

Occurrence, Isotopes, Preparation, Properties, Uses of Hydrogen

1. The first element in the periodic table is Hydrogen.
2. The lightest of all the elements is Hydrogen.
3. The only atom without neutrons is Protium.
4. The element without suitable position in the periodic table is Hydrogen.
5. Hydrogen should belong to the s-block as its electron configuration is $1s^1$.
6. The properties in which Hydrogen resembles alkali metals are
 - a) Like alkali metals, "H" has one electron in the valence shell
 - b) Like Alkali metals, H forms H^+ ion
 - c) Like Alkali metals, "H" forms monoxides and peroxides
 - d) Like Alkali metals, "H" acts as reductant
7. The properties in which Hydrogen resembles Halogens are
 - a) Like Halogens, it is diatomic molecule (H_2)
 - b) Like Halogens, it is short of one electron to attain inert gas configuration
 - c) The ionisation potential value of "H" is much nearer to those ionisation potential values of Halogens.
 - d) H can also form hydride ion H^-
8. Hydrogen has 3 isotopes. They are
Protium
Deuterium
Tritium
9. Theoretically the number of possible Hydrogen molecules is 6. They are H_2 , D_2 , T_2 , HD, HT and DT.
10. Ordinary Hydrogen is more reactive than Deuterium.
11. All the isotopes of Hydrogen have
 - a) The same position in the Long form of Periodic Table
 - b) Same electron configuration

- c) Similar chemical properties
- d) Same atomic radii

12. The isotopes of Hydrogen differ in their

- a) Mass number
- b) Number of neutrons
- c) Chemical reactivity
- d) Physical properties
- e) Bond energy of molecules

13. The radioactive isotope of Hydrogen is Tritium.

14. Generally ordinary Hydrogen contains Tritium and Protium in the ratio 1: 10¹⁷.

15. Tritium can be obtained in the nuclear transformations such as
(Occurs in nature) (Takes place in nuclear reactors)

16. The radioactive isotope of Hydrogen is **Tritium**. It exhibits radioactivity by Beta emission.

17. Tritium is harmless, since it emits only low energetic β -radiation but not harmful γ -rays.

18. In the study of mechanism of various chemical reactions, Deuterium and Tritium are used as tracers.

19. As the mass number increases, the chemical reactivity decreases. So chemically least reactive isotope of Hydrogen is Tritium.

20. The physical properties of Hydrogen and Deuterium are.

Property	Hydrogen H ₂	Deuterium D ₂
Bond length	0.7414A ⁰	0.7414A ⁰
Bond energy	436 KJ/mole	443.4 KJ/mole
Latent heat of fusion	0.117KJ/mole	0.197 KJ/mole
Latent heat of vapourisation	0.904 KJ/mole	1.226 KJ/mole
B.P	<u>252.6</u> ⁰ C	<u>249.4</u> ⁰ C
M.P	<u>259.2</u> ⁰ C	<u>254.4</u> ⁰ C
Molecular mass	2.016	4.03

- + Hydrogen is the most abundant element in the universe.
- + H₂ is absorbed by metals like Pd. This is known as **Occlusion of Hydrogen**.

- + Hydrogen accounts for 15.4% of all atoms in earth's crust. On this count it is second largest available element on earth's crust.
- + a) Metals having lower SRP than hydrogen reacts with acids to liberate H_2
This method is used to prepare hydrogen in the laboratory.
- b) Hydrogen is also prepared by the action of alkali on metals like, Zn, Al, Sn
- + H_2 is the byproduct in the electrolysis of brine. Pure H_2 is obtained in this process.
- + Large quantities of H_2 are prepared cheaply by the action of steam on red hot coke.
Where this gas mixture is passed over a catalyst (Fe_2O_3/Cr), CO is oxidised to CO_2
- + In petroleum industry cracking of naphtha and fuel oil produce H_2 as by product.
- + In an electric arc at the high temperature or under the influence of UV radiations atomic hydrogen is formed and it is extremely reactive and brings about many reductions at ordinary temperatures.
- + At high temperature (nearly about 2275 K), H_2 molecule decomposes to give atomic hydrogen.
- + H_2 burns in air or O_2 and forms water. This reaction takes place at ordinary temperature in presence of Pd or Pt black.
- + H_2 reduces metal oxides and their halides to the corresponding metals.
- + H_2 combines with many organic compounds in the presence of catalyst
 - i) Hydrogenation of oils to give fats
 - ii) Hydrogenation of olefins yields aldehydes.
- + Active metals like alkali metals and alkaline earth's to give hydrides at high temperatures.
 - i) By passing H_2 over fused Ca, Calcium hydride is formed
- + LiH is prepared by the union of Li and H_2
 $LiAlH_4$ is prepared by adding LiH to anhydrous $AlCl_3$ in dry ether.
- + Ionic hydrides are formed by high electropositive elements.
E.g.: LiH, BeH_2 , MgH_2

