Chapter 10 - Molecular Structure and Bonding Theories

Section 1 – Molecular Structure and Dipole Moment

Dr. Sapna Gupta

1

Introduction

All molecules have a 3D shapes including the diatomic ones because atoms have a volume thus occupy a 3D space.

- In tri atomic or polyatomic molecules and ions these shapes can get very important since physical properties of molecules can be predicted by the shape of molecule.
  - Why is H_2O liquid but CO_2 a gas at room temperature?
- How molecules will interact with each other in the 3D world can be predicted by shape of molecule.
- Biological functions occur because of proper molecular interactions.
  - Hemoglobin and oxygen binding
  - Sickle cell anemia – inability of hemoglobin to bind to oxygen. Difference of one amino acid (glutamic acid is replaced by valine) changes the shape of the whole protein.
  - (see https://evolution.berkeley.edu/evolibrary/article/mutations_06 for structures)

2

Molecular Structure

- Molecular structure is the three dimensional shape of a molecule.
- Geometry can be predicted by Lewis structures and VSEPR theory.
- VSEPR – Valence Shell Electron Pair Repulsion Theory states that electron pairs, bonding or nonbonding on the central atom, move as far away from each other as possible to minimize repulsion.
- To predict 3D structure of a molecule, the correct Lewis structure has to be drawn, followed by determining the electron groups around the central and finally predicting the geometry of the molecule.

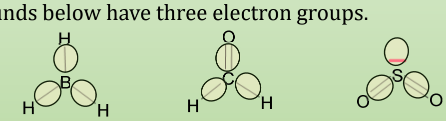
Lewis structure → Electron-domain geometry → Molecular geometry

VSEPR- Electron Groups

To determine the shape of the molecule one should first understand electron groups.. A lone pair of electron, a single bond, a double bond and a triple bond on the central atom are all considered one group.

All the compounds below have two electron groups regardless of the number of electrons in it (*double bond has 4 e⁻ and triple bond has 6 e⁻*). I have highlighted the groups in yellow.

All the compounds below have three electron groups.



You can see from the examples above how we determine the electron groups – single bonds, double bonds, triple bond and lone pair of electron.

We will use **AXE** formulas to learn more about electron groups and shapes, where A is the central atom, X is the number of terminal atom and E are lone pair of electron.

VSEPR- AXE Formula and Geometry

We will use **AXE** formulas to learn more about electron groups and shapes, where A is the central atom, X is the number of terminal atom and E are lone pair of electron.

Each of these AXE formulas has specific characteristics in shape of molecule and bond angles. AXE formulas are written as a formula, but they are just a generic representation of the central atom of a compound. If there is more than one central atom, then there is more than one AXE formula.

Example:

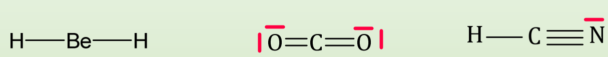
AX_2 indicates there are two terminal atoms, X on the central atom, A.

AX_2E indicates there are two terminal atoms, X, and one lone pair electron, E, on the central atom, A.

AXE formula helps us to determine the **electronic geometry** of the molecule which predicts the bond angle on the central atom. The electronic geometry is not necessarily the shape of the molecule. **Molecular geometry** is determined by the atoms, X, around the central atom. Lone pair of electrons don't occupy space as an atom can.

VSEPR- Electron Group – AX_2

AX_2 indicates that on the central atom A, there are two terminal atoms. Below are the compounds from a previous slide that had the two electron groups.

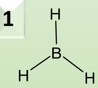


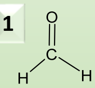
These electron groups be viewed as shown in the schematic on the right where there is a central atom and two atoms connected by the two groups are as far away from each other as possible, in accordance with the VSEPR theory. The black lines indicates one electron groups regardless of the number of electrons in it (*double bond has 4 e^- and triple bond has 6 e^-*).

