CHAPTER 11

SOME p-BLOCK ELEMENTS

LEARNING OBJECTIVES

(i) The general trends in the chemistry of p-block elements.
(ii) Describe the trends in physical and chemical properties of group 13 and 14 elements.
(iii) Explain anomalous behaviour of boron and carbon.
(iv) Describe allotropic forms of carbon. Carbon is a typical non-metal forming covalent bonds employing all its four valence electrons ($2s^22p^2$). It shows the property of catenation, the ability to form chains or rings, not only with C.C single bonds but also with multiple bonds ($C = C$ or $C \equiv C$). The tendency to catenation decreases as $C >> Si > Ge \approx Sn > Pb$. Carbon provides one of the best examples of allotropy. Three important allotropes of carbon are diamond, graphite and fullerenes. The members of the carbon family mainly exhibit +4 and +2 oxidation states; compounds in +4 oxidation states are generally covalent in nature. The tendency to show +2 oxidation state increases among heavier elements. Lead in +2 state is stable whereas in +4 oxidation state it is a strong oxidising agent. Carbon also exhibits negative oxidation states. It forms two important oxides: CO and CO_2. Carbon monoxide is neutral whereas CO_2 is acidic in nature. Carbon monoxide having lone pair of electrons on C forms metal carbonyls. It is deadly poisonous due to higher stability of its haemoglobin complex as compared to that of oxyhaemoglobin complex. Carbon dioxide as such is not toxic. However, increased content of CO_2 in atmosphere due to combustion of fossil fuels and decomposition of limestone is feared to cause increase in 'green house effect'. This, in turn, raises the temperature of the atmosphere and causes serious complications. Silica, silicates and silicones are important class of compounds and find applications in industry and technology.
(v) Know the chemistry of some important compounds of boron, carbon and silicon.
Boron is a typical non-metal and the other members are metals. The availability of 3 valence electrons ($2s^22p^1$) for covalent bond formation using four orbitals (2s, $2p_x$, $2p_y$ and $2p_z$) leads to the so called electron deficiency in boron compounds. This deficiency makes them good electron acceptor and thus boron compounds behave as Lewis acids. Boron forms covalent molecular compounds with dihydrogen as boranes, the simplest of which is diborane, B_2H_6. Diborane contains two bridging hydrogen atoms between two boron atoms; these bridge bonds are considered to be three-centre two-electron bonds. The important compounds of boron with dioxygen are boric acid and borax. Boric acid, $B(OH)_3$ is a weak monobasic acid; it acts as a Lewis acid by accepting electrons from hydroxyl ion. Borax is a white crystalline solid of formula $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$. The borax bead test gives characteristic colours of transition metals.
(vi) List the important uses of group 13 and 14 elements and their compounds.

INTRODUCTION

Elements of group 13 to 18 of the periodic table are collectively called 'p' block elements. The general electronic configuration of these elements is ns^2np^{1-6}. They involve the filling up of 'p' orbitals of their outermost shells, when their 's' orbitals are already filled. Some of the 'p' block elements such as boron, carbon, nitrogen, and oxygen, form very important compounds.
Group 13 (III A) of the periodic table consists of the elements boron-(B), aluminium (Al), gallium (Ga), indium (In) and thallium (TI). As we pass from the first group to the succeeding groups the metallic nature of elements goes on continuously decreasing and, therefore, compared to the first and second groups, the elements of the third group are less metallic. In group III A, aluminium is decidedly a metallic element while boron is usually classified amongst the non-metals like carbon and silicon.
It will be observed that the characteristic feature of this group is configuration s^2p^1 in the external-most shell. The shell preceding to the external-most contains the grouping s^2 in boron, s^2p^6 in aluminium and $s^2p^6d^{10}$ in other elements of the sub-group A. This also shows why boron differs from aluminium, and both of them from the members of the sub-group A viz. Ga, In and Tl.
Group 14 (IVA) of the periodic table consists of the elements, carbon, silicon, germanium, tin and lead. It forms a link between the more electropositive elements of groups IA to IIIA and the more electronegative elements of groups VA to VIIA for we find that in the elements of the group, the electropositive character is as well developed as the electronegative.
The common characteristic of the group is the arrangement s^2p^2 in the external-most shell. The spell previous to the external most contains in carbon the group s^2, in silicon s^2p^6 (both saturated and yet different, accounting for the similarities and dissimilarities of the two elements), in germanium $s^2p^6d^{10}$ (saturated), whereas, in tin and lead $s^2p^6d^{10}$ (unsaturated). This also shows why tin

and lead are so different from silicon and germanium.

