Unit 3

Molecular Structure

Slide Color Codes

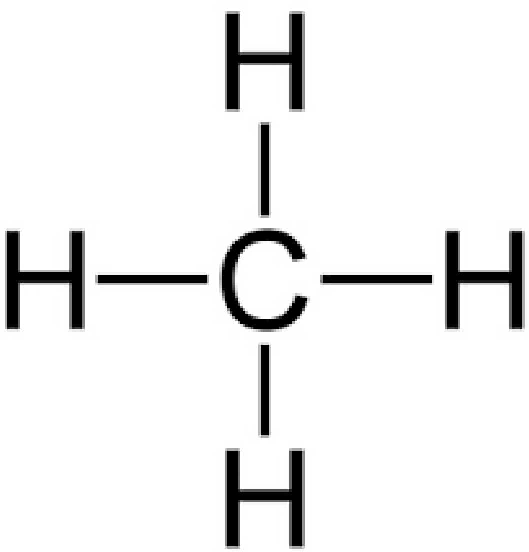
All Lectures: Required (black) | Required (blue) | OK to Skip (green)

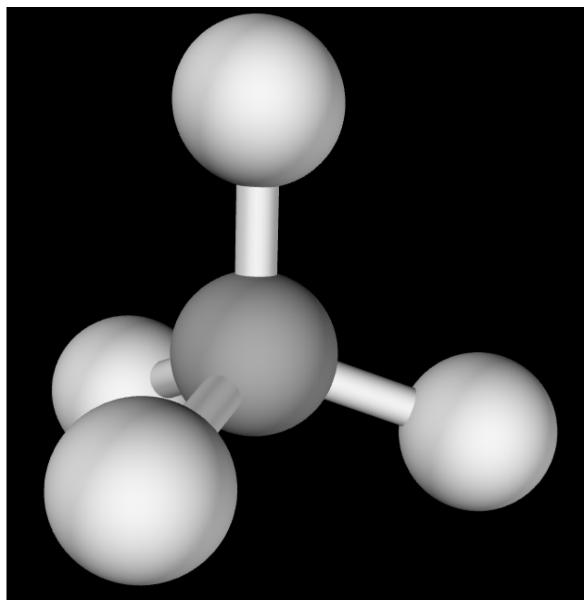
Section Only: Useful (yellow) | Not Examable (red)

Learning Objectives (Part 2)

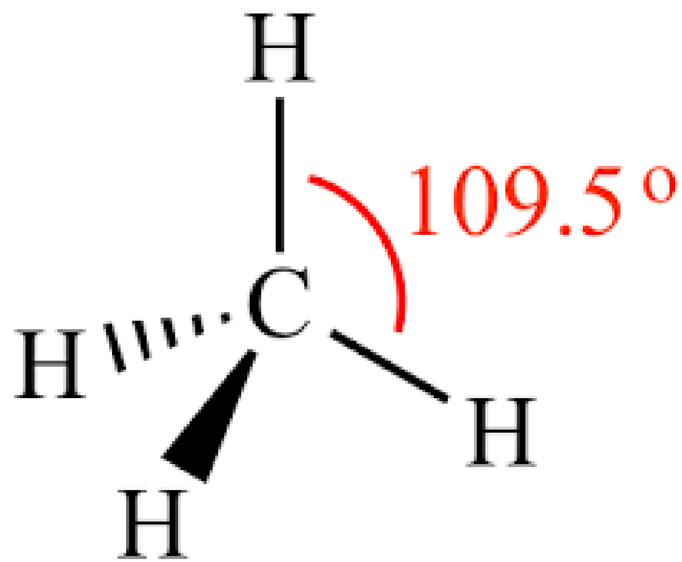
After mastering this unit you will be able to:

– Predict the geometry (shape, approximate bond angles, and trends in bond lengths) of molecules from their Lewis structures.





Minimized Energy

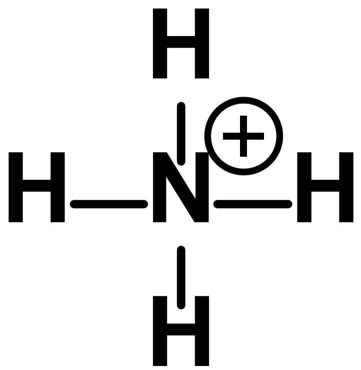


Shapes of Molecules

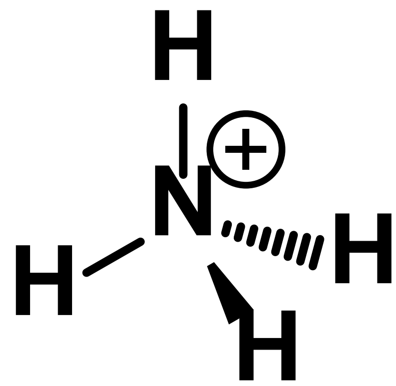
Lewis structures provide information about molecular bonding but they do NOT provide any information on molecular geometry. Molecular geometry is important in determining a substance's properties such as reactivity, solubility, and even conductivity in solids.

Valence Shell Electron Pair Repulsion (VSEPR)

VSEPR is a theory that predicts molecular shape by treating atoms in a molecule as point charges that are favoured to be as far away from each other as possible.



Lewis Structure (2D)

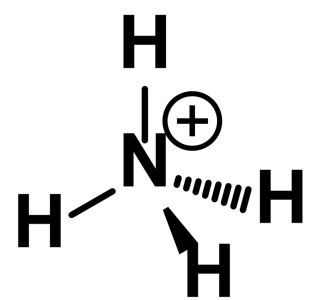


Perspective diagram (3D)

Perspective Diagram

A perspective diagram is a three-dimensional representation of a molecule in space. A wedge bond ( ) represents an atom coming out of the plane of the molecule. A dash bond ( ) represents an atom going into the plane of the molecule.

