

CHAPTER 10

CHEMICAL BONDING I

A chemical bond is formed between two atoms or ions which are strongly attached to each other. There are three general types of chemical bonds.

Ionic bond: Results from the transfer of one or more \bar{e} 's from one atom to another. Ionic substances are generally formed by the interaction of metals with nonmetals.

Covalent bond: Constructed by the sharing of \bar{e} 's between two atoms. This type of bonding is seen in the interactions of nonmetallic elements with each other.

Metallic bond: In metallic bonds each atom in a metal is bonded to several neighboring atoms.

Lewis Theory

- 1) Electrons play a fundamental role in chemical bonding.
- 2) If \bar{e} 's are transferred from one atom to another, positive and negative ions are formed and attract each other through electrostatic forces called ionic bonds.
- 3) A bond formed by the sharing of \bar{e} 's between atoms is called a covalent bond.
- 4) Each atom tries to acquire a stable \bar{e} configuration by sharing or transferring \bar{e} 's. Usually this is a noble gas configuration, one with eight outer-shell electrons, or an octet.

Lewis Symbols and Lewis Structures

A Lewis symbol consists of a chemical symbol to represent the nucleus and core \bar{e} 's. The valence (outer-shell) \bar{e} 's are placed around the symbol with dots.

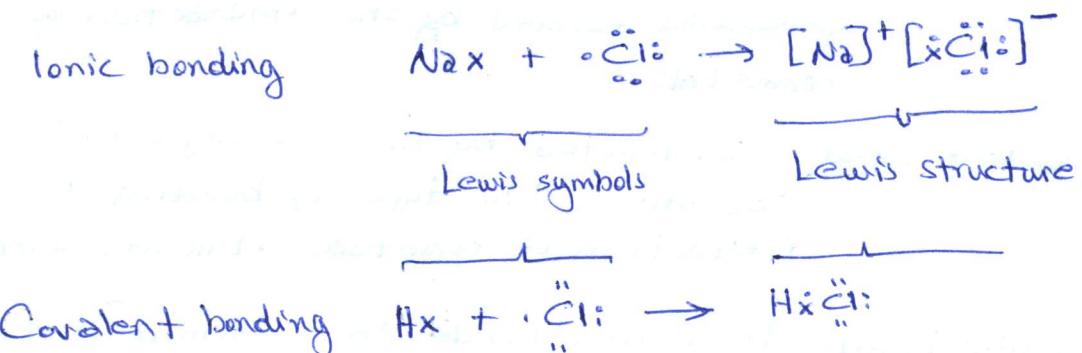
Silicon ($\text{Si} : [\text{Ne}] 3s^2 3p^2$)



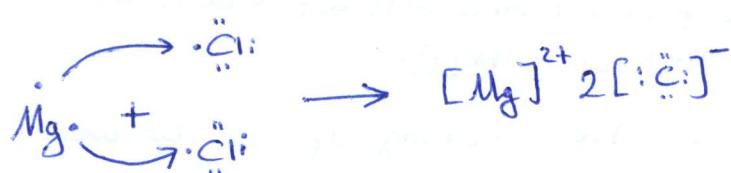
Lewis symbols of some elements

Group	<u>IA</u>	<u>2A</u>	<u>3A</u>	<u>IV A</u>	<u>VA</u>	<u>VIA</u>	<u>VIIA</u>	<u>VIII A</u>
	H:	Bc:	B:	C:	N:	O:	F:	He:
	Li:	Mg:	Al:	Si:	P:	S:	Cl:	Ne:
	Na:	Ca:						

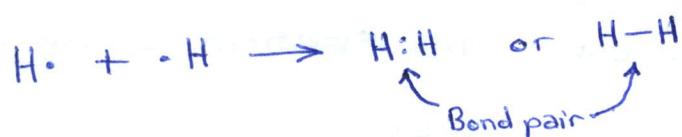
→ A Lewis structure is a combination of Lewis symbols



Example: Lewis structures of BaO and MgCl



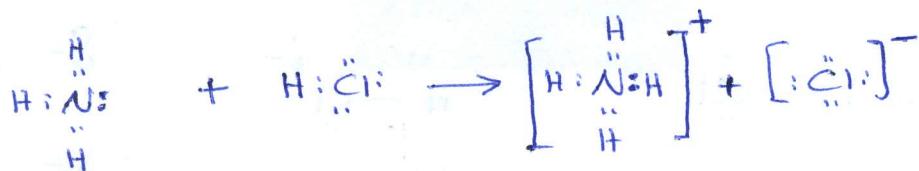
Example : Lewis structure of H_2 and Cl_2 molecules.



