P-BLOCK ELEMENTS

GENERAL CHARACTERISTICS :

- 1. General Electronic Configuration : ns^2np^{1-6} . The inner core of the electronic configuration influence the physical properties (such as atomic & ionic radii, IE, -ve $\Delta_{eg}H$, electronegativity etc) and the chemical properties.
- 2. Oxiation States : The oxidation states of elements are closely related to the number of electrons in the valence shell of their elements. The highest oxidation oxidation state = (gp no. -10).

INERT PAIR EFFECT : It is the tendency of having less availability of 'ns' electron in bonding on account of their penetration in (n-1)d sub shell. On descending the group, the inert pair effect increases & a lower oxidation state which is two less than the highest oxidation state becomes more stable in group 13 to 16.

| Group | 13 | 14 | 15 | 16 | 17 | 18 |
|-----------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| General E.C. | ns ² np ¹ | ns ² np ² | ns ² np ³ | ns ² np ⁴ | ns ² np ⁵ | ns ² np ⁶ |
| First member of | | | | | | |
| the group | В | С | Ν | 0 | F | Ne |
| Group Ox. state | +3 | +4 | +5 | +6 | +7 | +8 |
| Other Ox. state | +1 | +2, -4 | +3, -3 | +4, +2, -2 | +5, +3,+1 -1 | +6, +4, +2 |

- 3. Metallic & non-metallic character : The p block contains metallic & non-metallic elements. The non metals & metalloids exist only in the p block. The non metallic character decreases down the group. The most metallic elements are located in the lower left portion while the most nonmetallic character is present at the top right portion of the periodic table. The common metalloids are B, As, Ge, As, Sb, Te, Po, At etc.
- 4. IE & Electro negativity of nonmetals is higher & thus they readily form anions.
- 5. The nonmetal oxides are acidic or neutral whereas metal oxides are basic in nature, (Al₂O₃ is amphoteric)
- 6. The first member of each group differ in many respect from the other elements of the same group due to
 - (i) Small size of the atom & its ions
 - (ii) high electro negativity
 - (iii) absence of d-orbital in their valence shell

These factors have significant effect on the chemistry of the first element :

- (a) **Covalence up to four :** First member has one 2s & three 2p orbitals (& no vacant d orbital) available for taking part in chemical reaction. Thus, they may have maximum covalence of four Eg, Boron Forms BF_4 whereas Al form AIF₆ Carbon can form tetrahalides (CCl₄) whereas other members form hexahalides (SF₆, SiCl₆²⁻ etc), Nitrogen forms NF₃ while phosphorus forms PF₅.
- (b) Reactivity : Due to availability of d-orbitals of the elements of 3rd period, they can show higher covalence (beyond 4)
- (c) Tendency to form multiple bonds : Because of the combined effect of the smaller size & unavailability of d orbitals, the 1st member of each group show greater tendency to form $p\pi p\pi$ multiple bonds either with itself (C = C, C = C, N = N, O = O) or with other members of the second period of the elements (C = O, C = N, N = O). Heavier elements do not form $p\pi p\pi$ bonds because their atomic orbitals are too large and diffuse to have effective overlapping.

GENERAL CHARACTERISTICS OF GROUP 13 & 14

| Characteristics | Group 13 : BORON FAMILY | Group 14 : CARBON FAMILY |
|---|--|---|
| Occurence | Orthoboricacid (H_3BO_3) , Borax $(Na_2B_4O_7 10H_2O)$ Bauxite $(Al_2O_3 2H_2O)$ Cryolite (Na_3AlF_6) | Coal, Graphite & diamond Cassiterite (SnO ₂) Galena (PbS) |
| Electronic Configuration | B : $[He]2s^22p^1$ (has noble gas core) Al : $[Ne]3s^2 3p^1$ (has noble gas core) Ga : $[Ar]3d^{10} 4s^2 4p^1$ (has noble gas + 10d) ln : $[Kr]4d^{10}5s^2 5p1$ (has noble gas + 10d core) Tl : $[Xe] 4f^{14}5d^{10} 6s^2 6p^1$ (has noble gas + 14f + 10d core) | |
| Atomic Radii | On moving down the group both atomic & ionic radii are expected to increase due to addition of new shells. But atomic radii of Al > Ga because low screening & poor penetration of d orbitals in Ga. | Si is considerable but from Si to Pb is small increase due to presence of |
| ΙΈ | It decreases sharply from B to Al but IE of Ga & Al as well as ln & Tl is almost the same due to low screening of d & f electrons. | The 1st IE is higher. The decrease is small from Si to Ge to Sn & slightly increase from Sn to Pb (poor shielding & increasing size.) |
| Electronegativity | It is decreasing from B to Al but then increases due to discrepancies in atomic size. | More eletro-ve than gp13 |
| M.P & B.P | Decreases on moving down the group but the decreases in M.P is not regular (decreases from B to Ga & increases from Ga to Tl) as in B.P. B has unusually high MP due to very strong crystalline lattice & Ga has unusually low MP exists as discrete diatomic molecules. | binding forces. Thus higher MP & BP than gp 13. BP & MP decreases down the group. |
| Density | Increase down the group because increase in at mass outweights the effect of increase in size. | Same as group 13 elements |
| Electropositivity (metallic character) | Less electropositive than group 2 elements. On moving down the group, metallic character increases because IE decreases (eg B is a non metal.) | Metallic character increases because IE decreases Ge is metalloid. |
| Oxidation state | Maximum oxidation state +3 ($2e^{-1}$ in s & le^{-1} in p subshell). From B to Al, the sum of the three IE decreases, thus Al forms Al ³⁺ ions. Except boron, other elements also show +1 oxidation state which is more stable as we move down the group (inert pair effect). The relative stability of +1 : Al < Ga < ln < Tl. +3 state is highly oxidizing in nature & +1 | Maximum oxidation state $+4(2e^{-} \text{ in s } \& 2e \text{ in p subshell})$ Ge, Sn & Pb also show $+2$ which is more stable on moving down (inert pair effect) Ge < Sn < Pb. |
| | more ionic | |

CHEMICAL REACTION :

