Chemistry of Non-Metals–I
(Hydrogen, Oxygen, Nitrogen and their compounds)

Hydrogen

Hydrogen (Greek; hydro means water, gene means producing) is the first element in the periodic table and is the lightest element known. It was discovered by Henry Cavendish in 1766. Its name hydrogen was proposed by Lavoisier.

It's atomic number is 1 and it has the electronic configuration $1s^1$. It resembles both alkali metals and halogens and therefore, its position is anomalous.

Occurrence: Hydrogen is the 9th most abundant element in the earth's crust.

Isotopes : Isotopes are the different forms of the same element which have the same atomic number but different mass numbers.

Isotopes of hydrogen

Name	Symbol	Atomic number	Mass number	Relative abundance	Nature radioactive or non-radioactive
Protium or Hydrogen	${}_1^1H$ or H	1	1	99.985%	Non-radioactive
Deuterium	${}_1^2H$ or D	1	2	0.015%	Non-radioactive
Tritium	${}_1^3H$ or T	1	3	10^{-15} %	Radioactive

Physical constants of H_2, D_2 and T_2

Property	H_2	D_2	T_2
Molecular mass	2.016	4.028	6.03
Melting point (K)	13.8	18.7	20.63
Boiling point (K)	20.4	23.9	25.0
Heat of fusion (kJ mol^{-1})	0.117	0.197	0.250
Heat of vaporisation (kJ mol^{-1})	0.994	1.126	1.393
Bond energy (kJ mol^{-1})	435.9	443.4	446.9

Preparation of Dihydrogen : Dihydrogen can be prepared by the following methods:

(1) **Laboratory method :** In the laboratory, dihydrogen can be prepared by the action of dil. H_2SO_4 on granulated Zinc, $Zn + H_2SO_4(\text{dil.}) \rightarrow ZnSO_4 + H_2$

(2) **Industrial Method**

(i) *By the electrolysis of water* **:** The hydrogen prepared by this method is highly pure.

$$2H_2O(\text{l}) \xrightarrow{\text{Electrolysis}} 2H_{2(\text{g})} + O_{2(\text{g})}$$

dihydrogen is collected at cathode.

(ii) *Hydrocarbon steam process* **:** H_2 is prepared by the action of steam on hydrocarbon. e.g.

$$CH_4 + \underset{\text{(Steam)}}{H_2O} \xrightarrow{1170\ K} CO + 3H_2$$

(iii) *Bosch process* **:** $\underset{\text{water gas}}{H_2 + CO} + \underset{\text{steam}}{H_2O} \xrightarrow[Fe_2O_3,\ Cr_2O_3]{773\ K} CO_2 + 2H_2$

(iv) *Lane's process* **:** H_2 is prepared by passing alternate currents of steam and water gas over red hot iron. The method consists of two stages,

(a) Oxidation stage**:** $\underset{\textit{Iron filings}}{3Fe} + \underset{(\textit{Steam})}{4H_2O} \xrightarrow{1025-1075\ K} \underset{\text{Magnetic oxide of iron}}{Fe_3O_4} + 4H_2 + 161\ KJ$

(b) Reduction stage: $2Fe_3O_4 + \underset{\text{water gas}}{4CO + 4H_2} \rightarrow 6Fe + 4CO_2 + 4H_2O$

Physical properties of dihydrogen: It is a colourless, tasteless and odourless gas. It is slightly soluble in water. It is highly combustible. The Physical constants of atomic hydrogen are :

Atomic radius (pm) – 37 ; Ionic radius of H^- ion (pm) – 210; Ionisation energy $(kJ\ mol^{-1})$ – 1312;

Electron affinity $(kJ\ mol^{-1})$ –72.8; Electronegativity – 2.1.

Chemical properties of dihydrogen : Dihydrogen is quite stable and dissociates into hydrogen atoms only when heated above 2000 K, $H_2 \xrightarrow{2000\ K} H + H$.

Its bond dissociation energy is very high, $H_2 \rightarrow H + H$; $\Delta H = 435.9\ kJ\ mol^{-1}$.

Due to its high bond dissociation energy, it is not very reactive. However, it combines with many elements or compounds.

(1) **Action with metals:** To forms corresponding hydrides.

$$2Na + H_2 \xrightarrow{Heat} 2NaH\ ;\ \ Ca + H_2 \xrightarrow{Heat} CaH_2$$

With transition metals (elements of *d* – block) such as *Pd, Ni, Pt* etc. dihydrogen forms interstitial hydrides in which the small molecules of dihydrogen occupy the interstitial sites in the crystal lattices of these hydrides. As a result of formation of interstitial hydrides, these metals adsorb large volume of hydrogen on their surface. This property of adsorption of a gas by a metal is called **occlusion**. The occluded hydrogen can be liberated from the metals by strong heating.

(2) **Reaction with Non-metals :** $2H_2 + O_2 \xrightarrow{970\ K} 2H_2O$; $N_2 + 3H_2 \xrightarrow[750\ K,\ \text{Pressure}]{Fe,\ Mo} 2NH_3$

$$H_2 + F_2 \xrightarrow{Dark} 2HF\ ;\ \ H_2 + Cl_2 \xrightarrow[673\ K,\ \text{Pressure}]{Sunlight} 2HCl$$

$$H_2 + Br_2 \rightarrow 2HBr \; ; \; H_2 + I_2 \xrightarrow[Pt]{673\,K} 2HI$$

The reactivity of halogen towards dihydrogen decreases as: $F_2 > Cl_2 > Br_2 > I_2$

As a result, F_2 reacts in dark, Cl_2 in the presence of sunlight, Br_2 reacts only upon heating while the reaction with I_2 occurs in the presence of a catalyst.