- * Each chlorine atom is surrounded by 8 \bar{e} 's (the bond pair \bar{e} 's are double counted). Each atom conforms the octet rule: Atoms tend to gain, lose or share \bar{e} 's until they are surrounded by valance \bar{e} 's.
 - * The sharing of a pair of \bar{e} 's constitutes a single covalent bond, a single bond.

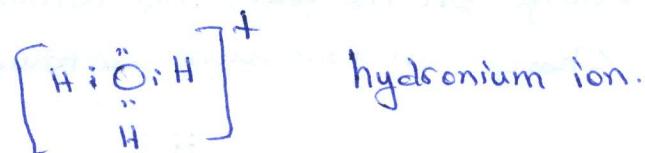
Coordinate Covalent Bond

A covalent bond in which a single atom contributes both of the \bar{e} 's to a shared pair is called a coordinate covalent bond.



- * The \bar{e} 's in the H-Cl bond remain on the Cl atom and a new bond between N and H atoms is formed by using the lone pair \bar{e} 's of N. This new bond is a coordinate covalent bond.

Example:

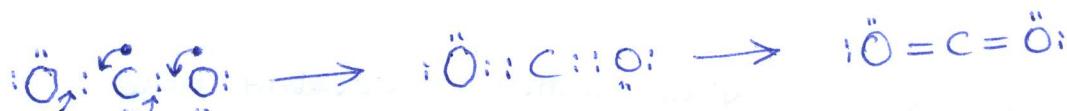


Multiple Covalent Bonds

Sometimes, more than one pair of \bar{e} 's must be shared if an atom is to attain an octet. CO_2 and N_2 , for instance, are two molecules in which atoms share more than one pair of \bar{e} 's.



- * Both O and C atoms still shy of an octet.



- * The unpaired \bar{e} 's are shifted into the region of the bond.

- * The bonded atoms are seen to share two pairs of \bar{e} 's between them form a double covalent bond(=).

Example



triple covalent bond
(three pairs of \bar{e} 's
are shared)

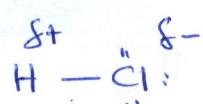
- * Double and triple covalent bonds are known as multiple covalent bonds.

Polar Covalent Bonds

A covalent bond in which \bar{e} 's are not shared equally between two atoms is called a polar covalent bond.



nonpolar cov.
bond.



polar cov. bond.

$\delta-$: partial negative
charge

$\delta+$: partial positive
charge

- * In polar covalent bond, \bar{e} 's are displaced toward the more nonmetallic element. The unequal sharing of \bar{e} 's leads to a partial (-) charge on the more nonmetallic elements ($\delta-$) and partial (+) charge on the more metallic element ($\delta+$).

Electronegativity

Electronegativity is the ability of an atom in a molecule to attract \bar{e} 's to itself. Electronegativity is related to ionization energy and \bar{e} affinity.

Electronegativity decreases from top to bottom in a group and increases from left to right in a period.

- * Electronegativity difference (ΔEN) allows us to estimate the polar character of a covalent bond.

ΔEN	very small	covalent bond
ΔEN	intermediate	polar covalent bond
ΔEN	Large	ionic bond

Writing Lewis Structures

- 1) Determine the total number of valence \bar{e} 's
- 2) Identify the central atom(s) and terminal atoms
 - C atoms are always central atoms
 - H is always terminal atoms
 - O atom is central atom in peroxy (-O-O-) and hydroxyl group (-O-H). Otherwise, O atom to be a terminal atom.

- central atoms have generally lowest electronegativity.

