

P-BLOCK ELEMENTS

INTRODUCTION TO CHEMISTRY OF P-BLOCK ELEMENTS

In p-block elements the last electron enters the outermost p orbital. As we know that the number of p orbitals is three and, therefore, the maximum number of electrons that can be accommodated in a set of p orbitals is six. Consequently there are six groups of p-block elements in the periodic table numbering from 13 to 18.

Boron, carbon, nitrogen, oxygen, fluorine and helium head the groups. Their valence shell electronic configuration is ns^2np^{1-6} (except for He). The inner core of the electronic configuration may, however, differ. The difference in inner core of elements greatly influences their physical properties (such as atomic and ionic radii, ionisation enthalpy, etc.) as well as chemical properties. Consequently, a lot of variation in properties of elements in a group of p-block is observed.

The maximum oxidation state shown by a p-block element is equal to the total number of valence electrons (i.e., the sum of the s- and p-electrons). Clearly, the number of possible oxidation states increases towards the right of the periodic table. In addition to this so called group oxidation state.

p-block elements may show other oxidation states which normally, but not necessarily, differ from the total number of valence electrons by unit of two. The important oxidation states exhibited by p-block elements are shown in Table 1.

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In boron, carbon and nitrogen families the group oxidation state is the most stable state for the lighter elements in the group. However, the oxidation state two unit less than the group oxidation state becomes progressively more stable for the heavier elements in each group. The occurrence of oxidation states two unit less than the group oxidation states are sometime attributed to the 'inert pair effect'.

The relative stabilities of these two oxidation states – group oxidation state and two unit less than the group oxidation state – may vary from group to group and will be discussed at appropriate places. It is interesting to note that the non-metals and metalloids exist only in the p-block of the periodic table. The non-metallic character of elements decreases down the group.

In fact the heaviest element in each p-block group is the most metallic in nature. This change from non-metallic to metallic character brings diversity in the chemistry of these elements depending on the group to which they belong.

In general, non-metals have higher ionisation enthalpies and higher electronegativities than the metals. Hence, in contrast to metals which readily form cations, non-metals readily form anions. The compounds formed by highly reactive non-metals with highly reactive metals are generally ionic because of large differences in their electronegativities. On the other hand, compounds formed between non-metals themselves are largely covalent in character because of small differences in their electronegativities. The change of non-metallic to metallic character can be

best illustrated by the nature of oxides they form. The non-metal oxides are acidic or neutral whereas metal oxides are basic in nature.

The first member of p-block differs from the remaining members of their corresponding group in two major respects: First is the size and all other properties which depend on size. Thus, the lightest p-block elements show the same kind of differences as the lightest s-block elements, lithium and beryllium. The second important difference, which applies only to the p-block elements, arises from the effect of d-orbitals in the valence shell of heavier elements (starting from the third period onwards) and their lack in second period elements.

The second period elements of p-groups starting from boron are restricted to a maximum covalence of four (using 2s and three 2p orbitals). In contrast, the third period elements of p-groups with the electronic configuration $3s^23p^n$ have the vacant 3d orbitals lying between the 3p and the 4s levels of energy. Using these d-orbitals the third period elements can expand their covalence above four. For example, while boron forms only $[BF_4]^-$, aluminium gives $[AlF_6]^{3-}$ ion. The presence of these d-orbitals influences the chemistry of the heavier elements in a number of other ways. The combined effect of size and availability of d orbitals considerably influences the ability of these elements to form π bonds.

The first member of a group differs from the heavier members in its ability to form $p \pi - p \pi$ multiple bonds to itself (e.g., $C=C$, $C\equiv C$, $N\equiv N$) and to other second row elements (e.g., $C=O$, $C=N$, $C\equiv N$, $N=O$). This type of π - bonding is not particularly strong for the

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heavier p-block elements. The heavier elements do form π bonds but this involves d orbitals ($d\pi - p\pi$ or $d\pi - d\pi$). As the d orbitals are of higher energy than the p orbitals, they contribute less to the overall stability of molecules than does $p\pi - p\pi$ bonding of the second row elements. However, the coordination number in species of heavier elements may be higher than for the first element in the same oxidation state. For example, in +5 oxidation state both N and P form oxoanions : NO_3^- (three-coordination with π - bond involving one nitrogen p-orbital) and 3 PO_4^- (four-coordination involving s, p and d orbitals contributing to the π - bond).

