Hydrogen Compounds

Hydrogen in atomic form consists of one proton and one electron but, in elemental form it exists as a diatomic (H_2) molecule. H_2 is called as dihydrogen.

Section (A) : Position of hydrogen in the periodic table; methods of preparation and properties

Position of hydrogen in the periodic table :

Hydrogen is the first element of the periodic table as its atomic number is 1.

The single electron is present in the K shell i.e. first shell with electron configuration $1s^1$.

Hydrogen resembles in many properties with alkali as well as halogen. This dual behaviour of hydrogen may arise due to its electronic configuration i.e. $1s^1$

Resemblance with alkali metals :

(a) Electronic configuration : The valance shell electron configuration of hydrogen and alkali metals are similar i.e. ns^1

(b) Formation of unipositive ion : Hydrogen as well as alkali metals lose one electron to form unipositive ions.

(c) Formation of oxides, halides and sulphides : Just like alkali metals hydrogen combines with electronegative elements such as oxygen, halogen and sulphur forming oxide, halide and sulphide respectively.

Example	Na_2O	NaCl	Na_2S
	H_2O	HCl	H_2S

(d) Reducing character : Like, alkali metals hydrogen also acts as reducing agent.

$$CuO + H_2 \xrightarrow{\Delta} Cu + H_2O \quad ; \quad B_2O_3 + 6K \xrightarrow{\Delta} 3K_2O + 2B$$

Resemblance with halogens .

(a) Electron configuration: Both have one electron less than that of preceding inert gas configuration.

(b) Atomicity: Like halogens, hydrogen forms diatomic molecule too. For example, Cl_2, Br_2, I_2 etc.

(c) Ionization enthalpy: Hydrogen as well as halogens both have higher ionization enthalpies.

H	F	Cl
1312 kJ/mol	1680 kJ/mol	1255 kJ/mol

(d) Formation of uninegative ion: Both hydrogen as well as halogens have the tendency to gain one electron to form uninegative ion so as to have the nearest noble gas electronic configuration.

(e) Formation of hydrides and covalent compounds: Hydrogen as well as halogens combine with elements to form hydrides and a larger number of covalent compounds.

For example;	CCl_4	$SiCl_4$	NaCl
	CH_4	SiH_4	NaH

Difference from alkali metals

(a) Ionization enthalpy of hydrogen (1312 kJ mol^{-1}) is very high as compared to that of alkali metals. (Li = 520 kJ mol^{-1}, Na = 495 kJ mol^{-1})

(b) Alkali metals possess metallic character but hydrogen does not possesses metallic character under normal conditions.

(c) The size of H^+ i.e. nucleus of H atom is 1.5×10^{-3} pm. Which is extremely small as compared to normal atomic and ionic sizes of alkali metals (50 to 200 pm). As a result, H^+ does not exist freely and is always associated with other atoms or molecules. It exists as hydrated proton with formula $H_9O_4^+$ in aqueous solution.

Difference from Halogens :

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

(b) Oxides of halogens are acidic while that of hydrogen is neutral.

Dihydrogen (H_2) :

Occurence

It is most abundent element of the universe (70% of the total mass) but it is much less abundent element (0.15% by mass) in the earth atmospher due to its light nature. In combined form it constitutes 15.4% of the earth crust and the oceans.

Isotopes

Hydrogen has three isotopes namely protium, ${}^{1}_{1}H$, deuterium, ${}^{2}_{1}H$ or D and tritium or T.

They differ from one another by the number of neutrons present in them, Protonium has no neutrons. Deuterium which is also known as heavy hydrogen has one and Tritium has two neutrons in the nucleus.

Property	Hydrogen	Deuterium	Tritium
Relative abundance (%)	99.985	0.0156	10^{-15}
Relative atomic mass (g mol^{-1})	1.008	2.014	3.016
Melting point / K	13.96	18.73	20.62
Boiling point / K	20.39	23.67	25.0
Density / gL^{-1}	0.09	0.18	0.27
Enthalpy of fusion/kJ mol^{-1}	0.117	0.197	
Enthalpy of vaporization/ kJ mol^{-1}	0.904	1.226	–
Enthalpy of bond dissociation /kJ mol^{-1} at 298.2 K	435.88	443.35	–
Internuclear distance / pm	74.14	74.14	–
Ionization enthalpy / kJ mol^{-1}	1312	–	–
Electron gain enthalpy/kJ mol^{-1}	–73	–	–
Covalent radius / pm	37	–	–
Ionic radius (H^-) / pm	208	–	–

Preparation of dihydrogen, (H_2)

(A) Laboratory method :

(i) By the action of dilute HCl on granulated zinc.

$$Zn(\text{granulated}) + 2H^+(\text{dilute}) \longrightarrow Zn^{2+} + H_2$$

(ii) By the action of aqueous alkali like NaOH on Zn, Al or Sn.

$$Zn + 2NaOH \xrightarrow{\Delta} \underset{\text{Sodium Zincate}}{Na_2ZnO_2} + H_2$$

$$2Al + 2H_2O + 2NaOH \xrightarrow{\Delta} \underset{\text{Sodium meta aluminate}}{2NaAlO_2} + 3H_2$$

(B) Commericial production :

(i) Electrolysis of acidified/alkaline water using platinum electrodes gives hydrogen gas.

$$2H_2O(\ell) \xrightarrow[\text{Traces of acid/base}]{\text{electrolysis}} 2H_2(g) + O_{2(g)}$$

(ii) Dihydrogen of high degree of purity (>99.95%) is obtained by the electrolysis of warm aqueous barium hydroxide solution between nickel electrodes.

(iii) It is obtained as a by-product in the manufacture of sodium hydroxide and chlorine by the electrolysis of brine solution.

At cathode : $2H_2O(\ell) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

At anode : $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

Over all reaction is :

$$2Na^+(aq) + 2Cl^-(aq) + 2H_2O(\ell) \longrightarrow Cl_2(g) + H_2(g) + 2Na^+(aq) + 2OH^-(aq)$$

(iv) By passing steam over hydrocarbons or coke at high temperature in the presence of catalyst.

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

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

Mixture of CO and H_2 is called water gas. As water gas is used for the synthesis of methanol and a number of hydrocarbons, it is also called synthesis gas or "syngas". Syngas is obtained now a day from sewage, saw-dust, scrap wood, news papers etc. The process of producing 'syngas' from coal is called 'coal gasification'

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

The yield of dihydrogen can be increased by reacting CO of syngas mixture with steam in the presence of iron chromate as catalyst

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

This reaction which involves the oxidation of CO into CO_2 is called water - gas shift reaction. The CO_2 formed is removed by scrubbing with sodium arsenite solution.

(v) By Lane's process. It involves two steps –

(a) Oxidation stage :

$$Fe(\text{fillings}) + H_2O\ (\text{super heated steam}) \xrightleftharpoons{1025\text{-}1075K} Fe_3O_4 + 4H_2$$

(b) Reduction stage :

$$Fe_3O_4 + \underbrace{2H_2 + CO}_{\text{coal gas}} \longrightarrow 3Fe + 2H_2O + CO_2$$

(vi) Common methods :

(i) Action of water with Na, K & Ca at room temperature .

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

(ii) Action of water with Mg, Al and Zn at boiling temperature of water.

$$Mg + H_2O \xrightarrow{\Delta} MgO + H_2$$

Properties of dihydrogen :

Physical properties :

(a) It is a colourless, odourless tasteless gas.

(b) It is combustible gas; so it can be carefully handled with care while using.

(c) It is lighter than air (density = 1/24th that of air) and insoluble in water.

Chemical properties :

The chemical reactivity of dihydrogen is very low at room temperature. It is attributed to its very high H–H bond dissociation enthalpy (439.9 kJ mol^{-1}). This bond enthalpy infact is the highest for any single bond enthalpy between two atoms of any element. The relatively inert nature of dihydrogen due to the high H–H bond enthalpy may be understood by the fact that the dissociation of dihydrogen into atoms is only 0.081 % around 2000 K which increases to 95.5% at 5000 K. Thus, the atomic hydrogen is produced at a high temperature in an electric arc or under ultraviolet radiations with its incomplete $1s^1$ electronic configuration.

It does combine with almost all the elements. It undergoes chemical reaction by :

(a) loss of the only electron to give H^+

(b) gain of an electron to form H^-, and

(c) sharing an electron to form a single covalent bond.

