Chapter 7
The p-Block Elements

Group-13 Elements: Boron Family

What are Group 13 Elements?

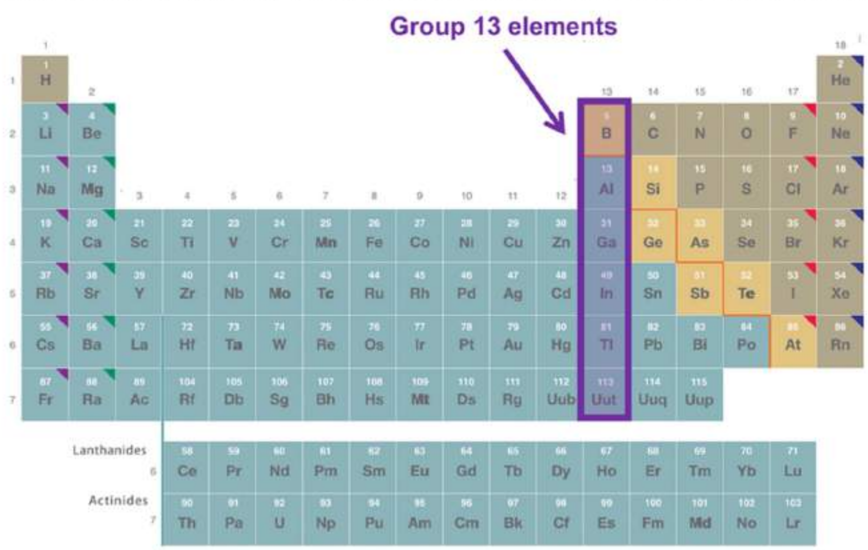
The group 13 elements are the first group in the p-block of the periodic table.

All the elements of group 13 are also called the boron family. The periodic table is segregated into s, p, d and f-blocks. This segregation is done based on the valence electron, if the valence electron falls on the p subshell, it comes in p-block and so on.

The members of Group 13 elements are:

- Boron
- Aluminium
- Gallium
- Indium
- Thallium

The general electronic configuration for the group 13 elements is ns^2np^1. Al is the most abundant metal and third most abundant element in the earth's crust.



General Physical Properties of Group 13 Elements:

- **Electronic Configuration**

  Their valence shell electronic configuration is ns^2np^1.

Electronic Configuration

Boron (5) – [He] $2S^2$ $2P^1$

Aluminium (13) – [Ne] $3S^2$ $3P^1$

Gallium (31) – [Ar] $3d^{10}$ $4S^2$ $4P^1$

Indium (49) – [Kr] $4d^{10}$ $5S^2$ $5P^1$

Thallium (81) – [Xe] $4f^{14}$ $5d^{10}$ $6S^2$ $6P^1$

- **Atomic Radii and Ionic Radii**

  Group 13 elements have a smaller size than those of alkaline earth metals due to greater effective nuclear charge, Z_{eff}.

  Atomic radii increase on going down the group with an anomaly at gallium (Ga). An unexpected decrease in the atomic size of Ga is due to the presence of electrons in d-orbitals which do not screen the attraction of the nucleus effectively. The ionic radii regularly increase from B^{3+} to TI^{3+}.

- **Density**

  It increases regularly on moving down the group from B to Tl.

- **Melting and Boiling Points**

  The Melting point and boiling point of group 13 elements are much higher than those of group 2 elements. The melting point decreases from B to Ga and then increases, due to structural changes in the elements.

  Boron has a very high melting point because of its three-dimensional structure in which B atoms are held together by strong covalent bonds. The low melting point of Ga is due to the fact that it consists of Ga_2 molecules, and Ga remains liquid upto 2276 K. Hence, it is used in a high-temperature thermometer.

- **Ionisation Enthalpy (IE)**

  The first ionisation enthalpy values of group 13 elements are lower than the corresponding alkaline earth metals, due to the fact that removal of the electron is easy. [ns^2 np^1 configuration] .

  On moving down the group, IE decreases from B to Al, but the next element Ga has a slightly higher ionisation enthalpy than Al due to the poor shielding of intervening d-electrons. It again decreases in In and then increases in the last element Tl.

- **Oxidation States**

  B and Al show an oxidation state of +3 only while Ga, In and Tl exhibit oxidation states of both +1 and +3.

  As we move down in group 13, due to the inert pair effect the tendency to exhibit +3 oxidation state decreases and the tendency to attain +1 oxidation state increases. Stability of +1 oxidation state follows the order Ga < In < Tl.

  Inert pair effect is the reluctance of the s-electrons of the valence shell to take part in bonding. It occurs due to poor shielding of the ns^2 – electrons by the intervening d and f – electrons. It increases down the group and thus, the lower elements of the group exhibit lower oxidation states.

- **Electropositive (metallic) Character**

  These elements are less electropositive than the alkaline earth metals due to their smaller size and higher ionisation enthalpies.

  On moving down the group, the electropositive character first increases from B to Al and then decreases from Ga to Tl, due to the presence of d and f-orbitals which causes poor shielding.

- **Reducing Character**

  It decreases down the group from Al to Tl because of the increase in electrode potential value for M^{3+} / M.

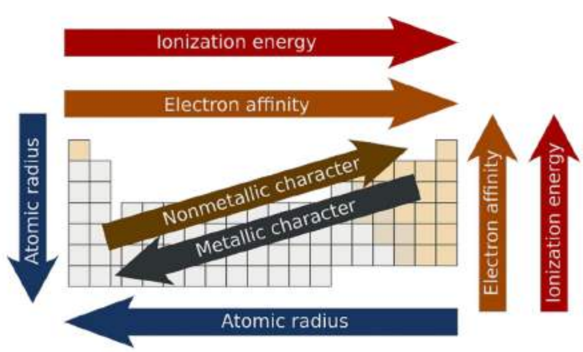
  Therefore, it follows the order: AI > Ga > In > Tl

- **Complex Formation**

  Due to their smaller size and greater charge, these elements have a greater tendency to form complexes than the s-block elements.

- **Nature of Compounds**

  The tendency of the formation of ionic compounds increases from B to Tl. Boron forms only covalent compounds whereas Al can form both covalent as well as ionic compounds. Gallium forms mainly ionic compounds, although anhydrous $GaCI_3$ is covalent.



Chemical Properties of 13 Group Elements

- **Action of Air**

  Crystalline boron is unreactive whereas amorphous boron is reactive. It reacts with air at 700°C as follows-

  $4B + 3O_2 \rightarrow 2B_2O_3$

  $2B + N_2 \rightarrow 2BN$

  Al is stable in air due to the formation of the protective oxide film.

  $4Al + 3O_2 \rightarrow 2Al_2O_3$

  Thallium is more reactive than Ga and In due to the formation of unipositive ion, Tl^+.

  $4Tl + O_2 \rightarrow 2Tl_2O$

- **Reaction with Nitrogen**

  $$2B + N_2 \xrightarrow{\Delta} \underset{\text{boron nitride}}{2BN}$$

  $$2Al + N_2 \xrightarrow{\Delta} \underset{\text{aluminium nitride}}{2AlN}$$

- **Action of Water**

  Both B and Al do not react with water but amalgamated aluminium reacts with H_2O evolving H_2.

  $2Al\ (Hg) + 6H_2O)\ 2AI(OH)_3 + 3H_2 + 2Hg$

  Ga and In do not react with pure cold or hot water but Tl forms an oxide layer on the surface.

- **Reaction with Alkalies**

  Boron dissolves in alkalies and gives sodium borates.

  $$2B + 6NaOH \xrightarrow{\text{Fusion}} 2Na_3BO_3 + 3H_2$$

  Aluminium also reacts with alkali and liberates hydrogen.

  $$2Al(s) + 2NaOH(aq) + 6H_2O(l) \longrightarrow \underset{\text{[sodium tetrahydroxo aluminate (III)]}}{2Na^+[Al(OH)_4]^-(aq)} + 3H_2(g)$$

• **Reaction with Carbon**

$$4B + C \xrightarrow{\Delta} \underset{\text{boron carbide}}{B_4C}$$

$$4Al + 3C \longrightarrow \underset{\text{aluminium carbide}}{Al_4C_3}$$

Aluminium carbide is ionic and forms methane with water.

• **Hydrides**

Elements of group 13 do not combine directly with H_2 to form hydrides, therefore their hydrides have been prepared by indirect methods, e.g

$$4BF_3 + 3LiAlH_4 \xrightarrow{\text{Dry ether}} \underset{\text{diborane}}{2B_2H_6} + 3LiF + 3AlF_3$$

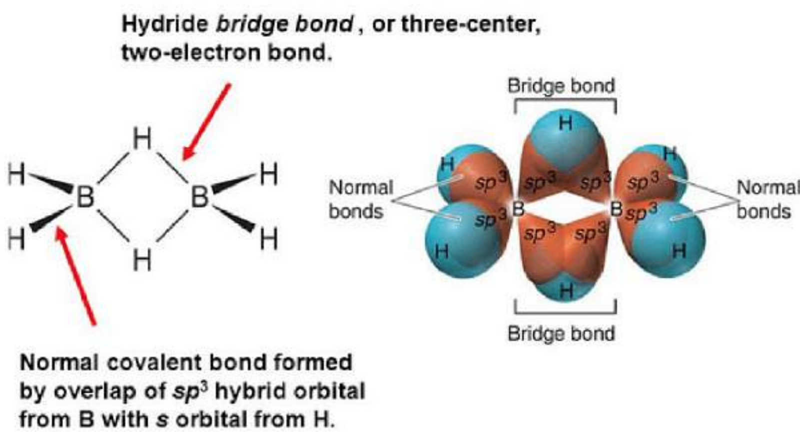
Boron forms a number of hydrides, they are known as boranes. Boranes catch fire in the presence of oxygen $B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$; & $\Delta_cH° = -1976\ kJ\ mol^{-1}$

Boranes are hydrolysed by water.

$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$

Boranes are stable but the stability of hydrides of Al, Ga, In, and Tl decreases on moving down the group because the strength of the M-H bond decreases.

Structure of diborane: BH_3 does not exist as such, but exists as a dimer, i.e; B_2H_6(diborane].



Diborane

In the above structure, B atoms are in sp^3 – hybrid state. There are six B-H bonds out of which four B-H bonds are normal bonds present in the same plane while rest two B-H bonds behave as bridge bonds, ie; 3c – 2e (three centre-two electrons, also known as a banana bond) and present above and below the plane of the molecules which do not have a sufficient number of electrons to form covalent bonds.
Aluminium (Al) forms a polymeric hydride of general formula $(AlH_3)_x$ which decomposes into its elements on heating.

- **Oxides**

  Except for Tl, all the elements of group 13 form oxides or general formula M_2O_3 on heating with oxygen.

$$4M + 3O_2 \xrightarrow{\Delta} 2M_2O_3$$

Tl forms thallium (l) oxide. Tl_2O is more stable than thallium (III) oxide Tl_2O_3 due to the inert pair effect.

- **Nature of Oxides and Hydroxides**

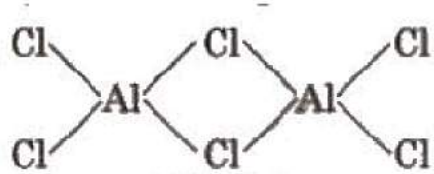
  $B(OH)_3$ or H_3BO_3 is soluble in water, while other hydroxides are insoluble in water.
  On moving down the group, there is a change from acidic to amphoteric and then to the basic character of oxides and hydroxides or group 13 elements.

