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HYDROGEN

Hydrogen is the most abundant element in the universe and is the third most abundant element on the surface of the globe. It is being visualized as the major source of energy in future. The global energy crisis can easily be overcome to a great extent by the use of hydrogen as the source of energy.

Hydrogen has the simplest atomic structure amongst all the elements of nature. In atomic form it consists of only one proton and one electron. However, in elemental form it exists as a diatomic (H_2) molecule and is called dihydrogen.

Position of Hydrogen In Periodic Table

Hydrogen shows similarities in properties with both alkali metals (Li, Na, K etc.) of group IA and halogens (F, Cl, Br, I) of group VIIA. Hence, in Mendeleev's periodic table it has been placed on two places i.e. in group IA along with alkali metals as well as in VIIA along with halogens.

Similarities of Hydrogen with Alkali Metals

(1)Both hydrogen and alkali metals have similar electronic configurations. Hydrogen has electronic configuration $1s^1$ and alkali metals have general outer shell electronic configuration (ns^1).

H (1) =$1s^1$ Li (3) =$1s^2$, $2s^1$

Na (11) =$1s^2$, $2s^2$, $2p^6$, $3s^1$

Thus, both hydrogen and alkali metals have only one electron in their outer most shell.

(2)Both hydrogen and alkali metals lose their valence electron to form unipositive ions.

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

(3)Both hydrogen and alkali metals form similar compounds.

HCl NaCl

H_2O Na_2O

(4) During electrolysis both hydrogen and alkali metals are obtained at cathode.

Dissimilarities of Hydrogen with Alkali Metals

(1) Unlike alkali metals hydrogen is non –metal.

(2) Alkali metals are monoatomic while hydrogen is diatomic.

(3) Ionization enthalpy of hydrogen is much more higher than the alkali metals.

Δ_iH (H) = 1312 kJ mol^{-1} Δ_iH (Li) = 520 kJ mol^{-1}

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Similarities of Hydrogen with Halogens

(1) Both hydrogen and halogens have similar electronic configurations. Both are short by one electron from the electronic configuration of their nearest inert gas.

H (1) $=1s^1$ He (1) $=1s^2$

F (9) $=1s^2, 2s^2, 2p^5$ Ne (10) $=1s^2, 2s^2, 2p^6$

(2) Both hydrogen and halogens gain one electron to form uninegative ions.

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

$$F + e^- \rightarrow F^-$$

(3) Both hydrogen and halogens form similar compounds.

H_2O Cl_2O

(4) Ionization enthalpy of hydrogen is more comparable to that of halogens.

$\Delta_i H$ (H) = 1312 kJ mol^{-1} $\Delta_i H$ (F) = 1680 kJ mol^{-1}

(5) Like halogens, it forms diatomic molecule and combines with other elements to form a large number of covalent compounds.

Dissimilarities of Hydrogen with Halogens

(1) Hydrogen is s-block element while halogens are p-block elements.

(2) In H_2 molecule both the hydrogen atoms do not contain any lone pair of electron while in halogen molecules both the halogen atoms contain three lone pair of electrons.

(3) The reactivity hydrogen is very low as compared to the reactivity of halogens.

- Loss of the electron from hydrogen atom results in nucleus (H^+) of ~1.5×10^{-3} pm size. This is extremely small as compared to normal atomic and ionic sizes of 50 to 200pm. As a consequence, H^+ does not exist freely and is always associated with other atoms or molecules. Thus, it is unique in behaviour and is, therefore, best placed separately in the Periodic table.
- Dihydrogen is the most abundant element in the universe (70% of the total mass of the universe) and is the principal element in the solar atmosphere.
- The giant planets Jupiter and Saturn consist mostly of hydrogen. However, due to its very light nature, it is much less abundant (0.15% by mass) in the earth's atmosphere.
- In the combined form it constitutes 15.4% of the earth's crust and the oceans.
- In the combined form besides in water, it occurs in plant and animal tissues, carbohydrates, proteins, hydrides including hydrocarbons and many other compounds.

