CHEMISTRY OF NON-METALS

Hydrogen: It is the smallest and the lightest element having atomic number one. Its electronic configuration is 1s¹. It behaves like both alkali and halogen atoms because it has tendency to lose and gain one electron.

Resemblance with Alkali Metals

- Electronic configuration: Like alkali metals, hydrogen has 1 electron in its outermost shell.
- (ii) Both show tendency to lose valence electron.
- (iii) Both possess strong affinity for electronegative elements like oxygen, sulphur, halogens etc.
- (iv) Both exhibit oxidation state of +1 and are strong reducing agents.

(v) On electrolysis, both hydrogen and alkali metals are liberated at cathode.

$$HCl \rightarrow H^+ + Cl^-$$

 $2H^+ + 2e^- \rightarrow H_2$ [at cathode]
 $NaCl \rightarrow Na^+ + Cl^-$
 $Na^+ + e^- \rightarrow Na$ [at cathode]

Resemblance with Halogens

(i) Electronic configuration: Both halogens and hydrogen lack one electron to attain configuration of nearest inert gas.

$$H \to 1s^1 \ F \to 1s^2 2s^2 2p^5$$
. etc.

- (ii) **Ionization energy**: Ionization energy of hydrogen is high like that of halogens.
- (iii) Atomic state: Both form diatomic molecules, like H₂, Cl₂, F₂, Br₂,
- (iv) Oxidation state: it shows -1 oxidation state like halogens.
 - (v) Electrolysis: In hydrolysis of NaCl, chlorine is liberated at anode while in NaH, hydrogen is liberated at anode.

$$2\text{NaCl} \rightarrow 2\text{Na} + \text{Cl}_2$$
 (at anode)

$$2NaH \rightarrow 2Na + H_2$$
 (at anode)

(vi) Electronegative character: Like halogens, hydrogen takes one electron and forms hydride ion.

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

 $Cl + e^- \rightarrow Cl^-$

(vii) Substitution reactions: Under suitable conditions, hydrogen is replaced by halogens and halogens are replaced by hydrogen.

$$CH_4 + Cl_2 \xrightarrow{Diffused} CH_3Cl + HCl$$

$$CH_3Cl + 2 [H] \xrightarrow{Sn/HCl \text{ or}} CH_4 + HCl$$

Difference of hydrogen from halogens and alkali metals

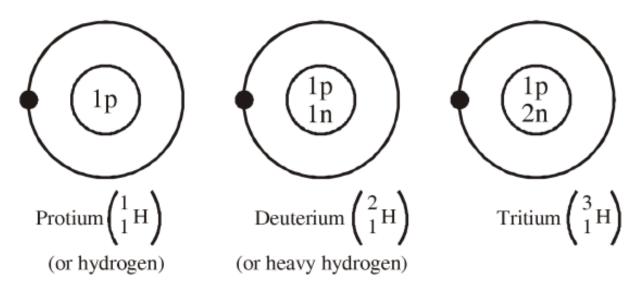
- Hydrogen is less electropositive than alkali metals but less electronegative than halogens.
- (ii) Hydrogen has less tendency to form ions as compared to alkali metals and halogens.
- (iii) Size of H ions is much smaller than those of alkali metals ions and halogen ions.
- (iv) alkali metal halides have high melting point while pure hydrogen halides have low boiling points.

(v) Hydrogen molecule does not have unshared pair of electrons, while halogen molecules have unshared pair of electrons.

- (vi) Oxides of alkali metals are basic, oxides of halogens are acidic while oxide of hydrogen (i.e. water) is neutral.
- (vii) Unlike alkali metals and halogens, hydrogen has one electron in extra nuclear part and one proton in nucleus.

Isotopes of Hydrogen

Hydrogen occurs in three isotopic forms: Protium (H), Deuterium (D) and Tritium (T):



Their chemical properties are the same as their electronic configuration is the same. But physical

properties are different due to different atomic masses.

Oxygen: It has atomic numbr 8, electronic configuration is $1s^2 2s^2 2p^4$. It exists as diatomic molecule. It is paramagnetic in nature because the presence of two unpaired electrons.

