SHAPES OF MOLECULES

- Determined by a theory known as VSEPR theory
  ↳ Valence Shell Electron Pair Repulsion

"Teachers Notes"
- The shapes of molecules are determined by the angles between the bonds within the molecule
- The bond angles are determined by the arrangement of electrons around each atom

→ listen to zoom recording here

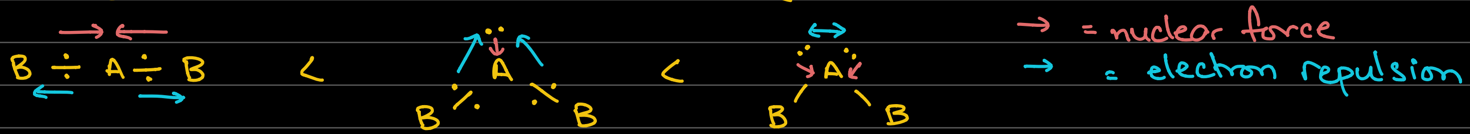
- Two "types" of electrons useful in figuring out molecule shape → ① Bonding ↓ Covalent and/or ② Non-Bonding ↓ Lone pairs

- Valence electrons → electrons (negatively charged) repel each other
  ↳ so, electrons in valence shell will experience the least repulsion when they are as far apart as possible.
    ↳ applies to both bonding / lone pairs

Simplified | Taking bond angles into consideration

Valence electron pair repulsion → depends on whether the electrons are bonded (BP) or they are non-bonding (LP)

BP-BP repulsion (least) < BP-LP repulsion < LP-LP repulsion (most)

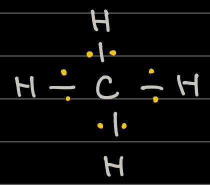


① Shapes of molecules with BP only (on central atom)
ie. central atom has no lone pairs

Steps:

① Draw a simple dot-cross diagram (only dots)

ie.



* Electron pair is a region of electron density

② Count the number of electron pairs around the central atom
- Electron pair = region of electron density
- Multiple bonds must be treated as single bonds or as single regions of electron density

C—C	C=C	C≡C
C : C	C ⋮ C	C ⋮ C
Single region	Single region	Single region

③ Note the arrangement that this number of electron pairs will adopt (given below):

No. of pairs: (around central atom)	Shape	Bond Angle
2	Linear	180°
3	Trigonal Planar	120°
4	Tetrahedral	109.5°
5	Trigonal Bipyramidal	90°, 120°
6	Octahedral	90°, 180°

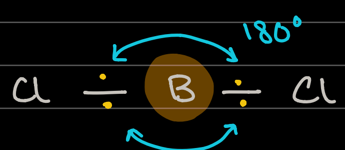
LINEAR (2 pairs of electrons)

ie. $BeCl_2$, CO_2, C_2H_2, C_2H_2 ethyne, HCN

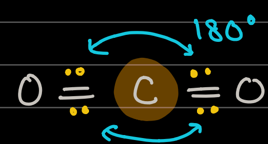
Be → group 2 but forms covalent bonds.

● = central atom

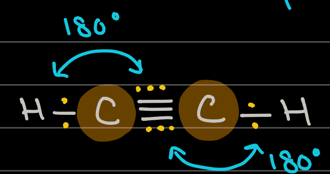
↔ = electron repulsion



$BeCl_2$

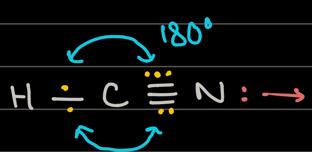


CO_2



Can have 2 angles:
∠HCC and ∠CCH = 180°

C_2H_2



→ this lone pair is irrelevant because it's not on the central atom

HCN → Hydrogen Cyanide

CO_2 : In CO_2, there are 2 separate regions of high electron density, corresponding to the bonding pairs in the two C=O bonds.

↳ These regions of electron density repel each other and are arranged so that they are as far apart as possible, making a bond angle of 180°

↳ Same goes for all the other linear molecules (with individual contexts)

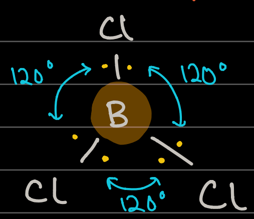
*All diatomic molecules are linear

TRIGONAL PLANAR (3 pairs of electrons / regions of electron density)

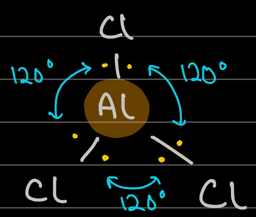
↳ "triangular" ↳ "flat" → 2D in shape

3 bonding pairs, eg. BCl_3, $AlCl_3$, C_2H_4 (ethene), HCOH (methanal)

