A Review of Gillespie Laws, its applications and limitations

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Abstract : In order to predict the geometry of covalent molecules, Valence Shell Electron Pair Repulsion Theory is used. This theory was given by Gillespie and Nyholm. According to this theory the geometry of a molecule depends upon the number of bonding and non-bonding electron pairs in the central atom. These arrange themselves in such a way that there is a minimum repulsion between them so that the molecule has minimum energy (i.e. maximum stability).

Gillespie Laws

The following rules have been reported by Gillespie to explain the shape of some covalent molecules:

1. If the central atom of a molecule is surrounded only by bonding electron pairs and not by non-bonding electron pairs (lone pairs), the geometry of the molecule will be regular.

    In other words we can say that the shape of covalent molecule will be linear for 2 bonding electron pairs, triangular for 3 bonding electron pairs. Tetrahedral for 4 bonding electron pairs, trigonal bipyramidal for 5 bonding electron pairs:

Name of Compound	Bonding Electron Pairs	Shape
$BeCl_2$	2	Linear
$BeCl_3$	3	Triangular Planar
$SnCl_4$	4	Regular Tetrahedral
PCl_5	5	Trigonal bipyramidal
SF_6	6	Regular Octahedral

2. When the central atom in a molecule is surrounded by both, bonding electron pairs as well as by lone pairs, then molecule will not have a regular shape. The geometry of the molecule will be disturbed. This alteration or distortion in shape is due to the alteration in bond angles which arises due to the presence of lone pairs on the central atom. How the presence of lone pairs causes an alteration in bond angles can be explained as follows:

    At a fixed angle the closer the electric-pairs to the central atom, the greater is the repulsion between them. Since the lone-pair electrons are under the influence of only one positive centre (i.e. nucleus), they are expected to have a greater electron density than the bond-pair electrons which are under the influence of two positive centres. Thus lone pair is much closer to the central atom than the bond pair. Hence it is believed that lone pair will exert more repulsion on any adjacent electron pair than a bond pair will do on the same adjacent electron pair.

$$(lp - lp) > (lp - bp) \qquad ....(i)$$

$$(lp = \text{ lone pair and } bp = \text{ bond pair})$$

If the adjacent electron pair is a bond pair, then repulsive force between lone pair and bond pair will be greater than repulsive force between two bond pairs.

$$(lp - bp) > (bp - bp) \quad \quad \ldots\ldots\ldots\ldots\ldots(ii)$$

On combining relations (i) and (ii) we get

$$(lp - lp) > (lp - bp) > (bp - bp)$$

Thus the repulsion between two lone pairs is maximum in magnitude, that between a bp and lp is intermediate while that between two bond pairs is the minimum.

The more the numbers of lone pairs on a central metal atom, the greater is the contraction caused in the angle between the bonding pairs. This fact is clear when we compare the bond angles in CH_4, NH_3 and H_2O molecules. (Table)

Molecules	No. of Lone pairs on central atom	Bond Angle	Contraction in bond angle w.r.t. CH_4
CH_4	0	109.5°	0
NH_3	1	107.5°	2°
H_2O	2	105.5°	4°

3. B-A-B bond angle decreases with the increase in electro negativity of atom B in AB_2 molecule where A is the central atom.

Example: $PI_3 (102°) > P Br_3 (101.5°) > PCl_3 (100°)$

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 the molecule.

5. Repulsion between electron pairs in filled shells are larger than the repulsion between electron pairs in incompletely filled shells

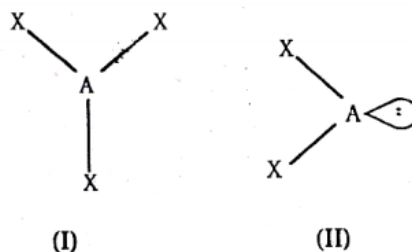Examples: $H_2O (105.5°) < H_2S (92.2°)$

Applications of Gillespie Laws

Let us take some examples in support of these laws:

(a) AX_2 molecule, which has only two bond-pairs, will be linear:

X----A-----X
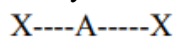
Examples in this groups will be $BeCl_2$, $CaCl_2$, CO_2 etc.

