**p Block Elements**

General Configuration: $ns^2 np^{1-6}$
Maximum oxidation state = Group 10

Across a period: Covalent radii and metallic character decreases, but electro negativity, electron affinity, oxidizing power and ionization energy increases.

Down the group: Covalent radii and metallic character increases, but electro negativity, electron affinity, oxidizing power and ionization energy decreases.

Inert pair effect: While going down the group, the $ns^2$ electrons become more and more reluctant to participate in bond formation. This is because down the group bond energy decreases and so the energy required to un-pair $ns^2$ electrons is not compensated by the energy released in forming two additional bonds.

**Group 15**

<table>
<thead>
<tr>
<th></th>
<th>2s² 2p³</th>
<th>Non Metals</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>2s² 2p³</td>
<td>Non Metals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>3s² 3p³</td>
<td>Metals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>4s² 4p³</td>
<td>Metalloids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>5s² 5p³</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>6s² 6p³</td>
<td>Metal</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Solids and show allotropic modifications
- $s$-orbitals in these elements are completely filled and $p$-orbitals are half filled, making their electronic configuration extra stable.

Down the group covalent radii increases and electro negativity decreases, Ionization energy decreases and hence metallic nature increases. Nitrogen has maximum electro negativity.

There is considerable increase in covalent radius from N to P. However from As to Bi only a small increase in covalent radius is observed.

Successive ionization enthalpy: $\Delta H_1 < \Delta H_2 < \Delta H_3$

Boiling point (bp) increases from top to bottom, but mp increases upto As and decreases upto Bi.

Except N, all elements show allotropy.

**Chemical properties of group 15**

**Oxidation State and Trends in group 15**

<table>
<thead>
<tr>
<th></th>
<th>-3, +3</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>-3, +3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>-3, +3, +5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>-3, +3, +5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>+3, +5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>+3, +5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Covalent character decreases down the group.
- Most common oxidation state are -3, +3 and +5
- -3 O.S decreases down the group due to increase in size and metallic nature.
- The stability of +5 O.S decreases due to inert pair effect down the group. Only Bi(V) compound is BiF₅.
Nitrogen exhibits +1, +2 and +4 O.S also when it reacts with oxygen. All these O.S tend to disproportionate in acid solution. e.g
\[ 3\text{HNO}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO} \]
Nitrogen is restricted to a maximum covalency of 4 since 4 orbitals (one s and three p) are available for bonding.
Phosphorous exhibits nearly all intermediate O.S from +5 and -3.
The heavier elements have vacant d-orbitals which can be used for bonding as in PF\textsubscript{6}^-. 

**Anomalous properties of nitrogen**

Nitrogen differs from the rest of the members of this group due to its smaller size, high electro negativity, high ionization enthalpy and non-availability of d-orbitals.
Nitrogen can form π-π multiple bond.
Nitrogen exists as diatomic molecule with a triple bond.
Heavier elements do not form π-π bonds as their atomic orbitals are so large and differs that they cannot have effective overlapping.
P, As and Sb form P-P, As-As and Sb-Sb single bonds whereas Bi forms metallic bonds. However, N-N single bond is weaker than P-P single bond, because of high inter electronic repulsion of non-bonding electrons owing to small bond length.
Catenation tendency is weaker in N as N-N bond is much weaker than P-P, As-As and Sb-Sb due to inter electronic repulsions because of small bond length.
Except nitrogen, the heavier elements can form dπ-pπ bonds, e.g R\textsubscript{3}P=O or R\textsubscript{3}P=CH\textsubscript{2} and also when transition elements like P(C\textsubscript{2}H\textsubscript{5})\textsubscript{3} and As(C\textsubscript{6}H\textsubscript{5})\textsubscript{3} act as ligands; they form dπ-dπ bonds.

1) **Reactivity towards hydrogen:** Form hydrides of formula EH\textsubscript{3}
   - Structure pyramidal
   - Bond angle decreases down the group due to decrease in electro negativity.
   - Stability decreases due to increase in size.
   - Reducing character increases due to decrease in stability. NH\textsubscript{3} is a mild reducing agent while BiH\textsubscript{3} is strongest.
   - Basic character decreases in the order: NH\textsubscript{3} > PH\textsubscript{3} > AsH\textsubscript{3} > SbH\textsubscript{3} > BiH\textsubscript{3}.

2) **Reactivity towards oxygen:** Form two types of oxides of the formula: E\textsubscript{2}O\textsubscript{3} and E\textsubscript{2}O\textsubscript{5}. The oxide in the higher oxidation is more acidic than that of lower oxidation state. Acidic character decreases down the group.
   - N\textsubscript{2}O\textsubscript{3}, P\textsubscript{2}O\textsubscript{5} → Acidic
   - As\textsubscript{2}O\textsubscript{3}, Sb\textsubscript{2}O\textsubscript{5} → Amphoteric
   - Bi\textsubscript{2}O\textsubscript{3} → Basic oxide

3) **Reactivity towards halogens:** They form halides of the formula: EX\textsubscript{3} and EX\textsubscript{5}.
   - Nitrogen does not form pentahalide due to absence of the d orbitals.
   - Pentahalides are more covalent than trihalides.
   - All trihalides except those of nitrogen are stable. Only NF\textsubscript{3} is stable. Trihalides except BiF\textsubscript{3} are predominantly covalent.
4) Reactivity towards metals: All these elements react with metals to form their binary compounds exhibiting -3 oxidation state, such as, Ca₃N₂ (calcium nitride) Ca₃P₂ (calcium phosphide), Na₃As₂ (sodium arsenide), Zn₃Sb₂ (zinc antimonide) and Mg₃Bi₂ (magnesium bismuthide).

**Dinitrogen**

**Preparation**

1. Dinitrogen is prepared commercially by the liquefaction and fractional distillation of air.
2. In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite:
   \[
   \text{NH}_4\text{Cl(aq)} + \text{NaNO}_2(\text{aq}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O(l)} + \text{NaCl(}\text{aq}\text{)}
   \]
3. \((\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{Heat}} \text{N}_2 + 4\text{H}_2\text{O} + \text{Cr}_2\text{O}_3\)
4. Pure nitrogen is obtained by the thermal decomposition of sodium or barium azide:
   \[
   \text{Ba(N}_3)_2 \rightarrow \text{Ba} + 3\text{N}_2
   \]
   \[
   2\text{NaN}_3 \rightarrow 2\text{Na} + 3\text{N}_2
   \]

**Properties**

1. Dinitrogen is a colourless, odourless, tasteless and non-toxic gas.
2. It is inert at room temperature because of the high bond enthalpy of \(\text{N} \equiv \text{N}\) bond.
3. At high temperature, it directly combines with some metals to form ionic nitrides and with non-metals to form covalent nitrides:
   \[
   6\text{Li} + \text{N}_2 \xrightarrow{\text{Heat}} 2\text{Li}_3\text{N}
   \]
   \[
   3\text{Mg} + \text{N}_2 \xrightarrow{\text{Heat}} 2\text{Mg}_3\text{N}_2
   \]
4. It combines with hydrogen at about 773 K to form ammonia:
   \[
   \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \xrightarrow{773\text{K}} 2\text{NH}_3(\text{g}); \quad \Delta H^\circ = -46.1 \text{kJmol}^{-1}
   \]
5. It combines with dioxygen only at about 2000 K to form nitric oxide, NO.
   \[
   \text{N}_2 + \text{O}_2(\text{g}) \xrightarrow{\text{Heat}} 2\text{NO(g)}
   \]
   Thermal decomposition of sodium azide gives dinitrogen gas. \((2\text{NaN}_3 \rightarrow 2\text{Na} + 3\text{N}_2)\)

**Ammonia**

**Preparation**

Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.

\[
\text{NH}_2\text{C\text{CNH}_2} + 2\text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{CO}_3 \rightleftharpoons 2\text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2
\]

On a small scale ammonia is obtained from ammonium salts which decompose when treated with caustic soda or lime.

\[
2\text{NH}_4\text{Cl} + \text{Ca(OH)_2} \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O} + \text{CaCl}_2
\]
\[
(\text{NH}_4)_2\text{SO}_4 + 2\text{NaOH} \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O} + \text{Na}_2\text{SO}_4
\]

On a large scale, ammonia is manufactured by Haber’s process.
The optimum conditions are a pressure of \(200 \times 10^5\) Pa (about 200 atm), a temperature of \(\approx 700\) K with iron oxide and small amount of \(\text{K}_2\text{O}\) and \(\text{Al}_2\text{O}_3\) as catalyst.