On electrolysis of these molten hydrides, H₂ gas is liberated at anode

- + Most of the p-block elements form covalent or molecular hydrides

E.g.: CH₄, NH₃, H₂O, HF

Molecular hydrides are of three types

- a) Electron deficient **E.g.:** B₂H₆, (AlH₃)_n
- b) Electron - Precise **E.g.:** CH₄, C₂H₆
- c) Electron rich **E.g.:** NH₃, H₂O.....

- + Many of the d-block elements form non-stoichiometric hydrides. These compounds may exist over a wide range of composition

E.g.: PdH_{0.7}; TiH_{1.8}; CrH, ZrH_{1.3-1.75}

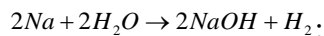
These lattices of these hydrides except few are different from those of the parent metals.

- + Unsaturated hydrocarbons add on one or more moles of hydrogen to form saturated hydrocarbons

Preparation Hydrogen:

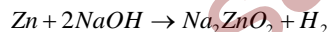
- + Action of water on active metals:

In cold



In hot

Action of alkalies on amphoteric metals: (Zn, Al, Pb, Sn, Sb)



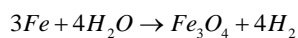
In steam



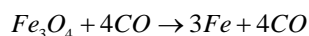
- + Action of water on metal hydride (hydrolith) CaH₂

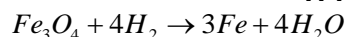
Manufacture

- + Lane process: super heated steam is passed over heated iron (1000°C)



Iron oxide is then reduced by water gas (CO + H₂) to iron at 1000°C.





This is called water gas shift reaction

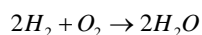
Properties of Hydrogen

Physical properties

- + Sparingly soluble in H₂O, inflammable, less reactive
- + Low M.P. (used as cryogenic fluid to lower temperature)

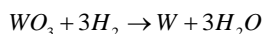
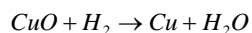
Chemical properties

- + Reacts slowly at room temperature. It is neutral towards litmus. It is combustible and burns in air with a pale blue flame.



- + Reducing action:

H₂ + Heated metal oxides metal



- + **Uses of Hydrogen**

Hydrogen is used

- i) In metallurgy
- ii) As a fuel.
- iii) H₂ is used in the synthesis of Ammonia by Haber's process.
- iv) When water gas mixed with H₂ is passed over ZnO + CrO₃ catalyst, then Methyl alcohol is obtained.
- v) The unsaturated vegetable oils like cotton seed oil, ground nut oil on hydrogenation give saturated fats. Here the catalyst is Raney Nickel. This is called **hardening of oils**.
(Or) production of vanaspati (margarine).

Hydrides, Ionic, Covalent and Interstitial Compounds

- * Hydride is used for binary compounds of hydrogen with other elements.
- * On the basis of properties and type of bonding, hydrides may be of following four types.
 - 1) Ionic or salt like or saline hydrides.
 - 2) Covalent or molecular hydrides.
 - 3) Metallic or interstitial hydrides.
 - 4) Polymeric hydrides and complex hydrides.

Ionic or Saline Hydrides

- * These are hydrides of elements having low electro negativity.
- * These are formed by alkali metals, alkaline earth metals (except Be and Mg).
- * Saline hydrides are generally white or light grey, non-volatile solids.

Ex: $LiH, NaH, KH, RbH, CaH_2, SrH_2$

Covalent or Molecular Hydrides

- * These hydrides are formed mainly by p-block elements. (Except noble gases)
- * These hydrides usually consist of discrete covalent molecules held together by weak Van der Waals' forces.
- * These hydrides are usually volatile.
- * The melting and boiling points of covalent hydrides are low.

