

Subject: Chemistry

Chapter: The p-Block Elements Top concepts

1. Elements in which the last electron enters the p-subshell of their outermost energy level are called p-block elements. The elements belonging to groups 13 to 18 constitute p-block elements.

2. General electronic configuration for elements belonging to p-block is ns^2np^{1-6}

3. General characteristics of p-block elements

1. Variation in oxidation states:

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
First member of group	B	C	N	O	F	He
Group oxidation state	+3	+4	+5	+6	+7	+8
Other oxidation states	+1	+2, -4	-3,+3	-2,+2,+4,	+5,+3,-1,+1	+2,+4,+6

2. Metallic and non-metallic character: Elements which show characteristics of both metals and non-metals and are called metalloids. Common metalloids in p-block elements are Si, Ge, As, Sb, Te, Po, At.

3. Differences in behaviour of first element of each group:

(a) Covalence upto four: First member of each group belongs to second period elements and have only four valence orbitals i.e., one 2s and three 2p orbitals. They do not have vacant d-orbitals in their valence shell. Therefore each member has maximum covalence of four (using one 2s and three 2p orbitals). Next members belonging to third or higher periods have vacant d-orbitals. For example elements of third period of p-block with the electronic configuration $3s^2 3p^x$ has vacant 3d-orbitals lying between 3p and 4s energy levels. Therefore, they can easily expand their octets and can show covalence above four. For example:

(i) Boron forms only BF_4^- (coordination number of B is four) whereas aluminium forms AlF_6^{3-} (coordination number of Al is six).

(ii) Carbon can form only tetrahalides (CX_4 , X = F, Cl, Br, I) whereas other members can form hexahalides, SF_6 , $SiCl_6^{2-}$ etc.

(iii) Nitrogen forms only NF_3 while phosphorous forms pentahalides like PCl_5 , PF_5 etc.

(iv) Fluorine does not form FCl_3 (F has more than octet) while chlorine forms ClF_3 (Cl has extended octet)

(b) Reactivity: Elements of second period do not have d – orbitals and are less reactive as compared to elements of third period which have d – orbitals. For example tetrahalides of carbon are not hydrolysed by water whereas tetrahalides of other elements of group 14 are readily hydrolysed (for e.g. Si)

(c) Tendency to form multiple bonds: Because of combined effect of smaller size and availability of p – orbitals, the first member of each group shows greater tendency to form $p\pi - p\pi$ multiple bonds either with itself (such as $\text{C} = \text{C}$, $\text{C} \equiv \text{C}$, $\text{N} \equiv \text{N}$, $\text{O} = \text{O}$) or with other members of the second period of elements (such as $\text{C} = \text{O}$, $\text{C} \equiv \text{N}$, $\text{N} = \text{O}$, etc.). Heavier elements of the group do not have strong tendency to form this type of $p\pi - p\pi$ bonding. The heavier elements do form π - bonding but they involve d – orbitals and form $d\pi - p\pi$ or $d\pi - d\pi$ bonding.

5. Group 13 Elements: The Boron family

1. Electronic Configurations: Elements of group 13 have the general outer electronic configuration of ns^2np^1

Elements	Symbol	Atomic No.	Electronic Configuration
Boron	B	5	$[\text{He}] 2s^2 2p^1$
Aluminium	Al	13	$[\text{Ne}] 3s^2 3p^1$
Gallium	Ga	31	$[\text{Ar}] 3d^{10} 4s^2 4p^1$
Indium	In	49	$[\text{Kr}] 4d^{10} 5s^2 5p^1$
Thallium	Tl	81	$[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^1$

2. Trends in properties of group 13 elements:

No.	Property	Variation along the group
1	Atomic radii	Atomic radii increases down the group but not regularly
2	Ionization Enthalpy	Ionization enthalpy decreases down the group but not regularly
3	Electronegativity	Down the group, electronegativity first decreases from B to Al and then increases marginally