(1) Reaction with halogens :

$$H_2\ (g) + X_2(g) \longrightarrow 2HX\ (g)\ (\ X = F, Cl, Br, I$$

Reaction with fluorine occurs even in the dark while reaction with iodine occurs in the presence of a catalyst. Order of reactivity is F > Cl > Br > I

(2) Reaction with oxygen :

It burns in air with a pale blue flame to form water This reaction is highly exothermic.

$$2H_2(g) + O_2(g) \xrightarrow[\text{heating}]{\text{catalyst or}} 2H_2O(l) \quad ; \quad \Delta H^0 = -285\ g\ kJ\ mol^{-1}$$

(3) Reaction with nitrogen (Haber process for manufacture of NH_3) :

$$3H_2(g) + N_2(g) \xrightarrow[Fe/Mo]{673\ K\ ,\ 200\ atm} 2NH_3(g) \quad ; \quad \Delta H^0 = -92.6\ kJ\ mol^{-1}$$

(4) Reaction with metals :

It combines with many metals at a high temperature to form the corresponding hydrides.

$$H_2\ (g) + 2M(g) \longrightarrow 2MH(s) \ ;\ M = \text{alkali metal}$$

With metals like, Pt, Pd, Ni, etc, hydrogen forms interstitial hydrides in which hydrogen atoms get trapped in the intersitial voids in the metallic crystals. This property is referred to as occlussion. The occuluded hydrogen liberates on strong heating.

(5) Reactions with metal ions and metal oxides.

Dihydrogen reduces some metal ions (lying below hydrogen) in aqueous solution and oxides of metals which are less reactive than iron into corresponding metals.

$H_2(g) + Pd^{2+}(aq) \longrightarrow Pd(s) + 2H^+(aq)$

$M_xO_y(s) + yH_2(g) \longrightarrow xM(s) + y\,H_2O(\ell)$

$CuO(s) + H_2(g) \xrightarrow{\Delta} Cu(s) + H_2O(\ell)$

(6) Reaction with organic compounds :

Dihydrogen combines with many organic compounds in the presence of catalyst to give useful hydrogenated products of commercial importance.

(a) Hydrogenation of vegetable oils :

$\text{Vegetable oil} + H_2(g) \xrightarrow[\text{Ni}]{473\ \text{K}} \text{Edible fats (margarine and vanaspati ghee)}$

(b) Hydroformylation of olefins :

It yields aldehydes which further undergo reduction to give alcohols.

$RCH = CH_2 + H_2 + CO \xrightarrow{\text{catalyst}} RCH_2CH_2CHO$

$RCH_2CH_2CHO + H_2 \xrightarrow{\text{catalyst}} RCH_2CH_2CH_2OH$

(c) Hydrogenation of unsaturated alkenes :

$CH_2 = CH_2 + H_2 \xrightarrow[473\ \text{K}]{\text{Ni or Pt}} CH_3–CH_3$

$CH{\equiv}CH + 2H_2 \xrightarrow[473\ \text{K}]{\text{Ni or Pt}} CH_3–CH_3$

Uses :

(i) In the manufacture of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers.

(ii) In the manufacture of vanaspati ghee by hydrogenation of polyunsaturated vegetable oils like, soyabean, cotton seed etc.

(iii) In the manufacture of bulk organic chemical, particularly methanol.

$CO(g) + 2H_2(g) \xrightarrow[\text{catalyst},\ \Delta]{\text{cobalt}} CH_3OH(\ell)$

(iv) In preparation of metal hydrides and hydrogen chloride which are highly useful chemicals.

(v) It is used in the metallurgical process to reduce heavy metal oxides in to metals.

(vi) Atomic hydrogen (where temperature required is 2500 K) and oxy-hydrogen torches (where temperature required is 4000 K) are used for cutting and welding purposes.

Dissociation of dihydrogen with the help of an electric arc produces atomic hydrogen atoms.

The atomic hydrogen atoms are allowed to recombine on the surface to be welded to regenerate the temperature of 4000K.

(vii) Mixed with liquid oxygen,it is used as a rocket fuel in space research.

(viii) It is used in fuel cells for generating electrical energy because it does not produce any pollution and releases greater energy per unit mass of fuel in comparision to gasoline and other fuels.

Solved Examples

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

Sol. The various, isotopes of hydrogen are :

${}_1^1H$ (Protium) ; ${}_1^2H$ or D(Deuterium) ; ${}_1^3H$ or T(Tritium)

The mass ratio of ${}_1^1H : {}_1^2H : {}_1^3H$ is 1 : 2 : 3

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

Sol. Hydrogen atom has only one electron and thus, to achieve stable inert gas configuration of helium, it shares its single electron with electron of other hydrogen atom to form a stable diatomic molecule. The stability of H_2 is further confirmed by the fact, that formation of one mole of gaseous H_2 molecules results in the release of 435.8 kJ of energy

$H(g) + H(g) \longrightarrow H_2(g)\ ;\ \Delta H = -\,435.8\ \text{kJ mol}^{-1}$

Ex-3. Which of the following can adsorb largest volume of hydrogen gas?

(1) Finely divided platinum
(2) Finely divided nickel
(3) Colloidal palladium
(4) Colloidal platinum

Ans. (3)

Sol. Order of adsorption of H_2(occlusion) is : Colloidal Palladium > Palladium > Platinum > Gold > Nickel.

Ex-4. Describe the bulk preparation of hydrogen by electrolytic method. What is the role of an electrolyte in this process ?

Sol.: The electrolyte (15–20% NaOH solution) increases conductivity of water.

Cathode (iron) : Reduction of water occurs.

$2H_2O + 2e^- \longrightarrow 2H_2 + 2OH^-$

Anode (nickel coated iron) : Oxidation of OH^- occurs.

$2OH^- \longrightarrow H_2O + 1/2\ O_2 + 2e^-$

Ex-5. Complete the following reactions :

(i) $H_2(g) + M_mO_n(s) \xrightarrow{\Delta}$ (ii) $CO(g) + H_2(g) \xrightarrow[\text{Catalyst}]{\Delta}$

(iii) $C_3H_8(g) + 3H_2O(g) \xrightarrow[\text{Catalyst}]{\Delta}$ (iv) $Zn(s) + NaOH(aq) \xrightarrow{\Delta}$

Ans. (i) $nH_2(g) + M_mO_n(s) \xrightarrow{\Delta} mM(s) + nH_2O(\ell)$

(ii) $CO(g) + 2H_2(g) \xrightarrow[\text{Catalyst}]{\Delta} CH_3OH(\ell)$ (methanol)

(iii) $C_3H_8(g) + 3H_2O(g) \xrightarrow[1270K]{Ni} 3CO(g) + 7H_2(g)$

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

Ex-6. Can conc. H_2SO_4 be used for drying H_2 gas ? Justify.

Sol. Conc. H_2SO_4 cannot be used for drying H_2 gas because H_2SO_4 does absorb moisture from moist H_2, but the process is highly exothermic. The heat so produced causes hydrogen to catch fire because of its inflammable nature.

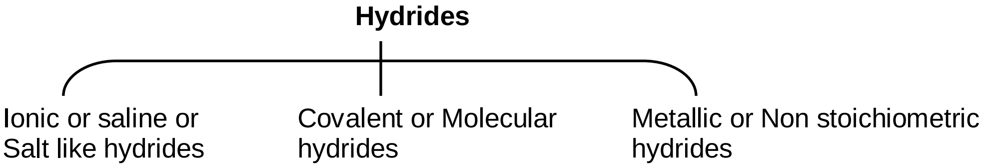
Ex-7. Can dihydrogen act as oxidising agent ? If so give chemical reactions to support the statement.

Sol.: Dihydrogen can act as oxidising agent when it forms metal hydrides.

$2Li + H_2 \longrightarrow 2LiH$

Section (B) : Hydrides

Dihydrogen combines with a large number of non-metals and metals, except noble gases, under certain suitable reaction conditions to form compounds. These binary compounds are called hydrides. The hydrides can be represented by the general formulaEH$_x$ (e.g. MgH_2) or EmHn (e.g. B_2H_6)



Ionic or saline hydrides :

These are stoichiometric compounds of dihydrogen with most of the s-block elements which are highly electropositive in nature.

However, the lighter metal hydrides such as LiH, BeH_2 and MgH_2 have significant covalent character. Infact BeH_2 and MgH_2 are polymeric in nature.

Ionic hydrides are crystalline, nonvolatile and non conducting in solid state. But their molten state conduct electricity and on electrolysis, liberate dihydrogen gas at anode. .Which confirms the existence of H^- ion.

$2H^-(\text{melt}) \longrightarrow H_2(g) + 2e^-$ at anode

These hydrides react with water violently libereting dihydrogen gas.

