exerted by bonding electron-pair on the electron-pair on atom A decreases. For example, PI_3 (102°) > PBr_3 (101.5°) > PCl_3 (100°)

Rule 4. *Bond angles involving multiple bonds are generally larger than those involving only single bonds. However, the multiple bonds do not affect the geometry of a molecule.*

Rule 5. *Repulsion between electron-pairs in filled shells are larger than the repulsion between electron pairs in incompletely filled shells,* e.g. compare H–O–H and H–S–H bond angles in H_2O and H_2S molecules: H_2O (105.50°) >> H_2S (92.20°)

The valence shell electron pair repulsion (VSEPR) model *predicts the shapes of molecules and ions in which valence-shell electron pairs are arranged about each atom so that electron pairs are kept as far away from one another as possible, thus minimizing electron-pair repulsions.* **Molecular geometry** *is the general shape of a molecule, as determined by the relative positions of the atomic nuclei.* Please remember, that even though VSEPR suggests pairs of electrons, VSEPR really refers to electron domains or regions. Remember, an electron region can exist as a single electron (one electron), two electrons (lone pair or bonded pair), four electrons (a double bond), or six electrons (triple bond). However, when we determine the geometry of a molecule, we locate the positions of the atoms, not the electron pairs. For the **General molecular formula, "A"** refers to central atom, "B" refers to atoms attached to central atom, and "E" refers to unbonded electron pairs. For example, AB_2E_2 is shown as the formula of water (H_2O), which has two bonded hydrogen atoms ("B") and two lone (unbonded) electron pairs ("E").

1. AB_2; Molecules with two electron pairs around a central atom

There are several molecules and ions that consists of a central atom plus two atoms of another element in which there are no lone pairs on the central atom. This kind of molecule is abbreviated as AB_2. Typical compounds include $BeCl_2$, $BeBr_2$, BeI_2, and CO_2, as well as CdX_2 and HgX_2, where X = Cl, Br or I. A polyatomic ion in this category is the nitronium ion NO_2^+. All of these are known to be **linear** (bond angle = 180°).

In the solid state, **Beryllium chloride,** $BeCl_2$, molecules are bonded to each other in a polymeric solid. However, $BeCl_2$ exists as discrete molecules in the gaseous state. The Lewis structure for $BeCl_2$ shows that the central atom Be has two bonding electron pairs and has no lone pairs of valence electrons, so it has two electron pairs. VSEPR theory, which assumes that electron pairs will be as far apart from one another as possible, predicts that the two electron pairs on Be will be 180° apart. Thus VSEPR theory predicts a **linear** structure for $BeCl_2$, and for all other molecules of this type.

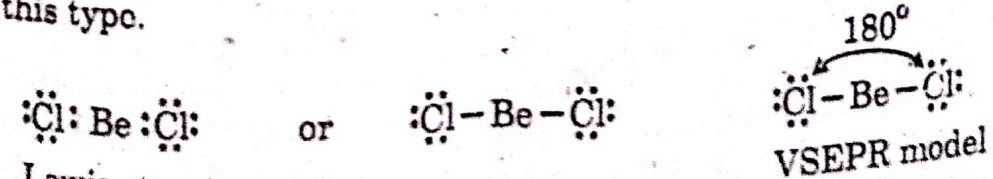
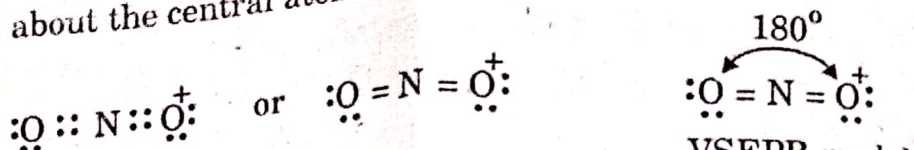


Fig. 2.13. $BeCl_2$ molecule

The Lewis structure for **nitronium ion,** NO_2^+, shows that the central nitrogen atom has two bonding electron pairs, since a double bond behaves as a single electron pair-bond in VSEPR model, and has no lone pair of valence electrons. Thus VSEPR theory predicts and experimental observations confirm that the **nitronium ion is linear,** which gives maximum separation between the two electron pairs about the central atom.