Table 1 General Electronic Configuration and Oxidation States of p-Block Elements

Group	13	14	15	16	17	18
General electronic configuration	ns^2np_1	ns^2np_2	ns^2np_3	ns^2np_4	ns^2np_5	ns^2np_6 ($1s^2$ for He)
First member of the group	B	C	N	O	F	He
Group oxidation state	+ 3	+ 4	+ 5	+ 6	+ 7	+ 8
Other oxidation states	+ 1	+2 , - 4	+3 , - 3	+4 ,+2 , - 2	+5 ,+3 ,+1 , - 1	+6 ,+4 ,+2

GROUP 13 ELEMENTS(THE BORON FAMILY)

The group 13 includes elements, Boron, Aluminium, Gallium, Indium and Thallium. Aluminium is the third most abundant element found in earth's crust. The important ores of aluminium are bauxite and cryolite. Variation in some properties of group 13 elements are like atomic radii and ionic radii, ionisation enthalpy, metallic character, electronegativity, melting point and boiling point, density, character as reducing and nature of compound are observed in elements of boron group i.e. Group 13 elements having electronic configuration $ns^2 np^1$. Hence, they possess +3 oxidation state and their stability goes on decreasing as the atomic number increases. These elements also possess +1 oxidation state and the stability goes on increasing as the atomic number increases.

Group 13 elements do not combine directly with hydrogen but they combine indirectly to form hydride compounds. Boron forms a number of hydrides having molecular formula $B_n H_{n+4}$ and $B_n H_{n+6}$ which are known as boranes. The other elements of this group form polymeric hydrides. Group 13 elements form MX_3 type trihalides, where X = F, Cl, Br and I is unknown. $AlCl_3$ exists in dimer form. The group 13 elements form oxides and hydroxides having formula $M_2 O_3$ and $M(OH)_3$ respectively. As the atomic number of elements goes on increasing, the acidic character of oxide and hydroxide goes on decreasing. Elements of these group form octahedral complexes.

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Aluminium sulphate reacts and forms double salts with sulphate of $+ 4\text{NH}$ and alkali metal ions having formula $\text{M}_2\text{SO}_4 \cdot \text{A}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ or $\text{MAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ where $\text{M} = \text{Na}^+, \text{K}^+, \text{Rb}^+$ and 4NH^+ . The first element (Boron) of group 13 shows anomalous behaviour. Boron is chemically less reactive and almost inert with normal chemical reagents at normal temperature but reacts with strong oxidising agents and with some typical reagents like non-metal, acid alkali and metals. Some important compounds of boron are borax powder, boric acid and boron hydride. The properties and uses of aluminium are as given in the text. Aluminium reacts with acid and base so it is amphoteric in nature.

1-Atomic Radii

On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase. However, a deviation can be seen. Atomic radius of Ga is less than that of Al. This can be understood from the variation in the inner core of the electronic configuration. The presence of additional 10 d-electrons offer only poor screening effect (Unit 2) for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

2- Ionization Enthalpy

The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group. The decrease from B to Al is associated with increase in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga, and between In and Tl are due to inability of d- and f-

electrons ,which have low screening effect, to compensate the increase in nuclear charge. The order of ionisation enthalpies, as expected, is $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$. The sum of the first three ionisation enthalpies for each of the elements is very high. Effect of this will be apparent when you study their chemical properties.

3- Electronegativity

Down the group, electronegativity first decreases from B to Al and then increases and then increases marginally. This is because of the discrepancies in atomic size of the elements.

4-Oxidation state and trends in chemical reactivity

Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form Al^{3+} ions. In fact, aluminium is a highly electropositive metal. However, down the group, due to poor shielding effect of intervening d and f orbitals, the increased effective nuclear charge holds ns electrons tightly (responsible for inert pair effect) and thereby, restricting their participation in bonding. As a result of this, only p-orbital electron may be involved in bonding. In fact in Ga, In and Tl, both +1 and +3 oxidation states are observed. The relative stability of +1 oxidation state progressively increases for heavier elements: $Al < Ga < In < Tl$. In thallium +1 oxidation state is predominant whereas the +3 oxidation state is highly oxidising in character. The compounds in +1 oxidation state, as expected from energy considerations, are more ionic than those in +3

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oxidation state. In trivalent state, the number of electrons around the central atom in a molecule of the compounds of these elements (e.g., boron in BF_3) will be only six. Such electron deficient molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. The tendency to behave as Lewis acid decreases with the increase in the size down the group. BCl_3 easily accepts a lone pair of electrons from ammonia to form $\text{BCl}_3 \cdot \text{NH}_3$.

