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CHAPTER

hydrogen & its compounds

- Hydrogen is the most abundant element in the universe. Some estimates are that 92% of the universe is made up of hydrogen, and 7% helium, leaving only 1% for all of the other elements.
- The abundance of H_2 in the earth's atmosphere is very small. This is because the earth's gravitational field is too small to hold so light an element, though some H_2 is found in volcano gases. In contrast, hydrogen is the tenth most abundant element in the earth's crust (1520 ppm or 0.152% by weight).
- Hydrogen has the simplest atomic structure of all the elements, and consists of a nucleus containing one proton with a charge +1 and one orbital electron. The electronic structure may be written as $1s^1$.
- Hydrogen is the first element in the periodic table, and is unique. There are only two elements in the first period, hydrogen and helium.

GENERAL	
Name, Symbol, Number	hydrogen, H, 1
Chemical series	nonmetals
Group, Period, Block	1, 1, *s*
Appearance	colourless
Atomic mass	1.00794 (7) g/mol
Electronic configuration	$1s^1$
Electrons per shell	1

PHYSICAL PROPERTIES	
Phase	gas
Density	(0°C, 101.325 kPa), 0.08988 g/L
Melting point	14.01 K, (–259.14°C, – 434.45°F)
Boiling point	20.28 K (–252.87°C, – 423.17°F)
Heat of fusion	(H_2) 0.117 kJ/mol
Heat of vapourisation	0.904 kJ/mol
Heat capacity	28.836 J/(mol.K)

ATOMIC PROPERTIES	
Crystal structure	hexagonal
Oxidation states	+1, –1 (amphoteric oxide)
Electronegativity	2.20 (Pauling scale)
Ionization energies	1st: 1312.0 kJ/mol
Atomic radius	25 pm
Atomic radius (calc.)	53 pm (Bohr radius)
Covalent radius	37 pm
van der Waals radius	120 pm

- The lightest gas is **hydrogen.**
- **Heavy water (D_2O)** is produced by repeated distillation and condensation. One part of D_2O is present in 6000 part of H_2O.
- Ionic hydrides are formed by **elements of very high electropositivity.**
- Hydrogen peroxide is generally prepared on industrial scale by the **electrolysis of 50% H_2SO_4.**
- Heavy water has found application in atomic reactor as **moderator.**
- **Heavy water** posseses high density and different physical properties than those of water.
- Hard water becomes free from Ca^{2+} ions when passed through ion exchange resin containing *R*COOH groups.
- Hydrogen gas is used in the hydrogenation of oils in presence of nickel as a catalyst.
- Hydrogen adsorbed on transition metals such as Pt, Pd, Ni, Os, Ca, Mn, Fe etc. is known as **occluded Hydrogen.**
- In solid hydrogen, the intermolecular bonding is **van der Waals.**
- The conversion of atomic hydrogen into ordinary hydrogen is **exothermic change.**
- The decomposition of H_2O_2 can be slowed down by the addition of small amount of phosphoric acid which act as **inhibitor** (negative catalyst for decomposition of H_2O_2).
- The bleaching properties of H_2O_2 are due to its **oxidising properties.**
- The **ortho and para hydrogen** possess different physical properties but same chemical properties. They have same electronic arrangement but different spin of nuclei.
- **Para hydrogen** is less stable than ortho hydrogen.
- **Tritium atom** $\left({}_1^3H\right)$ has two neutrons and one proton.
- Benzene is oxidised by H_2O_2 in presence of $FeSO_4$ to **phenol.**
- **BaO_2** is peroxide but oxides like MnO_2, PbO_2 and NO_2 do not have O – O bond, *i.e.* peroxide linkage and so are not peroxides.
- Fluorine reacts with water to form **oxygen and ozone.**
- Heavy water is used in nuclear reactors to **slow down the speed of neutrons.**
- The formula of heavy water is **D_2O.**
- The rubber foam is produced by passing oxygen through rubber foaming material. This oxygen is released from **hydrogen peroxide.**