(b) If the molecule is AX_3 (I) or AX_2 with a lone pair of electrons on the central atom A, i.e. AX^2E (II), then the molecule will be triangular (Fig 1):
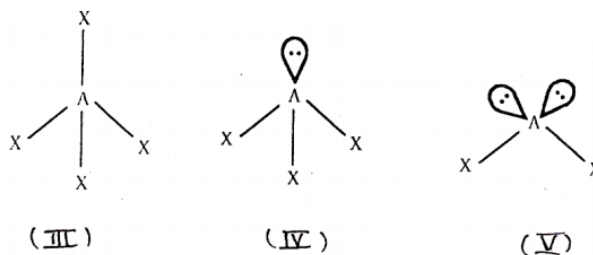

(I)   (II)

$$(I) = BCl_3, BF_3 \text{ etc.}$$

$$(II) = SO_2, SnCl_2 \text{ etc.}$$

Fig 1

(c) If the molecule is AX_4 (III) or AX_3E (IV) or AX_2E_2, then AX_4 will be tetrahedral; AX_3E will be pyramidal and AX_2E_2 will be angular. (Fig. 2):

(III)   (IV)   (V)

$$(III) = CCl_4, CH_4, SiCl_4, GeCl_4 \text{ etc.}$$

$$(IV) = NH_3, PCl_3, As_2O_3 \text{ etc.}$$

$$(V) = H_2O, SeCl_2, \text{ etc.}$$

Fig 2

(d) If the molecule is AX_5 (VI) or AX_4E (VII) or AX_3E_2 (VIII) or AX_2E_3 (IX) then AX_5 will be triangular bi pyramidal; AX_4E will irregular tetrahedral; AX_3E_2 will be T-shaped,; and AX_2E_3 will be linear. (Fig. 3)

(VI)   (IX)

(VIII)   (IX)
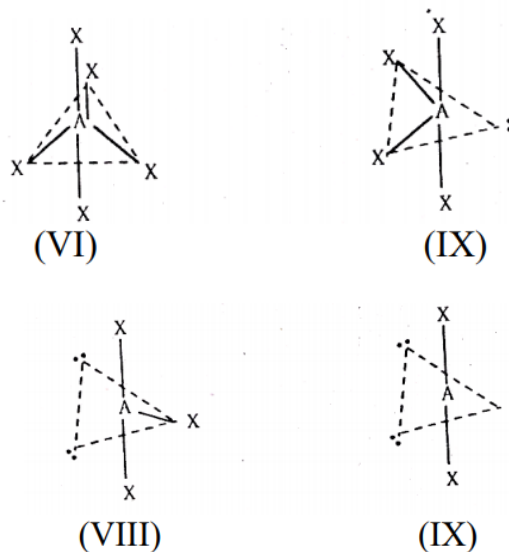
$$(VI) = PCl_5; (VII) SF_4, TeCl_4 \text{ etc.}$$

$$(VIII) = ClF_3, BrF_3 \text{ etc.}$$

$$(IX) = X_eF_2, ICl_2^-, \text{ or } I_3^- \text{ etc.}$$

Fig 3

(e) If the molecule is AX_6 (X) or AX_5E (XI) or AX_4E_2 (XII) then AX_6 will be octahedral, AX_5E will be square pyramidal; and AX_4E_2 will be square planar. (Fig. 4)

(X)   (XI)   (XII)
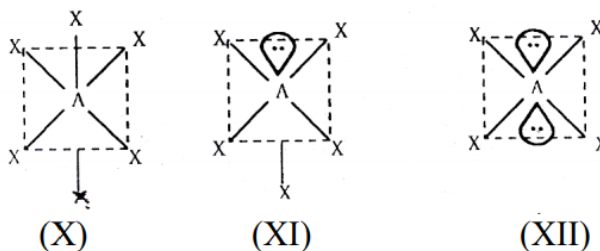
$$(X) = SF_6, WF_6, \text{ etc.}$$
$$(XI) = BrF_5, IF_5 \text{ etc.}$$
$$(XII) = ICl_4^-, X_eF_2^- \text{ etc.}$$

Limitations of VSEPR Theory
- This theory is not able to predict the shapes of certain transition element complexes.
- This theory is unable to explain the shapes of certain molecules with an inert pair of electrons.
- This theory is unable to explain the shapes of molecules having extensive delocalised π-electron system.
- This theory can not explain the shapes of molecules which have highly polar bonds.

References
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