Perspective Diagram



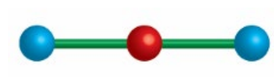
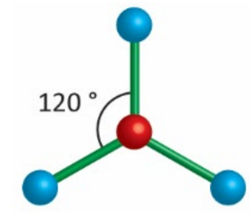
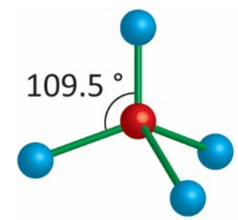
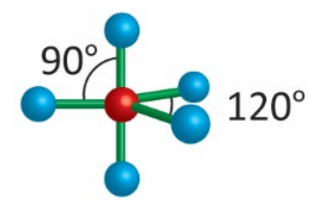
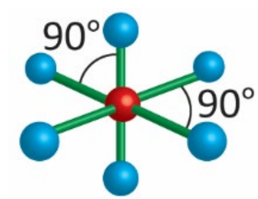
Note: for this tetrahedral shape, the dash and wedge bonds should both lie **below** a horizontal line drawn through the central atom.

VSEPR Guidelines

- You do NOT need to show lone pairs in VSEPR perspective diagrams
- You do NOT need to draw multiple bonds in VSEPR perspective diagrams

Parent Shapes

The five parent shapes describe how atoms and/or lone pairs arrange in a molecule to reduce electrostatic interactions.

# of bond pairs or lone pairs around the central atom	Parent shape	Bond angles	Structure (blue spheres represent atoms or lone pairs)
2	Linear	180°	
3	Trigonal planar	120°	
4	Tetrahedral	109.5°	
5	Trigonal bipyramidal	120° / 90°	
6	Octahedral	90 °	

Molecular Shapes

The molecular shape describes the three-dimensional arrangement of atoms in space to minimize electrostatic repulsions.

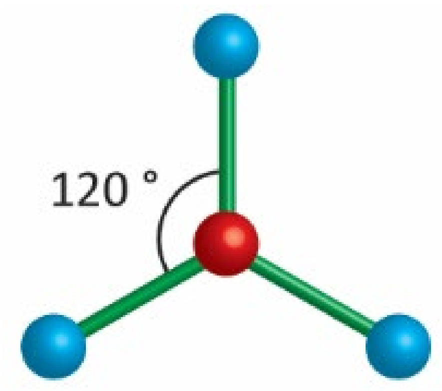
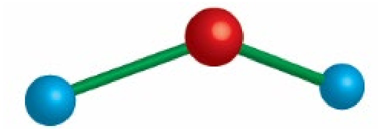
Note: LP – number of lone pairs

BP – number of bond pairs

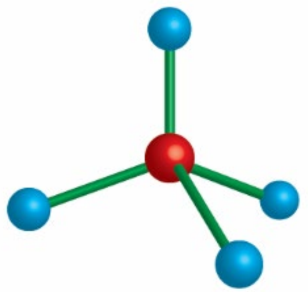
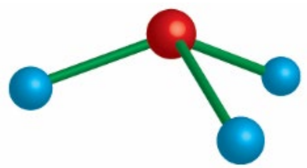
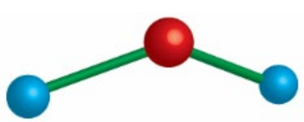
– multiple bonds count as one here

– same as number of atoms bonded

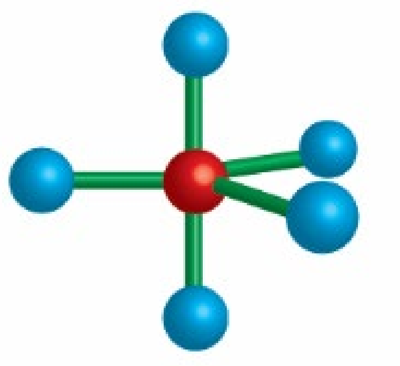
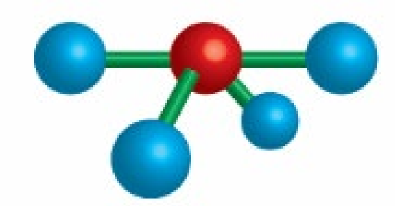
Trigonal Planar Parent Shape

Parent Shape	LP	BP	Molecular Shape	3D Structure
Trigonal Planar	0	3	Trigonal Planar	
Trigonal Planar	1	2	Bent	

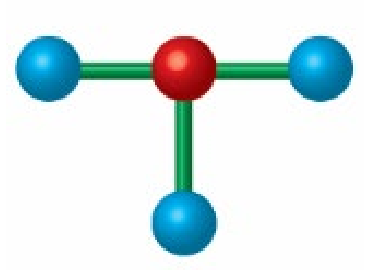
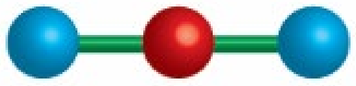
Tetrahedral Parent Shape

Parent Shape	LP	BP	Molecular Shape	3D Structure
Tetrahedral	0	4	Tetrahedral	
Tetrahedral	1	3	Trigonal pyramidal	
Tetrahedral	2	2	Bent	

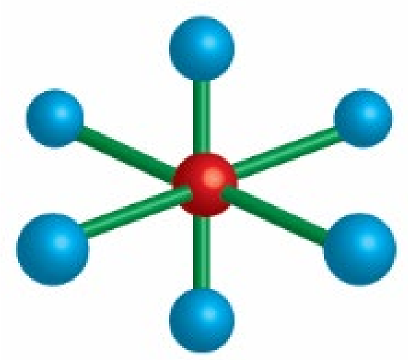
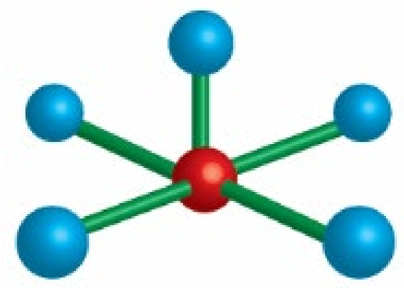
Trigonal Bipyramidal Parent Shape

Parent Shape	LP	BP	Molecular Shape	3D Structure
Trigonal Bipyramidal	0	5	Trigonal bipyramidal	
Trigonal Bipyramidal	1	4	See-saw	