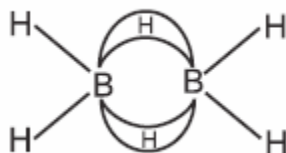
3. Some important compounds of boron:

No.	Name of compound	Formula of compound
1	Borax	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$

2	Orthoboric acid	H_3BO_3
3	Diborane	B_2H_6

4. Structure of diborane (B_2H_6):

The electron diffraction studies have shown bridged structure for diborane as shown below



Four hydrogen atoms (2 on the left and 2 on the right) are known as terminal hydrogens. These are different than the other two hydrogen atoms, which are known as bridged hydrogens. The two boron atoms and the four terminal H-atoms lie in the same plane while the two bridging H-atoms are in a plane perpendicular to the rest of the molecule. There are two types of bonds in the molecule:

- The four terminal hydrogens are bonded by normal covalent bonds formed by sharing of one electron each from B and H atoms
- The bridged hydrogens are bonded by three centre electron pair bond, which involve one electron pair only (i.e. two electrons) but binds three atoms i.e. two B atoms and one H atom.

Boron atom undergoes sp^3 hybridisation involving 2s and all the three 2p orbitals including one empty orbital. The four sp^3 hybrid orbitals adopt tetrahedral arrangement. Two hybrid orbitals of each B atom overlap with 1s orbital of two H atoms. Of the hybrid orbitals left on each B atom, one contains an unpaired electron while the other is vacant. The hybrid orbital containing an unpaired electron of one B atom and the vacant hybrid orbital of the second B atom overlaps simultaneously with 1s orbitals of H atom to form B-H-B bridge bond. B-H-B bond is called three centre electron pair bond.

5. Group 14 Elements: Carbon Family

1. Electronic Configuration: Elements of group 14 have the general outer electronic configuration of ns^2np^2

Element	Symbol	Atomic No.	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] $4d^{10} 5s^2 5p^2$



2. Trends in properties of group 14 elements:

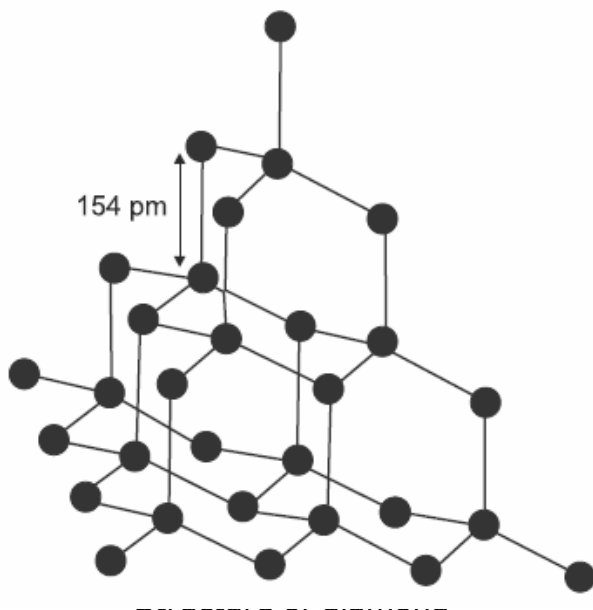
No.	Property	Variation along the group
1	Atomic radii	An atomic radius increases down the group. There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed
2	Ionization Enthalpy	Ionization enthalpy decreases down the group but not regularly. Small decrease in $\Delta_i H$ from Si to Ge to Sn and slight increase in $\Delta_i H$ from Sn to Pb is the consequence of poor shielding effect of intervening <i>d</i> and <i>f</i> 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

(3) Allotropes of Carbon: Allotrope forms or allotropes are the different forms of the same elements having different physical properties but similar chemical properties.

1. Crystalline form: Diamond and graphite are two crystalline forms of carbon having well defined structure
2. Amorphous form: Coal, wood charcoal, animal charcoal, lamp black, coke, etc. are many amorphous forms of carbon such as

(5) Structure of different allotropes of carbon:

(a) Diamond: Diamond has a network structure consisting of a very large number of carbon atoms bonded to each other. Each carbon atom is sp^3 hybridized and is bonded to four other carbon atoms by single covalent bonds. There is a three – dimensional network of strong covalent bonds in diamond. This makes diamond an extremely hard crystal with very high melting point (about 3843 K).

