Basic Concepts of Chemical Bonding

Chlorine

- pale yellow gas
- react with almost anything
- Responsible for the depletion of ozone layer
- if inhaled can cause death
- used as a chemical weapon during WWI

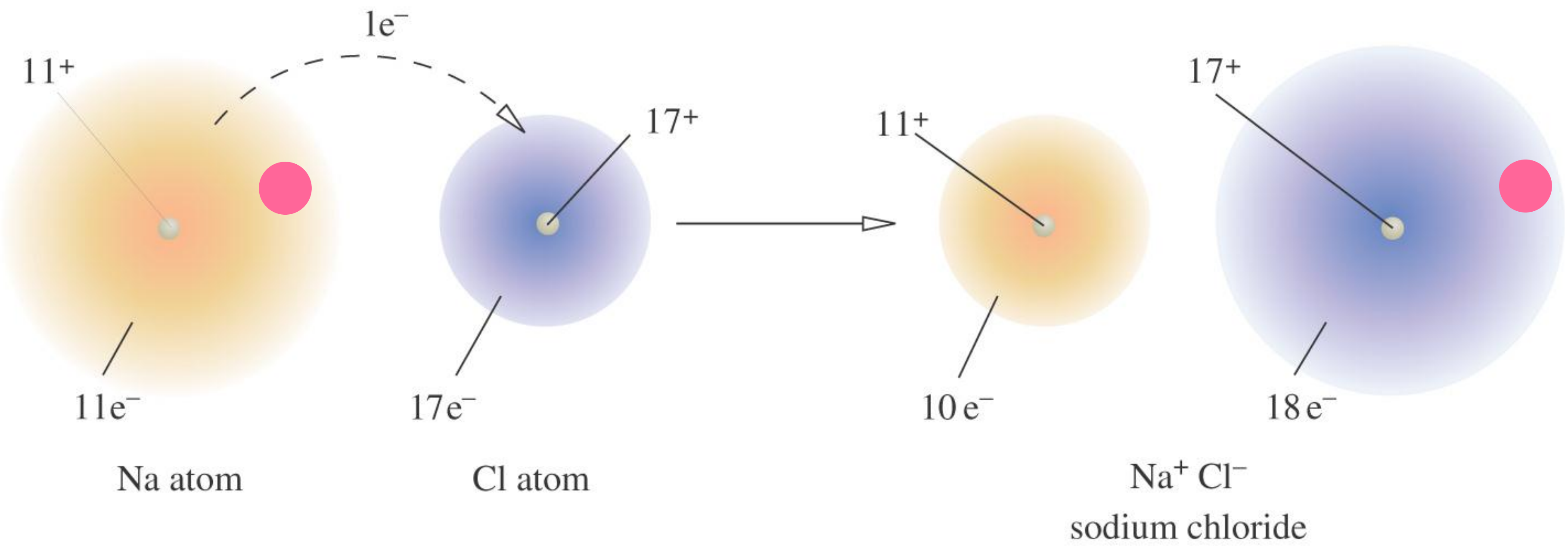
Sodium

- a shiny metal
- very reactive, toxic
- it explodes violently when dropped in water

Poison or Seasoning?

- How can two poisons (Na) and (Cl) combine to form a flavor enhancer (NaCl) that tastes great on steak?

- Answer: By an exchange of electrons that stabilizes both atoms–the formation of a chemical bond



Na 1 valence electron

Cl 7 valence electrons

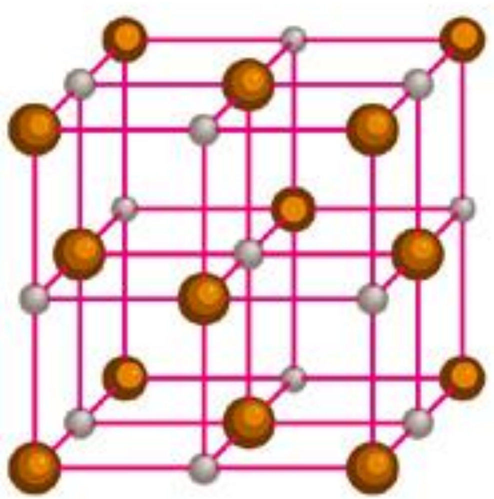
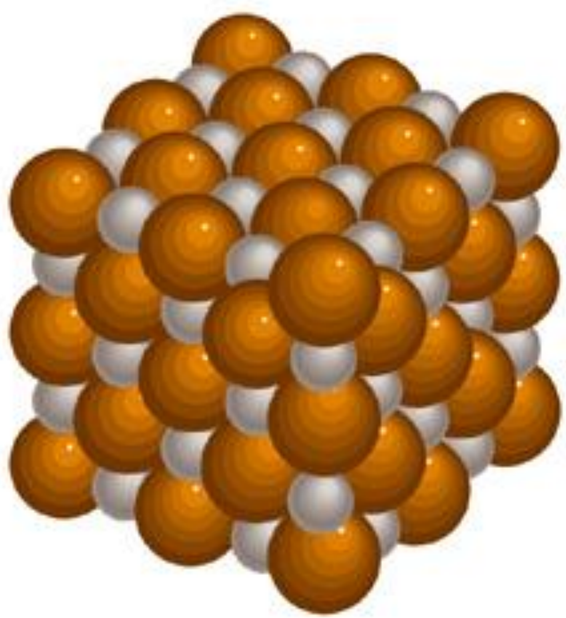
Na transfers electrons to Cl

Both (Na) and (Cl) are stabilized by the exchange

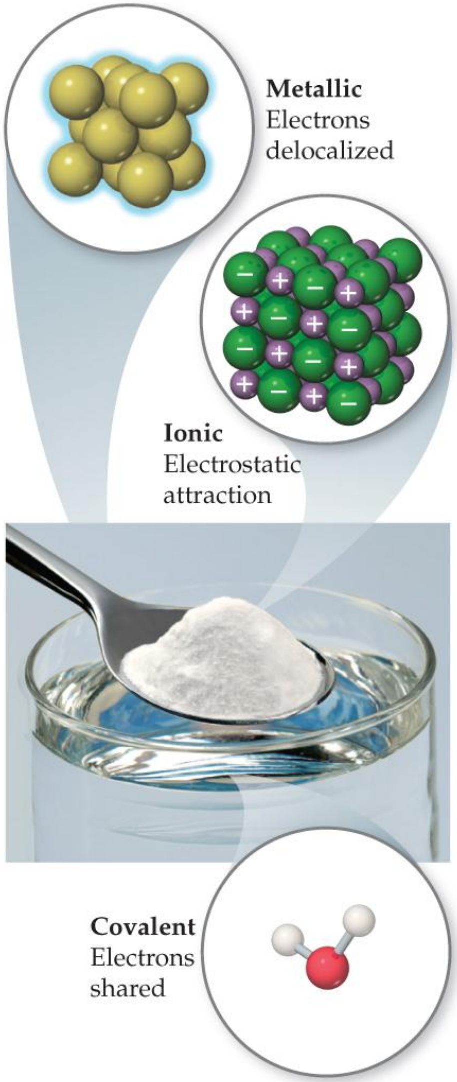
Both (Na^+) and (Cl^-) have full outer Bohr orbits.

Sodium chloride NaCl

The resulting substance (NaCl) is a stable, non toxic compound because both (Na^+) and (Cl^-) have stable electron configurations.

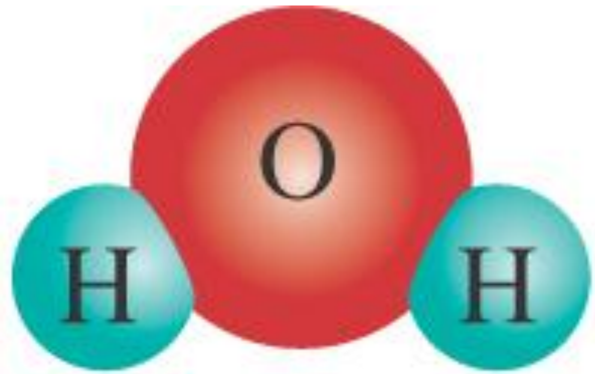




Chemical Bonds

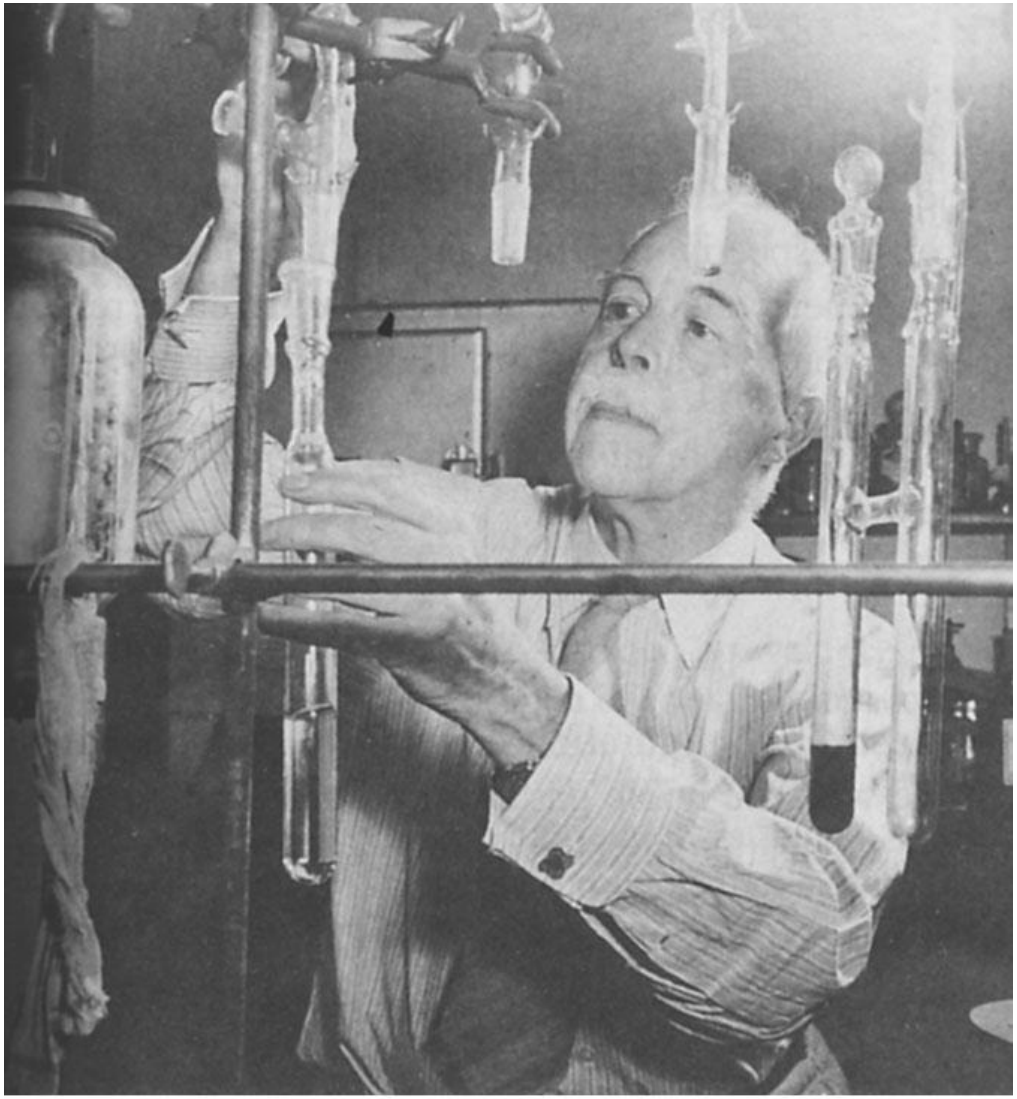


- Three basic types of bonds
  - Ionic
    - Electrostatic attraction between ions.
  - Covalent
    - Sharing of electrons.
  - Metallic
    - Metal atoms bonded to several other atoms.

Why particular elements combine in a particular Proportions?