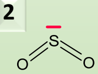
Characteristics of AX_2
Electronic geometry - Linear
Molecular geometry - Linear
Bond angle - 180°

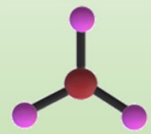
VSEPR- Electron Group – AX_3

AX_3 indicates that on the central atom A, with three terminal atoms. Below are the compounds from a previous slide that had the three electron groups. There are two variations of three electron groups – AX_3 and AX_2E. In AX_2E there is one lone pair on the central atom, which gives a different molecular geometry (shape) for the molecule as there is no atom in the third position.

1


1


2




Again, the schematic on the right shows central atom with three groups arranged as far away from each other as possible, in accordance with the VSEPR theory. As before the black line indicates one electron groups regardless of the number of electrons in it.

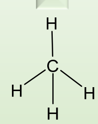
Characteristics of AX_3 *(molecule 1)*
Electronic geometry – Trigonal Planar
Molecular geometry – Trigonal Planar
Bond angle - 120°

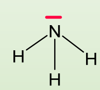
Characteristics of AX_2E *(molecule 2)*
Electronic geometry – Trigonal Planar
Molecular geometry – Bent
Bond angle - 120°

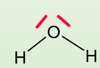
7

VSEPR- Electron Group – AX_4

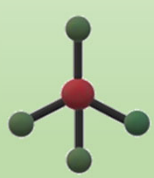
AX_4 indicates that on the central atom A, there are four terminal atoms. There are three variations of the four electron groups – AX_4 and AX_3E. In AX_2E_2 there are two lone pairs on the central atom. On the right are examples of these variations. Below is the schematic of a four electron group.

1


2


3


Characteristics of AX_4 *(molecule 1)*
Electronic geometry – Tetrahedral
Molecular geometry – Tetrahedral
Bond angle - 120°



Characteristics of AX_3E *(molecule 2)*
Electronic geometry – Tetrahedral
Molecular geometry – Trigonal Pyramidal
Bond angle - 120°

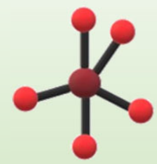
Characteristics of AX_2E_2 *(molecule 3)*
Electronic geometry – Tetrahedral
Molecular geometry – Bent
Bond angle - 120°

8

VSEPR – Electron Group – AX_5 and AX_6

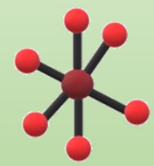
AX_5 has five electron groups pairs are arranged with three pairs in a plane 120° apart and two pairs at 90°to the plane and 180° to each other.

A trigonal bipyramidal geometry.



AX_6 Six electron pairs are 90° and 180° to each other apart.

An octahedral geometry.

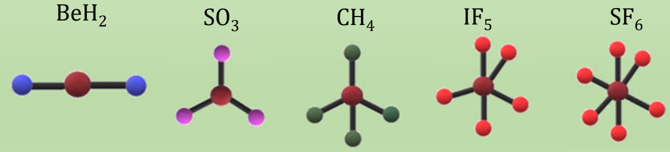


9

VSEPR – Electronic Geometry ALL

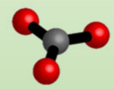
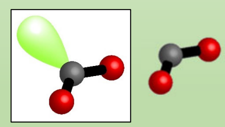
Space Filled Model

Number of e^- groups AXE formula	2 e^- groups AX_2	3 e^- groups AX_3	4 e^- groups AX_4	5 e^- groups AX_5	6 e^- groups AX_6
Shape	Linear	Trigonal Planar	Tetrahedral	Trigonal Bipyramidal	Octahedral
Example	BeH_2	SO_3	CH_4	IF_5	SF_6



10

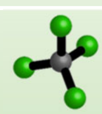
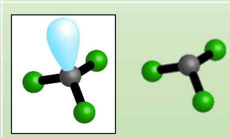
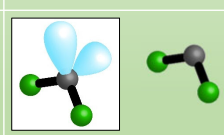
Shapes Possible – For AX_2 and AX_3