| | Group 13 | Group 14 |
|----|--|---|
| 1. | Boron is non metallic & the crystalline form is very hard, unreactive & non conducting (reacts only at very high temp) | Carbon is a typical non metal and exhibit allotropy. Silicon also behaves as non metal but in certain physical properties behave as semi metal. |
| 2. | Al is reactive but gets covered with a protective oxide layer. | Ge is a metalloid while Sn & Pb are typical metal. In tetravalent state the number of electrons around |
| | Ga, In & TI are relatively soft & reactive metals which readily dissolve in acids. The sum of the three IE for Boron in much greater | the central atom in a molecule (eg CCl_4 , Si Cl_4) is eight, thus they are ELECTRON PRECISE molecules. |
| | than that compensated by the lattice (solid) or hydration (aqueous) energies. Thus ionic compounds of boron are not easily formed. Other atoms of gp 13 form ionic compounds in aqueous solution. eg AlCl ₃ is covalent which hydrolyse to ionic $[Al(H_2O)_6]^{3+}$. Trichlorides on hydrolysis in water form tetrahedral $[M(OH)_4]$ species. | 5. Except carbon other members have d orbitals & can exceed its covalence more than 4. Due to this their halides can undergo hydrolysis & have tendency to form complexes by accepting electron pairs from donor species. Eg : [SiF₆]²⁻,[GeCl₆]²⁻,[Sn(OH)₆]²⁻ where the central atom has sp³d² hybridisation.entral atom can accept <i>e⁻</i> pair from H₂O due to availability of d -orbitals. |
| | $sp^{2}BCl_{3} \longrightarrow [B(OH)_{4}]^{-}sp^{3-}$ | |
| 6. | In +3 state, the number of electrons around the central atom in a molecule of these elements are only six (BF ₃) and are ELECTRON DEFICIENT molecules and behave as LEWIS ACIDS. | $\begin{array}{c c} Cl & Cl & OH \\ Sl &+ O &+ HCl \\ Cl & Cl & H & H & Cl & Cl \\ Cl & Cl & H & H & Cl & Cl \\ Cl & Cl & H & H & Cl & Cl \\ Cl & Cl & H & H & Cl & Cl \\ Cl & Cl & H & H & Cl & H \\ Silicic acid \\ \end{array}$ |
| | AlCl ₃ stabilizes by forming dimer. But BCl ₃ exists as molecule. (B atom is so small can accomodate 4 large sized atoms around it) | 6. Carbon has a tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation. Down the group |
| | $\begin{array}{c c} Cl \\ Cl \\ Cl \\ B \\ Cl \\ Cl \\ Cl \\ Cl \\ $ | catenation decreases as size increases and electronegativity decreases. Pb does not show catenation.7. Carbon shows allotropic forms due to catenation |
| | Planar Tetrahedral | and formation of $p\pi - p\pi$ bonds. |

| Property | Group 13 | Group 14 |
|---|---|---|
| Reactivity towards O ₂ (Nature of oxides) | $4B+3O_{2} \xrightarrow{\Delta} 2B_{2}O_{3}$ & $4Al+3O_{2} \xrightarrow{\Delta} 2Al_{2}O_{3}$ $2B+N_{2} \xrightarrow{\Delta} 2BN$ & $2Al+N_{2} \xrightarrow{\Delta} 2AlN$ Boron forms acidic. Al & Ga form amphoteric and In & Tl form basic oxides. | All elements when heated with oxygen form oxides (MO & MO ₂) Oxides of higher oxidation state are more acidic than those in lower ox. state CO_2 , Si O_2 , GeO ₂ are acidic whereas SnO_2 & PbO ₂ are amphoteric CO is neutral, GeO is acidic while SnO and PbO are amphoteric |
| Reactivity towards H_2O | B & Al do not react but Al amalgam reacts with cold water. ∴ oxide coating not formed $2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2$ | C, Si & Ge are not affected. Sn reacts with steam $Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$ Lead is unaffected due to formation of protective layer |

3

| Reactivity towards Halogen | Form trihalides $2E + 3X_2 \rightarrow 2EX_3$ BBr ₃ > BCl ₃ > BF ₃ (strength of Lewis acids) reason:- Due to back bonding BF ₃ is no longer remain electron deficient but in case of BCl ₃ and BBr ₃ , there is no back bonding between B & Cl or B & Br as size of Cl and Br is big enough, so that effective back bonding is not possible | Form halides $MX_2 \& MX_4$ Tetra halides are mostly covalent. Except carbon, all other members react directly with halogens under suitable conditions. Pbl_4 does not exist because Pb-1 bond initially formed does not release enough energy to unpair $6s^2$ electrons and excite one of them to higher orbital to have 4 unpair $6s^2$ electrons and excite one of them to higher orbital to have 4 unpaired e^- . Stability of dihalides increases down the group PbX ₂ more stable than PbX ₄ , but GeX ₄ more stable than GeX ₂ due to inert pair effect. |
|---|--|---|
| Reactivity towards Acids & Alkalis | B does not react & Al shows amphoteric nature. $2A1 + 6HC1 \rightarrow 2A1^{3+} + 6Cl^{-}$ $2Al + 2NaOH + 6H_2O \rightarrow 2Na[Al(OH)_4] + 3H_2$ Conc HNO ₃ Makes Al passive by forming a protective layer. | C, Si & Ge are unaffected by acids. Sn dissolve in dil HNO ₃ to form nitrate. Pb dissolve slowly in dil HCl forming PbCl ₂ but dissolve readily in dil HNO ₃ 4 Sn + 10HNO ₃ \rightarrow 4 Sn(NO ₃) ₂ + NH ₄ NO ₃ + 3 H ₂ O Pb + HNO ₃ \rightarrow Pb(NO ₃) ₂ + NO ₂ + H ₂ O |

SOME IMPORTANT COMPOUNDS :

- 1. BOROX : $Na_2B_4O_7.10H_2O$: a) It contains tetranuclear units $[B_4O_5(OH_4)]^{2-}$ thus the formula is $Na_2[B_4O_5(OH_4)] BH_2O$.
 - (b) Effect of heat : $\operatorname{Na}_{2}\operatorname{B}_{4}\operatorname{O}_{7}$. $\operatorname{10H}_{2}\operatorname{O} \xrightarrow{\Delta} \operatorname{Na}_{2}\operatorname{B}_{4}\operatorname{O}_{7} + \operatorname{10H}_{2}\operatorname{O} \xrightarrow{\Delta} 2\operatorname{NaBO}_{2} + B_{2}\operatorname{O}_{3}_{(\operatorname{Sodium metaborate})} B_{\operatorname{Borax}} B_{\operatorname{Bead}} \xrightarrow{(\operatorname{Boriz anhydride})} B_{\operatorname{Borax}} B_{\operatorname{Bead}}$
 - (c) $NaBO_2 + B_2O_3$ from transparent glassy bead which when touched with some colored cations as Ni^{2+} , Co^{2+} , Cu^{2+} etc & heated again gives characteristic colored beads. This is known as BOROX BEAD TEST.

e.g.
$$C \circ O + B_2 O_3 \longrightarrow C \circ (BO_{B/We})_2$$

$$N i O + B_2 O_3 \longrightarrow N i (B O_2)_2$$

- **2.** ORTHOBORIC ACID (H_3BO_3) :
 - (a) It is prepared by acidifying an aqueous solution of borax.

 $Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4B(OH)_3$.

(b) It is a weak monobasic acid which is not a protonic acid but acts as lewis acid by accepting electrons from a hydroxyl ion.

 $B(OH)_3 + 2HOH \rightarrow [B(OH)_4]^- + H_3O^+$

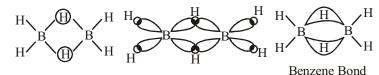
(c) Effect of heat : $H_3BO_3 \longrightarrow HBO_2 \longrightarrow B_2O_3$ _{Metaboric acid} $\longrightarrow B_2O_3$ _{Boric oxide}

3. DIBORANE (B_2H_6) :

(a) Reaction of NH_3 with dibrone gives initially B_2H_6 . $2NH_3$ formulated as $[BH_2(NH_3)_2]^+BH_4$. This gives borozine $B_2N_2H_6$ (ignorganic benzene) on heating.