G. N. Lewis

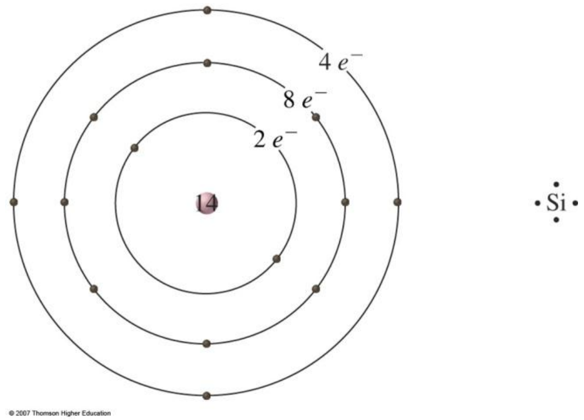


G. N. Lewis and Bonding

- Fundamental ideas:
  - Valence electrons are the most important.
  - Two types:
    - Ionic – valence electrons are transferred
    - Covalent – valence electrons are shared
  - Bond formation results in formation of full Bohr orbits. Because this stable configuration typically involves 8 electrons, this is commonly known as the OCTET rule.

Lewis Dot Structure

- Element symbol surrounded by a number of dots equal to the number of valence electrons.



  – Ignore the inner or CORE electrons.
  – The order in which electrons (dots) are drawn and their exact locations are not critical.

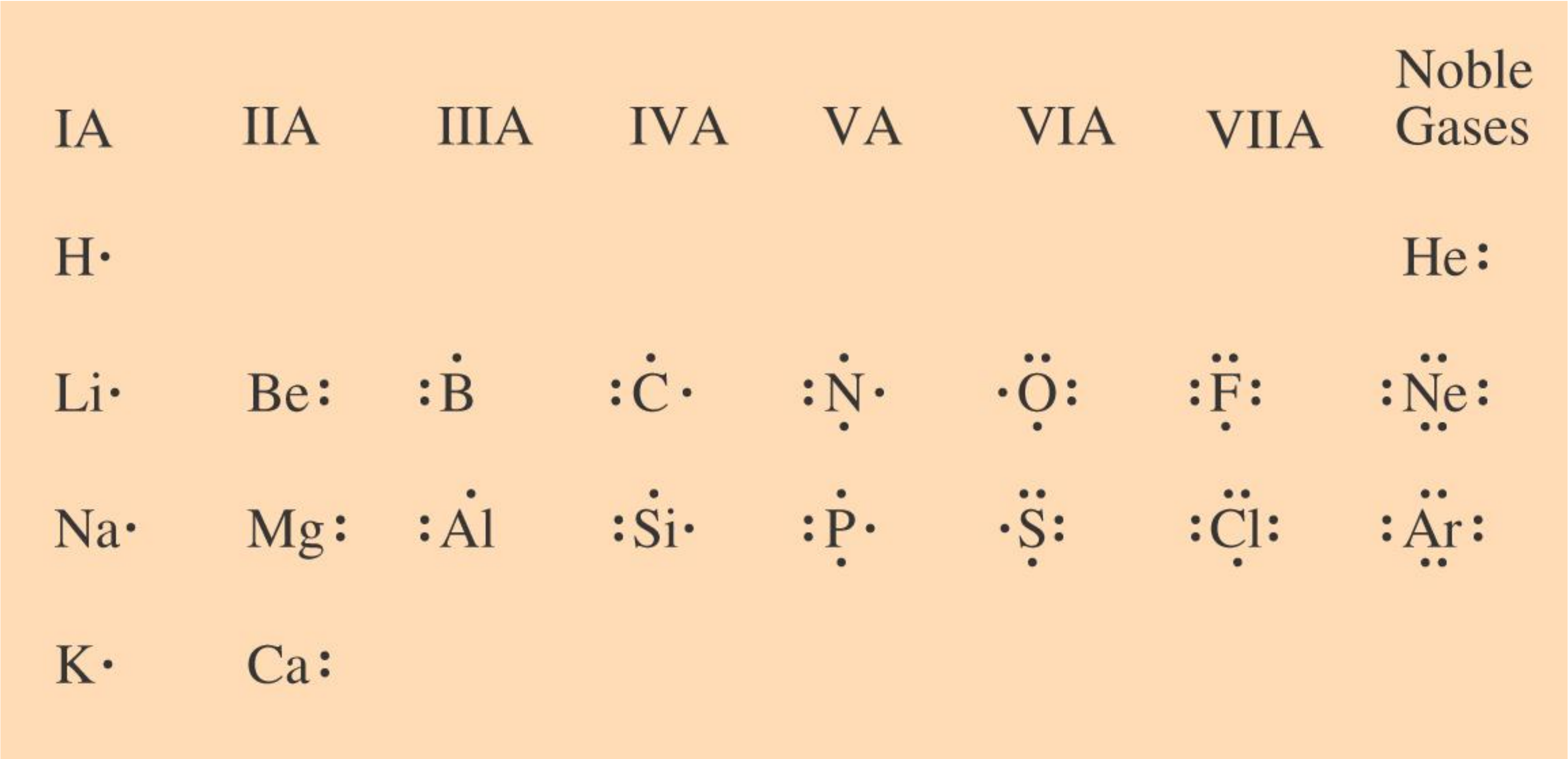
Lewis Symbols

Table 8.1 Lewis Symbols

Group	Element	Electron Configuration	Lewis Symbol	Element	Electron Configuration	Lewis Symbol
1A	Li	$[He]2s^1$	Li·	Na	$[Ne]3s^1$	Na·
2A	Be	$[He]2s^2$	·Be·	Mg	$[Ne]3s^2$	·Mg·
3A	B	$[He]2s^22p^1$	·Ḃ·	Al	$[Ne]3s^23p^1$	·Ȧl·
4A	C	$[He]2s^22p^2$	·Ċ̣·	Si	$[Ne]3s^23p^2$	·Ṩi·
5A	N	$[He]2s^22p^3$	·Ṇ̇:	P	$[Ne]3s^23p^3$	·Ṗ̣:
6A	O	$[He]2s^22p^4$	:Ọ̇:	S	$[Ne]3s^23p^4$	:Ṩ:
7A	F	$[He]2s^22p^5$	·F̤̈:	Cl	$[Ne]3s^23p^5$	·C̤̈l:
8A	Ne	$[He]2s^22p^6$	:N̤̈e:	Ar	$[Ne]3s^23p^6$	:Ä̤r:

- G. N. Lewis developed a method to denote potential bonding electrons by using one dot for every valence electron around the element symbol.
- When forming compounds, atoms tend to gain, lose, or share electrons until they are surrounded by eight valence electrons (the octet rule).

Lewis Dot Structures of the first 20 elements



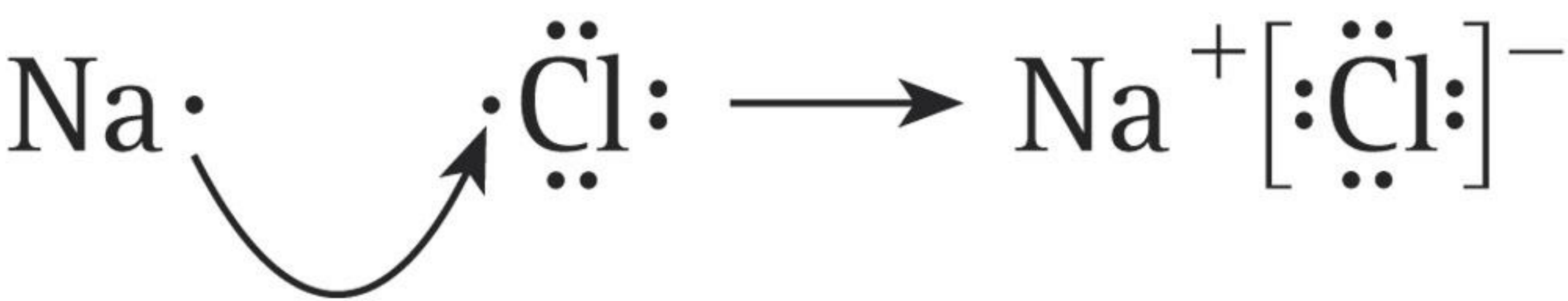
A simple, powerful theory

- According to Lewis theory, chemical bonding brings together elements in the correct ratios so that all of the atoms involved form an octet (8 electrons).

Ionic Lewis Structures

Ionic Lewis Structures

- Since ionic bonding involves the transfer of electrons from a metal to a nonmetal, the Lewis structure for an ionic compound involves moving dots. The metal becomes a cation and the nonmetal becomes an anion.



Charges

- The metal and the nonmetal each acquire a charge in the formation of an ionic bond.
- We indicate the magnitude of the charge in the upper right corner of the symbol.
- We enclose the anion in brackets.
- Charges on anions and cations within an ionic formula sum to zero.

EXAMPLE 5.1

Drawing Lewis Structures for Ionic Compounds

Draw a Lewis structure for MgO.

SOLUTION

The Lewis structures for Mg and O are as follows:

Mg: ·Ö:

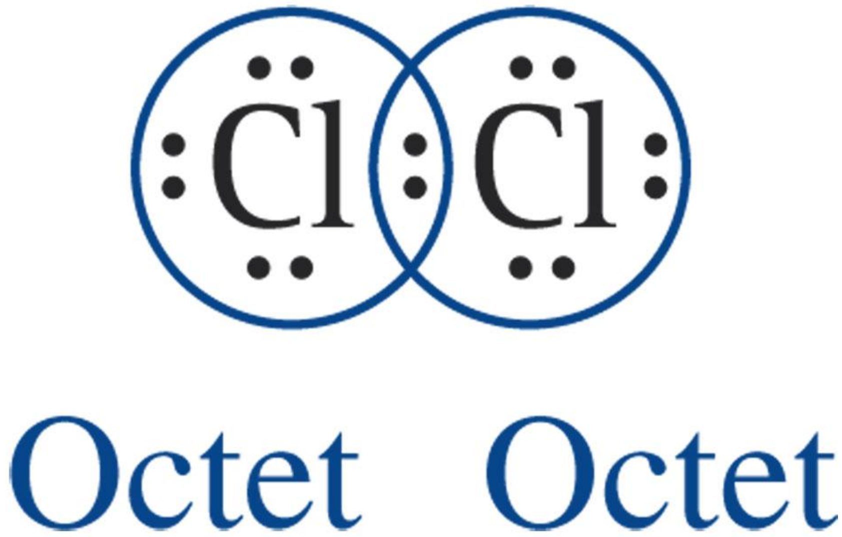
Mg must lose two electrons to form an octet, and O must gain two:

Mg^{2+} $[:\ddot{O}:]^{2-}$

Covalent Lewis Structures

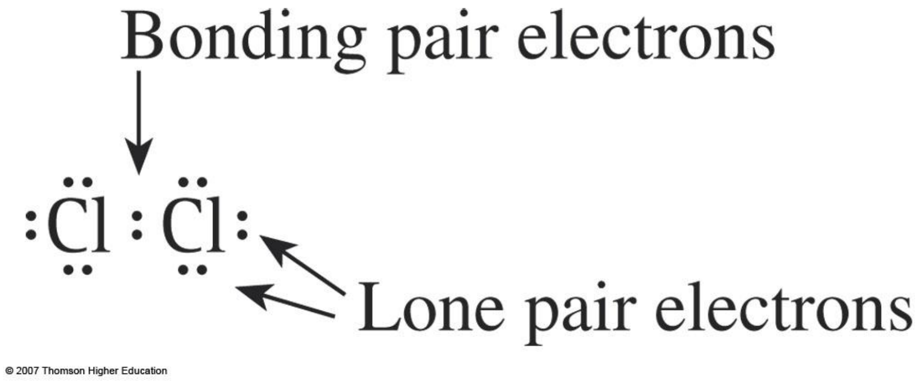
Covalent Lewis Structures

- Since covalent bonds involve the sharing of electrons, covalent Lewis structures contain dots that count for the octet of more than one atom.