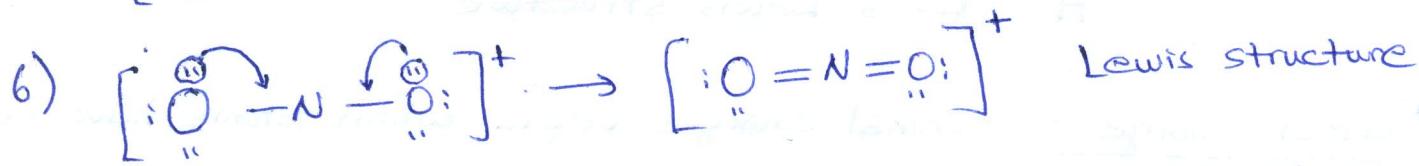
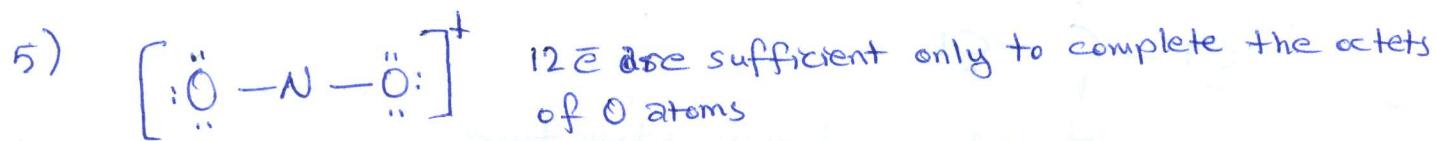
- 3) Draw a skeletal structure. Join the atoms by single covalent bonds.
- 4) For each bond in the structure, subtract two from the total number of valence \bar{e} 's.
- 5) Write the valence electrons remaining.
 - First complete the octets of the terminal atoms then central atoms.
 - if there is enough \bar{e} 's, complete octets for all the atoms.
- 6) If one or more central atoms are left with an incomplete octet after step 5, move lone pair electrons from one or more terminal atoms to form multiple covalent bonds to central atoms.

Example: Write the Lewis structure for the nitronium NO_2^+ ion.

1) t.n.v. \bar{e} = $5 + 6 + 6 = 17 - 1 = 16$



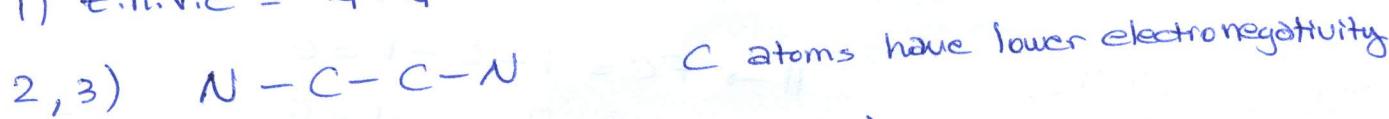
4) $16 - 4 = 12 \bar{e}$ (remaining valence \bar{e} 's)



N atom has two pairs \rightarrow move four more \bar{e} 's to complete the octet of N

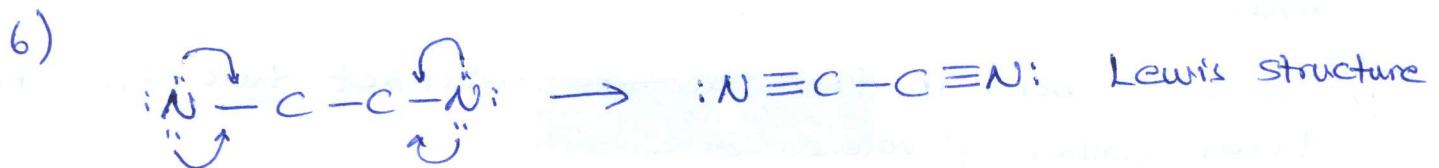
Example: Lewis structure of cyanogen C_2N_2

1) t.n.v. \bar{e} = $4 + 4 + 5 + 5 = 18$



4) $18 - 6 = 12 \bar{e}$ (to be assigned)

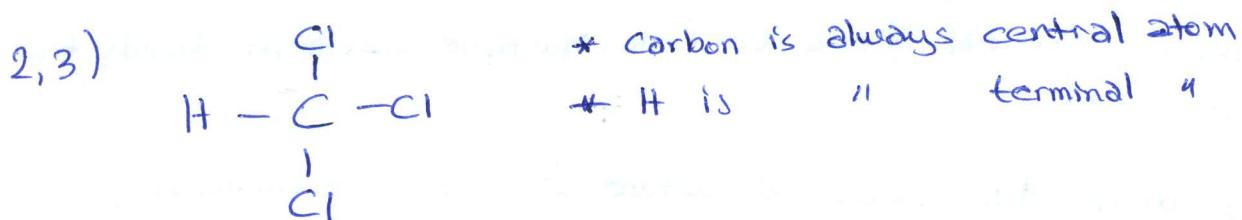
5) $\ddot{\text{N}}-\text{C}-\text{C}-\ddot{\text{N}}$: all 12 \bar{e} 's are assigned to terminal atoms