**HABER’S PROCESS**

**Properties**

1. Ammonia is a colourless gas with a pungent odour.
2. In the solid and liquid state there exists H-bond, which accounts for its higher melting and boiling points.
3. It is trigonal bipyramidal with three bond pairs and 1 lone pair.
4. Highly soluble
   \[
   \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+ (\text{aq}) + \text{OH}^- (\text{aq})
   \]
   (weakly basic in aq. Solution)
5. Forms ammonium salts with acids, e.g., \(\text{NH}_4\text{Cl}, (\text{NH}_4)_2\text{SO}_4\), etc. It precipitates the hydroxides of many metals from their salt solutions. For example,
   \[
   2\text{FeCl}_3 (\text{aq}) + 3\text{NH}_4\text{OH} (\text{aq}) \rightarrow \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O} (\text{s}) + 3\text{NH}_4\text{Cl} (\text{aq})
   \]
   (brown ppt)
   \[
   \text{ZnSO}_4 (\text{aq}) + 2\text{NH}_4\text{OH} (\text{aq}) \rightarrow \text{Zn(OH)}_2 (\text{s}) + (\text{NH}_4)_2\text{SO}_4 (\text{aq})
   \]
   (white ppt)
6. Presence of a lone pairs makes it a Lewis base. It donates the electron pair and forms linkage with metal ions.
**Uses**

To produce nitrogenous fertilizers and manufacture of inorganic nitrogen compounds. Liquid ammonia is also used as a refrigerant.

**Oxides of Nitrogen**

<table>
<thead>
<tr>
<th>Formula</th>
<th>Oxidation state</th>
<th>Resonance Structures</th>
<th>Common Methods of Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>+1</td>
<td>N=N=O ↔ N≡N−O</td>
<td>NH₄NO₃ → N₂O + 2H₂O</td>
</tr>
<tr>
<td>NO</td>
<td>+2</td>
<td>N=O : ↔ N = 0</td>
<td>2NaNO₂ + 2FeSO₄ + 3H₂SO₄ → Fe₂(SO₄)₃ + 2NaHSO₄ + 2H₂O + 2NO</td>
</tr>
<tr>
<td>N₂O₃</td>
<td>+3</td>
<td>:N−</td>
<td>2NO + N₂O₄ → N₂O₃</td>
</tr>
<tr>
<td>NO₂</td>
<td>+4</td>
<td>N</td>
<td>2Pb(NO₃)₂ → 4NO₂ + 2PbO</td>
</tr>
<tr>
<td>N₂O₄</td>
<td>+4</td>
<td>:O−</td>
<td>2NO₂ → N₂O₄ (Cool Heat)</td>
</tr>
<tr>
<td>N₂O₅</td>
<td>+5</td>
<td>N−</td>
<td>4HNO₃ + P₄O₁₀ → 4HPO₃ + 2N₂O₅</td>
</tr>
</tbody>
</table>

**Nitric Acid**

1. In the laboratory, nitric acid is prepared by heating KNO₃ or NaNO₃ and concentrated H₂SO₄ in a glass retort.
   NaNO₃ + H₂SO₄ → NaHSO₄ + HNO₃
2. On a large scale it is prepared mainly by Ostwald’s process.
3. \(2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)\)
4. \(3\text{NO}_2(g) + \text{H}_2\text{O}(l) \rightarrow 2\text{HNO}_3(\text{aq}) + \text{NO}(g)\)
5. NO thus formed is recycled and the aqueous HNO\(_3\) can be concentrated by distillation upto \(\sim 68\%\) by mass. Further concentration to 98\% can be achieved by dehydration with concentrated H\(_2\)SO\(_4\).

**Properties**

1. A colourless liquid. In gaseous state it has a planar structure.
2. In aq. Solution, behaves as a strong acid.
   \[ \text{HNO}_3(\text{aq}) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \]
3. Conc. HNO\(_3\) is a strong oxidizing agent and can react with metals and non-metals.
   - \(3\text{Cu} + 8\text{HNO}_3(\text{dil}) \rightarrow \text{Cu(NO}_3)_2 + 2\text{NO} + \text{H}_2\text{O}\)
   - \(\text{Cu} + 4\text{HNO}_3(\text{conc}) \rightarrow \text{Cu(NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}\)
   - \(4\text{Zn} + 10\text{HNO}_3(\text{dil}) \rightarrow 4\text{Zn(NO}_3)_2 + 5\text{H}_2\text{O} + \text{N}_2\text{O}\)
   - \(\text{Zn} + 4\text{HNO}_3(\text{conc}) \rightarrow \text{Zn(NO}_3)_2 + 2\text{H}_2\text{O} + 2\text{N}_2\text{O}\)

**With Non-metals**

- \(\text{I}_2 + 10\text{HNO}_3 \rightarrow 2\text{HICl}_3 + 10 \text{NO}_2 + 4\text{H}_2\text{O}\)
- \(\text{C} + 4\text{HNO}_3 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 4\text{NO}_2\)
- \(\text{S}_8 + 48\text{HNO}_3(\text{conc.}) \rightarrow 8\text{H}_2\text{SO}_4 + 48\text{NO}_2 + 16\text{H}_2\text{O}\)
- \(\text{P}_4 + 20\text{HNO}_3(\text{conc.}) \rightarrow 4\text{H}_3\text{PO}_4 + 20 \text{NO}_2 + 4\text{H}_2\text{O}\)

**Brown Ring Test:** Aq. Solution of nitrate ion + dil. FeSO\(_4\) solution + conc. H\(_2\)SO\(_4\) along the sides of the test tube.

- \(\text{NO}_3^- + 3\text{Fe}^{2+} + 4\text{H}^+ \rightarrow \text{NO} + 3\text{Fe}^{3+} + 2\text{H}_2\text{O}\)
- \([\text{Fe(H}_2\text{O)}]_6^{2+} + \text{NO} \rightarrow [\text{Fe}(\text{H}_2\text{O})]_6(\text{NO})]^{2+} + \text{H}_2\text{O}\) (brown)

**PHOSPHORUS**

**Occurrence:** Occurs as fluoroapatite Ca\(_5\)(PO\(_4\))\(_3\)F and hydroxyapatite Ca\(_5\)(PO\(_4\))\(_3\)(OH)

**Preparation:**

- Calcination of phosphate rock.
- Reduction with coke and sand

\[2\text{Ca(PO}_4)_3 + 6\text{SiO}_2 + 10\text{C} \rightarrow \text{P}_4 + 6\text{CaSiO}_3 + 10\text{CO}\]

Vapours condensed to solid under water
**Allotropes:**

1. **White Phosphorus:**

Condensation of gaseous or liquid state. It glows in dark (chemiluminescence). It is a waxy solid, insoluble in water, soluble in CS₂ and benzene. It is stored under water as it ignites spontaneously in air. It shows phosphorescence.

   - Each ‘P’ located at the corner of a tetrahedron is attached to 3 other ‘P’ atoms.
   - Angle is 60°. P₄ units face lot of angle strain.
   - It readily catches fire in air to give white dense fumes of P₄O₁₀
     
     \[ P₄ + 5O₂ \rightarrow P₄O₁₀ \]
   - It dissolves in NaOH (boiling) to give phosphine.
     
     \[ P₄ + 3NaOH + 3H₂O \rightarrow PH₃ + 3NaH₂PO₂ \text{(sodium hypophosphite)} \]

2. **Red Phosphorus:**

   White P \[ \rightleftharpoons \] 570K, inert atm. \[ \rightarrow \] Red P

   It is insoluble in water and CS₂.
   It does not glow in the dark.
   It has a high melting point (870K), amorphous, less reactive.
   Red P is less reactive than white P.
   Safe to handle and shows a polymeric structure.