- The helium nucleus contains **2 neutrons and 2 protons.**
- H_2O_2 gives off O_2 when heated, turns an acid solution of KI violet, and reduces acidified $KMnO_4$.
- **Atomic hydrogen** is obtained by passing silent electric discharge through hydrogen at low pressure.
- The ratio of electron, proton and neutron in tritium is **1 : 1 : 2.**
- **H_2O_2** is stored in plastic container after addition of stabilizer as H_2O_2 easily decomposes into water and oxygen and the decomposition speeds up in the presence of metallic impurities or strong bases and on exposure to light.
- Acidified $KMnO_4$ is decolourised by **Nascent hydrogen** (*i.e.* hydrogen at the moment of generation) is a more powerful reducing agent than ordinary H_2.
- Heavy water freezes at **3.8°C.**
- In aqueous solution, H_2 does not reduce **Zn^{2+}.**
- Hydrogen can be placed in halogens group because **it forms hydrides like chlorides.**
- Acidified solution of chromic acid on treatment with H_2O_2 yields **CrO_5+H_2O +K_2SO_4.**
- The melting points of most of the solid subtances increase with an increase of pressure. However ice melts at a temperature lower than its usual melting point when the pressure is increased. This is because **ice is less denser then water.**
- H_2O_2 converts potassium ferrocyanide to ferricyanide. The change observed in the oxidation state of iron is **$Fe^{2+} \rightarrow Fe^{3+}$.**
- Tritium emits **β-particles.** ${}_1H^3 \rightarrow {}_2He^3 + {}_{-1}e^0$
- H_2O_2 acts as a reducing agent in its **reaction with $KMnO_4$ in acid medium.**
- H_2O_2 turns an acidified solution of **TiO_2** to orange red (H_2TiO_4).
- The best method to test whether a clear liquid is water is to **add few drops on anhydrous copper sulphate and look for colour change.**
- **H_2O_2** is prepared in the laboratory when BaO_2 is added to CO_2 bubbling through cold water.
- **Colloidal solution of palladium** can adsorb large volumes of hydrogen gas as it has larger surface area.
- When silicon is boiled with caustic soda solution the gas evolved is **H_2.**
- **Hydrogen is not palced** with the group of alkali metals or halogens because ionization energy of hydrogen is too high for group of alkali metals but too low for halogen group.
- Water is permanently hard when it contains **nitrates of magnesium and calcium.**
- The acidified solution of $FeCl_3$ is reduced by passing **Nascent H.**
- The *n/p* ratio for ${}_1H^1$ is **zero.**
- In periodic table, tritium is placed in group **I.**
- Heavy water was discovered by **Urey band Washburn.**
- In the **hydrogen peroxide molecule,** the four atoms are arranged in a non-linear and non-planar manner.
- Ionic hydrides react with water to give **basic solutions.**
- Maximum density of heavy water is at **11.6°C.**

- Heavy hydrogen is used **in studying reaction mechanism.**
- In the preparation of hydrogenated oil the chemical reaction involving hydrogen is called **hydrogenation.**
- Ordinary hydrogen has perponderance of **hydrogen atoms.**
- The oxygen atoms of H_2O_2 used for oxidation is bound by **covalent bond.**
- Density of water is maximum at **4°C.**
- Ordinary hydrogen is a mixture of **75% ortho–H_2 + 25% para–H_2.**
- A mixture of hydrazine and 40 to 60 per cent of H_2O_2 solution is used as **rocket fuel.**
- Na_2O_2 gives H_2O_2 on treatment with a dilute acid.
- Calgon is an industrial name given to **sodium hexa meta phosphate $(NaPO_3)_6$ or $Na_2[Na_4(PO_3)_6]$.**
- **Permutit** is hydrated sodium aluminium silicate.
- For the bleaching of hair, the substance used is **H_2O_2.**
- Decolourisation of acidified potassium permanganate occurs when H_2O_2 is added to it. This is due to **reduction of $KMnO_4$.**
- Hydrogen reacts with **F_2** even in the dark.
- When zeolite (hydrated sodium aluminium silicate) is treated with hard water the sodium ions are exchanged with **Ca^{2+} ions.**
- The percentage by weight of hydrogen in H_2O_2 is **5.88.**
- When the same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide, the ratio of volumes of hydrogen evolved is **1 : 1.**
- Hydrogen may be prepared by heating a solution of caustic soda with **Zn.**
- The exhausted permutit is generally regenerated by percolating through it a solution of **sodium chloride.**
- **Hydrogen peroxide** has a half open book structure or bent structure.
- Hydrogen peroxide for the first time was prepared by **Thenard.**
- Ortho and para hydrogen differ in the **nature of spins of protons.**
- Hydrogen was discovered by **Cavendish.**
- H_2O_2 acts as an oxidising agent in **acidic as well as in alkaline medium.**
- H_2O_2 acts as antiseptic due to its **oxidising property.**
- Zeolites are extensivley used in **softening of water and catalyst.**
- Sodium zeolite is **$Na_2Al_2Si_2O_8$.**
- The formation of atomic hydrogen from molecular hydrogen will be favoured at **high temperature and low pressure.**
- Hydrogen peroxide is manufactured by the autoxidation of **2-ethylanthraquinol.**
- **Nascent hydrogen** consists of hydrogen atoms with excess energy.
- **Hydrogen molecules** are diatomic and form X^- ions.
- Water acts as excellent solvent due to **high dielectric constant.**
- **30 volume hydrogen** means 1 cm^3 of the solution liberates 30 cm^3 of O_2 at STP.
- An aqueous solution of hydrogen peroxide is **weakly acidic.**