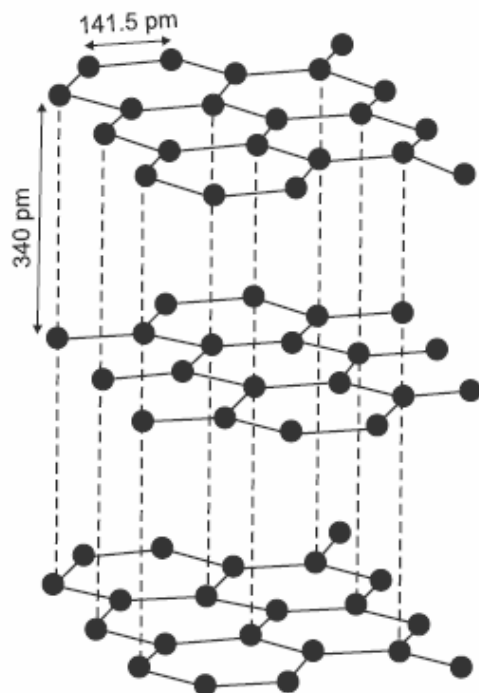


Since all the valence electrons of carbon are strongly held in carbon – carbon bonds, diamond is a poor conductor of electricity.

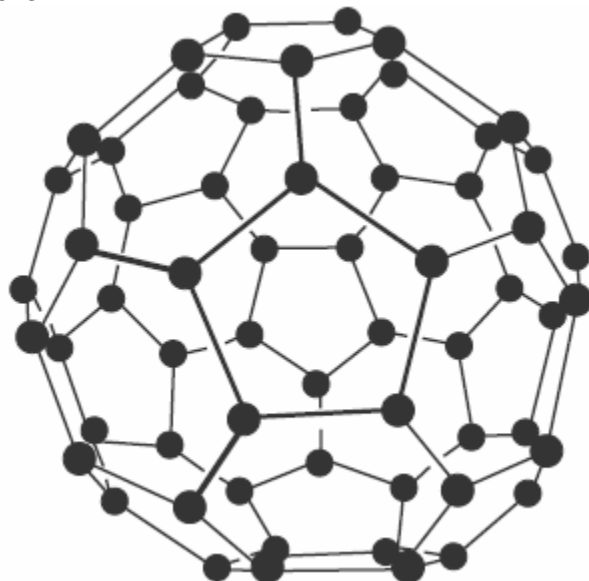
(b) Graphite: In graphite, each carbon atom undergoes sp^2 hybridisation and is covalently bonded to three other carbon atoms by single bonds. The fourth electron on each carbon atom forms π bonds. In this way, graphite consists of hexagonal rings in two dimensions. The C–C covalent distance in rings is 141.5 pm indicating strong bonding. These arrays of ring form layers. The layers are separated by a distance of 340 pm. The large distance between these layers indicates that only weak van der Waals' forces hold these layers together. The weak van der Waals' forces which hold these layers together are responsible for soft nature of graphite.

Because of the weak Van der Waals' forces between layers, one layer can move over the other layer and this account for the slippery nature of graphite. Therefore, graphite is used as lubricant. The electrons forming π bonds in the rings of graphite are delocalized and are relatively free to move under the influence of electric field. Therefore, graphite is a good conductor of electricity.