- **Halides**

  All the elements of the boron family (except Tl) form trihalides of type MX_3.

$$2B + 3X_2 \xrightarrow[\Delta]{} 2BX_3$$
$$B_2O_3 + 3C + 3Cl_2 \longrightarrow 2BCl_3 + 3CO$$
$$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO$$

All the boron trihalides [(BX_3) and aluminium trihalides AlX_3 (except AlF_3 which is ionic) are covalent compounds. AlX_3 exists as a dimer while BX_3 is a monomer because the boron atom is too small to coordinate with four large halide ions. The energy released during the formation of the bridge structure is not sufficient for the cleavage of the typical pπ – pπ bond in BF_3.



$[Al_2Cl_6]$

BF_3 is a colourless gas, BCl_3 and BBr_3 are colourless fuming liquids and BI_3 is a white solid at room temperature.
Trihalides of group 13 elements behave as Lewis acids because of their strong tendency to accept a pair of electrons. The relative strength of Lewis acids of boron trihalides is: **$BF_3 < BCI_3, < BBr_3, < BI_3$.**

This is due to pπ – pπ back bonding in BF_3 which makes it less electron deficient.

The halides of group 13 elements behave as Lewis acids and the acidic character is $BX_3 > AIX_3 > GaX_3 > InX_3$ (where, X = Cl, Br or I)
$TICI_3$ decomposes to TICl and Cl_2 and hence acts as an oxidising agent.

$$TlCl_3 \xrightarrow{\Delta} TlCl + Cl_2$$

Anomalous Behaviour of Boron

Boron shows anomalous behaviour with the other members of the group, due to the following reasons:

- The smallest size in the group.
- High ionisation energy.
- Highest electronegativity in the group.
- Absence of vacant d-orbital.

Few Points of Difference

- It is non-metal while other members of the group are metallic.
- It shows allotropy while other members do not.
- It has the highest melting point and boiling point in group 13.
- It forms only covalent compounds while other members form both ionic and covalent compounds.

- The halides of boron exist as monomers while $AlCl_3$ exists as a dimer.
- The oxides and hydroxides of boron are weakly acidic while those of aluminium are amphoteric and those of other elements are basic.
- It can be oxidised by concentrated HNO_3 while aluminium becomes passive due to the formation of an oxide layer on the surface.

$$2B + 6HNO_3 \longrightarrow \underset{\text{boric acid}}{2H_3BO_3} + 6NO_2$$

Diagonal Relationship between Boron and Silicon

Boron exhibit resemblance with its diagonal element silicon of group 14.

- Both Band Si are non-metals.
- Both are semi-conductors.
- Both Band Si form covalent hydrides, i.e.. boranes and silanes respectively.
- Both form covalent, and volatile halides which fume in moist air due to the release of HCI gas.
  $BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$
  $SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$

Boron and Its Compounds

Occurrence

It does not occur in a free state. Its important minerals are

- Borax (or Tineal), $Na_2B_4O_7 * 10H_2O$
- Kernite, $Na_2B_4O_7 * 4H_2O$
- Orthoboric acid, H_3BO_3

Isolation
Elemental boron is obtained by the following methods:

- By reduction of boric oxide with highly electropositive metals like K, Mg, AI, Na etc, in the absence of air.

$$2B + 6HNO_3 \longrightarrow \underset{\text{boric acid}}{2H_3BO_3} + 6NO_2$$

- By the reaction of boron halides with hydrogen.

$$2BCl_3 + 3H_2 \xrightarrow{1270K} 2B + 6HCl$$

Uses of Boron

- As a semi-conductor.
- Boron steel rods are used to control nuclear reactions.

  ${}_5B^{10} + {}_0n^1 \rightarrow {}_5B^{11}$

Compounds of Boron

- **Borax or Sodium Tetraborate Decahydrate [$Na_2B_4O_7.10H_2O$]**

  Preparation

  It occurs naturally as tineal in dried up lakes. It is obtained by boiling mineral colemanite with a solution of Na_2CO_3.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3 + 2NaBO_2 + \underset{\text{borax}}{Na_2B_4O_7}$$

  $NaBO_2$ can be removed by passing CO_2 through it.

  $4NaBO_2 + CO_2 \rightarrow Na_2CO_3 + Na_2B_4O_7$

  Properties

  (i) Its aqueous solution is basic in nature.

  $Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$

  (ii) On heating with ethyl alcohol and conc. H_2SO_4. It gives volatile vapours of triethyl borate which burn with a green flame.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$

$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\text{triethylborate}}{B(OC_2H_5)_3} + 3H_2O$$

  (iii) Action of heat:

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow[-10H_2O]{\text{Heat, swells}}$$

$$Na_2B_4O_7 \xrightarrow{\Delta} \underbrace{\underset{\text{sodium metaborate}}{2NaBO_2} + \underset{\text{boric anhydride}}{B_2O_3}}_{\text{glassy bead}}$$

  Borax bead is used for the detection of coloured basic radicals under the name borax bead test e.g.,

$$CoSO_4 \xrightarrow{\Delta} CoO + SO_3;$$

$$CoO + B_2O_3 \longrightarrow Co(BO_2)_2$$

cobalt metaborate (blue)

Basic radical or salt	Fe	Cr	Ni
Colours of borax bead	Green	Green	Brown

• **Boric Acid or Orthoboric Acid [H_3BO_3 or $B(OH)_3$]**

Preparation

By treating borax with dil. HCl or dil. H_2SO_4.

$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3$

Properties

(i) It is a weak monobasic acid (Lewis acid).

$H_3BO_3 + 2H_2O \rightarrow [B(OH)_4]^- + H_3O^+$

(ii) With C_2H_5OH and cone H_2SO_4, it gives triethyl borate.

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} B(OC_2H_5)_3 + 3H_2O$$

(iii)

Heating Effect:

$$\underset{\text{orthoboric acid}}{H_3BO_3} \xrightarrow{273\text{ K}} \underset{\text{metaboric acid}}{HBO_2} \xrightarrow{473\text{ K}} \underset{\text{tetraboric acid}}{H_2B_4O_7} \xrightarrow[\text{hot}]{\text{Red}} \underset{\text{boron trioxide (Boric anhydride)}}{B_2O_3}$$

Uses

It is used as an antiseptic and eye lotion under the name 'boric lotion', and as a food preservative.

• **Borazine or Borazole, [$B_3N_3H_6$]**

It is a colourless liquid having a six-membered ring of alternating B and N atoms. It is also called 'inorganic benzene'. It is prepared by B_2H_6 as follows:

$$3B_2H_6 + 6NH_3 \xrightarrow{\Delta} 2B_3N_3H_6 + 12H_2$$

1 : 2

The π electrons in borazine are only partially delocalised. It is more reactive than benzene.

Compounds of Aluminium

• **Anhydrous Aluminium Chloride [$AlCl_3$ or Al_2Cl_6]**

Preparation

O.

$$2AlCl_3 \cdot 6H_2O \xrightarrow{\Delta} 2Al(OH)_3 + 6HCl$$

$$2Al(OH)_3 \xrightarrow{\text{Heat}} Al_2O_3 + 3H_2O$$

(ii) By passing dry chlorine or HCl gas over heated Al.

$$2Al + 3Cl_2 \xrightarrow{\text{Heat}} 2AlCl_3$$

$$2Al + 6HCl \xrightarrow{\text{Heat}} 2AlCl_3 + 3H_2$$

(iii) By heating a mixture of alumina and carbon in a current of dry chlorine.

$$Al_2O_3 + 3C + 3Cl_2 \xrightarrow{\Delta} 2AlCl_3 + 3CO$$

Properties

(i) $AlC1_3$ fumes in moist air due to hydrolysis.

$AlC1_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCI$

(ii) It behaves as Lewis acid.

Uses

It is used as a catalyst in Friedel-Craft reaction and as a mordant dye.

• **Aluminium Oxide or Alumina [AI_2O_3]**

It is the most stable compound of aluminium and occurs in nature as colourless corundum and several coloured oxides, (it present in combination with different metal oxides) like ruby (red), topaz (yellow), sapphire (blue), and emerald (green), which are used as precious stones (gems).

Alum:

The term alum is given to double sulphates of the type X_2SO_4 * $Y_2(SO_4)_3$ * $24H_2O$ where, X represents a monovalent cation such as Na^+, K^+ and $NH^+{}_4$, while Y is a trivalent cation such a Al^3,Cr^{3+}, Fe^{3+} and Co^{3+}(Li^+ does not form alum).

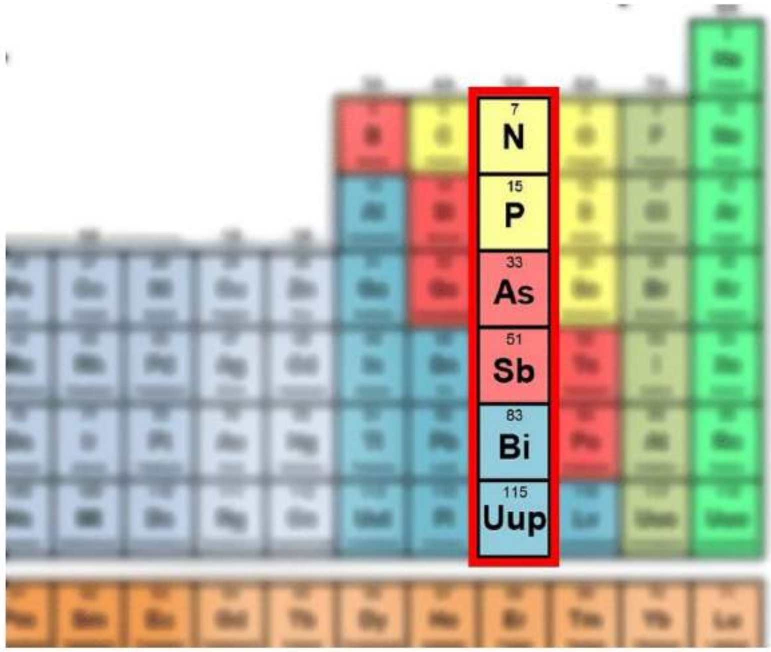
Fig: Potash Alum

Some important alums are:
(i) Potash alum $K_2SO_4 * Al_2(SO_4)_3 * 24H_2O$
(ii) Sodium alum $Na_2SO_4 * A1_2(SO_4)_3. 24H_2O$
(iii) Ammonium alum $(NH_4)_2SO_4 * AI_2(SO_4)_3 24H_2O$
(iv) Ferric alum $(NH_4)_2SO_4 * Fe_2(SO_4)_3 24H_2O$
Potash alum is prepared in the laboratory by mixing hot equimolar quantities of K_2SO_4 and $Al_2(SO_4)_3$. The resulting solution on concentration and crystallisation gives potash alum.
Note:
(i) A mixture of Al powder NH_4NO_3 is called ammonal and is lUed in bombs.
(ii) Al is the chief constituent of silver paints.
(iii) $A1_2(SO_4)_3$ 1.8 used for making fireproof clothes.

Group-15 Elements: Nitrogen Family

What are Group 15 Elements?

Group 15 elements are also called the Nitrogen family includes nitrogen phosphorus, arsenic, antimony and bismuth elements. The p-block elements are also known as the Representative Elements which is placed on the right side of the main periodic table. The 15 group of the Periodic Table consists of **nitrogen, phosphorus, arsenic, antimony and bismuth**. These elements are known as pnicogens and their compounds as **pniconides**.