$NaH\ (s) + H_2O\ (\ell) \longrightarrow NaOH\ (aq) + H_2(g)$

Similarly with protonic solvent such as ethanol and ammonia, they combine and liberates dihydrogen gas.

$LiH + CH_3OH \longrightarrow LiOCH_3 + H_2\uparrow$; $NaH + NH_3 \longrightarrow NaNH_2 + H_2\uparrow$

Note : LiH is unreactive at moderate temperature with O_2 or Cl_2 and therefore, it is used in the synthesis of other useful hydrides, e.g.

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

Ionic hydrides are powerful reducing agents

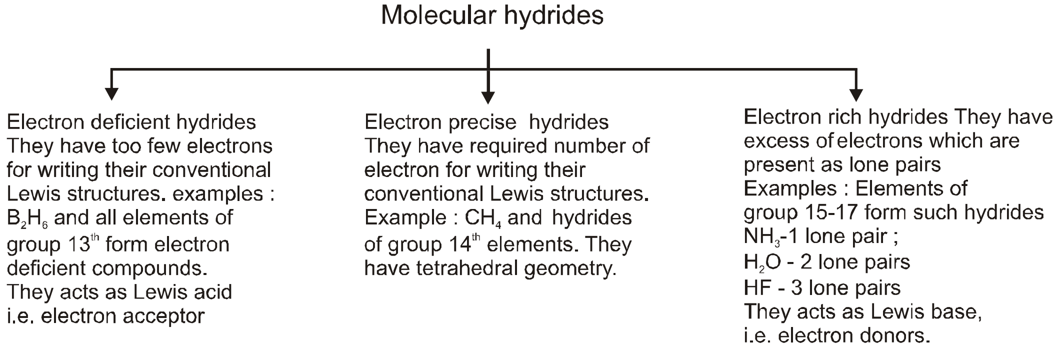
$2CO + NaOH \longrightarrow HCOONa + C$; $PbSO_4 + 2CaH_2 \longrightarrow PbS + 2Ca(OH)_2$

Covalent or molecular hydrides

These are the binary compounds of hydrogen with most of the p-block elements which have relatively high electronegativity. Covalent hydrides involves the formation of covalent bonds between H–atoms and other atoms by sharing of electrons. Some important examples of covalent hydrides are HCl, H_2O, CH_4, PH_3, NH_3 etc.

Being covalent they are volatile compounds and more soluble in organic solvents.

Molecular hydrides are further classified according to the relative numbers of electrons and bond in their Lewis structures.



Molecular hydrides

Electron deficient hydrides They have too few electrons for writing their conventional Lewis structures. examples : B_2H_6 and all elements of group 13th form electron deficient compounds. They acts as Lewis acid i.e. electron acceptor

Electron precise hydrides They have required number of electron for writing their conventional Lewis structures. Example : CH_4 and hydrides of group 14th elements. They have tetrahedral geometry.

Electron rich hydrides They have excess of electrons which are present as lone pairs Examples : Elements of group 15-17 form such hydrides NH_3-1 lone pair ; H_2O - 2 lone pairs HF - 3 lone pairs They acts as Lewis base, i.e. electron donors.

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

Metallic or non - stoichiometric (or interstitial) hydrides :

These are formed by many d-block and f-block elements except the metals of group 7,8 and 9. Chromium only the 6th group metals which form metallic hydrides, (CrH). These hydrides conduct electricity and heat not as efficiently as their parent metals do.

They are almost always non-stoichiometric, being deficient in hydrogen.

Examples : $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.5–1.8}$, $ZrH_{1.3–1.75}$, $VH_{0.56}$, $NiH_{0.6–0.7}$, $PdH_{0.6–0.8}$ etc.

Earlier it was thought that in these hydrides, hydrogen occupies interstices in the metal lattice producing distortion without any change in its type. This gave the name interstitial hydrides to this type of hydrides but recent studies have shown that except for hydrides of Ni, Pd, Ce and Ac, other hydrides of this class have lattice different from that of the parent metals.

This property of absorption of hydrogen on transition metal is largely used in the catalytic reduction, hydrogenation reaction for the preparation of large number of compounds.

Pd, Pt etc. can accomodate a very large volume of hydrogen and therefore can be used as its storage media.

Note : The inability of metals of group 7,8,9 of periodic table to form hydrides is referred to as hydride gap of d-block.

Dihydrogen as a fuel :

Dihydrogen on combustion liberates large quantities of heat.

Following table gives the data on energy release by combustion of fuels like dihydrogen, methane, LPG etc. in terms of the some amounts in mole, mass and volume.

Energy released on combustion in kJ	Dihydrogen (g)	Dihydrogen (□)	LPG	CH_4 (g)	octane (□)
Per mole	286	285	2220	880	5511
Per gram	143	142	50	53	47
Per litre	12	9968	25590	35	34005

It reveals that on a mass for mass basis dihydrogen can release more energy than that of petrol (about three times). Further pollutants in combustion of dihydrogen will be less than petrol. The only pollutant in this will be the oxides of nitrogen which is formed due to the presence of dinitrogen as impurity with dihydrogen. This can be minimised by injecting a small amount of water into the cylinder to lower the temperature, so that the reaction between dinitrogen and oxygen may not take place.

A cylinder of compressed dihydrogen weight about 30 times as much as a tank of petrol containing the same amount of energy. Also dihydrogen gas is converted into liquid state by cooling to 20K. This would require coastly insulated tanks of metal alloy, tanks of metal alloy like $NaNi_5$, Ti–TiH_2, Mg–MgH_2 etc, are used for storage of dihydrogen in small quantities.

These limitations have prompted the scientists to search for alternative techniques to use dihydrogen in an efficient way.

In this respect hydrogen economy is an alternative. The basic principle of hydrogen economy is the transportation and storage of energy in the form of liquid or gasseous dihydrogen.

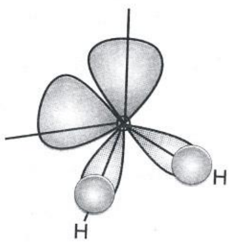
Advantage of hydrogen economy is that energy is transmitted in the form of dihydrogen and not as electric power.

1. In india in october 2005 a pilot project using dihydrogen as fule was launched for running automobiles Initially 5% hydrogen has been mixed in CNG for use in four wheeler vehicles.

2. Now a day it is also used in fule cells for generation of electric power.

Section (C) : Water

It is an important consituent of animal and vegetable matter and plays a vital role in their life processes. It constitutes about 65% of human body and about 95% by weight of some plants. It is a solvent of great importance. The distribution of water over the earth's surface is not uniform.



Physical properties :

It is a colourless and tasteless liquid. It has some unique and unusual properties in the condensed phase (liquid and solid states) which are due to the presence of extensive hydrogen bonding between water molecules. Hydrogen bonding leads to high freezing point, high boiling point, high heat of vaporisation and high heat of fusion in comparision to H_2S and H_2Se.

Water has a higher specific heat, thermal conductivity, surface tension, dipole moment and dielectric constant etc than most of the other liquids. Because of these properties water play a vital and key role in the biosphere.

Property	**H_2O**	**D_2O**
Molecular mass (g mol^{-1})	18.0151	20.0276
Melting point / K	273.0	276.8
Boiling point / K	373.0	374.4
Enthalpy of formation / KJ mol^{-1}	–285.9	–294.6
Enthalpy of vaporisation (373K) / KJ mol^{-1}	40.66	41.61
Enthalpy of fusion / KJ mol^{-1}	6.01	–
Temp of max. density / K	276.98	284.2
Density (298K) g cm^{-3}	1.0000	1.1059
Viscosity / centipoise	0.8903	1.107
Dielectric constant / $C_2/N.m^2$	78.39	78.06
Electrical conductivity	5.7×10^{-8}	–

The high heat of vaporisation and heat capacity are responsible for moderation of the climate and body temperature of living beings.

It is an excellent solvent for transportation of ions and molecules needed/essential for plant and animal metabolism.

Polar molecules and also the covalent compounds like alcohol and carbohydrates dissolve in water due to hydrogen bonding.

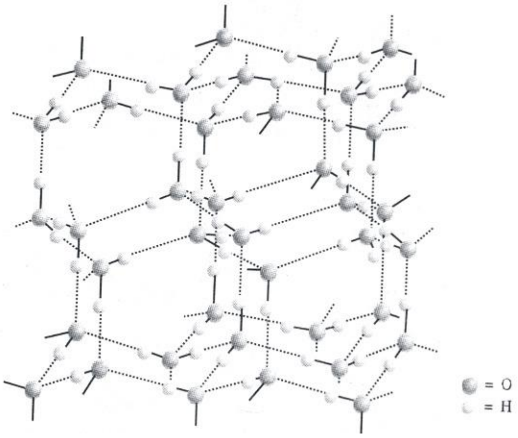
It is a highly polar molecule and in the liquid phase water molecules are associated together by hydrogen bonds. Its crystalline form is ice.