(3) **Reaction with unsaturated hydrocarbons:** H_2 reacts with unsaturated hydrocarbons such as ethylene and acetylene to give saturated hydrocarbons.

$$\underset{Ethylene}{H_2C = CH_2} + H_2 \xrightarrow[473\,K]{Ni\ or\ Pt\ or\ Pd} \underset{Ethane}{CH_3 - CH_3} \; ; \; \underset{Acetylene}{HC \equiv CH} + 2H_2 \xrightarrow[473\,K]{Ni\ or\ Pt\ or\ Pd} \underset{Ethane}{CH_3 - CH_3}$$

This reaction is used in the **hydrogenation or hardening of oils**. The vegetable oils such as groundnut oil or cotton-seed oil are unsaturated in nature because they contain at least one double bond in their molecules. Dihydrogen is passed through the oils at about 473 K in the presence of catalyst to form solid fats.

$$\underset{(liquid)}{\text{Vegetable oil}} + H_2 \xrightarrow[473\,K]{Ni} \underset{(solid)}{Fat}$$

The vegetable ghee such as Dalda, Rath, etc. are usually prepared by this process.

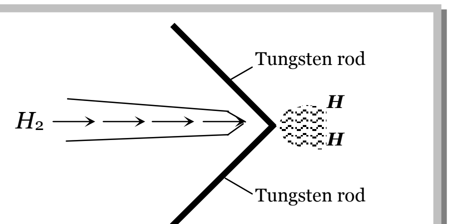
Uses of Dihydrogen

(1) As a reducing agent, (2) In the hydrogenation of vegetable oils, (3) As a rocket fuel in the form of liquid H_2, (4) In the manufacture of synthetic petrol, (5) In the preparation of many compounds such as NH_3, CH_3OH, Urea etc, (6) It is used in the oxy-hydrogen torch for welding if temperature around 2500°C is required. It is also used in atomic hydrogen torch for welding purposes in which temperature of the order of 4000°C is required.

Different forms of hydrogen

(1) **Atomic hydrogen :** It is obtained by the dissociation of hydrogen molecules.

The atomic hydrogen is stable only for a fraction of a second and is extremely reactive. It is obtained by passing dihydrogen gas at atmospheric pressure through an electric arc struck between two tungsten rods.



Atomic hydrogen torch

The electric arc maintains a temperature around 4000 – 4500°C. As the molecules of dihydrogen gas pass through the electric arc, these absorb energy and get dissociated into atoms as

$$H_2(g) \xrightarrow[arc]{Electric} 2H(g) : \Delta H = 435.90\,KJ\,mol^{-1}$$

This arrangement is also called atomic hydrogen torch.

(2) **Nascent hydrogen** : The hydrogen gas prepared in the reaction mixture in contact with the substance with which it has to react, is called nascent hydrogen. It is also called newly born hydrogen. It is more reactive than ordinary hydrogen. For example, if ordinary hydrogen is passed through acidified $KMnO_4$ (pink in colour), its colour is not discharged. On the other hand, if zinc pieces are added to the same solution, bubbles of hydrogen rise through the solution and the colour is discharged due to the reduction on $KMnO_4$ by nascent hydrogen.

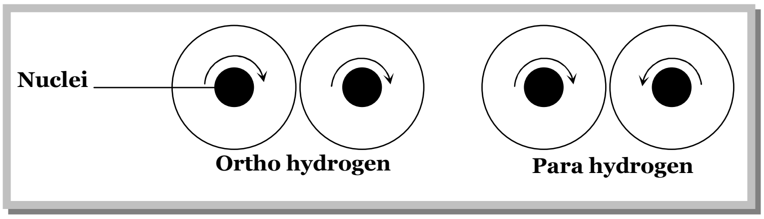
$$KMnO_4 + \underset{Molecular}{H_2} + H_2SO_4 \rightarrow No\ Reaction; \; Zn + H_2SO_4 \rightarrow ZnSO_4 + \underset{Nascent\ hydrogen}{2[H] \times 5}$$

$$2KMnO_4 + 3H_2SO_4 + 10H \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$$

(3) **Ortho and para hydrogen:** A molecule of dihydrogen contains two atoms. The nuclei of both the atoms in each molecule of dihydrogen are spinning. Depending upon the direction of the spin of the nuclei, the hydrogen is of two types:

(i) Molecules of hydrogen in which the spins of both the nuclei are in the same directions, called ortho hydrogen.

(ii) Molecules of hydrogen in which the spins of both the nuclei are in the opposite directions, called para hydrogen.



Ordinary dihydrogen is an equilibrium mixture of ortho and para hydrogen.

Ortho hydrogen $\rightleftharpoons$ Para hydrogen

The amount of ortho and para hydrogen varies with temperature as:

(i) At 0°K, hydrogen contains mainly para hydrogen which is more stable.

(ii) At the temperature of liquefaction of air, the ratio of ortho and para hydrogen is 1:1.

(iii) At the room temperature, the ratio of ortho to para hydrogen is 3:1.

(iv) Even at very high temperatures, the ratio of ortho to para hydrogen can never be more than 3:1.

Thus, it has been possible to get pure para hydrogen by cooling ordinary hydrogen gas to a very low temperature (close to 20 K) but it is never possible to get a sample of hydrogen containing more than 75% of ortho hydrogen. i.e., Pure ortho hydrogen can not be obtained.

Oxygen

Oxygen is the most abundant element in the earth crust (46.5%). It was discovered by **Karl Scheele** and **Joseph Priestley**. It occurs in three isotopic forms :

$\underset{(Abundance: 99.76\%)}{{}_8O^{16}}$ $\underset{(Abundance: 0.037\%)}{{}_8O^{17}}$ $\underset{(Abundance: 0.204\%)}{{}_8O^{18}}$

Out of the three isotopes, ${}_8O^{18}$ is radioactive.

Occurrence : In free state, it occurs in air and constitutes 21% by volume of air.