3. **Black Phosphorus:**

   It has two forms: α-black phosphorus and β-black phosphorus.
   
   \[ \text{Red P} \quad \xrightarrow{803k} \quad \text{Black P (α-form)} \]
   \[ \text{White P} \quad \xrightarrow{473k, \text{high pressure}} \quad \text{Black P (β-form)} \]
   It is the most stable variety with an extended layer structure

**Uses:**

In the form of phosphatic fertilizers.
Manufacture of food grade phosphates.
Detergents, pharmaceuticals, water industry.  
Manufacture of organo phosphorus compounds used as pesticides.

**Compounds: Hydrides: (MH₃)**

- NH₃ – Ammonia, most stable, shows H-bonding. Therefore, soluble in water
- PH₃ – Phosphine: When pure, it is non inflammable but becomes inflammable owing to the presence of P₂H₄ or P₄ vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH₄I) which on treating with KOH gives off phosphine.  
  \[ \text{PH}_4\text{I} + \text{KOH} \rightarrow \text{KI} + \text{H}_2\text{O} + \text{PH}_3 \]
- AsH₃  
- SbH₃  
- BiH₃  
  no H-bond insoluble in water. Strong reducing agent and poisonous.

**Preparation of PH₃:**

\[
\begin{align*}
\text{Ca}_3\text{P}_2 + 6\text{HCl} & \rightarrow 3\text{CaCl}_2 + 2\text{PH}_3 \\
\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} & \rightarrow 2\text{PH}_3 + 3\text{Ca(OH)}_2 \\
\text{P}_4 + 3\text{KOH} + 3\text{H}_2\text{O} & \rightarrow \text{PH}_3 + 3\text{KH}_2\text{PO}_2 \text{ (Potassium hypophosphite)} \\
\text{/NaOH} & \text{/3NaH}_2\text{PO}_2
\end{align*}
\]

**Preparation of AsH₃, SbH₃:**

\[
\text{Zn}_3\text{M}_2 + 6\text{HCl} \rightarrow 2\text{MH}_3(\text{g}) + 3\text{ZnCl}_2
\]

- Basic character of hydrides decrease down the group due to decrease in charge density. NH₃ is the most basic whereas ASH₃, SbH₃, BiH₃ do not show any basic properties.
- Thermal stability decreases down the group as the size of the central atom increases and the tendency to form stable M-H bond decreases.
- Reducing character increases down the group, because thermal stability of hydrides decreases.

**Properties of Phosphine:**

It is a colourless gas with rotten fish smell and is highly poisonous. It explodes in contact with traces of oxidising agents like HNO₃, Cl₂ and Br₂ vapours.

\[
\begin{align*}
\text{PH}_3(\text{aq}) \xrightarrow{\text{light}} \text{Red P} + \text{H}_2 \\
3\text{CuSO}_4 + 2\text{PH}_3 & \rightarrow \text{Cu}_3\text{P}_2 + 3\text{H}_2\text{SO}_4 \\
3\text{HgCl}_2 + 2\text{PH}_3 & \rightarrow \text{Hg}_3\text{P}_2 + 6\text{HCl} \text{ (mercury chloride)}
\end{align*}
\]

Phosphine is weakly basic and gives phosphonium compounds with acids e.g.,

\[
\text{PH}_3 + \text{HBr} \rightarrow \text{PH}_4\text{Br}
\]

**Halides:**

MX₃ (known for all)  MX₅ (except N)
N: 2s²2p³, It can easily form 3 covalent bonds and 1 coordinate bond. Thus total 4 bonds. Since there is non-availability of d-orbital, it cannot extend its coordination number beyond 4. However, for P and other group 15 elements, 5 covalent bonds can also be formed due to availability of d orbitals. (sp³d hybridization).

<table>
<thead>
<tr>
<th>MX₃</th>
<th>NX₃</th>
<th>Covalent</th>
<th>AsX₃</th>
<th>SbX₃</th>
<th>BiX₃ – ionic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>• Ionic character increases down the group, because of increased size of central atom, the electro positive character increases.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• MX₃ have pyramidal structure.</td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>• They are hydrolysed by water. (except NX₃)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Preparation:

\[
P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2
\]

\[
P_4 + 6X_2 \rightarrow 4PX_3 ;
\]

**PF₅ is pyramidal (in gas phase)**

\[
PCl₃ + 3H₂O \rightarrow H₃PO₃ + 3HCl (gives fumes)
\]

PCl₃ fumes in moisture due to formation of HCl(g)

\[
2PCl₃ + O₂ \rightarrow 2POCl₃ (phosphoryl chloride)
\]

3CH₃COOH + PCl₃ \rightarrow 3CH₃COCl + H₃PO₃

3C₂H₅OH + PCl₃ \rightarrow 3C₂H₅Cl + H₃PO₃

**Structure: Trigonal bipyramid**

PF₅ exist as PF₅ molecule in gas and solid state. There are 2 kinds of bond lengths, 3 equatorial and 2 axial bonds.

PCl₅ exist as PCl₅ molecule in gas or liquid and as [PCl₄]⁺ [PCl₆]⁻ in solid state.

PCl₅ reacts with organic compounds.

\[
\text{C}_2\text{H}_5\text{OH} + \text{PCl}_5 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{POCl}_3 + \text{HCl}
\]

\[
\text{CH}_3\text{COOH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{COCl} + \text{POCl}_3 + \text{HCl}
\]

Finely divided metals on heating with PCl₅ give corresponding chlorides.

\[
\text{2Ag} + \text{PCl}_5 \rightarrow \text{2AgCl} + \text{PCl}_3
\]

\[
\text{Sn} + 2\text{PCl}_5 \rightarrow \text{SnCl}_4 + 2\text{PCl}_3
\]
Preparation:

\[
\begin{align*}
\text{PCl}_3 + \text{Cl}_2 & \rightarrow \text{PCl}_5 \\
\text{P}_4 + 10\text{Cl}_2 & \rightarrow 4\text{PCl}_5 \\
\text{P}_4 + 10\text{SO}_2\text{Cl}_2 & \rightarrow 4\text{PCl}_5 + 10\text{SO}_2
\end{align*}
\]

Hydrolysis:

\[
\begin{align*}
\text{PCl}_5 + \text{H}_2\text{O} & \rightarrow \text{POCl}_3 + 2\text{HCl} \\
\text{PCl}_5 + 3\text{H}_2\text{O} \text{ (excess)} & \rightarrow \text{H}_3\text{PO}_3 + 2\text{HCl}
\end{align*}
\]

Oxoacids:

All oxoacids have at least one P=O and one P-OH bond. They have cyclic or linear structure.

- Monoprotic acid
- Hypophosphorous or Phosphinic acid

- Orthophosphoric acid
- Triprotic acid, Na\textsubscript{2}HPO\textsubscript{4}, NaH\textsubscript{2}PO\textsubscript{4}, Na\textsubscript{3}PO\textsubscript{4}
- Used for manufacture of phosphatic fertilizers.
Cyclotrimetaphosphoric acid

Polymetaphosphoric acid

+3 oxidation state

$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

The acids with P – H bond have strong reducing properties.

$4AgNO_3 + 2H_2O + H_3PO_2 \rightarrow 4Ag + 4HNO_3 + H_3PO_4$

That is why $H_3PO_2$ imparts reducing character to the acid as it has 2H atoms bonded to P.

Group 16

Elements in group 16 are Oxygen (O), Sulphur (S), Selenium (Se), Tellurium (Te) and Polonium (Po). Also called Chalcogens.

Occurrence:
1. Oxygen is the most abundant element.
2. Sulphur exists as gypsum $CaSO_4.2H_2O$, Epsom salt $MgSO_4.7H_2O$ or galena $PbS$, Zinc blende $ZnS$ etc.
3. Selenium and Tellurium as Selenides and Tellurides in sulphur ores.
4. Polonium exists as decay product of thorium and uranium minerals.