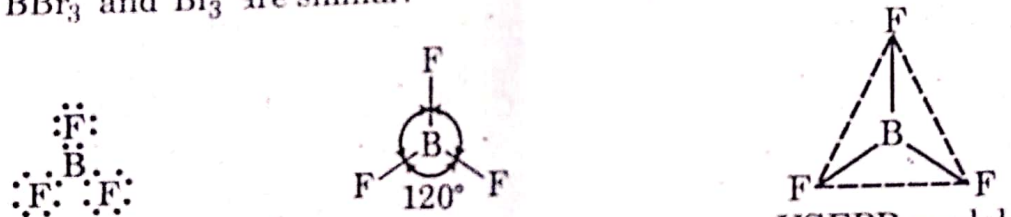
Lewis structure VSEPR model

Fig. 2.13 Geometry of NO_2^+ ion

2. Molecules with three electron pairs arounds a central atom

AB_3; When the central atom of a molecule is surrounded only by three bonding electron pairs, the geometry of the molecule will be **triangular planar.** Boron forms many covalent compounds by bonding to three other atoms. Typical examples include BF_3, BCl_3, BBr_3 and Bl_3. All are **trigonal planar** (that is, the flat molecules in which the bond angles are 120°).

The Lewis structure of boron trifluoride, BF_3, shows that the central atom B has three bonding electron pairs and has no lone pair of electrons. VSEPR theory predicts a trigonal planar structure for BF_3 molecule because this structure gives maximum separation among the three bonding electron pairs. The structures of BCl_3, BBr_3 and Bl_3 are similar.

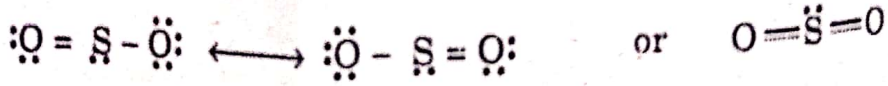


Lewis structure VSEPR model

Fig. 2.14 BF_3 molecule; trigonal planar.

AB_2E; When the central atom of a molecule is surrounded by two bonding electron pairs and by one lone-pair of electrons, the geometry of the molecule will be **bent, angular or V-shaped,** e.g., SO_2, $SnCl_2$

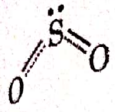
The Lewis formulas for the sulphur dioxide, SO_2, has two equivalent resonance structures.



Two equivalent resonance structures

In SO_2, the central atom sulphur is surrounded by three electron pairs. In SO_2 the resonance form contains a single bond, a double bond, and a lone pair of electrons, but a double bond is counted as a single electron pair for the purpose of VSEPR model. Therefore, in effect, S has three electron pairs around it. The VSEPR

theory predicts a trigonal planar arrangement for the three regions of electron density.



trigonal planar electonic geometry and angular molecular geometry

If all the three regions of electron density about the sulphur atom were equivalent, we would expect the O-S-O bond angle to be 120°. Clearly the three regions of electron density are not equivalent because the two regions are associated with the S-O bonds, while the third region is the lone pair of electrons that reside on the S atom. As the lone pair occupies more space, it will push the two bond pairs closer to each and the bond angle between two bond pairs becomes less than 120°.

The Lewis structure of stannous chloride, $SnCl_2$, shows that the central Sn atom has three election pairs, out of which one is lone pair. The VSEPR theory predicts a trigonal planar geometry for the three electron pairs. The lone pair of electrons exerts a greater repulsion on the bond pairs resulting in the shortening of Cl-Sn-Cl angle. Thus $SnCl_2$ in vapour phase is V shaped and arrangement is called angular.