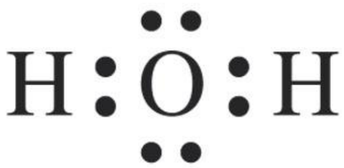
Types of Electron Pairs

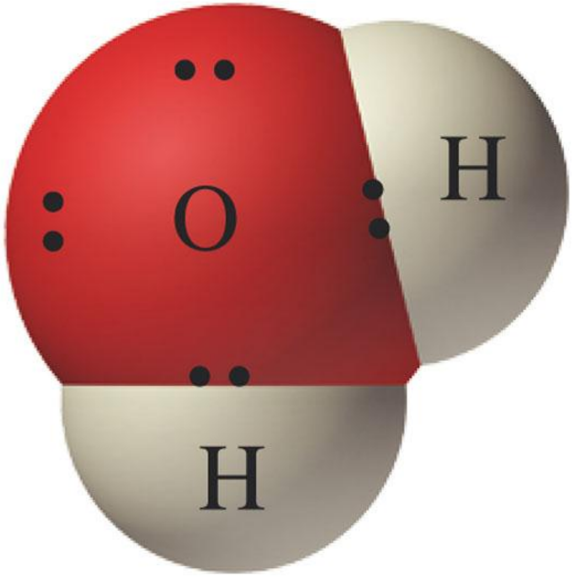
- The electrons between two atoms are called bonding pairs.
- Electrons on a single atom are called lone pairs.



Water

- The Lewis Structure shows a 2:1 ratio of hydrogen to oxygen.
- This corresponds to what is observed in nature.

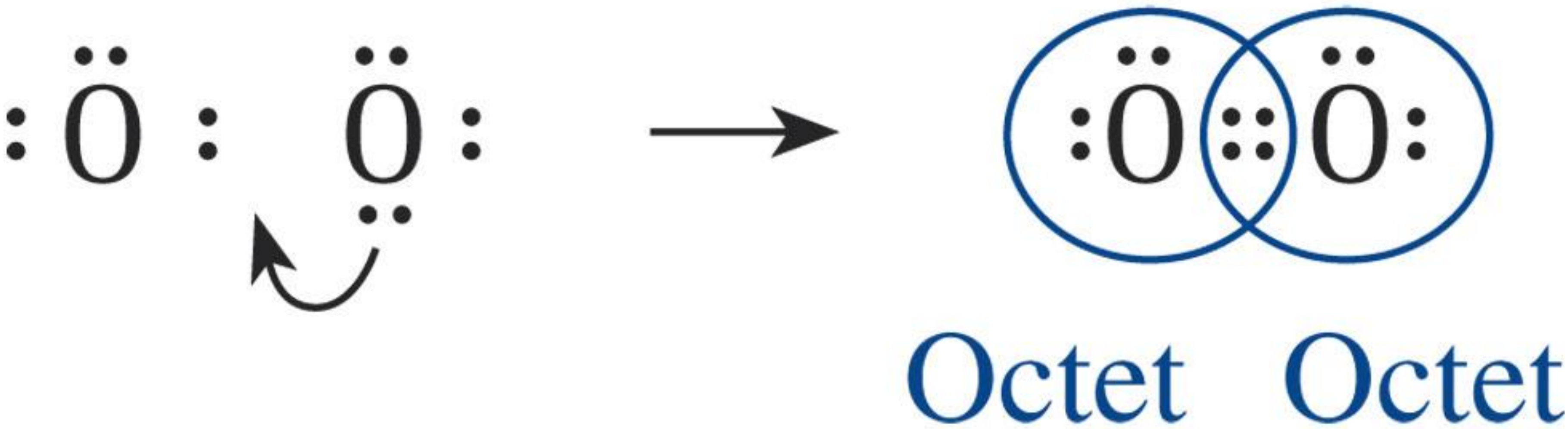


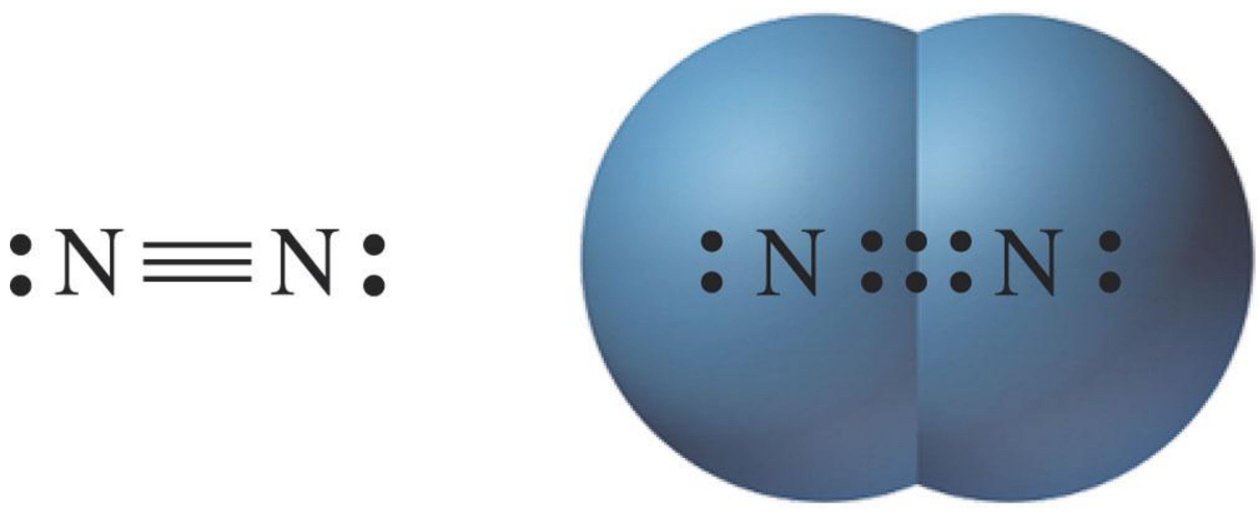


Multiple Bonds

- Sometimes multiple bonding pairs are necessary to complete the octets for each atom in the Lewis structure.
- Two bonding pairs are called a double bond. Three bonding pairs are a triple bond.

Multiple Bonds

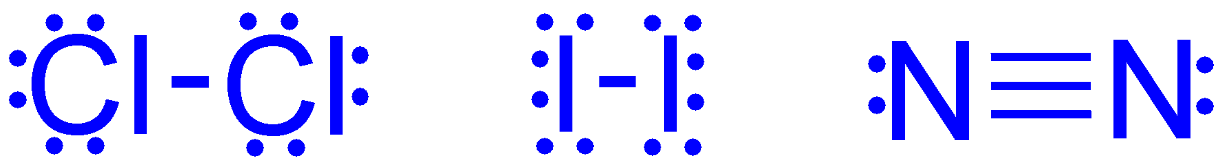




Multiple Bonds

hydrogen chlorine iodine nitrogen

A dash may replace a pair of dots.



Writing Lewis Structures

Writing Lewis Structures

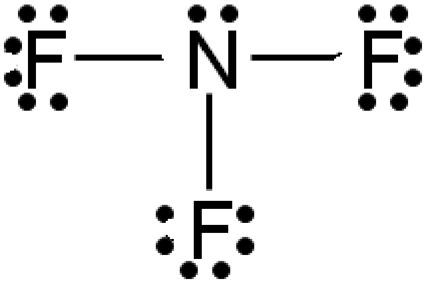
- Although the octet rule and Lewis structures do not present a complete picture of covalent bonding, they do help to explain the bonding scheme in many compounds and account for the properties and reactions of molecules.

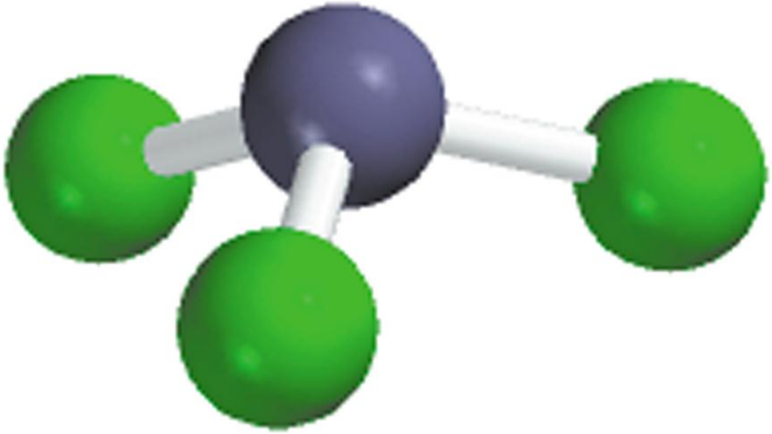
- For this reason, you should practice writing Lewis structures of compounds. The basic steps are as follows:

1. Place the atoms relative to each other. Put least electronegative element (lower group #) in the center. AB_n
2. Count total number of valence e^-. Add 1 for each negative charge. Subtract 1 for each positive charge.
3. Draw a single bond from each surrounding atom to the central atom, Complete an octet for all atoms ***except*** hydrogen
4. If structure contains too many electrons, form double and triple bonds on central atom as needed.

•Write the Lewis structure of nitrogen trifluoride (NF_3).

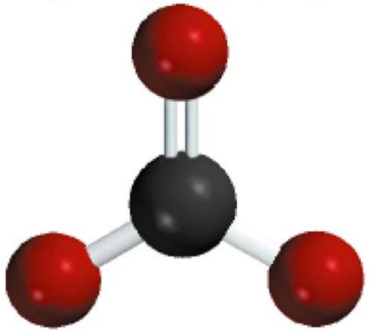
- Step 1 – N is less electronegative than F, put N in center
- Step 2 – Count valence electrons N - 5 ($2s^2 2p^3$) and F - 7 ($2s^2 2p^5$)
  - 5 + (3 x 7) = 26 valence electrons
- Step 3 – Draw single bonds between N and F atoms and complete
- octets on N and F atoms.
- Step 4 - Check, are # of e^- in structure equal to number of valence e^- ?
  - 3 single bonds (3x2) + 10 lone pairs (10x2) = 26 valence electrons





Write the Lewis structure of the carbonate ion (CO_3^{2-}).

- Step 1 – C is less electronegative than O, put C in center
- Step 2 – Count valence electrons C - 4 ($2s^22p^2$) and O - 6 ($2s^22p^4$)
  - -2 charge – $2e^-$
    - 4 + (3 x 6) + 2 = 24 valence electrons
- Step 3 – Draw single bonds between C and O atoms and complete
- octet on C and O atoms.
- Step 4 - Check, are # of e^- in structure equal to number of valence e^- ?
- 3 single bonds (3x2) + 10 lone pairs (10x2) = 26 valence electrons
- Step 5 - Too many electrons, form double bond and re-check # of e^-



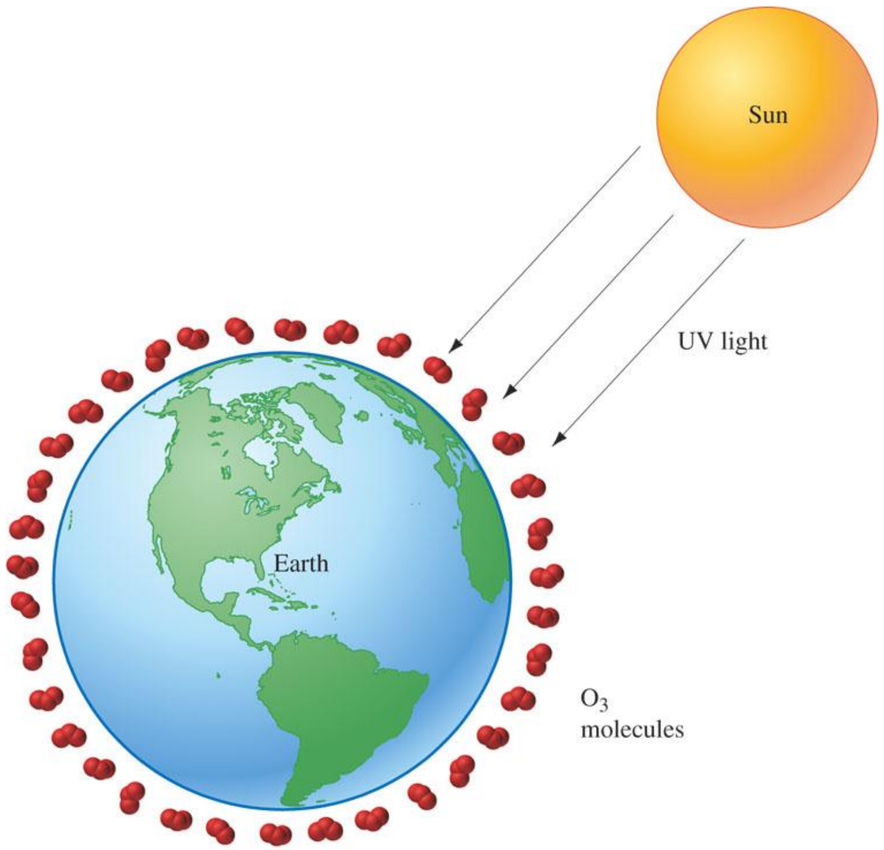
- 2 single bonds (2x2) = 4
- 1 double bond = 4
- 8 lone pairs (8x2) = 16