Occurrence: Most abundant and occurs both in free as well as in combined form. In free state it is present 21% by volume or 23% by weight in atmosphere. While in combined state it is present in water upto 89%. In earth crust it is present mainly in the form of silicates, aluminates, carbonates and oxides of metals. The balance of oxygen in nature is maintained as it is formed during photosynthesis in plants:

$$xH_2O + xCO_2 \xrightarrow{\text{Sunlight}} (CH_2O)_x + xO_2(g)$$
Water Carbon dioxide Carbohydrate Oxygen

Oxygen occurs in two molecular allotropic forms: dioxygen (O_2) is most stable while ozone (O_3) is less stable. Its three naturally occuring isotopes are ${}^{16}_{8}\mathrm{O}(99.76\%)$, ${}^{17}_{8}\mathrm{O}(0.037\%)$ and ${}^{18}_{8}\mathrm{O}(0.204\%)$.

Uses

- (i) In the manufacture of nitric acid, sulphuric acid, acetic acid etc.
- (ii) As an oxidising and bleaching agent.
- (iii) Used for artificial respiration.
- (iv) Mixture of liquid oxygen and finely divided charcoal is used as an explosive.
 - (v) As rocket fuel in liquid form.
- (vi) In oxy-acetylene flames.
- (vii) In manufacturing steel and in metal fabrication.

Ozone: It is one of the allotropic forms of oxygen. Ozone (O_3) is formed in the upper layer of atomosphere about 20 km above the earth's surface. It does not allow ultraviolet rays to reach the earth. Chlorofluoro carbons deplete ozone layer.

It is prepared by silent electric discharge through cold and dry oxygen in an apparatus called *ozoniser*.

$$3O_2(g) \stackrel{\text{Silent electric}}{=\!=\!=\!=} 2O_3(g)$$
 $\Delta H = +284 \text{ kJ},$

Commonly used ozonizers are (i) Siemen's ozoniser (ii) Brodie's ozoniser

Physical Properties

- (i) Pure ozone is pale bluish gas with strong pungent odour.
- (ii) It is slightly soluble in water, readily soluble in oils like turpentine oil, cinnamon oil.
- (iii) It is heavier than air.
- (iv) It is highly reactive because of low dissociation energy.
 - (v) It is netural towards litmus.
- (vi) It is poisonous in nature.
- (vii) It is a diamagnetic molecule.

Nitrogen: It exists both in combined and free state. In earth's atmosphere it is found upto about 78% by volume. It is present in the form of nitrates like nitre (NaNO₃), salt petre (KNO₃) and ammonium salts like ammonium chloride (NH₄Cl) and ammonium sulphate [(NH₄)₂ SO₄]. It is main constituent of animal and plant protein.

Preparation of Nitrogen

(i) From Nitrogen compounds:

(a) By heating ammonium nitrite or ammonium dichromate (laboratory preparation) : Sodium nitrite and ammonium chloride are heated:

$$\begin{aligned} \operatorname{NaNO}_2(\operatorname{aq}) + \operatorname{NH}_4\operatorname{Cl}(\operatorname{aq}) &\stackrel{\Delta}{\longrightarrow} \operatorname{NH}_4\operatorname{NO}_2(\operatorname{aq}) + \operatorname{NaCl}(\operatorname{aq}) \\ \operatorname{NH}_4\operatorname{NO}_2(\operatorname{aq}) &\stackrel{\Delta}{\longrightarrow} \operatorname{N}_2(g) + 2\operatorname{H}_2\operatorname{O}(l) \\ & \left(\operatorname{NH}_4\right)_2\operatorname{Cr}_2\operatorname{O}_7 &\stackrel{\Delta}{\longrightarrow} \operatorname{N}_2 + \operatorname{Cr}_2\operatorname{O}_3 + 4\operatorname{H}_2\operatorname{O} \\ \operatorname{Ammonium dichromate} \end{aligned}$$

(b) From ammonia: By passing ammonia vapours over heated copper oxide (CuO), pure dinitrogen can be obtained.

$$2NH_3 + 3CuO \rightarrow N_2 + 3Cu + 3H_2O$$

(c) From sodium azide:

$$2\text{NaN}_3 \xrightarrow{300^{\circ}\text{C}} 3\text{N}_2 + 2\text{Na}$$
Sodium azide

- (d) By the action of nitrous acid on urea : $NH_2CONH_2 + 2HNO_2 \rightarrow 2N_2 + CO_2 + 3H_2O$
 - (e) By passing vapours of ${\rm HNO_3}$ on strongly heated copper:

$$5\text{Cu} + 2\text{HNO}_3 \rightarrow 5\text{CuO} + \text{N}_2 + \text{H}_2\text{O}$$

(ii) From air (from liquified air): Liquified air is subjected to fractional distillation. Nitrogen has lower boiling point than oxygen, distills off first. This process is carried out in Claude's apparatus.