Physical Properties of Group 15 Elements

1. **Electronic configuration:** Their valence shell electronic configuration is $ns^2\ np^3$

Element	Electronic configuration
N	$[He]2s^22p^3$
P	$[Ne]3s^23p^3$
As	$[Ar]3d^{10}4s^24p^3$
Sb	$[Kr]4d^{10}5s^25p^3$
Bi	$[Xe]4f^{14}5d^{10}6s^26p^3$

1. **Metallic character:** N and P are non-metals, As and Sb are metalloids and Bi is metal.
2. **Physical state:** Nitrogen is the first element after hydrogen which is diatomic gas in native form. All other elements in the group are solids.
3. **Atomicity:** N_2 is diatomic while others are triatomic.
4. **Melting and boiling points:** The melting point increases from nitrogen to arsenic. The boiling points increase regularly on moving down the group.

5. **Density:** It increases down the group.
6. **Atomic radii:** It increases with an increase in atomic number as we go down the group.
7. **Allotropy:** All the elements (except Bi) exhibit allotropy. Nitrogens – α nitrogen, β – nitrogen.
   Phosphorus – White, red, black
   Arsenic – Grey, yellow, black
   Antimony – Metallic yellow (explosive)
8. **Oxidation state:**

N	P	As	Sb	Bi
−3 to +5	−3, +3, +4, + 5	+3, + 5	+3, + 5	+3, + 5

Nitrogen has a wide range of oxidation states. The stability of the +3 oxidation state increases and the stability of the +5 oxidation state decreases on moving down the group due to the inert pair effect.

1. **The ionization enthalpy:** The Ionisation energy of nitrogen is very high due to its small size and half-filled highly stable configuration. The ionization energy decreases down the group.
2. **Electronegativity:** It decreases from nitrogen to bismuth.
3. **Catenation:** 'They exhibit the property of catenation but to a lesser extent due to weak E – E bond than 14 group elements.
4. **Reactivity:** Elemental nitrogen is highly unreactive because of its strong triple bond. (almost as inert as noble gases). White phosphorus is extremely reactive and is kept in water. It is inflammable and can be ignited at 45°C.

Atomic and Physical Properties of Group 15 Elements

Property		N	P	As	Sb	Bi
Atomic number		7	15	33	51	83
Atomic mass/g mol^{-1}		14.01	30.97	74.92	121.75	208.98
Electronic configuration		$[He]2s^2 2p^3$	$[Ne]3s^2 3p^3$	$[Ar]3d^{10} 4s^2 4p^3$	$[Kr]4d^{10} 5s^2 5p^3$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^3$
Ionisation enthalpy	I	1402	1012	947	834	703
($\Delta_i H$/(kJ mol^{-1})	II	2856	1903	1798	1595	1610
	III	4577	2910	2736	2443	2466
Electronegativity		3.0	2.1	2.0	1.9	1.9
Covalent radius/pm[a]		70	110	121	141	148
Ionic radius/pm		171[b]	212[b]	222[b]	76[c]	103[c]
Melting point/K		63[*]	317[d]	1089[e]	904	544
Boiling point/K		77.2[*]	554[d]	888[f]	1860	1837
Density/[g cm^{-3}(298 K)]		0.879[g]	1.823	5.778[h]	6.697	9.808

Chemical Properties of Group 15 Elements:

1. **Hydrides:** All the elements of this group form hydrides of the type EH_3, which are covalent and pyramidal in shape. Some properties follow the order as mentioned:

NH_3	>	PH_3	>	AsH_3	>	SbH_3	>	BiH_3
ammonia		phosphine		arsine		stibine		bismuthine

1. **These properties are:**
   (i). Thermal stability,
   (ii). Basic strength,
   (iii). Solubility in water,
   (iv). Bond angle NH_3 (107.4°); PH_3 (92°),AsH_3 (91°), SbH_3(90°),
   (v). Strength of M – H bond

   Some properties follow the order: $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
   These properties are -
   (i). Reducing character
   (ii). Covalent character
   (iii). Rate of combustion
2. **Halides:** All the elements of this group form trihalides, MX_3 and except nitrogen all form pentahalides, MX_5, e.g., NCi_3, NI_3, PCI_3, $BiCI_3$, $AsCI_3$, PCl_5 etc. Trihalides (except of N) behaves as Lewis acid and the order of their strength is $PCl_3 > AsCl_3 > SbCl_3$. Trihalides of N behave as Lewis base and has the following order of strength-$NF_3 < NCl_3 < NBr_3 < NI_3$. NCl_3 is an explosive compound.
3. **Oxides:** All the elements of this group form oxides of the type M_2O_3 and M_2O_5.

Oxidation State	Oxides				
	N	P	As	Sb	Bi
+1	N_2O Nitrous oxide	-	-	-	-
+2	NO Nitric oxide	-	-	-	-
+3	N_2O_3 Dinitrogen trioxide	P_4O_6	As_4O_6	Sb_4O_6	Bi_2O_3
+4	N_2O_4 Dinitrogen tetroxide	-	-	-	-
+5	N_2O_5 Dinitrogen pentoxide	P_4O_{10}	As_4O_{10}	Sb_4O_{10}	⊗

1. N_2O_5 and N_2O_4 are strongly acidic, whereas, NO and N_2O are neutral.
   P_4O_{10} is also strongly acidic.
   As_4O_6 is called white arsenic and is a poison.
   The acidic strength of pentoxides and trioxides decrease on moving down the group, i.e., $N_2O_5 > P_2O_5 > As_2O_5 > Sb_2O_5$.
   BiOCl is called pearl white.

Nitrogen and its Compounds:

1. **Dinitrogen** (N_2)
   Preparation:

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

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$$

$$Ba(N_3)_2 \longrightarrow Ba + 3N_2 \quad \text{(pure nitrogen)}$$

Properties:

(i). Nitrogen does not react with alkali metals except Li but reacts with alkaline earth metals to give metal nitride.

$$6Li + N_2 \xrightarrow{\text{Heat}} 2Li_3N$$

$$3Mg + N_2 \xrightarrow{\text{Heat}} Mg_3N_2$$

(ii). Reaction with oxygen.

$$N_2(g) + O_2(g) \underset{}{\overset{2000\text{ K}}{\rightleftharpoons}} 2NO(g)$$

(iii). Reaction with non-metals.

$$2B + N_2 \xrightarrow{\text{Heat}} 2BN$$

(iv). Reaction with CaC_2.

$$CaC_2 + N_2 \xrightarrow{1273\ K} \underbrace{CaCN_2}_{\text{nitrolim}} + C$$

Uses:

Liquid N_2 is used as a refrigerant. N_2 is used in the manufacture of HNO_2, NH_2, $CaCN_2$(calcium cyanamide) and other nitrogenous compounds. It is used for filling electric bulbs.

Ammonia (NH_3)

Preparation:

(i) **Lab method:** $2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O$
(ii) **Haber's process**

$$N_2 + 3H_2 \xrightarrow[\text{Low temperature, high pressure}]{Fe/Mo} 2NH_3$$

(iii) $AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$

(iv) $NH_2CONH_2 \xrightarrow[2H_2O]{} 2NH_3 + H_2O + CO_2$

Properties:

(i). It is a colourless gas with a characteristic pungent odour. It is extremely soluble in water due to H – bonding.
(ii). It is a strong Lewis base and used in the metal ion detection as-

$$\underset{\text{[blue]}}{Cu^{2+}(aq)} + 4NH_3(aq) \longrightarrow \underset{\text{[deep blue]}}{[Cu(NH_3)_4]^{2+}}$$

$$Ag^+(aq) + Cl^-(aq) \longrightarrow \underset{\text{(white ppt)}}{AgCl(s)}$$

$$AgCl(s) + 2NH_3(aq) \longrightarrow \underset{\text{soluble}}{[Ag(NH_3)_2]}Cl(aq)$$

3. Reaction with chlorine:

When NH_3 is in excess, N_2 is the main product.

$8NH_3 + 3Cl_2 \rightarrow 6NH_4Cl + N_3$

When Cl_2 is in excess, NCl_3 is the main product.
$NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$

4. Reaction with Nessler's reagent:

$$NH_3 + \underbrace{2K_2HgI_4 + 3KOH}_{\text{Nessler's reagent}} \longrightarrow$$

Uses:

It is used as a refrigerant and to produce various nitrogenous fertilizers.

Table : Oxides of Nitrogen

Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N_2O	+ 1	$NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$	colourless gas, neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+ 2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	colourless gas, neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	N_2O_3	+ 3	$2NO + N_2O_4 \xrightarrow{250K} 2N_2O_3$	blue solid, acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO_2	+ 4	$2Pb(NO_3)_2 \xrightarrow{673K} 4NO_2 + 2PbO$	brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N_2O_4	+ 4	$2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$	colourless solid/ liquid, acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	N_2O_5	+5	$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$	colourless solid, acidic

NO_2 contains an odd number of valence electrons. On dimerisation, it is converted to a stable N_2O_4 molecule with an even number of electrons.

2. **Nitric acid (HNO_3):** It is a stronger acid than H_3PO_4.
   Preparation:
   (i) Lab method: $NaNO_3 + H_2SO_4$ (conc.) $\rightarrow NaHSO_4 + HNO_3$
   (ii) Ostwald's process

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

$$2NO + O_2 \rightleftharpoons 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

Physical properties: It is a syrupy, colourless, pungent liquid usually available as 68 % and 15.7 M aqueous solution is often yellow due to small concentrations of NO_2.

Chemical reactions:

(i). Action of nitric acid on zinc under different conditions:

Cold and dil HNO_3

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$$

Cold and concentrated HNO_3

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

(ii). Action of nitric acid on copper under different conditions:

Cold and dil. HNO_3

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$

Cold and concentrated HNO_3

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

(iii). Reaction with non-metals:

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

$$C + 4HNO_3 \longrightarrow CO_2 + 2H_2O + 4NO_2$$

$$S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

(iii). Reaction with non-metals:

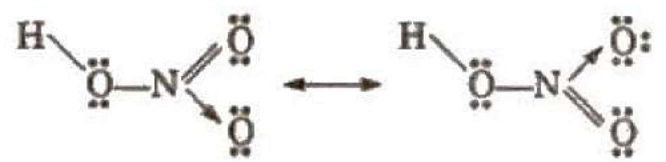
$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$
$$C + 4HNO_3 \longrightarrow CO_2 + 2H_2O + 4NO_2$$
$$S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$
$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

(iv). Brown ring test of nitrate:

$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$
$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{[brown]}}{[Fe(H_2O)_5NO]^{2+}} + H_2O$$

(v). Metals like Fe. Cr. Ni, AI or Co becomes inactive or passive due to stable oxide layers.

Structure of nitric acid:

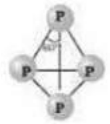


Uses: It is used
1.In the manufacturing of fertilizers.
2. For purification of silver and gold.
3. In the manufacturing of explosives and as oxidising agent.
4. As nitrating reagent.

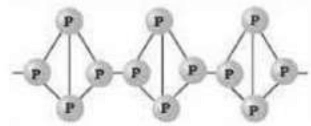
Phosphorus & its Compounds Allotropic Forms

- White phosphorus
- Red phosphorus
- Black phosphorus

Some Points of Distinction Between White and Red Phosphorus



White phosphorus



Red phosphorus

SL No.	Property	White Phosphorous	Red Phosphorous
1	Physical State	Soft Waxy Solid	Brittle Powder
2	Odour	Garlic	Odourless
3	Melting Point	317 K	Sublimes in absence of air at 563 K
4	Solubility in Water	Insoluble	Insoluble
5	Solubility in CS_2	Soluble	Insoluble
6	Stability	Unstable	Stable
7	Chemical Activity	Very Active	Less Active
8	Ignition Temperature	303 K (Low)	543 K (High)
9	Physiological Action	Poisonous	Non-poisonous
10	Phosphorescence	Glows in the dark	Does not glow in the dark

Black phosphorus is formed when red phosphorus is heated in a sealed tube at 803 K. It does not oxidise in air.
Matchbox side contains red P or P_2S_3+ glue and on tip of a match stick. red P, $KClO_3$ chalk and glue is deposited.