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Isotopes of Hydrogen

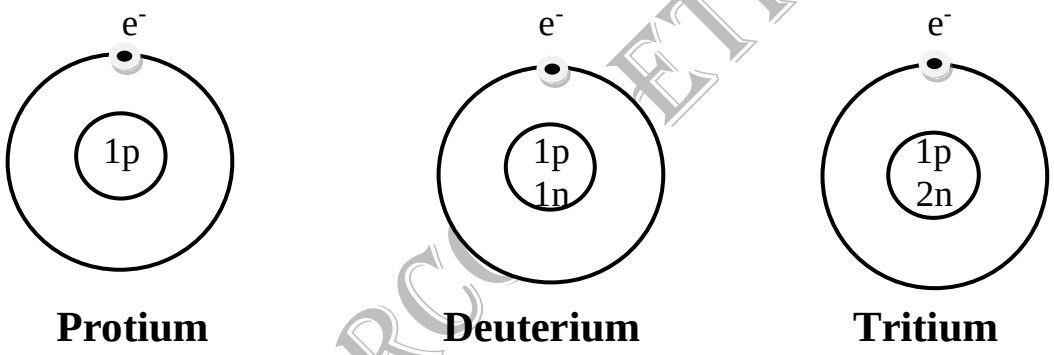
The atoms of same element having same atomic number but different atomic masses are called isotopes.

There are three isotopes of Hydrogen-

(1) Protium, ($_1H^1$)- It is lightest isotope of hydrogen and contains only one proton in its nucleus and one electron outside the nucleus. There is no neutron in its nucleus. Its natural abundance is 99.98%.

(2) Deuterium ($_1H^2$)or D- It contains one proton and one neutron in its nucleus and one electron outside the nucleus. It is also called heavy hydrogen and its natural abundance is 0.0156%.

(3)Tritium ($_1H^3$) or T- It contains one proton and two neutrons in its nucleus and one electron outside the nucleus. It is heaviest isotope of hydrogen and is radioactive in nature and emits low energy β- particles ($t_{1/2}$ = 12.33 years).



Protium **Deuterium** **Tritium**

- In the year 1934, an American scientist, Harold C. Urey, got Nobel Prize for separating hydrogen isotope of mass number 2 by physical methods.
- The predominant form of hydrogen is protium.
- Terrestrial hydrogen contains 0.0156% of deuterium mostly in the form of HD. The tritium concentration is about one atom per 10^{18} atoms of protium.
- Amongst different isotopes of hydrogen, only tritium is radioactive.
- Since the isotopes have the same electronic configuration, they have almost the same chemical properties. They differ only in their rates of reactions, mainly due to their different enthalpy of bond dissociation.
- The physical properties these isotopes differ considerably due to their large mass differences.

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DIHYDROGEN (H_2)

Preparation Methods

(1) Laboratory Preparation of Dihydrogen

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

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

OR

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

(ii) In laboratory it is also be prepared by the reaction of zinc with aqueous alkali.

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

Commercial Production of Dihydrogen

(i) By electrolysis of acidified water using platinum electrodes- When acidified water is electrolysed using platinum electrodes, hydrogen is obtained at cathode while oxygen is released at anode.

$$4H_2O\,(l) \rightarrow 4H^+(aq.) + 4OH^-(aq)$$

At anode-

$$4OH^-(aq) \rightarrow O_2(g) + 2H_2O + 4e^- \quad \text{(oxidation)}$$

At cathode-

$$4H^+(aq.) + 4e^- \rightarrow 2H_2(g) \quad \text{(reduction)}$$

Thus, the overall reaction will be as under-

$$2H_2O\,(l) \xrightarrow{\text{Electrolysis}} \underset{\text{(Cathode)}}{2\,H_2(g)} + \underset{\text{(Anode)}}{O_2(g)}$$

Here, the volume of $H_2(g)$ released at cathode is twice of the volume of $O_2(g)$ released at anode. It indicates that, in water molecule the hydrogen and oxygen atoms are present in ratio of 2:1.

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

(iii) It is obtained as a byproduct in appreciable amount during manufacture of sodium hydroxide and chlorine by the electrolysis of brine solution. The reactions that take place during electrolysis are as under-

$$2NaCl\,(aq.) \rightarrow 2Na^+(aq.) + 2Cl^-(aq)$$
$$2H_2O\,(l) \rightarrow 2H^+(aq.) + 2OH^-(aq)$$

At anode-

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \quad \text{(oxidation)}$$

At cathode-

$$2H^+(aq.) + 2e^- \rightarrow H_2(g) \quad \text{(reduction)}$$

Thus, the overall reaction will be as under-

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$$2NaCl\,(aq.) + 2H_2O\,(l) \rightarrow 2NaOH\,(aq.) + H_2(g) + Cl_2(g)$$

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

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

$$CH_4\,(g) + H_2O\,(g) \xrightarrow{1270\ K} CO\,(g) + 3H_2(g)$$

The mixture of CO and H_2, thus produced is called water gas. This mixture is used for the synthesis of methanol and a number of hydrocarbons. Hence, it is also called synthesis gas or 'syngas'.