	Electronic geometry	Bond angle	Shape	Model
AX_2	Linear	180°	Linear	
AX_3	Trigonal planar	120°	Trigonal planar	
AX_2E	Trigonal planar	120°	Bent *(The green balloon is the lone pair of electron)*	

Shutterstock Image

11

Shapes Possible – AX_4

	Electronic geometry	Bond angle	Shape	Model
AX_4	Tetrahedral	109°	Tetrahedral	
AX_3E	Tetrahedral	109°	Trigonal pyramidal*	
AX_2E_2	Tetrahedral	109°	Bent*	

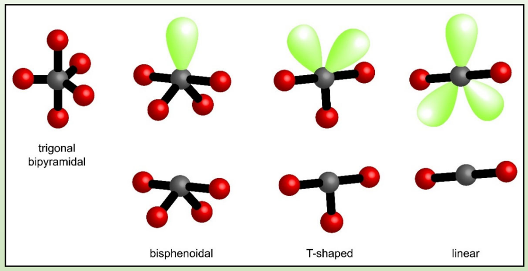
Shutterstock Image

*(*The blue balloon is the lone pair of electron)*

12

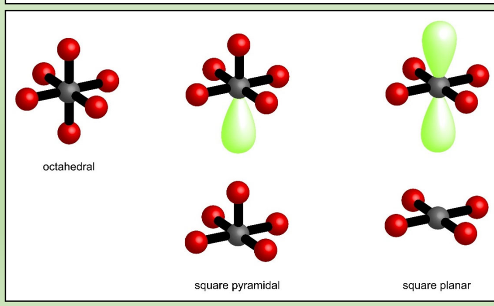
Shapes Possible – AX_5 andAX_6

AX_5
(The green balloon is the lone pair of electron)



Shutterstock Image

AX_6
(The green balloon is the lone pair of electron)



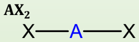
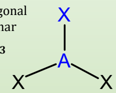
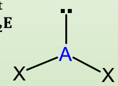
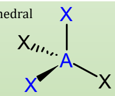
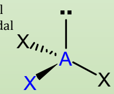
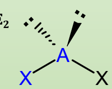
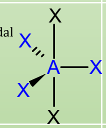
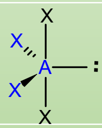
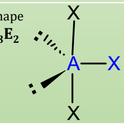
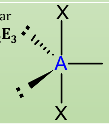
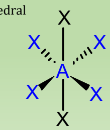
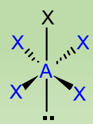
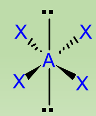
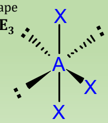
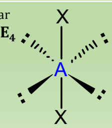
Shutterstock Image

13

Electron Groups	AXE formula	Bond Angle	E.g.	Electronic Geometry	Shape of Molecule
2	AX_2	180°	$BeCl_2$	Linear	Linear
3	AX_3	120 °	BF_3	Trigonal planar	Trigonal planar
3	AX_2E	120 °	SO_2	Trigonal planar	Bent
4	AX_4	109.5 °	CH_4	Tetrahedral	Tetrahedral
4	AX_3E	109.5 °	NH_3	Tetrahedral	Trigonal Pyramidal
4	AX_2E_2	109.5 °	H_2O	Tetrahedral	Bent
5	AX_5	90 °, 120 °, 180 °	PCl_5	Trigonal bipyramidal	Trigonal Bipyramidal
5	AX_4E	90 °, 120 °, 180 °	SF_4	Trigonal bipyramidal	Seesaw
5	AX_3E_2	90 °, 180 °	CIF_4	Trigonal bipyramidal	T – shape
5	AX_2E_3	180 °	XeF_2	Trigonal bipyramidal	Linear
6	AX_6	90 °, 180 °	SF_6	Octahedral	Octahedral
6	AX_5E	90 °	BrF_5	Octahedral	Square Pyramidal
6	AX_4E_2	90 °	XeF_4	Octahedral	Square Planar
6	AX_3E_3	90 °, 180 °		Octahedral	T – Shape
6	AX_2E_4	180 °		Octahedral	Linear