Ex: PH_3 -phosphane, H_2O -Oxidane, NH_3 -Azane

Metallic or Interstitial Hydrides

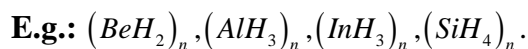
- * Hydrides are formed by d and f-block metals with electro negativity ranging from 1.2 to 1.4.
- * These hydrides are usually non-stoichiometric.

Ex: $TiH_{1.73}, LaH_{2.8}$

- * The transition metals of groups 7, 8 and 9 do not form hydrides and this region of periodic table is referred as hydride gap.

Polymeric Hydrides and Complex Hydrides

- * Polymeric hydrides are formed by elements having electro negativity in the range 1.4 to 2.0.



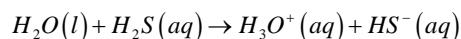
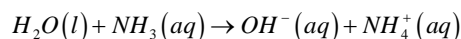
- * In the complex hydrides H^- ion acts as ligand and is attached to central metal atom.



Physical and Chemical Properties of Water

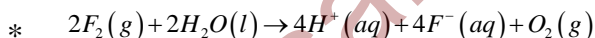
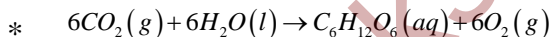
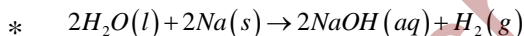
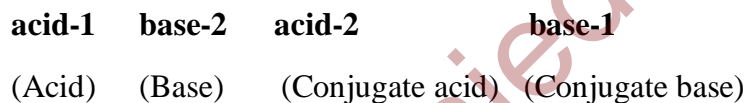
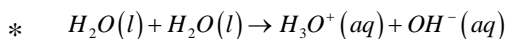
Chemical properties of water

- * It has the ability to act as an acid as well as a base.

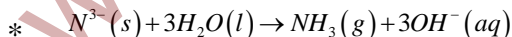
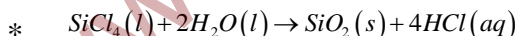


The above two reactions indicates that water as amphoteric nature.

Auto-protolysis

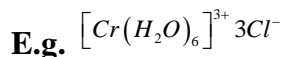


Hydrolysis Reaction



Hydrates Formation

(i) Coordinated water



(ii) Interstitial water

E.g. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

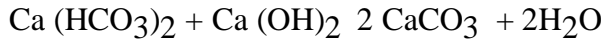
(iii) Hydrogen-bonded water

E.g. $[\text{Cu}(\text{H}_2\text{O})_4]^{2+} \text{SO}_4^{2-} \cdot \text{H}_2\text{O}$ in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Hard and soft water

- * Chemically soap is sodium stearate.
- * Water which gives good lather readily with soap is known as soft water.
- * Water which does not give lather readily with soap but precipitates soap is known as hard water.
- * Hardness of water is expressed in terms of ppm of CaCO_3 . That means the number of grams of CaCO_3 (or) its equivalent part present in 1 million grams of water is known as hardness.
- * The disadvantages of using hard water are
 - a) It produces boiler scales
 - b) It causes wastage of soap in laundries
- * Chemically boiler scales are CaCO_3 and MgCO_3 . Boiler scales can be removed by using calgon.
- * Hardness is of two types. They are
 - 1) Temporary hardness
 - 2) Permanent hardness
- * Temporary hardness of water arises due to the presence of the bicarbonates of Ca and Mg.
- * Permanent hardness of water arises due to the presence of the chlorides and sulphates of Ca and Mg (also salts of Fe).
- * Temporary hardness of water can be removed by
 - 1) Boiling
 - 2) Clark's Method
- * Boiling removes the temporary hardness due to the conversion of soluble bicarbonates into insoluble carbonates
$$\text{Ca}(\text{HCO}_3)_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$$
$$\text{Mg}(\text{HCO}_3)_2 \rightarrow \text{MgCO}_3 + \text{H}_2\text{O} + \text{CO}_2$$

- * In Clark's method, temporary hardness can be removed by adding a calculated quantity of milk of lime



In this method, addition of excess of lime is to be avoided since it will itself cause artificial permanent hardness.