Nowadays 'syngas' is being produced from sewage, saw-dust, scrap wood, news papers etc.

Coal Gasification

The process of producing 'syngas' from coal is called' coal gasification.

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

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

$$CO\,(g) + H_2O\,(g) \xrightarrow[673\ K]{FeCrO_4} CO_2\,(g) + H_2(g)$$

This is called **water-gas shift reaction.** Carbon dioxide is removed from the mixture by scrubbing with sodium arsenite solution.

- Presently about 77% of the industrial dihydrogen is produced from petro-chemicals, 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

Hydrides

The binary compounds of hydrogen with other elements are called hydrides.

Depending upon the nature of bonds, the hydrides may be classified into following three categories -

(1) Ionic or saline or saltlike hydrides

These hydrides involve ionic or electrovalent bond and are formed by highly electropositive s-block elements with hydrogen. For example, LiH, NaH, MgH_2, CaH_2, AlH_3 etc. These hydrides are crystalline, non-volatile and

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non-conducting in solid state. However, they conduct electricity in their molten state.

On electrolysis they liberates dihydrogen gas at anode, which confirms the existence of H^- ions in these hydrides.

- $BeH_2$and MgH_2 are polymeric in structure.
- Saline hydrides react violently with water producing dihydrogen gas.

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

- Lithium hydride is relatively unreactive at moderate temperatures and therefore does not react with O_2 or Cl_2. It is, therefore, used in the synthesis of other useful hydrides. For example,

$$8LiH + Al_2Cl_6 \rightarrow 2LiAlH_4 + 6LiCl$$
$$2LiH + B_2H_6 \rightarrow 2LiBH_4$$

(2) Covalent or Molecular Hydride

These hydrides involve covalent bond and are molecular in nature. These are mainly formed by p-block elements. For examples, CH_4, NH_3, H_2O, HF etc.

Being covalent, these hydrides are volatile in nature.

Molecular hydrides are further classified into following three catagories :

(i) Electron-deficient Hydrides-These hydrides do not contain sufficient number of electrons for conventional bonding. For example, e.g. diborane (B_2H_6). Being electron deficient, they act as Lewis acids i.e., electron acceptors.

(ii) Electron-precise Hydrides-These hydrides contain exactly same number of electrons as required for conventional bonding. For example e.g. CH_4, SiH_4 etc.

(iii) Electron-rich hydrides-These hydrides contain more number of electrons than that required for conventional bonding. For example NH_3, PH_3 etc. The excess electrons remain present as lone pairs. They behave as Lewis bases i.e., electron donors.

The presence of lone pairs on highly electronegative atoms like N, O and F in hydrides results in hydrogen bond formation between the molecules. This leads to the association of molecules.

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

These hydrides are mainly formed by d and f - block elements. These are formed by trapping of hydrogen in crystal lattice (interstitial sites) of metals and are usually non- stoichiometric in nature. For example, $NiH_{0.6\text{-}0.7}$, $PdH_{0.6\text{-}0.8}$, $LaH_{2.87}$, $YbH_{2.55}$ etc.

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HYDROGEN PEROXIDE (H_2O_2)

Preparation Methods

(1) By action of Sulphuric acid on Hydrated Barium peroxide

When hydrated barium peroxide is treated with dilute sulphuric acid and the excess water is removed by evaporation under reduced pressure hydrogen peroxide is obtained.

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

(2) By electrolytic oxidation of sodium hydrogen sulphate

When sodium hydrogensulphate is electrolysed using high current density, peroxo-disulphuric acid is obtained which on hydrolysis yields hydrogen peroxide.

$$Na_2SO_4\ (aq.) + H_2SO_4(aq) \rightarrow 2NaHSO_4(aq.)$$

$$2NaHSO_4(aq.) \rightarrow 2Na^+\ (aq.) + 2HSO_4^-(aq.)$$

(a) At anode-

$$2HSO_4^-(aq.) \rightarrow H_2S_2O_8 + 2e^- \quad \text{(oxidation)}$$

(b) At cathode-

$$2Na^+ + 2e^- \rightarrow 2Na \quad \text{(reduction)}$$

$$H_2S_2O_8 + H_2O\ (l) \rightarrow 2HSO_4^-(aq.) + 2H^+\ (aq.) + H_2O_2(aq)$$

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

$$K_2S_2O_8(s) + 2D_2O(l) \rightarrow 2KDSO_4(aq) + D_2O_2(l)$$

(3) By the auto-oxidation of 2-alklylanthraquinols

Industrially hydrogen peroxide is prepared by the autooxidation of 2-alklylanthraquinols.

$$\text{2-ethylanthraquinols} \xrightleftharpoons[H_2/Pd]{O_2\ (air)} \text{2-ethylanthraquinone} + H_2O_2$$

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

Physical Properties-

(1) In the pure state H_2O_2 is almost colourless (very pale blue) liquid.