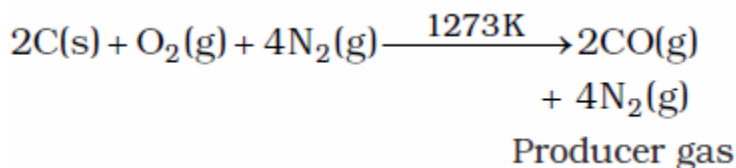
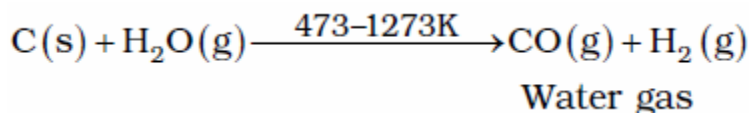
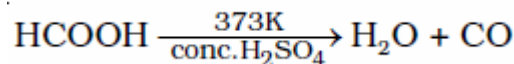
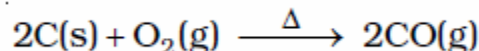


(c) Fullerene: It contains 20 six-membered rings and 12 five-membered rings. All the carbon atoms are equal and they undergo sp^2 hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in molecular orbitals, which in 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.



4. Some important Compounds of carbon and silicon
(i) Carbon Monoxide (CO)

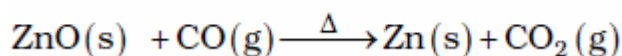
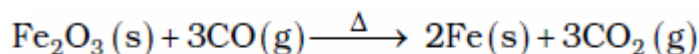
(a) Preparation of carbon monoxide (CO):



(b) Properties of carbon monoxide (CO):

(i) It is colourless, odourless and almost water insoluble gas

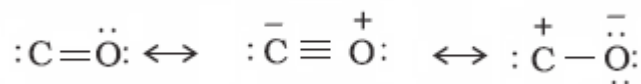
(ii) It is a powerful reducing agent and reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals



(iii) CO is highly poisonous because it has ability to form a complex with haemoglobin, which is about 300 times more stable than the oxygen-haemoglobin complex. This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death.

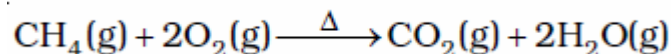
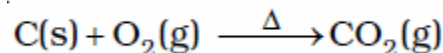
(c) Structure of carbon monoxide (CO): In CO molecule, there are one σ and two π bonds between carbon and oxygen: $\text{C} \equiv \text{O}:$. Because of the presence of a lone pair on carbon, CO molecule acts as a donor and reacts with certain metals when heated to form metal carbonyls.

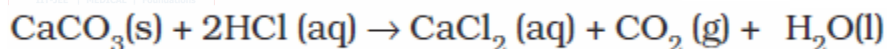
Carbon monoxide is regarded as resonance hybrid of the following structures:



(ii) Carbon dioxide (CO₂)

(a) Preparation of carbon dioxide (CO₂) :

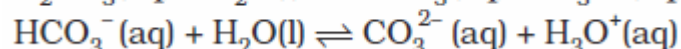
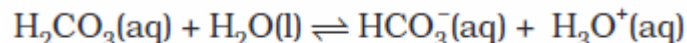




(b) Properties of carbon dioxide (CO₂):

(i) It is a colourless and odourless gas

(ii) With water, it forms carbonic acid, H₂CO₃ which is a weak dibasic acid and dissociates in two steps:

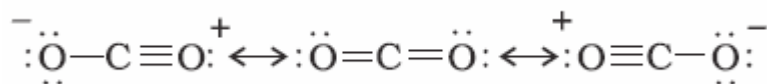


H₂CO₃/HCO₃⁻ buffer system helps to maintain pH of blood between 7.26 to 7.42

(iii) Being heavy and non-supporter of combustion carbon dioxide is used as fire extinguisher

(c) Structures of carbon dioxide:

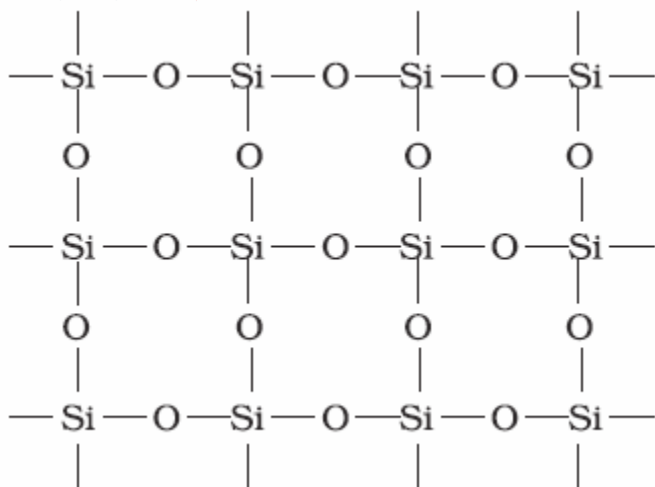
In CO₂ molecule carbon atom undergoes sp hybridisation. Two sp hybridised orbitals of carbon atom overlap with two p orbitals of oxygen atoms to make two sigma bonds while other two electrons of carbon atom are involved in pπ – pπ bonding with oxygen atom. This results in its linear shape [with both C–O bonds of equal length (115 pm)] with no dipole moment. The resonance structures are shown below:



(iii) Silicon dioxide (SO₂):

Silicon dioxide is a covalent, three dimensional network solid. In this structure each silicon atom is tetrahedrally surrounded by four oxygen atoms. Each oxygen atom in turn is covalently bonded to other silicon atoms. Each corner is shared with another tetrahedron. The entire crystal may be considered as giant molecule in which eight membered rings are formed with alternate silicon and oxygen atoms. Thus, there are no discrete SiO₂ units and it is a network solid.

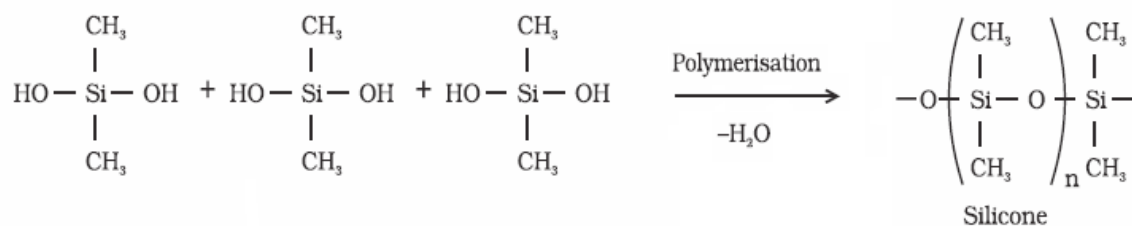
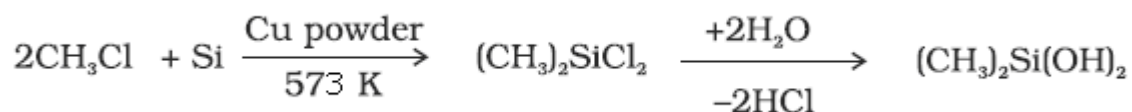




(iv) Silicones

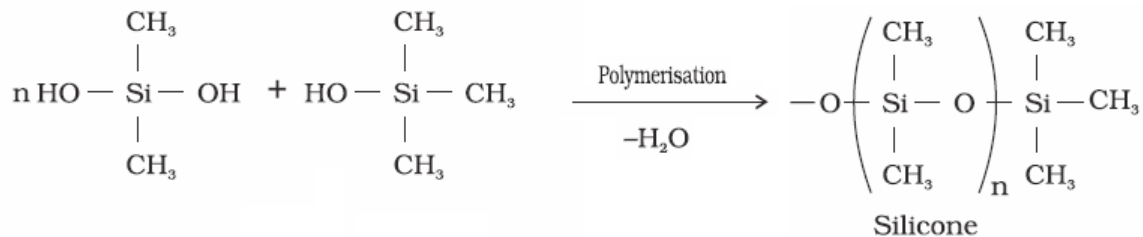
Silicones are organosilicon polymeric compounds containing Si-O-Si linkages. These have the general formula $(R_2SiO)_n$ having (R_2SiO-) as a repeating unit. Starting materials for the manufacture of silicones are alkyl or aryl substituted silicon chlorides, $R_nSiCl_{(4-n)}$, where R is alkyl or aryl group.