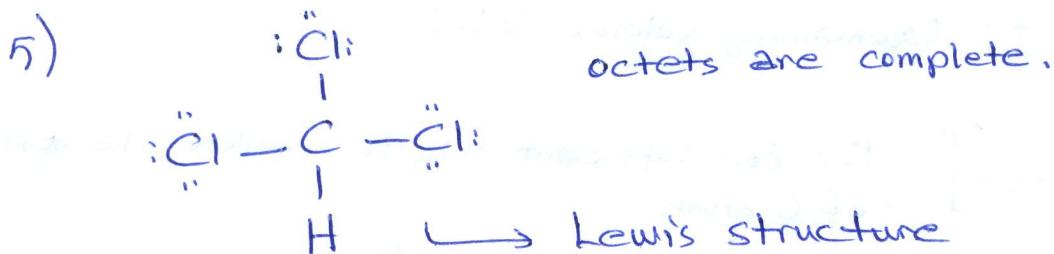
complete the octet of central C atoms by moving 4 \bar{e} 's from each of the terminal N atoms.

Example: Lewis structure of chloroform CHCl_3

1) t.n.v. \bar{e} = $4 + 1 + (7 \times 3) = 26$



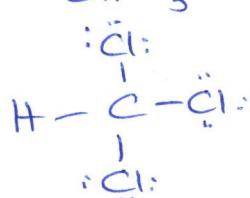
4) $26 - 8 = 18 \bar{e}$ (to be assigned)



Formal Charge: Formal charges occur when atoms have not contributed equal numbers of \bar{e} 's to the covalent bonds.

$$\boxed{FC = \frac{\text{number of valence } \bar{e} \text{ in free atom}}{\text{number of bonds}} - \frac{\text{number of lone pair } \bar{e}}{2}}$$

Example CHCl_3



$$\text{H} \rightarrow FC = 1 - 0 - 1 = 0$$

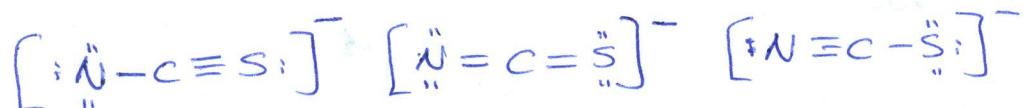
$$\text{Cl} \rightarrow FC = 7 - 6 - 1 = 0$$

$$\text{C} \rightarrow FC = 4 - 0 - 4 = 0$$

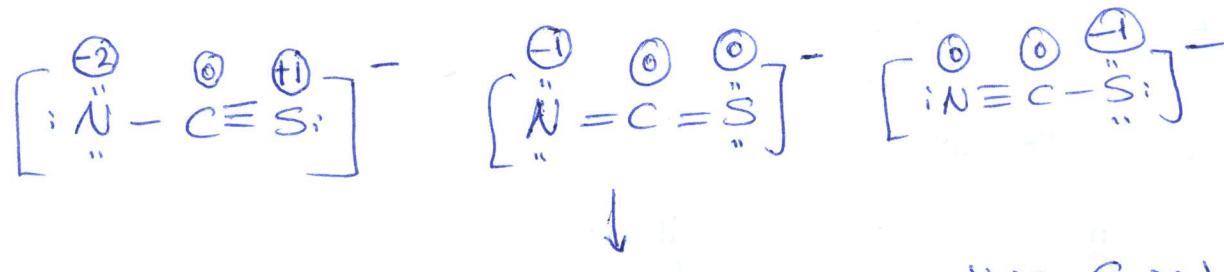
→ General Rules:

- 1) The sum of the formal charges in a Lewis structure
 - a) must be equal zero for a neutral molecule
 - b) must be equal the magnitude of the charge for a polyatomic ion. $\left[\ddot{\text{O}}^+ \equiv \text{N} - \ddot{\text{O}}^- \right]^+ \Rightarrow \text{the sum} = +1 + 1 - 1 = +1\right]$
- 2) They should be as small as possible
- 3) (-) FC usually appear on the most electronegative atom
(+) FC " " " on the least "
- 4) FC with the same sign on adjacent atoms are unlikely.

Example: The following are three possible Lewis structures for the thiocyanate ion, NCS^- .

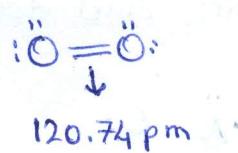
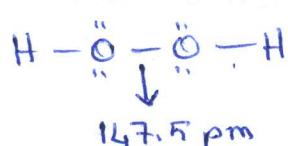
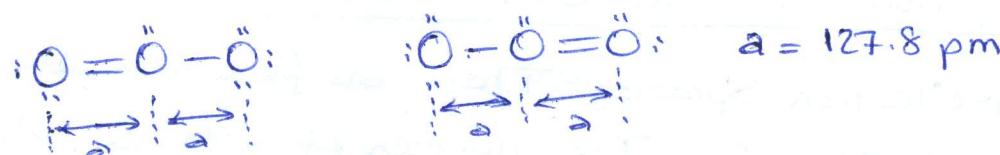


- a) Find the FC of the atoms in each structure
- b) Which L. structure is the perfect one



N is more electronegative than C and S.
This structure is the preferred Lewis structure.