(2) It is miscible with water in all proportions and forms mono hydrate $H_2O_2.H_2O$ (mp221K).

(3) A 30% aqueous solution of H_2O_2 is marketed as '100 volume' hydrogen peroxide. It means that one millilitre of 30% H_2O_2 solution will give 100 V of oxygen at STP.

Commercially, it is marketed as 10 V, which means it contains 3% H_2O_2.

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Q. Calculate the strength of 10 volume solution of hydrogen peroxide.
Sol^{n}- 10 volume solution of H_2O_2 means that 1L of this H_2O_2 will give 10 L of oxygen at STP

$$2H_2O_2\,(l) \rightarrow 2H_2O\,(l) + O_2(g)$$
2 moles 1 mole
(2× 34)g 22.4 L

22.4 L of O_2 at STP is produced from H_2O_2 = 68 g
10 L of O_2 at STP is produced from H_2O_2 = (68 × 10/22.4)g=30.34g
Therefore, strength of H_2O_2 in 10 volume H_2O_2 = 30.36 g/L

Structure

Hydrogen peroxide has a **non-planar open book like structure**, where both the oxygen atoms are present on the axis while, the hydrogen atoms are present on either of the pages. Its geometry can be represented as under-

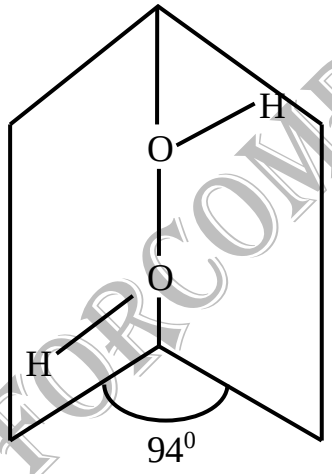


Fig.- Non-planar open book like structure of H_2O_2

Chemical Properties

It acts both like an oxidising as well as reducing agent in both acidic and alkaline media.

Oxidising action in acidic medium

(1) In acidic medium, hydrogen peroxide oxidizes green coloured ferrous ions into yellow coloured ferric ions.

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

(2) In acidic medium, hydrogen peroxide oxidizes black coloured lead sulphide into white coloured lead sulphate.

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

Hence, hydrogen peroxide is used in restoring the colour of blackened oil paintings.

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Oxidising action in basic medium

(1) In alkaline medium, hydrogen peroxide oxidizes green coloured ferrous ions into yellow coloured ferric ions.

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

(2) In alkaline medium, hydrogen peroxide oxidizes Mn^{2+} ions into Mn^{4+} ions.

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

Reducing action in acidic medium

(1) In acidic medium, hydrogen peroxide reduces permanganate ions into manganous ions.

$$2MnO^{4-} + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

(2) In acidic medium, hydrogen peroxide reduces hypochlorous ions into chloride ions.

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

Reducing action in basic medium

(1) In alkaline medium, hydrogen peroxide reduces iodine into iodide ions.

$$I_2 + H_2O + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$$

(2) In alkaline medium, hydrogen peroxide reduces permanganate ions into manganese dioxide.

$$2MnO^{4-} + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$$

Storage

H_2O_2 decomposes slowly on exposure to light.

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

This reaction gets catalyzed in the presence of metals or traces of alkali (present in glass containers). It is, therefore, stored in wax-lined glass or plastic vessels in dark. Here, urea can be added as a stabiliser.

It is kept away from dust because, dust can induce explosive decomposition of H_2O_2 .

Uses

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

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

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

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

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

HEAVY WATER (D_2O)

It is extensively used as a moderator in nuclear reactors and in exchange reactions for the study of reaction mechanisms. It can be prepared by exhaustive electrolysis of water or as a by-product in some fertilizer industries.. It is used for the preparation of other deuterium compounds. For example,

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

$$SO_3 + D_2O \rightarrow D_2SO_4$$

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

Q. Can phosphorus with outer electronic configuration $3s^2,3p^3$ form PH_5 ?
Ans. Although phosphorus exhibits +3 and +5 oxidation states, it cannot form PH_5. It is because, high energy of atomization (Δ_aH) of dihydrogen and $\Delta_{eg}H$ value of atomic hydrogen do not favour +5 oxidation state of P and therefore, they do not favour the formation of PH_5.

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