At atmospheric pressure ice crystallises in the hexagonal form, but at very low temperature it condenses to cubic form. Density of ice is less than that of water. Therefore, an ice floats on water.

Note : In winter season ice formed on the surface of a lake gives thermal insulation and this ensures the survival of the aquatic life.

Structure of ice

Ice has a highly ordered three dimensional hydrogen bonded structure



According to X–rays analysis of ice crystals, each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 2.76 Å. There are four H atoms around each O atom. Two of the four H atmos are bonded by covalent bonds (bonds lengths 100 pm) where as the other two are bonded through H–bonds (bond lengths 176 pm)

Hydrogen bonding gives ice open cage like structure with wide holes. As a consequence of this, ice has a relatively large volume for a given mass of liquid water.

Chemical properties :

(1) Amphoteric nature :

$H_2O(\ell) + NH_3(aq) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$

$H_2O(\ell) + H_2S\ (aq) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$

The auto -protolysis (self ionisation) of water occurs as :

$H_2O(l)$	+	$H_2O\ (l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$OH^-(aq)$
Acid-1		base-1		acid-2		base-2
(acid)		(base)		conjugate acid		conjugate base

(2) Redox reaction involving water :

$2H_2O\ (l) + 2Na(s) \xrightarrow[\text{reduction}]{\text{oxidation}} 2NaOH(aq) + H_2(g)$

Water is a great source of dihydrogen

$6CO_2(g) + 12\ H_2O(\ell) \longrightarrow C_6H_{12}O_6(aq) + 6H_2O(l) + 6O_2(g)$

This reaction occurs during photosynthesis

$2F_2(g) + 2H_2O(\ell) \longrightarrow 4H^+\ (aq) + 4F^-\ (aq) + O_2(g)$

(3) Hydrolysis reaction :

It has a very strong hydrating tendency because of its high dielectric constant.

Hydrolysis of certain covalent and some ionic compounds takes place in water.

$P_4O_{10} + 6H_2O(\ell) \longrightarrow 4H_3PO_4(aq)$; $SiCl_4(l) + 2H_2O(\ell) \xrightarrow{\Delta} SiO_2(s) + 4\ HCl(aq)$

$N^{3-}\ (s) + 3H_2O\ (\ell) \longrightarrow NH_3(g) + 3OH^-\ (aq)$

(4) Hydrates formation :

Many salts on crystallisation from their aqueous solutions yield hydrate salts. There are three ways of association of water as given below.

(i) Coordinated water: Attached to central metal ion through coordinate–covalent bond. $[Cr(H_2O)_6]^{3+}3Cl^-$

(ii) Interstitial water: Water molecules occupy the interstices of the crystal lattice of the compound e.g. $BaCl_2.2H_2O$.

(iii) Hydrogen bonded water: Water is attached to the compound making hydrogen bond.

$[Cu(H_2O)_4]^{2+}\ SO_4^{2-}.\ H_2O$ in $CuSO_4.5H_2O$

Solved Examples

Ex-8. What characteristics do you expect from electron deficient hydrides with respect to their structure and chemical reactivity ?

Sol. Electron deficient hydrides do not have sufficient number of electrons to form normal covalent bonds. They generally exist in polymeric forms such as B_2H_6, B_4H_{10}, $(AlH_3)_n$, etc.

Due to deficiency of electrons, these hydrides act as Lewis acids and thus, form complex entities with Lewis bases such as : NH_3, H^- ions, etc.

$$B_2H_6 + 2\ddot{N}H_3 \longrightarrow [BH_2(NH_3)_2]^+[BH_4]^-$$
$$B_2H_6 + 2NaH \longrightarrow 2Na^+[BH_4]^- \text{ (sodium borohydride)}$$

Ex-9. Do you expect the carbon hydride of the type (C_nH_{2n+2}) to act as Lewis acid or base ? Justify your answer.

Sol. Carbon hydride of the type (C_nH_{2n+2}) are electronprecise hydrides. In other words, they have exact numbers of electrons required to form covalent bonds. Therefore, they do not have tendency to either gain or lose electrons and hence, they do not act as Lewis acids or Lewis bases.

Ex-10. 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 character

(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.

Sol. (i) BeH_2 is a covalent hydride, therefore, it does not conduct electricity at all. CaH_2 conducts electricity in the fused state while TiH_2 conducts electricity at room temperature. Thus, the order of increasing electrical conductance is : $BeH_2 < CaH_2 < TiH_2$.

(ii) Electronegativity decreases down the group from Li to Cs, therefore, the ionic character of their hydrides also increases in the same order, i.e., LiH, < NaOH < CsH.

(iii) F – F bond dissociation enthalpy is the minimum. This is due to high concentration of electron density around each F atom in the form of 3 lone pairs which cause significant repulsive interactions. The bond enthalpy of D–D bond is slightly higher than that of H–H bond. It is due to marginally smaller size of D. Thus, the bond dissociation enthalpy increases in the order : F–F < H–H < D–D.

(iv) Ionic hydrides are powerful reducing agents. Both MgH_2 and H_2O are covalent hydrides but the bond dissociation of O–H bonds in H_2O is much higher than that of Mg–H bond in MgH_2. Therefore, the reducing character increases in the order : $H_2O < MgH_2 < NaH$.

Ex-11. How do you expect the metallic hydrides to be useful hydrogen storage ? Explain.

Sol. In some of the transition metal hydrides, hydrogen is absorbed as H atoms. Due to the inclusion of H-atoms, the metal lattice expands and thus becomes less stable. Therefore, when such metallic hydride is heated, it decomposes to release hydrogen gas and very finely divided metal. The hydrogen evolved in this manner can be used as a fuel. Thus, transition metals or their alloys can act as sponge and can be used to store and transport hydrogen to be used as a fule.

Ex-12. Explain the meaning of term hydride gap.

Ans. Elements of group 7, 8, 9 of d-block do not form hydrides at all. This inability of metals of group 7, 8, 9 of periodic table to form hydrides is referred to as hydride gap of d-block.

Ex-13. Explain the following :

(a) Water is excellent solvent for ionic compounds.

(b) Lakes freeze from top to bottom.

Sol. (a) Water has a high dielectric constant (78.39) due to the polar character of its molecule. Water is an excellent solvent for many ionic as well as covalent compounds. Dissolution of ionic compounds takes place because of ion-dipole interactions. Dissolution of molecular compounds such as alcohols, amides, urea, sugar, glucose, honey, etc., in water takes place because of the tendency of these substances to form hydrogen bonds with water molecules.

(b) This is due to the fact that the frozen water does not sink to the bottom but keeps floating at the surface due to its lesser density. This provides thermal insulation to the water below it. The lesser density of ice can be attributed to open cage-like structure on account of hydrogen bonding.

Soft water and Hard water :

	Soft water		Hard water
1.	Water free from soluble salts of calcium and magnesium is called soft water. It gives lather with soap easily.	1.	Water containing calcium and magnesium in the form of hydrogen carbonate, chloride and sulphate does not give lather with soap. This type of water is called hard water.
2.	Distilled water and rain water are common examples of soft water.	2.	River water, sea water, tap water are common examples of hard water.
3.	It does not form scum/precipitate with soap.	3.	It forms scum/precipitate with soap. It reacts with soap (containing sodium sterate) to precipitate out Ca/Mg sterate. $2C_{17}H_{35}COONa(aq) + M^{+}(aq)$ $\downarrow$ $(C_{17}H_{35}COO)_2M \downarrow + 2Na^{+}(aq)$ M = Ca/Mg
4.	It is suitable for laundry as well as for boilers.	4.	It is not suitable for laundry because of the above reason. It is also harmful for boilers becasue of the deposition of salts in the form of scales. The scale formation reduces the efficiency of the boiler.

Hardness of water :

(1) Temporary hardness :

It is due to the presence of the soluble bicarbonates of magnesium and calcium.

Methods used for removing the temporary hardness of water are as follows -

(a) Boiling :

$$Mg(HCO_3)_2 \xrightarrow{Boil} Mg(OH)_2\downarrow + 2CO_2\uparrow$$

$Mg(OH)_2$ is precipitated because of high solubility product of $Mg(OH)_2$ as compared to that of $MgCO_3$

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

Filtrate is soft water.