Preparation of Dioxygen : Oxygen is prepared by the following methods

(1) **By the decomposition of oxygen rich compounds** : e.g.

$$\underset{Pot.\,Nitrate}{2KNO_3} \xrightarrow{Heat} 2KNO_2 + O_2\,; \quad \underset{Pot.\,Chlorate}{2KClO_3} \xrightarrow[MnO_2]{Heat} 2KCl + 3O_2$$

(2) **By heating dioxides, Peroxides and higher oxides** : e.g.

$$\underset{Silver\ oxide}{2Ag_2O} \xrightarrow{Heat} 4Ag + O_2\,; \quad \underset{Manganese\ dioxide}{3MnO_2} \xrightarrow{Heat} Mn_3O_4 + O_2\,; \quad \underset{Barium\ peroxide}{2BaO_2} \xrightarrow{Heat} \underset{Barium\ oxide}{2BaO} + O_2$$

(3) **Laboratory Method:** In the laboratory, O_2 is prepared by thermal decomposition of potassium chlorate.

$$2KClO_3 \xrightarrow[MnO_2]{420\,K} 2KCl + 3O_2$$

Note : ❑ In the absence of MnO_2 catalyst, the decomposition takes place at 670-720 K. Therefore, MnO_2 acts as a catalyst and also lowers the temperature for the decomposition of $KClO_3$.

O_2 can also be prepared by the action of water on sodium peroxide as, $2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$.

(4) **Industrial preparation:** The main sources for the industrial preparation of dioxygen are air and water.

(i) *From air:* O_2 is prepared by fractional distillation of air. During this process, N_2 with less boiling point (78 K) distills as vapour while O_2 with higher boiling point (90 K) remains in the liquid state and can be separated.

(ii) *From water:* O_2 can also be obtained by the electrolysis of water containing a small amount of acid or alkali, $2H_2O \xrightleftharpoons{Electrolysis} 2H_2(g) + O_2(g)$.

Physical properties of O_2: It is a colourless, tasteless and odourless gas. It is slightly soluble in water and its solubility is about $30\ cm^3$ per litre of water at 298 K.

Physical properties of atomic and molecular oxygen.

Atomic properties	Molecular properties
Atomic radius (pm) – 73	Bond length (pm) – 120.7
Ionic radius O^{2-} (pm) – 140	Bond energy $(kJ\ mol^{-1})$ – 493
Electronegativity – 3.5	Density at S.T.P. $(g\ cm^{-3})$ – 1.429
Ionisation energy $(kJ\ mol^{-1})$ – 1310	Melting point (*K*) – 54.4
Electron affinity $(kJ\ mol^{-1})$ – 140	Boiling point (*K*) – 90.2

Chemical properties of O_2: It does not burn itself but helps in burning. It is quite stable in nature and its bond dissociation energy is very high. Therefore, it is not very reactive as such, $O_2 \rightarrow O + O$

bond dissociation energy $= 495\ kJ\ mol^{-1}$

Therefore, dioxygen reacts at higher temperatures. However, once the reaction starts, it proceeds of its own. This is because the chemical reactions of dioxygen are exothermic and the heat produced during the reaction is sufficient to sustain the reactions.

(1) **Action with litmus :** Like dihydrogen, it is also neutral and has no action on blue or red litmus.

(2) **Reaction with metals :** Active metals like *Na, Ca* react at room temp. to form their respective oxides.

$$4Na + O_2 \rightarrow 2Na_2O; \quad 2Ca + O_2 \rightarrow 2CaO$$

It reacts with *Fe, Al, Cu* etc. metals at high temperature

$$4Al + 3O_2 \rightarrow 2Al_2O_3; \quad 4Fe + 3O_2 \rightarrow 2Fe_2O_3$$

(3) **Action with Non-metals :** It form oxides.

$$2H_2 + O_2 \xrightarrow[\text{Electric discharge}]{1073\ K} 2H_2O; \quad N_2 + O_2 \xrightarrow{3273\ K} \underset{\text{Nitric oxide}}{2NO}$$

$$S + O_2 \xrightarrow{Heat} SO_2; \quad C + O_2 \xrightarrow{Heat} CO_2$$

(4) **Reaction with compounds** : Dioxygen is an oxidising agent and it oxidises many compounds under specific conditions. e.g. $4HCl + O_2 \xrightarrow[CuCl_2]{700\,K} 2H_2O + 2Cl_2$; $4NH_3 + 5O_2 \xrightarrow[Pt]{1073\,K} 4NO + 6H_2O$

$CS_2 + 3O_2 \xrightarrow{Heat} CO_2 + 2SO_2$; $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Oxides : A binary compound of oxygen with another element is called oxide. On the basis of acid-base characteristics, the oxides may be classified into the following four types:

(1) **Basic oxides :** Alkali, alkaline earth and transition metals form basic oxides - Na_2O, MgO, Fe_2O_3 etc. their relative basic character decreases in the order : alkali metal oxides>alkaline earth metal oxides>transition metal oxides.

(2) **Acidic oxides :** Non-metal oxides are generally acidic - $CO_2, SO_2, SO_3, NO_2, N_2O_5, P_4O_{10}, Cl_2O_7$ etc.

(3) **Amphoteric oxides :** Al_2O_3, SnO_2 etc.

(4) **Neutral oxides :** H_2O, CO, N_2O, NO etc.