Physical properties

- (i) It is colourless, tasteless and odourless gas.
- (ii) It is neither combustable nor supports combustion.
- (iii) It is slightly lighter than air, sparingly soluble in water.
- (iv) It is non-poisonous in nature but animal do not survive in its atmosphere due to absence of oxygen.

Uses

- (i) In manufacture of ammonia, nitric acid, nitrides, calcium cyanamide and fertilizers etc.
- (ii) In filling electric bulbs and gas thermometers due to its low chemical reactivity.
- (iii) It provids inert atmosphere in metallurgical operations.
- (iv) Regulates the combustion of oxygen in air.
 - (v) Liquid dinitrogen is used as a refrigerant.

Silicon

It has atomic number 14 and it is the second member of group-14.

It possess certain similarities with carbon, such as

- (a) Both show covalency of four.
- (b) Both form hydrides (SiH₄ and CH₄) and halides (SiX₄ and CX₄) of tetrahedral shape.

Silicon also behaves in different manner from carbon due to low electronegativity, availability of d-orbitals and less tendency to form multiple bonds. So, silicon shows following dissimilarities with carbon.

- (a) Silicon also shows covalency of six unlike carbon which shows covalency of four only.
- (b) Silicon tetrahalide undergoes hydrolysis while carbon tetrahalide is stable.
- (c) Carbon dioxide is a gas while silicon dioxide is a solid.

Silicon is the second most abundant element in the earth's crust. It occurs in combined state as silica (SiO₂) in form of sand, flint and quartz and as silicates in the form of mica, felspar (K₂O.Al₂O₃.6SiO₂) and kaolinite (Al₂O₃.2SiO₂.2H₂O).

Phosphorus: It has atomic number 15 and it is the second member of group-15 after nitrogen. It differs from nitrogen in certain respect due to its large size, low electronegativity and availability of d-orbitals such as nitrogen in sp

and sp² hybridized state forms stable compounds but compounds of phosphorus in these hybridized states are unstable.

It occurs as phosphates in rocks, in vegetables, in animal bones, blood, teeth and nervous tissues, in egg yolk etc. The important ores of phosphorus are phosphorite $[Ca_3(PO_4)_2]$, fluoropatite $[3Ca_3(PO_4)_2]$, CaF_2 , hydroxyapatite $[3Ca_3(PO_4)_2]$, $Ca(OH)_2$, chloropatite $[3Ca_3(PO_4)_2]$. Ca Cl_2 and bone-ash $[Ca_3(PO_4)_2]$. Ores of phosphorus are collectively known as phosphate rock.

Phosphorus occurs in three alllotropic forms, white, red and black phosphorus.

White Phosphorus

- White phosphorus is a white, transparent, soft waxy crystalline solid.
- II. It is insoluble in water and alcohol but soluble in carbon disulphide (CS₂) and benzene.
- III. It has garlic like odour and is toxic in nature.
- IV. It ignites spontaneously in moist air and gives out light (Chemiluminescence). Therefore it is stored under water.

Red Phosphorus

I. It is prepared by heating white phosphorus to about 250° C

White
$$P \xrightarrow{240^{\circ}C} Red P$$

- II. It is odourless and less toxic.
- III. It is dark red powder.
- IV. It is stable in air and insoluble in organic solvents.

Black Phosphorus

It is prepared by heating white phosphorus under high pressure. It is thermodynamically most stable allotrope.

Fertilizers: These are the chemical substances which are added to the soil to make up for the deficiency of essential elements in plants.