(b) Clark's method (calcium hydroxide/lime water method) :

$$Ca(HCO_3)_2 + Ca(OH)_2 \text{ (calculated amount)} \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2\text{(calculated amount)} \longrightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O$$

(2) Permanent hardness :

It is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates.

Methods used for removing the permanent hardness of water are as follows -

(a) Addition of washing soda (sodium carbonate) : It reacts with chloride and sulphate of Mg^{2+} and Ca^{2+} to precipitate out as $MgCO_3$ and $CaCO_3$.

$$MCl_2 + Na_2CO_3 \longrightarrow MCO_3\downarrow + 2\ NaCl \qquad (M = Mg/Ca)$$

$$MSO_4 + Na_2CO_3 \longrightarrow MCO_3\downarrow + Na_2SO_4 \qquad (M = Mg/Ca)$$

(b) Calgon's method :

Sodium hexametaphosphate ($Na_6P_6O_{18}$ or $Na_2[Na_4(PO_3)_6]$) is commerically called 'calgon' forms soluble complexes with Mg^{2+} and Ca^{2+} ions.

$2Ca^{2+} + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6]$ (soluble complex) $+ 4Na^{+}$
Hard water

$2Mg^{2+} + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Mg_2(PO_3)_6]$ (soluble complex) $+ 4Na^{+}$
Hard water

OR

$$Na_6P_6O_{18} \longrightarrow 2Na^{+} + Na_4P_6O_{18}^{2-}$$

$$M^{2+} + Na_4P_6O_{18}^{2-} \longrightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^{+} \ (M = Mg/Ca)$$

(c) Ion-exchange method : (Zeolite/permutit method) With zeolite (hydrated sodium aluminium silicate) $NaAlSiO_4$, hard water gives following exchange reaction.

$$2NaZ(s) + M^{2+}(aq) \longrightarrow MZ_2(s) + 2Na^{+}(aq) \qquad (M = Ca^{2+}/ Mg^{2+})$$

The exhausted zeolite is regenerated for further use by treating with aqueous solution of NaCl

$$MZ_2(s) + 2NaCl(aq) \longrightarrow 2NaZ(s) + MCl_2(aq)$$

(d) Synthetic resin method : This method is more efficient than zeolite. It involves the use of cation exchange resin and anion exchange resin for softening of water. Cation exchange resin contain large organic molecules with $–SO_3H$ group and are insoluble. Anion exchange resin contain large organic molecules with –OH group and are insoluble.

Reaction with cation exchange resin.

$$RSO_3H + NaCl \longrightarrow RSO_3Na + HCl$$

$$2RNa(s) + \underset{\text{Hard water}}{M^{2+}(aq)} \longrightarrow R_2M(s) + 2Na^+(aq) \qquad (M^{2+} = Ca^{2+} / Mg^{2+})$$

Exhausted resin is then regenerated by treating with NaCl solution.

Pure de-mineralised water which is 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).

$2RH(s) + M^{2+}(aq) \quad MR_2(s) + 2H^+(aq)$

Here in this H^+ exchange for Na^+, Mg^{2+}, Ca^{2+} and other cation present in the water. This process results in the release of proton and thus makes the water acidic.

In the anion exchange process as given below, $OH^–$ exchanges for anion like, $Cl^–$, $HCO_3^–$, $SO_4^{2–}$ etc, present in the water, this process results in the release of $OH^–$ which neutralise the H^+ ions released in the catio exchange.

$RNH_2(s) + H_2O(\square) \rightleftharpoons RNH_3^+ + OH^–(s)$; $\qquad RNH_3^+.OH^–(s) + X^–(aq) \rightleftharpoons RNH_3X^– + OH^–$

$H^+(aq) + OH^–(aq) \longrightarrow H_2O(\square)$

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

Heavy water (D_2O) :

Preparation :

(a) By prolonged/exhaustive electrolysis of water. **(b)** Obtained as a by product in some fertilizer industries.

Properties :

Heavy water is colourless, tasteless and odourless liquid. All physical constants of heavy water are higher than the corresponding values of ordinary water. Chemically heavy water is similar to ordinary water but the chemical reactions are slower than those of ordinary water.

Uses :

(i) It is widely used as moderator in nuclear reactors.

(ii) It is used in exchange reactions for the study of the reaction mechanism.

(iii) It is used for the preparation of other deuterium compounds.

$$CaC_2 + D_2O \longrightarrow C_2D_2 + Ca(OD)_2$$

$$SO_3 + D_2O \longrightarrow D_2SO_4 \; ; \qquad Al_4C_3 + 12D_2O \longrightarrow 3CD_4 + 4Al(OD)_3$$

Section (D) : Hydrogen Peroxide (H_2O_2)

Methods of preparation :

(A) Laboratory method

$$BaO_2 + 2\ \ HCl \longrightarrow \underbrace{BaCl_2 + H_2O_2}_{\text{not possible to isolate } H_2O_2 \text{ from this solution}}$$

Anhydrous BaO_2 cannot be used, as $BaSO_4$ formed by the reaction with H_2SO_4, forms a thin protective film around BaO_2 and reaction slowly ceases and finally stops after sometime. So hydrated barium peroxide is used.

$$H_2O_2 + \underset{\text{sat.soln.}}{Ba(OH)_2} + 6\ H_2O \longrightarrow BaO_2\ .\ 8\ H_2O$$

Acidifying barium peroxide and removing excess of water by evaporation under reduced pressure gives H_2O_2. $BaSO_4$ is removed by filteration.

$$BaO_2.8H_2O + \underset{\text{cold}}{H_2SO_4} \longrightarrow \underset{\text{ppt.}}{BaSO_4 \downarrow} + H_2O_2 + 8\ H_2O$$

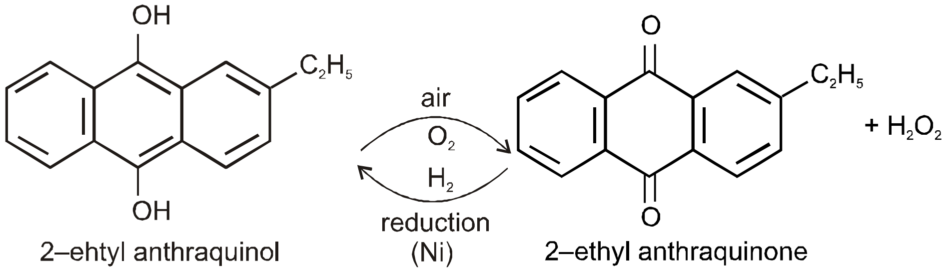
Since H_2SO_4 can decompose H_2O_2 at a higher temperature, therefore, this reaction should be carried out at low temperature. H_3PO_4 can be used in place of H_2SO_4.

$3BaO_2 + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2\downarrow + H_2O_2$;

$Ba_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3BaSO_4\downarrow + 2H_3PO_4$ (can be used again)

(B) Industrial Method

(i) Auto oxidation :



(ii) By electrolysis of conc. H_2SO_4 (50%) at 0^0C using inert electrodes :

Cathode : Platinum

Anode : Graphite

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

At anode : $2\,HSO_4^- \longrightarrow S_2O_8^{-2} + 2\,H^+ + 2e^-$

Or $(2\,HSO_4^-\,(aq) \longrightarrow HO_3SOOSO_3)$

Cathode : $H^+ + e^- \longrightarrow \frac{1}{2}H_2$

$$H_2S_2O_8 + H_2O \xrightarrow[\text{distillation}]{80\text{–}90^{0}C} \underbrace{2\,H_2SO_4 + H_2O_2}_{\substack{\big\downarrow BaCl_2 \\ BaSO_4\downarrow + H_2O_2(aq)}}$$

❖ $K_2S_2O_8\,(s) + 2\,D_2O\,(\square) \longrightarrow 2\,KDSO_4\,(aq) + D_2O_2\,(\square)$

(iii) Modified method :

Equimolar mixture of sulphuric acid and ammonium sulphate is used for electrolysis.

$(NH_4)_2\,SO_4 + H_2SO_4 \longrightarrow 2NH_4HSO_4$ (ammonium hydrogen sulphate)

$NH_4HSO_4 \longrightarrow NH_4SO_4^- + H^+$

At cathode : $H^+ + e^- \longrightarrow \frac{1}{2}\,H_2.$

At anode : $2\,NH_4SO_4^- \longrightarrow (NH_4)_2\,S_2O_8$ (ammonium persulphate) $+ 2e^-$

$(NH_4)_2\,S_2O_8 + H_2O \xrightarrow{\text{distillation}} 2\,NH_4\,HSO_4 + H_2O_2$

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

Properties of H_2O_2 :

(a) Physical properties :

(1) It is a colourless viscous liquid which appears blue in the large quantity.