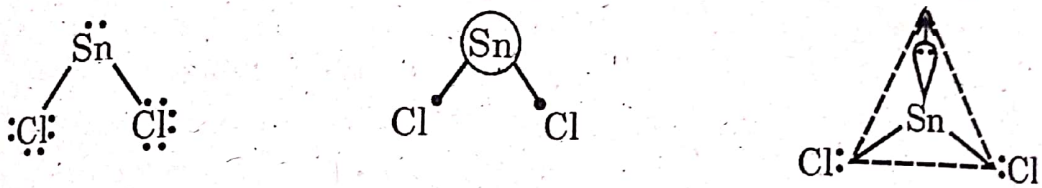


Fig. 2.15. $SnCl_2$ molecule V shaped

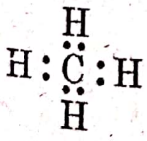
The trigonal planar molecular geometry occurs when there are three atoms bonded and no lone pair of electrons on the central atom and the bond angle is 120°. The angular molecular geometry occurs when there are two atoms bonded and one lone pair of electrons on the central atom and the bond angle is slightly less than 120°.

3. Molecules with four electron pairs around a central atom

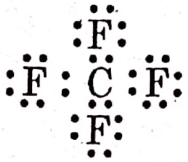
AB_4; When the central atom of a molecule is bonded to the four other atoms and has no lone-pair of electrons on it, the molecular geometry will be **tetrahedral,** e.g., CH_4, CCl_4, SiF_4.

The Group IVA elements form numerous covalent compounds by sharing their four electrons with four other atoms and are abbreviated as AB_4 molecules.

The lewis structures for **methane,** CH_4 and **carbon tetrafluoride,** CF_4 are



Methane



Carbon tetrafluoride

The central carbon atoms in both molecules have four bonding electron pairs, so VSEPR theory predicts **tetrahedral geometry** since this gives maximum separation. The four H atoms in CH_4 and four F atoms in CF_4, lie at the corners of a regular tetrahedron. The H-C-H bond angles are all 109°28′.

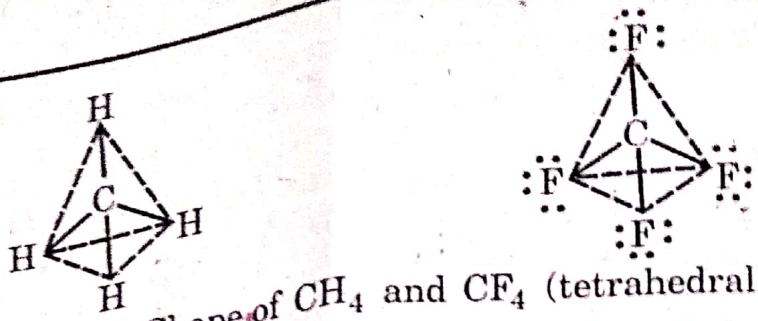
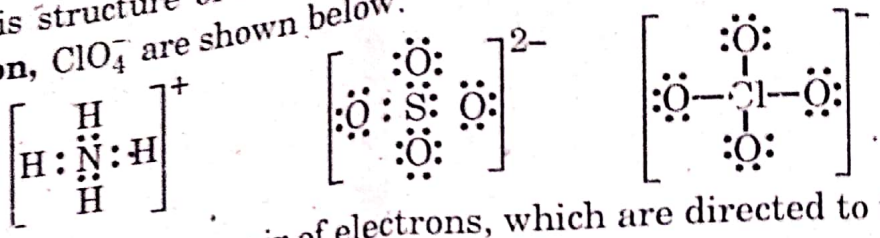
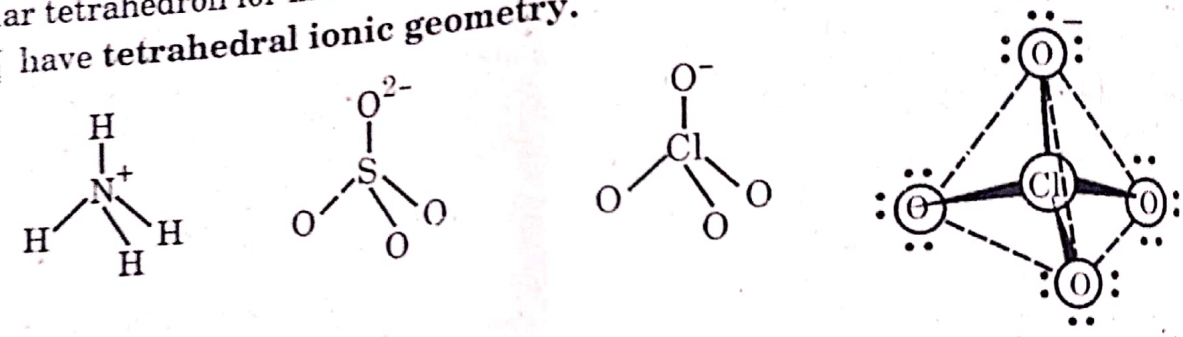


