Chapter_07

p-Block Elements

Group 15 Elements (The Nitrogen Family)

1. **Molecular nitrogen** comprises about 78% by volume of Earth's atmosphere. It exhibits anomalous properties due to its smaller size, has high ionisation enthalpy, high electronegativity and absence of *d*-orbitals.
2. The valence shell electronic configuration of group 15 elements is ns^2np^3.
3. **Physical properties** All the elements are polyatomic. Dinitrogen is a diatomic gas while all others are solids. The boiling point increase from top to bottom but the melting point increases upto arsenic and then decreases upto bismuth.
4. **Oxidation states** The common oxidation states of these elements are $-3, +3$ and $+5$. The tendency to exhibit -3 oxidation state decreases down the group due to increase in size and metallic character.
5. Nitrogen differs from the rest of the members due to its small size, high electronegativity, high ionisation enthalpy and non-availability of *d*-orbitals. It has a unique ability to form $p\pi$-$p\pi$ multiple bonds with itself and with other atoms like C and O. That's why it exists as N_2 molecule with a triple bond and has high bond enthalpy.
6. Heavier members of nitrogen family form $p\pi$-$d\pi$ bond and show **catenation** due to their high sigma bond energy.
7. **Reducing character of hydrides of nitrogen family** increases down the group due to decrease in bond dissociation enthalpy.

   Basic character and **bond angle** in the hydrides of nitrogen family decreases down the group, i.e.

   $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$
8. **Dinitrogen** It is produced commercially by the liquifaction and fractional distillation of air. In the laboratory, N_2 is prepared by the following process:

   $$NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$$

   - It can also be obtained by thermal decomposition of $(NH_4)_2Cr_2O_7$ and $Ba(N_3)_2$.
   - It is colourless, tasteless, odourless and non-toxic gas.
   - Following chemical reactions are shown by nitrogen :

   $$6Li + N_2 \xrightarrow{\text{Heat}} 2Li_3N, \qquad 3Mg + N_2 \xrightarrow{\text{Heat}} Mg_3N_2$$
9. **Ammonia** is manufactured by **Haber's process**.

   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta_f H° = -46.1 kJ/mol$

   The optimum conditions for the production of ammonia are high pressure of 200×10^5 Pa (about 200 atm) and temperature $\approx$ 700 K and use of a catalyst such as iron oxide with small amount of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium. Earlier iron was used as a catalyst with molybdenum as a promoter.
10. **Nitric acid** is manufactured by **Ostwald's process** and involves the following steps :

    $$4NH_3(g) + 5O_2(g) \xrightarrow[500K,\ 9\ bar]{\text{Pt /Rh gauge}} 4NO(g) + 6H_2O(l)$$

    $$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

    $$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

    It is being a strong oxidising agent oxidises most of the metals (except gold and platinum) and non-metals. Its oxidises Cu to Cu^{2+}, iodine to iodic acid, C to CO_2, S to H_2SO_4 and P to phosphoric acid (H_3PO_4).

Group 16 Elements (The Oxygen Family)

11. The general electronic configuration of group 16 elements is ns^2np^4.
12. **Electron gain enthalpy of oxygen** is less negative than that of sulphur due to compact size of oxygen atom i.e. (inter-electronic repulsion is more in O). From sulphur onwards, enthalpy again becomes less negative upto Po.
13. **Properties of oxygen** are different from other elements of the group due to its small size, high electronegativity and absence of *d*-orbital.

    Due to the absence of *d*-orbital, oxygen shows covalency of 4 and in practice it rarely exceeds the covalency by two, while other members of the group can exceed their covalency beyond four. Oxygen atom can only form $p\pi$-$p\pi$ bond (if required) due to small size.

    H_2O undergoes extensive H-bonding due to high electronegativity of O-atom and hence, exists as liquid. On the other hand, H_2S does not undergo H-bonding and hence, exists as a discrete molecule and is a gas.
14. **Reducing property** and **acidic strength** increase from H_2O to H_2Te due to decrease in bond dissociation enthalpy. However, their thermal stability decreases from H_2O to H_2Te.
15. **Dioxygen** is a colourless and odourless gas. It is prepared by heating oxygen containing salts or by thermal decomposition of the oxides of metals. It directly reacts with nearly all metals and non-metals.