(2) It is H–bonded and therefore, miscible with water in all proportions and forms a hydrate $H_2O_2.\,H_2O$ (melting point 221 K).

(3) Its boiling point (144°C) is more than water, freezing point (–4°C) is less and density is more than water.

Its aqueous solution is more stable than the anhydrous liquid where it decomposes into water and O_2, slowly on exposure to light.

$$2\,H_2O_2 \rightleftharpoons 2\,H_2O + O_2$$

☞ H_2O_2 is not kept in glass/metal containers because traces of alkali metal ions and metal ions from the glass and metal surface respectively can catalyse the explosive decomposition of H_2O_2. Therefore, H_2O_2 aqueous solution is stored in the plastic or wax–lined glass containers in dark and some urea, phosphoric acid or glycerol is added to that solution because these compounds have been found to behave as negative catalyst for the decomposition of H_2O_2. It is also kept away from the dust because dust can also induce explosive decomposition. Commercially it is marketed as 10 V, which means it contains 3% H_2O_2.

(b) Chemical properties :

(1) Acidic nature :

Aqueous H_2O_2 behaves as a weak acid according to following equation.

$H_2O_2(aq) \rightleftharpoons H^+ + HO_2^-$ $K_a = 1.5 \times 10^{-12}$ at 25ºC

A 30% soln. of H_2O_2 has pH = 4

Aqueous H_2O_2 turns blue litmus red, which is bleached by oxidising property of H_2O_2.

$Na_2CO_3 + H_2O_2 \longrightarrow Na_2O_2 + H_2O + CO_2 \uparrow$

$Ba(OH)_2 + H_2O_2 + 6\,H_2O \longrightarrow BaO_2.\,8\,H_2O$

(2) H_2O_2 as an oxidising agent :

$2e^- + 2\,H^+ + H_2O_2 \longrightarrow 2\,H_2O$ SRP = + 1.77 V (in acidic medium)

$2e^- + H_2O_2 \longrightarrow 2\,OH^-$ SRP = + 0.87 V (in basic medium)

On the basis of above potential, we can say that H_2O_2 is a stronger oxidising agent in acidic medium than in basic medium but kinetically it is found that reactions are faster in basic medium.

(a) Oxidation by H_2O_2 in acidic medium :

$2\,Fe^{2+} + 2\,H^+ (aq). + H_2O_2 \longrightarrow 2\,F^{3+} (aq) + 2\,H_2O$ (□)

$2H_2O_2 + \underset{\text{hydrazine}}{NH_2.NH_2} \longrightarrow N_2 + 4H_2O$. (reaction is explosive)

$H_2O_2 \longrightarrow H_2O + [O] \times 4$

$PbS + 4[O] \longrightarrow PbSO_4$

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

This property is utilized in restoring the white colour in old paintings which turns black due to the formation of PbS by the action of atmospheric H_2S.

$H_2O_2 \longrightarrow H_2O + [O]$

$H_2S + [O] \longrightarrow H_2O + S$

$H_2O_2 + H_2S \longrightarrow 2\,H_2O + S$

(b) Oxidation by H_2O_2 in basic medium :

$2\,Cr(OH)_3 + 4\,NaOH + 3\,H_2O_2 \longrightarrow 2\,Na_2CrO_4 + 8\,H_2O$.

Or $10\,OH^- + 3\,H_2O_2 + 2Cr^{+3} \longrightarrow 2\,CrO_4^{2-} + 8\,H_2O$

$Pb^{2+}(aq) + CrO_4^{2-}$ (yellow solution) $PbCrO_4 \downarrow$ (yellow)

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

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

(3) H_2O_2 as reducing agent :

$H_2O_2 \longrightarrow O_2 + 2\,H^+ + 2e^-$

$2\,OH^- + H_2O_2 \longrightarrow O_2 + 2\,H_2O + 2e^-$

In alkaline medium, its reducing character is more than in acidic.

(a) Reducing action in acidic medium :

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

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

(b) Reducing action in basic medium :

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

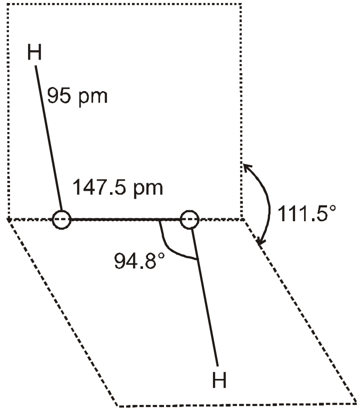
$2\,MnO_4^- + 3\,H_2O_2 \longrightarrow 2\,MnO_2 + 3\,O_2 + 2\,H_2O + 2\,OH^-$

$2[Fe(CN)_6]^{3-}(s) + H_2O_2(aq) + 2OH^-(aq) \longrightarrow 2[Fe(CN)_6]^{4-}(aq) + 2H_2O$(□) $+ O_2(g)$

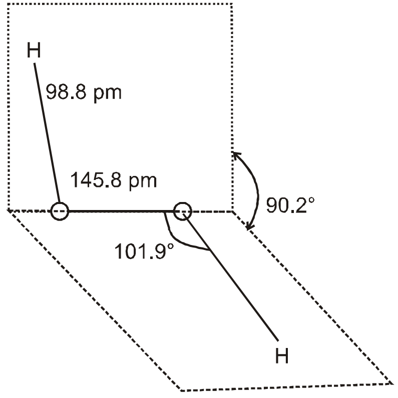
$Ag_2O + H_2O_2 \longrightarrow 2\,Ag + H_2O + O_2$

Structures :

Hydrogen peroxide is non planar structure. The two oxygen atoms are linked to each other by a single covalent bond and each oxygen is further linked to a hydrogen atom by a single covalent bond. The O–H bonds are in different planes due to repulsions between different bonding and antibonding orbitals.



(a) Gas phase



(b) Solid phase

Uses :

(i) 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 used in high quality detergents.

(iii) It is used in 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.

(v) Also used in Environmental (Green) chemistry. e.g., in pollution control treatment of domestic and industrial effluents, oxidation of cyanides, restoration of aerobic conditions to sewage wastes, etc.?

Solved Examples

Ex-14. What causes the temporary and permanent hardness of water ?

Sol. Temporary hardness is caused by presence of soluble bicarbonates of calcium and magnesium, i.e. $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ in water whereas permanent hardness is caused by presence of soluble chlorides and sulphates of calcium and magnesium, i.e. $CaCl_2$, $CaSO_4$, $MgCl_2$ and $MgSO_4$ in water.

Ex-15. What is 'demineralised water' and how can it be obtained ?

Sol. Water which is free from all cations and anions is called demineralised water. It is obtained by passing hard water first through cation exchange resin and then through anion exchange resin.

Ex-16. Explain the following :

(i) Soft water lathers with soap but not hard water.
(ii) Temporary hard water becomes soft on boiling.
(iii) Water can extinguish most fires but not petrol fire.
(iv) Hard water is softened before use in boilers.

Sol. (i) Hard water contains calcium and magnesium salts. These react with soap to form insoluble calcium and magnesium salts of fatty acids, i.e., form scum and not lather.

$$2RCOONa\text{ (soap)} + Ca^{2+} \longrightarrow (RCOO)_2Ca\text{ (insoluble)} + 2Na^+$$
$$2RCOONa\text{ (soap)} + Mg^{2+} \longrightarrow (RCOO)_2Mg\text{ (insoluble)} + 2Na^+$$

(ii) Temporary hardness of water is due to the presence of soluble bicarbonates of calcium and magnesium. On boiling, the bicarbonates are converted into insoluble carbonates which can be removed by filtration.

$$Ca(HCO_3)_2\text{ (soluble)} \longrightarrow CaCO_3\downarrow + H_2O + CO_2$$
$$Mg(HCO_3)_2\text{ (soluble)} \longrightarrow MgCO_3\downarrow + H_2O + CO_2$$

(iii) When water poured over petrol fire, petrol being lighter than water floats over water and thus fire spreads instead being extinguished.

(iv) Hard water consists bicarbonates and other soluble salts of calcium and magnesium. When hard water is evaporated in boilers, scales of precipitated carbonates of calcium and magnesium along with other salts such as sulphates, chlorides, etc., are formed. In order to avoid the formation of scales hard water is first softened before use in boilers.

Ex-17. What happens when ?
(i) Heavy water reacts with magnesium nitride.
(ii) Heavy water reacts with sodium.