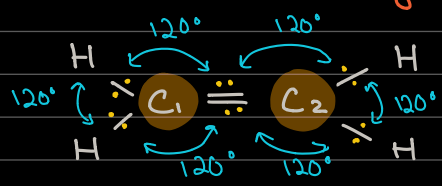
All of the following have three regions of electron density:



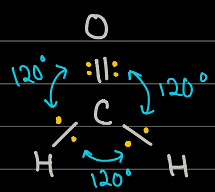
BCl_3



$AlCl_3$



C_2H_4 (ethene)



HCOH (methanal)

BCl_3 : In BCl_3, the three chlorine atoms are joined by single covalent bonds to the central boron atom

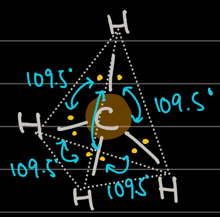
- there are three separate regions of high electron density, corresponding to the three B–Cl bonding pairs of electrons. → they repel each other equally (as all are bonding pairs)
- As a result, BCl_3 is planar (flat), and the arrangement of electrons is trigonal, that is, the three B–Cl bonds point towards the three corners of an equilateral triangle
- All bond angles are 120°

↳ Also applies to other trigonal planar atoms – with individual context

TETRAHEDRAL (4 pairs of electrons / regions of electron density)

ie. CH_4, CH_3Cl, $CHCl_3$, CCl_4

- Tetrahedron is a 3D shape with 4 triangular faces

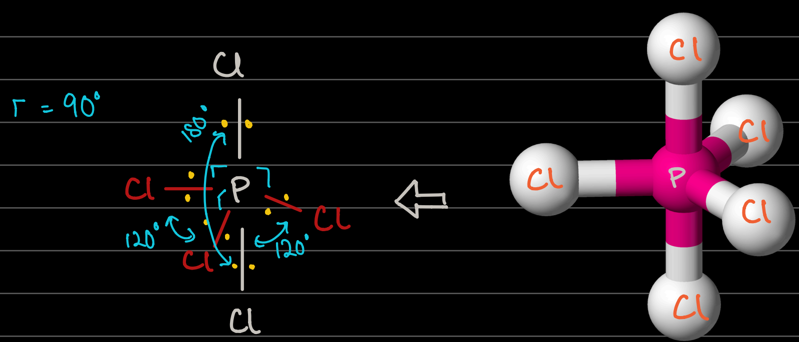


- The four H atoms are covalently bonded to the central C atom
- The four separate regions of high electron density correspond to the four C-H bonding pairs of electrons
- The four BP repel each other equally, so that the four CH bonds point towards the four corners of a regular tetrahedron
- The four H atoms surround the central carbon atom symmetrically
- All the bond angles are equal (109.5°)
  ↳ This is known as the tetrahedral angle

TRIGONAL BYPYRAMIDAL (5 bonding pairs of electrons / regions of electron density)

- A trigonal bipyramid is a three dimensional shape with two triangular pyramids joined together with a triangular base

eg. PCl_5, PF_5

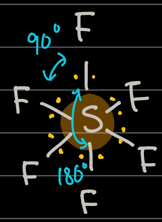


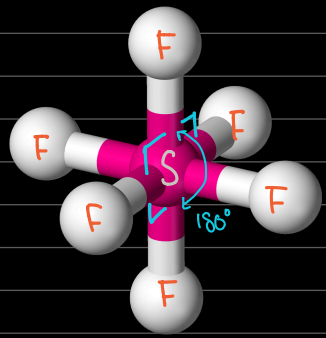
- The five chlorine atoms are joined to the central phosphorous atom by five single covalent bonds
- The five regions of high electron density correspond to the five bonding pairs in the five P-Cl bonds
- The five P-Cl bonds point towards the five corners of a trigonal bipyramid
- The structure is not totally symmetrical
- The Cl-P-Cl bond angles within the horizontal plane are 120°
- The Cl-P-Cl bond angles above and below the plane are 90°
- The Cl-P-Cl bond angle in the vertical plane is 180°

OCTAHEDRAL (6 pairs of electrons)
e.g SF_6 sulfur hexafluoride

- Octahedron is a 3D shape with eight

triangular faces
ie. it is 2 square based pyramids joined by their square base





- In SF_6, there are six S-F covalent bonds, corresponding to 6 regions of high electron density, which repel each other equally.