Chemical properties:

1. **With non-metals:**

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

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

2. $$P_4 + 10Cl_2 \longrightarrow 4PCl_5$$

3. **With compounds:**

$$P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{sodium hypophosphite}}{3NaH_2PO_2} + PH_3$$

$$P_4 + 20HNO_3 \longrightarrow \underset{\text{orthophosphoric acid}}{4H_3PO_4} + 4H_2O + 20NO_2$$

Uses
It is used in matchboxes, explosives, as rat poison, in fertilizers and alloys
Compounds of Phosphorous

1. **Phosphine (PH_3)**
   Preparation It is prepared by following methods:

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$
$$Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$$
$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$$
$$PH_4I + KOH \longrightarrow KI + H_2O + PH_3$$

Properties

(i). It is a colourless gas with a rotten fish-like smell and is highly poisonous. It explodes in contact with traces of oxidising agents like HNO_3, Cl_2 and Br_2 vapours.

$3CuSO_4 + 2PH_3 \rightarrow CU_3P_2 + 3H_2SO_4$

$3HgCl_2 + 2PH_3 \rightarrow Hg_3P_2 + 6HCl$

(ii). Phosphine is weakly basic.

$PH_3 + HBr \rightarrow PH^+_4 + Br^-$

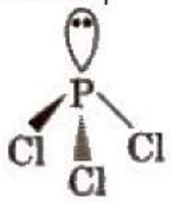
Uses: It is used to prepare smoke screens in warfare. A mixture of CaC_2 and Ca_3P_2 is used in Holme's signals.

1. **Phosphorus Trichloride (PCl_5)**
   Preparation:

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$
$$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

Properties: It is a colourless oily liquid having a pyramidal shape [sp^3 – hybridised].

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$
$$3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$$
$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$



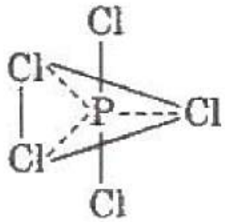
Structure of PCl_3

2. **Phosphorus Pentachloride (PCl_5)**
   Preparation:

$P_4 + 10\ Cl_2 \rightarrow 4\ PCl_5$

$P_4 + 10\ SO_2CI_2 \rightarrow 4PCl_5 + 10\ SO_2$

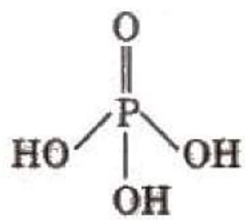
Structure: PCl_5 in gaseous and liquid phases has sp^3d – hybridization and its shape is trigonal-bipyramidal. The three equatorial P – Cl bonds are equivalent while the two axial bonds are longer equatorial bonds.



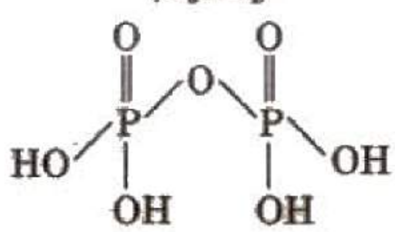
Properties: In solid-state, PCl_5 exists as an ionic solid, $[PCI_4]^+$ $[PCl_6]^-$ in which, the cation, $[PCI_4]^+$ is tetrahedral and the anion $[PCl_6]^-$ is octahedral.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$
$$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$$
$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$
$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$
$$2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3$$
$$Sn + 2PCl_5 \longrightarrow SnCl_4 + 2PCl_3$$

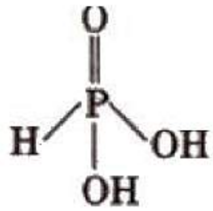
Oxoacids of Phosphorus:



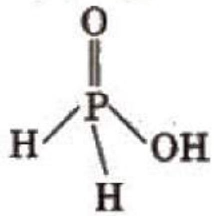
orthophosphoric acid
(H_3PO_4)



pyrophosphoric acid
($H_4P_2O_7$)



orthophosphorous acid
(H_3PO_3)



hypophosphorous acid
(H_3PO_2)

In toothpaste, $CaHPO_4 \cdot 2H_2O$ is added as a mild abrasive and polish agent.

Group-14: Carbon Family

What are Group 14 Elements?

The group 14 elements are the second group in the p-block of the periodic table. It is also called the carbon group. The members of this group are:

1. Carbon (C)
2. Silicon (Si)
3. Germanium (Ge)
4. Tin (Sn)
5. Lead (Pb)
6. Flerovium (Fl)

General Physical Properties of Group 14 Elements

1. **Electronic configuration:** Their valence shell electronic configuration is $ns^2\ np^2$.

Element	Atomic number	Electronic configuration
Carbon (C)	6	$[He]\ 2s^2\ 2p^2$
Silicon (Si)	14	$[Ne]3s^2\ 3p^2$
Germanium (Ge)	32	$[Ar]\ 3d^{10}, 4s^2\ 4p^2$
Tin (Sn)	50	$[Kr]\ 4d^{10}, 5s^2\ 5p^2$
Lead (Pb)	82	$[Xe]\ 4f^{14}, 5d^{10}, 6s^2\ 6p^2$

1. **Metallic character:** C and Si are non-metals,Ge is a metalloid and Sn and Pb are metals.
2. **Appearance:** C is black. Si is light-brown, Ge is greyish, Sn and Pb are silvery white.
3. **Density:** Density increases with an increase in atomic number due to an increase in mass per unit volume down the group.
4. **Melting points and Boiling points:** The melting points and boiling points decrease from carbon to lead but carbon and silicon have very high melting and boiling points due to their giant structure.
5. **Oxidation state:** They exhibit +2 and +4 oxidation state.
   The compounds of Pb in the +4 oxidation state are powerful oxidizing agents since the +2 oxidation state of Pb is more stable due to the **inert pair effect**.
   The compounds in the +2 oxidation state are ionic in nature and the + 4 oxidation state are covalent in nature (According to Fajan's rule).
6. **Ionisation enthalpy:** It decreases from C to Sn. For Pb, it is slightly higher than Sn.
7. **Electronegativity values:** The value decreases from C to Pb but not in a regular manner probably due to the filling of d-orbitals III and Sn and f-orbitals in Pb.
8. **Catenation:** The greater the strength of the element-element bond, the greater is the strength of catenation. $C >> Si > Ge = Sn > Pb$ (catenation).
9. **Allotropy:** All the elements of this group except Pb exhibit allotropy.
10. **Valency:** All elements exhibit tetra valency. In the case of carbon, 406 kJ mol^{-1} of energy is required for the promotion of 2s – electron to 2p. The formation of two extra bonds provides this energy.
11. **Atomic and ionic radii:** Both increase from C to Pb.

12. Multiple bonding Carbon forms pπ – pπ bonds with itself and with S, N and O. Other elements show a negligible tendency of this type due to their large size. Others form dπ – pπ multiple bonds.

Chemical Properties of Group 14 Elements

1. Hydrides:

- All members of the group form covalent hydrides. Their number and ease of formation decrease down the group.
- Hydrides of carbon are called hydrocarbons (alkanes, alkenes or alkynes).
- Hydrides of Si and Ge are known as silanes and germanes.
- The only hydrides of Sn and Pb are SnH_4 (stannane) and PbH_4 (plumbane).
- Their thermal stability decrease down the group.
- Their reducing character increases down the group.

2. Halides:

- All the elements give tetrahedral and covalent halides of the type MX_4 except $PbBr_4$, and PbI_4.
- Thermal stability: $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$
- Order of thermal stability with common metals: $MF_4 > MCl_4 > MBr_4 > MI_4$
- Except CX_4 other tetrahalides can be hydrolysed due to the presence of vacant d-orbitals.
  $SiX_4 + 2H_2O \rightarrow SiO_2 + 4HX$.
- Ease of hydrolysis: $SiX_4 > GeX_4 > SnX_4 > PbX_4$
- Except for C, other elements form dihalides of the type MX_2 which are all ionic and have higher melting points and boiling points, e.g., $SnCl_2$ is a solid whereas $SnCl_4$ is a liquid at room temperature.

Note:
$SnCl_2 . 5H_2O$ is called **bitter of tin** and is used as a mordant in dyeing.

3. Oxides:

- They form two types of oxides. mono-oxides of the type MO and dioxides of the type MO_2.
  Example: CO (neutral) and SiO, GeO, SnO, PbO(all basic)
  $$\underbrace{CO_2, SiO_2}_{\text{acidic}} \quad \underbrace{GeO_2, SnO_2 \text{ and } PbO_2}_{\text{amphoteric}}$$
- CO_2 is linear gas at ordinary temperature. Solid CO_2 is known as **dry ice** or **drikold**.

- SiO_2 is solid with a three-dimensional network in which Si is bonded to four oxygen atoms tetrahedrally and covalently. A mass of hydrated silica (SiO_2) formed from skeletons of minute plants, known as diatoms, is called **kieselguhr**. It is a highly porous material and is used in the manufacture of dynamite.

Carbon

- The amount of carbon present in the earth's atmosphere and its crust is very less. There is only 0.02% of carbon in the earth's crust. This carbon exists as minerals like coal, carbonates and hydrogen carbonates etc. 0.03 % of the carbon exists in the atmosphere of the earth as carbon dioxide.

- Carbon is of utmost importance for our existence and it finds extensive usage in chemistry.
- Because of its indisputable importance, chemistry has been divided into two branches:
  (a) Organic Chemistry: This deals with the various compounds containing carbon.
  (b) Inorganic Chemistry: This branch deals with compounds that do not have any carbon content.
- Free states (diamond. graphite, coal etc.) and combined states (oxides, carbonates, hydrocarbons etc.)

Anomalous Behaviour of Carbon

- Since most of the first members of a group have peculiar characteristics and properties. On similar grounds, even carbon behaves differently than the other members of the group. These properties of carbon are very unique.
- We can attribute this behaviour to carbon mainly due to:
  (i) Small size of the atom
  (ii) High electronegativity
  (iii) High ionization enthalpy
  (iv) Unavailability of d-orbital's

Unique Properties of Carbon

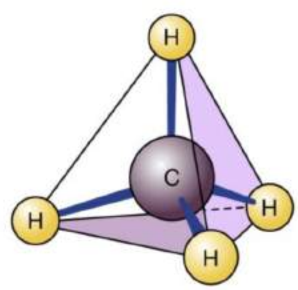
1. Small Size of Carbon

- Carbon derives a lot of its properties from its small size.

- The compounds that carbon forms are highly stable and this is also because of their small size. Due to its small size, the nucleus effectively holds on to the bonded and non-bonded electrons.

2. Tetravalency of Carbon

- Carbon exhibits tetravalency. It means it can share four electrons to complete its octet. Thus, we know it bonds to four different monovalent atoms.
- Carbon forms a large variety of compounds with oxygen, nitrogen, hydrogen, halogens. This results in a different set of compounds that have distinctive characteristics and properties.
- Carbon has the availability of only s and p orbitals. Therefore, it can hold only four pairs of electrons in its valence shell. Thus, we can restrict the covalence to four. However, the other elements in the group can easily grow their covalence due to the availability of d-orbitals.



3. Catenation

- One of the unique properties of Carbon is its ability to form long carbon chains. It implies that carbon attaches with other carbon atoms to form long carbon chains. This property is known as catenation. Sometimes, this chain could be as big as to have a total of 70-80 carbons.
- This gives rise to a variety of complex compounds. Some of the compounds have a straight carbon chain while some others have branched carbon chain or rings.
- The carbon compounds having only a single bond are saturated hydrocarbons. On the other hand, the compounds with the double or triple bond are unsaturated hydrocarbons.
- As we move down the group, the size of the elements increases. This results in decreasing electronegativity. Thus, the propensity to show

catenation also decreases. This can be clearly observed from bond enthalpy values.