GROUP 13 (III A) :

Trends in physical and chemical properties of group 13 elements :

(i) Density, melting point, boiling point and heat of sublimation : Density increases from B to Tl. Melting points decrease from B to Ga and then increase upto Tl. Boiling points and heats of sublimation show a continuous decrease. The successive decrease in heat of sublimation indicates that the atoms of these elements are held less and less closely as we move from B to Tl.

(ii) Ionisation energies : The first ionisation energies which correspond to the removal of np^1-electron from ns^2p^1 configuration are relatively low while the second and third ionisation energies are considerably higher. Since boron atom is the smallest in size, its ionisation energy is the highest.

(iii) Electropositive (metallic) character : This increases from B to TI. Boron is predominantly a non-metal due to its small size and relatively high nuclear charge whereas other members are metals.

(iv) Oxidation states : Boron and aluminium show an oxidation state of +3 while other members show both + 1 and +3 oxidation states. Since the inert pair effect increases from Ga to TI (Boron and aluminium do not show inert pair effect), the stability of +3 oxidation state decreases while that of + 1 state increases. Thus Ga (I) compounds are unstable, In(I) compounds are moderately stable whereas those of Tl(I) are the most stable. Among the M(III) compounds, Tl(III) compounds are stable and tend to change to Tl(I) compounds. Consequently Tl(III) compounds are strong oxidising agents due to this tendency viz.

$$\underset{\substack{\text{unstable}\\ \text{(oxidising}\\ \text{agent)}}}{\text{Tl(III)}} \xrightarrow[\text{reduction}]{+2e^-} \underset{\text{stable}}{\text{Tl(I)}}$$

(v) Reactivity : Pure boron is almost unreactive at ordinary temperature. It reacts with air only when heated; it does not react with water. It is attacked only by hot conc. acids.

Aluminium decomposes water and reacts readily in air at ordinary temperature to form a protective layer to its oxide which protects it from further action. Calcium and indium are not affected by air even when heated whereas thallium is a little more reactive and forms an oxide on its surface.

(vi) Nature of M^{3+} compounds : From the electronic configurations of these elements it is clear that all of them would be expected to form M^{3+} ions. The nature of the compounds of M^{3+} ions is decided by Fajan's rule according to which the smaller the cation, the greater is its tendency to form covalent compounds. Thus with the increase of the size of M^{3+} ions from B^{3+} to Tl^{3+}, the tendency of these ions to form covalent compounds decreases. Consequently the compounds of B^{3+} are predominantly covalent while Al^{3+}, Ga^{3+}, In^{3+} and TI^{3+} give ionic compounds as well.

(vii) Oxides and hydroxides : As we move from boron to thallium, the oxides and hydroxides of these elements change from acidic through amphoteric to basic. Thus oxides and hydroxides of boron are acidic, those of Al and Ga are amphoteric while those of In and Tl are basic.

(viii) Hydrides : Boron forms a large number of covalent hydrides. Al and Ga form complex anionic hydrides such as $Li^+[AIH_4]^-$, $Li^+[GaH_4]^-$.

(ix) Halides : The trihalides of boron are covalent and act as Lewis acids. The fluorides of Al, Ga, In and Tl are ionic. The other halides (i.e. chlorides, bromides and iodides) of these metals are, however, largely covalent.

BORON FAMILY :

The boron family consists of five elements : Boron, aluminium, gallium, indium and thallium.

This group elements show a wide variation in properties. Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron, and gallium, indium and thallium are almost exclusively metallic in character.