 $2 \operatorname{B}_{2}\operatorname{H}_{6} + 6 \operatorname{N}\operatorname{H}_{3} \rightarrow 3 [\operatorname{B}\operatorname{H}_{2}(\operatorname{N}\operatorname{H}_{3})_{2}]^{+} [\operatorname{B}\operatorname{H}_{4}]^{-} \xrightarrow{\Delta} 2 \operatorname{B}_{3}\operatorname{N}_{3}\operatorname{H}_{6} + 12 \operatorname{H}_{2} \xrightarrow{B_{0} \operatorname{razine}(\operatorname{inorganic benzene})} + 12 \operatorname{H}_{2} \operatorname{Razine}(\operatorname{Inorganic benzene)} + 12 \operatorname{H}_{2} \operatorname{Razine}($

(b) Structure of diborane : There are two types of hydrogen : (i) four terminal hydrogen are bonded to B by normal covalent bonds sharing one e⁻ each by B & H atom (ii) The bridged hydrogen are bonded by three centre e⁻ pair bonds, which involve one e⁻ pair only (2e⁻) but binds three atoms B, H & B known as three centre electron pair bond.



(c) Boron also forms a series of hydridoborates; the most important one is the tetrahedral $[BH_4]^-$ ion. Lithium and sodium tetrahydridoborates, also known as borohydrides, are prepared by the reaction of metal hydrides with B_2H_6 in diethyl ether. MBH_4 (metal borohydrides) used as reducing agent in organic synthesis

4.SILICON DIOXIDE (SiO₂)

- (a) Also called silica, forms 95% of the earth's crust. The crystalline forms are quartz, cristobalite & tridymite. They are interconvertible at suitable temperature.
- (b) It is a covalent, three dimensional network solid in which each Si atom is covalently bonded in a tetrahedral manner to four Oxygen atoms. Each Oxygen atom in turn is covalently bonded in another Si atom. The entire crystal is a giant molecule in which eight member rings are formed. Silica in normal form is almost non-reactive because of very high Si-O bond enthlpy, however, it is attacked by HF and NaOH.

5. SILICONES

- (a) They are polymeric compounds containing Si-O linkage with general formula R₂SiO as repeating unit.
- (b) The starting material for the manufacture of silicones is alkyl substituted chlorosilanes.

 $2CH_{3}Cl + Si \xrightarrow{Cu/570K} (CH_{3})_{2}SiCl_{2} \xrightarrow{+2H_{2}O} (CH_{3})_{2}Si(OH)_{2} + 2HCl$

The polymers are obtained by the hydrolysis of the chloro derivative. When two molecules of dialkyl silinol combine, dimer is obtained with the elimination of the molecule of water.

$$HO \xrightarrow{H}_{O} OH + HO \xrightarrow{H}_{O} OH \xrightarrow{-H_2O} HO \xrightarrow{CH_3} OH \xrightarrow{-H_2O} HO \xrightarrow{H}_{O} OH \xrightarrow{I}_{O} OH$$

Since an active -OH group is left on each end of the chain, polymerization reaction continues & the length of the chain increases.

$$HO - \begin{array}{c} CH_{3} & CH_{3} & CH_{3} \\ I & I \\ CH_{3} & CH \\ CH_{3} & CH_{3} \end{array} - OH + HO - \begin{array}{c} Si - OH \\ I \\ CH_{3} & CH_{3} \end{array} - OH - \begin{array}{c} CH_{3} \\ Polymerise \\ -H_{2}O \end{array} - O - \begin{array}{c} CH_{3} \\ Si - O \\ CH_{3} \\ CH_{3} \end{array} - \begin{array}{c} CH_{3} \\ I \\ CH_{3} \\ CH_{3} \end{array} - \begin{array}{c} CH_{3} \\ I \\ CH_{3} \\ CH_{3} \\ CH_{3} \end{array} - \begin{array}{c} CH_{3} \\ I \\ CH_{3} \\ CH_$$

- (c) Silicones are surrounded by non polar alkyl groups which are water repelling. They are used as sealant, greases, electrical insulators & for water proofing of the fabric. They are also used in surgical & cosmetic plants
- 6. SILICATES : (SiO_4^4) and ZEOLITE

Do Uses of SiO₄⁴⁻(silicates), SiO₂ (Silicon dioxide) from N.C.E.R.T. BOOK.

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

Structure of different allotropes of carbon:

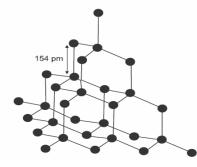
(a) Diamond: Diamond has a network structure consisting of a very large number of carbon atoms bonded to each other. Each carbon atom is sp³ hybridized and is bonded to four other carbon atoms by single covalent bonds. There is a three – dimensional network of strong covalent bonds in diamond. This makes 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.

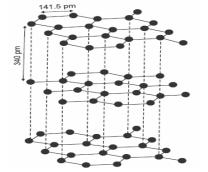
(b)Graphite: In graphite, each carbon atom undergoes sp² hybridisation and is covalently bonded to three other carbon atoms by single bonds. The fourth electron on each carbon atom forms π bonds. In this way, graphite consists of hexagonal rings in two dimensions. The C–C covalent distance in rings is 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.

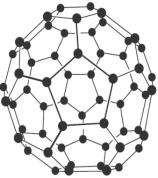
(c)Fullerene: It contains 20 six- membered rings and 12 five membered rings. All the carbon atoms are equal and they undergo sp² hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in molecular orbitals, which in 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.



Structure of diamond



Structure of graphite



Structure of fullerene

Some important compounds of Carbon

(i) CARBON MONOXIDE (CO)

(a)Preparation of carbon monoxide (CO):

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

HCOOH
$$\xrightarrow{373K}$$
 conc.H₂SO₄ $\xrightarrow{H_2O}$ + CO

$$C(s) + H_2O(g) \xrightarrow{473-1273K} CO(g) + H_2(g) = 2C(s)$$

Water gas

(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

$$\begin{array}{l} \operatorname{Fe}_{2}O_{3}\left(s\right) + 3\operatorname{CO}\left(g\right) \xrightarrow{\Delta} 2\operatorname{Fe}\left(s\right) + 3\operatorname{CO}_{2}\left(g\right) \\ \operatorname{ZnO}\left(s\right) + \operatorname{CO}\left(g\right) \xrightarrow{\Delta} \operatorname{Zn}\left(s\right) + \operatorname{CO}_{2}\left(g\right) \end{array}$$

(iii) CO is highly poisonous because it has ability to form a complex with haemoglobin, which is about 300 times more stable than the oxygenhaemoglobin 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:C = 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:

 $:C = \overset{..}{O}: \longleftrightarrow : \overset{..}{C} \equiv \overset{+}{O}: \longleftrightarrow : \overset{+}{C} = \overset{..}{\overset{..}{O}:}$

(ii) Carbon dioxide (CO₂)

(a) Preparation of carbon dioxide (CO₂) :

$$C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g) \qquad CH_4(g) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(g)$$

 $CaCO_3(s) + 2HCl (aq) \rightarrow CaCl_2 (aq) + CO_2 (g) + H_2O(l)$

(b) Properties of carbon dioxide (CO₂):

(i) It is a colourless and odourless gas

(ii) With water, it forms carbonic acid, H_2CO_3 which is a weak dibasic acid and dissociates in two steps:

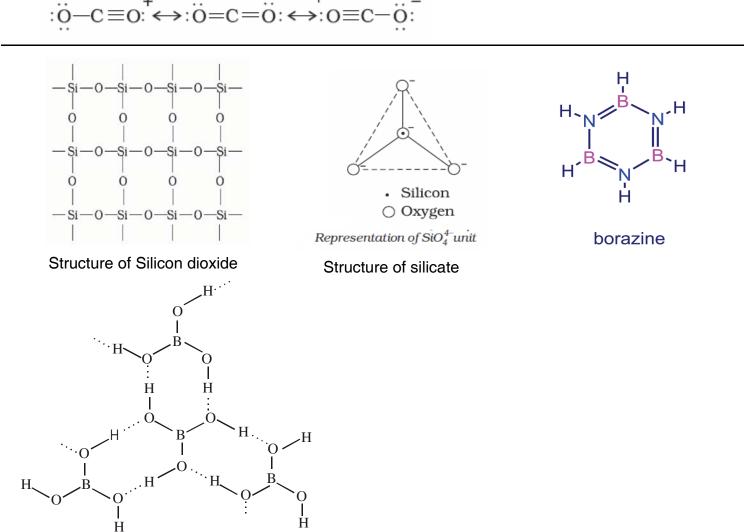
$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3(aq) + H_3O^{\dagger}(aq)$$
$$HCO_3(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^{\dagger}(aq)$$

 H_2CO_3/HCO_3^- 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

+ $O_2(g)$ + $4N_2(g)$ $\xrightarrow{1273K}$ 2CO(g) + $4N_2(g)$ Producer gas (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 $p\pi - p\pi$ 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:



Structure of boric acid; the dotted lines represent hydrogen bonds

Zeolites:

Aluminosilicate 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.

S BLOCK ELEMENTS

| Properties | Alkali metals (group 1) \rightarrow Why | Alkali Earth Metals (group 2) |
|---------------------|--|---|
| - | General configuration $-ns^1(n=2-7)$ | General configuration –ns ² |
| Electronic | Li : [He]2s ¹ | Be. $[He]2s^2$ |
| configuration | Na : $[Ne]2s^1$ | $Mg:Ne]3s^2$ |
| | K. $[Ar] 4s^1$ | $Ca: [Ar] 4s^2$ |
| | $Rb : [Kr]5s^1$ | $Sr : [Kr]5s^2$ |
| | $Cs : [Xe]6s^1$ | Ba : $[Xe]6s^2$ |
| | $Fr : [Rn]7s^1$ | $Ra: [Rn]7s^2$ |
| | | They are smaller than alkali metals. It |
| Atomic & ionic | They have largest size in their respective | increases on moving down the group due |
| radii | period. It increases on moving down the | to addition of new energy shells. The |
| | group due to addition of new energy shells. | ••• |
| | The monovalent ions (M^+) are smaller than | devalent ions (M^{2+}) are smaller than the |
| | the parent atom. | parent atom $M^{2+} < M^+ < M$ (due to |
| | | decreased effective nuclear charge) |
| Ionisation enthalpy | The 1 st IE is quite low due to large size. The | _ |
| | value decreases down the group. After | than that of alkali metals due to smaller size. |
| | loosing one e^- , it attains stable noble gas | But the 2 nd IE are smaller than |
| | configuration. | corresponding alkali metals I.E. ₂ (group 1) |
| | | is greater than I.E. $_2$ (group 2). |
| | Decreases with increase in ionic size | Larger than alkali metals due to greater |
| Hydration Enthalpy | $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+ > Fr^+$ | charge density |
| | Li ⁺ has maximum degree of hydration thus | $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ |
| | its salts exist as hydrated salts e.g. LiCl. | Salts are more extensively hydrated eg. |
| | 2H ₂ O. | MgCl ₂ $6H_2O$, CaCl ₂ . $6H_2O$. |
| | 2 | |
| | Low density due to large atomic volume & | Denser, heavier & harder than alkali metals |
| Density | can but cut with a knife. The density increases | due to small size & strong metallic bonds. |
| Density | down the group from Li to Cs but k is lighter | Show regular trend. |
| | than Na as increase in size is more than mass. | |
| State | Silvery white, soft & light metals. | Silvery white, lustrous & relatively harder |
| | Silvery white, son & light fields. | than alkali metals. |
| Conductors | Good conductors of heat & electricity. | Cood conductors of heat & electricity |
| | | Good conductors of heat & electricity. |
| Malting Pr | Low MP & BP due to weak metallic bonds | |
| Melting & | (Presence of only one valence electron) & | Higher than alkali metals due to smaller |
| Boiling points | decreases down the group | size. Does not show a regular trend. |
| | | (2 valence $e^- \rightarrow$ metalic bonding strong. |
| Flame | Li : Crimson red, Na : Yellow | Be & Mg do not impart color as the |
| Coloration | K : Violet, Rb : Red Violet | electrons are strongly bound to get excited |
| (due to | Cs : Blue | by flame (due to small size) |
| excitation & de- | due to low I.E. e^- excited by light of particular | Ca : Brick red |
| excitation of | λ ; while coming back complementary colour | Sr : Crimson red |
| valence electron) | is observed by energing λ . | |
| | is observed by energing A. | Ba : Apple green |

GENERAL TRENDS IN PROPERTIES :

| Reducing | 1 | | |
|---------------------------|---|--|--|
| Reducing Properties | Strong reducing agent as they have low IE (tendency to lose e ⁻) E ^o is less | They are weaker reducing agents than alkal metals because of higher I.E. + 2 (noble gas config. & high lattice enthalpy.) | |
| Oxidation State | +1 | +2 | |
| Photoelectric effect | Cs shows maximum due to low I.E. | · - | |
| Basic Strength | | | |
| Reaction with Air | Tarnish in air due to formation of a layer of oxides which in turn form hydroxides Reactivity with oxygen increases from Li to Cs, (they are stored under kerosene oil) 4Li + O₂ → 2Li₂O(Oxide) 2Na + O₂ → Na₂O₂(Peroxide) K(or Rb or Cs)+O₂ → KO₂ (superoxide) The stabilities of these oxides are linked with the relative sizes of cations & anions involved & also upon the charges present | to formation of an oxide layer (BeO, MgO) • With the exception Ba & Ra which form peroxides (MO ₂) rest of the elements from normal oxides on heating with excess Oxygen. $2Be+O_2 \rightarrow 2BeO$ $2Mg+O_2 \rightarrow 2MgO$ $2Mg+O_2 \rightarrow 2MgO$ | |
| | on them. A smaller cation can stabilize a smaller anion while a larger cation can stabilize larger anion. Thus Li⁺ forms oxide (O²⁻) but Na⁺, K⁺ being larger form peroxide & superoxide. Li react directly with nitrogen to form nitrides 6Li + N₂ → 2Li₃N | $2Ba + O_2 \rightarrow BaO_2$ $\begin{bmatrix} \vdots \vdots \vdots \end{bmatrix}^{2^-} \begin{bmatrix} \vdots \vdots & -\vdots & \vdots \end{bmatrix}^{2^-} \begin{bmatrix} \vdots & \vdots & -\vdots & \vdots \end{bmatrix}^{2^-} \begin{bmatrix} \vdots & \vdots & \cdots & \vdots \end{bmatrix}^{-}$ Oxide (O ²) Peroxide (O ² ₂) Superoxide (O ² ₂) | |
| Reaction towards Acids | Readily react with acids to liberate H₂ 2M+2HCl→2MCl+H₂↑ | • Readily react with acids to liberated H_2 M+2HCl \rightarrow MCl ₂ +H ₂ \uparrow | |
| Nature of Oxides | Oxides & peroxides are colorless but superoxide is yellow or orange. The superoxides are paramagnetic and used as oxidizing agents. All oxides are basic in nature & are easily hydrolysed by water to form hydroxides. M₂O + H₂O → 2M⁺ + 2OH⁻ M₂O₂ + H₂O → 2M⁺ + 2OH⁻ + H₂O₂ | BeO is a covalent solid, the oxides of the rest of the metals are white crystalline ionic solids Except for BeO which is amphoteric in nature rest of the oxides are basic & the | |
| | $2\mathrm{MO}_2 + 2\mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{M}^+ + 2\mathrm{OH}^- + \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2$ | Sodium beryllate BeO+2HCl \rightarrow BeCl ₂ +H ₂ O | |
| Reaction with water | React with water to form hydroxides & release H₂. 2M + 2H₂O → 2MOH + H₂ Reaction of Li with water is less vigorous than Na due to its small size & high hydration energy. Other metals react vigorously. | Ca, Sr & Ba are readily react with water with increasing vigour even in cold to form hydroxides | |

