**Electron deficient Molecules**

There are certain molecules in which the central atom has lesser number of electrons than the number of electrons required attaining the inert gas electronic configuration. These molecules are called electron deficient species and have half-filled or empty orbitals. For example B in BF3 has 8 electrons in total whereas it requires 10 electrons to attain the electronic configuration of Ne (2, 8).

These molecules do not have enough electrons to form two-electron bonds between the atoms. For instance (BH3)2. [Be(CH3)2]2, [AI(CH3)3]n are electron deficient molecules, since they do not contain enough electrons to form the two-electron bonds between the atoms. The elements of group IIA and IIIA form electron deficient molecules. These elements have strong tendency to accept electrons and acquire tetrahedral geometry. The species having lone pairs of electrons react with electron deficient species and share electrons to make up their electron deficiency. Nature of bonding in these species is explained by taking the example of diborane, (BH3)2.

**2.5.1 Structure and Bonding in Diborane**

Diborane is made up of two BH3 units. Each BH3 is short of two electrons to complete the octet.The two BH3 unit form dimeric structure in which B atom undergoes sp3 hybridization and one sp3 orbital overlap with the 1s orbital of H atom as shown in Figure 2.53. Electron diffraction studies have shown that B2H6 has a hydrogen-bridged structure in which two irregular BH4 tetrahedra are joined by one common edge.



Figure 2.53: Formation of two (3c-2e MO's in B2H6 on the basis of MOT.

(a): BH3units; (b) Overlapping of sp3 and sp3orbitals (c) 3c 2e bond (d) bond lengths and bond angles in B2H6.

Two B atoms (B(I) and B(II) and four terminal H atoms (Ht) lie in the plane of paper. Two H bridging atoms (Hb) are located centrally above and below the plane. The four terminals B—H bonds are conventional, localized electron pair bonds. The other B—H bonds consist of 3c—2e bonds and are called hydrogen bridge bonds. The atoms in electron deficient compounds usually formthree-center two-electron (3c—2e) bonds.  In a 3c—2e bond, the two electrons are shared by three atoms with each atom contributing one orbital to the formation of the bond.



Figure 2.54: Formation of 2e -3c bonds in diborane.

It is assumed that two sp3 hybridized BH2 fragments come together with two H atoms. Each boron atom use two of its sp3 hybrid orbitals and two electrons to form the terminal B — H bonds.  Each boron atom has one electron and two sp3 orbitals remaining as shown in the Figure 2.54. The 1s orbital of a hydrogen atom can overlap with an occupied sp3 orbital from one boron atom and an unoccupied sp3 hybrid from the other boron atom. The result is the formation of a three-center two-electron hydrogen bridge bond. The other bridge bond is formed similarly.

**Evidence in Favorof BridgeStructure**

1. Nuclear magnetic resonance study and Raman spectra have shown that there are two types of H atoms in diborane. Four terminal hydrogen are similar and two bridging H atoms are similar
2. Specific heat measurements have shown that the two ends of the molecule cannot be rotated against each other. This hindered rotation clearly indicates that the two bridging hydrogen atoms lie in a plane at right angles to the plane of two boron and four H atoms.
3. The entire four terminal B—H bonds have the same length as those inboron-carbonyl, which is not electron-deficient. The electron-deficiency in B2H6 lies with the B(I)—Hb—B(II) bridge system in which B(I) —Hb or Hb —B(II) bond is longer than the terminal bonds