Trends of oxides in the periodic Table : On moving from left to the right in periodic table, the nature of the oxides change from basic to amphoteric and then to acidic. For example, the oxides of third period has the following behaviour :

Na_2O strongly basic	MgO basic	Al_2O_3 amphoteric	SiO_2 weakly acidic	P_4O_{10} acidic	SO_2 strongly acidic	Cl_2O_7 very strongly acidic

Basic to acidic character increases →

However, on moving down a group, acidic character of the oxides decreases. For example in the third group, the acidic character of oxides decreases as:

B_2O_3 acidic	Al_2O_3 amphoteric	Ga_2O_3 (weakly basic)	In_2O_3, Tl_2O_3 basic

Acidic character decreases →

On the basis of oxygen content the oxides may be classified into the following types :

(1) **Normal oxides :** These contain oxygen atoms according to the normal oxidation number i.e. – 2. For example, $MgO, H_2O, CaO, Li_2O, Al_2O_3$ etc.

(2) **Polyoxides :** These contain oxygens atoms more than permitted by the normal valency. Therefore, these contain oxygen atoms in oxidation state different than –2.

(3) **Peroxides :** These contains O_2^{2-} ion having oxidation number of oxygen as –1. For example, $H_2O_2, Na_2O_2, BaO_2, PbO_2$ etc.

(4) **Superoxides :** These contains O_2^- ion having oxidation number of oxygen as –1/2. For example, KO_2, PbO_2, etc.

(5) **Suboxides :** These oxides contain less oxygen than expected from the normal valency. For example, N_2O.

(6) **Mixed oxides :** These oxides are made up of two simple oxides. For example, red lead $Pb_3O_4(2PbO_2 + PbO_2)$, magnetic oxide of iron, $Fe_3O_4(FeO + Fe_2O_3)$ and mixed oxide of manganese, $Mn_3O_4(MnO_2 + 2MnO)$.

Uses of dioxygen

(1) It is used in the oxy-hydrogen or oxy-acetylene torches which are used for welding and cutting of metals.

(2) It is used as an oxidising and bleaching agent, (3) Liquid O_2 is used as rocket fuel.

(4) It is used in metallurgical processes to remove the impurities of metals by oxidation.

Ozone or trioxygen

Ozone is an allotrope of oxygen. It is present in the upper atmosphere, where it is formed by the action of U. V. radiations on O_2, $3O_2 \xrightarrow{U.V \text{ radiation}} \underset{\text{Ozone}}{2O_3}$

O_3 protects us from the harmful U. V. radiations which causes skin cancer. Now a days, ozone layer in the stratrosphere is depleting due to *NO* released by supersonic aircrafts and chlorofluoro carbons (CFC'S) i.e. freon which is increasingly being used in aerosols and as a refrigerant.

Preparation : Ozone is prepared by passing silent electric discharge through pure, cold and dry oxygen in a specially designed apparatus called ozoniser. The formation of ozone from oxygen is an endothermic reaction.

$$3O_2 \underset{\text{discharge}}{\overset{\text{Silent electric}}{\rightleftharpoons}} 2O_3 \quad \Delta H = +285.4\, kJ$$

Ozone is prepared in the laboratory by the following two types of ozonisers :

(a) Siemen's ozoniser, (b) Brodie's ozoniser

For the better yield of ozone : (a) Only pure and dry oxygen should be used. (b) The ozoniser must be perfectly dry. (c) A fairly low temperature $(\approx 273\ K)$ must be maintained. (d) The electric discharge must be sparkless.

Physical properties : Ozone is a light blue coloured gas, having pungent odour. It is heavier than air. Its vapour density is 24. It is slightly soluble in water.

Chemical properties : The important chemical properties of ozone are discussed below:

(1) **Decomposition :** Pure ozone decomposes on heating above 475 K to from O_2 gas.

$$2O_3 \xrightarrow{475\ K} 3O_2 \quad \Delta H = -285.4\, kJ$$

(2) **Oxidising agent :** Ozone is one of the most powerful oxidising agent with the liberation of dioxygen. In fact, ozone is a stronger oxidising agent than molecular oxygen because ozone has higher energy content and decomposes to give atomic oxygen as: $O_3 \rightarrow O_2 + \underset{\text{Atomic oxygen}}{O}$

Therefore, ozone oxidises a number of non-metals and other reducing agents. e.g.

$$\underset{\text{Metal}}{2Ag} + O_3 \rightarrow \underset{\text{Silver oxide}}{Ag_2O} + O_2;\quad \underset{\text{Non-metal}}{S} + 3O_3 \rightarrow SO_3 + 3O_2;\quad \underset{\text{Compound}}{PbS} + 4O_3 \rightarrow PbSO_4 + 4O_2$$

Mercury is oxidised to mercurous oxide, $2Hg + O_3 \rightarrow \underset{\text{Mercurous oxide}}{Hg_2O} + O_2$

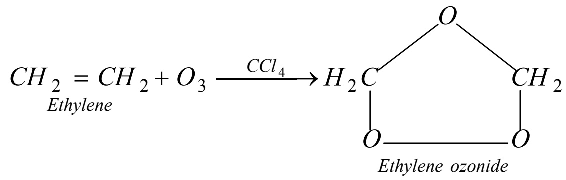
During this reaction mercury loses its meniscus and starts sticking to the sides of the glass. This is known as tailing of mercury. Mercurous oxide formed in this reaction dissolves in mercury and starts sticking to the glass surface.

(3) **Bleaching agent :** Due to the oxidising action of ozone, it acts as a mild bleaching agent as well as a sterilizing agent. It acts as a bleaching agent for vegetable colouring matter.

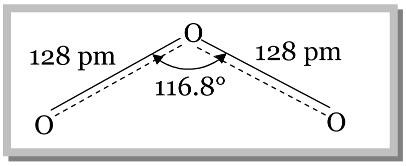
$$Vegetable\ \ colouring\ \ matter + O_3 \rightarrow \underset{(Colourless)}{Oxidised\ coloured\ \ matter} + O_2$$

For example, ozone bleaches indigo, ivory, litmus, delicate fabrics etc.

(4) **Formation of ozonides :** Ozone reacts with alkenes in the presence of CCl_4 to form an ozonide. e.g.