Fig. 2.16. Shape of CH_4 and CF_4 (tetrahedral)

The lewis structure of **Ammonium ions,** NH_4^+, **sulphate ion,** SO_4^{2-} and **perchlorate ion,** ClO_4^- are shown below:



Each has four bonding pair of electrons, which are directed to the corners of a regular tetrahedron for maximum separation from each other. Thus NH_4^+, SO_4^{2-} and ClO_4^- have **tetrahedral ionic geometry.**



AB_3E; When the central atom of a molecule has three bonding electron pairs and one lone-pair of electrons on it, the molecular geometry is **trigonal pyramidal,** e.g., NH_3, PCl_3.

The Lewis structure for **ammonia** molecule, NH_3, shows that the central N atom has three bonding electron pairs and one lone electron pair. The VSEPR theory predicts tetrahedral geometry with bond angles of 109°28′. The shape of the molecule is determined by the arrangement of atoms and not the lone pair of electrons. Therefore, the NH_3 molecule is described as **pyramidal.** The N atom lies at the apex and the three H atoms lie at the corners of a pyramid with a triangular base. Also, repulsions between the lone pair and the bonding electron pairs are greater than repulsions between bonding electron pairs. The VSEPR theory thus predicts that the H-N-H bond angles will be less than 109°28′. Experimentally, we find that the H-N-H bond angles are 107°20′.

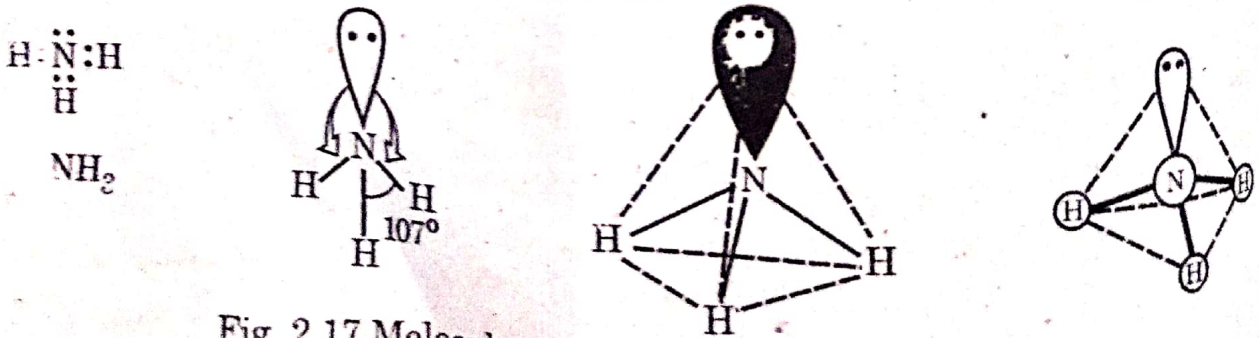
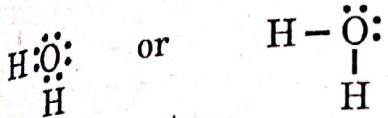