14

VSEPR Geometries

No of e-groups	Geometry (all atoms)	1 Lone Pair	2 Lone Pairs	3 Lone Pairs	4 Lone Pairs
2	Linear AX_2 				
3	Trigonal Planar AX_3 	Bent AX_2E 			
4	Tetrahedral AX_4 	Trigonal pyramidal AX_3E 	Bent AX_2E_2 		
5	Trigonal Bipyramidal AX_5 	Seesaw AX_4E 	T-Shape AX_3E_2 	Linear AX_2E_3 	
6	Octahedral AX_6 	Square Pyramid AX_5E 	Square Planar AX_4E_2 	T-shape AX_3E_3 	Linear AX_2E_4 

15

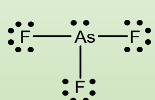
Solved Problem: Electron Geometry Prediction

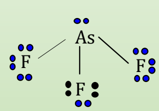
Use the VSEPR model to predict the geometries of the following molecules:

a. AsF_3

b. PH_4^+

AsF_3 has 1(5) + 3(7) = 26 valence electrons; As is the central atom.



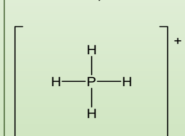


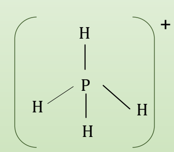
There are 4 pairs of electrons around As; three bonding and one lone pair.

AX_3E

The electronic geometry is tetrahedral. One of these regions is a lone pair, so the molecular geometry is trigonal pyramidal.

PH_4^+ has 1(5) + 4(1) – 1 = 8 valence electrons; P is the central atom.





There are 4 pairs of electrons around P; all four bonding electron pairs.

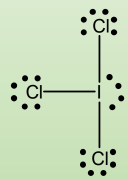
AX_4

The electronic geometry is tetrahedral. All regions are bonding, so the molecular geometry is tetrahedral.

16

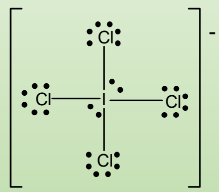
Solved Problem: Predicting Electronic Geometry
Use the VSEPR model to predict the electronic geometries of the following molecules:
a. ICl_3
b. ICl_4^-

ICl_3 has 1(7) + 3(7) = 28 valence electrons. I is the central atom.



There are five regions: three bonding and two lone pairs.
AX_3E_2
The electronic geometry is trigonal bipyramidal.
The geometry is T-shaped.

ICl_4^- has 1(7) + 4(7) + 1 = 36 valence electrons. I is the central element

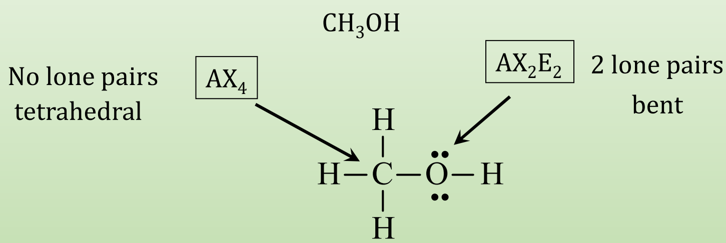


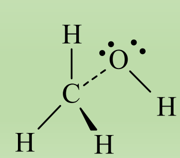
There are six regions around I: four bonding and two lone pairs.
AX_4E_2
The electronic geometry is octahedral.
The geometry is square planar.

17

Molecule With More Than One Central Atom

For CH_3OH there are two central atoms so each will have its own geometry.





18

Dipole Moment and Polarity of Molecule

- In case of HCl, where we see that there is a charge separation, there is also dipole moment. The dipole moment arrow will go towards Cl since it is more electronegative than H.