Structure of O_3 : The structure of O_3 molecule is angular as shown in fig. The $O-O-O$ bond angle is 116.8° and $O-O$ bond length is 128 pm.



Uses of ozone

(1) O_3 is used for disinfecting water for drinking purposes because ozone has germicidal properties.

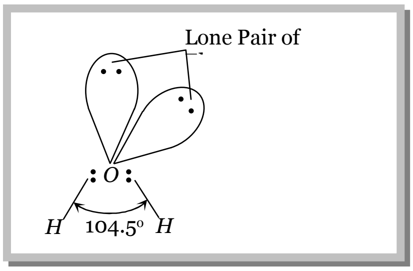
(2) It is used for purifying air of crowded places such as cinemas, under ground railway, auditoriums, tunnels, mines etc.

(3) It is used in industry for the manufacture of $KMnO_4$, artificial silk, synthetic camphor etc.

Water

Water is the oxide of hydrogen. It is an important component of animal and vegetable matter. Water constitutes about 65% of our body. It is the principal constituent of earth's surface.

Structure : Due to the presence of lone pairs, the geometry of water is distorted and the $H-O-H$ bond angle is 104.5°, which is less than the normal tetrahedral angle (109.5°) . The geometry of the molecule is regarded as angular or bent. In water, each $O-H$ bond is polar because of the high electronegativity of oxygen (3.5) in comparison to that of hydrogen (2.1). The resultant dipole moment of water molecule is 1.84D.



In ice, each oxygen atom is tetrahedrally surrounded by four hydrogen atoms; **two by covalent bonds and two by hydrogen bonds**. The resulting structure of ice is open structure having a number of vacant spaces. Therefore, the density of ice is less than that of water and ice floats over water.

It may be noted that water has maximum density $(1 g\, cm^{-3})$ at 4°C.

Heavy water : Chemically heavy water is deuterium oxide (D_2O). It was discovered by **Urey**. It has been finding use in nuclear reactors as a moderator because it slows down the fast moving neutrons and therefore, helps in controlling the nuclear fission process.

Physical properties : Water is colourless, odourless and tasteless liquid at ordinary temperature.

Some physical constants of H_2O and D_2O at 298 K

Constant	Ordinary water (H_2O)	Heavy water (D_2O)
Molecular mass	18.015	20.028
Maximum density $(g\,cm^{-3})$	1.000	1.106
Melting point (K)	273.2	276.8
Boiling point (K)	373.2	374.4
Heat of fusion $(kJ\,mol^{-1})$ at 273K	6.01	6.28
Heat of vaporisation $(kJ\,mol^{-1})$ at 373K	40.66	41.61
Heat of formation $(kJ\,mol^{-1})$	– 285.9	– 294.6
Ionisation constant	1.008×10^{-14}	1.95×10^{-15}

Chemical properties : Water shows a versatile chemical behaviour. It behaves as an acid, a base, an oxidant, a reductant and as ligand to metals.

(1) **Dissociation of water :** Water is quite stable and does not dissociate into its elements even at high temperatures. Pure water has a small but measurable electrical conductivity and it dissociates as:

$$H_2O + H_2O \rightleftharpoons \underset{Hydronium\ ion}{H_3O^+} + OH^- ;\ K_W = 1.0\times10^{-14}\ mol^2L^2 \text{ at 298K}$$

(2) **Amphoteric nature :** Water can act both as an acid and a base and is said to be amphoteric. However, water is neutral towards litmus and its pH is 7.

(3) **Oxidising and reducing nature :** Water can act both as an oxidising and a reducing agent in its chemical reactions. e.g. $2Na + \underset{Oxidising\ agent}{2H_2O} \rightarrow 2NaOH + H_2$; $2F_2 + \underset{Reducing\ agent}{2H_2O} \rightarrow 4HF + O_2$

Hard and Soft water

(1) **Soft water :** Water which produces lather with soap solution readily is called soft water. e.g. distilled water, rain water and demineralised water.

(2) **Hard water :** Water which does not produce lather with soap solution readily is called hard water. e.g. sea water, river water, well water and tap water.

Cause of hardness of water : The hardness of water is due to the presence of bicarbonates, chlorides and sulphates of calcium and magnesium.

Hard water does not produce lather because the cations $(Ca^{+2}\ and\ Mg^{+2})$ present in hard water react with soap to form insoluble precipitates, $\underset{From\ hard\ water}{M^{+2}} + \underset{Sodium\ stearate(soap)}{2C_{17}H_{35}COONa} \rightarrow \underset{Metal\ stearate(PPt.)}{(C_{17}H_{35}COO)_2M} + 2Na^+$, Where

$M = Ca\ or\ Mg$

Therefore, no lather is produced until all the calcium and magnesium ions are precipitated. This also results into wastage of lot of soap.

Type of hardness of water : The hardness of water is of two types :

Temporary hardness : This is due to the presence of bicarbonates of calcium and magnesium. It is also called carbonate hardness.

Permanent Hardness : This is due to the presence of chlorides and sulphates of calcium and magnesium. It is also called non-carbonate hardness.

Softening of water : The process of the removal of hardness from water is called softening of water.