- The catenation order: C >> Si > Ge >> Sn.

4. Electronegativity

- Additionally, carbon has an extraordinary capacity to shape pp – pp multiple bonds with itself and with different molecules. This can also be related to its smaller size and high electronegativity. Some of the examples would include C = C, C° C, C = O, C = S and C° N.
- As a matter of fact, the heavier elements don't shape pp – pp bonds. This is mainly because of the reason that their nuclear orbitals are too vast and diffused to have viable overlapping.
  Example: Lead does not indicate catenation.

Q. Give some practical uses of carbon.

Ans. There are many important uses of carbon. Some of them are:

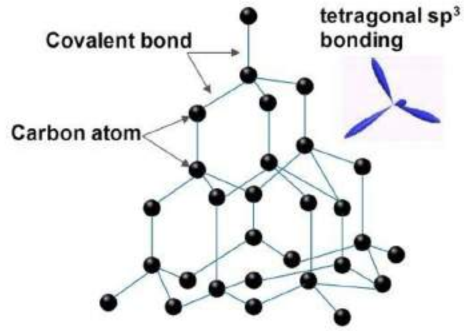
- We use impure carbon in the form of charcoal (from wood) and coke (from coal) in metal smelting.
- Graphite is a common use in pencils. We also use graphite to make brushes in electric motors and in furnace linings.
- Activated charcoal finds its usage in purification and filtration in respirators and kitchen extractor hoods.
- Industrial diamonds are a common tool for cutting rocks and drilling.

Allotropic Forms of Carbon

The crystalline forms include:

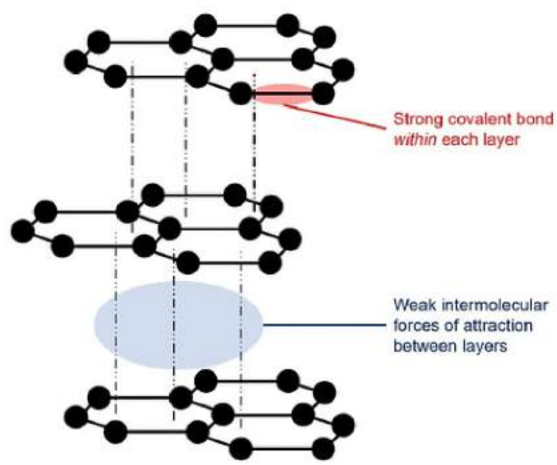
1. Diamond:

- It is the hardest and has a three-dimensional polymeric structure in which the hybridization of C is sp^3.
- It is a covalent solid.
- Melting point = 3650 °C
- Density = 3.51 g/cm^3
- Bad Conductor of heat and electricity



2. Graphite:

- It is dark grey having hexagonal plates, hybridization of each C is sp^2.
- It is a good conductor of heat and electricity due to the presence of free electrons.
- It was also known as the black lead.
- It is a very good lubricant.
- Aqua dag: Suspensions of graphite in water.
- Oil dag: Suspension of graphite in oil lubricants.



Structure of Graphite

3. Fullerenes:

- These are the only pure form of carbon.
- C_{60} molecule contains 12 five-membered rings and 20 six-membered rings.
- The five-membered rings are connected to six-membered rings while six-membered rings are connected to both five and six-membered rings.
- These are used in microscopic ball bearings, lightweight batteries, in the synthesis of new plastics and new drugs.

Amorphous forms of carbon are:

- **Coal:** The different forms of coal are peat (60 % C), lignite (70 % C), Bituminous (78 % C), Semi Bituminous (83 % C) and anthracite (90 % C). Bituminous is the most common variety of coal.
- **Coke** is obtained by the destructive distillation of coal.

$$\text{Coal} \xrightarrow{\text{DD}} \text{coke } (80° - 90\% \text{ C})$$

- **Charcoal or wood charcoal:** It is obtained by heating wood strongly in absence of air. When heated with steam, it becomes more activated. It is used to remove colouring matters and odoriferous gases.
- **Bone black or animal charcoal** It is obtained by destructive distillation of bones in iron retort. By-products are bone oil or pyridine. It is used as an adsorbent. On burning, it gives bone ash which is calcium phosphate and used in the manufacture of phosphorous and phosphoric acid.
- **Lamp-black** It is obtained by burning vegetable oils in a limited supply of air. It is used in the manufacture of printing ink, black paint, varnish and carbon paper.
- **Carbon-black** It is obtained by burning natural gas in a limited supply of air. It is added to a rubber mixture for making automobile tyres.

Gaseous Forms of Carbon

1. **Coal Gas:**
   Preparation: By destructive distillation of coal.
   Composition: H_2 = 45 – 55%, N_2 = 2 – 12%, CH_4 = 25 – 35%, CO_2 = 0 – 3%, CO = 4 – 11%, O_2 = 1 – 1.5%, Ethylene, acetylene, benzene, etc. = 3 – 5 %
   Uses: It is used as an illuminant, as fuel and to provide an inert atmosphere in the metallurgical processes.

2. **Natural Gas:**
   It is found along with petroleum below the surface of the earth.
   Composition: CH_4 = 60 – 80 %, Higher hydrocarbons = 2 – 12%, C_2H_6 = 5 – 10 %, C_3H_8 = 3 – 18 %
   Uses: It is used as a fuel. Its partial combustion yields carbon black (reinforcing agent for rubber).
3. **Oil Gas:**
   Preparation:

$$\text{Kerosene} \xrightarrow[\text{absence of air}]{\text{Heated in}} \text{Mixture of simple hydrocarbons}$$

1. **Uses:** It is used as fuel in laboratories in Bunsen burners.
2. **Wood-Gas:**
   Preparation: Destructive distillation of wood gives wood gas (CH_4, C_2H_6 H_2)
   Uses: It is used as fuel.
3. **Liquified Petroleum Gas (LPG):**
   Composition: n-butane + Iso-butane
   Uses: It is used as domestic fuel.
4. **Carbon Monoxide (CO):**
   Preparation:

$$\text{(i)}\ 2C(s) + O_2(g) \xrightarrow{\Delta} 2CO(g)$$

$$\text{(ii)}\ HCOOH \xrightarrow[\text{Conc. } H_2SO_4]{373\text{ K}} H_2O + CO$$

It is manufactured in the form of water and produces gas.

$$C(g) + H_2O(g) \xrightarrow[473\text{ K} - 1273\text{ K}]{} \underbrace{CO(g) + H_2(g)}_{\text{water gas}}$$

$$2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273\text{ K}} \underbrace{2CO(g) + 4N_2(g)}_{\text{producer gas}}$$

Properties:

(i) It is a colourless, odourless and almost water-insoluble gas.
(ii) It is a powerful reducing agent.
(iii) CO is used in the extraction of many metals from their oxide ores.

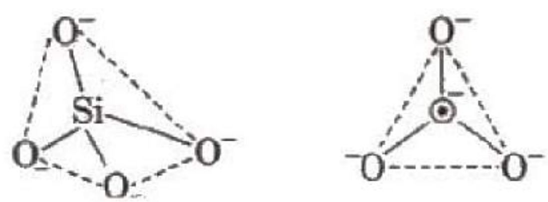
$$Fe_2O_3(s) + 3CO(g) \xrightarrow{\Delta} 2Fe(s) + 3CO_2(g)$$

$$ZnO(s) + CO(g) \xrightarrow{\Delta} Zn(s) + CO_2(g)$$

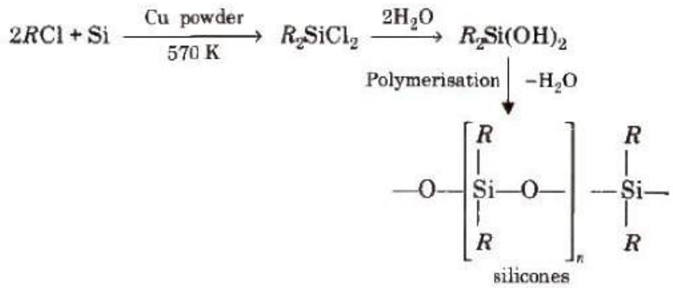
1. **Carbon Dioxide (CO_2):**
   Preparation:
   (i) $C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$
   (ii) $CH_4(g) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(g)$
   (iii) $CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$
   Properties:
   (i) It is a colourless and odourless gas.
   (ii) With water, it forms carbonic acid.
   $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$
   (iii) Photosynthesis
   $6CO_2 + H_2O \xrightarrow[\text{Chlorophyll}]{h\nu} C_6H_{12}O_6 + 6O_2 + 6H_2O$

Compounds of Silicon

1. **Silicates**
   Silicates are metal derivatives of silicic acid, H_2SiO_3 and can be obtained by fusing metal oxides or metal carbonates with sand. The basic structural unit of silicates is SiO_4^{4-}.



1. Mica (abrak) is naturally occurring aluminium silicate $[KH_2Al_3(SiO_4)_3$ or $KAl_3Si_3O_{10}(OH)_2$.
2. **Silicones**
   The linear, cyclic or cross-linked polymeric compounds containing (R_2SiO) as a repeating unit, are known as silicones. They are manufactured from alkyl-substituted chlorosilanes.



1. Silicones are chemically inert, water repellent, heat resistant, good electrical insulators. These are used as lubricants (vaseline), insulators etc
2. **Carborundum**It is the second hardest material known and has the formula SiC (silicon carbide). It is used as a high-temperature semiconductor, in transistor diode rectifiers.
3. **Glass**It is a transparent or translucent amorphous substance obtained by fusion of sodium carbonate (or sodium sulphate), calcium carbonate and sand (silica). It is not truly solid, so its melting point is not sharp. The general formula of glass is $Na_2O.CaO.6SiO_2$
   Coloured glasses are obtained by adding a certain substance to the molten mass.

Colour	Substance added
Blue	CoO
Green	Fe^{2+} and Cr
Yellow	Fe^{3+} uranate of sodium
Purple	MnO_2
Lemon-yellow	CdS
Red	CiO, selenium oxide
Amber	Organic matter and C
Ruby	$AuCl_3$

<u>Different Varieties of Glass:</u>

Glass type	Composition	Properties
Hard glass	K_2O-CaO.4SiO_2	Resistant to acid and chemicals
Flint glass	K_2O-PbO.4SiO_2	High refractive index so used in optical lenses and prisms
T Rex glass	Mixture of borosilicate of Pb, Ca and Na	Low coefficient of thermal expansion so can with stand sudden changes in temperature
Crookes glass	Contains CeO_2 along with general composition	Absorbs UV radiations so used In making goggles
Jena glass	Contains mixture of Zn and Ba borosilicates	Resistant to heat, shock, etc.
Quartz glass	Pure silica	Optical instruments (vitreous)

Glass is attacked by HF. This property is used in the **etching of glass**.

$$Na_2SiO_3 + 8HF \longrightarrow 2NaF + H_2SiF_6 + 3H_2O$$
$$CaSiO_3 + 8HF \longrightarrow CaF_2 + \underset{\text{hydrofluoro silicic acid}}{H_2SiF_6} + 3H_2O$$

Compounds of Lead

1. **Chrome yellow ($PbCrO_4$):**
   It is prepared by adding potassium chromate to lead chromate and is used as a yellow pigment under the name chrome yellow. On treating with alkali, it gives basic lead chromate or chrome red, $PbCrO_4.PbO$.
2. **Basic lead carbonate, $Pb(OH)_2.2PbCO_3$**
   It is also known as white lead and is prepared by adding sodium carbonate solution to any lead salt.
   $3Pb(NO_3)_2 + 3Na_2CO_3 + H_2O \rightarrow Pb(OH)_2.2PbCO_3 + 6NaNO_3 + CO_2$

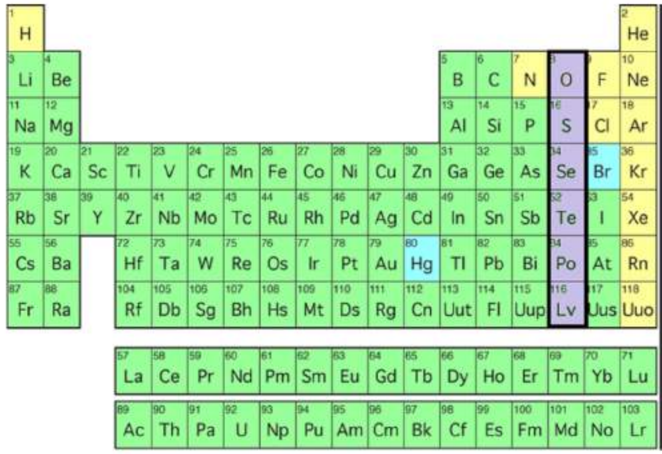
   It is used as white paint. The disadvantage of using white lead in paints is that it turns black by the action of H_2S of the atmosphere.