When methyl chloride reacts with silicon in the presence of copper as a catalyst at a temperature 573K various types of methyl substituted chlorosilane of formula $MeSiCl_3$, Me_2SiCl_2 , Me_3SiCl with small amount of Me_4Si are formed. Hydrolysis of dimethyldichlorosilane, $(CH_3)_2SiCl_2$ followed by condensation polymerisation yields straight chain polymers.



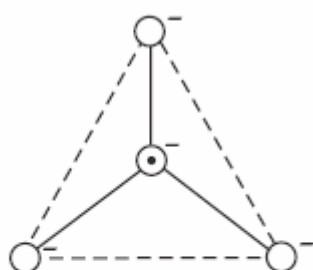
The chain length of the polymer can be controlled by adding $(CH_3)_3SiCl$ which blocks the ends.





(v) Silicates:

Basic building unit of all silicates is the tetrahedral SiO_4^{4-} ion. In silicates either the discrete unit is present or a number of such units are joined together via corners by sharing 1, 2, 3 or 4 oxygen atoms per silicate units. If all the four corners are shared with other tetrahedral units, three-dimensional network is formed.



- Silicon
- Oxygen

Representation of SiO_4^{4-} unit

(vi) Zeolites:

Aluminosilicates are formed when few Si atoms are replaced by Al atoms in three-dimensional network of silicon dioxide. Zeolites are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation, e.g., ZSM-5 (A type of zeolite) used to convert alcohols directly into gasoline.

(7) Some important reasons:

(1) Atomic and ionic radii group 13 elements are smaller as compared to corresponding elements of group 2

Explanation: On moving from left to right in a periodic table, magnitude of nuclear charge increases but the electrons are added to the same shell. Since the electrons in the same shell do not screen each other, therefore, the electrons experience greater nuclear charge. In other words, effective nuclear charge increases and thus, size decreases. Therefore, the elements of group 13 have smaller size than the corresponding elements of second group.



(2) On moving down the group both atomic and ionic radii are expected to increase due to addition of new shells. But the atomic radius of Al is slightly more than that of Ga

Explanation: While going from Al ($Z = 13$) to Ga ($Z = 31$) there are ten elements of the first transition series of d – block from ($Z = 21$ to 30) which have electrons in the inner d – orbitals. The d – orbitals do not screen the nucleus effectively because of their shapes and poor penetration power. As a result, the effective nuclear charge in Ga becomes more than in Al and its atomic radius, therefore, decreases slightly.

(3) Ionization enthalpy decreases sharply from B to Al and then the ionization enthalpy of Ga is unexpectedly higher than that of Al

Explanation: The sharp decrease in ionization enthalpy from B to Al is due to increase in size. In case of Ga, there are ten d – electrons in its inner electronic configuration. Since, the d – electrons shield the nuclear charge less effectively than the s – and p – electrons, the outer electron is held strongly by the nucleus. As a result, the ionization enthalpy increases on moving from Al to Ga. Similar increase is also observed from In to Tl which is due to presence of 14 f-electrons in inner electronic configuration of Tl which have very poor shielding effect

(4) BCl_3 act as Lewis acid

Explanation: In trivalent state, the number of electrons around the central atom i.e. B in BCl_3 is only six. BCl_3 has two electrons less than the octet and therefore is electron deficient molecule. BCl_3 has a tendency to accept a pair of electrons to achieve stable electronic configuration and therefore, behave as Lewis acid

(5) AlCl_3 exist as dimer Al_2Cl_6 while BCl_3 exist as monomer, though both are electron deficient compounds

Explanation: In AlCl_3 , there are six electrons around Al atom and these are two less than the octet. In the dimeric structure, each aluminium atom completes its octet by accepting a lone pair of electron from the chlorine atom of another AlCl_3 molecule. Boron because of its small size cannot accommodate four large sized halide ions around it to form a dimer