- Total = 24

- **<u>Solve Examples</u>:** H_2O, CO_2, CN^-, HF, NH_3, N_2, CH_4, CF_4, NO^+

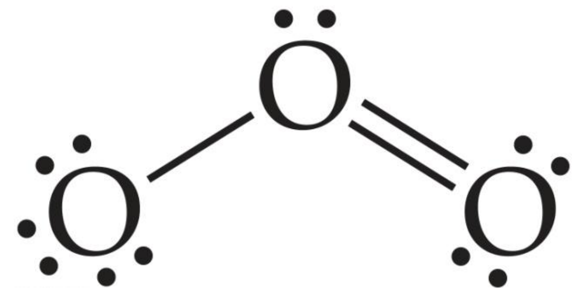
Ozone

- Ozone is an atmospheric gas that protects life on Earth from excessive exposure to UV light.

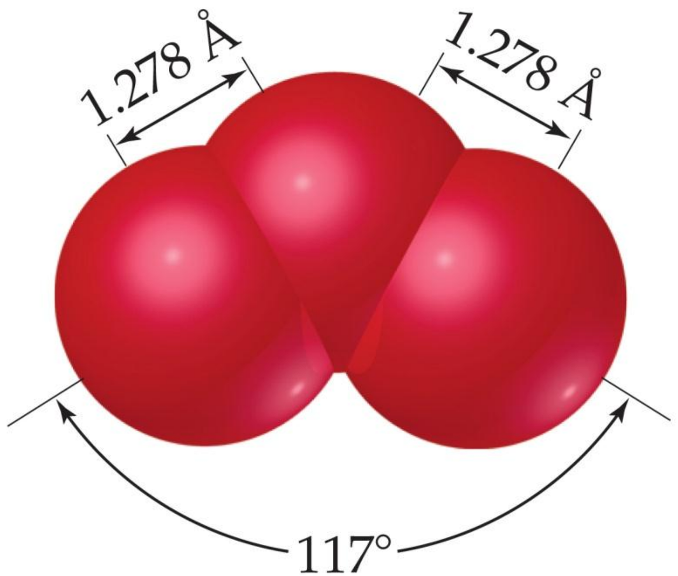


The Best Lewis Structure?

- Following our rules, this is the Lewis structure we would draw for ozone, O_3.

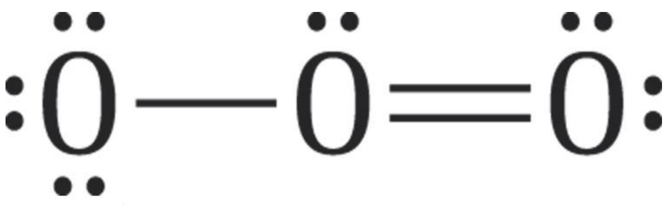


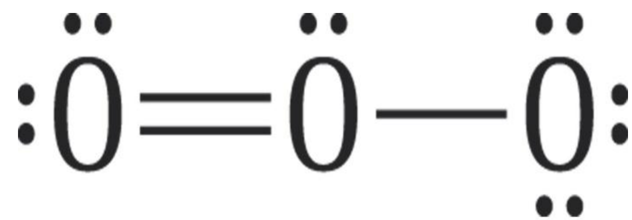
- However, it doesn't agree with what is observed in nature: Both O to O connections are the same.



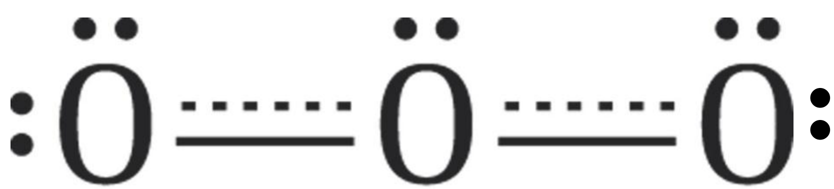
Ozone’s Lewis Structure

- There appear to be two equally valid Lewis structures.



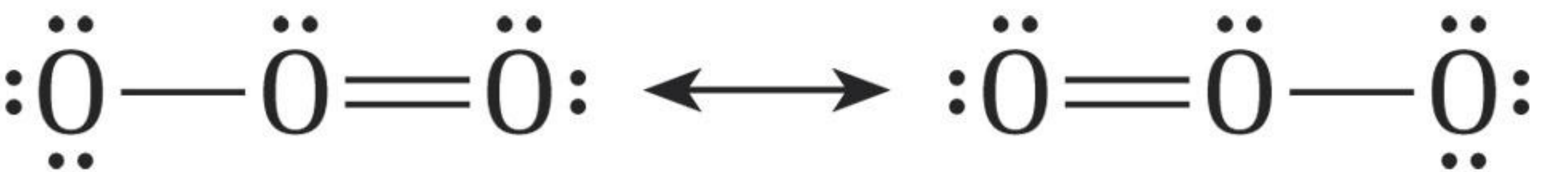


- The ozone molecule is actually best represented with two identical bonds, each one shorter than a single bond, but longer than a double bond.



Resonance Structures

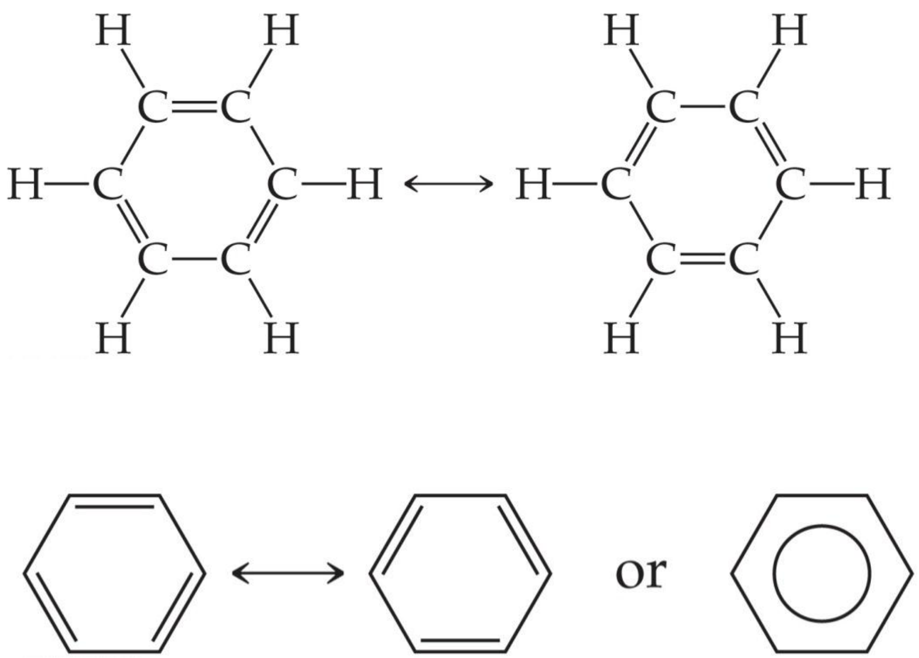
- Resonance is the averaging of two identical Lewis structures.
- Resonance structures are usually represented with a double-centered arrow between them.



Oxygen vs. Ozone

- Molecular oxygen’s double bond is stronger than ozone’s “bond and a half.”
- UV light is not energetic enough to break oxygen’s strong bond.
  - Oxygen does not *absorb* UV light.
- UV light will break one of ozone’s two bonds.
  - Ozone *absorbs* UV light.

Resonance



- The organic compound benzene, C_6H_6, has two resonance structures.
- It is commonly depicted as a hexagon with a circle inside to signify the delocalized electrons in the ring.

•*Localized* electrons are specifically on one atom or shared between two atoms; *Delocalized* electrons are shared by multiple atoms.

Formal charge

Formal charges can be used to help in the assessment of resonance structures and molecular topology

It can help in assigning bonding when there are several possibilities

N.B.: *Formal charge is only a tool for assessing Lewis structures, not a measure of any actual charge on the atoms*

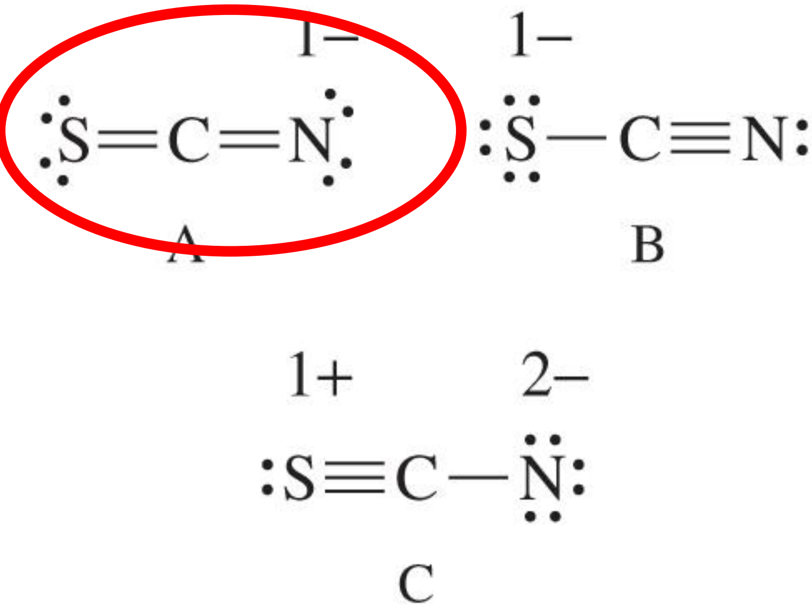
Formal charge is the apparent electronic charge of each atom in a molecule, based on the electron-dot structure

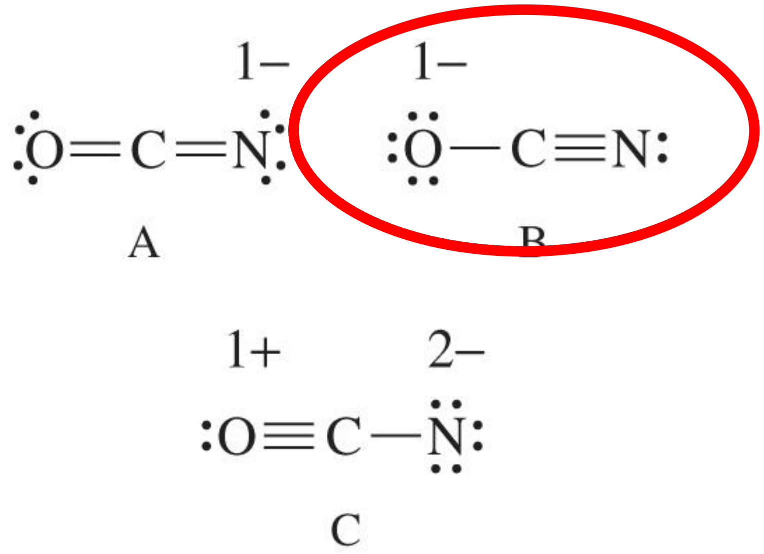
Formal Charge **=** *No. of valence electrons in a free atom of the element* **-** *No. of unshared electrons on the atom* **-** *No. of bonds to the atom*

Formal charge and Lewis dot structure

Resonance structures that contribute more to the electronic ground state :

- Have smaller magnitudes of formal charges
- Place negative formal charges on more electronegative elements
- Have smaller separation of charges



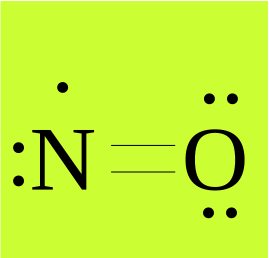


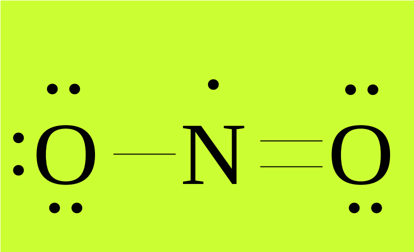
Exceptions to the Octet Rule

- There are three types of ions or molecules that do not follow the octet rule:
  - ions or molecules with an odd number of electrons,
  - ions or molecules with less than an octet,
  - ions or molecules with more than eight valence electrons (an expanded octet).