GROUP 14 ELEMENTS (THE CARBON FAMILY)

The group 14 includes elements carbon, silicon, germanium, tin and lead. The first element of this group is carbon, so it is also known as carbon group elements. Carbon shows catenation property due to its small size, high electronegativity and very high carbon-carbon bond energy. Due to typical characteristic of catenation it forms number of compounds which are studied in organic chemistry. It also forms compounds with metals and non-metals. Group 14 elements have variation in properties like atomic radii, ionisation enthalpy electropositive character, electronegativity, melting points and boiling points density, catenation and allotropy.

The oxidation state of group 14 elements are +2 and +4. The carbon shows anomalous behaviour. The crystalline allotropes of carbon are diamond, graphite and fullerenes. Some important compounds of carbon are halides of carbon, carbon disulphide, carbide compounds, carbon monoxide and carbon dioxide. The important compounds of silicon are silicon hydrides having general formula $\text{Si}_n \text{H}_{2n+2}$. The value of bond enthalpy for silicon-silicon is 297 kJmol^{-1} hence catenation character is observed in

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silicon and it forms limited hydride compounds, having formula $\text{Si}_n \text{H}_{2n+2}$ where $n = 1$ to 8, and these compounds are also known as silanes. The stability of silane compounds are less compared to hydrides of carbon and hence reducing power is more. Silicon also forms silicon dioxide known as silica and more than 22 allotropic structures are known in which some are crystalline and some are amorphous. Silica is acidic and hence it dissolves in liquid alkali or alkaline carbonate to form silicate compounds. Silicon reacts with only F_2 and form SiF_4 while reacts with Cl_2 and form SiCl_4 . The hydrolysis of SiCl_4 gives silicic acid and the mechanism for hydrolysis are in two steps. The silicones are synthetic materials containing Si - O - Si bond linkage. These compounds are polymeric substances containing R_2SiO repeating unit. The general formula is $(\text{R}_2\text{SiO})_n$, where R is methyl or phenyl group. The empirical formula is R_2SiO which is similar to that of organic compound, ketone, so it is called silicone. Approximately 95% of earth's crust consists of silicates and silica compounds, containing independent SiO_4^{4-} having tetrahedral structure. The types of silicates depending upon the number of corners (0, 1, 2, 3 and 4) of the SiO_4^{4-} tetrahedron are shared with other tetrahedrons and based on . In a three dimensional structure of SiO_2 , its Si^{4+} partially substituted by Al^{3+} gives aluminosilicate are called feldspar and zeolites. In zeolites the SiO_4^{4-} and AlO_4^{5-} . tetrahedron joined together in simple way to form three dimensional network. The uses of silicates are as a molecular sieves and shape selectives catalyst. One important catalyst of silicate is ZSM-5 used in petrochemical industry which converts alcohol directly into gasoline.

1- Covalent Radius

There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled d and f orbitals in heavier members.

2- Ionization Enthalpy

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electrons is visible here also. In general the ionisation enthalpy decreases down the group. Small decrease in Δ_iH from Si to Ge to Sn and slight increase in Δ_iH from Sn to Pb is the consequence of poor shielding effect of intervening d and f orbitals and increase in size of the atom.

3- Electronegativity

Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity values for elements from Si to Pb are almost the same.

4- Physical Properties

All group 14 members are solids. Carbon and silicon are non-metals, germanium is a metalloid, whereas tin and lead are soft metals with low melting points. Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13.

5- Oxidation states

The group 14 elements have four electrons in outermost shell. The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since the sum of the first four ionization enthalpies is very high, compounds in +4 oxidation state are generally

covalent in nature. In heavier members the tendency to show +2 oxidation state increases in the sequence $\text{Ge} < \text{Sn} < \text{Pb}$. It is due to the inability of ns^2 electrons of valence shell to participate in bonding. The relative stabilities of these two oxidation states vary down the group. Carbon and silicon mostly show +4 oxidation state. Germanium forms stable compounds in +4 state and only few compounds in +2 state. Tin forms compounds in both oxidation states (Sn in +2 state is a reducing agent). Lead compounds in +2 state are stable and in +4 state are strong oxidising agents. In tetravalent state the number of electrons around the central atom in a molecule (e.g., carbon in CCl_4) is eight. Being electron precise molecules, they are normally not expected to act as electron acceptor or electron donor species. Although carbon cannot exceed its covalence more than 4, other elements of the group can do so. It is because of the presence of d orbital in them. Due to this, their halides undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species. For example, the species like, SiF_6^{2-} , $[\text{GeCl}_6]^{2-}$, $[\text{Sn}(\text{OH})_6]^{2-}$ exist where the hybridisation of the central atom is sp^3d^2 .