Fig. 2.17 Molecular geometry of NH_3, pyramidal

AB_2E_2; When the central atom of a molecule is bonded to the other two atoms and two non-bonding pair on it, the molecular geometry is **angular** or **bent**, e.g., H_2O, SCl_2.

The Lewis structure for **water** molecule, H_2O, shows that the central O atom is surrounded by two bonding electron pairs and two lone electron pairs. For four electron pairs, VSEPR theory predicts tetrahedral geometry, with bond angles of 109°28′. Since there are two lone pairs of electrons, in the H_2O molecule, VSEPR theory satisfactorily explains the ***angular molecular structure*** of water molecule. The two lone pairs occupy more space than the two bonding pairs and generate greater repulsion between two lone pairs than the repulsion between a lone pair and a bonding pair, which in turn is greater than the repulsion between two bonding pairs. Thus the two O-H bonds in H_2O will be forced to come closer together than N-H bonds in NH_3 and account for the observed bond angle of 104.5° in H-O-H. Typical examples are H_2O, H_2S, N_2O and Cl_2O and all are angular molecules.



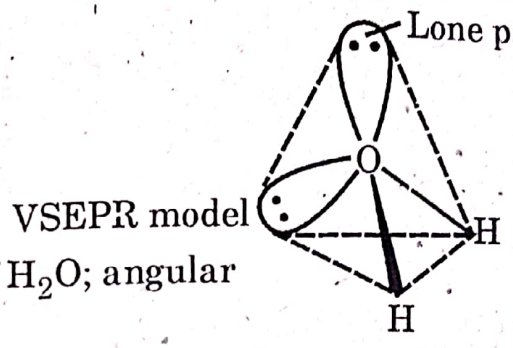


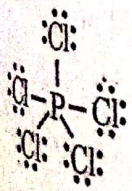
Fig 2.18. Shape of H_2O; angular

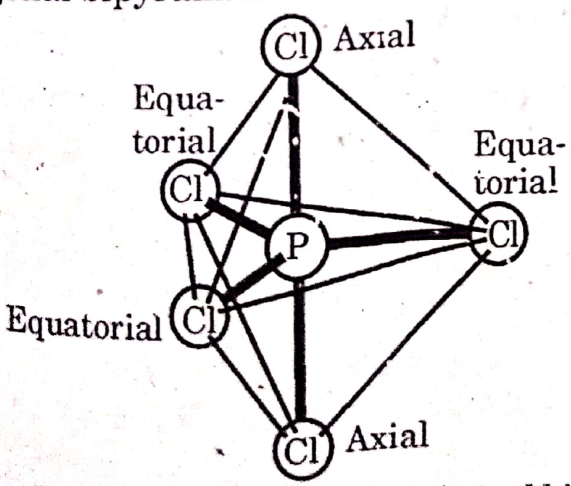
Greater the number of lone pairs on a central atom, the greater is the contraction in the bond angle.

4. Compounds with five electron pairs around a central atom

AB_5; When the central atom of a molecule is surrounded only by five bonding electron pairs, the molecular geometry is **trigonal bipyramidal.**

The heavier group VA elements, P, As, Sb, form some covalent compounds by sharing all five of their valence electrons with five other atoms. PF_5 and PCl_5 are such compounds. The Lewis structure for PCl_5 shows five bonding electron pairs around the central P atom. The VSEPR theory predicts **trigonal bipyramidal geometry,** because maximum separation of five bonding electron pairs around a central P atom is achieved when the five Cl atoms lie at the corners and P atom in the centre of a trigonal bipyramid.