(1) *Removal of temporary hardness* **:** It can be removed by the following methods:

(i) *By boiling* **:** During boiling, the bicarbonates of *Ca* and *Mg* decompose into insoluble carbonates and give CO_2. The insoluble carbonates can be removed by filtration.

$$\underset{Cal.bicarbonate}{Ca(HCO_3)_2} \xrightarrow{Heat} \underset{PPt.}{CaCO_3} + CO_2 + H_2O\ ;\ \underset{Mag.bicarbonate}{Mg(HCO_3)_2} \xrightarrow{Heat} \underset{PPt.}{MgCO_3} + CO_2 + H_2O$$

(ii) *Clark's method* **:** This process is used on a commercial scale. In this process, calculated amount of lime $[Ca(OH)_2]$ is added to temporary hard water.

$$\underset{\text{Soluble}}{Ca(HCO_3)_2} + \underset{\text{Lime}}{Ca(OH)_2} \longrightarrow \underset{\text{Insoluble}}{2CaCO_3} \downarrow + 2H_2O$$

$$\underset{\text{Soluble}}{Mg(HCO_3)_2} + \underset{\text{Lime}}{Ca(OH_2)} \longrightarrow \underset{\text{(Insoluble)}}{MgCO_3 \downarrow + CaCO_3} \downarrow + 2H_2O$$

(2) *Removal of permanent hardness :* Permanent hardness can be removed by the following methods :

(i) *By washing soda method :* In this method, water is treated with a calculated amount of washing soda (Na_2CO_3) which converts the chlorides and sulphates of *Ca* and *Mg* into their respective carbonates which get precipitated.

$$CaCl_2 + Na_2CO_3 \longrightarrow \underset{ppt.}{CaCO_3} + 2NaCl\ ;\ \ MgSO_4 + Na_2CO_3 \longrightarrow \underset{ppt.}{MgCO_3} + Na_2SO_4$$

(ii) *Permutit method :* This is a modern method employed for the softening of hard water. hydrated sodium aluminium silicate $(Na_2Al_2Si_2O_8.xH_2O)$ is called permutit. These complex salts are also known as zeolites.

The permutit as loosely packed in a big tank over a layer of coarse sand. Hard water is introduced into the tank from the top. Water reaches the bottom of the tank and then slowly rises through the permutit layer in the tank. The cations present in hard water are exchanged for sodium ions. Therefore this method is also called ion exchange method.

$$\underset{\text{Sodium zeolite}}{Na_2Z} + \underset{\text{(From hard water)}}{Ca^{+2}} \longrightarrow \underset{\text{Cal zeolite}}{CaZ} + 2Na^+\ ;\ Na_2Z + \underset{\text{(From hard water)}}{Mg^{+2}} \longrightarrow \underset{\text{Magnesium zeolite}}{MgZ} + 2Na^+$$, where $Z = Al_2Si_2O_8.\ xH_2O$

Hydrogen peroxide

Hydrogen peroxide (H_2O_2) was discovered by French chemist Thenard.

Preparation : it is prepared by

(1) **Laboratory method** : In laboratory, H_2O_2 is prepared by Merck's process. It is prepared by adding calculated amounts of sodium peroxide to ice cold dilute (20%) solution of H_2SO_4.

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

(2) **Industrial method** : On a commercial scale, H_2O_2 can be prepared by the electrolysis of 50% H_2SO_4 solution. In a cell, peroxy disulphuric acid is formed at the anode.

$$2H_2SO_4 \xrightarrow{\text{Elecrolysis}} \underset{\text{Peroxy disulphuric acid}}{H_2S_2O_8(aq.)} + H_2(g)$$

This is drawn off from the cell and hydrolysed with water to give H_2O_2

$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$ The resulting solution is distilled under reduced pressure when H_2O_2 gets distilled while H_2SO_4 with high boiling point, remains undistilled.

Physical properties : Pure H_2O_2 is a thick syrupy liquid with pale blue colour. It is more viscous and dense than water. It is completely miscible with water, alcohol and ether in all proportions.

Chemical properties :

(1) **Decomposition :** Pure H_2O_2 is an unstable liquid and decomposes into water and O_2 either upon standing or upon heating, $2H_2O_2 \longrightarrow 2H_2O + O_2;\ \Delta H = -196.0\,kJ$

(2) **Oxidising character :** It is a powerful oxidising agent. It acts as an oxidising agent in neutral, acidic or in alkaline medium. *e.g.* $2KI + H_2O_2 \longrightarrow 2KOH + I_2$ [In neutral medium]

$2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$ [In acidic medium]

$MnSO_4 + H_2O_2 + 2NaOH \longrightarrow MnO_2 + Na_2SO_4 + 2H_2O$ [In alkaline medium]

(3) **Reducing nature :** H_2O_2 has tendency to take up oxygen from strong oxidising agents and thus, acts as a reducing agent, $H_2O_2 + \underset{\text{From oxidising agent}}{O} \longrightarrow H_2O + O_2$

It can act as a reducing agent in acidic, basic or even neutral medium.

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

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

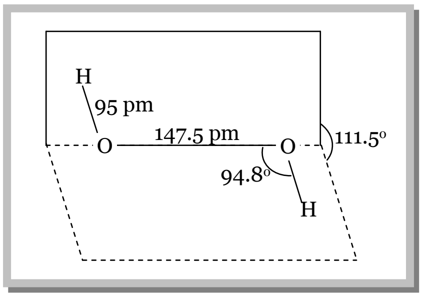
(4) **Bleaching action :** H_2O_2 acts as a bleaching agent due to the release of nascent oxygen.

$$H_2O_2 \longrightarrow H_2O + O$$

Thus, the bleaching action of H_2O_2 is due to oxidation. It oxidises the colouring matter to a colourless product, Colouring matter +O $\rightarrow$ Colour less matter

H_2O_2 is used to bleach delicate materials like ivory, silk, wool, leather etc.

Structure of H_2O_2 : H_2O_2 has non-planar structure in which two H-atoms are arranged in two directions almost perpendicular to each other and to the axis joining the two oxygen atoms. The O – O linkage is called peroxide linkage.



Strength of H_2O_2 : The strength of H_2O_2 is expressed in terms of weight or volume :

(1) *As weight percentage* **:** The weight percentage of H_2O_2 gives the weight of H_2O_2 in 100 *g* of solution. For example, a 40% solution by *wt*. means 40 g of H_2O_2 are present in 100 *g* of solution.

