hydogen forms compounds with elements having atomic numbers 9,11,12 and 17. Give their chemical formulae and compare their properties.

Ans: HF, NaH, MgH_2 and HCl are the hydrides formed by hydrogen and elements with atomic numbers 9,11,12 and 17 repectively.
HF and HCl are covalent compounds with partial ionic character. They are polar. They dissociate into H^+ in solution and hence acidic. NaH and MgH_2 are ionic hydrides contacting H^- ions. They are crystalline compounds which dissolve in water to form hydrogen gas and the corresponding hydroxides which are alkaline.

6. (i) Hydrogen bonding is the cause for several peculiar properties of water in the liquid and solid states. What are those properties?

(ii) Water forms several types of hydrates with metal salts. Discuss any two of them with examples. **(HSE March 2006)**

Ans:

(i) Water has high boiling point due to association by intermolecular hydrogen bonding. Density of ice is less than that of water because ice has an ordered three dimensional hydrogen bonded structure which contains vacant spaces which lower its density.

(ii) (a) In certain hydrates, water molecules are coordinated to the metal ion in complexes e.g., $[Cr(H_2O)_6]Cl_3$

(b) In certain metal salt hydrates, water molecules occupy voids or interstitial sites in the crystal lattice e.g., $BaCl_2 . 2H_2O$

7. Water behaves as an ampoteric substance.

(i) Illustrate the statement with suitable examples.

(ii) Name an element that oxidises water. Write equation for the reaction.

(iii) How does silicon tetrachloride react with water?

Ans:

(i) Water has the ability to act as an acid as well as a base

$$\underset{(base)}{H_2O} + HCl \rightleftharpoons H_3O^+ + Cl^-$$

$$\underset{(acid)}{H_2O} + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

(ii) Fluorine. $2Fe + 2H_2O \longrightarrow 4HF + O_2$

(iii) $SiCl_4$ undergoes hydrolysis with water to form SiO_2

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$$

8. For the removal of permanent hardness of water, it is treated with a chemical substance, calgon. It is believed that this substance renders calcium and magnesium ions present in water passive so as to cause no hinderance in lather formation with soap .

(i) What is calgon chemically?

(ii) How does this substance make water soft?

(iii) Give chemical equations to support your answer?

Ans:

(i) sodium hexametaphosphate ($Na_6P_6O_{18}$) is known as calgon.

(ii) Ca^{2+} and Mg^{2+} of hard water react with calgon to form soluble complexes which remain dissolved in water. The ions are not free to react with soap as they are tied up in stable complexes.

(iii) See theory

9. A sample of river water does not give lather with soap easily when it is cold. But on heating it gives ready lather

(i) Account for this observation. Give chemical equations.

(ii) In certain cases water does not give lather even when heated. Explain.

Ans:

(i) It is because of temporary hardness of water due to the presence of dissolved bicarbonates of *Mg* and *Ca*. On heating, these salts decompose to form insoluble compounds and are precipitated.

$$Ca(HCO_3)_2 \xrightarrow{heat} CaCO_3 + H_2O + CO_2$$

$$Mg(HCO_3)_2 \xrightarrow{heat} MgCO_3 + H_2O + CO_2$$

Thus water becomes free of *Ca* and *Mg* ions and forms ready lather with soap.

(ii) This is due to permanent hardness caused by dissolved chlorides and sulphates of *Ca* and *Mg*

10. (i) Bring out the difference between hydration and hydrolysis using suitable examples.

(ii) Comment on the different types of hydrates

Ans:

(i) Decomposition of a compound by the action of water is called hydrolysis. Many compounds are hydrolysed by water

e.g., $SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$

The process by which water molecules combine with ions or molecules to form hydrated species is called hydration.

e.g., $CuSO_4.5H_2O$, $BaCl_2.2H_2O$

(ii) There are three types of hydrates

1. Water molecules co-ordinated to the metal ion in complexes. e.g., $[Cr(H_2O)_6]Cl_3$
2. Water molecules occupying voids in the crystal lattice. e.g., $BaCl_2.2H_2O$
3. Hydrates containing hydrogen bonded water molecules. e.g., $CuSO_4.5H_2O$

11. (i) Dalda available in the market is prepared from vegetable oil. Write the science behind it

(ii) Water from a river can't be used for washing clothes by soap. So people there are using detergents. Give reason for this and suggest a remedy. **(HSE March 2007)**

Ans:

(i) Dalda is prepared by passing H_2 through vegetable oil in presence of Ni at about 473K. Then addition of H_2 takes place at the $C = C$ of the oil converting it into saturated vegetable ghee such as dalda.