    Some reactions are as follows :

    $$2Ca + O_2 \longrightarrow 2CaO$$

    $$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

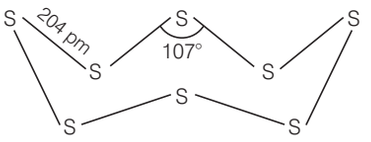
    $$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$
16. **Oxides** are binary compounds of oxygen with another element. These may be simple (e.g MgO, Al_2O_3) or mixed (Pb_3O_4, Fe_3O_4). These can be acidic oxide (SO_2, Cl_2O_7) basic oxide (Na_2O, CaO) or amphoteric oxide (Al_2O_3), etc.
17. **Ozone** is thermodynamically less stable than oxygen because its decomposition into oxygen results with the liberation of heat (ΔH is negative) and increase in entropy (ΔS is positive). These two effects result in a large negative Gibbs energy change (ΔG) for its conversion into oxygen.
    - Ozone oxidises iodide ions to iodine and lead sulphide to lead sulphate.

    $$2I^-(aq) + H_2O(l) + O_3(g) \longrightarrow 2OH^-(aq) + I_2(s) + O_2(g)$$

    $$PbS(s) + 4O_3(g) \longrightarrow PbSO_4(s) + 4O_2(g)$$

    - In quantitative method for estimating O_3 gas, ozone is treated with an excess of KI solution buffered with a borate buffer (pH = 9.2). Iodine is liberated which can be titrated against a standard solution of sodium thiosulphate.
18. **Sulphur** forms numerous allotropes of which yellow rhombic (α-sulphur) and monoclinic (β-sulphur) are the most important.

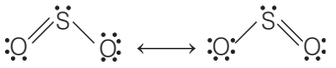
- The S_8 ring in both the monoclinic and rhombic form is puckered and has a crown shape.



- At elevated temperatures (~1000 K) sulphur exists as S_2 and is paramagnetic in nature.

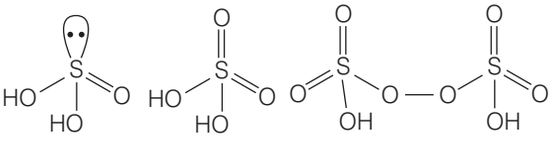
19. **Moist sulphur dioxide** behaves as a reducing agent. It converts Fe^{3+} ions to Fe^{2+} ions. It also decolourises acidified potassium permanganate solution (a confirmative test for SO_2 gas).

SO_2 molecule is angular and is a resonance hybrid of the following two structures :



The two S—O bonds are equal.

20. *The structure of some* ***oxoacids of sulphur*** *are as follows* :



Sulphurous acid H_2SO_3 | Sulphuric and H_2SO_4 | Peroxodisulphuric acid ($H_2S_2O_8$) (Marshall's acid)

Peroxomonosulphuric acid (H_2SO_5) and peroxodisulphuric acid or Marshall's acid ($H_2S_2O_8$) contain peroxide linkages in their structure.

21. **Sulphuric acid** (H_2SO_4), the king of chemicals or oil of vitriol, is manufactured by contact process, *reactions involved are as follows* :

$$S_8 + 8O_2 \longrightarrow 8SO_2$$

$$2SO_2(g) + O_2(g) \underset{}{\overset{V_2O_5}{\rightleftharpoons}} 2SO_3(g);$$

$$\Delta H° = -ve$$

$$SO_3 + H_2SO_4 \longrightarrow \underset{\text{Oleum}}{H_2S_2O_7} \xrightarrow[\text{Dilution}]{H_2O} 2H_2SO_4$$

The favourable conditions for the maximum yield of SO_3 are pressure of about 2 bar and optimum temperature of 720 K.

22. In SF_6, S is sterically protected by six F-atoms which do not allow H_2O molecules to attack at S-atoms. As a result of this, SF_6 does not undergo hydrolysis.