(2) *As volume* **:** The strength of H_2O_2 is commonly expressed as volume. This refers to the volume of oxygen which a solution of H_2O_2 will give. For example, a "20 volume" of H_2O_2 means that 1 litre of this solution will give 20 litres of oxygen at NTP.

Uses of H_2O_2

(1) It is used as an antichlor in bleaching because it can reduce chlorine.

$$Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$$

(2) It is used for restoring the colour of lead paintings.

(3) It is used as an antiseptic for washing wounds, teeth and ears under the name perhydrol

Nitrogen

N_2 was discovered by **Daniel Rutherford**. It is the first member of group 15 in the periodic table

Occurrence : N_2, occurs both in the free state as well as in the combined state. N_2 occurs in atmosphere to the extent of 78% by volume in free state. N_2 is present in many compounds such as potassium nitrate (nitre). Sodium nitrate (Chile salt peter) and many ammonium compounds. N_2 is an important constituent of proteins in plants and animals in combined state.

Preparation : It is prepared by the following methods

(1) **Laboratory method** : In the laboratory N_2 is prepared by heating an aqueous solution containing an equivalent amounts of NH_4Cl and $NaNO_2$.

$$NH_4Cl(aq.) + NaNO_2(aq.) \xrightarrow{\text{Heat}} N_2(g) + 2H_2O(l) + NaCl$$

(2) **Commercial preparation :** Commercially N_2 is prepared by the fractional distillation of liquid air.

Physical properties : N_2 is a colourless, odourless and tasteless gas. It is a non-toxic gas. It's vapour denstiy is 14. It has very low solubility in water.

Chemical properties

(1) N_2 is neutral towards litmus. It is chemically unreactive at ordinary temp. It is neither combustible nor it supports combustion.

(2) The N – N bond in N_2 molecule is a triple bond $(N \equiv N)$ with a bond distance of 109.8 *pm* and bond dissociation energy of 946 $kJ\ mol^{-1}$

(3) **Combination with compounds :** N_2 combines with certain compounds on strong heating . eg

$$\underset{\text{Calsium carbide}}{CaC_2} + N_2 \xrightarrow{1300\,K} \underset{\text{Calsium cyanamide}}{CaCN_2} + C \;;\; \underset{\text{Aluminium oxide}}{Al_2O_3} + N_2 + 3C \xrightarrow{2100\,K} \underset{\text{Al.nitride}}{2AlN} + 3CO$$

Both these compounds are hydrolysed on boiling with water to give ammonia.

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3 ;\; AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

Therefore, calcium cyanamide is used as a fetilizer under the name nitrolim $(CaCN_2 + C)$

Uses of nitrogen : N_2 is mainly used in the manufacture of compounds like $NH_3, HNO_3, CaCN_2$ etc.

Compounds of nitrogen

(1) **Ammonia :** Ammonia is the most important compound of nitrogen. It can be manufactured by Haber's process. In this process, a mixture of N_2 and H_2 in the ratio of 1 : 3 is passed over heated *Fe* at 650 – 800*K* as catalyst and *Mo* as promotor,

$N_2 + 3H_2 \rightleftharpoons 2NH_3,\ \Delta H = -93.6\,kJ\ mol^{-1}$ This is a reversible exothermic reaction.

Ammonia is prepared in the laboratory by heating ammonium salt (NH_4Cl) with a strong alkali like $NaOH$

$NH_4Cl + NaOH \longrightarrow NH_3 + H_2O + NaCl$ Ammonia can be dried by passing over quick lime (CaO). How ever, it can not be dried with dehydrating agents such as conc. H_2SO_4, P_2O_5 and anhydrous $CaCl_2$ because ammonia reacts with these compounds.

NH_3 is a colourless gas with a characteristic pungent smell called ammonical smell. It is highly soluble in water and its solution is basic in nature, $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

NH_3 is expected to have a tetrahedral geometry, but the lone pair distorts its geometry and the molecule has pyramidal geometry with N – H bond length of 101.7 *pm* and a bond angle of 107.5°.

Liquid ammonia is widely used as a refrigerant due to its high heat of vaporization.

(2) **Oxides of nitrogen :** Nitrogen combines with O_2 under different conditions to form a number of binary oxides which differ with respect to the oxidation state of the nitrogen atom. The important oxides are $N_2O, NO, N_2O_3, NO_2, N_2O_4$ and N_2O_5.

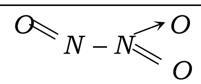
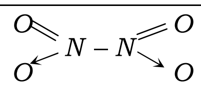
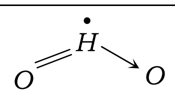
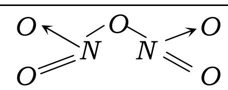
$$NH_4NO_3 \xrightarrow{\text{Heat}} \underset{\substack{\text{Nitrous oxide} \\ \text{(laughing gas)}}}{N_2O} + 2H_2O \; ; \; 4NH_3 + 5O_2 \xrightarrow[pt]{1100\,K} 4NO + 6H_2O$$

$$NO + NO_2 \underset{}{\overset{-20^{o}C}{\rightleftharpoons}} N_2O_3 \; ; \; 2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

NO_2 exists in equilibrium with N_2O_4 as,

$$\underset{\text{Colourless}}{N_2O_4} \rightleftharpoons \underset{\text{Brown}}{2NO_2} \; ; \; 4HNO_3 + P_4O_{10} \longrightarrow 2N_2O_5 + 4HPO_3$$