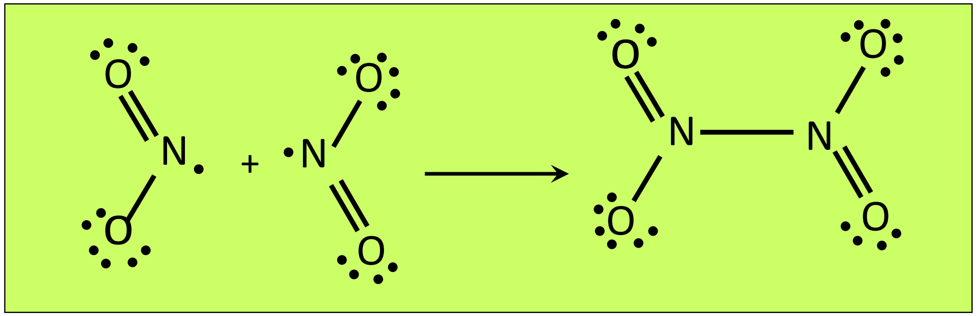
Odd e- molecules (Free radicals)

- These molecules have uneven numbers of electrons therefore no way that they can form octets.
- Examples: NO and NO_2. These species have an odd number of electrons.





- NO_2 (present in smog from photochemical reaction of NO with O_3).
- Radicals react to form dimeric N_2O_4 $^{-}$ obeys Octet rule.

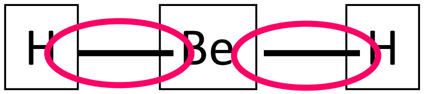


Exceptions to the Octet Rule

- Be compounds $\Rightarrow$ BeH_2, $BeCl_2$

BeH_2

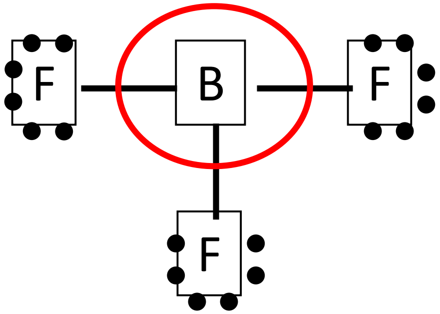
$$\begin{array}{l} Be - 2e^- \\ 2H - 2\times1e^- \\ \hline \quad 4e^- \end{array}$$



- Boron and Al compounds $\Rightarrow$ BF_3, $AlCl_3$, BCl_3

BF_3

$$\begin{array}{l} B - 3e^- \\ 3F - 3\times7e^- \\ \hline \quad 24e^- \end{array}$$



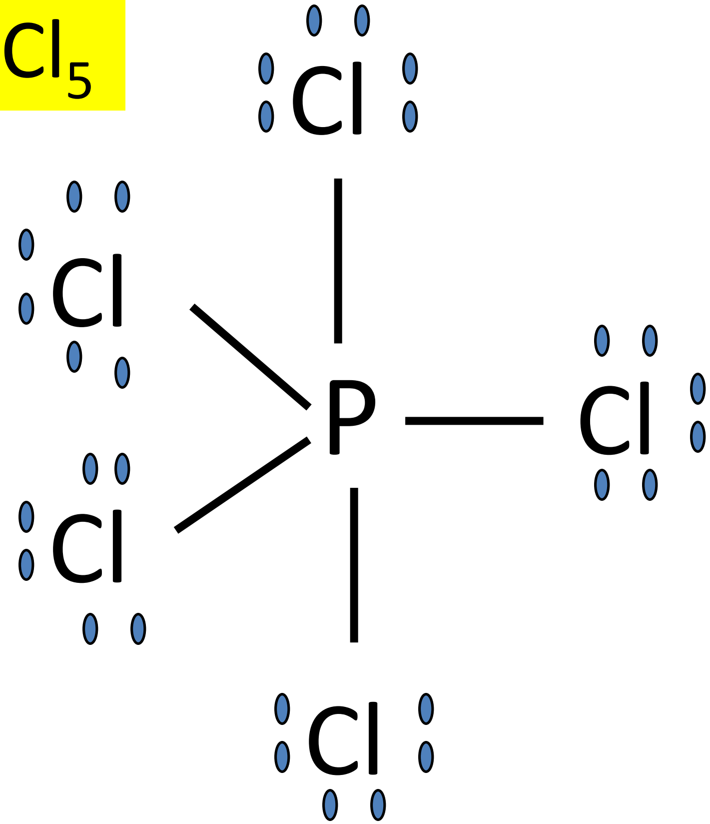
3 single bonds (3x2) = 6

9 lone pairs (9x2) = 18

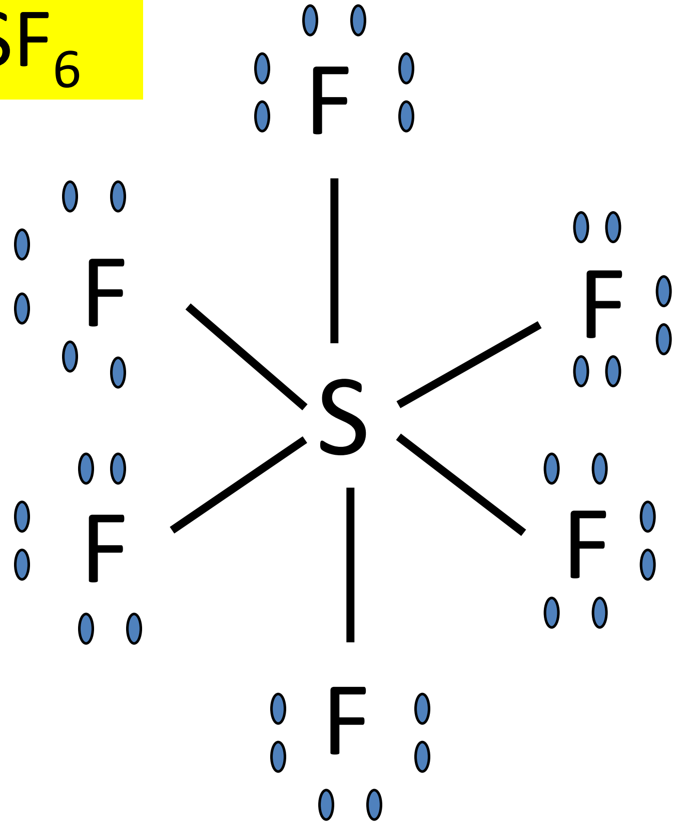
Total = 24

Exceptions to the Octet Rule

PCl_5



SF_6



P = 5

<u>Cl = 5 x 7</u>

40 valence electrons

10 ve on P

S = 6

<u>F = 6 x 7</u>

48 valence electrons

12 ve on S

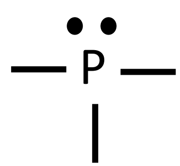
Exceptions to the Octet Rule

"An exception to the Octet Rule occurs for Expanded valence shells…."

– Occurs because of atoms with vacant d-orbitals can expand their valence shells to form > 4 bonds (lowers energy), i.e for non-metals from P onwards.

– P is $3s^2\ 3p^3\ 3d^0$

– If we treat it just as $3s^2\ 3p^3$, then must apply Octet rule, ie.



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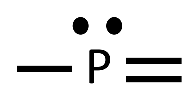
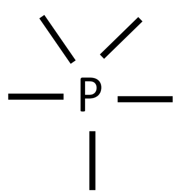


- But if we consider it as $3s^2\ 3p^3\ 3d^0$, then there is room to accommodate extra bonding pairs, ie. Up to 5 bonding pairs



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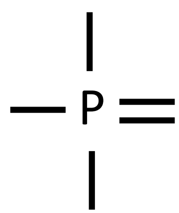

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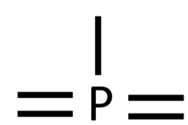


The Shapes of Molecules

- Molecular shape is an important factor in determining the properties of substances.

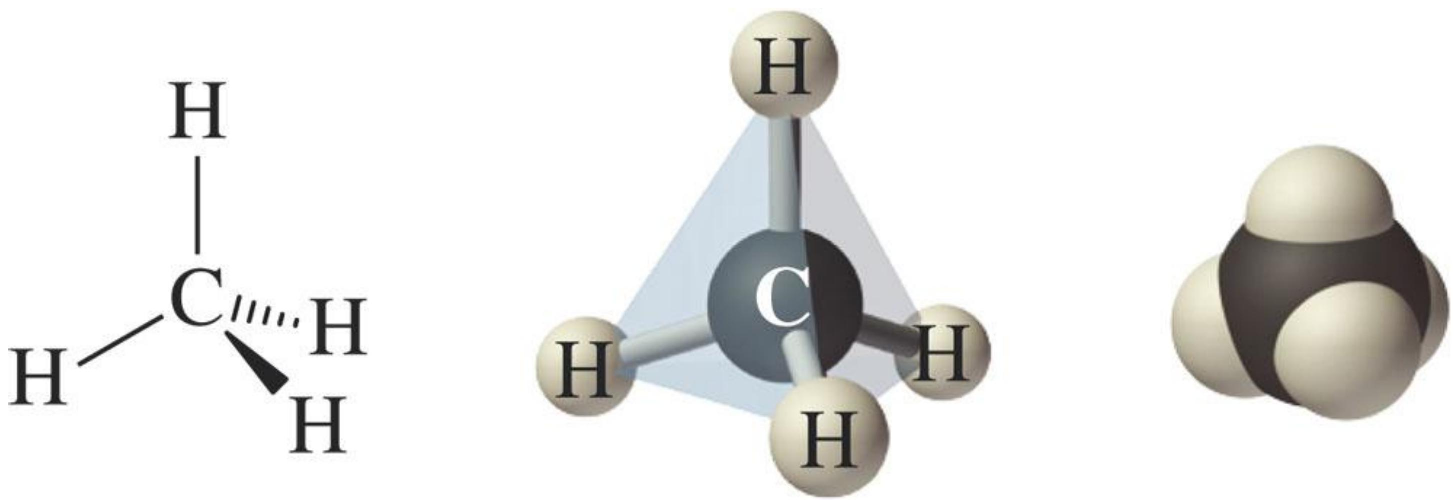
- Valence shell electron pair repulsion theory (VSEPR theory) allows us to predict molecule shapes from their Lewis structures.

VSEPR Theory

- Is based on the idea that the negative charges of bonding electrons and lon pairs electrons in a molecule repel each other.
- The molecular shape is determined by the position of the atoms in the molecule.

The Ideal Shape

- The three-dimensional geometry that puts the greatest angle (minimum repulsions, maximum distance) between four bonding electron pairs on a central atom is *tetrahedral*.