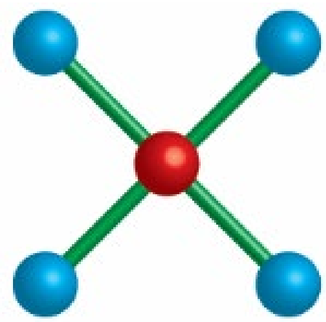
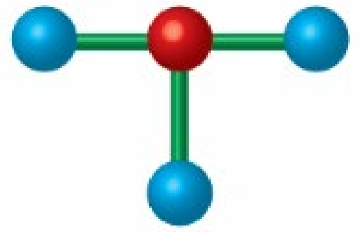
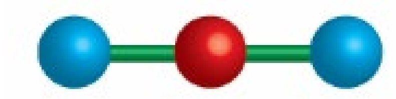
Trigonal Bipyramidal Parent Shape

Parent Shape	LP	BP	Molecular Shape	3D Structure
Trigonal Bipyramidal	2	3	T-shape	
Trigonal Bipyramidal	3	2	Linear	

Octahedral Parent Shape

Parent Shape	LP	BP	Molecular Shape	3D Structure
Octahedral	0	6	Octahedral	
Octahedral	1	5	Square Pyramidal	

Octahedral Parent Shape

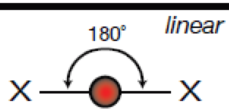
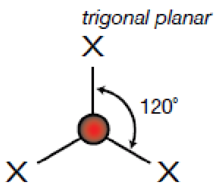
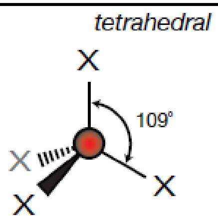
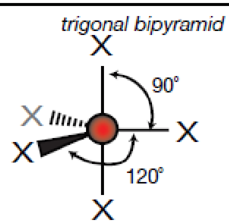
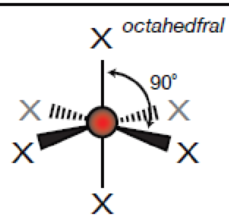
Parent Shape	LP	BP	Molecular Shape	3D Structure
Octahedral	2	4	Square planar	
Octahedral	3	3	T-shape	
Octahedral	4	2	Linear	

Worksheet Question #16

https://phet.colorado.edu/en/simulation/molecule-shapes

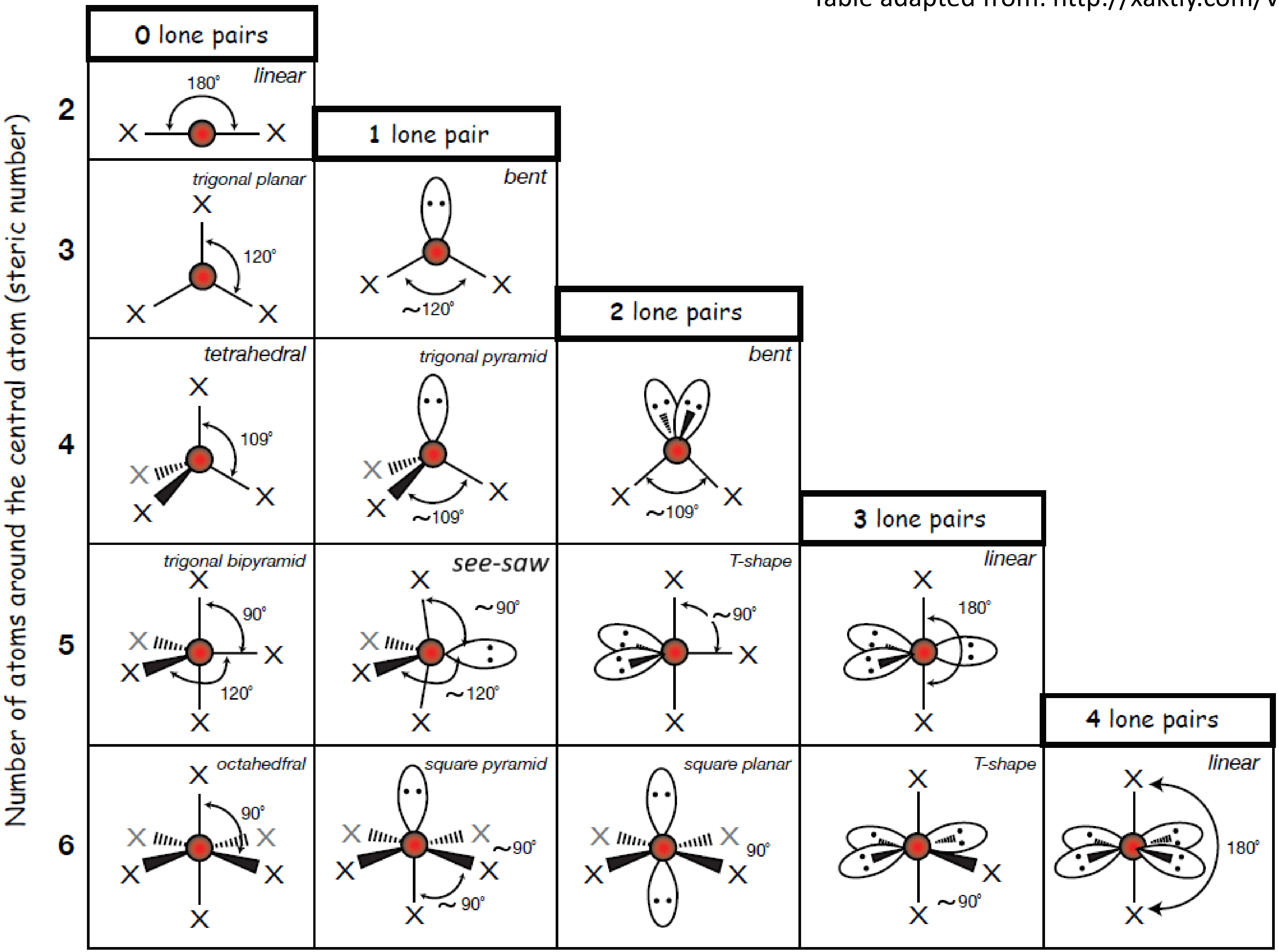
Using the PhET applet, complete the table below by drawing perspective diagrams, naming the shapes and giving the bond angles formed when bonds are replaced with lone pairs in the given parent shapes.