- Moist hydrogen cannot be dried over concentrated H_2SO_4 because **it is oxidised by H_2SO_4.**
- Hydrogen burns with **blue flame.**
- The most reactive isotope of H is **$_1H^1$.**
- H_2 acts as an oxidant in its reaction with **Ca.**
- The most dangerous method of preparing hydrogen would be by the action of HCl and **K.**
- **Liquid H_2** gas in cold, liquid form expands when it is further cooled.
- The life period of atomic hydrogen is **only one third of a second.**
- The percentage of para hydrogen in ordinary hydrogen increases when **temperature is lowered.**

Strength of H_2O_2 solution

The strength of H_2O_2 solution available in the market is expressed in terms of "volume strength". It is defined as the volume of O_2 liberated in ml at NTP from 1ml of the H_2O_2 solution.

Suppose, 1 ml of a H_2O_2 solution on heating decomposes giving 20 ml of O_2 gas at NTP. Then its volume strength is '20V'. Similarly it may be 10V, 12V, 15V, etc.

The relationship between normality and volume strength is:-

$$\text{Normality} = \frac{\text{Volume strength}}{5.6}$$

Again the relationship between % strength and volume strength is :

% strength = volume strength × 0.3035

- The **bond energy of covalent** O—H bond in water is greater than bond energy of hydrogen bond.
- At **absolute zero,** only para hydrogen exists.
- Hydrogen shows **+1, –1 and zero oxidation states.**
- Ozone reacts with H_2O_2 to give oxygen. One volume of ozone gives **two volumes of oxygen.**
- When hydrolith is treated with water it yields **H_2.**
- Hydrogen gas is used on industrial scale in the manufacture of **margarine.**
- Ammonium persulphate solution on heating under reduced pressure gives **H_2O_2.**
- The O—O bond length in H_2O_2 is **1.48 Å.**
- H_2O_2 restores the colour of old lead paintings, blackened by the action of H_2S gas, **by oxidising PbS to $PbSO_4$.**
- Hydrogen has a tendency to gain one electron in order to acquire helium configuration. It thus resembles **halogens.**
- In the case of H_2O_2 the angle between the planes containing the hydrogen atom is **90º.**
- Water contracts on heating **from 0ºC to 4ºC.**
- The geometry of water molecule is same as that of **chlorine oxide.**
- Decomposition of H_2O_2 is accelerated by **finely divided metals.**
- Tritium is obtained by **nuclear reactions.**

Photohydrogen
"Photohydrogen" is hydrogen produced with the help of artificial or natural light. It is sometimes discussed in the context of obtaining renewable energy from sunlight, by using microscopic organisms such as bacteria or algae.