Note:
Lead poisoning is called plumbosolvency which increases in the excess of nitrates, organic acids and ammonium salts.

Group-16: Oxygen Family

What are Group 16 Elements?

The group 16 elements of the modern periodic table consist of 5 elements oxygen, sulphur, selenium, tellurium and polonium. The elements in this group are also known as the chalcogens or the ore-forming elements because many elements can be extracted from sulphide or oxide ores.
The name sulphur has been derived from Sanskrit word 'Sulvezi' meaning 'killer of copper'.



General Physical Properties of Group 16 Elements

1. **Electronic configuration:** Their valence shell electronic configuration is ns^2, np^4.

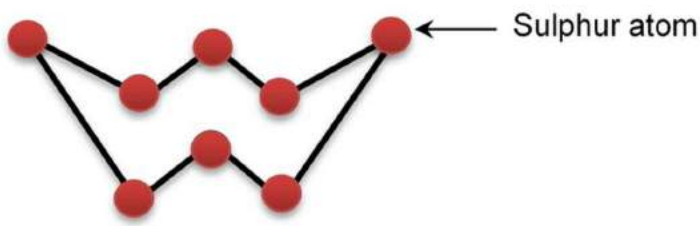
Element	Atomic number	Electronic configuration
Oxygen (O)	8	[He] $2s^2$ $2p^4$
Sulphur (S)	16	[Ne] $3s^2$ $3p^4$
Selenium (Se)	34	[Ar] $3d^{10}$, $4s^2$ $4p^4$
Tellurium (Te)	52	[Kr] $4f^{10}$, $5s^2$ $5p^4$
Polonium (Po)	84	[Xe] $4f^{14}$,$5d^{10}6s^2$ $6p^4$

2. **Metallic and non-metallic character:**

3. **Abundance:** O > S > Se > Te > Po
4. **Density:** It increases down the group regularly,
5. **Melting point and boiling point:** Both show a regular increase down the group due to an increase in molecular weight and Van der Waals' forces of attraction.
6. **Oxidation state:**

O	S	Se	Te	Po
-1,-2	-2 to +6	-2 to +6	-2 to +6	-2 to +6

7. In OF_2, the oxidation state of oxygen is +2.
8. **Ionisation energy:** They possess a large amount of ionisation energy which decreases gradually from O to Po due to an increase in the size of atoms and an increase in the screening effect.
9. **Electron affinity:** They have high electron affinity which decreases from O to Po. As the size of the atom increases, the extra added electron feels lesser attraction by the nucleus and hence, electron affinity decreases.
10. **Electronegativity:** It decreases down the group due to a decrease in effective nuclear charge down the group.
11. **Catenation:** Group 16 elements follow the order as shown below: S-S > Se-Se > O-O > Te-Te
12. **Atomicity:** Oxygen is diatomic, sulphur and selenium are octatomic with a puckered ring structure.



1. **Allotropy:** Allotropy or allotropism is the property of some chemical elements to exist in two or more different forms, in the same physical state, known as allotropes of the elements.
   - Oxygen – Dioxygen (O_2) and ozone (O_3)
   - Sulphur – Rhombic (01′ a) sulphur S_8
   - Monoclinic (or β) sulphur, S_8(most stable), plastic sulphur
2. **Atomic radii and ionic radii:** They increase regularly from O to Po.

Chemical Properties of Group 16 Elements:

1. **Hydrides:** All these elements form stable hydrides of the type H_2E. (Where E = O, S, Se, Te and Po).
   $2H_2 + O_2 \Leftrightarrow 2H_2O$
   $FeS + H_2SO_4 \rightarrow H_2S + FeSO_4$
   H_2O is a liquid due to hydrogen bonding, while others are colourless gases with an unpleasant smell.

[Down the group acidic character increases from H_2O to H_2Se. All the hydrides except water possess reducing property and this character increases from H_2S to H_2Te].

2. **Halides:** The stability of the halides decreases in the order: $\mathbf{F^- > Cl^- > Br^- > I^-}$Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. SF_6 is exceptionally stable for steric reasons.
   SF_4 is a gas, SeF_4 is a liquid and TeF_4 is solid. These fluorides have sp_3 d hybridization and see-saw geometry. They behave Lewis acid as well as Lewis base e.g.,
   $SF_4 + BF_3 \rightarrow SF_4 \rightarrow BF_3$
   $SeF_4 + 2F^- \rightarrow [SeF_6]^{2-}$
   The well known mono halides are dimeric in nature. Example are S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2. These dimeric halides undergo disproportion as given below:
   $2\ SeCl_2 \rightarrow SeCl_4 + Se$
3. **Oxides:** They form AO_2 and AO_3 type oxides. **Their acidic nature follow the order:** $SO_2 > SeO_2 > TeO_2 > PoO_2$ and $SO_3 > SeO_3 > TeO_3$
   Ozone is considered as oxides of oxygen.
   SO_2 is a gas having sps -hybridisation and V-shape.
   SO_3 is a gas that is sp^2-hybridised and planar in nature.
   SeO_2 is a volatile solid consist of non-planar infinite chains.
   SeO_3 has a tetrameric cyclic structure in solid-state. SO_2 and SO_3 are the anhydrides of sulphurous (H_2SO_3) and sulphuric acid (H_2SO_4) respectively.

Oxygen and its Compounds:

1. **Dioxygen:**
   Priestley and **Scheele** prepared oxygen by heating suitable oxygen compounds.
   Preparation: By action of heat on oxygen-rich compounds.
   (i) From oxides:

$$2HgO \xrightarrow{\Delta} 2Hg + O_2 \uparrow$$
$$2Ag_2O \longrightarrow 4Ag + O_2 \uparrow$$
$$2PbO_2 \longrightarrow 2PbO + O_2 \uparrow$$

(ii) From peroxides and other oxides:

$$2H_2O_2 \xrightarrow{MnO_2} 2H_2O + O_2$$

(iii) **From certain compounds:**

$$2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$$

$$2CaOCl_2 \longrightarrow 2CaCl_2 + O_2$$

Physical properties: It is colourless, odourless, tasteless, slightly heavier than air and sparingly soluble in water.

Chemical properties: On heating, it combines directly with metals and nonmetals, e.g.,

$$C + O_2 \longrightarrow CO_2$$

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

$$S + O_2 \longrightarrow SO_2$$

$$N_2 + O_2 \xrightarrow{3000°C} 2NO$$

$2Mg + O_2 \rightarrow 2MgO$

$4Na + O_2 \rightarrow 2\ Na_2O \rightarrow Na_2O_2$

Combination with O_2 is accelerated by using catalyst. Platinum is particularly an active catalyst.

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O$$

Uses: It is used in welding and cutting oxy-hydrogen or oxy-acetylene torch and in the iron and steel industry to increase the content of blast in the Bessemer and open-hearth process. It is also used for life support systems e.g., in hospitals, for divers, miners and mountaineers.

Tests:

1. With NO it gives reddish-brown fumes of NO_2.
2. It is adsorbed by alkaline pyrogallol.

1. **Ozone (O_3)**
   Preparation: Bypassing silent electric discharge through cold, dry oxygen in ozonised.
   Lab method: $3O_2 \Leftrightarrow 2O_3$; + 284.3 kJ

   Physical properties: It is pale blue gas with a characteristic strong smell. It is slightly soluble in water.

   Chemical reactions:
   1.Decomposition:

$$2O_3 \xrightarrow{573\,K} 3O_2;\ \Delta H = 284\ kJ/mol$$

2. **2. Oxidising action:**

$$O_3 \longrightarrow O_2 + [O]$$
$$PbS + 4[O] \longrightarrow PbSO_4$$
$$H_2S + [O] \longrightarrow H_2O + S$$
$$2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O$$

3. It acts as a powerful oxidizing agent. It liberates iodine from neutral KI solution and the liberated I_2 turns starch paper blue.
$2KI + H_2 + O_3 \rightarrow 2KOH + I_2 + O_2$
I_2 + Starch → Blue colour

Uses: It is used
1. as a germicide and disinfectant for sterilizing water.
2. as a bleaching agent for oils, ivory wax and delicate fibres.
3. for detecting 'the position of the double bond in unsaturated compounds.
4. in destroying odours coming from the cold storage room, slaughterhouses and kitchen of hotels.

Compounds of Sulphur

1. **Sulphur Dioxide (SO_2)**
   Method of preparation:
   (i) By heating sulphur in the air

$$S + O_2 \xrightarrow{\Delta} SO_2$$ **(ii)** Roasting iron pyrites in excess of air

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$ **(iii)** Lab method

$$SO_3^{2-}(aq) + 2H^+(aq) \longrightarrow H_2O(l) + SO_2(g)$$

Physical Properties: SO_2 is a colourless gas with a pungent smell and is highly soluble in water.

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3$$

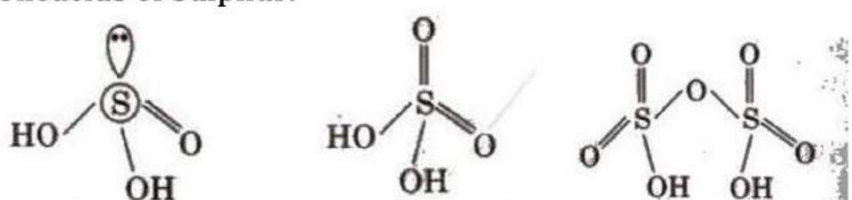
Chemical reactions: It turns lime water milky due to the formation of calcium bisulphite. However, in excess of SO_2 milkiness disappears due to the formation of calcium bisulphite.

$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$ (milkiness)
$CaSO_3 + SO_2 + H_2O \rightarrow Ca(HSO_3)_2$ (soluble)
$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$
$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$
$SO_2(g) + CL_2(g) \rightarrow SO_2Cl_2(l)$
$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

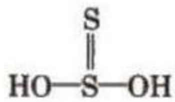
Reducing agent

$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$
$5SO_2 + 2MnO_4^{2-} + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$
When H_2S gas is passed through a saturated solution of SO_2 till its smell disappears, it turns in a milky solution, the Wacken roder's liquid. When H_2S is passed through H_2SO_4 the reaction is called Wacken roder's reaction.