Number of atoms around the central atom (steric number)

	0 lone pairs	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2					
3					
4					
5					
6					

PhET – VSEPR

Table adapted from: http://xaktly.com/VSEPR.html



Predicting Molecular Geometry

1. Draw the best Lewis structure
2. Determine the parent shape (lone pairs + number of atoms directly bonded to the central atom)
3. Determine the molecular shape

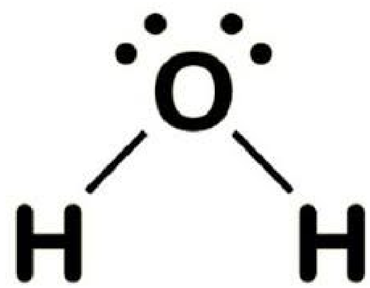
VSEPR practice

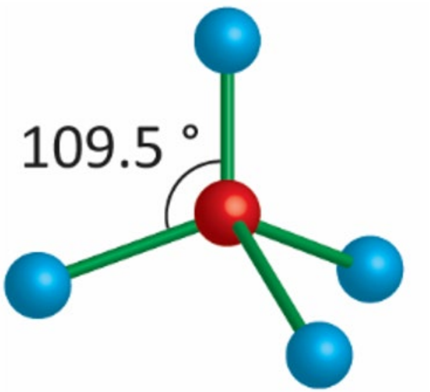
Draw Lewis structures and then predict and rationalize the molecular shapes and bond angles of the following molecules:

a) H_2O

b) CO_2

c) SO_2





2 lone pairs

Parent Shape: Tetrahedral

Molecular Shape: Bent

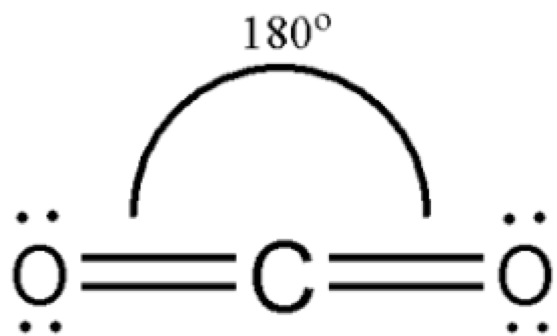
VSEPR practice

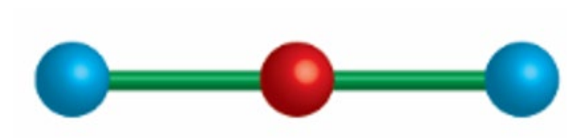
Draw Lewis structures and then predict and rationalize the molecular shapes and bond angles of the following molecules:

a) H_2O

b) CO_2

c) SO_2





No lone pairs

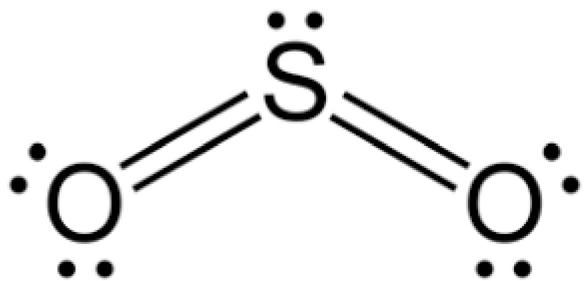
Parent Shape: Linear

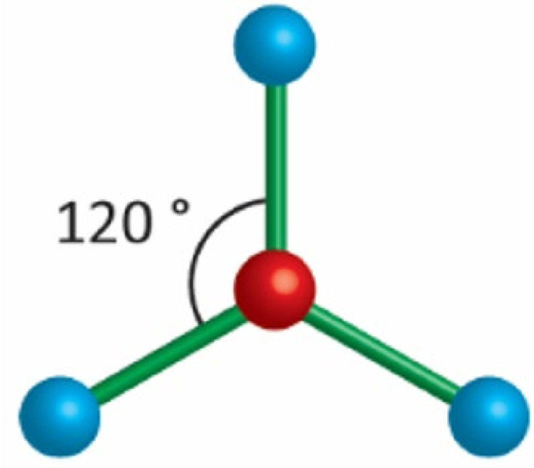
Molecular Shape: Linear

VSEPR practice

Draw Lewis structures and then predict and rationalize the molecular shapes and bond angles of the following molecules:

a) H_2O
b) CO_2
c) SO_2



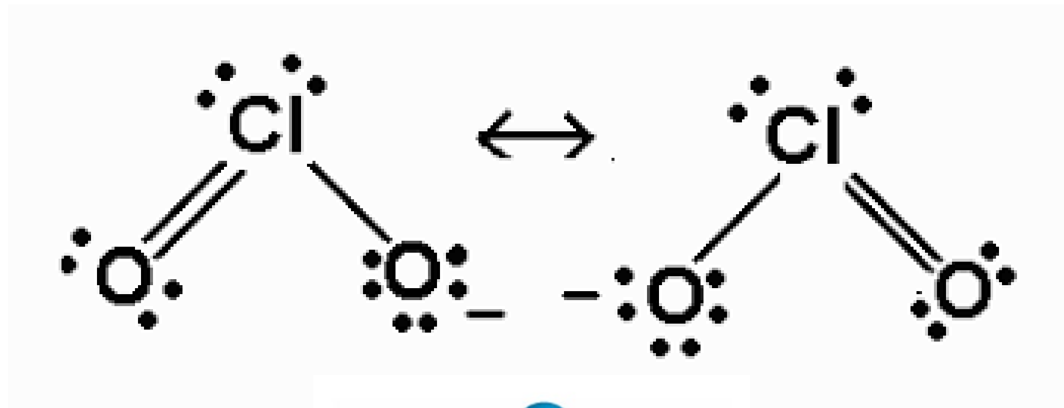


1 lone pairs

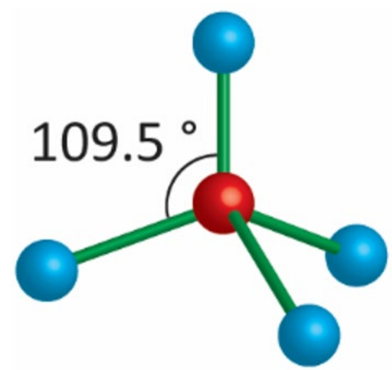
Parent Shape: Trigonal Planar
Molecular Shape: Bent