LH_2
LH_2 is an acronym used in the aerospace industry, which stands for liquid hydrogen. LH_2 is a common liquid fuel for rocket applications. Hydrogen is found naturally in the H_2 form, thus the H_2 part of the name. Hydrogen at normal temperatures is a gas and to exist as a liquid must be cooled to a very low level, 20.268 K (& 8722; 423 °F). Liquid hydrogen has a very low density of 70.8 kg/m³ (at 20 K), so storage tanks for it have to be quite large.

- Hydrogen is evolved by the action of cold dilute HNO_3 on **Mg or Mn.**
- $H_2O_2$when added to a solution containing $KMnO_4$ and H_2SO_4 acts **as a reducing agent.**
- H_2O_2 is **diamagnetic.**
  A saturated solution of CO_2 loses weight on exposure to the atmosphere.
- Smell of H_2O_2 resembles **nitric acid.**
- MnO_2 liberates oxygen from a solution of H_2O_2(the action being catalytic) only if the solution is **acidic.**
- H_2O_2 is concentrated by **distillation under reduced pressure.**
- Deuterium an isotope of hydrogen is **non-radioactive.**
- **Hydrogen peroxide** restores the colour of the lead paintings.
- The ionisation energy of hydrogen is **closer to halogens.**
- If water is boiled for sometime it becomes free from **temporary hardness.**
- Zeolite which shows ion-exchanging ability **is a sodium alumino silicate**.
- Hydrogen combines with O_2 to form H_2O. In this reaction **hydrogen gets oxidised.**
- The boiling point of heavy water is **101.4°C.**
- Atomic hydrogen produces formaldehyde when it reacts with **CO.**
- Nucleus of deuterium contains **one proton and one neutron.**
- **Density of heavy water** is higher than ordinary water.
- Deuterium resembles hydrogen in chemical properties but reacts **slower than hydrogen.**
- The electronic configuration of deuterium is **$1s^1$.**
- Decomposition of H_2O_2 is accompanied by **decrease in free energy.**
- The weight percentage of deutrium in heavy water is **20.**
- One of the most important uses of H_2O_2 is **as rocket fuels.**
- **Pure H_2O_2** is pale blue syrupy liquid.
- Tailing of mercury is a laboratory test for **O_3.** In this test, O_3 reacts with Hg to form Hg_2O which sticks on the walls of glass. This is called tailing of mercury
  $$O_3 + 2Hg \rightarrow Hg_2O + O_2.$$
  The tailing is removed by the action of H_2O_2 on Hg_2O.
  $$H_2O_2 + Hg_2O \rightarrow 2Hg + H_2O + O_2.$$
- A molten ionic hydride on electrolysis **H_2 is liberated at anode.**

- Experimental evidence for the presence of ortho and para hydrogen was shown by **Melceman and Mcleod.**
- Hydrogen loses its electron to form H^+ ion. In this respect it resembles to **alkali metals.**
- Heavy water is manufactured in India at **Trombay.**
- Oxygen and hydrogen react to form water. This discovery was made by **Cavendish.**
- The catalyst used in Bosch process of manufacture of H_2 is **Fe_2O_3 + Cr_2O_3.**
- The number of radioactive isotopes of hydrogen is **one** as only tritium is radioactive.
- The number of protons, electrons and neutrons respectivley in a molecule of heavy water is **10, 10, 10.**
- Hydrogen is obtained by the action of an alloy of silicon and iron with NaOH. The process is called **silicol process.**
- The O—O bond is present in **peroxide.**
- When different metals like Zn, Sn, Fe are added to dilute sulphuric acid, **H_2 gas,** which burns explosively in air, is evolved.
- The ionisation of hydrogen atom gives **proton.**
- The hybridisation of the orbitals of oxygen in H_2O_2 is ***sp*³.**
- High boiling point of water is due to **hydrogen bonding.**
- H_2O_2 on treatment with chlorine gives **oxygen.**
- The most reactive state of hydrogen is **atomic hydrogen.**
- The oxidising property of H_2O_2 is due to the fact that two oxygen atoms in its molecule are **bonded differently.**