- I. Nitrogeneous fertilizers: These are the fertilizers which mainly supply nitrogen to the plants. Such as urea (NH₂CONH₂), ammonium sulphate [(NH₄)₂SO₄], calcium ammonium nitrate (CAN) [Ca(NO₃)₂. NH₄NO₃].
- II. Phosphatic fertilizers: These are the fertilizers which mainly supply phosphorus

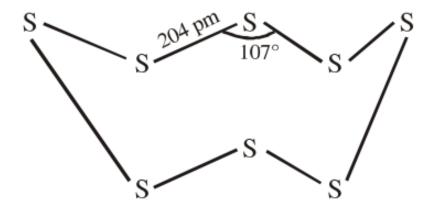
to the plants. Such as triple phosphtate of lime $[Ca(H_2PO_4)_2]$, superphosphate of lime, Thomas slag (double salt of tricalcium phosphate and calcium silicate).

Sulphur: It has atomic number 16 and it is the second member of group-16 after oxygen. Unlike oxygen, sulphur exists in oxidation state of -2, +2, +4 and +6 due to availability of empty d-orbitals.

Sulphur comprises of 0.05% of earth's crust. It occurs in free and combined state both. In free state it occurs in volcanic areas, in limestone cares etc. In combined form as sulphide ores like zinc blende (ZnS), cinnabar (HgS), galena (PbS), copper pyrites (CuFeS₂) and iron pyrites (FeS₂) and as sulphate ores like gypsum (CaSO₄ . 2H₂O), barytes (BaSO₄), epsom salt (MgSO₄ . 7H₂O) and celesite (SrSO₄).

Sulphur exists in following allotropic forms:

I. Rhombic sulphur (α): It is pale yellow crystalline solid (M.P. 114°C) and most stable of all allotropes of sulphur. It consists of S₈ structural unit packed together into octahedral shape. It is soluble in carbon disulphide and prepared by evaporating sulphur solution in CS₂.



Structure of S₈ molecule

II. Monoclinic (β): It is bright yellow crystalline solid (M.P. 119°C). It also exists as S₈ molecules but differs from rhombic sulphur in arrangement. It is soluble in carbon disulphide (CS₂) and is prepared by melting and cooling sulphur. It changes into rhombic form above transition temperature (95.6°C).

Rhombic sulphur $\stackrel{95.6^{\circ}\text{C}}{=}$ Monoclinic sulphur

III. Plastic sulphur (γ): It is soft rubbe like yellowish brown mass (M.P.: not sharp). It has random molecular structure which consists of long chains of sulphur atoms as well as some S₈ rings. It is insoluble in CS₂. It is prepared by pouring boiling sulphur into cold water.

- IV. Colloidal sulphur (δ): It can be prepared by passing H₂S through a solution of an oxidising agent in water.
 - V. Milk of sulphur: It can be formed by boiling milk of lime with sulphur and decomposing the product with HCl. It is soluble in CS₂.

Halogens: Fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At) are collectively known as halogens. These are all non-metals.

Halogens are very reactive due to high electronegativity and therefore do not exist in free state.

Fluorine: It mainly occurs in fluorspar (CaF_2) , cryolite $(AlF_3.3NaF)$, fluoropatite $[CaF_2.3Ca_3(PO_4)_2]$. In traces it occurs in sea water, bones, teeth, milk and plants.

Chlorine: Its important sources are sodium chloride (NaCl), potassium chloride (KCl), carnallite (KCl, MgCl₂.6H₂O).

Bromine: It is found in sea water as sodium bromide (NaBr), potassium bromide (KBr) and magnesium bromide (MgBr₂).

Iodine: Its main sources are sea weeds which contain iodine as alkali metal iodide, caliche contains iodine as sodium iodate (NaIO₃), cod liver oil and thyroid glands of animals.

Physical Properties

Fluorine: It is a pale greenish yellow, pungent smelling poisonous gas. It condenses to a pale yellow liquid (B.P. –188°C) and crystallizes to a pale yellow solid (M.P. –233°C). It is heavier than air.

Chlorine: It is a greenish yellow, pungent smelling gas. It dissolves in water and is used as a germicide for water purification.

Bromine: It is reddish brown mobile liquid. It boils at 58.8°C and freezes to a yellowish brown crystalline soild at -7.3°C.

Iodine: It is violet-coloured crystalline solid having metallic lustre.

Noble gases: Group-18 constitues helium (He), neon (Ne), argon (Ar,), krypton (Kr), xenon (Xe) and radon (Rn). These are known as noble gases or inert gases because they have their outermost shell complete and hence do not react normally.