δ+ δ-
H——Cl

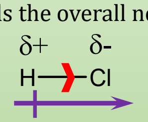
- Dipole moment a measure of how much a molecule can move in an electrical field. The movement occurs only if there is a charge separation.
- Polar molecules have dipole moment, while nonpolar molecules have zero dipole moment. Dipole moment is represented by the letter "μ" (*mu*).
- To determine dipole moment:
  1. Draw the Lewis structure
  2. Determine the molecular shape of the molecule
  3. Determine the electronegativity from the periodic table
  4. See if the molecule is symmetrical as that will nullify the charge separation.
  5. Determine if the molecule is polar of not (yes – if molecule is asymmetric)

Dipole Moment of Diatomic Molecules

In homonuclear diatomics such as H_2, Cl_2, there is no dipole moment since they have the same electronegativity and are thus nonpolar molecules.

For HCl, we can represent the charge separation using δ+ and δ- to indicate partial charges. Because Cl is more electronegative than H, it has the δ- charge, while H has the δ+ charge.

(The **red arrow** on the bond from here on indicates the polarity in the bond. The arrow will point towards the more electronegative element. The **purple arrow** indicates dipole moment. Note that it has a crosshair on it and is drawn to indicate towards the overall negative charge on the molecule)



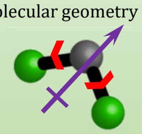
Dipole moment will occur in any diatomic molecule with polarity. How much is dependent on the electronegativity.

Dipole moment can be measured in lab and is called dielectric constant. This numerical value indicates how polar a molecule will be.

Dipole Moment of Triatomic Molecules

In case of molecules with more than two atoms, the shape of the molecule has to be taken into account because bond dipoles are additive since they are ***vectors***. Write the AXE formula, it is good practice and gives a lot of information about the molecule.

H_2O
AX_2E_2
Electronic geometry – tetrahedral
Molecular geometry - bent



dipole moment > 0

BeH_2
AX_2
Electronic geometry – tetrahedral
Molecular geometry - bent

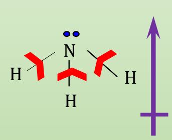
dipole moment (μ) = 0

21

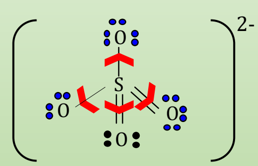
Dipole Moment of Larger Molecules and Ions

The rules are the same no matter how large the molecule is. Always draw the correct Lewis structure, determine the shape of the molecule and the polarity of the bonds. Here are some more examples.

NH_3
AX_3
Electronic geometry – tetrahedral
Molecular geometry – trigonal planar



SO_4^{2-}
AX_4
Electronic geometry – tetrahedral
Molecular geometry - tetrahedral



μ = 0

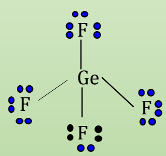
22

Solved Problem: Predicting dipole moment

Which of the following molecules have dipole moment?

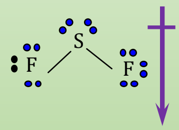
a. GeF_4
b. SF_2
c. AsF_3

GeF_4: 1(4) + 4(7) = 32 valence electrons.
Ge is the central atom.
8 electrons are bonding; 24 are nonbonding. Tetrahedral molecular geometry. (AX_4)



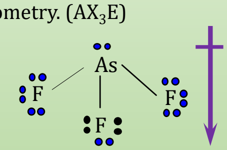
GeF_4 is nonpolar and has no dipole moment.

SF_2: 1(6) + 2(7) = 20 valence electrons.
S is the central atom.
4 electrons are bonding; 16 are nonbonding.
Bent molecular geometry. (AX_2E_2)



SF_2 is polar and has a dipole moment.

AsF_3: 1(5) + 3(7) = 26 valence electrons.
As is the central atom.
6 electrons are bonding; 20 are nonbonding.
Trigonal pyramidal molecular geometry. (AX_3E)



AsF_3 is polar and has a dipole moment.

23

Key Words/Concepts

- Molecular Geometry
- Shapes/VSEPR
- AXE formula
- Bonding and nonbonding electrons
- Bond angles
- Electronegativity
- Bond polarity
- Polarity of molecule
- Dipole moment

24