Compounds of Hydrogen

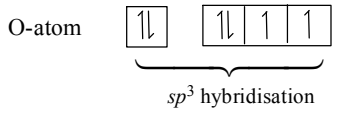
Formula of Compound	Name of Compound	Some Uses of Compound
H_2S	Hydrogen sulphide	Hydrogen sulphide, although it has a strong odour of rottten eggs, it is used by chemists to prouce other compounds and analyse the composition of mixtures. Hydrogen sulphide is more often an nuisane than its uses because its odour is present among decaying organic matter, such as garbage and sewage. It is also common for H_2S to be given off during the removal of tarnish from silver, the exhaust of cars and some buses and around some hot springs.
H_2O_2	Hydrogen peroxide	Rocket propellant, sterilize milk industry, used as bleach in paper, wood pulp, textile and food industries, used as antiseptic, germicide and skin cleanser, used to clean, etch and oxidise PCB and semiconductors/other metals and electronics.
H_2SO_4	Sulphuric acid	Processing metals - cleaning/pickling iron and steel before plating them with tin or zinc; production of fertilizers; manufacture of chemicals in making nitric acid, HCl, synthetic detergents, explosives, dyes, pigments, drugs and sulphate salts; in refining of petroleum and the making of rayon.

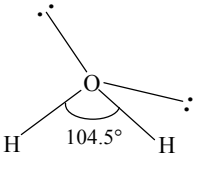
Formula of Compound	Name of Compound	Some Uses of Compound
HCl	Hydrochloric acid or hydrogen chloride	Just like hydrogen peroxide, HCl taken part in pickling/ cleaning metals. Helps to digest food in the walls of the stomach where HCl is present, to separate cotton from wool, manufacture of ammonium chloride, phosphoric acid, dies, pigments in paint, iron, steel, production of corn starch and glucose, make solvents, chloride salts and bleaches, neutralise soap refining, leather tanning, brewing, textiles, waste streams, prevent bacterial in toilet bowls, produces tin and tantalum, used in making glue and gelatin and acts as a starch modifier.
HCN	Hydrogen cyanide	Very dangerous compound that has been used in the past WW1/nazi gas chambers to kill people, used to make the base product, acrylonitrile, for acrylic fibres, plastics, and synthetic rubbers, commercially used as an insecticide and rodenticide and used to make pharmaceuticals.

- **Water**

Water is one of the most plentiful and readily available of all chemicals. It has special importance because of its ability to dissolve so many other substances. Oxygen atom in water molecule is sp^3-hybridised, four hybrid orbitals directed towards the corners of a tetrahedral are formed.

The bond angle is less than the expected angle in tetrahedron due to the presence of two lone pairs of electrons on two uncombined hybrid orbitals which repel each other and the bonded pairs and cause them to come closer and thereby reducing the bond angle from 109° 28′ to 104.5°.

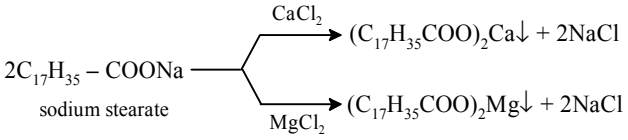




- **Hard and soft water**

The water which lathers easily on shaking with soap solution is called as soft water. While the water which does not produce lather with soap solution readily, rather it forms an insoluble white scum is called as hard water.

- **Cause of hardness of water -** The hardness of water is due to presence of soluble salts of calcium, magnesium and other heavy metals in it. Such water when treated with soap (sodium or potassium salt of higher fatty acid) does not produce lather but produce soluble calcium and magnesium salts of fatty acid, which separate out as scum from water.



Soap will not produce l ather until all the Ca^{2+} and Mg^{2+} ions from water have been removed. Hence the water free from soluble calcium and magnesium salts and containing soluble salts of 'Na' and 'K' is called as soft water.

- **Types of hardness -** It is of two types, such as temporary and permanent hardness. The temporary hardness is due to presence of dissolved bicarbonates of calcium and magnesium and the carbonates of iron. This type of hardness can be easily removed by simply boiling the water, when insoluble carbonates and hydroxides will be formed. Such precipitates are deposited as scale at the bottom of the vessel.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\downarrow + H_2O + CO_2\uparrow$$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3\downarrow + H_2O + CO_2\uparrow$$

$$FeCO_3 + 6H_2O + O_2 \xrightarrow{\Delta} Fe(OH)_3\downarrow + 4CO_2\uparrow$$

On the other hand permanent hardness is due to presence of dissolved chlorides and sulphates of Ca, Mg, Fe and other heavy metals. The softening of this type of water can't be done by boiling, rather it needs chemical treatment.