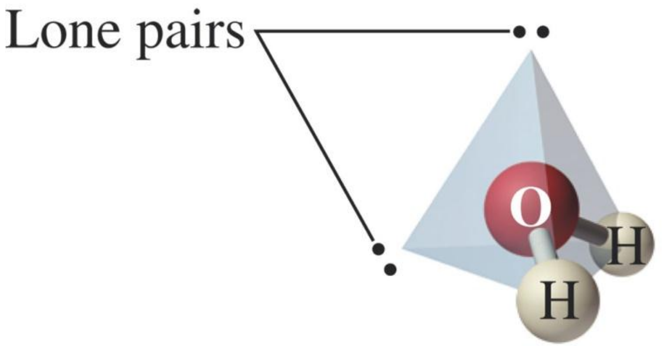
Two types of geometry

- The combination of lone pairs and multiple bonds with bonded pairs makes possible other geometries.

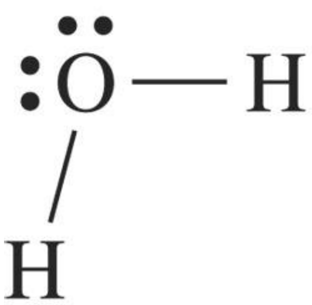
- Important to distinguish between electron geometry and molecular geometry

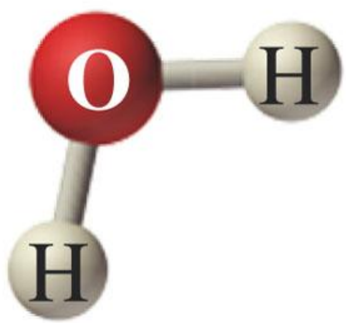
Water

- Electron geometry is tetrahedral.

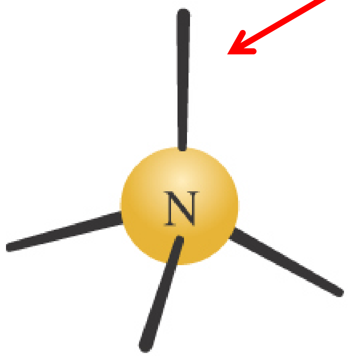


- Molecular geometry is bent.

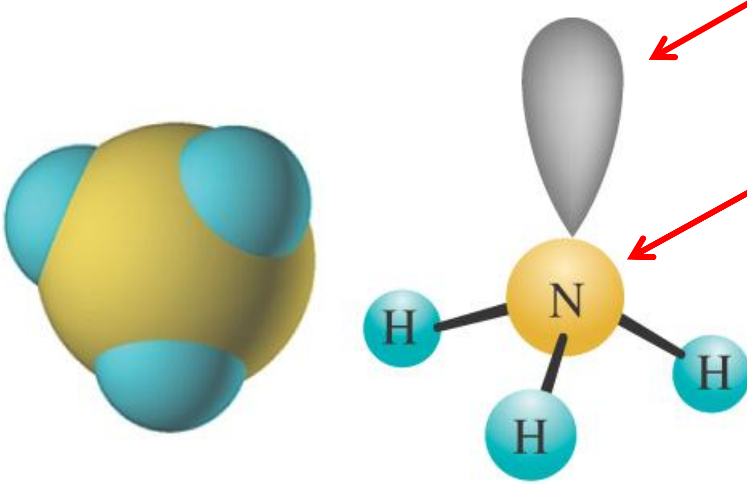




- Ammonia, NH_3, has four electron pairs around nitrogen.



The arrangement of electron pairs around nitrogen is tetrahedral.



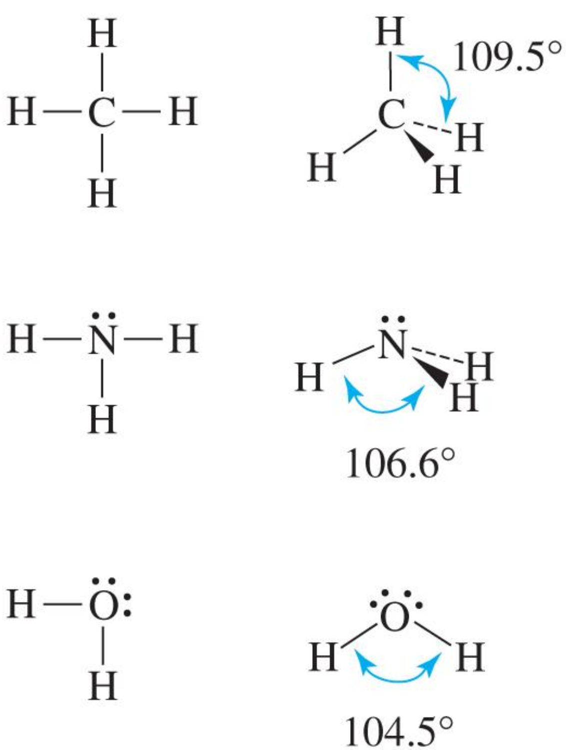
NH_3 has one unbonded pair of electrons.

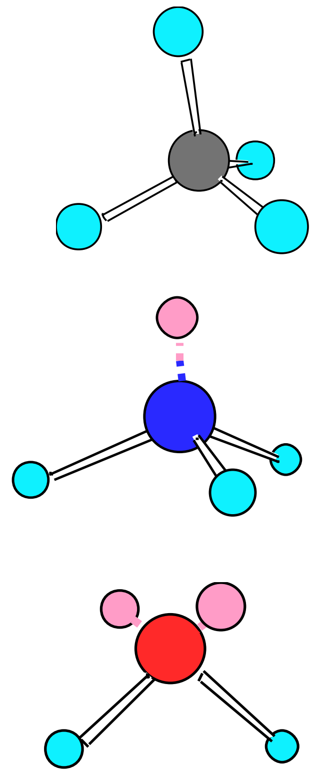
cule

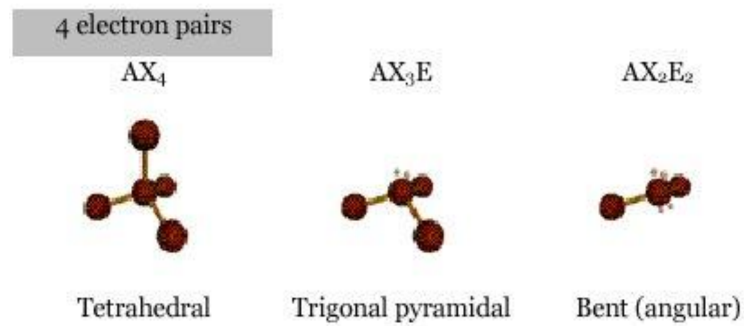
is pyramidal.

Lone pair repulsion

The isoelectronic molecules CH_4, NH_3, and H_2O illustrate the effect of lone pairs on molecular shape







Predicting Molecular Geometry

1. Draw Lewis structure for the molecule.
2. Count number of lone pairs and bonding pairs on the central atom
3. Use VSEPR to predict the geometry of the molecule.

A double or triple bond acts exactly like a single bond in determining molecular geometry

VSEPR Theory

- **Valence Shell Electron Pair Repulsion** theory provides a method for predicting the shape of molecules, based on the electron pair electrostatic repulsion

- This method predicts shapes that compare favorably with those determined experimentally

- Electrons repel each other because they are negatively charged. The quantum mechanical rules force some of them to be fairly close to each other in bonding pairs or lone pairs, but each pair repels all other pairs

- *According to the VSEPR model, molecules adopt geometries in which their valence electron pairs position themselves as far from each other as possible*

- A molecule can be described by the generic formula $\mathbf{AX_mE_n}$

  A: the central atom

  X: stands for any atom or group of atoms surrounding A

  E: lone pair of electrons

  SN=m + n: number of positions occupied by atoms or lone pairs around A

VSEPR Theory

Number of Objects	2	3	4	5	6
Electron Geometry	linear	trigonal planar	tetrahedral	trigonal bipyramidal	Octahedral
Formula (Shape/Molecular Geometry)	AX_2	AX_3 (trig. planar) AX_2E (bent)	AX_4 (tetrahedral) AX_3E (pyramidal) AX_2E_2 (bent)	AX_5 (t.b.p.) AX_4E (seesaw) AX_3E_2 (T-shaped) AX_2E_3 (linear)	AX_6 (octahedral) AX_5E (square pyramidal) AX_4E_2 (square planar) AX_3E_3 (T-shaped)

VSEPR Theory

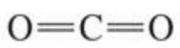
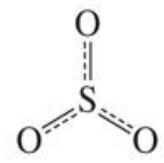
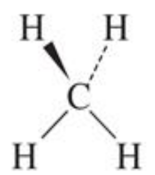
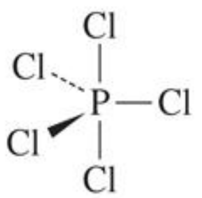
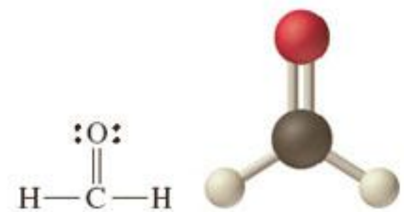
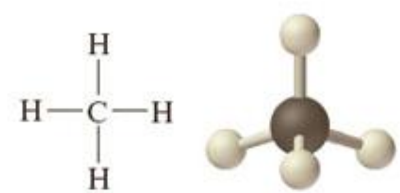
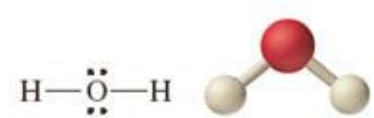
Steric Number	Geometry	Examples	Calculated Bond Angles	
2	Linear	CO_2	180°	
3	Trigonal (triangular)	SO_3	120°	
4	Tetrahedral	CH_4	109.5°	
5	Trigonal bipyramidal	PCl_5	120°, 90°	
6	Octahedral	SF_6	90°	

TABLE 1

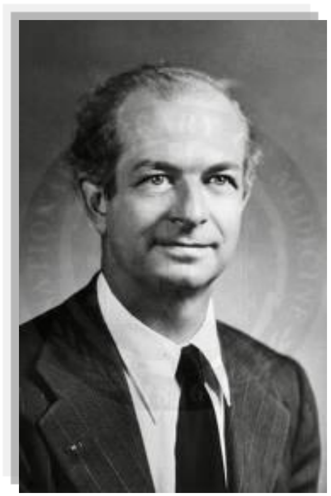
VSEPR Geometries

Total Electron Groups	Bonding Groups	Lone Pairs	Electron Geometry	Molecular Geometry	Example
2	2	0	Linear	Linear	
3	3	0	Trigonal planar	Trigonal planar	
3	2	1	Trigonal planar	Bent	
4	4	0	Tetrahedral	Tetrahedral	
4	4	1	Tetrahedral	Pyramidal	
4	2	2	Tetrahedral	Bent	

Electronegativity

The different affinities of atoms for the electrons in a bond are described by a property called **electronegativity**.

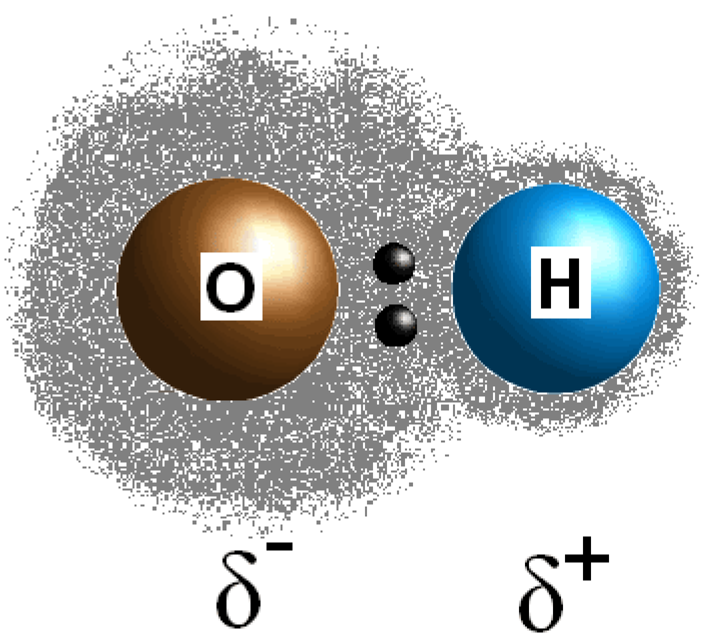
Electronegativity is the ability of atom in a molecule to attract shared electrons to itself.