| Nature of Hydroxides | heat due to intense hydration. | Less basic and less stable than alkali metals Due to low IE of metals, M-OH bond ionizes, releasing OH⁻; Basic strength increases down the group due to decrease in IE. Be(OH)₂ is amphoteric in nature. Be(OH)₂+2OH⁻ → [Be(OH)₄]²⁻(Berylate ion) Be(OH)₂+2HCl+2H₂O → [Be(OH)₄]Cl₂ |
|--|---|--|
| Reactivity towards halogens | React vigorously with halogens to form ionic halides. Li forms covalent halides due to high polarisibility. Among halides, the covalent character increase from F to 1 (Fajan's Rules) MP & BP follow : F > C1 > Br > 1 increase in lattice enthalpy) Low solubility of LiF in water is due to high lattice enthalpy. Low solubility of CsI is due to small hydration enthalpy of two ions | Combine with halogens at elevated temperature. Ionic character increases from Be to Ra. BeCl₂ in solid state has a chain structure. Cl Cl Cl Be Cl Cl |
| Reactivity towards hydrogen | All metals react to form ionic hydrides which have high melting points Ionic nature increases from Li to Cs | All the elements except Be combine with H₂ to form MH₂ BeH₂ & MgH₂ are covalent & polymeric whereas others are ionic. |
| Salts of Oxo- acids (H ⁺ on hydroxyl group) (Carbonates & bicarbonates) | Forms salts with all oxo acids (H₂CO₃, H₂SO₄). Salts are soluble in water & thermally stable. Thermal stability increases down the group. Li₂CO₃ decomposes on heating & its bicarbonates does not exist as a solid, Li₂CO₃ → Li₂O + CO₂ Bicarbonates of other metals decomposes at low temperature. Nitrates : Lithium nitrate on heating gives oxide whereas other alkali metals give nitrites. 4LiNO₃ → 2Li₂O + 4NO₂ + O₂ 2NaNO₃ → 2NaNO₂ + O₂ | Carbonates are insoluble in water & their solubility decreases with increases in at no of metal ion. Thermal stability increases with increase in cationic size BeCO₃ is unstable & is stored only in the atmosphere of CO₂. Sulphates are thermally stable & white in color. The solubility of sulphates decreases down the group because SO²⁻₄ is large & masks the cation in lattice thus the size of cation does not influence lattice energy but hydration energy decreases from Be²⁺ to Ba²⁺. Nitrates are prepared by dissolution of carbonates in dil HNO₃. |

| $2M(NO_3)_2 \rightarrow 2MO + 4NO_2 + O_2$ |
|--|
|--|

Solutions in liquid NH₃

• Alkali metals as well as alkali earth metals dissolve in liquid NH₃ giving deep blue solutions which are conducting in nature.

Alkali metals: $M + (X + Y)NH_3 \rightarrow [M(NH_3)_X]^+ + [e(NH_3)_Y]^-$ (ammoniated cation) (ammoniated electron)

Alkali earth metals $M + (X + Y)NH_3 \rightarrow [M(NH_3)_X]^{2+} + 2[e(NH_3)_Y]^{-}$

- When light falls on the ammoniated electron, they absorb energy corresponding to red color and the transmitted light has a blue color.
- The blue solution is paramagnetic which on standing slowly liberate H₂ & formaton of metal amide.

$$\mathbf{M}^{+}_{(\mathrm{aq})} + e + \mathbf{NH}_{3(1)} \rightarrow \mathbf{MNH}_{2(\mathrm{aq})} + \frac{1}{2}\mathbf{H}_{2}$$

- The electrical conductivity of the solution is due to ammoniated cation as well as ammoniated electron.
- In concentrated solution the color changes from blue to bronze due to pairing of electron.
- The concentrated solutions are diamagnetic in nature.

ANOMALOUS BEHAVIOUR OF HEAD ELEMENTS

The elements belonging to second period sometimes called the head elements of their respective groups. The first element in each group (1, 2, 13, 14, 15, 16, 17) exhibit certain properties which are different from that of other elements in their respective groups. This anomalous behavior of the first element in each group is due to :

(i) Smaller size of their atoms

(v) Non availability of 'd' orbitals

- (iii) High polarizing power
- (iv) Low electropositive character

(ii) Higher ionisatio enthalpies

Difference betwen Lithium & other Difference between Beryllium & other alkali alkali metals (Anomalous behaviour of Li) earth Metals : (Anomalous behavior of Be) 1. Li is much harder with high MP & BP than other 1. Be has higher MP & BP than other alkali alkali metals earth metals 2. Li is less reactive but strongest reducing agent 2. BeO is amphoteric while others are strong (due to high hydration energy) bases. 3. Li forms Lithium monoxide with O_2 & reacts 3. Be & Mg do not impart color to the flame. 4. Be does not form peroxides. directly with N_2 to form nitrides. 4. LiCl is deliquescent & forms hydrates like 5. BeSO₄ is soluble in water. LiCl.2H₂O 6. Be does not liberate H_2 from acids whereas others do 5. Lithium hydrogen carbonate is not formed in solid state. 6. Lithium nitrate on heating gives oxide whereas other alkali metals give nitrites $4\text{LiNO}_3 \rightarrow 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2$ 2NaNO₃ \rightarrow 2NaNO₂ + O₂ 7. LiF & Li₂O are less soluble in water.

Important Compounds of alkali metals:

| Name of compound | Name of process & Brief about the process | Related chemical equations |
|---|--|--|
| Sodium Carbonate (Washing Soda), Na ₂ CO ₃ ·10H ₂ O | Solvay Process: When CO ₂ gas is passed through a brine solution saturated with ammonia, sodium bicarbonate is formed. Sodium bicarbonate on heating forms sodium carbonate | $\begin{array}{l} 2\mathrm{NH}_3 + \mathrm{H}_2\mathrm{O} + \mathrm{CO}_2 \rightarrow \left(\mathrm{NH}_4\right)_2 \mathrm{CO}_3 \\ \left(\mathrm{NH}_4\right)_2 \mathrm{CO}_3 + \mathrm{H}_2\mathrm{O} + \mathrm{CO}_2 \rightarrow 2\mathrm{NH}_4\mathrm{HCO}_3 \\ \mathrm{NH}_4\mathrm{HCO}_3 + \mathrm{NaCl} \rightarrow \mathrm{NH}_4\mathrm{Cl} + \mathrm{NaHCO}_3 \\ \overline{2}\mathrm{NaHCO}_3 \rightarrow \mathrm{Na}_2\mathrm{CO}_3 + \mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} \end{array}$ |
| Sodium Chloride, NaCl | Evaporation of sea water: Evaporation of sea water gives crude salt which contains impurities of CaSO ₄ , Na ₂ SO ₄ etc. To obtain pure sodium chloride, the crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with HCl gas. Crystals of pure sodium chloride separate out. | |
| Sodium Hydroxide (Caustic Soda), NaOH | Electrolysis of NaCl in Castner- Kellner cell: A brine solution is electrolysed using a mercury cathode and a carbon anode. Na metal discharged at the cathode combines with mercury to form sodium amalgam. Chlorine gas is evolved at the anode. Sodium amalgam on treatment with water forms sodium hydroxide | Cathode : Na ⁺ + e ⁻ \xrightarrow{Hg} Na – amalgam Anode : Cl ⁻ $\rightarrow \frac{1}{2}$ Cl ₂ + e ⁻ 2Na-amalgam + 2H ₂ O \rightarrow 2NaOH+ 2Hg +H ₂ |

| | sodium carbonate with | $Na_2CO_3 + H_2O + CO_2 \rightarrow 2 NaHCO_3$ |
|--|-----------------------|--|
|--|-----------------------|--|