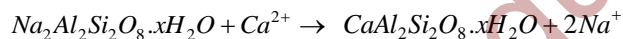
a) Using Na_2CO_3 , both temporary and permanent hardness can be removed.

- * The methods used for removing permanent hardness are

- Permutit method/Ion exchange method
- Synthetic resins method
- Calgon method

- * a) Permutit is an artificial zeolite. Chemically permutit is hydrated sodium aluminosilicate. Its formula is $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$.

Gan's permutit process is also known as Base Exchange process. Here the reaction involved is



This method is also called ion exchange method or zeolite process.

- * The exhausted permutit is regenerated by soaking it with 10% NaCl solution [Brine solution]

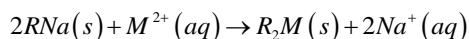
b) Nowadays hard water is softened by using synthetic cation exchangers.

- * This method is more efficient than zeolite process.

- * Cation exchange resins contain large organic molecule with $-\text{SO}_3\text{H}$ group and are water insoluble.

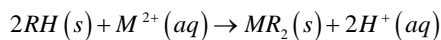
- * Ion exchange resin (RSO_3H) is changed to RNA by treating it with NaCl.

- * The resin exchanges Na^+ ions with Ca^{2+} and Mg^{2+} ions present in hard water to make the water soft.

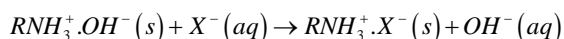
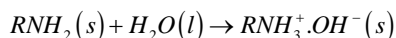


- * The resin can be regenerated by adding aqueous NaCl solution.

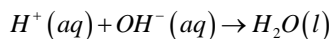
- * Pure de-mineralised water free from all soluble mineral salts is obtained by passing water successively through a cation exchange (in the H^+ form) and an anion-exchange (in the OH^- form) resins.



- * In this cation exchange process, H^+ exchanges for Na^+ , Ca^{2+} , Mg^{2+} and other cations present in water.
- * This process results in proton release and thus makes the water acidic. In the anion exchange process:



- * OH^- exchanges for anions like Cl^- , HCO_3^- , SO_4^{2-} etc. present in water. OH^- ions, thus, liberated neutralise the H^+ ions set free in the cation exchange.



- * The exhausted cation and anion exchange resin beds are regenerated by treatment with dilute acid and alkali solutions respectively.

(c) Calgon is sodium hexameta phosphate. Its formula is $Na_2 [Na_4 (PO_3)_6]$ or $(Na PO_3)_6$

- * Calgon forms water soluble complex compounds with Calcium and Magnesium salts and thus removes boiler scales.
- * Calgon removes hardness by forming complex compounds with the Ca^{2+} and Mg^{2+} ions of hard water.

Geometry of water

- + In the gas phase water is a bent molecule with a bond angle 104.5° and O-H bond length of 95.7 pm.
- + In the liquid phase water molecules are associated together by hydrogen bonds.
- + The crystalline form of water is ice. At normal pressure ice crystallises in the hexagonal form, but at very low temperatures it condenses to cubic form.
- + Density of ice is less than that of water. Therefore, an ice cube floats on water.

- + In winter season ice formed on the surface of a lake provides thermal insulation which ensures the survival of the aquatic life. This fact is of great ecological significance.

Geometry of ice

- + Ice has a highly ordered three dimensional hydrogen bonded structure.
- + Examination of ice crystals with X-rays shows that each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 276 pm.
- + Hydrogen bonding gives ice a rather open type structure with wide holes. These holes can hold some other molecules of appropriate size interstitially.
- + The Physical constants of H₂O and D₂O are

S.No Physical Property

	H ₂ O	D ₂ O
1. Molecular weight	18	20
2. Freezing point	0°C	3.82°C
3. Boiling point	100°C	101.42°C
4. Max. density	1g/cc	1.1g/c.c.
5. Temp. of max density	4°C	11.6°C
6. Dielectric constant	82	80.5
7. Ionic product	1x10 ⁻¹⁴	3x10 ⁻¹⁵
8. Viscosity at 20°C (millipoises)	10.09	12.6
9. Specific heat at 20°C	1	1.018
10. Latent heat of vaporisation (J/g)	2253	2329
11. Solubility of NaCl/100g water at 25°C	35.9	30.5