Clicker Question

The O-Cl-O bond angle in ClO_2^- is *approximately*:



A. 90˚
B. 109.5˚
C. 120˚
D. 180˚
E. Not well defined

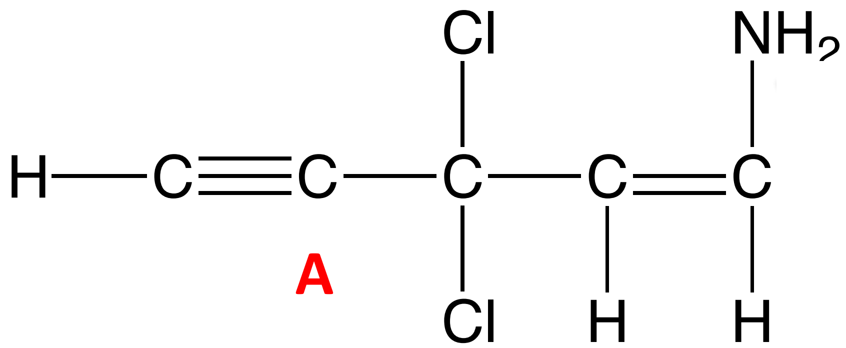


2 lone pairs

Parent Shape: Tetrahedral
Molecular Shape: Bent

Clicker Question

Determine the parent shape of the atom labelled "A":



Line structure (lone pairs not shown)

A) Linear

B) Trigonal Planar

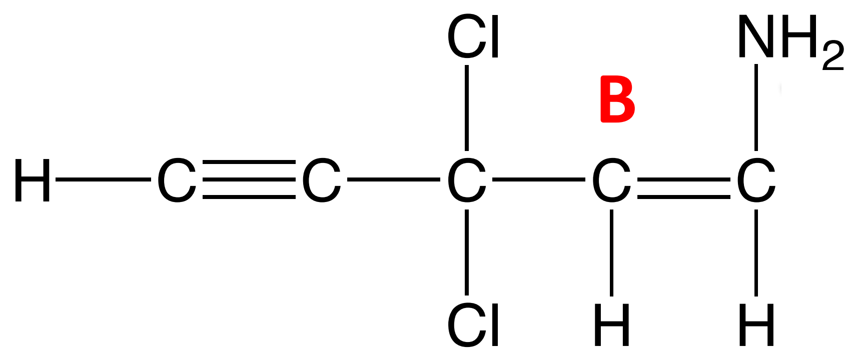
C) Tetrahedral

D) Trigonal Bipyramidal

E) Octahedral

Clicker Question

Determine the molecular shape of the atom labelled "B":



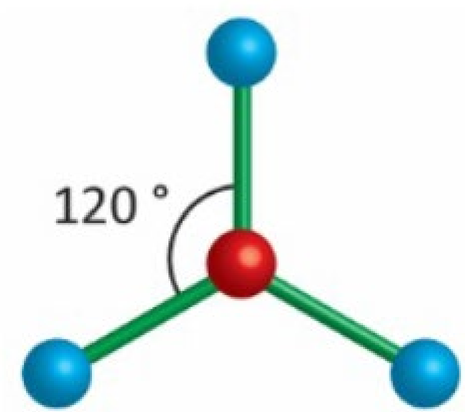
A) Linear

B) Trigonal Planar

C) Tetrahedral

D) Trigonal Bipyramidal

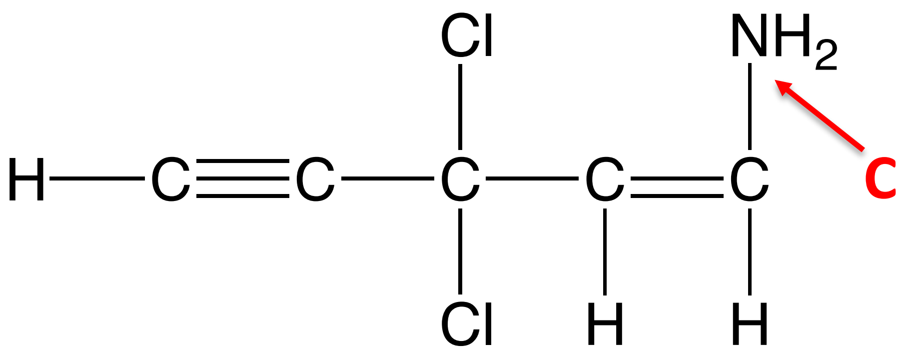
E) Octahedral



No lone pairs

Clicker Question

Determine the molecular shape of the atom labelled "C":



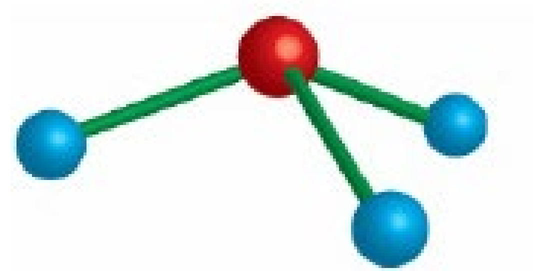
A) Bent

B) Trigonal Planar

C) Tetrahedral

D) Trigonal Pyramidal

E) Octahedral



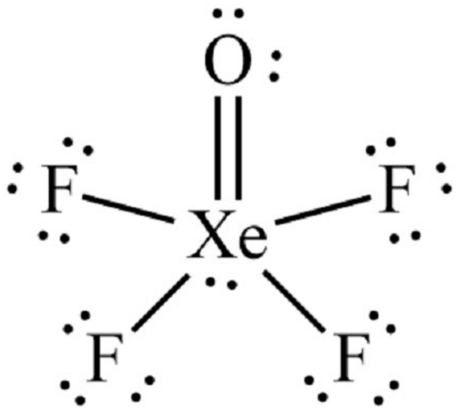
N has 1 lone pairs

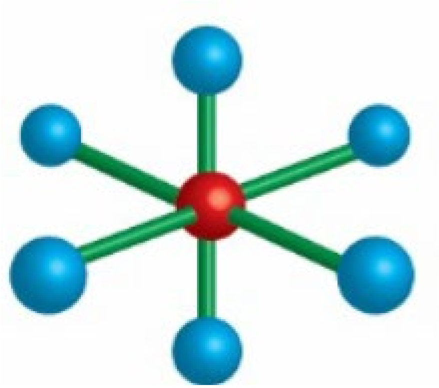
Parent Shape: Tetrahedral

Clicker Question

What is the molecular shape of $XeOF_4$?