(6) Anhydrous AlCl_3 covalent in nature but hydrated AlCl_3 is ionic

Explanation: In anhydrous AlCl_3 Al atom is linked to three Cl atoms by covalent bonds. This is due to the fact that a large amount of energy is needed to convert aluminium atom (Al) to aluminium ion (Al^{3+}). Therefore, it prefers to form covalent bonds with Cl atoms. However, when aluminium chloride is dissolved in water, it undergoes hydration as:



Hydration of Al_2Cl_6 is an exothermic process and a large amount of energy is released. Thus energy liberated during hydration process is responsible for the removal of three electrons from Al to form Al^{3+} ion. In fact, in dissolved

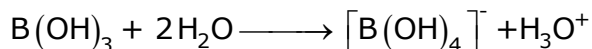
state, Al exists as $[\text{Al}(\text{H}_2\text{O}_6)]^{3+}$. Therefore, the hydrated aluminium chloride is ionic in nature.

(7) Basic character of hydroxides increase on moving down the group

Explanation: On moving down the group, the magnitude of the ionization energy decreases. As a result, the strength of the M–O bond also decreases accordingly. Therefore, its cleavage becomes easy resulting in the increased basic strength down the group

(8) Boric acid is not a protonic acid but a Lewis acid

Explanation: A species that accepts electron pair acts as Lewis acid. Boric acid accepts electrons from hydroxyl ion of water and a Lewis acid



(9) PbCl_4 is a good oxidizing agent

Explanation: An oxidizing agent reduces itself easily. Pb in PbCl_4 is in +4 oxidation state. Due to inert pair effect because Pb^{2+} is more stable than Pb^{4+} . Thus Pb^{4+} easily reduces to Pb^{2+} and thus PbCl_4 acts as good oxidizing agent

(10) Boron does not form B^{3+} ions

Explanation: Boron has a very small size. The sum of first three ionisation enthalpies ($\text{IE}_1 + \text{IE}_2 + \text{IE}_3$) is very high. Therefore, it cannot lose its three electrons to form B^{3+} ions.

(11) BCl_3 is more stable than TlCl_3

Explanation: B exhibits +3 oxidation state and can form stable BCl_3 . Thallium shows +3 oxidation state as well as +1 oxidation state but +1 oxidation state is more predominant stable than +3 oxidation state because of inert pair effect. Therefore, TlCl_3 is not as stable as BCl_3

(12) Molten aluminium bromide is a poor conductor of electricity

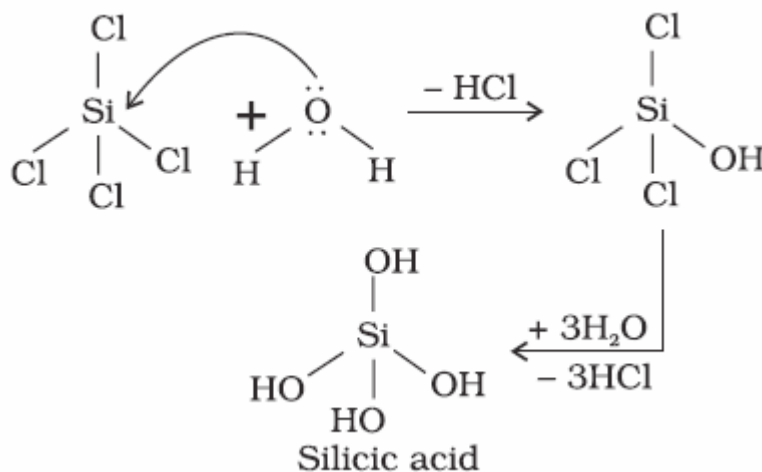
Explanation: AlBr_3 is predominantly a covalent compound. Even in molten state it does not have ions which can conduct electricity. Molten aluminium bromide is a poor conductor of electricity

(13) Tendency to catenation decreases in order $\text{C} \gg \text{Si} > \text{Ge} \approx \text{Sn} > \text{Pb}$