- The 6 S-F bonds point towards the six corners of regular octahedron.
- All F-S-F bond angles in the horizontal plane are 90°
- All F-S-F bond angles between the vertical and horizontal plane are also 90°
- There is one F-S-F bond angle in the vertical plane which is 180°.

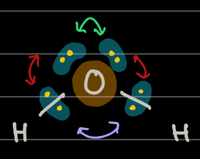
SHAPES OF MOLECULES WITH LONE PAIRS (as well) + BONDING PAIRS on the central atom

Valence electrons — BP + LP

- Lone pair orbitals, on average, are larger than orbitals containing bonding pairs only. (as they are only attracted to their own nucleus).
  ↳ Therefore, they take up more space around the central atom

- They have a greater repulsive effect on the other pairs of electrons that surround the central atom
  ↳ and this causes the angle between two lone pairs to be larger than the angle between a lone pair and a bonding pair, which, in turn, is larger than the angle between two bonding pairs

● = region of high electron density



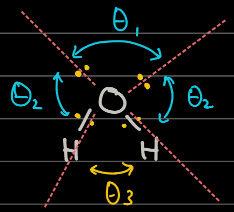
- 4 regions of high electron density → tetrahedral

BUT

LP-LP repulsion > LP-BP repulsion > BP-BP repulsion

- The bond angle is therefore smaller than the tetrahedral angle (109.5°) because the two lone pairs repel more effectively than the bonding pairs and they "squeeze" the hydrogens together

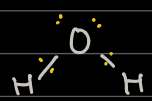
- The bond angle decreases to 104.5°.



$\theta_1 > \theta_2 > \theta_3 = 104.5°$

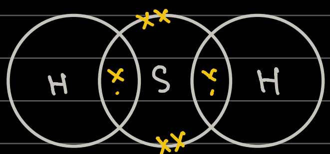
Rule of thumb for bond angles:
- For every lone pair, the bond angle decreases by approximately 2°.

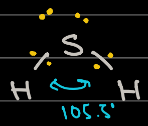
H_2O → 4 regions → 109.5°
but 2LP → − 4.0°
105.5° → Approximate value



→ bent / v-shaped / non-linear

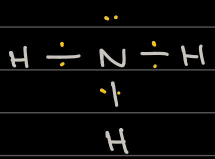
Q. Draw a dot-cross for H_2S. What is the shape? What is the H-S-H bond angle?

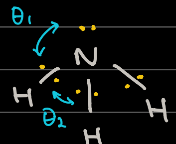




refer to "rule of thumb"
↑
Bond angle ≑ 105.5°
↳ we'll take approximate value for this because we don't know the exact theoretical value.

One lone pair on the central atom
ie. NH_3 → N is in group 5, 5 valence electrons



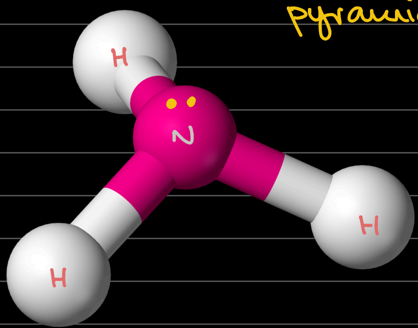


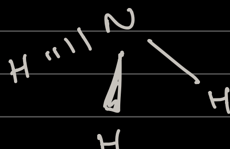
trigonal pyramidal

$\theta_1 > \theta_2$
LP-BP > BP-BP

Bond angle should decrease by about 2°
109.5° − 2 = 107.5° (approximately)

Actual H-N-H bond angle is <u>107°</u>.



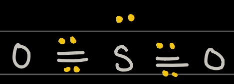


* Regions of electron density include both BP and LP on the central atom

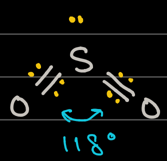
PH_3

trigonal pyramidal

SO_2

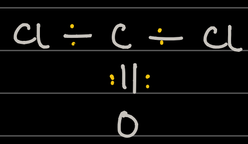


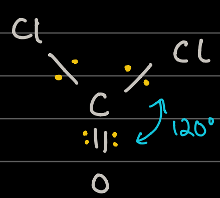
3 regions → so angle would be 120° if they were all bonding pairs
However, since there's a lone pair present, 120 − 2 = 118° approx.