(ii) Water is hard. (See text).

12. (a) Account for the following observations

(i) Density of ice is lower than that of water.

(ii) Hard water does not form ready lather with soap.

(b) Justify the position of hydrogen in the periodic table. **(HSE March2011)**

Ans:

(i) Ice has an ordered three dimensional hydrogen bonded structure in which each oxygen atom is tetrahedrally surrounded by four other oxygen atoms. The resulting structure contains vacant spaces and hence the density of ice is less than that of water.

(ii) Hardness of water is due to the presence of dissolved salts of calcium and magnesium. These cations present in hard water form insoluble salts with soap and prevent the formation of lather. For example,

$$2C_{17}H_{35}COONa + M^{2+} \longrightarrow (C_{17}H_{35}COO)_2\,M + 2Na^{+}$$

(sodium stearate)

$(M = Ca \text{ or } Mg)$

NCERT Exercise Questions and Answers

1. Write the names of isotopes of hydrogen. What is the mass ratio of these isotopes?

Ans: Protium $\left({}_{1}^{1}H\right)$, Deuterium $\left({}_{1}^{2}H\right)$ and Tritium $\left({}_{1}^{3}H\right)$ having the mass ratio 1:2:3

2. Why does hydrogen occur in diatomic state rather than monoatomic form under normal conditions?

Ans: $H\,(1s^1)$ is one electron short of stable inert gas configuration $(1s^2)$ of helium. To achieve this stable state, it shares the electron with another hydrogen atom to form stable H_2 molecule.

3. How can the production of dihydrogen obtained from coal gasification, be increased?

Ans: Coal gasification involves the formation of water gas (syn gas) from coal or coke by passing steam over it. The production of H_2 may be increased by mixing syn gas with steam and passing over iron chromate catalyst. Then CO is oxidised to CO_2 and produces more H_2 from steam.

4. Complete the following reactions

(i) $CO\,(g) + H_2\,(g) \xrightarrow[\text{catalyst}]{\Delta}$ (ii) $C_3H_8\,(g) + 3H_2O\,(g) \xrightarrow[\text{catalyst}]{\Delta}$

(iii) $Zn\,(s) + NaOH\,(aq) \xrightarrow{\text{heat}}$

Ans: (i) $CO(g) + 2H_2(g) \xrightarrow[\text{cat}]{\Delta} CH_3OH(l)$

(ii) $C_3H_8(g) + 3H_2O(g) \xrightarrow[\text{cat}]{\Delta} 3CO(g) + 7H_2(g)$

(iii) $Zn(s) + 2NaOH(aq) \xrightarrow[\text{heat}]{} Na_2ZnO_2(aq) + H_2(g)$

5. Discuss the consequences of high bond enthalpy of $H-H$ bond in terms of chemical reactivity.

Ans: High bond enthalpy makes hydrogen inert at ordinary temperatures. However, H_2 is active at higher temperatures or in presence of catalyst.

6. What characteristics do you expect from an electron deficient hydride with respect to its structure and chemical reactions?

Ans: Due to lack of sufficient electrons, they do not form normal covalent bonds but exist in polymeric state (e.g., B_2H_6). These compounds compensate their electron deficiency by reacting with many metals, non metals and their compounds. ($2NaH + B_2H_6 \rightarrow 2NaBH_4$). They are Lewis acids capable of reacting with Lewis bases.

7. Do you expect carbon hydrides of the type C_nH_{2n+2} to act as Lewis acid or base? Justify your answer.

Ans: This type of carbon hydrides neither gain nor lose electrons because they contain exact number of electrons (electron precise) to form covalent bonds. They do not show either Lewis acid or Lewis base nature.

8. What do you mean by non-stoichiometric hydrides? Do you expect this type of hydrides to be formed from alkali metals? Justify.

Ans: Metallic hydrides whose compositions do not correspond to simple whole number ratio are called non-stoichiometric hydrides. In these compounds H atoms occupy voids in the metal lattice and some voids remain vacant making it non-stoichiometric. Alkali metal hydrides are ionic hydrides and contain H^- ions. Since H^- is formed by complete transfer of an electron from metal to H, the metal - hydrogen ratio is always fixed. Hence alkali metals form only stoichiometric hydrides.