Explanation: Carbon has unique property of catenation i.e. property to form bonds with itself. Tendency to catenation depends upon the strength of M–M bond where $\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$ or Pb . If M–M bond formed is strong then catenation is favoured. As we go down the group the strength of M–M bond decreases due to increase in size of the atom and hence tendency to catenation decreases

(14) CCl_4 cannot be hydrolysed while SiCl_4 can be easily hydrolyzed

Explanation: SiCl_4 is readily hydrolysed by water because silicon has vacant 3d orbitals in its outermost shell. As a result, silicon can extend its coordination number beyond four. The vacant 3d orbitals of silicon accept electrons from water molecule and thus SiCl_4 can be easily hydrolysed



Carbon does not contain any d – orbitals in the valence shell. Carbon has only s and p – orbitals. As a result carbon cannot increase its coordination number beyond four and therefore, it cannot accept electrons from water molecules and eventually does not undergo hydrolysis

(15) Silanes are a few in number while alkanes are large in number

Explanation: Carbon has a maximum tendency for catenation due to strong C-C bonds. So, it forms a large number of alkanes. Silicon has a reduced tendency for catenation due to weak Si-Si bonds and hence it forms only a few silanes.

(16) Concentrated HNO_3 can be stored in an aluminium container but cannot be stored in a zinc container.

Explanation: In the presence of conc. HNO_3 , Al becomes passive, due to a thin protective layer of its oxide (Al_2O_3), which is formed on its surface and prevents further action between the metal and the acid. Therefore Al containers can be used for storing conc. HNO_3 . It cannot be stored in zinc vessels because zinc reacts with HNO_3 .

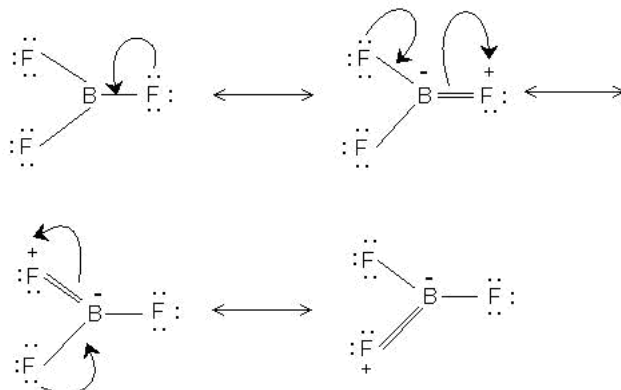
(17) BBr_3 is a stronger Lewis acid than BF_3

Explanation: BBr_3 is a stronger Lewis acid than BF_3 because of the back donation of electrons into empty 2p orbital of the B atom from filled p-orbital of the Br atom is much less than that by F atoms. This is due to larger size of the Br atom as compared to the F atom. As a result the electron deficiency of B is much higher in BBr_3 than that in BF_3 . Hence BBr_3 is a stronger Lewis acid than BF_3



(18) BF_3 exists whereas BH_3 does not exist

Explanation: BF_3 is trigonal planar molecule. Due to $p\pi - p\pi$ back bonding lone pair of electrons of F is back donated to B atom. This delocalization reduces the deficiency of electrons of boron thereby increasing the stability of BF_3 molecule. The mechanism is as follows:



Due to absence of lone pair of electrons on H atom this compensation does not occur in BH_3 .

In other words electron deficiency of B stays & hence it reduces its electron deficiency as BH_3 dimerises to form B_2H_6 .

(19) SiO_2 is solid but CO_2 is a gas at room temperature

Carbon is able to form $p\pi - p\pi$ bond with O atom and constitute a stable non-polar molecule $\text{O}=\text{C}=\text{O}$. Due to weak inter molecular force its boiling point is low and it is gas at room temperature.

Si on the other hand is not able to form $p\pi - p\pi$ bond with O atoms because of its relatively large size. In order to complete its octet Si is linked to four O atoms around it by sigma bond & these constitute three dimensional network structures, which is responsible for its solid state.