Important Compounds of alkaline earth metals:

| Name of compound Calcium Oxide or Quick Lime, CaO | Name of process & Brief about the process It is prepared by heating limestone (CaCO ₃) in a rotary kiln at 1070-1270 K. The carbon dioxide is removed as soon as it is produced to enable the reaction to proceed to completion | Related chemical equations $CaCO_3 \xrightarrow{heat} CaO + CO_2$ |
|---|--|--|
| Calcium Hydroxide (Slaked lime), Ca(OH) ₂ | It is prepared by adding water to quicklime, CaO | $CaO + H_2O \rightarrow Ca(OH)_2$ |
| Calcium Carbonate, CaCO ₃ | It is prepared by passing carbon dioxide through slaked lime. Excess of carbon dioxide should be avoided since this leads to the formation of water soluble calcium hydrogen- carbonate | $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ |
| | It is prepared by the addition of sodium carbonate to calcium chloride. | $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$ |
| Calcium Sulphate (Plaster of Paris), CaSO ₄ · $\frac{1}{2}$ H ₂ O | It is obtained when gypsum, CaSO ₄ ·2H ₂ O, is heated to 393 K | $2(CaSO_4.2H_2O) \rightarrow 2(CaSO_4).H_2O + 3H_2O$ |

✤ Diagonal relationship between Li and Mg

Li resembles Mg mainly due to similarity in sizes of their atoms and ions. The main points of similarity are:

- i) Both are quite hard.
- ii) Both LiOH and Mg(OH)₂ are weak bases.
- iii) Carbonates of both on heating decompose to produce oxides and carbondioxide.
- iv) Both react with nitrogen to give ionic nitrides.
- v) Nitrates of both decompose on heating to give oxides.
- vi) Both Li and Mg do not form solid bicarbonates.
- vii) Because of covalent character LiCl and MgCl₂ are soluble in ethanol.
- viii) The hydroxides, bicarbonates and fluorides of both Li and Mg are sparingly soluble in water.

***** Biological importance of Na and K

- i) Sodium ions participate in the transmission of nerve signals.
- ii) Sodium ions also regulate flow of water across the cell membranes and in transport of sugars and amino acids into the cells.
- **iii)** Potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in oxidation of glucose to produce ATP.
- iv) Potassium ions in combination with sodium ions are responsible for transmission of nerve signals.
- v) The functional features of nerve cells depend upon the sodium potassium ion gradient that is established in the cell.

* Biological importance of Ca and Mg

- i) Magnesium ions are concentrated in animal cells and Calcium ions are concentrated in body fluids, outside the cell.
- ii) All enzymes that utilize ATP in phosphate transfer require magnesium ion as cofactor.
- iii) In green plants magnesium is present in chlorophyll.
- iv) Calcium and magnesium ions are also essential for the transmission of impulses along nerve fibres.
- v) Calcium ions are important in blood clotting and are required to trigger the contraction of muscles.
- vi) Calcium ions also regulate the beating of the heart.

S BLOCK AND P BLOCK ELEMENTS REASONING

1. Explain why is sodium less reactive than potassium?

lonization energy of K < Na i.e. the outermost electron in potassium can be lost easily as compared to sodium 2. Why is the Li is trongest reducing agent or SRP is most -ve, ie= -3.0 V

- Due to high heat of hydration which compensate its high heat of ionization make total heat to be more exothermic
 Why is Group I elements known as the most electropositive element
 Ionization energy is least for 1st on. The loosely held s-electron in the outermost valence shell of these elements make
- Ionization energy is least for Ist gp. The loosely held s-electron in the outermost valence shell of these elements makes them the most electropositive metals. They readily lose electron to give monovalent M+ ions.
- 4. What do you mean by diagonal relationship and its reason in the periodic table,? Similarities in few property of two elements placed diagonally in second and 3rd period, The diagonal relationship is due to the similarity in ionic sizes and /or charge / radius ratio of the elements.
- 5. Why alkali metal hydroxides are make the strongest bases? The alkali metal hydroxides are the strongest of all bases because the dissolve freely I water with evolution of much heat on account of intense hydration.
- 6. What makes lithium show properties different from rest of the alkali metals? Lithium is a small atom and it forms smaller Li+. As a result, it has very high charge to radius ratio. This is primarily responsible for the anomalous behavior of lithium.
- 7. Explain why alkali and alkaline earth metals cannot be obtained by chemical reduction methods? Alkali metals and alkaline earth metals are among the strongest reducing agents and the reducing agents that are stronger than them are not available
- 8. Why are potassium and cesium, rather than lithium used in photoelectric cells? because as compared to Cs and K, Li is smaller in size and therefore, requires high energy to lose an electron. While on the other hand, K and Cs have low ionization energy
- When an alkali metal dissolves in liquid ammonia the solution can acquire different colours. Explain the reasons for this type of colour change
 When an alkali metal is dissolved in liquid ammonia, it results in the formation of a deep blue coloured solution.
 M+(x+y) NH₃→M⁺(NH₃), +e⁻¹(NH₃),
- 10. Why are peroxides and super oxides stable in comparison to other oxides down the group? The stability of peroxides and super oxides is due to the stabilization of large anions by larger cat ions through lattice energy effects.
- 11. Why are lithium compounds soluble in organic solvents Due to high polarizing power, there is increased covalent character of lithium compounds which is responsible for their solubility in organic solvents.
- 12. Why does table salt get wet in rainy season? Table salts contains impurities of CaCl2 and MgCl2 which being deliquescent compounds absorbs moisture from the air in rainy reason.
- **13.** The atomic radii of alkaline earth metals are smaller than those of the corresponding alkali metals. Explain why? Beryllium, Magnesium, Calcium, Strontium, Barium and Radium.
- 14. The second ionization enthalpy of calcium is more than the first. How is that calcium forms CaCl₂ and not CaCl give reasons.

The higher value of second ionization enthalpy is more than compensated by the higher enthalpy of lattice formation of Ca^{2+} . Therefore formation of $CaCl_2$ becomes more favorable than CaCl energetically.

15. Compounds of alkaline earth metals are more extensively hydrated than those of alkali metals. Give reason The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions because of smaller six.

16. Why does the solubility of alkaline earth metal hydroxides in water increase down the group? Among alkaline earth metal hydroxides, the anion being common the cationic radius will influence the lattice enthalpy. Since lattice enthalpy decreases much more than the hydration enthalpy with increasing ionic size, the solubility increases as we go down the group.