Resonance: When we apply the usual rules for Lewis structures for ozone, we come up with two possibilities. ($\text{Ozone} = \text{O}_3$)

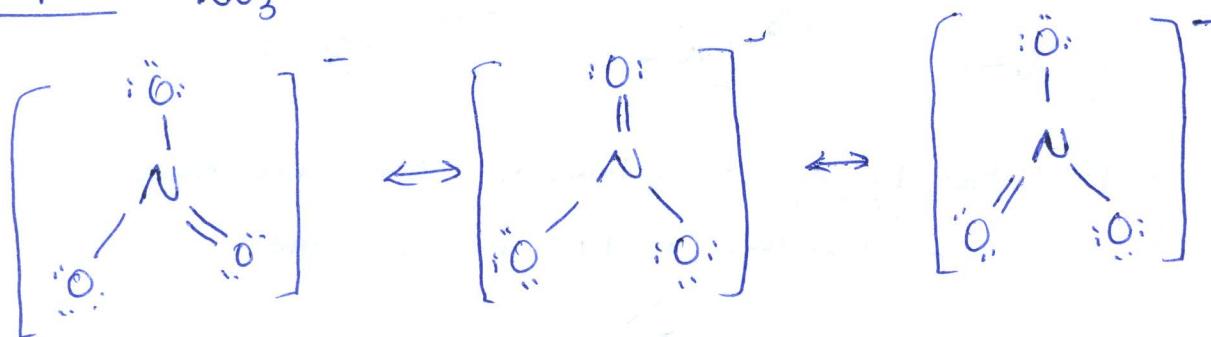


The bonds in ozone are intermediate between a single and a double bond. The structure of ozone is a hybrid of the two.

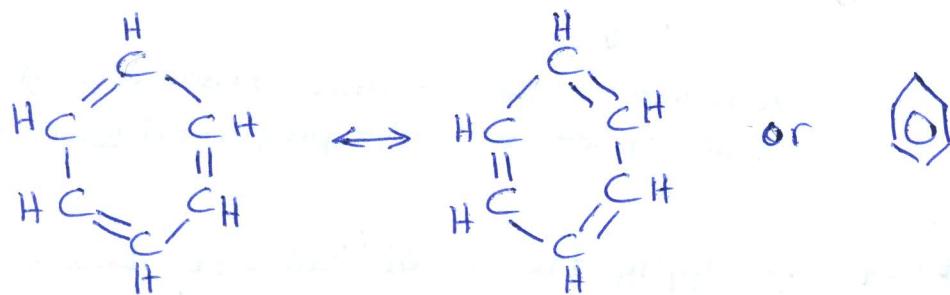


- * The situation in which two or more possible Lewis structures contribute to the "correct" structure is called resonance.
- * In resonance structures:
 - arrangement of atoms is the same
 - " " " electrons is different

Example: NO_3^-



Example: Benzene

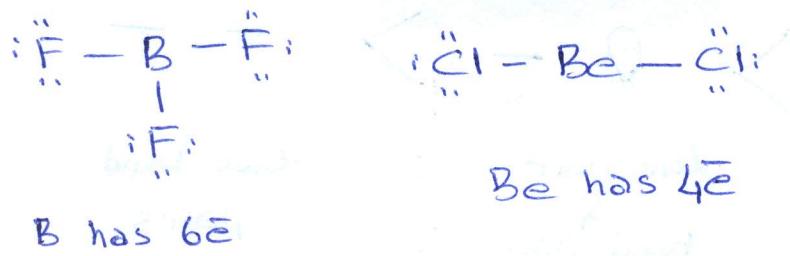


Exceptions to the Octet Rule

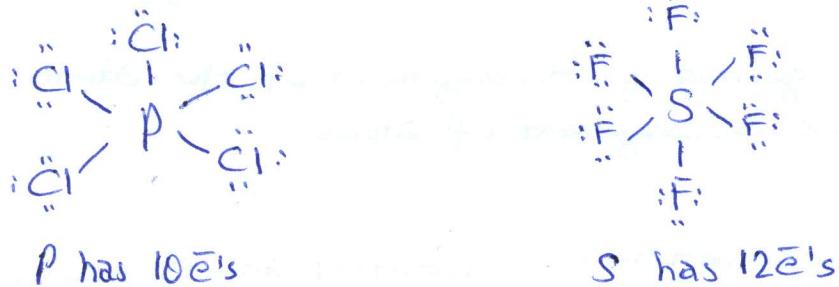
- 1) Odd-Electron Species: There are few molecules or ions such as NO , NO_2 , O_2 . The number of valence \bar{e} 's are odd. Lewis theory deals with \bar{e} pairs and does not tell us where to put the unpaired \bar{e} .