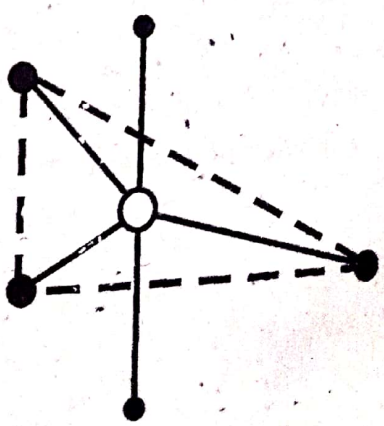
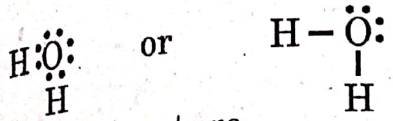


Fig.2.19 PCl_5 molecule, trigonal bipyramid

AB_2E_2; When the central atom of a molecule is bonded to the other two atoms and two non-bonding pair on it, the molecular geometry is **angular** or **bent**, e.g., H_2O, SCl_2.

The Lewis structure for **water** molecule, H_2O, shows that the central O atom is surrounded by two bonding electron pairs and two lone electron pairs. For four electron pairs, VSEPR theory predicts tetrahedral geometry, with bond angles of 109°28′. Since there are two lone pairs of electrons, in the H_2O molecule, VSEPR theory satisfactorily explains the ***angular molecular structure*** of water molecule. The two lone pairs occupy more space than the two bonding pairs and generate greater repulsion between two lone pairs than the repulsion between a lone pair and a bonding pair, which in turn is greater than the repulsion between two bonding pairs. Thus the two O–H bonds in H_2O will be forced to come closer together than N-H bonds in NH_3 and account for the observed bond angle of 104.5° in H-O-H. Typical examples are H_2O, H_2S, N_2O and Cl_2O and all are angular molecules.



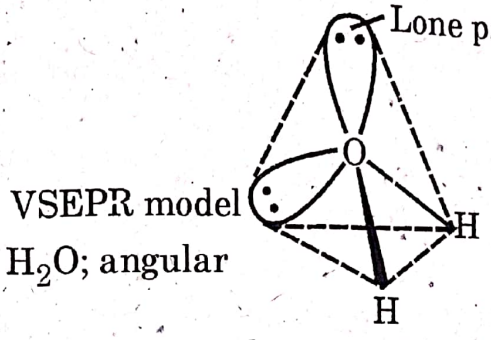


Fig 2.18. Shape of H_2O; angular

Greater the number of lone pairs on a central atom, the greater is the contraction in the bond angle.

4. Compounds with five electron pairs around a central atom

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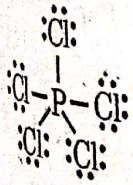
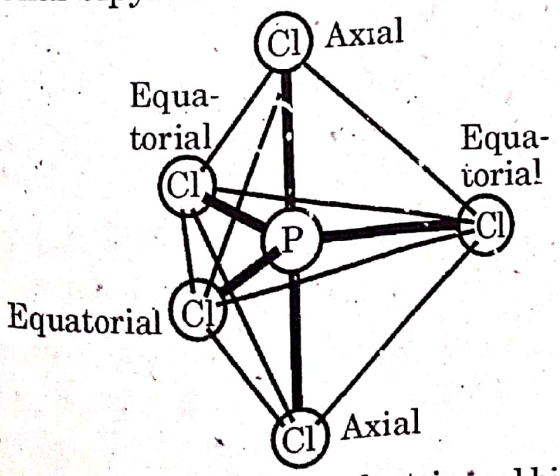
The heavier group VA elements, P, As, Sb, form some covalent compounds by sharing all five of their valence electrons with five other atoms. PF_5 and PCl_5 are such compounds. The Lewis structure for PCl_5 shows five bonding electron pairs around the central P atom. The VSEPR theory predicts **trigonal bipyramidal geometry,** because maximum separation of five bonding electron pairs around a central P atom is achieved when the five Cl atoms lie at the corners and P atom in the centre of a trigonal bipyramid.