ALLOTROPES OF CARBON

Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985, third form of carbon known as fullerenes was discovered by H.W.Kroto, E.Smalley and R.F.Curl. For this discovery they were awarded the Nobel Prize in 1996.

A- Diamond

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It has a crystalline lattice. In diamond each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. The C–C bond length is 154 pm. The structure extends in space and produces a rigid three-dimensional network of carbon atoms.

It is very difficult to break extended covalent bonding and, therefore, diamond is a hardest substance on the earth. It is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.

B- Graphite

Graphite has layered structure. Layers are held by van der Waals forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C—C bond length within the layer is 141.5 pm. Each carbon atom in hexagonal ring undergoes sp^2 hybridisation and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π bond. The electrons are delocalised over the whole sheet. Electrons are mobile and, therefore, graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

C- Fullerenes

Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourised C_n small molecules consists of mainly C_{60} with smaller quantity of C_{70}

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and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules. C₆₀ molecule has a shape like soccer ball and called Buckminsterfullerene. It contains twenty six- membered rings and twelve five membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo sp² hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in molecular orbitals, which in turn give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C-C distances of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called bucky balls in short.

It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore, $\Delta_f H^\circ$ of graphite is taken as zero. $\Delta_f H^\circ$ values of diamond and fullerene, C₆₀ are 1.90 and 38.1 kJ mol⁻¹, respectively. Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes. Carbon black is obtained by burning hydrocarbons in a limited supply of air. Charcoal and coke are obtained by heating wood or coal respectively at high temperatures in the absence of air.

GROUP 15 ELEMENTS(THE NITROGEN FAMILY)

The first element of group 15, differs in many aspects from the other elements in the group. The reason for which is its smaller size, the capacity of formation of $p \pi - p \pi$ triple bond between, nitrogen atoms and the nonavailability of d-orbitals. As we go down from above in the group, variations are found in properties. Dinitrogen (N_2) can be prepared in the laboratory as well as on commercial level. The oxides of nitrogen element are N_2O , NO , N_2O_3 , N_2O_4 and N_2O_5 which possess resonance forms. Ammonia and nitric acid are compounds of nitrogen. Phosphorus element exists as P_4 molecule. It has many allotropes. It forms hydrides, halides and oxoacid compounds.

1- Atomic and ionic radii

Covalent and ionic radii increase down the group. There is appreciable increase in covalent radii from N to P. There is small increase from As to Bi due to presence of completely filled d or f orbitals in heavy elements.

2-Ionisation energy

It goes on decreasing down the group due to increase in atomic size. Group 15 elements have higher ionisation energy than group 14 elements due to smaller size of group 15 elements. Group 15 elements have higher ionization energy than group 16 elements because they have stable electronic configuration i.e., half filled p-orbitals.

3- Allotropy

All elements of Group 15 except nitrogen show allotropy.

4- Catenation

Nitrogen shows catenation to some extent due to triple bond but phosphorus shows catenation to maximum extent. The tendency to show catenation decreases down the group.

5- Oxidation states

The common oxidation states are +3, +5, -3. The tendency to show -3 oxidation state decreases down the group due to decrease in electronegativity which is due to increase in atomic size.

The stability of +5 oxidation state decreases whereas stability of +3 oxidation state increases due to inert pair effect.

Nitrogen shows oxidation states from -3 to +5.

Nitrogen and phosphorus with oxidation states from +1 to +4 undergo oxidation as well as reduction in acidic medium. This process is called disproportionation.



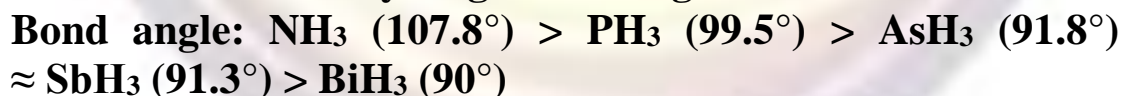
6-Reactivity towards hydrogen

All group 15 elements form trihydrides, MH_3 .
Hybridisation - sp^3

The stability of hydrides decrease down the group due to decrease in bond dissociation energy down the group.