- **17.** Why does the solubility of alkaline earth metal carbonates and sulphates in water decrease down the group? The size of anions being much larger compared to cations, the lattice enthalpy will remain almost constant within a particular group. Since the hydration enthalpies decrease down the group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.
- **18.** Beryllium and magnesium do not give colour to flame whereas other alkaline earth metals do so. Why? In Be and Mg, the electrons are strongly bound. The energy required to excite these electrons is very high
- 19. Potassium carbonate cannot be prepared by Solvay process. Why? This is because unlike sodium bicarbonate, potassium bicarbonate is fairly soluble in water and does not precipitate out.
- **20.** Why is KO₂ paramagnetic ? The superoxide O_2^- is paramagnetic because of one unpaired electron in π^*2p molecular orbital.
- 21. Why is Li₂CO₃ decomposed at a lower temperature whereas Na₂CO₃ at higher temperature? This is because lithium carbonate is covalent. Lithium ion, being very small in size, polarizes a large carbonate ion,
- 22. The hydroxides and carbonates of sodium and potassium are easily soluble in water while the corresponding salts of magnesium and calcium are sparingly soluble in water. Explain. the lattice energies of carbonates and hydroxides formed by calcium and magnesium are much more than those of sodium and potassium
- **23.** Why are lithium salts commonly hydrated and those of the other alkali metal ions usually anhydrous? Lithium is the smallest in size among the alkali metals. Hence, Li⁺ ion can polarize water molecules more easily than other alkali metals.
- 24. Why is LiF almost insoluble in water whereas LiCl soluble not only in water but also in acetone? This is mainly because of the greater ionic character of LiF as compared to LiCl
- 25. The mobilities of the alkali metal ions in aqueous solution are Li⁺ < Na⁺ < K⁺ < Rb⁺ < Cs⁺ Smaller the size of an ion, the more highly is it hydrated. Since Li⁺ is the smallest, it gets heavily hydrated in an aqueous solution. On the other hand, Cs⁺ is the largest and so it is the least hydrated, Greater the mass of a hydrated ion, the lower is its ionic mobility

26. Lithium is the only alkali metal to form a nitride directly.

Li reacts directly with nitrogen to form lithium nitride. This is because Li^{\dagger} is very small in size and so its size is the most compatible with the N³⁻ ion. Hence, the lattice energy released is very high. This energy also overcomes the high amount of energy required for the formation of the N³⁻ ion.

a solution of Na₂CO₃ is alkaline ? its hydrolyses to give sodium bicarbonate and sodium hydroxide (a strong base). As a result, the solution becomes alkaline. Na₂CO₃ + H₂O → NaHCO₃ + NaOH

28. alkali metals are prepared by electrolysis of their fused chlorides ?

as they themselves are very strong reducing agents. They cannot be prepared by displacement reactions Neither can electrolysis of aqueous solutions be used to extract these elements. This is because the liberated metals react with water.

29. sodium is found to be more useful than potassium ?

Sodium ions are involved in the transmission of nerve signals, in regulating the flow of water across the cell membranes,

30. Why does beryllium show similarities with AI?

Because of their similarity in charge / radius ratios

- **31.** Why is beryllium carbonate unusually unstable thermally as compared to the other carbonates of this group? This is due to strong polarizing effect of small Be²⁺ on the large CO3²⁻ anion and leading to the formation of more stable BeO
- 32. BeO is almost insoluble but $BeSO_4$ in soluble in water,

The size compatibility of Be^{2^+} and O^{2^-} is high. Therefore, the lattice energy released during their formation is also very high and can not be overcome by Hyd.Energy On the other hand, $SO_4^{2^-}$ ion is a large anion. Hence, Be^{2^+} can easily polarise $SO_4^{2^-}$ ions, making $BeSO_4$ unstable. Thus, the lattice energy of $BeSO_4$ is not very high and so it is soluble in water

33. BaO is soluble but BaSO₄ is insoluble in water,

The size compatibility of Ba²⁺ and O²⁻ is not high. As a result, BaO is unstable. The lattice energy released during its formation is also not very large. It can easily be overcome by the hydration energy of the ions.

Therefore, BaO is soluble in water. In BaSO₄, Ba²⁺ and SO_4^{2-} are both large-sized. The lattice energy released is high. Hence, it is not soluble in water

34. Lil is more soluble than KI in ethanol.

As a result of its small size, the lithium ion has a higher polarising power than the potassium ion. It polarises the electron cloud of the iodide ion to a much greater extent than the potassium ion. This causes a greater covalent character in Lil than in KI. Hence, Lil is more soluble in ethanol.

35. What is 'inert pair effect'?

Inertness of the electron pair of ns orbital which occurs down the group due to poor overlapping bond energy can not compensate for excitation energy ,which fails to promote e- from ns orbital and oxidation states decreases by to unit than the group oxidation states are attributed to the 'inert pair effect'.

36. How can you explain higher stability of BCI_3 as compared to $TICI_3$?

In TI, the +3 state is highly oxidising and it reverts back to the more stable +1 state. due to inert pair effect ,+3 In TI, is unstable

37. Why does boron trifluoride behave as a Lewis acid?

It has three electrons in its valence shell. Thus, it can form only three covalent bonds and one p orbital is vacant . This means that there are only six electrons around boron and its octet remains incomplete.

38. Consider the compounds, BCI_3 and CCI_4 . How will they behave with water? Justify

Being a Lewis acid, $\ensuremath{\mathsf{BCI}}_3$ readily undergoes hydrolysis. Boric acid is formed as a result

 $BCl_3 + 3H_2O \longrightarrow 3HCl + B(OH)_3$ CCl₄ completely resists hydrolysis. Carbon does not have any vacant orbital

39. Is boric acid a protic acid? Explain.

Boric acid is not a protic acid. It is a weak monobasic acid, behaving as a Lewis acid. $^{B(OH)_{3}} + ^{2HOH} \longrightarrow [B(OH)_{4}]^{-} + ^{H_{3}O^{+}}$ It behaves as an acid by accepting a pair of electrons from ^{-}OH ion.

40. Lead is known not to form an iodide, Pbl₄.

Due to inert pair effect Pb(IV) is highly unstable and can reduce to reduces to Pb(II). $PbI_4 \longrightarrow PbI_2 + I_2$

41. Lead(IV) chloride is highly unstable towards heat.

On moving down group IV, the higher oxidation state becomes unstable because of the inert pair effect. Pb(IV) is highly unstable and when heated, it reduces to Pb(II).

 $PbCl_{4(I)} \longrightarrow PbCl_{2(s)} + Cl_{2(g)}$

^{42.} Suggest reasons why the B–F bond lengths in BF₃ (130 pm) and BF_4^- (143 pm) differ.

 $p^{p-orbital} = F remove this$ p p - p r back bonding (130 pm).

With a vacant *p*-orbital on boron, the fluorine and boron atoms undergo $p\pi - p\pi$ back-bonding to remove this This (130 pm). Tetrahedral structure tetr

hybridisation from sp^2 (in BF₃) to sp^3 (in BF_4^-) occurs. Boron now forms 4 σ bonds and the double-bond character is lost.

This accounts for a B–F bond length of 143 pm in BF_4^- ion.