Linus Pauling

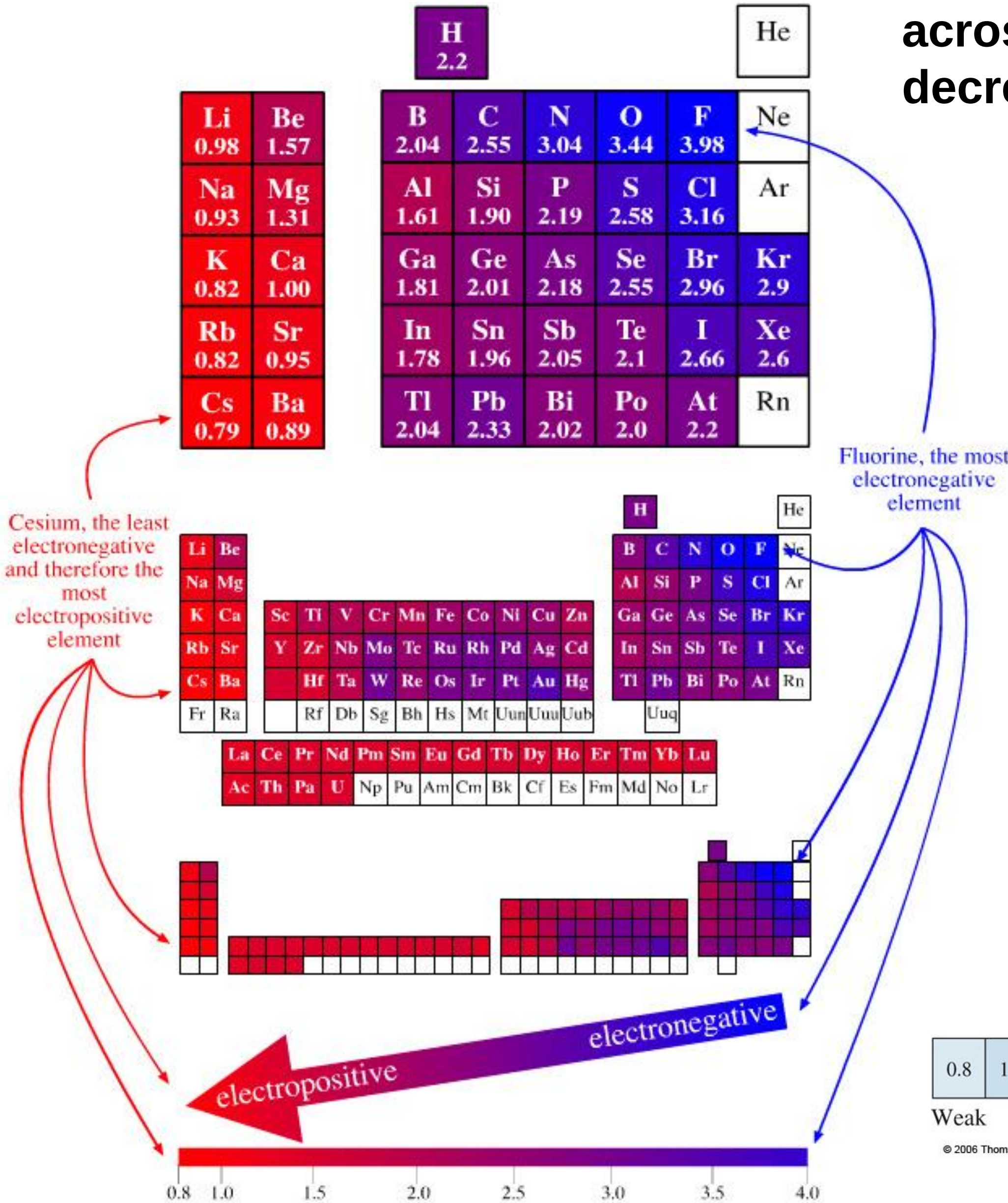
(1901 – 1994)

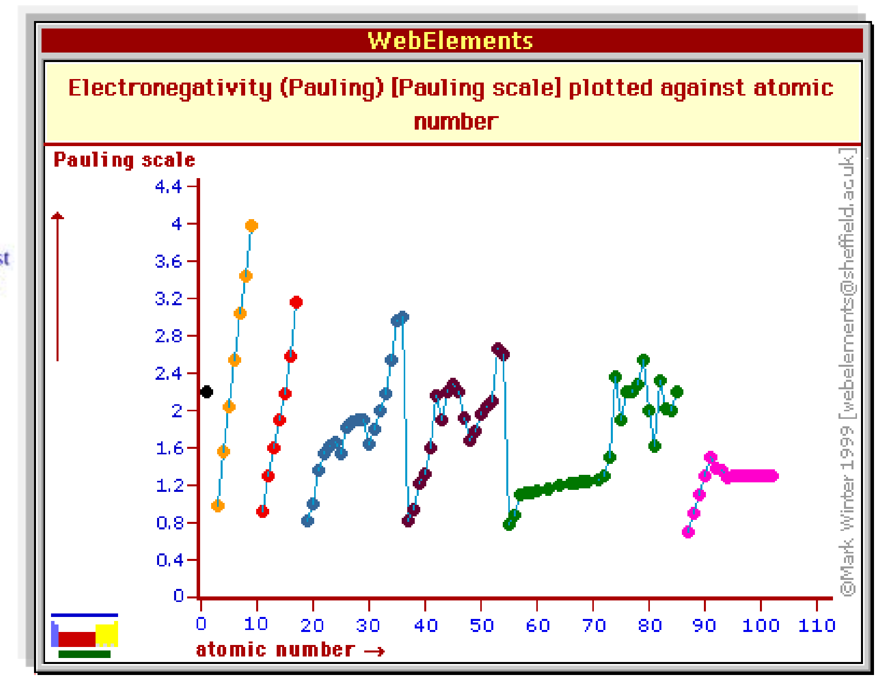
Nobel Prize in Chemistry 1954

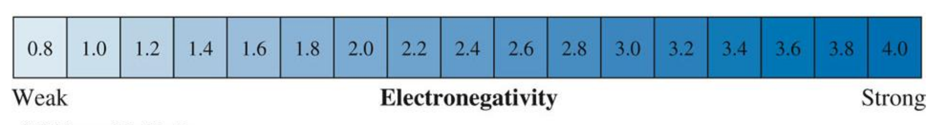


Electronegativity & Periodicity

Electronegativity increases as you move right across a row on the periodic table and decreases as you move down a column.

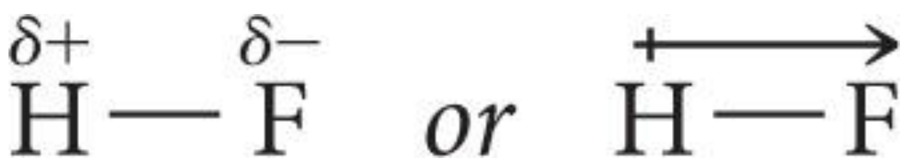






Electronegativity and Polar Covalent Bonds

- When two atoms share electrons unequally, a **polar covalent bond** results.
- Electrons tend to spend more time around the more electronegative atom. The result is a partial negative charge (*not* a complete transfer of charge). It is represented by δ–.
- The other atom is “more positive,” or δ+.

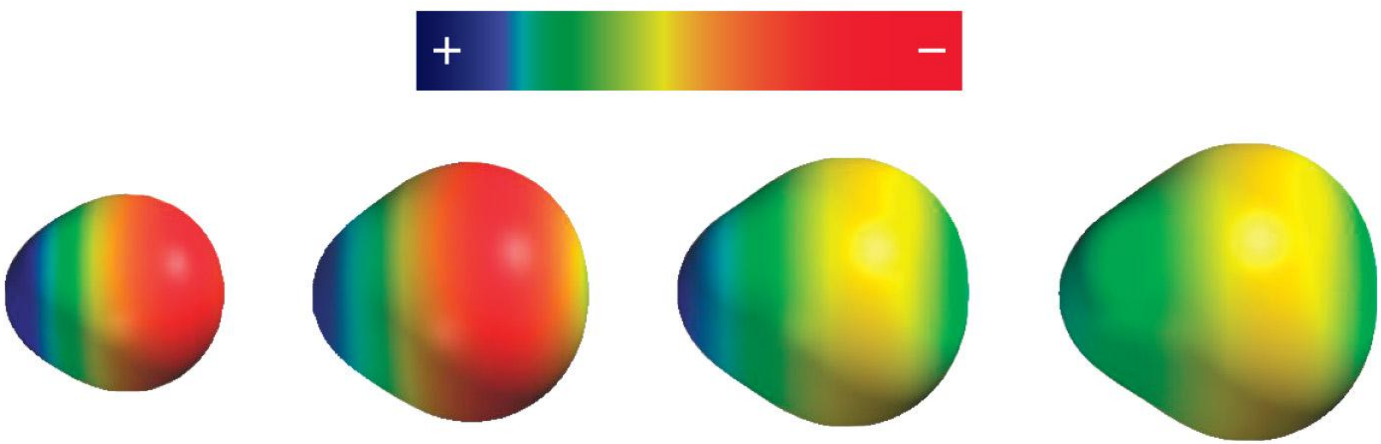


Polar Covalent Bonds

Table 8.3 Bond Lengths, Electronegativity Differences, and Dipole Moments of the Hydrogen Halides

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

The greater the difference in electronegativity, the more polar is the bond.



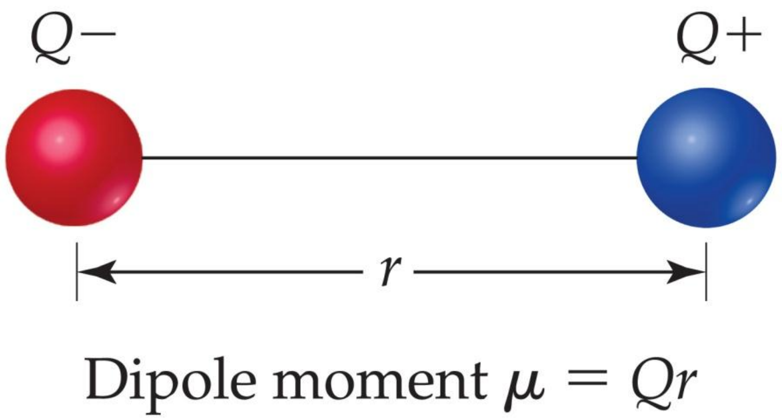
HF HCl HBr HI

Dipoles

- When two equal, but opposite, charges are separated by a distance, a **dipole** forms.
- A **dipole moment**, μ, produced by two equal but opposite charges separated by a distance, *r*, is calculated:

$$\mu = Qr$$

- It is measured in debyes (D).