Boiling point increases with increase in size due to increase in van der Waals forces. Boiling point of NH_3 is more because of hydrogen bonding.



Electronegativity of N is highest. Therefore, the lone pairs will be towards nitrogen and hence more

repulsion between bond pairs. Therefore bond angle is the highest. After nitrogen, the electronegativity decreases down the group.

Basicity decreases as



This is because the lone pair of electrons are concentrated more on nitrogen and hence the basicity will be maximum in the case of NH_3 . It will decrease down the group as the electronegativity decreases down the group.

The reducing power of hydrides increases down the group due to decrease in bond dissociation energy down the group.

7- Reactivity towards oxygen

All group 15 elements form trioxides (M_2O_3) and pentoxides (M_2O_5).

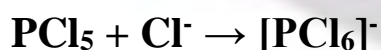
Acidic character of oxides decreases and basicity increases down the group. This is because the size of nitrogen is very small. It has a strong positive field in a very small area. Therefore, it attracts the electrons of water's O-H bond to itself and release H^+ ions easily. As we move down the group, the atomic size increases. Hence, the acidic character of oxides decreases and basicity increases as we move down the group.

8- Reactivity towards halogen

Group 15 elements form trihalides and pentahalides.

Trihalides – covalent compounds and become ionic down the group. sp^3 hybridisation, pyramidal shape
Pentahalides - sp^3d hybridisation, TBP shape.

They are lewis acids because of the presence of vacant d – orbitals.



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**PCl₅ is ionic in solid state and exist as [PCl₄]⁺ [PCl₆]⁻
In PCl₅, there are three equatorial bonds and two axial bonds. The axial bonds are longer than equatorial bonds because of greater repulsion from equatorial bonds.**

Nitrogen does not form pentahalides due to absence of d- orbitals.

9-Reactivity towards metals

All elements react with metals to form binary compounds in –3 oxidation state.

10- Anomalous behaviour of nitrogen

The behaviour of nitrogen differs from rest of the elements.

Reason:

- i. It has a small size.**
- ii. It does not have d – orbitals**
- iii. It has high electronegativity**
- iv. It has high ionization enthalpy**

GROUP 16 ELEMENTS(THE OXYGEN FAMILY)

1- Oxidation states

They show -2, +2, +4, +6 oxidation states. Oxygen does not show +6 oxidation state due to absence of d – orbitals. Po does not show +6 oxidation state due to inert pair effect.

The stability of -2 oxidation state decreases down the group due to increase in atomic size and decrease in electronegativity.

Oxygen shows -2 oxidation state in general except in OF₂ and O₂F₂

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The stability of +6 oxidation state decreases and +4 oxidation state increases due to inert pair effect.

2- Ionisation enthalpy

Ionisation enthalpy of elements of group 16 is lower than group 15 due to half filled p-orbitals in group 15 which are more stable. However, ionization enthalpy decreases down the group.

3-Electron gain enthalpy

Oxygen has less negative electron gain enthalpy than S because of small size of O.

From S to Po electron gain enthalpy becomes less negative to Po because of increase in atomic size.

4- Melting and boiling point

It increases with increase in atomic number. Oxygen has much lower melting and boiling points than sulphur because oxygen is diatomic (O_2) and sulphur is octatomic (S_8).

5-Reactivity with oxygen: EO_2 and EO_3

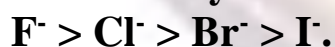
Reducing character of dioxides decreases down the group because oxygen has a strong positive field which attracts the hydroxyl group and removal of H^+ becomes easy.

Acidity also decreases down the group.

SO_2 is a gas whereas SeO_2 is solid. This is because SeO_2 has a chain polymeric structure whereas SO_2 forms discrete units.

6-Reactivity with halogens: EX_2 EX_4 and EX_6

The stability of halides decreases in the order



This is because E-X bond length increases with increase in size.

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Among hexa halides, fluorides are the most stable because of steric reasons. Dihalides are sp^3 hybridised, are tetrahedral in shape.

Hexafluorides are only stable halides which are gaseous and have sp^3d^2 hybridisation and octahedral structure.

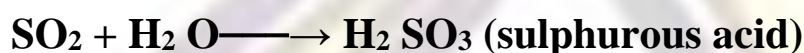
H_2O is a liquid while H_2S is a gas. This is because strong hydrogen bonding is present in water. This is due to small size and high electronegativity of O.