43. If B-Cl bond has a dipole moment, explain why BCl₃ molecule has zero dipole moment.

This is because BCI₃ is trigonal planar in shape. It is a symmetrical molecule. Hence, the respective dipole-moments of

3

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the B-CI bond cancel each other, thereby causing a zero-dipole moment.

44. Aluminium trifluoride is insoluble in anhydrous HF but dissolves on addition of NaF

(HF) is a covalent compound and has a very strong intermolecular hydrogen-bonding. Thus, it does not provide ions and aluminium fluoride (AIF) does not dissolve in it. Sodium fluoride (NaF) is an ionic compound and when it is added to the mixture, AIF dissolves. This is because of the availability of free F⁻. The reaction involved in the process is:

 $AIF_3 + 3 NaF \longrightarrow Na_3[AIF_6]$

Sodium hexafluoroaluminate (III)

45. Aluminium trifluoride precipitates out of the resulting solution when gaseous BF₃ is bubbled through. Give reasons.

This happens because the tendency of boron to form complexes is much more than that of aluminium. Therefore, when BF_3 is added to the solution, B replaces Al from the complexes according to the following reaction: Na₃[AlF₆] + 3 BF₃ \longrightarrow 3 Na[BF₄] + AlF₃

46. Suggest a reason as to why CO is poisonous.

Carbon monoxide is highly-poisonous because of its ability to form a complex with haemoglobin. The CO–Hb complex is more stable than the O_2 –Hb complex. The former prevents Hb from binding with oxygen. Thus, a person dies because of suffocation on not receiving oxygen. It is found that the

47. How is excessive content of CO₂ responsible for global warming?

Carbon dioxide has the property of trapping the heat provided by sunrays. Higher the level of carbon dioxide, higher is the amount of heat trapped. This results in an increase in the atmospheric temperature, thereby causing global warming.

48. Conc. HNO_3 can be transported in aluminium container.

Conc. HNO₃ form a thin protective oxide layer on the aluminium surface. This oxide layer renders aluminium passive.

49. A mixture of dilute NaOH and aluminium pieces is used to open drain.

Sodium hydroxide and aluminium react to form sodium tetrahydroxoaluminate(III) and hydrogen gas. The pressure of the produced hydrogen gas is used to open blocked drains.

 $2 \text{ Al} + 2 \text{ NaOH} + 6 \text{H}_2\text{O} \longrightarrow 2 \text{ Na}^+[\text{Al}(\text{OH})_4]^+ + 3 \text{H}_2$

50. Graphite is used as lubricant.

different layers of graphite are bonded to each other by weak van der Waals' forces. These layers can slide over each other. Graphite is soft and slippery

51. Aluminium utensils should not be kept in water overnight.

However, when water is kept in an aluminium vessel for long periods of time, some amount of aluminium oxide may dissolve in water. As aluminium ions are harmful, water should not be stored in aluminium vessels overnight.

52. How would you explain the lower atomic radius of Ga as compared to AI?

Although Ga has one shell more than Al, its size is lesser than Al. This is because of the poor shielding effect of the 3*d*-electrons. The shielding effect of *d*-electrons is very poor and the effective nuclear charge experienced by the valence electrons in gallium is much more than it is in the case of Al.

53. Classify following oxides as neutral, acidic, basic or amphoteric: CO, B₂O₃, SiO₂, CO₂, Al₂O₃, PbO₂, Tl₂O₃

(1) CO = Neutral

(2) $B_2O_3 = Acidic$

Being acidic, it reacts with bases to form salts. It reacts with NaOH to form sodium metaborate.

 $B_2O_3 + 2 \text{ NaOH} \longrightarrow 2 \text{ NaBO}_2 + H_2O$

(3) $SiO_2 = Acidic$

Being acidic, it reacts with bases to form salts. It reacts with NaOH to form sodium silicate.

 $SiO_2 + 2 NaOH \longrightarrow 2 Na_2SiO_3 + H_2O$

(4) $CO_2 = Acidic$

Being acidic, it reacts with bases to form salts. It reacts with NaOH to form sodium carbonate. $CO_2 + 2 NaOH \longrightarrow Na_2CO_3 + H_2O_3$

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(5) $AI_2O_3 = Amphoteric$

Amphoteric substances react with both acids and bases. Al_2O_3 reacts with both NaOH and H_2SO_4 . Al,O, + 2 NaOH \longrightarrow NaAlO,

£ 3 £

 $\mathrm{Al_2O_3} + 3\mathrm{H_2SO_4} \longrightarrow \mathrm{Al_2(SO_4)_3} + 3\mathrm{H_2O}$

(6) PbO₂ = Amphoteric Amphoteric substances react with both acids and bases. PbO₂ reacts with both NaOH and PbO₂ + 2 NaOH → Na₂PbO₃ + H₂O

 H_2SO_4 , 2 PbO₂ + 2 H₂SO₄ \longrightarrow 2 PbSO₄ + 2 H₂O + O₂

(7) TI_2O_3 = Basic Being basic, it reacts with acids to form salts. It reacts with HCl to form thallium chloride. $TI_2O_3 + 6 HCl \longrightarrow 2 TICI_3 + 3 H_2O$

54. Aluminium forms $[AIF_6]^{3-}$ whereas $[BF_6]^{3-}$ in not formed why?

Due to presence of vacant d-orbital's, AI can expand its octet to form bonds with six fluoride ions whereas B cannot . Boron does not have d-orbital's

- **55.** Some halides of group 14 elements form complexes of the type $[Mx_6]^{2-}$ Give reason. the central atom can increase its coordination number from 4 to 6 due to availability of vacant d–orbital's.
- 56. Why is carbon different from other member of the group? Carbon differs from rest of the members of its group due to its smaller size, higher electro negativity, higher ionization enthalpy and unavailability of d-orbital's.
- 57. Why does the covalence of carbon not expand beyond four?

In carbon, only s and p orbital's are available for bonding and therefore it can accommodate only four pairs of electrons around it. This limit the maximum covalence to four whereas other members can expand their covalence due to the presence of d-orbital's.

- **58.** Why does the heavier elements do not form $p\pi p\pi$ multiple bond as carbon do? because their atomic orbital's are too large and diffuse to have effective overlapping.
- 59. Why solid CO₂ is called dry ice?Solid CO₂ on heating sublimates without melting
- 60. Why does CO_2 have a linear shape with no dipole moment In CO_2 molecule carbon atom undergoes sp hybridization. Two sp hybridized orbital of carbon atom overlap with two p-orbital's of oxygen atoms to make two sigma bonds while other two electrons of carbon atom are involved in $p\pi - p\pi$ bonding with oxygen atom. This results in its linear shape [with both c-o bond of equal length (115 pm)] with no dipole moment.

61. Why does graphite conduct electricity? Graphite forms hexagonal ring and undergoes sp2 hybridization. The electrons are delocalized over the whole sheet. Electrons are mobile and therefore graphite conducts electricity over the sheet.

- **62.** White fumes appear around the bottle of anhydrous aluminium chloride. Give reason. Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture to liberate HCI gas. Moist HCI appears white in colour.
- **63.** Boron is unable to form BF₆³⁻ ion. Explain. Due to non-availability of *d* orbitals, boron is unable to expand its octet. Therefore, the maximum covalence of boron cannot exceed 4.
- **64.** Diamond is covalent, yet it has high melting point. Why ? Diamond has a three-dimensional network involving strong C—C bonds, which are very difficult to break and, in turn has high melting point.