2) Incomplete Octets: This exception occurs when there are fewer than 8 \bar{e} around an atom. Mostly seen in compounds of boron and beryllium.



3) Expanded Valence Shells: If there are more than 8 \bar{e} 's in the valence shell of an atom, it is called expanded valence shell. Especially the nonmetal atoms of the 3rd period and beyond that are bonded to highly electronegative atoms.



SHAPES OF MOLECULES

Lewis structures do not indicate the shapes of molecules. They simply shows the number and types of bonds between atoms.

Actually the overall shape of a molecule is determined by its bond angles and lengths.

Bond length: The distance between the nucleus of bonded atoms.

Bond angle: The angles between adjacent lines representing bonds.

Valence-Shell Electron-Pair Repulsion (VSEPR) Theory

\bar{e} pairs repel each other, whether they are in chemical bond or unshared \bar{e} pairs (lone pair). The best arrangement of \bar{e} pairs is the one that minimizes the repulsion among them.

* The shapes of molecules or ions depend on the number of \bar{e} 's (also the repulsion between them) around the central atom.

Repulsion



between two lone pairs lone pair & bond pair two bond pairs

The order of repulsive forces.

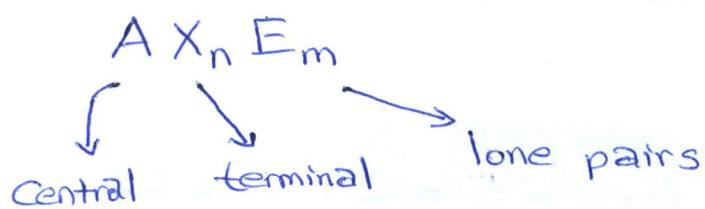
* There are two geometries

- Electron-group geometry: The arrangement of \bar{e} domains about the central atom of a molecule. Or geometric distribution of \bar{e} 's.
- Molecular geometry: Arrangement of the atoms in a molecule. Or geometric arrangement of atoms.

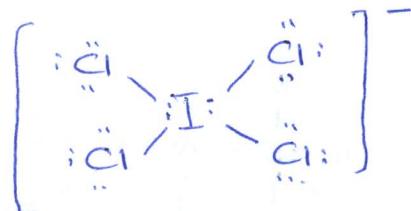
Electron Group Geometries: Central atoms may have two, three, four, five, or six electron groups distributed around them.

2 \bar{e} groups	linear	
3 \bar{e}	trigonal planar	
4 \bar{e}	tetrahedral	
5 \bar{e}	trigonal bipyramidal	
6 \bar{e}	octahedral	

- * Lone-pair \bar{e} 's spread out more than bond-pair \bar{e} 's. As a result the repulsion of one lone-pair \bar{e} for another lone-pair is greater than between two bond-pair \bar{e} 's.
- * The closer together the two groups of electrons, the stronger the repulsion between them. The repulsion between two \bar{e} groups is much stronger at an angle of 90° than a 120° or 180° .

VSEPR NotationUsing VSEPR Theory to Predict a Geometric Shape:

1) Draw a plausible Lewis structure



2) Determine the number of electron groups around the central atom, and identify them as bond-pair or lone-pair electrons.

6 \bar{e} groups around I

4 bond-pairs

2 lone-pairs

3) Establish the electron - group geometry

the orientation of 6 electron groups is octahedral



① In a multiple covalent bond, all \bar{e} 's constitute one group of \bar{e} .

4) Determine the molecular geometry



Molecular geometry is
Square planar

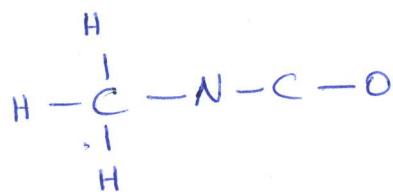
SEE APPENDIX
TABLE 10.1

Example: More than one central atom.