a. Tetrahedral
b. See-saw
c. Square planar
d. Trigonal bipyramidal
e. Square pyramidal





1 lone pairs

Parent Shape: Octahedral
Molecular Shape: Square Pyramidal

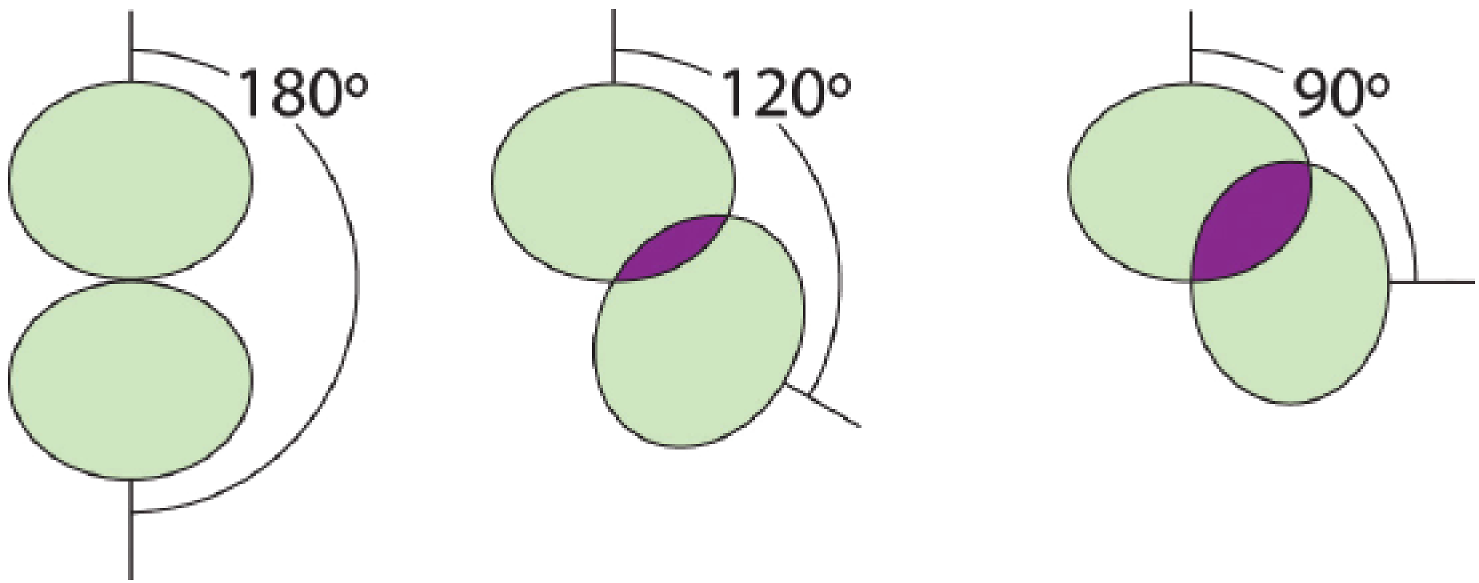
Electron repulsion

- Determining the number of 90° repulsions and their type can be used to rationalize the molecular shape adopted by a molecule.

LP – LP	Stronger repulsions
LP – BP	
BP – BP	Weaker repulsions

- Lone pairs (LP) require more space than bonding pairs BP) due to their higher electron density.
- The greater repulsion from lone pairs (LP-BP repulsion) compresses the bond angles between bonded atoms

Why 90˚ Repulsions?



- At 90˚, electron pairs overlap in space significantly leading to stronger repulsion (e- don't like to share space!)
- LPs are more spread out, so have more overlap
- BPs are more confined between the nuclei so have less overlap

https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/09._Molecular_Geometry_and_Bonding_Theories/9.2%3A_The_VSEPR_Model

Worksheet Question #19

ClF_3 has a trigonal bipyramidal parent shape with two lone pairs on the central atom. As such, it can take have two possible molecular shapes: T-shape or trigonal planar (see below).

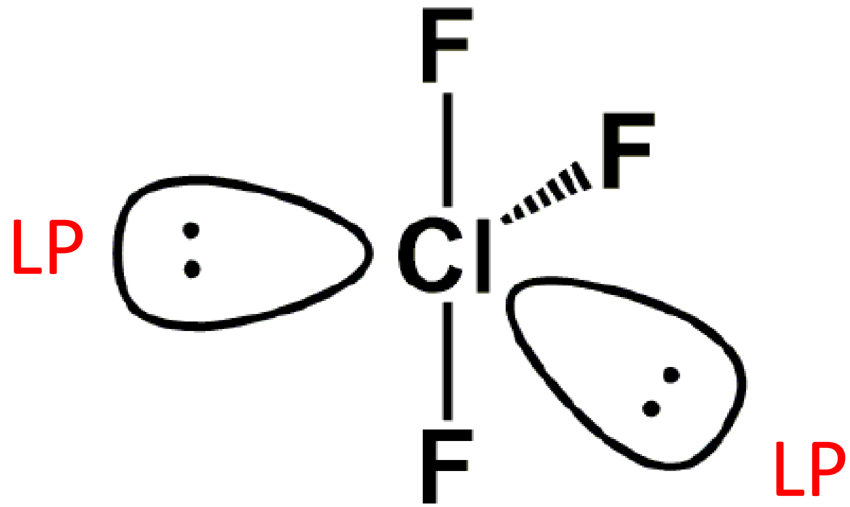
a) Determine the number of 90° LP-LP, LP-BP, and BP-BP interactions in each of these geometries. Write your answers in the table below.

b) Based on your answers to a., which molecular geometry is ClF_3 more likely to exhibit? Briefly explain your answer.