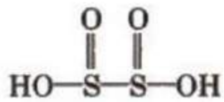
Oxoacids of Sulphur:



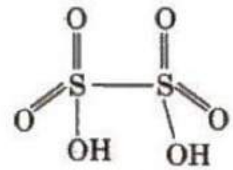
sulphurous acid (H_2SO_3) sulphuric acid (H_2SO_4) oleum (pyrosulphuric acid) ($H_2S_2O_7$)



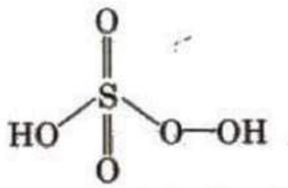
thiosulphurous acid
($H_2S_2O_2$)



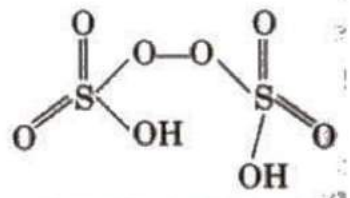
dithionous acid
($H_2S_2O_4$)



dithionc acid
($H_2S_2O_6$)



peroxomonsulphuric acid
or Caro's acid
(H_2SO_5)



peroxodisulphuric acid
($H_2S_2O_8$)

2. **Sulphuric Acid (H_2SO_4)**

Sulphuric acid is one of the most important industrial chemicals worldwide. It is called the king of chemicals. It is manufactured by the lead chamber process or contact process. The contact process involves three steps:

(i) Burning of sulphur or sulphur ores in air to generate SO_2.
(ii) Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5).
(iii) Absorption of SO_3 in H_2SO_4 to give oleum ($H_2S_2O_7$) which upon hydrolysis gives H_2SO_4.

Properties:

1. Sulphuric acid is a colourless, dense, oily liquid.
$MX + H_2SO_4 \rightarrow 2HX + M_2SO_4$
2. Concentrated sulphuric acid is a strong dehydrating agent.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

The burning sensation of concentrated H_2SO_4 on skin.
3. Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric acid and nitric acid.

$$S + 2H_2SO_4 (conc.) \longrightarrow 3SO_2(g) + 2H_2O$$
$$C + 2H_2SO_4(conc.) \longrightarrow CO_2 + 2SO_2 + 2H_2O$$
$$Cu + 2H_2SO_4(conc.) \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

Uses: It is used in petroleum refining, in pigments paints and in detergents manufacturing.

3. **Hypo:** It is chemically sodium thiosulphate pentahydrate, $Na_2S_2O_3.5H_2O$. The solid is an efflorescent (loses water readily) crystalline substance that dissolves well in water. It is also called sodium hyposulfite or "hypo".

   Preparation:
   1. It is prepared by boiling sodium sulphite solution with flowers of sulphur and stirring till the alkaline reaction has disappeared.
   $Na_2SO_3 + S \rightarrow Na_2S_2O_3$
   2. It is also prepared by **spring's reaction.**
   $Na_2S + Na_2SO_3 + I_2 \rightarrow Na_2S_2O_3 + 2NaI$

   Properties:
   (i). It is a colourless, crystalline and efflorescent substance.
   (ii). It gives white ppt with a dilute solution of $AgNO_3$ which quickly changes into black due to the formation of Ag_2S.

   $$S_2O_3^{2-} + 2Ag^+ \longrightarrow \underset{\text{white ppt}}{Ag_2S_2O_3}$$

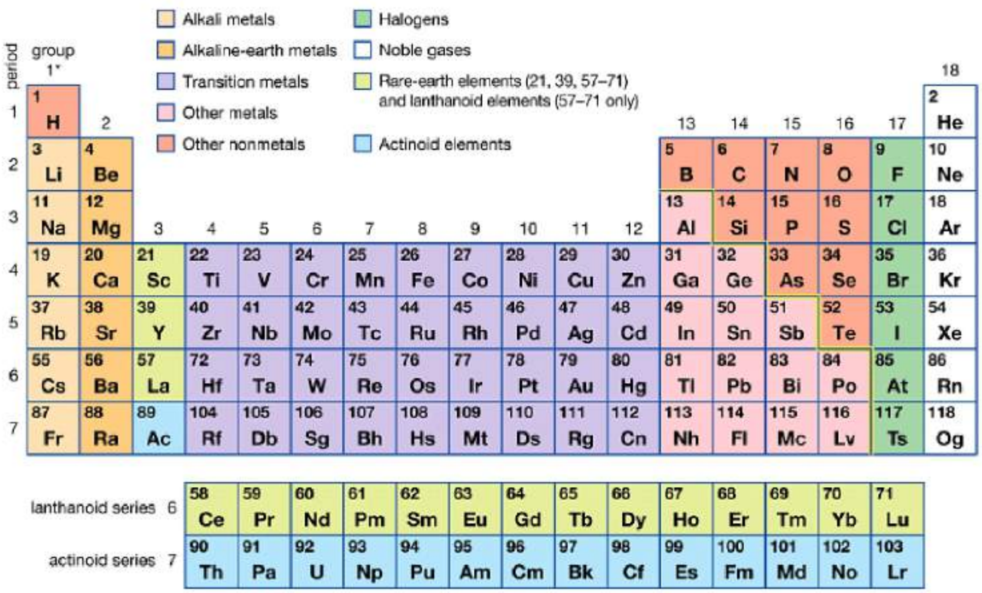
   $$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$$

   Uses:
   1. Due to its property of dissolving silver halide, it is used in photography for fixing under the name hypo.
   $2Na_2S_2O_3 + AgBr \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$
   2. During bleaching, it is used as an antichlor.
   $Na_2S_2O_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + S + 2HCl$
   3. It is used to remove iodine stain, for volumetric estimation of iodine and in medicines.

Group-17: Halogens

What are Halogens?

The halogens are the elements that form group 17 of the periodic table. They are reactive nonmetals and include fluorine, chlorine, bromine, and iodine. Halogens are highly reactive non-metals. These elements greatly resemble in property with each other. Group 17 elements are collectively called halogens (In Greek: halo means salt and genes mean producing, so collectively salt-producing) and it consists of fluorine, chlorine, bromine, iodine, and astatine.
The similarity to this extent is not found in other groups of the periodic table. They have a regular gradation in the physical and chemical properties. Astatine is the only radioactive element in the group. They have seven electrons in their outermost shell (ns_2np_5) and are short of one electron from the configuration of the nearest noble gas. The chemical properties and reactivity of an element are determined by the oxidation state exhibited by them.



Group 17 – Halogens

General Physical Properties of Group 17 Elements:

1. **Electronic configuration:** Their valence shell electronic configuration is $ns^2 np^5$.

Element	Atomic Number	Electronic configuration
Fluorine (F)	9	[He] $2s^2$ $2p^5$
Chlorine (Cl)	17	[Ne] $3s^2$ $3p^5$
Bromine (Br)	35	[Ar] $3d^{10}$, $4s^2$ Ap^5
Iodine (I)	53	[Kr] $4d^{10}$, $5s^2 5p^5$
Astatine (At)	85	[Xe] $4f^{14}$ $5d^{10}$, $6s^2$ $6p^5$

1. **Physical state:** Intermolecular forces in halogens are weak and increase down the group. Thus, F_2 and Cl_2 are gases, Br_2 is volatile liquid and I_2 is solid.
2. **Atomicity:** All are diatomic in nature.
3. **Abundance:** Being very reactive in nature, they are not found free in nature. Their presence in the earth's crust follows the order: $F_2 > Cl_2 > Br_2 > I_2$
4. **Colour:** They absorb light in the visible range forming excited states and are thus, coloured in nature.
   $F_2 \Rightarrow$ pale Yellow
   $Cl_2 \Rightarrow$ yellowish green
   $Br_2 \Rightarrow$ reddish brown
   $I_2 \Rightarrow$ deep violet
5. **Metallic character:** All the elements are non-metals and metallic character increases down the group. Thus, 1 forms 1+.
6. **Oxidation state:**

F	Cl	Br	I	At
-1	-1 to +6	-1 to +6	-1 to+7	-1, +1, +5

7. **Bond energy & bond length:** The bond length increases from fluorine to iodine and in the same order bond energy decreases. However, the bond dissociation energy of F_2 is lesser due to its smaller size. The order of bond energy is:

$$Cl_2 > Br_2 > F_2 > I_2$$

$$F{-}F < Cl{-}Cl < Br{-}Br < I{-}I$$

8. **Density:** It increases down the group in a regular fashion and follows the order F > Cl > Br >I.
9. **Ionisation enthalpy:** The ionisation enthalpy of halogens is very high and decreases down the group. The iodine also forms I^+ and I^{3+} and forms compounds like LiI, lCN, IPO_4. In a molten state, the compounds conduct electricity showing ionic character.
10. **Electron affinity:** The halogens have high values for electron affinity. The order of electron affinity is: $\mathbf{Cl_2 > F_2 > Br_2 > I_2}$
    Due to the small size of fluorine (hence, high electron density), the extra electron to be added feels more electron-electron repulsion. Therefore, fluorine has less value for electron affinity than chlorine.
11. **Reduction potentials and oxidising nature:** $E°_{red}$ of halogens are positive and decrease from F to I. Therefore, halogens act as strong oxidising agents and their oxidising power decreases from fluorine to iodine. Fluorine is the strongest oxidising agent and is most reactive. That's why it is prepared by the electrolysis of a mixture of KHF_2 and anhydrous HF using Monel metal as a catalyst.
12. **Solubility:** Halogens are soluble in water which follows the order: $\mathbf{F_2 > Cl_2 > Br_2 > I_2}$
    The solubility of iodine in water is enhanced in the presence of KI.
    $KI + I_2 \Leftrightarrow KI_3 \Leftrightarrow K^+ + I^-{}_2$
    I_2 forms a blue colour complex with starch.

Chemical Properties of Group 17 Elements:

1. **Hydrides:** HF is a low boiling liquid due to intermolecular hydrogen bonding, while HCI, HBr, HI are gases. The boiling point follows the trend: HF > Hi > HBr > HCl
   Some other properties show the following trend:

HI > HBr > HCl > HF	HI < HBr < HCl < HF
Acid strength, Reducing character, Bond length	Thermal stability, Dipole moment, Bond strength, Stability

2. **Oxides:** Fluorine forms two oxides, OF_2 and O_2F_2, but only OF_2 is thermally stable at 298K. O_2F_2 oxidises Plutonium to PuF_6 and the reaction is used for removing plutonium as PuF_6 from spent nuclear fuel. Chlorine forms a number of oxides such as, CI_2O, CI_2O_3, Cl_2O_5 , Cl_2O_7 , CIO_2 and CIO_2 is used as a bleaching agent for paper pulp, textiles and in water treatment.
   Br_2O, BrO_2, BrO_3 are the least stable bromine oxides and exist only at low temperatures. They are very powerful oxidising agents.
   The iodine oxides, i.e., I_2O_4, I_2O_5, I_2O_7 are insoluble solids and

decompose on heating. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

$$\underset{\text{(cold dilute)}}{2F_2 + 2NaOH} \longrightarrow 2NaF + OF_2 + H_2O$$

$$\underset{\text{(hot conc.)}}{2F_2 + 4NaOH} \longrightarrow 4NaF + O_2 + 2H_2O$$

3. **Reaction with alkali:** Other halogens form hypohalite with dilute NaOH and hypohalite with conc.

$$X_2(g) + \underset{\text{(cold dilute)}}{2OH^-} \xrightarrow{150^\circ C} X^- + \underset{\text{(hypohalite ion)}}{OX^-} + H_2O$$

$$X_2(g) + \underset{\text{(hot conc.)}}{6OH^-} \xrightarrow{70^\circ C} 5X^- + \underset{\text{(halate ion)}}{XO_3^-} + 3H_2O$$

$NaOH_4$.