Electronic Configuration:
General electronic config – $ns^2np^4$

Atomic and Ionic Radii:
Due to increase in number of shells, atomic and ionic radii increase from top to bottom in the group.

Ionization Enthalpy:
1. Decreases down the group due to increase in size.
2. Group 16 elements have lower ionization enthalpy than corresponding elements of group 15 due to stability of half filled p-orbital electronic configuration in group 15.

Electron Gain Enthalpy:
1. Oxygen has less negative electron gain enthalpy due to its compact nature.
2. Sulphur onwards the value again becomes negative upto Po.
Electronegativity:
Oxygen is the second most electronegative element, next to fluorine. Within a group electronegativity decreases with increase in atomic number.

Metallic Character:
Increase from oxygen to polonium.

Physical Properties:

<table>
<thead>
<tr>
<th>O, S → Non-Metals</th>
<th>Se, Te → Metalloids</th>
<th>Po → Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. All of them exhibit Allotropy.</td>
<td>2. M.P and B.P increases with increase in atomic number but there is large difference in m.p of O and S due to its atomicity – O₂ and S₈.</td>
<td></td>
</tr>
</tbody>
</table>

Chemical Properties:
2. Oxygen shows only negative oxidation state of -2 and in case of OF₂, oxidation state of +2.
3. Other elements of the group easily show +2, +4, and +6 oxidation state.
4. Stability of +4 oxidation state increase down the group due to inert pair effect.

Reactivity with Hydrogen:
All the elements form hydrides of the formula H₂E (E = S, Se, Te, Po).

Chemical Properties:
1. Allotropy is exhibited by all members.
2. M.P and B.P increases with increase in atomic number but there is large difference in m.p of O and S due to its atomicity – O₂ and S₈.

Reactivity with Oxygen:
All these elements form oxides of the formula EO₂ and EO₃ where E = S, Se, Te or Po.
1. SO₂ is gas but SeO₂ is solid.
2. Reducing property decreases from SO₂ and TeO₂. SO₂ is reducing and TeO₂ is an oxidising agent.
3. Also form EO₃ type oxides. Both types are acidic.

Reactivity towards halogens:
1. Form halides of the formula EX₆, EX₄ and EX₂.
2. Stability of halides decrease in the order F⁻ > Cl⁻ > Br⁻ > I⁻.
3. Amongst hexahalides, hexafluorides are only stable. They (hexafluorides) are gaseous octahedral in nature. Most stable is SF₆ due to steric reasons.
4. Amongst tetrafluorides, SF₄ is gas, SeF₄ is liquid and TeF₄ a solid. They have Sp³d hybridization and have trigonal bipyramidal structures and are regarded as see-saw geometry.
5. All elements except Se form dichlorides and dibromides. Dihalides have Sp³ hybridisation.
6. Monohalides are dimeric in nature. E.g – S₂Fe, S₂Cl₂, S₂Br₂, Se₂Cl₂ and Se₂Br₂. Dimeric halides undergo disproportionation as:- 2Se₂Cl₂ → SeCl₄ + 3Se.
DIOXYGEN

Methods of Preparation:
1. By heating chlorates, nitrates and permanganates.
   \[ 2KClO_3 \xrightarrow{\text{Heat}} MnO_2 \rightarrow 2KCl + 3O_2 \]
2. Thermal decomposition of oxides.
   \[ 2Ag_2O(s) \rightarrow 4Ag(s) + O_2(g); \quad 2Pb_3O_4(s) \rightarrow 6PbO(s) + O_2(g) \]
   \[ 2HgO(s) \rightarrow 2Hg(l) + O_2(g); \quad 2PbO_2(s) \rightarrow 2PbO(s) + O_2(g) \]
3. \( 2H_2O_2 \rightarrow 2H_2O + O_2 \) Catalyst used – finely divided metals and manganese dioxide.
4. On large scale, prepared by electrolysis of water.
5. Industrially, from air \( \rightarrow \) first carbon dioxide and water vapour are removed and remaining gases liquefied are fractionally distilled.

Properties of DIOXYGEN:
1. Colourless and odourless gas.
2. Directly reacts with nearly all metals and non-metals except Au, Pt and some noble gases. Its combination with other elements is exothermic.

3. Some reactions with metals and non-metals are:
   \[ 2Ca + O_2 \rightarrow 2CaO \]
   \[ 4Al + 2O_2 \rightarrow 2Al_2O_3 \]
   \[ P_4 + 5O_2 \rightarrow P_4O_{10} \]
   \[ C + O_2 \rightarrow CO_2 \]
   \[ 2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \]
   \[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \]
4. Some compounds are catalytically oxidized.
   \[ 2SO_2 + O_2 \xrightarrow{\text{V}_2\text{O}_5} 2SO_3 \]
   \[ 4HCl + O_2 \xrightarrow{\text{CuCl}_2} 2H_2O \]

Uses:
1. Importance in normal respiration and combustion.
2. Oxyacetylene welding.
4. Oxygen cylinders are used in hospitals, high altitude flying and in mountaineering.
5. Combustion of fuels, e.g. hydrazine in liquid oxygen provides thrust in rockets.

OXIDES
A binary compound of oxygen with another element is called oxide.

Oxides can be simple (MgO, Al_2O_3) or mixed (Pb_3O_4, Fe_3O_4). Simple oxides can be acidic, basic or amphoteric oxides.

An oxide which combines with water to give an acid is termed as acidic oxide. (e.g \( SO_2, CO_2, N_2O_5 \))
\[ SO_2 + H_2O \rightarrow H_2SO_3 \] (Non metal oxides are acidic)
The oxide which gives a base with water is called basic oxides. Metal oxides are basic (e.g- Na₂O, CaO, BaO)

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2
\]

Some metal oxides exhibit dual behavior. They show characteristics of both acidic as well as basic oxides. They are known as amphoteric oxides. E.g Al₂O₃

\[
\begin{align*}
\text{Al}_2\text{O}_3 + 6\text{HCl} + 9\text{H}_2\text{O} & \rightarrow 2[\text{Al(H}_2\text{O})_6]^{3+} + 6\text{Cl}^- \\
\text{Al}_2\text{O}_3 + 6\text{NaOH} + 3\text{H}_2\text{O} & \rightarrow 2\text{Na}_3[\text{Al(OH)}_6]
\end{align*}
\]

Some oxides are neither acidic nor basic. E.g CO, NO and N₂O

**OZONE**

Ozone is an allotrope of oxygen. It is too reactive to remain at sea level. At a height of 20km above sea level it is formed from atmospheric oxygen in the presence of sunlight. The ozone layer protects earth’s surface from excessive concentration of UV radiation.

**Preparation:**
When silent electric discharge is passed through dry oxygen, ozonised oxygen (10%) is produced.

\[
3\text{O}_2 \rightarrow 2\text{O}_3 (\Delta H=142\text{KJmol}^{-1})
\]

**Properties:**

1. Pale blue gas, dark blue liquid and violet black solid.
2. In small concentrations, it is harmless and if concentration rises above 100ppm breathing becomes uncomfortable.
3. Ozone is thermodynamically unstable. Its decomposition to oxygen results in liberation of heat and increase in entropy. The two effects results in negative Gibb’s energy change for conversion into oxygen. High concentration of ozone can be dangerously explosive.
4. Acts as good oxidising agent because \([\text{O}_3 \rightarrow \text{O}_2 + \text{O}]\) due to liberation of nascent oxygen.

\[
\begin{align*}
\text{PbS} + 4\text{O}_3 & \rightarrow \text{PbSO}_4 + 4\text{O}_2 \\
2\text{I}^- + \text{H}_2\text{O} + \text{O}_3 & \rightarrow 2\text{OH}^- + \text{I}_2 + \text{O}_2
\end{align*}
\]

This reaction can be used for estimating O₃ gas. I₂ liberated titrated against standard Na₂S₂O₃ solution helps in estimation.
5. Nitrogen oxides emitted from exhaust system of supersonic aeroplanes might be slowly depleting ozone layer in upper atmosphere.