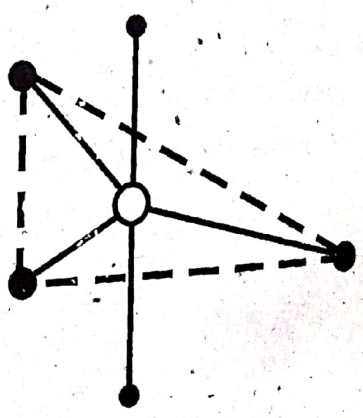
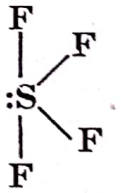


Fig.2.19 PCl_5 molecule, trigonal bipyramid

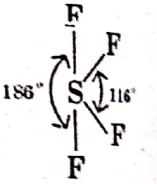
The repulsion of the five electron pairs is minimized in this arrangement. The five positions and hence the five bonds of a trigonal bipyramid are not all equivalent. Two of the positions are called *axial*. In the PCl_5 molecule they form a linear system. The other three positions are called *equatorial*. They lie in a plane at the corners of an equilateral triangle. The bond angle between the equatorial Cl atoms is 120°, the bond angle between the two axial Cl atoms is 180°, and the bond angle between an axial Cl atom and an equatorial Cl atom is 90°. The axial bonds are somewhat longer than the equatorial bonds in such molecules. The two axial Cl atoms and the three equatorial Cl atoms in PCl_5 can be distinguished experimentally because of the different bond angles and bond lengths.

AB_4E. When the central atom of a molecule is surrounded by four bonding electron pairs and by one lone-pair of electrons, the molecular geometry is **seesaws** (irregular tetrahedral), e.g., SF_4, $TeCl_4$.

The sulphur has five electron pairs around it; four from the S-F bonds and one from the nonbonding pair. The five electron pairs about sulphur should have a trigonal bipypramidal arrangement. Because the axial and equatorial positions of the electron pairs are not equivalent, we must decide in which of these positions the lone pair appears. It is experimentally observed, the nonbonding (lone) pair occupies an equatorial position and the four bonding pairs occupy the remaining four positions. This gives a **seesaw** (or distorted tetrahedral) geometry. The axial and equatorial S-F bonds are slightly bent back away from the nonbonding electron region, suggesting that the bonding regions are "pushed" by the nonbonding regions, which is larger and greater repulsion.



Lewis Structure



Geometry of SF_4

AB_3E_2; When the central atom of a molecule is surrounded by three bonding electron pairs and two lone pair of electrons gives a **T-shaped geometry,** e.g., ClF_3.

Chlorine Trifluoride, ClF_3, has five electron pairs around the central Cl atom, two of them are lone pairs and the rest of the three are bonding pairs. The VSEPR theory predicts *trigonal bipyramidal geometry* for the presence of five electron pairs. The two lone-pairs would set up repulsive interactions with the bond-pairs and will distort its symmetry from true trigonal bipyramidal geometry. Experimental evidence indicates that it is more favourable for the lone pairs to be in the equatorial positions. Therefore, two of the three F atoms lie in the axial positions. The four atoms form a distored "T", and this structure gives minimum

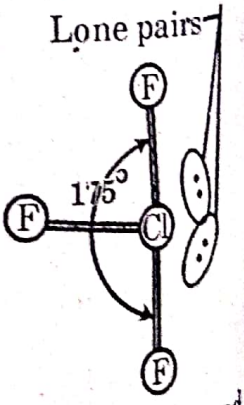
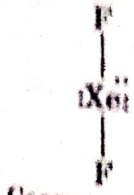


Fig. 2.20 Molecular geometry of ClF_3; T-shaped

repulsion. One F-Cl- F bond has bond angle 180° and two F - Cl - F have bond angles of 90° each.