Worksheet Question #19 (a)

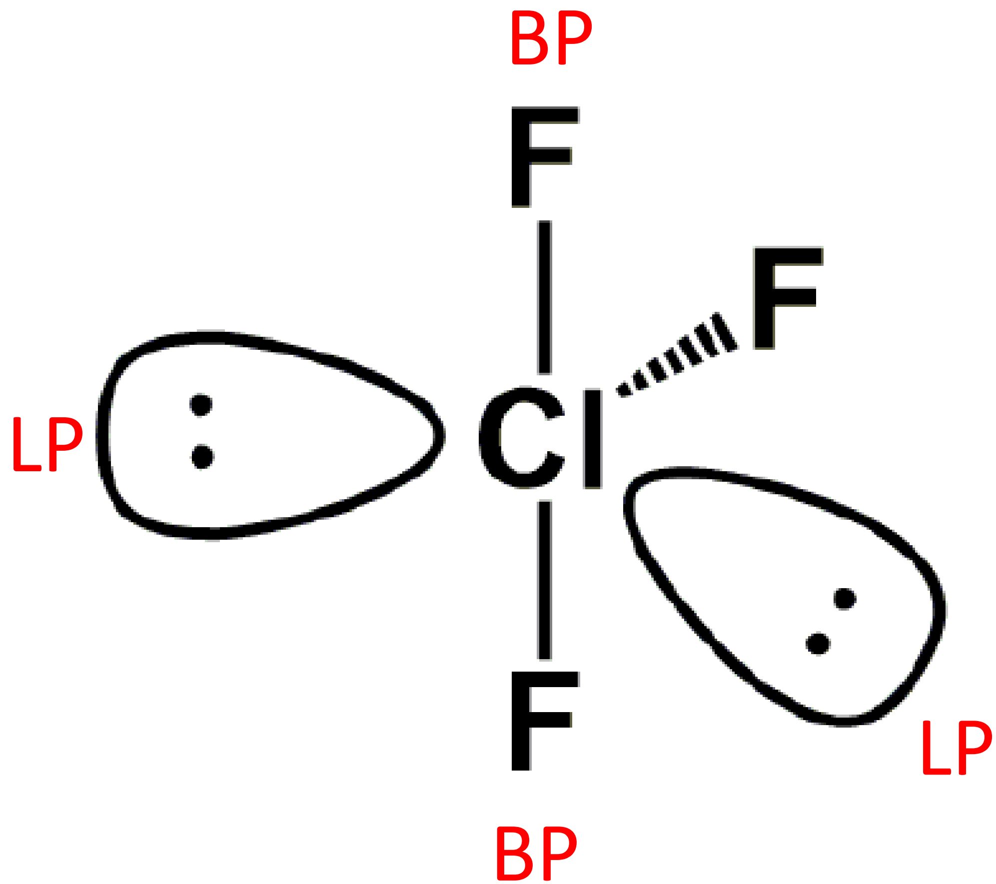
	T-shape
L.P. - L.P.	0
L.P. - B.P.	
B.P. - B.P.	

LP-LP at 120°, not 90°



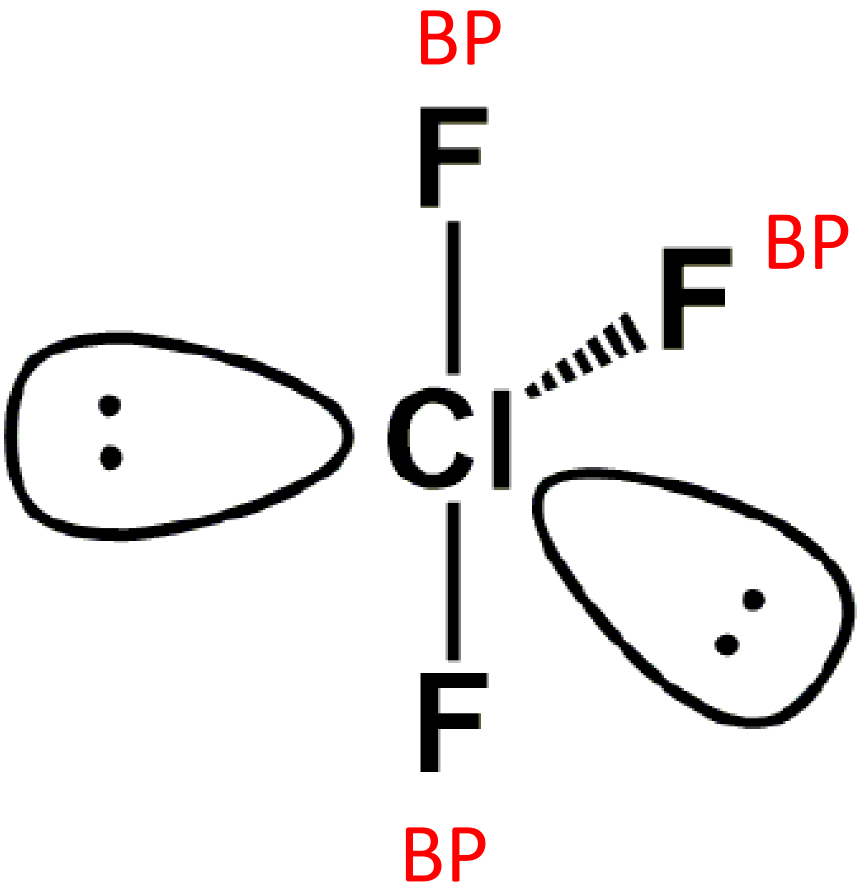
Worksheet Question #19 (a)

	T-shape
L.P. - L.P.	0
L.P. - B.P.	4
B.P. - B.P.	