Degree of hardness of water

It is defind as the number of parts by weight of $CaCO_3$ or its equivalent present in one million parts by weight of water. It is shortly expressed in ppm. For example, suppose 12 mg of $MgSO_4$ is present per litre of water sample.

$\Rightarrow$ 12 mg. $MgSO_4$ corresponds to 10^3gm water (Assuming density of water = 1gm/ml)

$\therefore$ 10^6 gm water contains = 12×10^3 mg of $MgSO_4$

= 12 gm of $MgSO_4$

Again 12 gm $MgSO_4$ = 0.1 mole $MgSO_4$

$\equiv$ 0.1 mole $CaCO_3 \equiv$ 10 gm $CaCO_3$

$\Rightarrow$ 10 gm $CaCO_3$ present per 10^6 gm of water.

$\therefore$ Hardness of water sample is 10 ppm.

- **Softening of hard water**

By boiling- This has been already discussed in types of hardness.

By Clark's process - In this process temporary hardness of water can be removed by adding calculated quantity of slaked lime to it. The slaked lime reacts with soluble calcium and magnesium bicarbonates giving $CaCO_3$ and $Mg(OH)_2$ precipitate, which settle down at the bottom of the tank and can be removed.

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$

$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O$

Excess amount of slaked lime may cause artificial hardness by forming soluble $Ca(HCO_3)_2$ with CO_2 from air.

By lime soda process- In this process both temporary and permanent hardness of water can be removed by adding a mixture of lime and sodium carbonate to it. Some times NaOH is

also added to water in order to neutralise any free acid present and to remove magnesium salts as hydroxide.

$MgCl_2 + Na_2CO_3 \rightarrow MgCO_3\downarrow + 2NaCl$

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$

$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$

$MgSO_4 + NaOH \rightarrow Mg(OH)_2\downarrow + Na_2SO_4$

By permutit process- In this process water is allowed to pass through zeolite, which is a complex substance containing sodium and aluminium silicate. So that sodium ions are displaced by Ca^{2+}, Mg^{2+} ions forming insoluble calcium and magnesium zeolite. Now a days synthetic zeolites, which are also called as permutit are widely used.

$CaCl_2 + Na_2–Ze \rightarrow Ca – Ze\downarrow + 2NaCl$

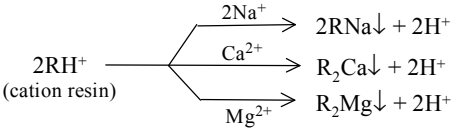
$MgSO_4 + Na_2–Ze \rightarrow Mg – Ze\downarrow + Na_2SO_4$

After long use the sodium permutit loses its ability of softening the hard water, as insoluble calcium permutit deposits over sodium permutit.

Ion - exchange resin process - Ion-exchange resins are insoluble, cross linked, long chain organic compounds containing a sulphonic ($–SO_3H$) group or carboxylic (–COOH) group capable of exchanging their H^+ ion with other cations, which is called as cation exchange resin. Where as those containing basic functional groups like amino or quarternary ammonium or quarternary phosphonium, etc. are called as anion exchange resin. These resins after treatment with dilute NaOH solution become capable of exchanging their OH^- ion with the anions present in water.

Dowex-50, Amberlite IR-120 are the cation exchange resins and their function can be represented as :-

Dowex-3, Amberlite - 400 are the anion exchange resins and their function can be represented as :-



From the above it is clear that if hard water is passed first through cation exchange resin and then through anion exchange resin, then the resulting water will be free from both cations and anions. Again H^+ ions from first step combines with OH^- ions from second step giving water.

- **Demineralisation of water**

The soft water obtained by any of the above methods is not free from all soluble minerals. It also contains some soluble salts of Na and K. But in ion-exchange resin process all the cations and anions can be removed from water as discussed above. The water obtained in this process is called as demineralised water or de-ionised water. It is different from distilled water, as the former contains some dissolved silica, CO_2, O_2 etc. This type of water is very much useful for high pressure boilers.

End