9. How do you expect metal hydrides to be useful for hydrogen storage? Explain.

Ans: Due to the inclusion of H atoms into the metal lattice, the lattice becomes unstable. So upon heating, the hydride easily decomposes to form H_2 gas. Many transition metals can be used for the storage (and transport) of H_2 (as hydrides) which is a good fuel (Hydrogen economy).

10. How does atomic hydrogen or oxy hydrogen torch function for cutting and welding purposes?

Ans: Atomic hydrogen is formed by passing H_2 through an electric arc struck between tungsten electrodes at 3700–4300K. Atomic hydrogen being very short lived, recombines to form

molecular hydrogen liberating large amount of energy. This energy is used in welding and cutting in atomic hydrogen torch.

11. Among NH_3, H_2O and HF which would you expect to have highest magnitude of hydrogen bonding? Why?

Ans: HF. Due to high electronegativity of F, $H-$ bonding will be the strongest in HF.

12. Saline hydrides are known to react with water violently producing fire. Can CO_2 a well known fire extinguisher be used in this case? Explain.

Ans: No. The fire produced by the action of water on saline hydrides cannot be put out by CO_2 because the hot metal hydride reduces CO_2 readily. $NaH + CO_2 \rightarrow HCOONa$ (sodium formate)

13. Arrange the following
    (i) CaH_2, BeH_2 and TiH_2 in order of increasing electrical conductance
    (ii) LiH, NaH and CsH. in order of increasing ionic nature
    (iii) $H-H$, $D-D$, and $F-F$ in order of increasing bond dissociation enthalpy
    (iv) NaH, MgH_2 and H_2O in order of increasing reducing property

Ans: (i) BeH_2 (covalent) $< CaH_2 < TiH_2$ (ii) $LiH < NaH < CsH$
(iii) $F-F < H-H < D-D$ (iv) $H_2O < MgH_2 < NaH$

14. What is meant by 'autoprotolysis' of water? What is its significance?

Ans: Self ionisation of water is called autoprotolysis of water

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

This makes water capable of reacting with both acids and bases (amphoteric). H_2O acts as an acid with bases stronger than itself and acts as a base with acids stronger than itself.

15. Complete the chemical reactions
    (i) $PbS\,(s) + H_2O_2\,(aq) \rightarrow$ (ii) $MnO_4^-\,(aq) + H_2O_2\,(aq) \rightarrow$
    (iii) $CaO\,(s) + H_2O\,(g) \rightarrow$ (iv) $AlCl_3\,(s) + H_2O\,(l) \rightarrow$
    (v) $Ca_3N_2\,(s) + H_2O\,(l) \rightarrow$

Ans: (i) $PbS\,(s) + 4H_2O_2\,(aq) \rightarrow PbSO_4\,(s) + 4H_2O\,(l)$
(ii) $2MnO_4^-\,(aq) + 5H_2O_2\,(aq) + 6H^+ \rightarrow 2Mn^{2+}\,(aq) + 8H_2O\,(l) + 5O_2\,(g)$
(iii) $CaO\,(s) + H_2O\,(g) \rightarrow Ca(OH)_2\,(aq)$
(iv) $AlCl_3\,(s) + H_2O\,(l) \rightarrow Al\,(OH)_3\,(s) + 3HCl\,(aq)$
(v) $Ca_3N_2\,(s) + 6H_2O\,(l) \rightarrow 3Ca\,(OH)_2\,(aq) + 2NH_3\,(aq)$

16. What is meant by 'demineralised water'? How can it be obtained?

Ans: Water free from all cations and anions is called demineralised water. Hard water is passed through cation exchange resin followed by anion exchange resin to form demeneralised water.

17. Is demineralised water or distilled water useful for drinking purposes? If not, how can it be made useful?

Ans: No. Demineralised (or distilled) water does not contain essential minerals. It can be made useful by adding required amounts of useful minerals.

18. Knowing the properties of H_2O and D_2O, do you think that D_2O can be used for drinking purpose?

Ans: No. D_2O does not support life because it slows down the reactions in plants and animals.

19. What do you expect the nature of hydrides formed by elements of atomic number 15, 19, 23 and 44 with hydrogen? Compare their behaviour towards water.

Ans: Atomic number 15 is a non-metal (P) and its hydride is PH_3 which is covalent. Element with atomic number 19 is an alkali metal (K) which forms ionic hydride. Element with atomic number 23 is a transition metal (V) which can form interstitial hydride and the element with atomic number 44 (Ru) is a transition metal of group 8 which does not form hydride (hydride gap). Among these only KH reacts with water to form KOH and H_2.