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2
\]
6. Ozone layer is also depleted by refrigerants and aerosol sprays.
7.

Bond length is 128pm and bond angle is 117°.

**Uses:**
1. Used as germicide, disinfectant and sterilizing water.
2. Used for bleaching oils, ivory, flour and starch.
3. Acts as oxidising agent in manufacture of KMnO₄.

**SULPHUR**

**Allotropic forms of Sulphur:**
1. Yellow rhombic sulphur (α-sulphur)
2. Monoclinic sulphur (β-sulphur)

Rhombic is stable at room temperature which transforms to monoclinic when heated above 369k. Rhombic sulphur is yellow in colour, insoluble in water and dissolves to some extent in benzene, alcohol and ether. It is readily soluble in CS₂.

Monoclinic sulphur is stable above 369K and α-sulphur below 369K, called transition temperature, both forms are stable. Both exist as S₈ molecules. At high temperature (~1000k), S₂ is dominant and it is para magnetic.

![Sulphur Molecule](image)

**SULPHUR DIOXIDE**

**Preparation:**
1. S + O₂ → SO₂ Sulphur burnt in air or oxygen gives SO₂ along with a little (6-8%) SO₃.
2. Sulphites with dilute sulphuric acid.
   \[ \text{SO}_3^{2-}(aq) + 2\text{H}^+ (aq) \rightarrow \text{H}_2\text{O}(l) + \text{SO}_2(g) \]
3. By product of roasting sulphide ores.
   \[ 4\text{FeS}_2 + 11\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s) + 8\text{SO}_2(g) \]

**Properties:**
1. Colourless gas with pungent smell.
2. Highly soluble in water.
3. Liquifies at room temp. under a pressure of 2atm and boils at 263K.
4. \[ \text{SO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{SO}_3(aq) \] (sulphurous acid)
5. \[ \text{NaOH} + \text{SO}_2 \rightarrow \text{Na}_2\text{SO}_3 \] (sodium sulphite) + H₂O
   \[ \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + \text{SO}_2 \rightarrow 2\text{NaHSO}_3 \] (sodium hydrogen sulphite)
6. Reacts with chlorine in the presence of charcoal as catalyst to give sulphuryl chloride.
   \[ \text{SO}_2(g) + \text{Cl}_2(g) \rightarrow \text{SO}_2\text{Cl}_2(l) \]
7. Oxidised to sulphur trioxide in the presence of V₅O₅
   \[ 2\text{SO}_2(g) + \text{O}_2(g) \rightarrow \text{V}_2\text{O}_5 \]
   \[ \rightarrow 2\text{SO}_3(g) \]
8. Moist SO₂ behaves as reducing agent. Converts Iron(III) ions to Iron(II) ions and
2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+

decolourizes acidified KMnO_4 solution

5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}

9. SO_2 is angular.

**Uses of SO_2:**
1. In refining petroleum.
2. In bleaching wool and silk.
3. As an anti-colour, disinfectant and preservative.
4. Sulphuric acid, NaHSO_3 and Ca(HSO_3)_2 are manufactured from sulphur dioxide.
5. Liquid SO_2 is used as a solvent to dissolve a number of organic and inorganic chemicals.

**Oxoacids of Sulphur**
Forms oxoacids of the formula H_2SO_x, H_2S_2O_y, H_2S_3O_6, H_2S_4O_7, H_2SO_5, H_2S_2O_8.

**Sulphuric Acid**

**Manufacture:**
By contact process. The steps are:
1. Burning of sulphur or sulphide ores in air to generate SO_2.
   S + O_2 \rightarrow SO_2
   4FeS_2 (Iron pyrites) + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2
2. Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of catalyst V_2O_5.
   2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g) \quad \Delta H^\circ=-196.6\text{KJmol}^{-1}
   This is the key reaction in the process. High yield of SO_3 will lead to more production of H_2SO_4.
3. Absorption of SO_3 in 98% H_2SO_4 to give Oleum (H_2S_2O_7).
   SO_3 + H_2SO_4 \rightarrow H_2S_2O_7
4. Dilution of oleum with water to get desired concentration of sulphuric acid.
   H_2S_2O_7 + H_2O \rightarrow 2 H_2SO_4 \quad \text{(Sulphuric acid prepared is 96-98% pure)}

**Conditions favouring maximum yield of sulphur trioxide:**
Key step in the manufacture of sulphuric acid is catalytic oxidation of SO_2 with O_2 to give SO_3.

\[ 2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g) \quad \Delta H^\circ=-196.6\text{KJmol}^{-1} \]
The reaction is exothermic and reversible.

a) **Low temperature**: Favours oxidation of \( \text{SO}_2 \) as reaction is exothermic (according to Le-Chatelier’s principle). But it is essential to have a minimum temperature of 720K, to give maximum yield.

b) **High Pressure**: Favours oxidation as volume of gaseous products are less. A pressure of 2 to 3 bar is sufficient. Very high may cause corrosion of the vessel.

c) **Use of catalyst**: \( \text{V}_2\text{O}_5 \) increases the speed of reaction.

**Description of the Plant (Manufacture of \( \text{H}_2\text{SO}_4 \) by Contact Process):**

![Flow diagram for the manufacture of sulphuric acid](image)

1. **Sulphur burners**: Sulphur or Iron pyrites are burnt.

2. **Purification unit**: The gaseous mixture coming out of sulphur burner is generally impure.
   Purified as:
   - I. **Dust Chambers**: Steam is introduced to remove dust.
   - II. **Coolers**: The gases are cooled to about 373K by passing them through cooling pipes.
   - III. **Scrubber**: Gases are passed into washing tower which dissolves mist and other soluble impurities.
   - IV. **Drying Tower**: A spray of conc. \( \text{H}_2\text{SO}_4 \) used for drying gases.
   - V. **Arsenic purifier**: This chamber contains shelves with gelatinous ferric hydroxide. The impurities of arsenic oxide are absorbed by ferric hydroxide.

3. **Testing Box**: The purifies gases are tested by passing a strong beam of light. Impurities present will scatter the light.

4. **Contact Chamber or Converter**: Pure gases are then heated to about 723-823K in a pre-heater and then introduced into contact chamber. It is a cylindrical chamber fitted with iron pipes packed with catalyst \( \text{V}_2\text{O}_5 \). In this \( \text{SO}_2 \) is oxidized to \( \text{SO}_3 \). As the forward reaction is exothermic, the pre-heating is stopped once the oxidation has started.

5. **Absorption tower**: It is a cylindrical tower packed with acid proof flint. \( \text{SO}_3 \) escaping out from converter is led from the bottom of the tower and conc. \( \text{H}_2\text{SO}_4 \) (98%) is sprayed from top. \( \text{SO}_3 \) gets absorbed by \( \text{H}_2\text{SO}_4 \) to form oleum or fuming sulphuric acid.
   \[
   \text{H}_2\text{SO}_4 + \text{SO}_3 \rightarrow \text{H}_2\text{SO}_7 \quad \text{(oleum)}
   \]
   Oleum is then diluted with calculated amount of water to get acid of desired concentration.
H₂S₂O₇ + H₂O → 2H₂SO₄