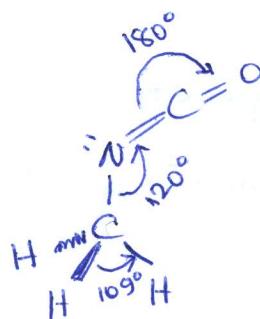
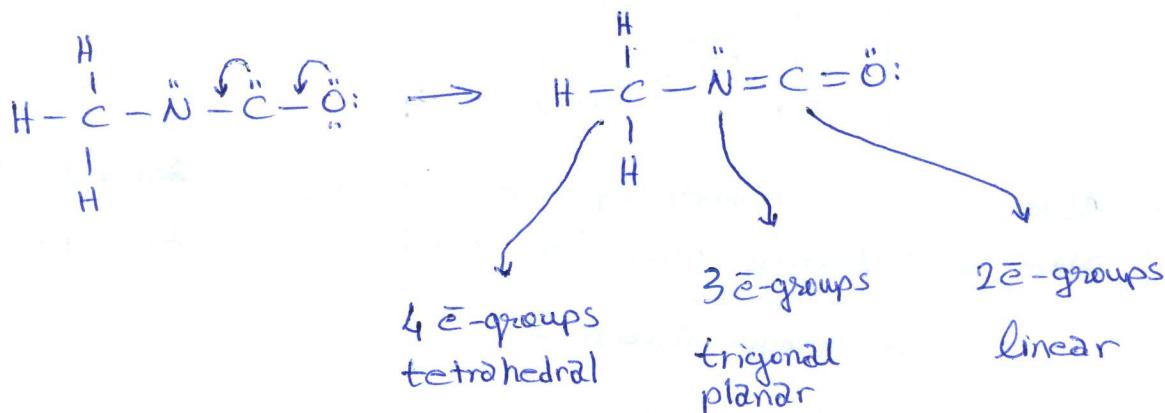


1) Lewis structure

$$\text{t.n.v.e} = 4 + (1 \times 3) + 5 + 4 + 6 = 22$$
$$\begin{array}{ccccc} & & & & \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ \text{C} & \text{H} & \text{N} & \text{C} & \text{O} \end{array}$$



$$22 - 12 = 10 \text{ remaining } \bar{\text{e}}\text{'s}$$

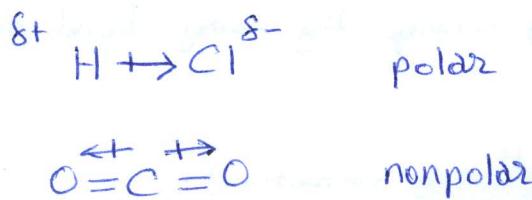


Molecular Shapes and Dipole Moments

The difference in electronegativity between H and Cl leads to a polar covalent bond in the HCl molecule. The Cl atom is more electronegative than the H atom. So, electrons are displaced toward the Cl atom. A molecule such as HCl is called a polar molecule.



* A cross-base arrow is used (\rightarrow) to show the atom that attracts $\bar{\text{e}}$'s more strongly.

Example:

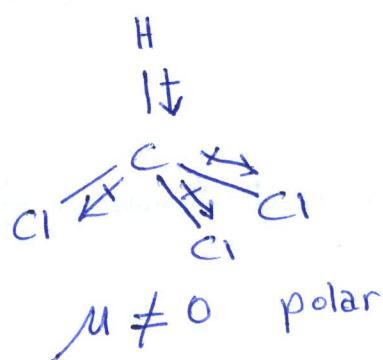
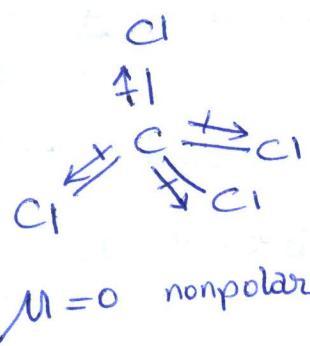
$\bar{\text{e}}\text{'s}$ are displaced to the O atom in each C and O bond and this gives rise to a bond dipole. However, the two bond dipoles are equal and point in opposite directions. They

cancel each other and lead to dipole moment of zero.