All noble gases occcur in atmosphere except radon which is radioactive. The noble gases occupy 1% by volume of the atmosphere. Helium is second most abundant element in the universe (about 23%) after hydrogen and also occurs in natural gas, in the water of certain springs and in radioactive minerals.

Helium: It is obtained from natural gas. Natural gas is compressed and cooled when nitrogen, hydrocarbons get liquefied. Helium is not liquefied, thus is purified.

Argon, neon, krypton and xenon: Fractional distillation followed by condensation of liquefied air yields neon, argon, krypton and xenon as byproducts.

Radon: Radon is a decay product of radium.

$$^{226}_{88}$$
 Ra \rightarrow $^{222}_{86}$ Rn + $^{4}_{2}$ He Radium Radon Helium

The most important compunds of noble gases are fluorides of xenon. They are prepared as follows:

Uses

Helium:

- I. Used in filling metereological balloons and inflating aeroplane tyres.
- II. Helium-oxygen mixture is used by divers for artificial respiration and also used in treatment of asthma.
- III. To create inert atmosphere and in vacuum tubes, radiotubes, signal lamps etc.
- IV. Liquid helium is used to produce extremely low temperature.

Neon: Neon and its combination with other gases is used in discharge tubes called as "Neon signs."

Argon:

- Used in filling incandescent and fluorescent lamps.
- II. For creating inert atmosphere in welding and metallurgical purposes.

Krypton and xenon:

- I. Mixture of krypton and xenon is used in electrical flash bulbs for high speed photography.
- II. Krypton and xenon are better choice than argon for filling tubes and valves.

Radon: In treacment of cancer and malignats growth.

Some Important Facts

- Hydrate: Many substances combine with water to form crystalline compounds called as hydrates.
- Polar nature of water molecules is because of charge separation between oxygen and hydrogen atoms.
- A hydrate crystal contains a definite amount of water, called as water of crystallisation.
- Efflorescence: The phenomenon of crystal becoming anhydrous by losing water of crystallisation is known as efflorescence. e.g. Na₂CO₃. 10H₂O; CuSO₄. 5H₂O.
- 5. **Deliquescence:** The process in which salt absorbs moisture from the air and then becomes solution, is known as deliquescence.
- Dehydration: Removal of water form crystals or compounds by heating, is known as dehydration.
- Heavy water is used as neutron moderator, for production of deuterium, as tracer compound.
- Calcium hydroxide causes permanent hardness.

- Soaps are sodium or potassium salts of monovalent long chain fatty acids.
- Mixture of 3 parts of conc. HCl and 1 part of conc. HNO₃ is called aqua regia.
- 11. Fuming nitric acid contains dissolved NO_2 in conc. HNO_3 . It is brown in colour.
- 12. Nitrous oxide is known as laughing gas.
- 13. During generation of steam in boiler, if hard water is used, calcium bicarbonate decomposes into insoluble calcium carbonate, that sticks to inner surface of boiler known as boiler scale. Which causes heat wastage, clogs the tubes of steam and sudden crack in scale cuses boiler to burst.
- H₂O₂ is a weak acid and forms two series of salts: hydroperoxides and normal peroxides.

$$H_2O_2 + H_2O \rightarrow H_3O^+ + HO_2^-$$
Hydroperoxide ion
$$HO_2^- + H_2O \rightarrow H_3O^+ + O_2^{2-}$$
Peroxide ion

 H₂O₂ acts as a bleaching agent as it releases nascent oxygen that causes oxidation of colouring matter.

- 16. H_2O_2 should be stored in coloured, wax-lined bottles in presence of stabilizer like H_3PO_4 etc.
- 17. Boron compounds are electron deficient compounds and therfore act as Lewis acids.
- Boron forms covalent bonds because of its small atomic size and high ionization energy.
- 19. Boric acid behaves as a strong monobasic acid in presence of polyhydroxy compounds.
- 20. Concentrated solution of sodium silicate in water is known as water glass.
- 21. Quartz is the most stable form of silica.
- 22. White phosphorus is always kept under water.
- Fluorine cannot be obtained as a product in any chemical reaction
- Dry chlorine cannot act as bleaching agent.
 For that moisture is required.
- There are 8 sulphur atoms in a sulphur molecule.