Heavy Water, Hydrogen Peroxide Preparations, Reactions, Uses and Structure

Heavy water

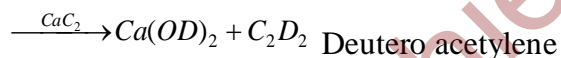
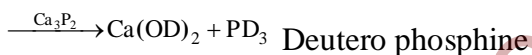
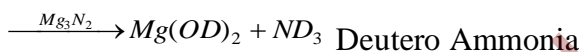
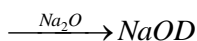
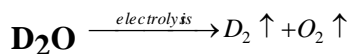
- * Heavy water was prepared by Urey by the exhaustive electrolysis of alkaline water.
 - * Heavy water is Deuterium oxide.
 - * Natural water contains 1 part of heavy water in 6000 parts of ordinary water.
- 100% D₂O can be obtained by 3 methods. They are
- a) Exhaustive electrolysis of alkaline water
 - b) Fractional distillation
 - c) Exchange reactions
- * Heavy water is prepared by the exhaustive electrolysis of water containing N/2 NaOH.
 - * In the preparation of heavy water by electrolytic method, the cathode is steel vessel and anode is a perforated cylindrical Nickel sheet.
 - * D₂O can be prepared by exchange reactions. When H₂S gas is passed through hot water, the hydrogen atoms in H₂S exchange their places with deuterium from D₂O present in water. Thus H₂S becomes enriched with D₂S. On passing the H₂S gas enriched with D₂S through cold water, the deuterium from D₂S and Hydrogen from H₂O exchange places and the cold water becomes richer in D₂O. The process is repeated.
 - * The Physical constants of H₂O and D₂O are

S.No Physical Property

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2. Freezing point	0°C	3.82°C
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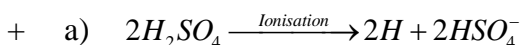
* **Chemical Properties of D₂O:**



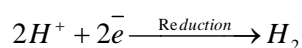
Hydrogen peroxide

- + The formula of Hydrogen peroxide is H₂O₂.
- + H₂O₂ is also known as oxygenated water.
- + (-O-O-) bond is known as peroxy linkage.
- + H₂O₂ is a dibasic acid. Its molecular weight is 34 and its equivalent weight is 17.
- + Perchloric acid, MnO₂, PbO₂, TeO₂, KMnO₄ etc. do not contain peroxy bond.
- + In the laboratory, H₂O₂ is prepared by the action of ice cold dil. H₂SO₄ on Na₂O₂ (or) hydrated Barium Peroxide [BaO₂, 8H₂O].
- + H₂O₂ can also be obtained by passing CO₂ gas through a suspension of Barium peroxide in water.

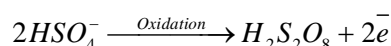
- + In the preparation of H_2O_2 from BaO_2 , Phosphoric acid is preferred to dil H_2SO_4 . This is because H_3PO_4 increases the stability of H_2O_2 .
- + In auto oxidation method, the starting substance is 2-ethyl anthraquinone.
- + The reagent used for reducing 2-ethyl anthraquinone to 2-ethyl anthraquinol is H_2/Pd .
- + On aerial oxidation 2-ethylanthraquinol gives H_2O_2 .
- + In electrolytic method, H_2O_2 is manufactured by the electrolysis of 50% H_2SO_4 (or) a mixture of $(NH_4)_2 SO_4$ + dil. H_2SO_4 using platinum anode and lead cathode.
- + The product obtained at anode by the electrolysis of 50% H_2SO_4 is $H_2S_2O_8$.
- + During the electrolysis of 50% H_2SO_4 , the gas liberated at the cathode is H_2 .



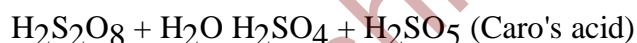
At cathode



At anode



- b) Peroxy disulphuric acid solution on distillation under reduced pressure gives H_2O_2 .

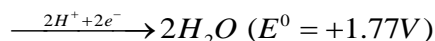


- + The common name of $H_2S_2O_8$ is Marshall's acid. Its chemical name is Perdisulphuric acid.
- + During distillation, H_2O_2 undergoes decomposition below its boiling point. So it is purified by distillation under reduced pressure.
- + The strength of H_2O_2 can be expressed in
 - a. Volume strength b. Molarity
 - c. Normality d. Weight-Volume Percentage
- + The volume of O_2 gas at S.T.P. obtained by the decomposition of 1 c.c. of H_2O_2 solution is known as its volume strength. It is denoted by V.