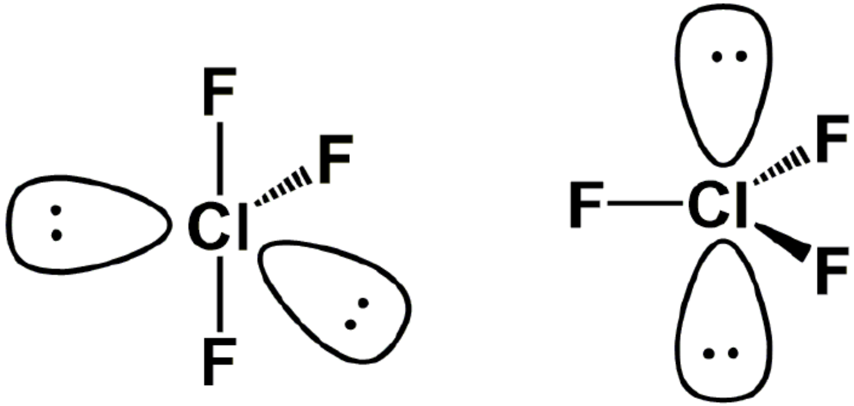


Worksheet Question #19 (a)

	T-shape
L.P. - L.P.	0
L.P. - B.P.	4
B.P. - B.P.	2



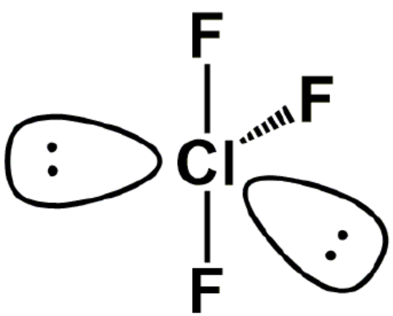
Worksheet Question #19 (a)



	T-shape	Trigonal Planar
L.P. - L.P.	0	0
L.P. - B.P.	4	6
B.P. - B.P.	2	0

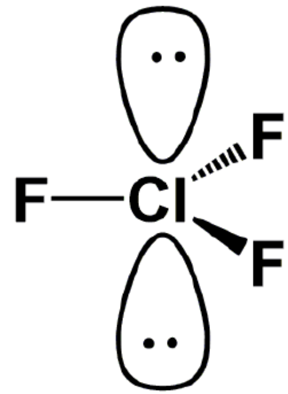
Worksheet Question #19 (b) CLICKER

- which molecular geometry is ClF_3 more likely to exhibit? Briefly explain your answer.



T-shape

(A)



Trigonal planar

(B)

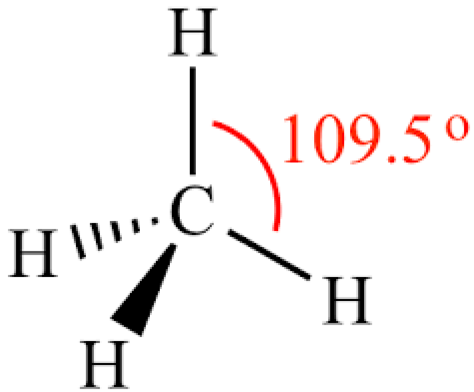
Non-ideal Geometries

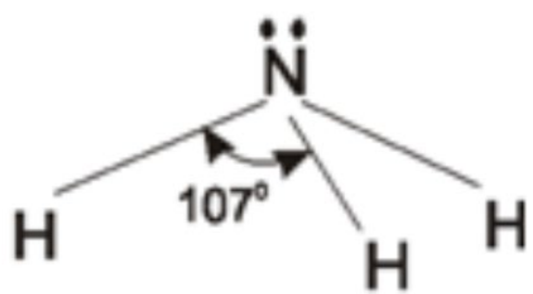
- The greater repulsion from lone pairs causes distortions of molecules away from the ideal geometries predicted by VSEPR theory.
- Lone pairs tend to push other pairs away, making bond angles distort from ideal values.
- These distortions are also affected by formal partial charges on terminal atoms.

Worksheet Question #21

Rationalize the trend in experimental bond angles for the two chemical series shown in the table to the right.

Series 1	
Species	Bond Angle
CH_4	109.5°
NH_3	106.7°
H_2O	104.5°

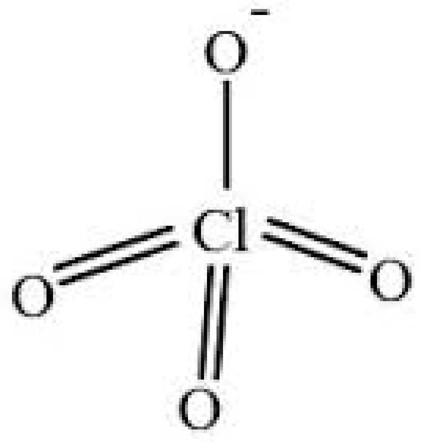


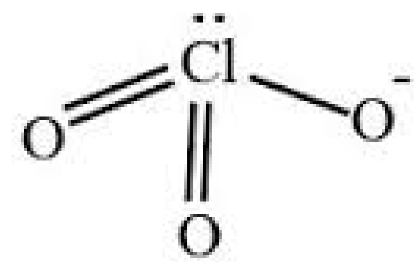


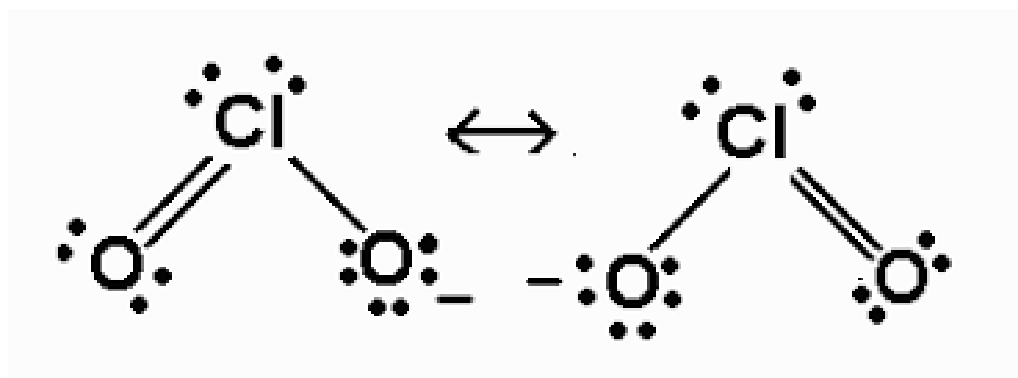
Worksheet Question #21

Rationalize the trend in experimental bond angles for the two chemical series shown in the table to the right.

Series 2	
Species	Bond Angle
ClO_4^-	109.5°
ClO_3^-	108.6°
ClO_2^-	113°







For ClO_2^-, formal charges repulsion is greater than the lone pair repulsion.