Dipole Moment: The magnitude of the charge displacement in a polar covalent bond is given by the dipole moment (μ). Dipole moment is the product of a partial charge and distance.

$$\boxed{\mu = q \times d}$$

$$\begin{aligned} \mu &= 3.34 \times 10^{-30} \text{ coulomb-meter (C.m)} \\ &= 1 \text{ debye (D)} \end{aligned}$$

Example:Bond Order and Bond Lengths

Bond order	=	for a single covalent bond $\rightarrow 1$
\downarrow Describes whether a covalent bond is single, double or triple	=	" " double " " $\rightarrow 2$
	\equiv	" " triple " " $\rightarrow 3$

Bond Length \downarrow
Distance between
the centers of atoms

$\text{single} > \text{double} > \text{triple}$

Bond Energies

We can determine the enthalpy change by using bond energies.

$$\Delta H_{rxn} = \Delta H_{(bond\ breakage)} + \Delta H_{(bond\ formation)}$$

$$\Delta H_{rxn} = \sum BE_{(reactants)} - \sum BE_{(products)}$$

* Bond-dissociation energy (D), is the quantity of energy required to break one mole of covalent bonds in a gaseous species.

Example: The rxn. of methane (CH_4) and chlorine produces a mixture of products. Calculate ΔH for this rxn.

Bond energies: $\text{C-H} = 414 \text{ kJ}$ $\text{Cl-Cl} = 243 \text{ kJ}$
 $\text{C-Cl} = 339 \text{ kJ}$ $\text{H-Cl} = 431 \text{ kJ}$

$$\begin{aligned}\Delta H \text{ for net bond breakage} &\Rightarrow 1 \text{ mol C-H bond} & 414 \text{ kJ} \\ & 1 \text{ mol Cl-Cl} " & + 243 \text{ kJ} \\ & \hline & 657 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta H \text{ for net bond formation} &\Rightarrow 1 \text{ mol C-Cl bond} & -339 \text{ kJ} \\ & 1 \text{ mol H-Cl} " & + -431 \text{ kJ} \\ & \hline & -770 \text{ kJ}\end{aligned}$$

$$\Delta H_{rxn} = 657 - 770 = -113 \text{ kJ}$$

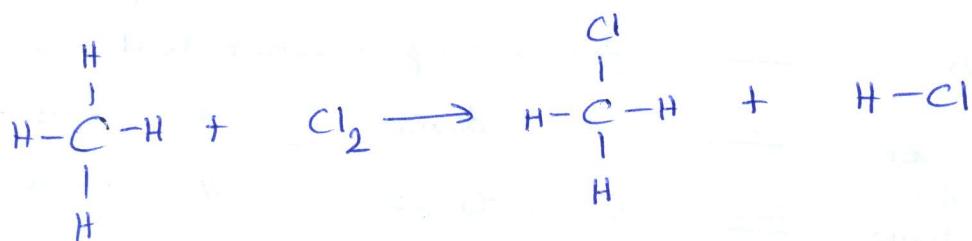
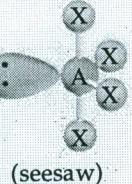
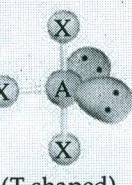
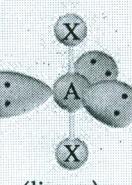
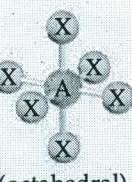
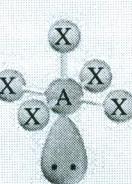


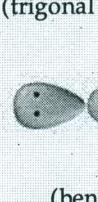
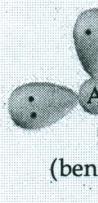
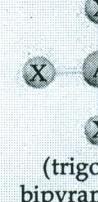
TABLE 10.1 Molecular Geometry as a Function of Electron-Group Geometry (Continued)

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example
	trigonal bipyramidal	1	AX_4E^b		90°, 120°	SF_4
	trigonal bipyramidal	2	AX_3E_2		90°	ClF_3
	trigonal bipyramidal	3	AX_2E_3		180°	XeF_2
6	octahedral	0	AX_6		90°	SF_6
	octahedral	1	AX_5E		90°	BrF_5
	octahedral	2	AX_4E_2		90°	XeF_4

^aFor a discussion of the structure of SO_2 , see page 428.

^bFor a discussion of the placement of the lone-pair electrons in this structure, see page 427.

TABLE 10.1 Molecular Geometry as a Function of Electron-Group Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example
2	linear	0	AX_2	 (linear)	180°	BeCl_2
3	trigonal planar	0	AX_3	 (trigonal planar)	120°	BF_3
	trigonal planar	1	AX_2E	 (bent)	120°	SO_2^a
4	tetrahedral	0	AX_4	 (tetrahedral)	109.5°	CH_4
	tetrahedral	1	AX_3E	 (trigonal pyramidal)	109.5°	NH_3
	tetrahedral	2	AX_2E_2	 (bent)	109.5°	OH_2
5	trigonal bipyramidal	0	AX_5	 (trigonal bipyramidal)	$90^\circ, 120^\circ$	PCl_5

(continued)