- + Peroxydrol is 30% (w/v) H_2O_2 solution. Its molarity is 8.93M. Its Normality is 17.86 N and it contains 300g/Lit (or) 0.3g/ml.
- + On long standing or on heating, H_2O_2 undergoes decomposition. The equation for the decomposition of H_2O_2 is $2H_2O_2 \rightarrow 2H_2O + O_2$
- + 90% H_2O_2 is used as an oxidant for rocket fuel.
- + The boiling point of H_2O_2 is $152^{\circ}C$.
- + H_2O_2 exhibits
 - a) Oxidising properties b) Reducing properties
 - c) Bleaching property d) Acidic PropertyIt cannot exhibit dehydrating property.
- + H_2O_2 has greater reactivity in basic medium. It is because bases catalyse the decomposition of H_2O_2 .
- + H_2O_2 is a stronger oxidising agent and a weaker reducing agent.
- + The antiseptic action and the bleaching action of H_2O_2 involve the oxidising properties.
- + During decomposition, H_2O_2 undergoes disproportionation.
- + When H_2O_2 acts as an oxidising agent, it undergoes reduction. H_2O_2 is a powerful oxidant, but poor reductant.
- + The reactions in which H_2O_2 acts as a reducing agent, there will be the liberation of O_2 .
- + $H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$. $E^0 = -0.67V$ represents the reducing property of H_2O_2 .
- + The fundamental equation for oxidising property of H_2O_2 is



- + The oxidising properties of H_2O_2 in both acidic and basic media are due to



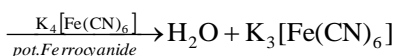
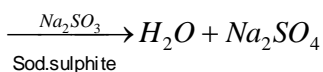
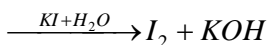
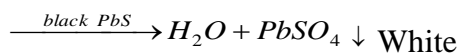
(Reduction)



(Reduction)

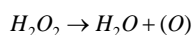
- + The SRP values indicate that H_2O_2 is a strong oxidising agent in acidic medium and weak oxidising agent in basic medium.

+ **Oxidising properties of H_2O_2**



POT. Ferricyanide

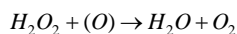
- + The bleaching action of H_2O_2 is due to its oxidising nature.



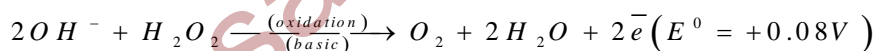
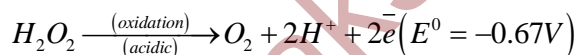
- + H_2O_2 is used to bleach silk, wool, ivory and hair.

- + H_2O_2 is used to bleach black hair to golden yellow colour under the common name Auricome.

- + The fundamental equation for reducing property of H_2O_2 is



- + In both acidic and basic media, H_2O_2 shows reducing properties as



- + **The reducing properties of H_2O_2 are**

- + H_2O_2 is used to clean wounds since it acts as disinfectant and germicide.

- + H_2O_2 is used to restore the colour of old oil paintings.

These two are specific tests for H_2O_2 .

- + H_2O_2 turns starch - Iodide paper to blue colour. It is not a specific test for H_2O_2 .

Because it is a general test given by all oxidising agents

- + H_2O_2 can be estimated by Iodometric method.

H_2O_2 is treated with KI liberating I_2 . Then the liberated Iodine is titrated against standard Hypo solution.

- + The structure of H_2O_2 in **gaseous state** can be shown as:
- + In H_2O_2 molecule the HOO bond angle is $94^\circ 48'$
- + In H_2O_2 molecule the dihedral angle is $111^\circ 30'$
- + In H_2O_2 molecule the O—O bond length is 1.48Å and the O—H is 0.97Å
- + In crystalline H_2O_2 , the dihedral angle $111^\circ 30'$ is reduced to 90° , due to Hydrogen bonding.

The values of bond length and bond angles in gaseous H_2O_2 are different from that of solid and liquid states.

- + The difference in the bond lengths and bond angles from one state to another state of H_2O_2 is due to difference in hydrogen bonding.