Group 17 Elements : (The Halogen Family)

23. All elements have seven electrons in their outermost shell (ns^2np^5). They have little tendency to lose electrons.

24. Halogens have maximum negative electron gain enthalpy in the corresponding periods. The electronegativity decreases down the group.

25. Ionisation enthalpy, electronegativity, and electrode potential are higher for fluorine than expected from other halogens, whereas ionic and covalent radii, melting and boiling points and electron gain enthalpy are quite low than expected.

This is due to the small size, highest electronegativity, low F—F bond dissociation enthalpy and non-availability of *d*-orbital.

26. **Fluorine** has smaller bond dissociation enthalpy than chlorine, while *X*—*X* bond dissociation enthalpies from Cl onwards show the expected trend Cl—Cl > Br—Br > F—F > I—I. Due to small size and large electron- electron repulsion among the lone pairs of fluorine, F—F bond length is more than Cl — Cl and Br — Br bond lengths.

- Fluorine reacts with water to produce oxygen or ozone.

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

$$3F_2 + 3H_2O \longrightarrow 6HF + O_3$$

27. **Chlorine** can be prepared by heating manganese dioxide with conc. HCl.

(i) $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

(ii) $4HCl + O_2 \xrightarrow[\text{(Deacon's process)}]{CuCl_2} 2Cl_2 + 2H_2O$

- Chlorine reacts with sodium hydroxide solution in the following manner :

(i) $\underset{\text{(Cold, dilute)}}{2NaOH} + Cl_2 \longrightarrow NaCl + \underset{\substack{\text{Sodium}\\\text{hypochlorite}}}{NaOCl} + H_2O$

(ii) $\underset{\text{(Hot, conc.)}}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + \underset{\substack{\text{Sodium}\\\text{chlorate}}}{NaClO_3} + 3H_2O$

- It has great affinity for hydrogen. It reacts with compounds containing hydrogen to form hydrogen chloride.

$$H_2 + Cl_2 \longrightarrow 2HCl$$

- On standing, chlorine water loses its yellow colour due to the formation of HCl and HOCl.

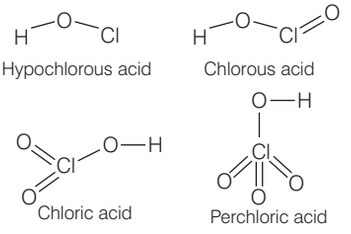
$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

$$HOCl \longrightarrow HCl + \underset{\substack{\text{Nascent}\\\text{oxygen}}}{[O]}$$

Nascent oxygen formed by HOCl is responsible for oxidising and bleaching properties of chlorine.

28. **Hydrogen chloride** is a colourless and pungent smelling gas. It is easily liquefied to a colourless liquid and freezes to a white crystalline solid. It can be prepared by heating sodium chloride with conc. H_2SO_4.

29. Various oxoacids of halogens are HOF, HOCl, HOBr, HOI etc. The structures of some important oxo acids are :



30. **Interhalogen compounds** Two different halogens may react to form interhalogen compounds of the type *XX*', XX'_3, XX_5', XX_7', where, *X* = higher molecular mass halogen, *X*' is lower molecular mass halogen. Their geometry is respectively

linear, T-shaped, square pyramidal and pentagonal bipyramidal.

In all interhalogen compounds, *X*—*X*′ bond is weaker than *X*—*X* bond (except F—F bond). So, these compounds are more reactive than individual halogens.

Group 18 Element : (The Noble Gases)

31. General electronic configuration of noble gases is ns^2np^6. Due to the completely filled shell, these gases exhibit very high ionisation enthalpies.

32. The first compound of Xe was $Xe^+PtF_6^-$ which was discovered by Neil Bartlett.

33. **Xenon fluorides** are readily hydrolysed even by traces of water.

$$2XeF_2(s) + 2H_2O(l) \longrightarrow 2Xe\ (g) + 4HF\ (aq) + O_2(g)$$

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

The geometry of XeF_2, XeF_4, XeF_6, $XeOF_4$ and XeO_3 are linear, square planar, distorted octahedral, square pyramidal and pyramidal, respectively.

34. **Helium** is used in gas-cooled nuclear reactors and as diluent for oxygen in modern diving apparatus because of its very low solubility in blood.