7- Oxides

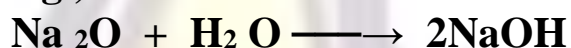
The compounds of oxygen and other elements are called oxides.

Types of oxides:

a. Acidic oxides: Non- metallic oxides are usually acidic in nature.



b. Basic oxides: Metallic oxides are mostly basic in nature. Basic oxides dissolve in water forming bases e.g.,



c. Amphoteric oxides: They show characteristics of both acidic as well as basic oxides.



d. Neutral oxides: These oxides are neither acidic nor basic.

Example: Co, NO and N_2O

GROUP 17 ELEMENTS (THE HALOGENS FAMILY)

1- Atomic and ionic radii

Halogens have the smallest atomic radii in their respective periods because of maximum effective nuclear charge.

2- Ionisation enthalpy

They have very high ionization enthalpy because of small size as compared to other groups.

3- Electron gain enthalpy

Halogens have maximum negative electron gain enthalpy because these elements have only one electron less than stable noble gas configuration.

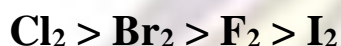
Electron gain enthalpy becomes less negative down the group because atomic size increases down the group.

4- Electronegativity

These elements are highly electronegative and electronegativity decreases down the group. They have high effective nuclear charge.

5- Bond dissociation enthalpy

Bond dissociation enthalpy follows the order



This is because as the size increases bond length increases.

Bond dissociation enthalpy of Cl_2 is more than F_2 because there are large electronic repulsions of lone pairs present in F_2 .

5- Colour

All halogens are coloured because of absorption of radiations in visible region which results in the excitation of outer electrons to higher energy levels.

6- Oxidising power

All halogens are strong oxidizing agents because they have a strong tendency to accept electrons.

Order of oxidizing power is $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

7- Reactivity with H_2

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Acidic strength: $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$

Stability: $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

This is because of decrease in bond dissociation enthalpy.

Boiling point

$\text{HCl} < \text{HBr} < \text{HI} < \text{HF}$

HF has strong intermolecular H bonding

As the size increases van der Waals forces increases and hence boiling point increases.

% Ionic character: $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

Dipole moment: $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

Electronegativity decreases down the group.

Reducing power: $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$

8-Reactivity with metals

Halogens react with metals to form halides.

Ionic character: $\text{MF} > \text{MCl} > \text{MBr} > \text{MI}$

Halides in higher oxidation state will be more covalent than the one in the lower oxidation state.

9- Interhalogen compounds

Reactivity of halogens towards other halogens:

Binary compounds of two different halogen atoms of general formula

$\text{X X}'_n$ are called interhalogen compounds where $n = 1, 3, 5, \text{ or } 7$ These are covalent compounds.

All these are covalent compounds.

Interhalogen compounds are more reactive than halogens because $\text{X}-\text{X}'$ is a more polar bond than $\text{X}-\text{X}$ bond.

All are diamagnetic.

Their melting point is little higher than halogens.

XX' (ClF , BrF , BrCl , ICl , IBr , IF) (Linear shape)

XX'_3 (ClF_3 , BrF_3 , IF_3 , ICl_3) (Bent T- shape)

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**XX'5 – ClF₅, BrF₅, IF₅, (square pyramidal shape)
XX'7 – IF₇ (Pentagonal bipyramidal shape)**

GROUP 18 ELEMENTS)(THE NOBLE GAS FAMILY)

1- Ionisation enthalpy

They have very high ionization enthalpy because of completely filled orbitals.

Ionisation enthalpy decreases down the group because of increase in size.

2- Atomic radii

Increases down the group because number of shells increases down the group.

3- Electron gain enthalpy

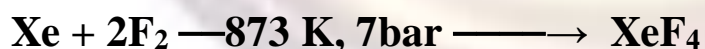
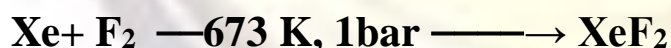
They have large electron gain enthalpy because of stable electronic configuration.

4- Melting and boiling point

Low melting and boiling point because only weak dispersion forces are present.

5- XeF₂ is linear, XeF₄ is square planar and XeF₆ is distorted octahedral. KrF₂ is known but no true compound of He Ne and Ar are known.

6- Compounds of Xe and F



7- Compounds of Xe and O

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