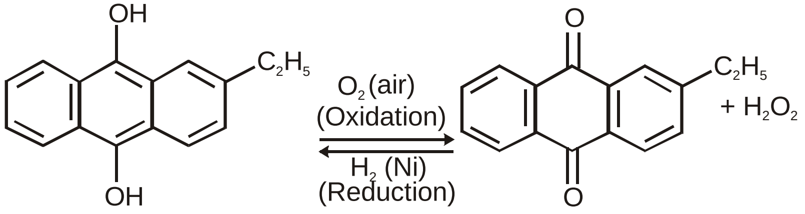
Sol. (i) $Mg_3N_2 + 6D_2O \longrightarrow Mg(OD)_2 + 2ND_3$ (Deutrammonia)
(ii) $Na + 2D_2O \longrightarrow 2NaOD + D_2$

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

Sol. Heavy water is injurious to human beings, plants and animals since it slows down the rates of reactions occuring in them. Thus, heavy water does not support life. In fact it retards certain cellular process, such as mitosis, cell division, etc. Thus, prolonged use of D_2O leads to degeneration of tissues.

Ex-19. **Assertion :** Anhydrous BaO_2 is not used for preparing H_2O_2.
Reason : H_2O_2 is prepared on large scale by air oxidation of 2-Ethyl anthraquinol.
(1) If both Assertion and Reason are true and Reason is a correct explanation of Assertion.
(2) If both Assertion and Reason are true and Reason is not a correct explanation of Assertion.
(3) If Assertion is true but Reason is false.
(4) If Assertion is false but Reason is true.

Sol. **Assertion :** $BaO_2 + H_2SO_4 \longrightarrow BaSO_4 \downarrow$ (white) $+ H_2O_2$
Insoluble $BaSO_4$ forms a thin layer around BaO_2 and therefore reaction occurs slowly and finally stops. So anhydrous BaO_2, is not used.
Reason : Industrial method (Auto oxidation)



2- Ethyl anthraquinol 2-Ehtylanthraquinone

It is cheaper method as only O_2 from air and H_2 are consumed. **Ans.** (2)

Ex-20. Write chemical reactions to justify that hydrogen peroxide can function as an oxidising as well as a reducing agent.

Sol. H_2O_2 can act as an oxidising as well as a reducing agent both in acidic and basic media as illustrated below.
(i) Oxidising agent in acidic medium : $2Fe^{2+}(aq) + 2H^+(aq) + H_2O_2(aq) \longrightarrow 2Fe^{3+}(aq) + 2H_2O(\ell)$
(ii) Oxidising agent in basic medium : $Mn^{2+}(aq) + H_2O_2(aq) + 2HO^-(aq) \longrightarrow \underset{\text{manganese dioxide}}{MnO_2(s)} + 2H_2O(\ell)$
(iii) Reducing agent in acidic medium :

$$2MnO_4(aq) + 6H^+(aq) + 5H_2O_2(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(\ell) + 5O_2(g)$$

(iv) Reducing agent in basic medium :

Ex-21. Explain the following :
(i) Why hydrated barium peroxide is used in the preparation of hydrogen peroxide instead of the anhydrous variety ?
(ii) Phosphoric acid is preferred to sulphuric acid in the preparation of H_2O_2 from barium peroxide.
(iii) Statues coated with white lead on long exposure to atmosphere turns black and the original colour can be restored on treatment with H_2O_2.

Sol. (i) If anhydrous barium peroxide is used in the preparation, the barium sulphate, thus formed, forms an insoluble protective coating on the surface of solid barium peroxide hydrated.
This prevents the further reaction of the acid, i.e., causing the reaction to stop. If, however, hydrated barium peroxide (in the form of the paste) is used, the water causes to dislodge the insoluble $BaSO_4$ from the surface of BaO_2. Hence $BaSO_4$ settles at the bottom of the reaction vessel and the reaction continues without any difficulty.
(ii) When phosphoric acid is used in the preparation of H_2O_2 from BaO_2, it plays the dual role. It liberates H_2O_2 and also acts as a preservator by retarding its decomposition.
(iii) White lead is used as a pigment. The statues coated with white lead get blackened due to the action of H_2S present in atmosphere in traces.

$$Pb(OH)_2 \text{(white lead)}.2PbCO_3 + 3H_2S \longrightarrow 3PbS + 2CO_2 + 4H_2O$$

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. Which of the following is correct for hydrogen ?
(1) It is always collected at cathode.
(2) Its ionization energy is very low incomparision with alkali metals.
(3) It can form bonds in +1 as well as in –1 oxidation states.
(4) Its oxide is not stable.

Sol. $2Na + H_2 \longrightarrow 2\overset{+1}{Na}\ \overset{-1}{H}$; $N_2 + 3H_2 \longrightarrow 2\overset{-3}{N}\ \overset{+1}{H_3}$ **Ans.** (3)

2. Metal which does not react with cold water but evolves H_2 with steam is :
(1) Na (2) K (3) Pt (4) Fe

Sol. $4H_2O(g) + 3Fe(s) \xrightarrow{1000\ K} Fe_3O_4 + 4H_2\uparrow$ **Ans.** (4)

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

Sol. Coal gasification is the process of producing 'syngas' from coal and steam

$$C(s) + H_2O(g) \xrightarrow[Ni]{1270K} \underbrace{CO(g) + H_2(g)}_{syngas}$$

The production of hydrogen can be increased by the reaction carbon monooxide of syngas with steam in presence of iron chromate as catalyst at 673 K when it is oxidised to CO_2.

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

The CO_2 thus produced is removed by scrubbing with a solution of sodium arsenite.

4. Discuss the consequences of high enthalpy of H–H in terms of chemical reactivity.

Sol. Due to high bond enthalpy of H–H bon, dihydrogen molecule (H_2) is quite unreactive at room temperature. However, at high temperature or in presence of catalysts, it combines with many metals and non-metals to form respectively hydrides.

5. What do you understand by (i) electron-deficient, (ii) electron-precise, and (iii) electron rich compounds of hydrogen ? Provide justification with suitable examples.

Sol. (i) Hydrides of elements of group–13 such as BH_3, AlH_3, etc., do not have sufficient number of electrons to form normal covalent bond and hence are called electron-deficient hydrides. To make up this deficiency, they generally exist in polymeric forms such as B_2H_6, B_4H_{10}, $(AlH_3)_n$, etc.

(ii) Hydrides of elements of group-14 like CH_4, SiH_4, GeH_4, etc. have exact number of electrons to form covalent bonds and hence are called electron-precise hydrides. All these hydrides have tetrahedral shapes.

(iii) Hydrides of elements of group 15, 16 and 17, like NH_3, PH_3, H_2O, H_2S, HF, HCl, etc. have more electrons than required to form normal covalent bonds and hence are called electron-rich hydrides. The excess electron in these hydrides are present as lone pairs of electrons.

6. What do you understand by the term "non-stoichiometric hydrides" ? Do you expect this type of hydrides to be formed by alkali metals ? Justify your answer.

Sol. These are hydrides which have low hydrogen content. In these hydrides the ratio of the metal to hydrogen atoms is fractional and they are called non-stoichiometric hydrides. Furthermore, even this fractional ratio of atoms is not fixed but varies with the temperature and the pressure conditions. This type of hydrides are formed by d-and f-block elements. In these hydrides, the hydrogen atoms occupy holes in the metal lattice. Usually some holes alway remain unoccupied and hence these metals form non-stoichiometric hydrides.

Alkali metals are highly reducing as they transfer their lone electron to the H atom, thereby, forming H^- ions. In other words, alkali metals hydrides are ionic in nature. SInce such hydrides are formed by complete transfer of an electron, therefore, the ratio of metal to hydrogen is always fixed. Therefore, alkali metals form only stoichiometric hydrides. They do not form non-stoichiometric hydrides at all.

7. How does the atomic hydrogen or oxy-hydrogen torch function for cutting and welding purposes ? Explain.

Sol. Atomic hydrogen is produced when moleculer hydrogen is passed through an electric arc struck between tungsten electrodes (3773–4273 K).

$H_2(g) \xrightarrow{\text{electric arc}} H(g) + H(g)$: $\Delta H = 436.0\ kJ\ mol^{-1}$

The life span of atomic hydrogen is about 0.3 sec and therefore, it immediately gets converted into the molecular hydrogen (H_2) liberating a large amount of energy which is used for cutting and welding purposes in the form of atomic hydrogen torch.

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

Sol. Strength of H-hydrogen depends upon the atomic size and electronegativity of the other atom to which H-atom is covalently bonded. Smaller size and higher electronegaivity favour H-bonding. Now among N, F, O atoms, atomic size of F is lowest and its electronegativity is highest. Hence H–F will have highest mgnitude of H–bonding.