AB_2E_3: When the central atom of a molecule is bonded to the two atoms of another element and has three nonbonding pair on it, the molecular geometry is **linear,** e.g., XeF_2. The three lone pairs on Xe occupy the equatorial positions of the trigonal bipyramidal arrangement, giving a linear geometry.



Geometry of XeF_2

5. Molecules with six electron pairs around a central atom

AB_6: When the central atom of a molecule is surrounded only by six bonding electron pairs and has no bonding pair, the geometry of the molecule is **octahedral.** The halides of the group VIA elements in the +6 oxidation state are examples of the **AB_6 type.** The Lewis structure of **sulphur hexafluoride,** SF_6, shows that there are six bond pairs around the central S atom. The octahedron VSEPR model correctly predicts octahedral geometry, since the maximum separation possible for six F atoms surrounding one S atom is achieved when the F atoms are situated at the corners and the S atoms in the centre of a regular octahedron and thus repulsion of the six electron pairs is minimized in this arrangement. An octahedron is a regular solid figure whose corners are all identical. Therefore, all the bonds and all the F atoms are equivalent in SF_6 molecule. The F - S - F bond angles are 90 or 180°.

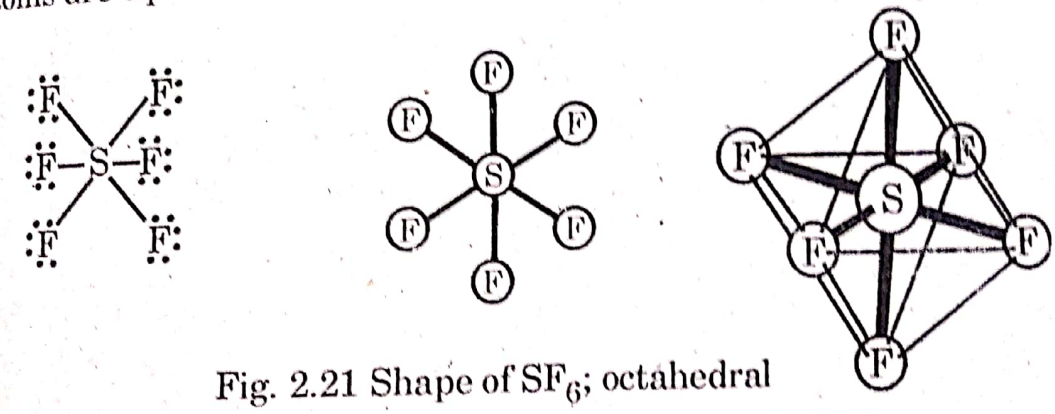


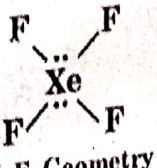
Fig. 2.21 Shape of SF_6; octahedral

The examples of such type molecules or ions are SF_6 and PCl_6^- etc.

AB_5E: Molecules in which the central atom is surrounded by six electron pairs, of which one is lone pair. The molecule adopts the shape of a square pyramid as shown in Table 2.2. Thus BrF_5, IF_5 and $SbCl_5^{2-}$ etc., containing one lone pair would adopt square pyramidal geometry. In IF_5, the lone pair on iodine occupies one of the six equivalent positions in the octahedral arrangement, giving a square pyramidal geometry.

IF_5 Geometry

AB_4E_2: Molecules in which the central atom is surrounded by six electron pairs, out of which two are lone pairs and they are placed on opposite sides of the molecule, resulting in a square planar shape. Examples of this type are ICl_4^-, BrF_4^- etc., as shown in table 2 2. In XeF_4, the two lone pairs on Xe occupy opposing positions in the octahedral arrangement to minimize their repulsion. The result is a square planar geometry.



XeF_4 Geometry