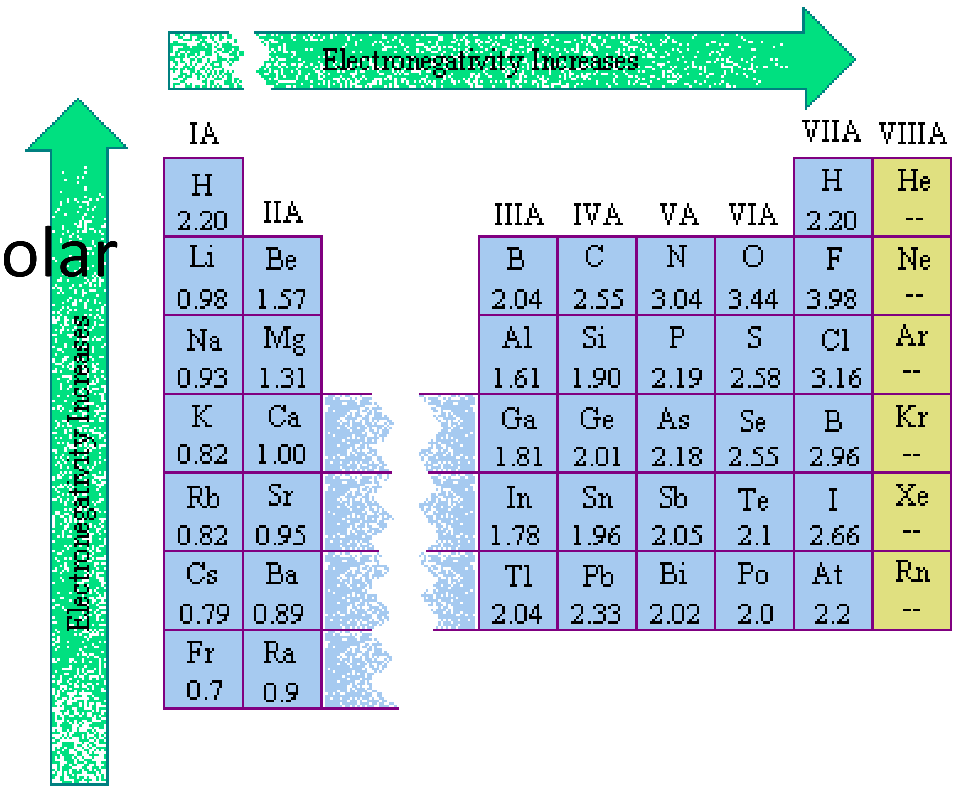
Electronegativity & Bond Polarity

- Polar bonds arise whenever elements with different electronegativity form a bond.

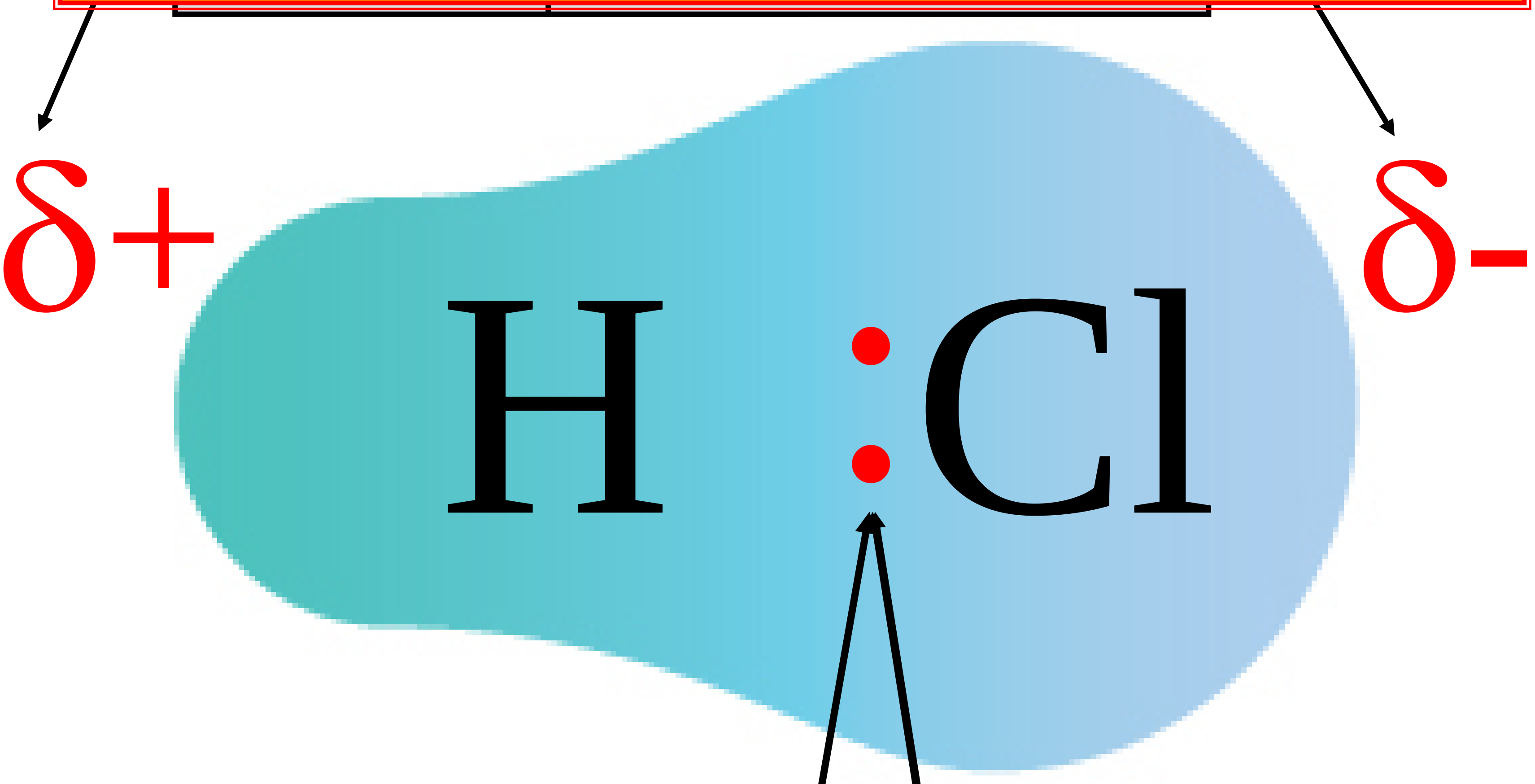
•The ionic character, must be related to the difference in the electronegativities of A and B. Pauling calculated this difference as follows:

•Electronegativities of A & B

- $X_A - X_B < 0.5$ → • Slightly Polar
- $0.5 < X_A - X_B < 2$ → •Polar
- $X_A - X_B > 2$ → •Ionic



Polar Covalent Bonding in HCl



The attractive force that an atom has for shared electrons is known as its **electronegativity**.

A Magnet Analogy

- A polar bond is analogous to a bar magnet; its uneven electron distribution results in a negative pole and a positive pole.
- Similarly, an entire molecule may be polar if uneven electron distribution within the molecule results in a negative pole and a positive pole.

Polar or Nonpolar Molecule?

- Look at the Lewis structure and ask two questions.
  - Does the molecule contain polar bonds?
  - Do the polar bonds together give overall polarity to the molecule?

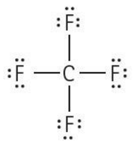
EXAMPLE 5.10

Determining If a Molecule Is Polar

Is CF_4 a polar molecule?

SOLUTION

Here is the Lewis structure for CF_4:



Because carbon and fluorine have different electronegativities, the bonds are polar. VSEPR theory predicts that CF_4 is tetrahedral. If we think of each bond as an arrow, then the four equal arrows in a tetrahedral arrangement cancel as shown in Table 2. Consequently, the molecule is nonpolar.

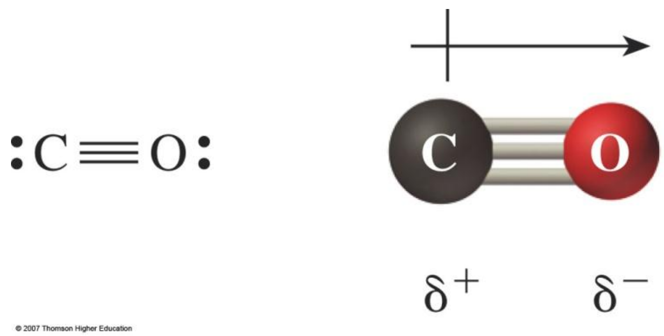
YOUR TURN

Determining If a Molecule Is Polar

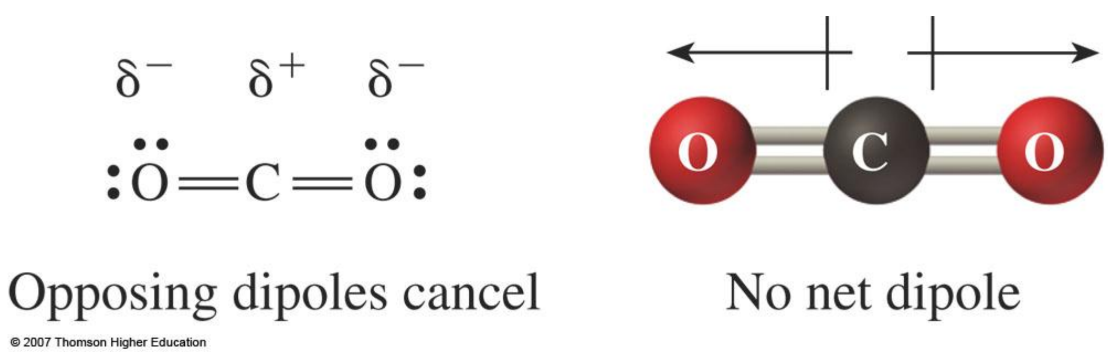
Is H_2S polar or nonpolar?

Examples

- Carbon monoxide, CO, is a polar molecule.



- Carbon dioxide, CO_2, contains polar bonds but is a nonpolar molecule. CO_2 is linear (VSEPR) so the polar bonds *cancel* each other.



Symmetry

- In general, polar bonds result in polar molecules unless the symmetry of the molecule is such that the bonds cancel each other.

- Polar molecules contain asymmeterically distributed centers of charge.

TABLE 2

Common Molecular Geometries and Their Resulting Polarities

Nonpolar

Linear

Two identical polar bonds pointing in opposite directions cancel. The molecule is nonpolar.

Polar

Bent

Two polar bonds at an angle of less than 180° between them will not cancel. The molecule is polar.

Nonpolar

Trigonal planar

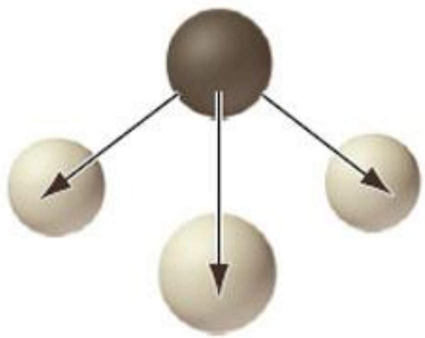
Three identical polar bonds at 120° from each other will cancel. The molecule is nonpolar.

Nonpolar

Tetrahedral

Four identical polar bonds in a tetrahedral arrangement will cancel. The molecule is nonpolar.

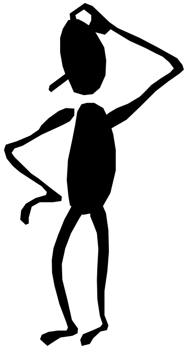
Polar



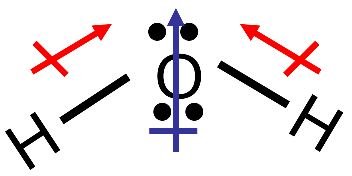
Pyramidal

Three polar bonds in pyramidal arrangement will not cancel. The molecule is polar.

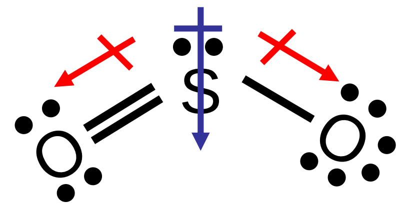
In all cases where the bonds cancel, they are assumed to be identical bonds (i.e., between the same two elements). If the bonds are not identical, they most likely do not cancel, and the molecule will be polar.



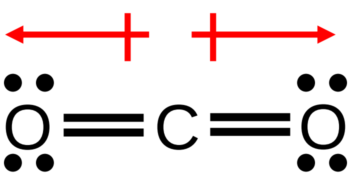
Which of the following molecules is polar?
H_2O, CO_2, SO_2, and CH_4



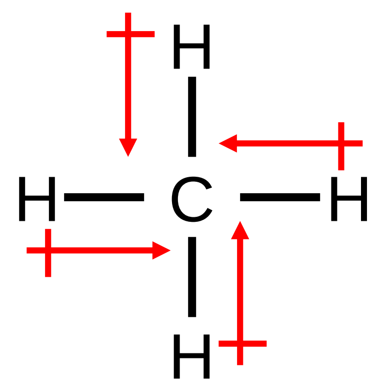
dipole moment
polar molecule



dipole moment
polar molecule



no dipole moment
nonpolar molecule



no dipole moment
nonpolar molecule