**PROPERTIES of H₂SO₄:**

1. Colourless, dense and oily liquid.
3. Chemical reactions of H₂SO₄ are as a result of:
   a) Volatility
   b) Strong acidic character
   c) Strong affinity of water
   d) Ability to act as oxidising agent
4. In aqueous solution, sulphuric acid ionizes as:
   \[ \text{H}_2\text{SO}_4(aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{HSO}_4^-(aq) \quad \text{K}_{a1} = \text{very large (}>10) \]
   \[ \text{H}_2\text{SO}_4^-(aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{SO}_4^{2-}(aq) \quad \text{K}_{a2} = 1.2 \times 10^{-2} \]
   Larger \( K_{a1} \) means – easily dissociated into \( H^+ \) and \( \text{HSO}_4^- \) and is a stronger acid.
5. Forms two types of salt:
   Normal sulphates (e.g. sodium sulphate, copper sulphate)
   Acid sulphates (e.g. hydrogen sulphate)
6. Can be used to form more volatile acids from their corresponding salts.
   \[ 2\text{MX} + \text{H}_2\text{SO}_4 \rightarrow 2\text{HX} + \text{M}_2\text{SO}_4 \quad (\text{X=F, Cl, NO}_3) \]
7. Acts as dehydrating agent. Can dry gases and also removes water from organic compounds.
   \[ \text{C}_1\text{2H}_2\text{O}_{11} + \text{H}_2\text{SO}_4 \rightarrow 12\text{C} + 11\text{H}_2\text{O} \]
8. Hot conc. H₂SO₄ is a strong oxidising agent. Both metals and non-metals are oxidized and itself is reduced to SO₂.
   \[ \text{Cu} + 2\text{H}_2\text{SO}_4 \text{(conc.)} \rightarrow \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O} \]
   \[ 3\text{S} + 2\text{H}_2\text{SO}_4 \text{(conc.)} \rightarrow 3\text{SO}_2 + 2\text{H}_2\text{O} \]
   \[ \text{C} + 2\text{H}_2\text{SO}_4 \text{(conc.)} \rightarrow \text{CO}_2 + 2\text{SO}_2 + 2\text{H}_2\text{O} \]

**USES:**

1. Important industrial chemical.
2. Used in manufacture of fertilizers (e.g. ammonium sulphate, superphosphate)
3. Petroleum refining
4. Paints, pigments and dyestuff
5. Detergent industry
6. Metallurgical applications
7. storage batteries
8. Laboratory reagent
9. In the manufacture of nitrocellulose products

**GROUP 17**

F, Cl, Br, I, At (radioactive) are called halogens. Most reactive non-metals and most electronegative.

F₂: Pale yellow gas
Cl₂: Greenish yellow gas
Br₂: Reddish brown liquid, sparingly soluble in H₂O
I₂: Lustrous, grayish black solid, sublimes on heating sparingly soluble in H₂O, soluble in org. solvents.

**Bond Energy:**

\[ F_2 < Cl_2 > Br_2 > I_2 \]

Anomalous behavior of F₂ is due to the fact that the lone pair of electrons are very close which lead to repulsions.

**Electron Affinity:**

\[ F < Cl > Br > I \]

This is because F being small in size repels the incoming electron.

**Occurs as:**

- F – Fluorides
- Cl – NaCl in oceans
- Br – Bromides
- I – Iodides and iodates (IO₃⁻)

<table>
<thead>
<tr>
<th>Oxidizing power</th>
<th>F₂ &gt; Cl₂ &gt; Br₂ &gt; I₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radii</td>
<td>F &lt; Cl &lt; Br &lt; I</td>
</tr>
<tr>
<td>I.E</td>
<td>F &gt; Cl &gt; Br &gt; I</td>
</tr>
<tr>
<td>E.N</td>
<td>F &gt; Cl &gt; Br &gt; I</td>
</tr>
</tbody>
</table>

**Preparation of Halogens:**

As halogens are oxidizing, they are prepared by electrolysis.

**F₂:**

Electrolytic is molten KF + HF, Cathode – mild steel, Anode – Carbon rod

Cathode: \[ 2H^+ + 2e^- \rightarrow H_2(g) \]

Anode: \[ 2F^- \rightarrow F_2(g) + 2e^- \]

Teflon separates the 2 electrodes to avoid the explosive mixing of H₂ and F₂.

**Chemical Method:**

\[ K_2MnF_6 + 2SbF_5 \rightarrow 2KSbF_6 + MnF_3 + 0.5F_2 \]

**Cl₂:**

Electrolysis of natural brine (NaCl)

By oxidation of HCl by MnO₂ or KMnO₄ (Lab Method)

\[ 2KMnO₄ + 16HCl \rightarrow 2KCl + 2MnCl₂ + 8H₂O + Cl₂ \]

By oxidation of NaCl

\[ 2NaCl + 2H₂SO₄ + MnO₂ \rightarrow Na₂SO₄ + MnSO₄ + 2H₂O + Cl₂ \]

**Br₂:**

Oxidation of bromide ions from natural brine with Cl₂

\[ 2Br⁻ + Cl₂ \rightarrow Br₂ + 2Cl⁻ \]
I₂:
Oxidation of bromide ions from natural brine with Cl₂
\[ 2I^- + Cl_2 \rightarrow I_2 + 2Cl^- \]
Reduction of iodates with NaHSO₃.
\[ NaIO_3 + 3NaHSO_3 \rightarrow NaI + 3NaHSO_4 \]
\[ NaIO_3 + 5NaI + 3H_2SO_4 \rightarrow 3I_2 + 3H_2O + 3Na_2SO_4 \]

**Trends in Group 17:**

<table>
<thead>
<tr>
<th>F₂</th>
<th>Cl₂</th>
<th>Br₂</th>
<th>I₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>F is the most electronegative element i.e. has good acceptance of an electron and is therefore the strongest oxidizing agent.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Oxidizing character decreases down the group. Thus one halogen oxidises halide ions of higher atomic number halogens.

- F₂ + 2X⁻ → 2F⁻ + X₂ (X=Cl, Br, I)
- Cl₂ + 2X⁻ → 2Cl⁻ + X₂ (X=Br, I)
- Br₂ + 2I⁻ → 2Br⁻ + I₂

Reactivity of halogens with metals or non-metals decreases down the group. F₂ > Cl₂ > Br₂ > I₂

- Mg + Br₂ → MgBr₂
- Xe + 3F₂ → XeF₆

Ionic character of M-X bond decreases down the group. M-f > M-Cl > M-Br > M-I

- Low O.S of M → MCl₂
- High O.S of M → MCl₄ → more covalent than MCl₂

**Compounds: Hydrogen Halides:** HF, HCl, HBr, HI

**Preparation:**

- CaF₂ + H₂SO₄ → CaSO₄ + 2HF
- 2NaCl + H₂SO₄ → Na₂SO₄ + 2HCl

**Oxidizing Action:**

- F₂ > Cl₂ > H₂SO₄ > Br₂ > I₂

Similar reactions as above cannot be used for the preparation of HBr and HI as H₂SO₄ is a stronger oxidizing agent and will oxidize the HBR, HI formed to BR₂, I₂ respectively.

- NaBr + H₂SO₄ → HBr + Br₂
- NaI + H₂SO₄ → HI + I₂

**Methods of preparation for HBr and HI:**

- H₂ + Br₂ → 2HBr (Pt / asbestos)
- 2I₂ + N₂H₄ → 4HI + N₂ (573K)

HX are colourless, irritating gases.
HF has a higher b.p due to H-bonding.
Acidic Character:

HF << HCl < HBr < HI

Low acidic character of HF is due to strong H-bonding and higher bond dissociation enthalpy. HF is corrosive and attacks glass.

NF₃ is an exothermic compound but BCl₃ is endothermic because bond energy of F₂ is lower than Cl₂ and N-F bond is smaller and stronger than N-Cl bond.

Stability:

Decreases down the group due to decreased bond dissociation enthalpy.

HF > HCl > HBr > I

Reducing Nature:

HF < HCl < HBr < HI

Oxides:

Halogens form many oxides with oxygen. Fluorine forms only OF₂ and O₂F₂ – oxygen fluorides, they are good fluorinating agents.

Pu + 3O₂F₂ → PuF₆ + 3O₂ (removed as PuF₆)

O₂F₂ oxidises Pu to PuF₆ and the reaction is used in removing Pu as PuF₆ from spent nuclear fuel.

Chlorine, Bromide and iodine form oxides where o.s ranges from +1 to +7. The higher oxides of halogens tend to be more stable than the lower ones.

Chlorine oxides, Cl₂O, ClO₂, Cl₂O₆ and Cl₂O₇ are highly reactive oxidizing agents. ClO₂ is used as bleaching agent for paper pulp and textiles and in water treatment.

Bromine oxides Br₂O, BrO₂, BrO₃ are least stable halogen oxides. They are powerful oxidizing agents.