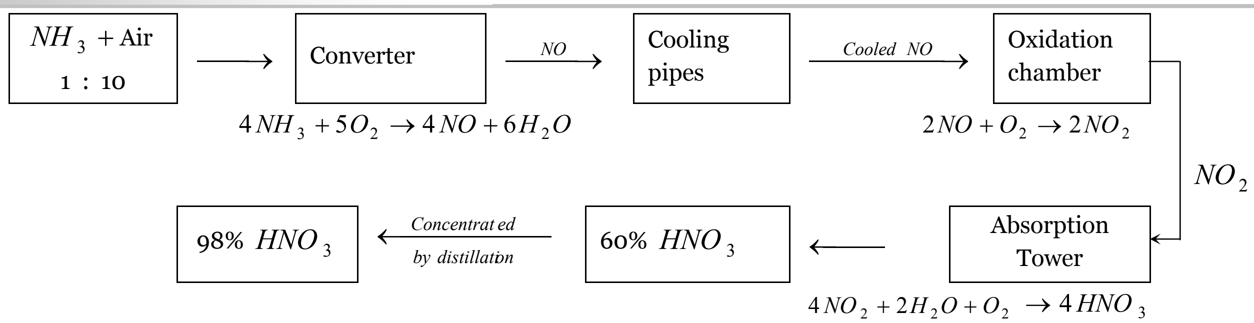
Oxides of Nitrogen

Oxide	**Oxidation State of N**	**Physical appearance**	**Structure**
Nitrous oxide (N_2O)	+1	Colourless gas	$N \equiv N \rightarrow O$
Nitric oxide (NO)	+2	Colourless	$N = O$
Dinitrogen trioxide (N_2O_3)	+3	Blue solid	
Dinitrogen tetraoxide (N_2O_4)	+4	Colourless liquid	
Nitrogen dioxide (NO_2)	+4	Brown gas	
Dinitrogen pentoxide (N_2O_5)	+5	Colourless gas	

(3) **Nitric acid** (HNO_3) **:** Nitric acid is one of the important mineral acid to act as an oxidising agent. Nitrogen shows an oxidation state of +5 in nitric acid.

Laboratory preparation : It is prepared in laboratory by heating of KNO_3 or $NaNO_3$ with conc. H_2SO_4. Vapours of HNO_3 get collected in a receiver. On cooling receiver with cold water vapours of HNO_3 condense into liquid form, $NaNO_3 + H_2SO_4 \longrightarrow HNO_3 + NaHSO_4$.

Ostwald process : HNO_3 is commonly manufactured by Ostwald process in which it is prepared from NH_3.



Flow sheet diagram for manufacture of HNO_3 by Ostwald's process

Physical properties : Pure HNO_3 is a colourless liquid. It boils at 86°C and freezes to a white solid at – 42°C . The impure acid is generally yellow due to the presence of nitrogen dioxide as impurity. HNO_3 containing dissolved nitrogen di oxide is known as fuming nitric acid.

Chemical properties

(1) HNO_3 acts as a strong oxidising agent both in the concentrated as well as in the dilute form.

(2) Metals which are more electropositive than hydrogen react with HNO_3 to first liberate nascent hydrogen which then reduces HNO_3 to NO_2, NO, NH_3, NH_4NO_3 and N_2O depending upon the nature of metal, concentration of the acid used and the temperature *eg* :

(i) *Mg* and *Mn* react with very dil. HNO_3 (1– 2%) to liberate H_2 gas, $\underset{\text{(metal)}}{M} + 2HNO_3 \longrightarrow M(NO_3)_2 + H_2 \uparrow$.

(ii) Cold dil. HNO_3 reacts with metals like *Mg*, *Zn*, *Sn*, *Fe* etc, producing NH_4NO_3. Lead gives *NO* under these conditions *eg*. $4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$.

(iii) With hot dil HNO_3, Zn gives N_2O. $4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$.

(iv) With conc. HNO_3, metals like *Zn*, *Mg*, *Bi*, *Pb*, etc give NO_2 and the corresponding metal nitrate.

$$Zn + 4HNO_3 \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O.$$

(v) With, conc. HNO_3, Sn gives metastannic acid. i.e. $SnO_2.H_2O$ or H_2SnO_3.

(vi) HNO_3 attacks proteins giving a yellow nitro compound called xantho protein. Therefore, HNO_3 cause stains on skin and renders wool yellow.

(vii) The gas NO reacts with iron (II) salts to form complex cation $[Fe(NO)(H_2O)_5]^{+2}$ which is dark brown liquid. It is responsible brown ring test for nitrates.

(viii) Metals such as *Cu*, *Ag*, *Hg*, etc. which are less reactive than hydrogen react with conc. HNO_3 forming NO_2 and the corresponding metal nitrate. With dil. HNO_3 metal nitrate and NO are formed.

(ix) Noble metals like gold and platinum do not react with conc. HNO_3 However, These metals dissolve in aqua regia (1 part conc. HNO_3 +3 part conc. *HCl*) forming their respective chlorides. The high reactivity of aqua regia is due to the nascent chlorine which is formed by the action of conc. HNO_3 and conc. *HCl*

$HNO_3 + 3HCl \longrightarrow NOCl + 2H_2O + 2[Cl]$

(x) **Passivity** Metals like Fe, Cr, Ni and Al become passive, i.e. lose their normal activity when dipped in conc. HNO_3. This passivity is due to the formation of a thin protective layer of the metal oxide (i.e. $Fe_3O_4, Cr_2O_3, NiO, Al_2O_3$ on the surface of the metal).

(xi) Conc. HNO_3 oxidises cane sugar to oxalic acid.

(xii) Nitration of toluene with fuming HNO_3 gives the well-known explosive, TNT.

(xiii) Glycerol on nitration with a mixture of conc. HNO_3 + conc. H_2SO_4 gives trinitroglycerine.

(xiv) Dynamite which is widely used for shooting oil wells, building roads, dams and tunnels in rocks is a mixture of glyceryl trinitrate and glyceryl dinitrate absorbed over kieslguhr.

(xv) All nitrates are soluble in water.

(xvi) Nitrate ion (NO_3^-) is a planar species since the N-atom in is sp^2 - hybridized.

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