Boron is a fairly rare element, mainly occurs as orthoboric acid (H_3BO_3), borax. $Na_2B_4O_7.10H_2O_7.10H_2O$, and kernite, $Na_2B_4O_7.4H_2O$.

There are two isotopic forms of boron ^{10}B (19%) and ^{11}B(81%). Aluminium is the most abundant metal and the third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%). Bauxite, $Al_2O_3.2H_2O$ and cryolite, Na_3AlF_6 are the important minerals of aluminium.

The atomic, physical and chemical properties of these elements are :

Electronic configuration : The outer electronic configuration of these elements is ns^2np^1. A close look at electronic configuration suggest that while boron and aluminium have noble gas core, gallium and indium have noble gas plus 10 d-electrons, and thallium has noble gas plus 14 f-electrons plus 10 d-electrons cores.

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 for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium is less than that of aluminium.

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 change.

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

BORON CHEMISTRY

Properties :

(A) Physical :

(a) Small atomic size

(b) Low electronegativity and hard, absorbs neutron, steel grey in colour. Some dissimilarities of boron with other elements of this group are :

(i) Boron is a non-metal while all other elements of this group are metals.

(ii) Boron forms only covalent compounds, while other elements of this group form both covalent and ionic compounds.

(iii) Boron shows a maximum covalency of four, while other elements of this group show a maximum valency of six, absorbs neutron, steel grey in colour. Its density is 2.34 gm/cc.

(B) Chemical :

1. Crystalline Boron is not active. Amorphous Boron reacts.

$$4B + 3O_2 \xrightarrow{700^\circ C} 2B_2O_3$$

$$2B + N_2 \xrightarrow{700^\circ C} 2BN$$

2. Action in alkalis and acids

$$2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2$$

$$2B + 3H_2SO_4 \xrightarrow{\text{oxidation}} 2H_3BO_3 + 3SO_2$$

$$B + 3HNO_3 \xrightarrow{\text{oxidation}} H_3BO_3 + 3NO_2$$

3. Boron reduces silica and CO_2

$$3SiO_2 + 4B \longrightarrow 2B_2O_3 + 3Si$$

$$3CO_2 + 4B \longrightarrow 2B_2O_3 + 3C$$

Preparation of Boron :

1. **From boric oxide** Boric oxide can be reduced to boron by highly electropositive metals.

$$B_2O_3\,(s) + 3Mg\,(s) \longrightarrow 2B\,(s) + 3MgO\,(s)$$

2. **From boron trichloride** By reducing volatile boron compound (boron trichloride) by dihydrogen at high temperature, boron is obtained

$$2BCl_3 + 3H_2\,(g) \xrightarrow{1270K} 2B\,(s) + 6HCl\,(g)$$

3. Crystalline boron may be obtained from BCl_3, by heating it with zinc

$$2BCl_3\,(g) + 3Zn\,(s) \xrightarrow{900^\circ C} 2B\,(s) + 3ZnCl_2\,(s)$$

4. **By electrolytic reduction of boron compounds** Boron can be obtained by the electrolysis of fused mixture containing boric anhydride (B_2O_3), magnesium oxide (MgO) and magnesium fluoride at 1100°C. The reactions taking place during electrolysis are,

$$2MgO \longrightarrow 2Mg + O_2(g)$$

$$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$$

5. **By thermal decomposition of boron hydrides and halides** Boron hydrides / halides on heating decompose to give amorphous boron.

$$B_2H_6\,(g) \xrightarrow{1170K} 2B\,(s) + 3H_2(g)$$

Compounds of boron :

Boron trioxide or boric anhydride, B_2O_3 : It is obtained by burning boron in oxygen or by heating boric acid to dull red heat when it forms a glassy transparent mass :

$$4B + 3O_2 \longrightarrow 2B_2O_3$$

$$3H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$$

It is hygroscopic and slowly combines with water to form boric acid, therefore, it is boric anhydride.

Boric oxide is an acidic oxide ; it combines with water to form boric acid. Mainly orthoboric acid, H_3BO_3, and to some extent metaboric acid, HBO_2 are the products formed :

$$B_2O_3 + H_2O \longrightarrow 2HBO_2$$

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