non-linear / v-shaped / bent

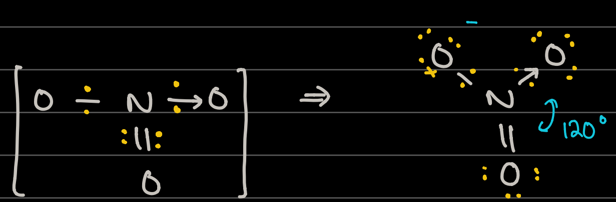
CCl_2O → phosgene



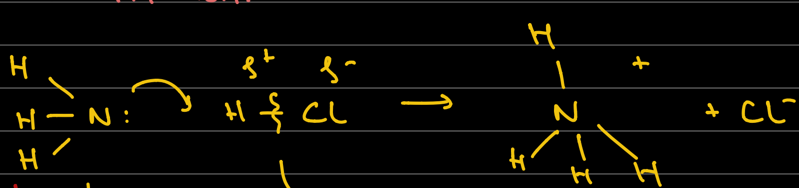


trigonal planar

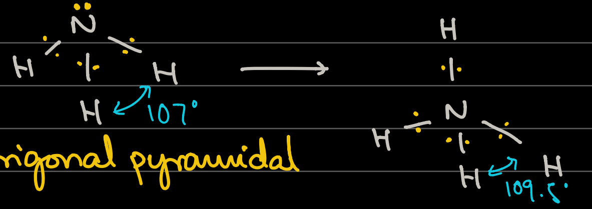
NO_3^- ion
nitrate



Q. what is the change in bond angle and shape when NH_3 reacts with HCl to form the NH_4^+ ion.



* Important

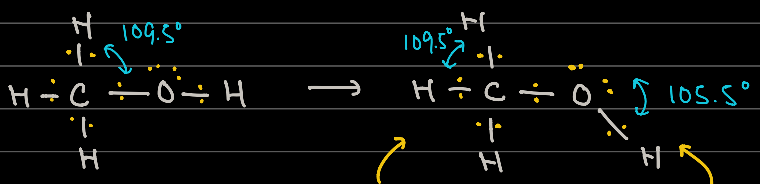


trigonal pyramidal

tetrahedral

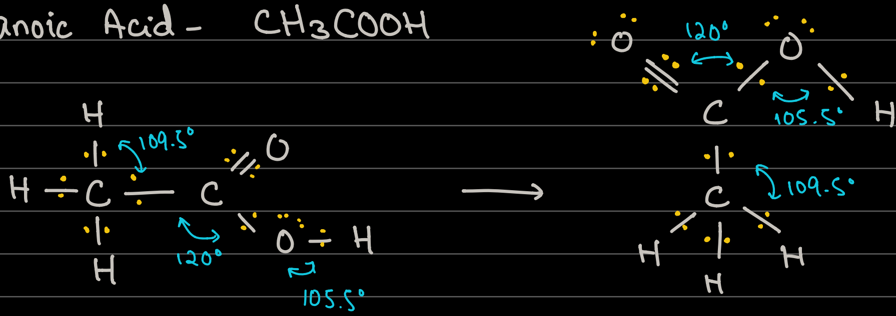
∴, the bond angle increases from 107 to 109.5°