The iodine oxides, I₂O₄, I₂O₅, I₂O₇ are insoluble solids and decompose on heating. I₂O₅ is a very good oxidizing agent and is used in the estimation of CO.

Reactivity towards Metals:

Halogens react with metals to form metal halides. Mg(s) + Br₂(l) → MgBr₂(s)

Ionic character of the halides decreases in the order: MF > MCl > MBr > MI where M is a monovalent metal.

If metal exhibits more than one O.S, higher O.S halides are more covalent than low O.S halides

Oxoacids of Halogens:

<table>
<thead>
<tr>
<th>Halic (l) acid (Hypohalous acid)</th>
<th>HOF (Hypofluorous acid)</th>
<th>HOCl (Hypochlorous acid)</th>
<th>HOBr (Hypobromous acid)</th>
<th>HOI (Hypoiodous acid)</th>
</tr>
</thead>
</table>

Inter Halogen Compounds:

When two different halogens react with each other, interhalogen compounds are formed. E.g. \(XX', XX'_3, XX'_5\) and \(XX'_7\) where \(X\) is halogen of larger size and \(X'\) of smaller size and \(X\) is more electropositive than \(X'\).

**Preparation:**

They are prepared by the direct combination or by the action of halogen on lower interhalogen compounds. For e.g.,

\[
\begin{align*}
\text{Cl}_2 + F_2 & \rightarrow 2\text{ClF} \quad (\text{equal volume}) \\
\text{Cl}_2 + 3F_2 & \rightarrow 2\text{ClF}_3 \quad (\text{excess}) \\
I_2 + 3\text{Cl}_2 & \rightarrow 2\text{ICl}_3 \quad (\text{excess}) \\
Br_2 + 3F_2 & \rightarrow 2\text{BrF}_3 \quad (\text{diluted with water}) \\
I_2 + \text{Cl}_2 & \rightarrow 2\text{ICl} \quad (\text{equimolar}) \\
Br_2 + 5F_2 & \rightarrow 2\text{BrF}_5 \quad (\text{excess})
\end{align*}
\]

**Properties:**

\(XX'\) | ClF, BrF, IF (unstable), BrCl, ICl, IBr
### Table

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{ClF}_3$ (Bent T-Shaped, because it is sp$^3d$ hybridized)</td>
<td>![ClF3 Structure]</td>
</tr>
<tr>
<td>$\text{BrF}_3$ (Bent T-Shaped, because it is sp$^3d$ hybridized)</td>
<td></td>
</tr>
<tr>
<td>$\text{IF}_3$ (Bent T-Shaped, because it is sp$^3d$ hybridized)</td>
<td></td>
</tr>
<tr>
<td>$\text{ClF}_5$ (Square pyramid)</td>
<td>![ClF5 Structure]</td>
</tr>
<tr>
<td>$\text{BrF}_5$ (Square pyramid)</td>
<td></td>
</tr>
<tr>
<td>$\text{IF}_5$ (Square pyramid)</td>
<td></td>
</tr>
<tr>
<td>$\text{IF}_7$ (Pentagonal bipyramidal)</td>
<td>![IF7 Structure]</td>
</tr>
</tbody>
</table>

### Notes

1. They are all covalent and diamagnetic in nature. They are volatile solid or liquid except ClF which is a gas.
2. They are more reactive than halogens because X-X’ bond in inter halogens is weaker than X-X bond in halogens except F-F bond.
3. All these undergo hydrolysis giving halide ion.
   \[
   XX’ + H_2O \rightarrow HX’ + HOX
   \]
   the bigger one forms hypohalous acid.

### Uses:
The compounds are used as non aqueous solvents. They are useful fluorinating agents. ClF$_3$ and BrF$_3$ are used for the production of UF$_6$ in the enrichment of $^{235}$U.

\[
\text{U(s) + 3ClF}_3(\text{l}) \rightarrow \text{UF}_6(\text{g}) + 3\text{ClF(g)}
\]

### Properties of Chlorine:
1. Greenish yellow gas with pungent and suffocating odour.
2. Reacts with metals and non-metals to form chlorides.
   - $2\text{Al} + 3\text{Cl}_2 \rightarrow 2\text{AlCl}_3$
   - $2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl}$
   - $2\text{Fe} + 3\text{Cl}_2 \rightarrow 2\text{FeCl}_3$
   - $\text{P}_4 + 6\text{Cl}_2 \rightarrow 4\text{PCl}_3$
   - $\text{S}_8 + 4\text{Cl}_2 \rightarrow 4\text{S}_2\text{Cl}_2$
3. Can react with hydrogen to form HCl.
   - $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$
   - $\text{H}_2\text{S} + \text{Cl}_2 \rightarrow 2\text{HCl} + \text{S}$
   - $\text{C}_{10}\text{H}_{16} + 8\text{Cl}_2 \rightarrow 16\text{HCl} + 10\text{C}$
4. With excess of NH$_3$, chlorine gives nitrogen and ammonium chloride while with excess of chlorine, nitrogen trichloride is formed.
   - $8\text{NH}_3 + 3\text{Cl}_2 \rightarrow 6\text{NH}_4\text{Cl} + \text{N}_2$; $\text{NH}_3 + 3\text{Cl}_2 \rightarrow \text{NCl}_3 + 3\text{HCl}$
     (excess) (excess)
5. With cold and dilute alkalies chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate.

\[
2\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaCl} + \text{NaOCl} + \text{H}_2\text{O} \\
\text{(cold and dilute)} \\
\text{NaOH} + 3\text{Cl}_2 \rightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O} \\
\text{(hot and conc.)}
\]

6. With dry slaked lime it gives bleaching powder.

\[
2\text{Ca(OH)}_2 + 2\text{Cl}_2 \rightarrow \text{Ca(OCl)}_2 + \text{CaCl}_2 + 2\text{H}_2\text{O}
\]

The composition of bleaching powder is \( \text{Ca(OCl)}_2 \cdot \text{CaCl}_2 \cdot \text{Ca(OH)}_2 \cdot 2\text{H}_2\text{O} \).

7. Chlorine reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with unsaturated hydrocarbons. For example,

\[
\text{CH}_4 + \text{Cl}_2 \xrightarrow{\text{UV}} \text{CH}_3\text{Cl} + \text{HCl} \\
\text{C}_2\text{H}_4 + \text{Cl}_2 \xrightarrow{\text{Room temp.}} \text{C}_2\text{H}_4\text{Cl}_2
\]

8. Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl.

9. It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.

\[
2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{Cl}_2 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{HCl} \\
\text{Na}_2\text{SO}_3 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl} \\
\text{SO}_2 + 2\text{H}_2\text{O} + \text{Cl}_2 \rightarrow \text{H}_2\text{SO}_4 + 2\text{HCl} \\
\text{I}_2 + 6\text{H}_2\text{O} + 5\text{Cl}_2 \rightarrow 2\text{HIO}_3 + 10\text{HCl}
\]

10. It is a powerful bleaching agent; bleaching action is due to oxidation.

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{O} \\
\text{Coloured substance} + \text{O} \rightarrow \text{Colourless substance}
\]

**Uses:**
1. Used for bleaching wood pulp, bleaching cotton and textiles.
2. In extraction of gold and platinum.
3. In manufacture of dyes, drugs and organic compounds.
4. In sterilizing drinking water.
5. Preparation of poisonous gases such as phosgene (COCl₂), tear gas and mustard gas.

**HYDROGEN CHLORIDE:**

**Preparation:**

Prepared by heating sodium chloride with concentrated sulphuric acid.

\[
\text{NaCl} + \text{H}_2\text{SO}_4 \xrightarrow{420\text{K}} \text{NaHSO}_4 + \text{HCl} \\
\text{NaHSO}_4 + \text{NaCl} \xrightarrow{823\text{K}} \text{Na}_2\text{SO}_4 + \text{HCl}
\]

HCl gas can be dried by passing through concentrated sulphuric acid.