9. What do you understand by the term 'auto-protolysis' of water. What is its significance ?

Sol. Auto-protolysis refers to self ionization of water. It may be represented as :

$$\underset{\text{Acid}_1}{H_2O(\ell)} + \underset{\text{Base}_2}{H_2O(\ell)} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+(aq)} + \underset{\text{Base}_1}{OH^-(aq)}$$

Due to auto-protolysis, water acts as amphoteric substance i.e., it reacts with both acids and bases. It acts as a base towards acids stronger than itself and as an acid towards bases stronger than itself.

For example, $$\underset{\text{Acid}_1}{H_2O(\ell)} + \underset{\text{Base}_2}{NH_3(aq)} \longrightarrow \underset{\text{Acid}_2}{NH_4^+(aq)} + \underset{\text{Base}_1}{OH^-\ (aq)}$$

$$\underset{\text{Base}_1}{H_2O(\ell)} + \underset{\text{Acid}_2}{H_2S(aq)} \longrightarrow \underset{\text{Acid}_1}{H_3O^+(aq)} + \underset{\text{Base}_2}{HS^-\ (aq)}$$

10. Consider the reaction of water with F_2 and suggest in terms of oxidation and reduction which species are oxidised/reduced ?

Sol. $$\underset{\text{(oxidant)}}{2F_2(g)} + \underset{\text{(reducant)}}{2H_2O(\ell)} \longrightarrow O_2(g) + 4H^+(aq) + 4F^-(aq)$$

or $$\underset{\text{(oxidant)}}{3F_2(g)} + \underset{\text{(reducant)}}{3H_2O(\ell)} \longrightarrow O_3(g) + 6H^-(aq) + 6F^-(aq)$$

In these reactions, water acts as a reducing agent and gets oxidised to either O_2 or O_3 on the other hand, F_2 acts as an oxidising agent and gets reduced to F^- ion.

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

Sol. Demineralised or distilled water is not useful for drinking purpose because it does not contain even useful minerals. Therefore, to make it useful for drinking purposes, useful minerals in proper amounts should be added to demineralised or distilled water.

12. Match list-I with list-II and select the correct answer :

Column-I	**Column-II**
(A) Heavy water	(p) Bicorbonates of Mg and Ca in water
(B) Temporary hard water	(q) Distilled water
(C) Soft water	(r) Deuterium oxide
(D) Permanent hard water	(s) Sulphates and chlorides of Mg and Ca in water.

Ans. (A - r); (B - p); (C - q); (D - s)

Sol. (A) Chemically heavy water is D_2O, i.e. deuterium oxide.

(B) Temporary hardness of water is due to the presence of bicarbonates of calcium and magnesium and can be removed by simple boiling.

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

(C) Water which produces lather with soap solution readily, is called soft water e.g., distilled water, rain water and demineralised water. It contains no foreign ions.

(D) Permanent hardness of water is due to the presence of sulphates and chlorides of calcium and magnesium and can be removed by chemical methods.

$$CaCl_2 + Na_2CO_3 \xrightarrow{\Delta} CaCO_3\downarrow + 2NaCl$$

13. Describe the usefulness of water in biosphere and biological systems.

Sol. Water is essential for all forms of life. It constitutes about 65-70% of the body mass of animals and plants, In comparison to other liquids, water has high specific heat, thermal conductivity, surface tension, dipole moment and dielectric constant, etc. These properties allow water to play a key role in biosphere. The high heat of vaporisation and high heat capacity are responsible for moderation of the climate and body temperature of living beings. It is an excellent solvent for transportation of minerals and other nutrients for plant and animal metabolism. Water is also required for photosynthesis in plants which releases O_2 into the atmosphere.

14. What properties of water make it useful as a solvent ? What type of compounds can it (i) dissolve (ii) hydrolyse ?

Sol. Water has high dielectric constant (79.39) and high dipole moment (1.84D). Because of these properties, water dissolves most of the inorganic (ionic) compounds and many covalent compounds. That is why water is called a universal solvent. Ionic compounds dissolve in water due to ion dipole interaction but, covalent compounds such as alcohol, amines, urea, glucose, sugar, etc., dissolve in water due to H-bonding.

Water can hydrolyse many metallic or non-metallic oxides, hydrides, carbides, nitrides, phosphides and other salts. Some of the important hydrolytic reactions are given below.

$$CaO(s) + H_2O(\ell) \longrightarrow Ca(OH)_2(aq)$$

$$CaH_2\ (s) + 2H_2O(\ell) \longrightarrow Ca(OH)_2(aq) + 2H_2(g)$$

$$Ca_3N_2(s) + 6H_2O(s) \longrightarrow 3Ca(OH)_2(aq) + 2NH_3(g)\ \text{(ammonia)}$$

15. What is the difference between hydrolysis and hydration ?

Sol. Hydrolysis refers to the reaction of salt or more precisely ions of the salt to form acidic or basic solution. For example,

$$Na_2CO_3 + 2H_2O \rightleftharpoons 2Na^+ + 2OH^- + H_2CO_3$$

$$NH_4Cl + H_2O \rightleftharpoons H^+ + Cl^- + NH_4OH$$

Hydration, refers to the addition of H_2O to ions or molecules to form hydrated ions or hydrated salts.

For example, $NaCl(s) + H_2O \longrightarrow \underbrace{Na^+(aq) + Cl^-(aq)}_{\text{Hydrated ions}}$

$$\underset{\text{Anhydrous salt}}{CuSO_4(s)} + 5H_2O(\ell) \longrightarrow \underset{\text{Hydrated salt}}{CuSO_45H_2O(s)}$$

16. Do you expect different products in solution when aluminium (III) chloride and potassium chloride are treated separately with (i) normal water (ii) acidified water, and (iii) alkaline water ?

Sol. KCl is the salt of a strong acid and a strong base. It does not undergo hydrolysis in normal water. It just dissociates to give $K^+(aq)$ and $Cl^-(aq)$ ions giving neutral solution.

$$KCl(s) \xrightarrow{\text{water}} K^+(aq) + Cl^-(aq)$$

$AlCl_3$, on the other hand, is a salt of a weak base $Al(OH)_3$ and a strong acid HCl. Therefore, in normal water, it undergoes hydrolysis, as follows giving acidic solution.

$$AlCl_3(s) + 3H_2O(\ell) \longrightarrow Al(OH)_3(s) + H^+(aq) + Cl^-(aq)$$

In acidic water, both KCl and $AlCl_3$ undergo ionisation.

$$KCl \xrightarrow{\text{acidified water}} K^+(aq) + Cl^-(aq)$$

$$AlCl_3(s) \xrightarrow{\text{acidified water}} Al^{3+}(aq) + 3Cl^-(aq)$$

In alkaline water, $AlCl_3$ reacts to form soluble tetrahydroxoaluminate(III) complex or metaaluminate ion, i.e. AlO_2^-.

$$AlCl_3(s) + 4OH^-(aq) \longrightarrow \underset{\text{tetrahydroxoaluminate}}{[Al(OH)_4^-](aq)} + 3Cl^-(aq)$$

$$\underset{\text{Meltaaluminate ion}}{AlO_2^-(aq) + 2H_2O(\ell)}$$

KCl does not react and only undergoes ionisation as K^+ and Cl^- ions.

17. **Assertion :** H_2O_2 is not stored in glass bottles.

Reason : Alkali metal oxides present in glass catalyse the decomposition of H_2O_2.

(1) If both Assertion and Reason are true and Reason is a correct explanation of Assertion.
(2) If both Assertion and Reason are true and Reason is not a correct explanation of Assertion.
(3) If Assertion is true but Reason is false.
(4) If Assertion is false but Reason is true.

Sol. Assertion and reason both are correct statements and the reason is the correct explanation of the assertion.

$$2H_2O_2 \xrightarrow{\text{Alkali metal oxide}} 2H_2O + O_2.$$

Ans. (1)

18. Consider the following statements.

S_1 : Water at 4°C having maximum density is known as heavy water.
S_2 : Heavy water is formed by the combination of hydrogen and oxygen.
S_3 : D_2O has higher density than H_2O.
S_4 : D_2O is obtained by exhaustive electrolysis of water.

Which of the statements are correct ?

(1) S_1 and S_2 (2) S_2 and S_3 (3) S_3 and S_4 (4) S_2 and S_4

Sol. S_3 : Heavy water is oxide of deuterium. Its density is 1.106 gm^{-3} and that of H_2O is 1.00 gm^{-3}.
S_4 : Correct statement.

Ans. (3)