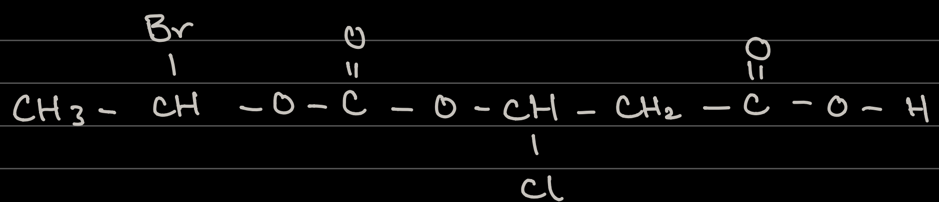
Methanol - CH_3OH

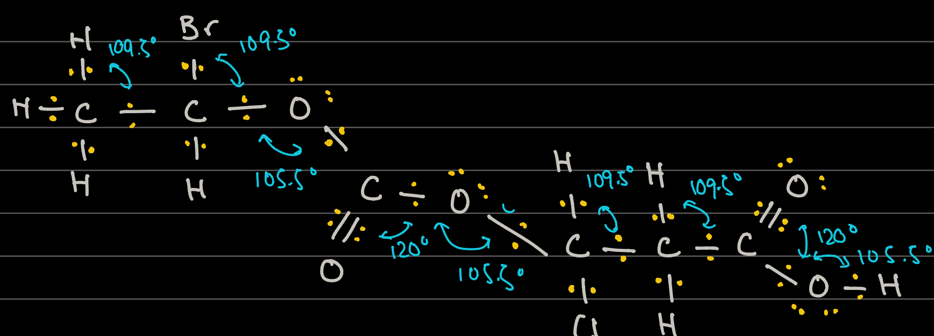


tetrahedral + non-linear

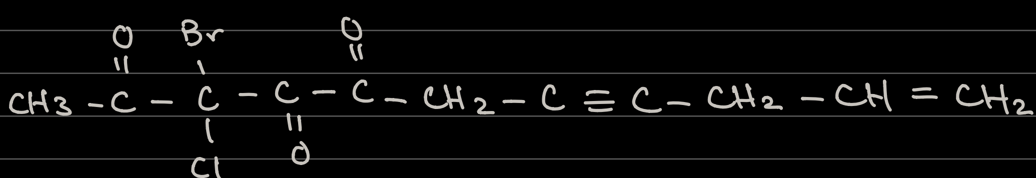
Ethanoic Acid - CH_3COOH

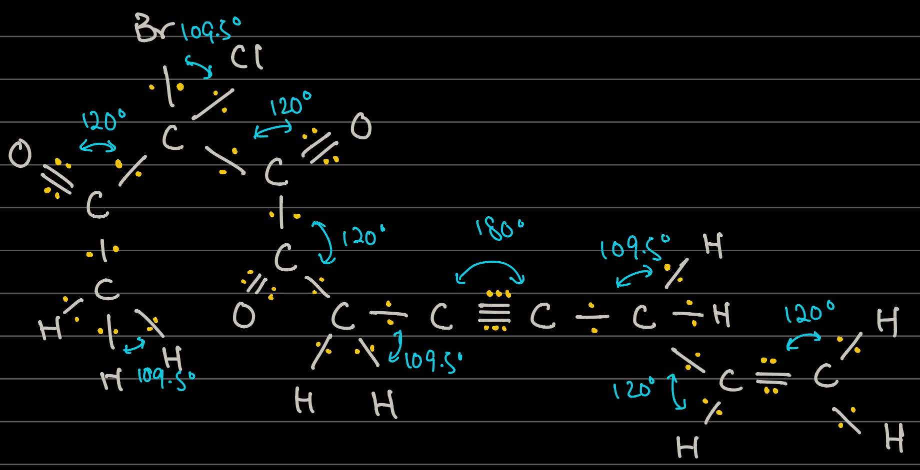






tetrahedral + tetrahedral + v-shaped + trigonal planar + v-shaped + tetrahedral + tetrahedral + trigonal planar + v-shaped

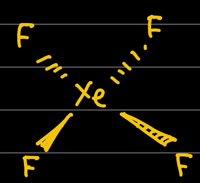




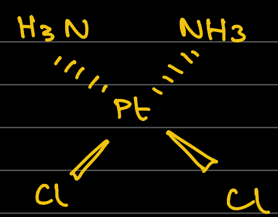
4 regions of electron density

tetrahedral 109.5° or square planar 90°

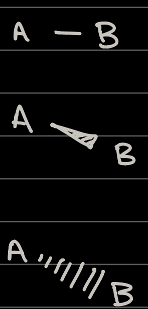
- in transitional metal complexes
- XeF_4



usually platinum compounds
cis-platin



3D BOND NOTATION: Draw bonds to show their 3D orientation
ie. where is the bond pointing

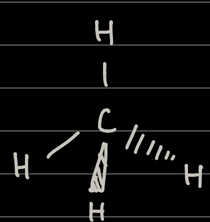


Flat Bond

wedge, is a bond "coming at you"
ie. in front of the plane of the paper

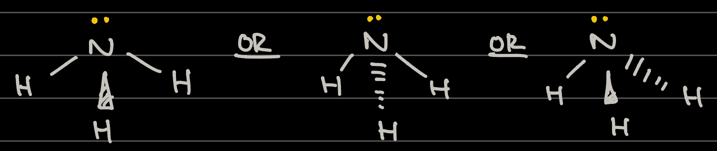
Dotted Bond, is a bond going back into the paper
ie. away from you

ie. tetrahedral with proper 3D bond notation =

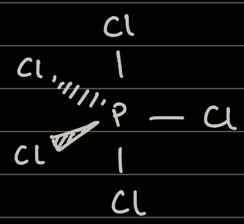


*Always draw the two straight bonds adjacent to each other (by convention), then one wedge and one dotted

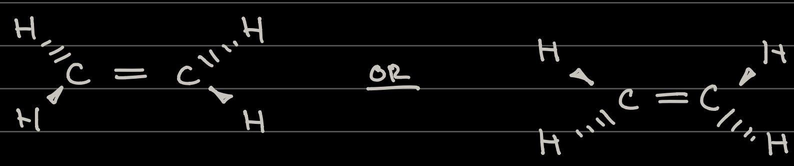
Trigonal Pyramidal



Trigonal Bipyramidal



PCl_5



Ethene