4. **Oxoacids of halogens:** Higher oxoacids of fluorine such as HFO_2, HFO_3 do not exist because fluorine is the most electronegative and has the absence of d-orbitals.
   +3 oxidation state of bromine and iodine are unstable **due to the inert pair effect.** Therefore, $HBrO_2$ and HIO_2 do not exist.
   Acidic character of oxoacids decreases as the electronegativity of the halogen atom decreases. Thus, the order of acidic strength.

$$\underset{\text{(hypofluorous > acid)}}{HOF} > \underset{\text{(hypochlorous acid)}}{HOCl} > \underset{\text{(hypobromous acid)}}{HOBr} \xrightarrow{\text{Acidic nature decreases}} \underset{\text{(hypoiodous acid)}}{HOI}$$

   For the oxoacids of the same halogens. acidic strength and thermal stability increase as the number of O atoms increases.

Interhalogen Compounds:

- When two different halogens react with each other, interhalogen compounds are formed. These compounds are covalent and diamagnetic in nature. They are volatile solids or liquids except for elf which is a gas at 298 K. Interhalogen compounds are more reactive than halogens (except fluorine).
- The XY_3 type compounds have bent 'T' shape, XY_5 type compounds have square pyramidal shape and IF_7 has pentagonal bipyramidal structure.
- BrF_3 has "T" shaped structure due to 3 bp and 2 lp.
- ICI is more reactive than I_2 due to a weak bond. ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.
- $U(s) + 3ClF_3(l) \rightarrow UF_6(g) + 3ClF(g)$

Pseudohalogens and Pseudohalides:
The substances behaving like halogens are known as pseudohalides. Some examples are

Pseudohalogenn	Pseudohalide ion
$(CM)_2$ Cyanogen	CN^- Cyanide
$(OCN)_2$ Oxycyanogen	OCN^- Cyanate
$(SCN)_2$ Thiocyanogen	SCN^- Thiocyanate

Chlorine and its Compounds:

Occurrence:

Common salt, NaCl is most important. Chlorine is also present in sea water and as rock salt.

Preparation of Chlorine:

1. **By oxidation of conc. HCl:**
   $4NaCl + Mn0_2 + 4H_2SO_4 \rightarrow 4NaHSO_4 + MnCl_2 + 2H_2O + Cl_2$
2. **Weldon's process**
   $MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$
3. **Deacon's process**
   In this process, HCl is oxidised by O_2 in the presence of $CuCl_2$ as a catalyst at 400°C.
   $4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$
4. **Electrolytic process:** By the electrolysis of brine solution in Nelson cell.
   $NaCl \rightleftharpoons Na^+ + Cl^-$ $2Na^+ + 2e^- \rightarrow 2Na + H_2O \rightarrow 2NaOH + H_2$ (at cathode)
   $2Cl^- \rightarrow 2Cl + 2e^- \rightarrow Cl_2$ (at anode)

Properties:
It is yellowish-green gas, collected by upward displacement of air poisonous in nature, soluble in water. Its aqueous solution is known as chlorine water.

Chemical Reactions:

1. **Action of water:**
   $$Cl_2 + H_2O \longrightarrow HOCl + HCl$$
   $$HOCl \longrightarrow HCl + \underset{\text{nascent oxygen}}{[O]}$$
   Coloured matter + [0] →

colourless matter. The bleaching action of chlorine is due to oxidation and is permanent.

2. **Action of hydrogen:**

$$H_2 + Cl_2 \xrightarrow[\text{Charcoal catalyst}]{\text{UV light}} 2HCl$$

3. **Displacement reactions:**

$$2KBr + Cl_2 \longrightarrow 2KCl + Br_2$$
$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

4. **Action of NaOH (cold):**

$$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$$

5. An aqueous solution of NaOCl is called Javelle water,
6. **Action of H_2S:**

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$

7. **Action of dry SO_2:**

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$

8. **Action of CO:**

$$CO + Cl_2 \longrightarrow COCl_2$$

9. **Oxidising properties:**

$$SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$$

$$2FeSO_4 + Cl_2 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2HCl$$

10.**Reaction with ammonia:**

(a) When ammonia is in excess

$$8NH_3 + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$$

(b) When chlorine is in excess

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$

11.**Chromyl chloride test:** When a mixture of chloride and solid $K_2Cr_2O_7$ is heated with concentrated H_2SO_4 in a dry test tube, deep red vapours of chromyl chloride are evolved.

$$Cl^- + K_2Cr_2O_7 + H_2SO_4 \longrightarrow \underset{\text{red vapours}}{CrO_2Cl_2} + KHSO_4 + HSO_4^- + H_2O$$

When these vapours are passed through NaOH solution, the solution becomes yellow due to the formation of sodium chromate.

$$CrO_2Cl_2 + 4NaOH \longrightarrow \underset{\text{yellow}}{Na_2CrO_4} + 2NaCl + 2H_2O$$

12.The yellow solution is neutralised with acetic acid and on the addition of lead acetate gives a yellow precipitate of lead chromate.

$$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow \underset{\text{yellow ppt.}}{PbCrO_4} + 2CH_3COONa$$

Uses: It is used as a bleaching agent, disinfectant and in the manufacture of $CHCl_3$, CCl_4, DDT, anti-knocking compounds and bleaching powder.

2. Hydrochloric Acid (HCl)

Preparation:

$$NaCl + H_2SO_4 \xrightarrow{420\ K} NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \xrightarrow{823\ K} Na_2SO_4 + HCl$$

Properties:

It is a colourless and pungent-smelling gas. It is extremely soluble in water and ionises as below:

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

Its other reaction are as

$$NH_3 + HCl \longrightarrow NH_4Cl$$
$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$
$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$
$$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$$

[Noble metals like gold, platinum can dissolve in aqua-regia [three part conc. HCl and one part of conc. HNO_3].

Uses:

It is used in the manufacture of chlorides. Chlorine, in textile and dyeing industries, in medicine and in the extraction of glue from animal tissues and bones.

Iodine (I_2)

1. Its major source is deep seaweeds of laminaria variety. Their ashes which are called kelp contain 0.5% iodine as iodides.
2. Another source of I_2 is caliche or crude chile saltpetre ($NaNO_3$) which contains 0.2%, $NaIO_3$. Iodine is purified by sublimation.
3. It shows no reaction with water. The tincture of iodine is a mixture of I_2 and KI dissolved in rectified spirit.

Group-18: Inert Gases

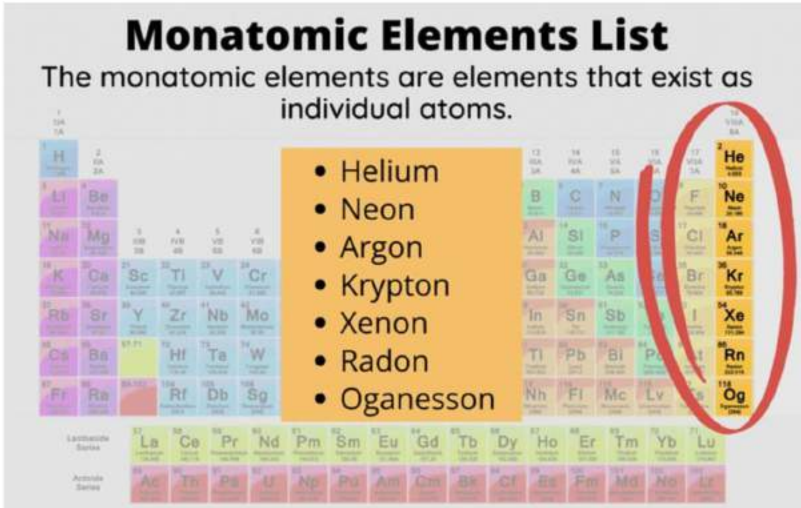
What are Inert Gases?

Members of group 18 in the modern periodic table are known as noble gases. They are colourless, odourless gases at room temperature, isolated by William Ramsay in 1898 from the air.

Inert Gases are:

1. Helium (He)
2. Neon (Ne)
3. Argon (Ar)
4. Krypton (Kr)
5. Xenon (Xe)

6. Radon (Rn)



The members of the group have eight electrons in their outermost orbit (except helium which has two electrons). Thus, they have a stable configuration. Group 18 elements are gases and chemically unreactive, which means they don't form many compounds. Thus, the elements are known as inert gases. Like the other group elements, noble gas elements also exhibit trends in their physical and chemical properties. The general characteristics of noble gases are discussed below.

General/Physical Characteristics of Group 18 Elements:

1. **Electronic configuration:** Their valence shell electronic configuration is $ns^2\ np^6$ except He.

Element	Atomic number	Electronic configuration
Helium (He)	2	$1s^2$
Neon (Ne)	10	$[He]2s^2 2p^6$
Argon (Ar)	18	$[Ne]3s^2 3p^6$
Krypton (Kr)	36	$[Ar]\ 3d^{10} 4s^2 4p^6$
Xenon (Xe)	54	$[Kr]4d^{10} 5s^2 5p^6$
Radon (Rn)	86	$[Xe]\ 4f^{14}\ 5d^{10} 6s^2 6p^6$

1. **Physical state:** They are all gases under ordinary conditions of temperature and pressure.
2. **Abundance:** In 1.0% air, the abundance follows the order: **Ar > Ne > He > Kr > Xe**

3. **Atomicity:** The $C_p/C_v = 1.67$ shows their monoatomic nature. However, under high energy conditions, several molecular ions such as He^+, HeH^+, $HeH^{2+}$and Ar^{2+} are formed in discharge tubes. They only survive momentarily and are detected spectroscopically.
4. **Melting and boiling points:** Due to the increase in the magnitude of Van der Waals' forces, the melting point and boiling point increase from He to Rn.
5. **Atomic radii:** The atomic radii increase from He to Rn. It corresponds to the Van der Waals' radii. So it has the greatest atomic size in the respective period.
6. **Density:** The density of noble gases increases down the group.
7. **Heat of vaporisation:** They have very low values of heat of vaporisation due to weak Van der Waals' forces of attraction. The value increases down the group.
8. **Solubility in water:** They are slightly soluble in water and solubility increases from He to Rn.
9. **Liquefication:** It is extremely difficult to liquefy inert gases due to weak Van der Waals' forces of attraction among their molecules. Hence, they possess a low value of critical temperature also.
10. **Ionisation energy:** All noble gases possess a very stable (ns^2 and $ns^2\ np^6$) electronic configuration. Therefore, the ionisation energy of noble gases is very high and decreases down the group.
11. **Electron affinity:** Due to the presence of stable electronic configuration, they have no tendency to accept an additional electron. Therefore, electron affinity is almost zero.

Chemical Properties of Group 18 Elements:

The noble gases are inert in nature because of their completely filled subshells. In 1962, the first compound of noble gases was prepared. It is hexafluoroplatinate (prepared by Bartlett).
$Xe + PtF_6 \rightarrow Xe[PtF_6]$
Now, many compounds of Xe and Kr are known with fluorine and oxygen.

Preparation of Compounds of Xenon:

$$\text{(i)}\quad \underset{\text{(Xe in excess)}}{Xe(g)} + F_2(g) \xrightarrow{\text{673 K, 1 bar}} XeF_2(s)$$

$$\text{(ii)}\quad \underset{\text{(1: 5 ratio)}}{Xe(g)} + 2F_2(g) \xrightarrow{\text{873 K, 7 bar}} XeF_4(s)$$

$$\text{(iii)}\quad \underset{\text{(1: 20 ratio)}}{Xe(g)} + 3F_2(g) \xrightarrow{\text{573 K, 60-70 bar}} XeF_6(s)$$

$$\text{(iv)}\quad XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$

Chemical Reactions of Xenon Compounds:

$$XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$$

$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+ [SbF_6]^-$$

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