**Properties:**
2. Extremely soluble. \( \text{HCl(g)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq) \)
   
   Its aqueous solution is called hydrochloric acid.
3. Reacts with NH₃ and gives white fumes. \( \text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl} \)
4. 3 parts of conc. HCl and 1 part of con. HNO₃ forms aqua regia.

\[
\text{Au} + 4\text{H}^+ + \text{NO}_3^- + 4\text{Cl}^- \rightarrow \text{AuCl}_4^- + \text{NO} + 2\text{H}_2\text{O} \\
3\text{Pt} + 16\text{H}^+ + 4\text{NO}_3^- + 18\text{Cl}^- \rightarrow 3\text{PtCl}_6^{2-} + 4\text{NO} + 8\text{H}_2\text{O}
\]
5. It decomposes salts of weaker acids, e.g., carbonates, hydrogen carbonates, sulphites, etc.

\[
\begin{align*}
\text{Na}_2\text{CO}_3 + 2\text{HCl} & \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \\
\text{NaHCO}_3 + \text{HCl} & \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \\
\text{Na}_2\text{SO}_3 + 2\text{HCl} & \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{SO}_2
\end{align*}
\]

**Uses:**
1. In manufacture of chlorine, NH₄Cl and glucose.
2. In medicine and as laboratory reagent.

**Uses of halogens and its compounds:**

<table>
<thead>
<tr>
<th>Halogen</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>Manufacture of UF₆ for nuclear power generation and SF₆ for dielectrics.</td>
</tr>
<tr>
<td>HF</td>
<td>Chemicals obtained are chlorofluorocarbons like Freon used as a refrigerator and polytetra-fluorethylene called Teflon used in nonstick pans. Also used in glass industry as an etching agent and in the manufacture of fluoride salts.</td>
</tr>
<tr>
<td>NaF</td>
<td>Used for fluoridation of water, (1ppm of fluoride in drinking ware prevents tooth decay)</td>
</tr>
<tr>
<td>SnF₂</td>
<td>Used in fluoride toothpastes.</td>
</tr>
<tr>
<td>Cl₂</td>
<td>Used for bleaching paper, pulp, textiles. Used as disinfectant for sterilizing drinking water. Used in production of organic compounds- PVC, chlorinated hydrocarbons, pharmaceuticals. Used in production of inorganic compounds. E.g. HCL, PCl₃, NaOCl</td>
</tr>
<tr>
<td>C₂H₂Br₂</td>
<td>Used as gasoline additive.</td>
</tr>
<tr>
<td>Br₂</td>
<td>Used to make AgBr for photography.</td>
</tr>
<tr>
<td>I₂</td>
<td>Used for preparation of iodoform and KI</td>
</tr>
<tr>
<td>NaI, NaIO₃ or KI, KIO₃</td>
<td>Added to table salt and is called iodised salt. (Insufficient iodine in the diet leads to Goitre.</td>
</tr>
</tbody>
</table>

**GROUP 18**

Known as Noble gases as their valance shell orbitals are completely filled and react with a few elements under certain conditions.

<table>
<thead>
<tr>
<th>Noble gas</th>
<th>Configuration</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1s²</td>
<td>Atmospheric abundance of the noble gases in dry air ~1% by volume of which Ar is major constituent.</td>
</tr>
<tr>
<td>Ne</td>
<td>2s²2p⁶</td>
<td></td>
</tr>
</tbody>
</table>
Electronic Configuration:
General electronic configuration is ns²np⁶ except He (1s²). Due to fully filled configuration noble gases are inactive in nature.

Ionization Enthalpy:
Due to stable electronic configuration, they have high I.E. Decreases down the group due to increase in atomic size.

Atomic Radii:
Increases down the group due to increase in number of shells.

Electron Gain Enthalpy:
Noble gases have stable electronic configuration, so no tendency to accept electron and hence have large positive values of ΔₑgH.

Physical Properties:
1. Monoatomic, colourless, odourless and tasteless.
2. Sparingly soluble in water.
3. Low m.p and b.p due to weak dispersion forces.
4. Can be liquefied at low temperature due to weak forces.

Chemical Properties:
Chemically inert due to:
1. Completely filled electronic config. ns²np⁶ in their valance shell.
2. High ionization enthalpy.
3. More positive electron gain enthalpy.

Uses of Noble Gases:

Helium:
- Non inflammable and light gas. Used in filling balloons for meteorological observations.
- Used in gas cooled nuclear reactors.
- Liquid He (b.p. 4.2K) is used as cryogenic agent for carrying out various experiments at low temperatures.
- Used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems.

Neon:
- Used in discharge tubes.
• Used in fluorescent bulbs for advertisement display purpose.

**Argon:**
• Used to provide an inert atmosphere in high temperature metallurgical processes.
• Used for filling electric bulbs.
• Used in lab for handling substances that are air sensitive.

**Kr, Xe:**
• Used in light bulbs used for special purposes.

**Energy of Compounds of Noble Gases:**

In 1962, Neil Bartlett prepared a red compound $O_2^+PtF_6^-$. He realised that the first I.E of $O_2=1175 \text{ kJmol}^{-1}$ was almost identical to I.E of $Xe=1170 \text{ kJmol}^{-1}$. He prepared a similar red colour compound by mixing $Xe$ and $PtF_6$.

$$Xe + PtF_6 \rightarrow Xe^+[PtF_6]^-$$

After this, a number of compounds of $Xe$ with electronegative elements like fluorine and oxygen have been synthesised.

**Xenon-fluorine compounds**

Xenon forms three binary fluorides, $XeF_2$, $XeF_4$ and $XeF_6$ by the direct reaction of elements.

\[
\begin{align*}
Xe (g) + F_2 (g) \quad & 673k, 1\text{bar} \quad \rightarrow \quad XeF_2 (s) \\
(Xe \text{ in excess}) \\
Xe (g) + 2F_2 (g) \quad & 873k, 7\text{bar} \quad \rightarrow \quad XeF_4 (s) \\
(1:5 \text{ ratio}) \\
Xe (g) + 3F_2 (g) \quad & 573k, 60-70\text{bar} \quad \rightarrow \quad XeF_6 (s) \\
(1:20 \text{ ratio})
\end{align*}
\]

$XeF_6$ is also prepared as $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$ at 143K.

**Structure:**

![Structure of XeF2, XeF4, and XeF6](image)
Properties:

1. XeF₂, XeF₄ and XeF₆ are colourless crystalline solids.
2. Sublime readily at 298 K.
3. They are powerful fluorinating agents. They react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.
   \[
   \begin{align*}
   \text{XeF}_2 + \text{PF}_5 & \rightarrow [\text{XeF}]^+ [\text{PF}_6]^- ; \\
   \text{XeF}_4 + \text{SbF}_5 & \rightarrow [\text{XeF}_3]^+ [\text{SbF}_6]^- \\
   \text{XeF}_6 + \text{MF} & \rightarrow \text{M}^+ [\text{XeF}_7]^+ \quad (\text{M} = \text{Na}, \text{K}, \text{Rb or Cs})
   \end{align*}
   \]
4. They are readily hydrolysed even by traces of water.
   \[
   2\text{XeF}_2 (s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{Xe} (g) + 4\text{HF(aq)} + \text{O}_2(g)
   \]

Xenon-oxygen compounds:

Hydrolysis of XeF₄ and XeF₆ with water gives XeO₃.
\[
\begin{align*}
6\text{XeF}_4 + 12\text{H}_2\text{O} & \rightarrow 4\text{Xe} + 2\text{XeO}_3 + 24\text{HF} + 3\text{O}_2 \\
\text{XeF}_6 + 3\text{H}_2\text{O} & \rightarrow \text{XeO}_3 + 6\text{HF}
\end{align*}
\]
Partial hydrolysis of XeF₆ gives oxyfluorides
\[
\begin{align*}
\text{XeF}_6 + \text{H}_2\text{O} & \rightarrow \text{XeOF}_4 + 2\text{HF} \\
\text{XeF}_6 + 2\text{H}_2\text{O} & \rightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}
\end{align*}
\]
Hydrolysis of XeF₆ is not a redox reaction as there is no change in oxidation state.

Structure: