Chapter 10

Chemical Bonding

Why is it important to understand Bonding Example: HIV-Protease

- HIV-protease is a protein synthesized by the human immunodeficiency virus (HIV).
- This particular protein is crucial to the virus's ability to multiply and cause AIDS
- Pharmaceutical companies designed molecules that would disable HIV-protease by sticking to the molecule's active site – ***protease inhibitors***
- To design such a molecule, researchers used ***bonding theories*** *to simulate* the shape of potential drug molecules and how they would interact with the protease molecule

Why is it important to understand Bonding

Example: Taste

- The taste of a food depends on the interaction between the food molecules and taste cells on your tongue
- The main factors that affect this interaction are the shape of the molecule and charge distribution within the molecule
- The food molecule must fit snugly into the active site of specialized proteins on the surface of taste cells
- When this happens, changes in the protein structure cause a nerve signal to transmit

Sugar & Artificial Sweeteners

- Sugar molecules fit into the active site of taste cell receptors called Tlr3 receptor proteins
- When the sugar molecule (the key) enters the active site (the lock), the different subunits of the T1r3 protein split apart
- This split causes ion channels in the cell membrane to open, resulting in nerve signal transmission
- Artificial sweeteners also fit into the Tlr3 receptor, sometimes binding to it even stronger than sugar
  - making them “sweeter” than sugar

Structure Determines Properties

- Properties of molecular substances depend on the structure of the molecule
- The structure includes many factors, such as:
  - the skeletal arrangement of the atoms
  - the kind of bonding between the atoms
    - ionic, polar covalent, or covalent
  - the shape of the molecule
- Bonding theory should allow you to predict the shapes of molecules

Bonding Theories

- Explain how and why atoms attach together to form molecules
- Explain why some combinations of atoms are stable and others are not
  - why is water H_2O, not HO or H_3O
- Can be used to predict the shapes of molecules
- Can be used to predict the chemical and physical properties of compounds

- What is meant by “chemical bond”?
- Why do atoms bond with each other to form compounds?
- How do atoms bond with each other to form compounds?

What is a “Chemical Bond”?

A “strong” attractive force between atoms

How strong is “strong”?

- Strong enough to not break when the “bonded” atoms move away from each other due to thermal motion
- Strong enough to not break up when “bonded” atoms collide with other particles (the higher the temperature, the more forceful those “thermal” collisions are)
- Strong enough to compete with attractions to <u>other</u> atoms

When they form bonds, atoms strongly prefer to have an "octet" of electrons in their valence shell

ns^2 np^6

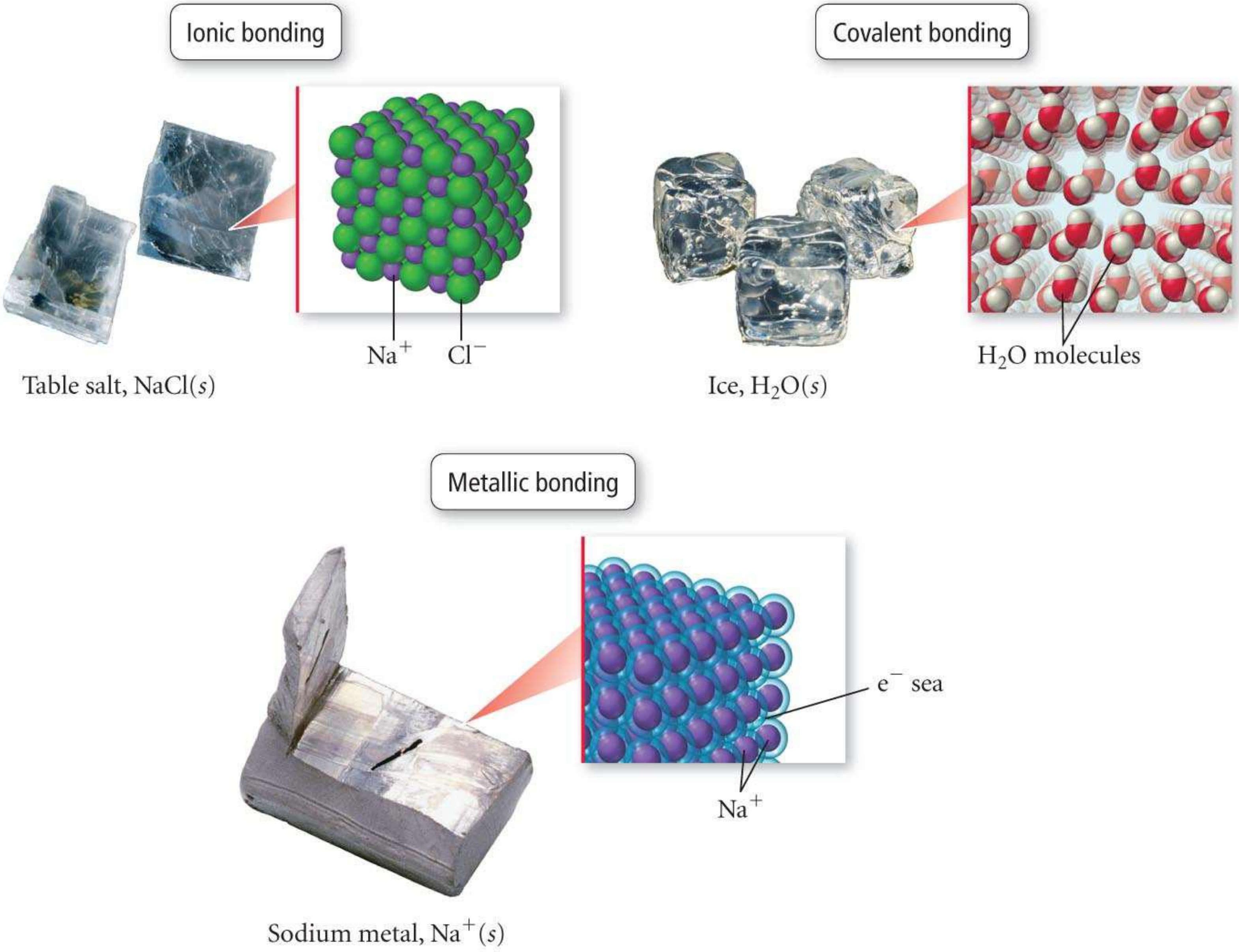
where n is the uppermost shell in the atom

We often loosely refer to this as "attaining a noble gas configuration".

A useful way to classify chemical bonds

- Ionic (Metal-Nonmetal or Cation-Anion)
  - Due to the electrostatic attraction between a cation (+) and an anion (–).
- Covalent (Nonmetal-Nonmetal)
  - Due to the attraction of the nuclei of two atoms to a higher density of electrons between them (therefore “shared” by both atoms.
- We will not consider other kinds of bonding (which, ultimately, can often be understood in terms of these two major categories)

Types of Bonding



Ionic bonding

The strong attraction between two oppositely charged ions.

Formation of an ionic bond is often conceptualized as the “transfer” of electron(s) from the atom that forms the cation to the atom that forms the anion, both attaining a noble-gas electron configuration as a result.

$$\mathrm{Na} \quad + \quad \mathrm{Cl} \quad \rightarrow \quad \mathrm{Na}^+ \quad + \quad \mathrm{Cl}^-$$

$$\begin{tikzcd}
{[\mathrm{Ne}]3s^1} \arrow[rr, bend left] & + & {[\mathrm{Ne}]3s^2\,3p^5} & \rightarrow & {[\mathrm{Ne}]} & + & {[\mathrm{Ne}]3s^2\,3p^{\mathbf{6}}} \\
 & & & & & & {[\mathrm{Ar}]} \arrow[u]
\end{tikzcd}$$

But:

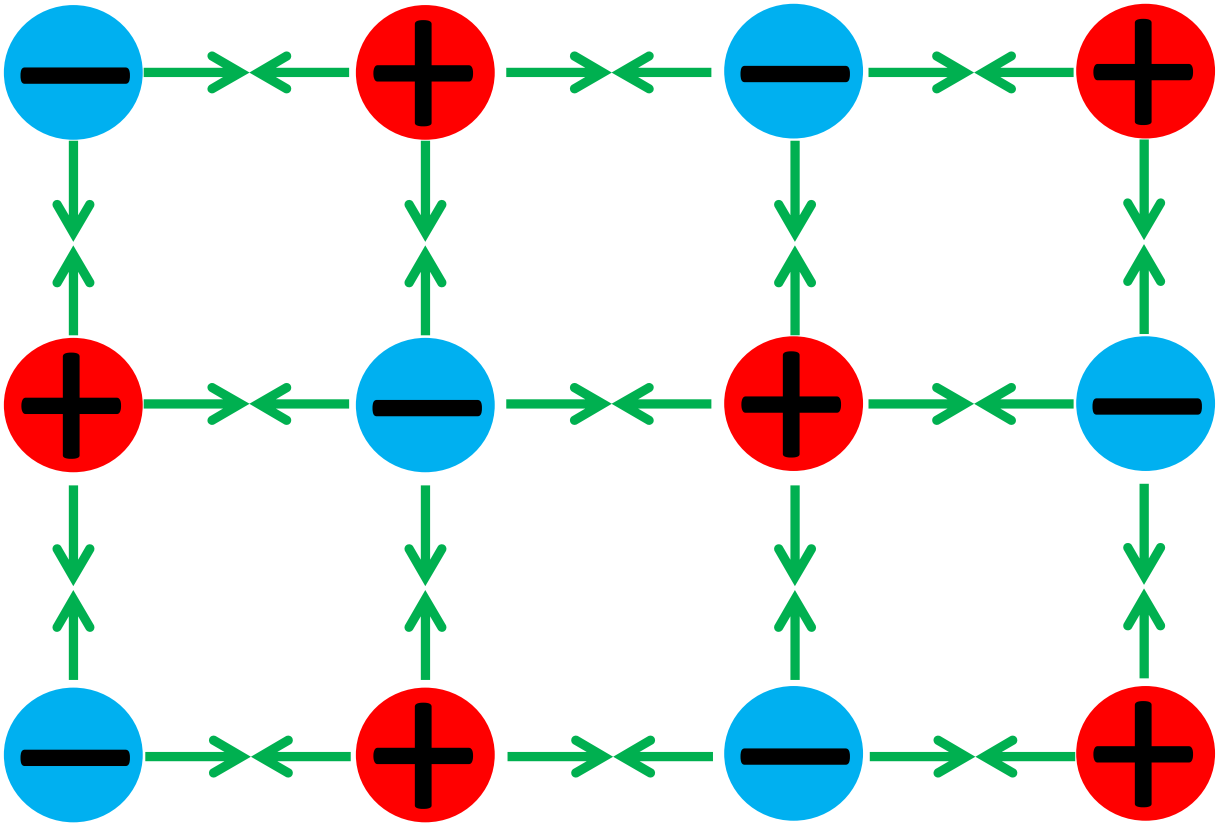
The ionic bond doesn’t need to be formed as a result of a direct transfer of an electron between two atoms.

All we need are oppositely charged ions. They may be brought together long after they were formed quite separately from one another.

Ionic bonds do not lead to molecules.

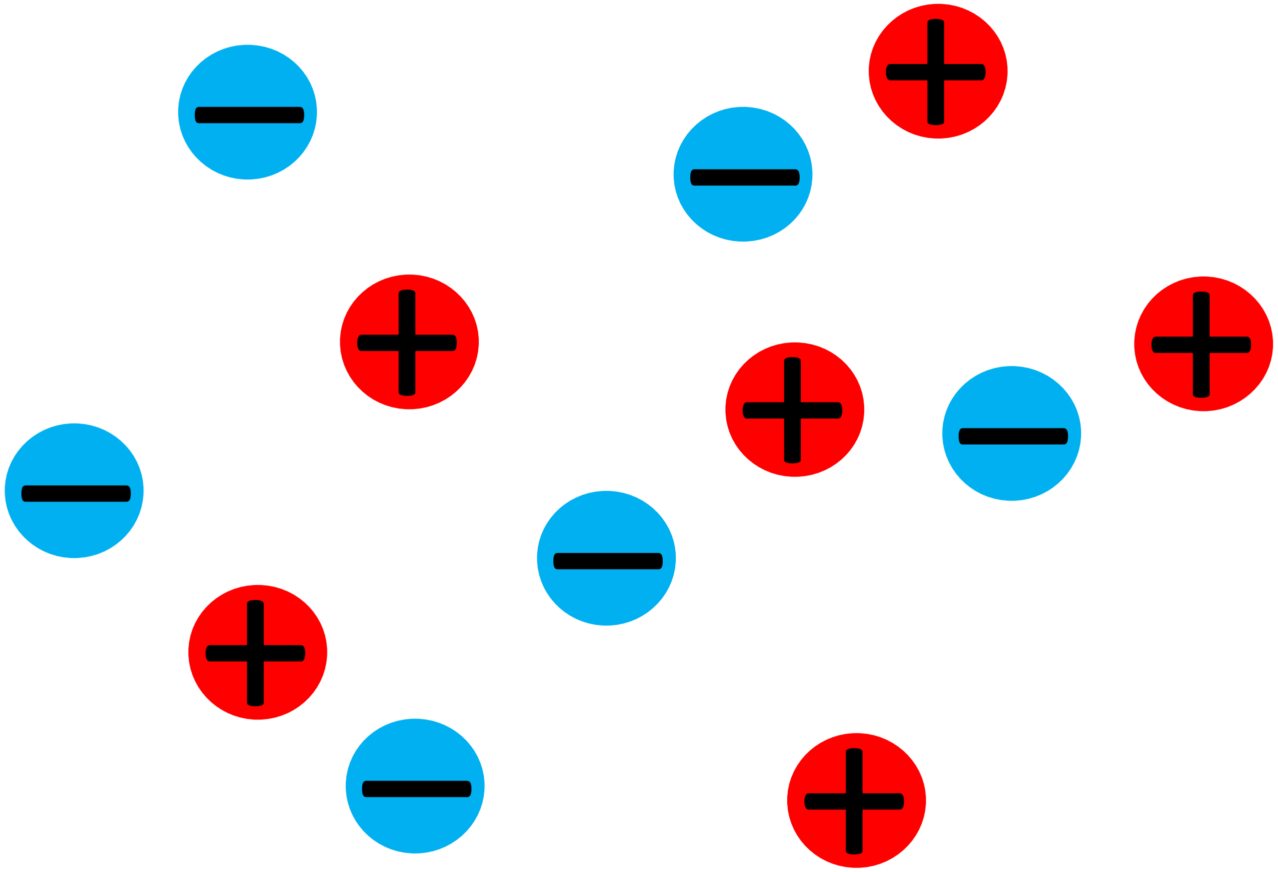
They lead to “ionic compounds”.

In solid form, ionic compounds form regular crystals where the (+) and (–) charges stack in a way that maximizes the force of attraction (and minimizes the potential energy).



How do we know they are not in the form of molecules?

When we melt an ionic substance, individual ions start floating away separately. They **<u>don’t</u>** melt as neutral units where the cation and the anion are stuck together.



Covalent bonding

Another way two atoms can be more stable together than apart is by offering the valence electrons the chance to spend more time between the nuclei.

The (–) electron would be near not one but <u>**two**</u> (+) <u>**nuclei**</u>, making the system more stable (lower in potential energy)

When this opportunity arises, there is no reason for only one atom's electron to do it. <u>An electron from **both atoms**</u> will want to concentrate in the space between them.

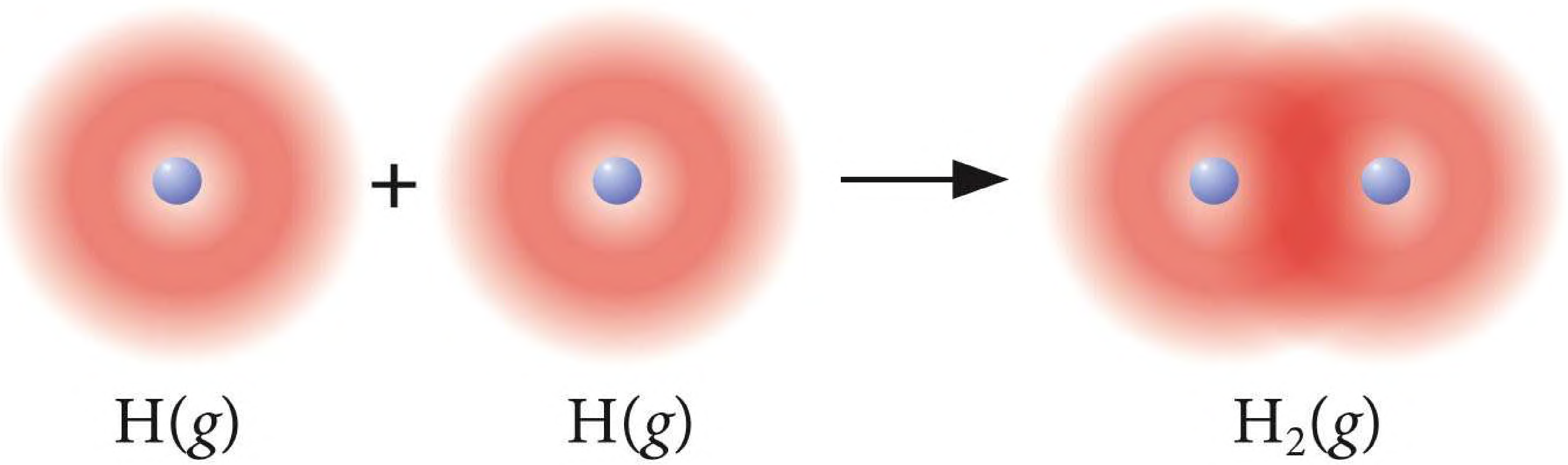
When two electrons (one from each atom) are concentrating between the two nuclei, the limitation imposed by Pauli Exclusion Principle still applies.

So the two electrons will “pair up” in an orbital that is now involved in bonding.

And that **pair of electrons** would be called a “bonding pair”, or a “**covalent bond**”

Covalent bonding example

As two hydrogen atoms approach each other, the electron on each atom has an opportunity to lower its potential energy by spending most of its time between the two nuclei. At a certain distance, “bond length”, minimum energy is achieved.

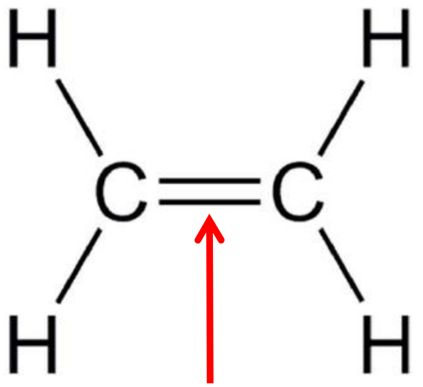


Multiple bonds

We often show a covalent bond as a line (or a "dash") between the two atoms.

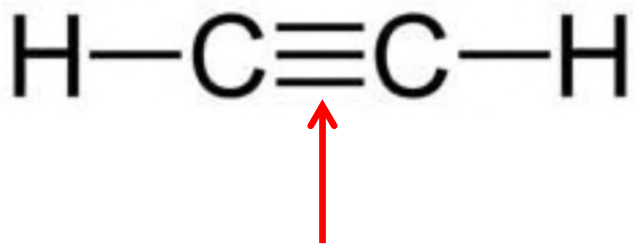
Just as we can have an ionic bond between multiply charged cations and anions (e.g. MgO where we have Mg^{2+} and O^{2-}, or AlN where we have Al^{3+} and N^{3-}), we can have multiple covalent bonds between two atoms.

Multiple covalent bonds are shown with multiple parallel lines.



Double bond

An "extra" bond added to a "single bond" between the C atoms here



Triple bond

Two "extra" bonds added to a "single bond" between the C atoms here

Multiple bonds

For a bond between a given pair of atoms:

Single < Double < Triple
weakest strongest

which is intuitive.

But we also have, for a bond between a given pair of atoms:

Single < Double < Triple
longest shortest

which makes sense if we realize that “stronger bond” means stronger attraction of atoms towards one another, which makes them come closer.

Polar covalent bonds and Electronegativity

We learned earlier that some elements “like” electrons more than others, as indicated by their larger ionization energy.

- It costs more to remove an electron from them

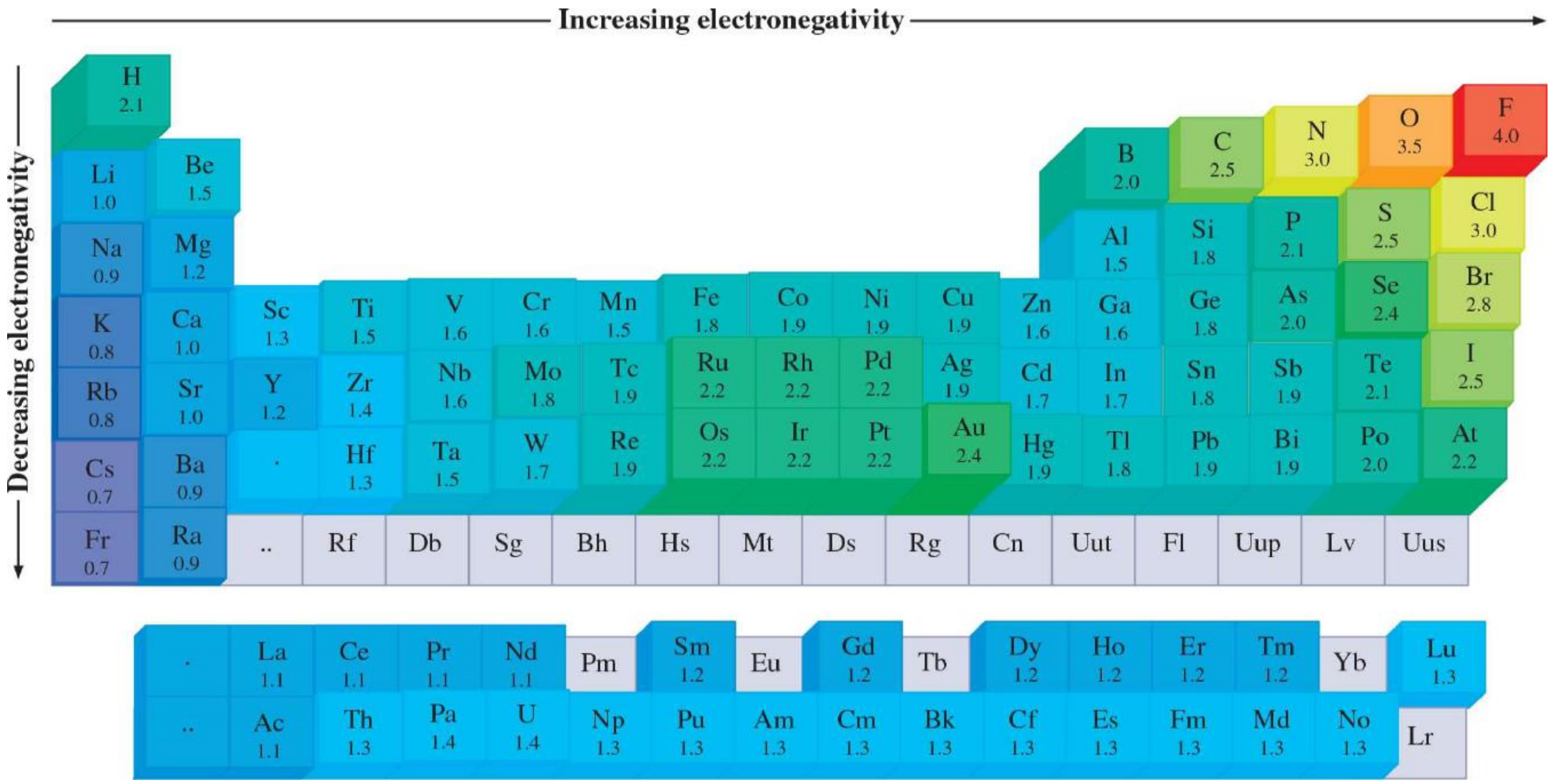
When an element is making a covalent bond, its relative attraction to electrons doesn’t go away.

If it attracted electrons strongly alone, it will still do that when bonded.

Polar covalent bonds and Electronegativity

The tendency of a bonded atom to attract electrons towards itself is called “electronegativity”.

Polar covalent bonds and Electronegativity



H 2.1																
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	·	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	··	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus

·	La 1.1	Ce 1.1	Pr 1.1	Nd 1.1	Pm	Sm 1.2	Eu	Gd 1.2	Tb	Dy 1.2	Ho 1.2	Er 1.2	Tm 1.2	Yb	Lu 1.3
··	Ac 1.1	Th 1.3	Pa 1.4	U 1.4	Np 1.3	Pu 1.3	Am 1.3	Cm 1.3	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr

Not surprisingly, electronegativity increases from left to right and from bottom to top in the periodic table, following the same trend as ionization energy.

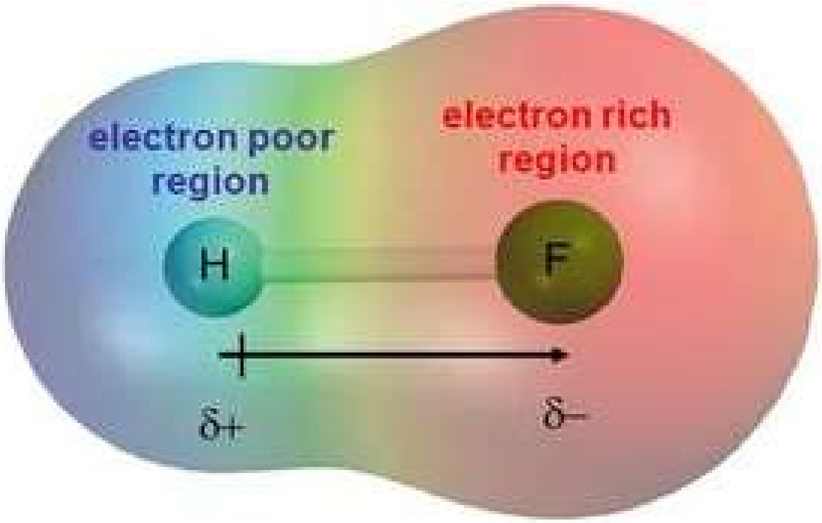
F, O, N, and Cl have the highest electronegativity values.

Polar covalent bonds and Electronegativity

The “shared” bonding electrons spend more time near the more electronegative atom.

Increased electron density around the more electronegative atom gives it an extra “partial” negative charge (shown as δ–).

Conversely, the less electronegative atom develops a partial positive charge (shown as δ+).



δ: greek lower-case letter “delta”

Polar covalent bonds and Electronegativity

Larger difference in electronegativies of bonded atoms

↓

Larger polarization of the bond

When the atoms forming a covalent bond develop partial negative and positive charges, the bond is called a “polar covalent bond”, or simply a “polar bond”.

A “polar bond” has a “dipole moment”

Dipole moment:

A (+) and (-) charge separated by a distance

Larger the charges, larger the dipole moment

More polar bonds have larger dipole moments

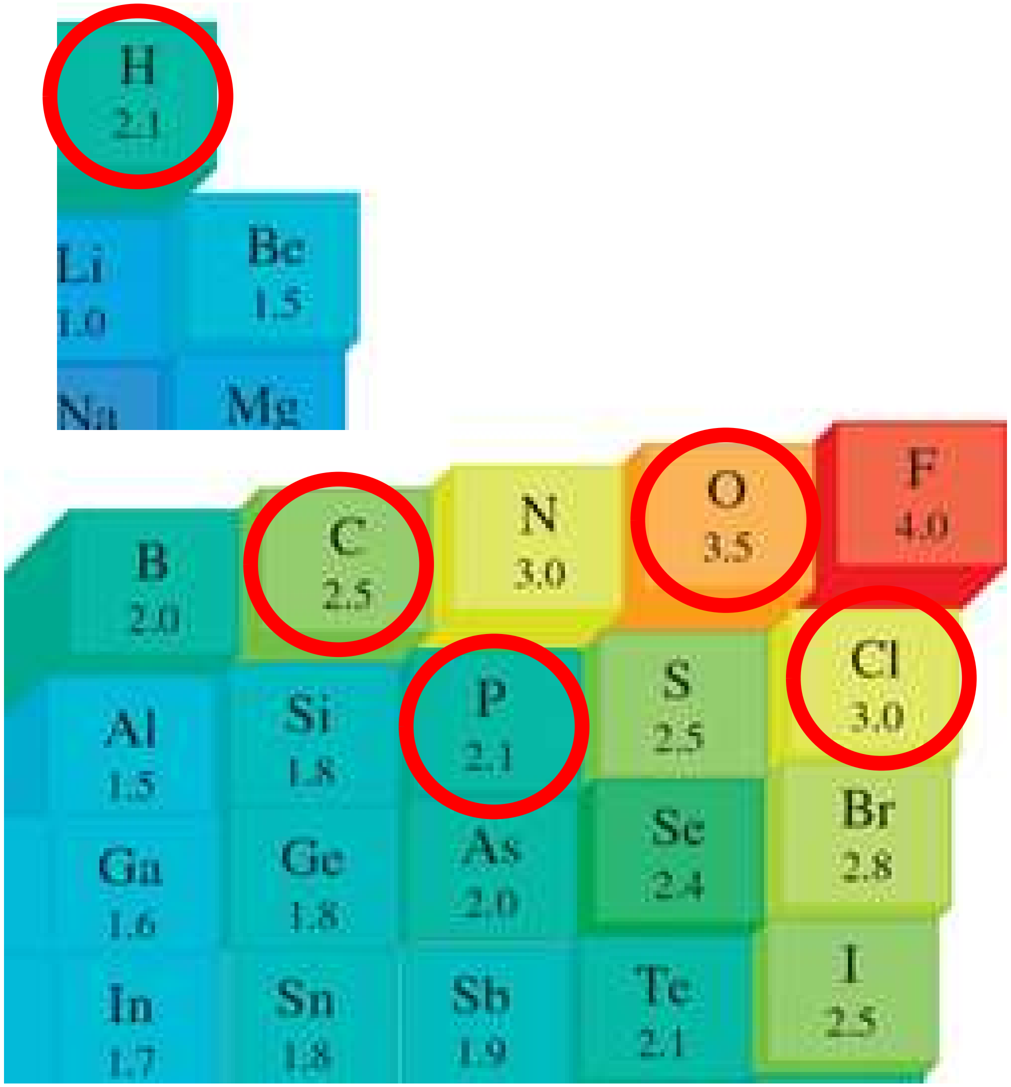
Polar covalent bonds and Electronegativity

We can roughly estimate how polar a bond is by examining the electronegativity difference between the two bonded atoms.

And we can use electronegativity values to compare the polarity of different bonds.

Example

Using electronegativities, arrange the following bonds in order by increasing polarity: P—H, H—O, C—Cl.



Electronegativity differences:

P—H	2.1 – 2.1 = 0
H—O	3.5 – 2.1 = 1.4
C—Cl	3.0 – 2.5 = 0.5

Bond polarities:

P—H < C—Cl < H—O

Even though we just used the numerical values of electronegativity differences in the previous example, it would be unwise to over-interpret them.

Electronegativity of an element can be defined and calculated in various ways.

If derived from the actual polarization of the bonds the element makes with various other elements, electronegativity of a given element is an average value, not applying to any particular bond exactly.

If derived from ionization energy and related quantities, the electronegativity of a given element only approximately applies to the polarization of the bonds it makes with various other elements.

Polar covalent bonds and Electronegativity

Even if Carbon and Iodine have the same electronegativity values (say, 2.5), it doesn’t mean that a C—I bond will have exactly zero polarization. It will still be somewhat polarized.

Polar covalent bonds and Electronegativity

In many cases, we can rank bond polarities by simply using the trends of electronegativity (EN) in the periodic table.

Pick the more polar bond:

O—F $\boxed{\text{N—F}}$

O is less electronegative than F

N is further left than O, compared with F

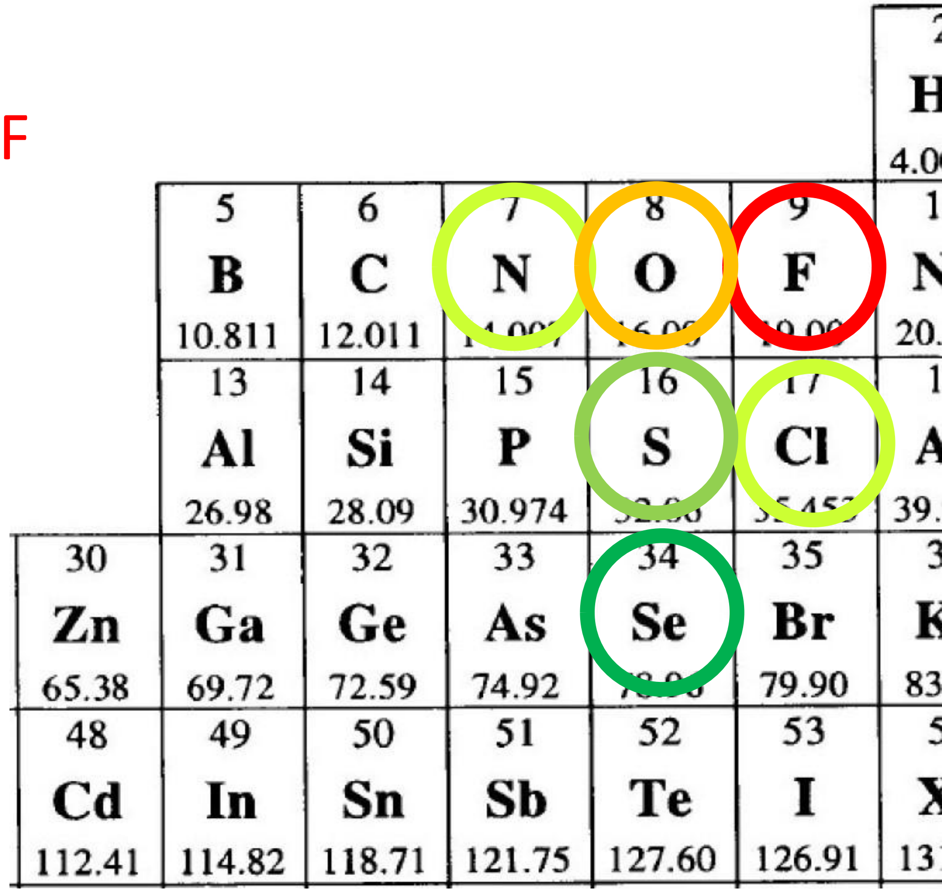
N and F have a larger EN difference

S—Cl $\boxed{\text{Se—Cl}}$

S is less electronegative than Cl

Se is below S in the same group, so it has even lower EN

Se and Cl have a larger EN difference



						2 H 4.0
	5 B 10.811	6 C 12.011	7 N [illegible]	8 O [illegible]	9 F [illegible]	1 N 20.
	13 Al 26.98	14 Si 28.09	15 P 30.974	16 S [illegible]	17 Cl [illegible]	1 A 39.
30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se [illegible]	35 Br 79.90	3 K 83
48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	5 X 13

Polar covalent bonds and Electronegativity

In other classes or websites or books, you might have seen electronegativity differences used to classify bonds as “nonpolar”, “polar”, and “ionic”.

That has value, and also reflects the how chemists use the term “nonpolar” to describe bond polarity.

But we won’t do that here.

Polar covalent bonds and Electronegativity

We won’t do that here because:

- Electronegativity alone is not good enough to accurately gauge the actual polarization in a given molecule with more than 2 atoms (and sometimes not even in that case)
- We want to focus on the more clear-cut distinction between zero polarity and non-zero polarity

So, here, “nonpolar” means “zero polarity”
And “polar” means “non-zero polarity” (no matter how small)

So, in practice, we will use those terms as follows:

“**nonpolar bond**”:
Bond between two identical atoms, like H-H, F-F
Both atoms attract the bonding electrons equally

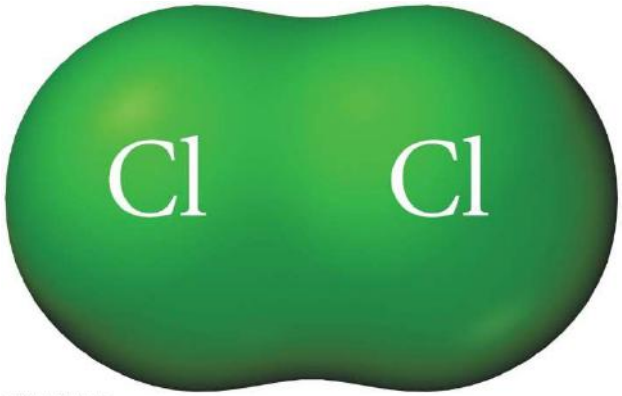
“**polar bond**”:
Bond between two different elements, like H-Cl, O-H
There will always be some polarization (small or large)

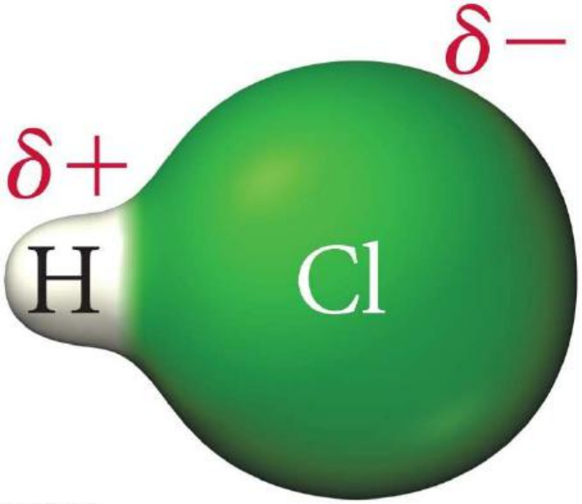
We will come back to the issue of polarity at the end of this chapter, when we think about the polarity of an **entire molecule**.

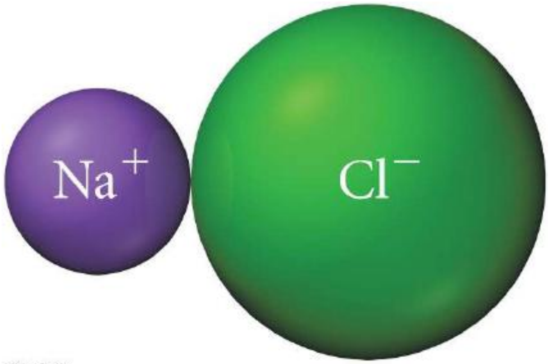
To do that:

- We will first learn to derive how the valence electrons are distributed in a molecule, using Lewis Structures
- Then we will learn to derive the molecular shapes from the Lewis Structures. The molecular shape will also tell us whether the molecule is polar or not

Bond Polarity







Lewis Structures

A simple way to do “quantum chemistry” for “covalent structures”, i.e. molecules and polyatomic ions

Surprisingly powerful!

Why do we draw “Lewis Structures”?

- It shows if there are double or triple bonds in a molecule, and where they are
- It shows where the non-bonding electrons are
  - <u>Hugely important in determining molecular shape</u>

Lewis structures are based on these principles:

- Only **valence electrons** count
- When bonded, atoms form **octets** (have 8 electrons in their valence shells)
  - H needs only 2 electrons, and forms a “duet”
- When bonded, electrons on atoms exist in **pairs**, regardless of whether they are used in bonding or not
  - “**bond**” = bonding pair (two electrons in a bond)
  - “**lone pair**” = two electrons lumped together, not used in a bond

General steps for writing Lewis structures:

1. Calculate the number of valence electrons.
2. Draw the “skeletal bonds” that show which atom is connected to which. Each bond is a pair of electrons.
3. Complete the octets of atoms (except H) by creating lone pairs, starting with the peripheral atoms.
4. If the central atom doesn’t have an octet when you run out of your valence electron budget, turn a peripheral atom’s lone pair into an extra bond with the central atom.
5. Repeat Step 4 if needed, using a lone pair of another (rather than the same one as before) peripheral atom whenever possible.

<u>Step 1</u>: Calculate the number of valence electrons

- Sum up the valence electrons brought by each atom
- <u>Subtract the charge</u> (so, a positive charge reduces the number of electrons, and a negative charge increases it)
- **This is our "budget" of electrons**

Example: H_2O

1 valence electron from each H

6 valence electrons from O

(2)(1) + (1)(6) = **8** val. e^-

Example: H_3O^+

Each H: 1 val. e^-; each O: 6 val. e^-

1 (+) charge to subtract

(3)(1) + (1)(6) – **1** = **8** val. e^-

Example: OH^-

1 val. e^- from H, 6 val. e^- from O

1 (–) charge to subtract

(1)(1) + (1)(6) – (-**1**) = **8** val. e^-

Step 2: Draw the "skeletal bonds"

I prefer drawing bonding pairs as a "line" (or a "dash"): —

Others might prefer to use : for all electron pairs

This is when we decide which atom is "central", and which is "peripheral"

Example: H_2O

H—O—H H is never central

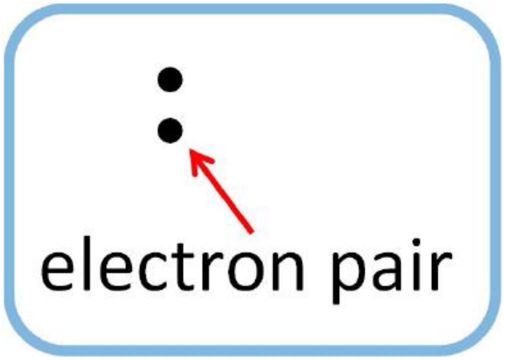
Example: CO_2

O—C—O Why not C—O—O ?

- Symmetry is preferred
- "More metallic" atom more likely to be central
- Single C, two O suggests C is central

Step 3: Complete the octets

- By putting enough lone pairs on each atom
- Start with peripheral atoms
- Put remaining (if any) pairs on the central atom

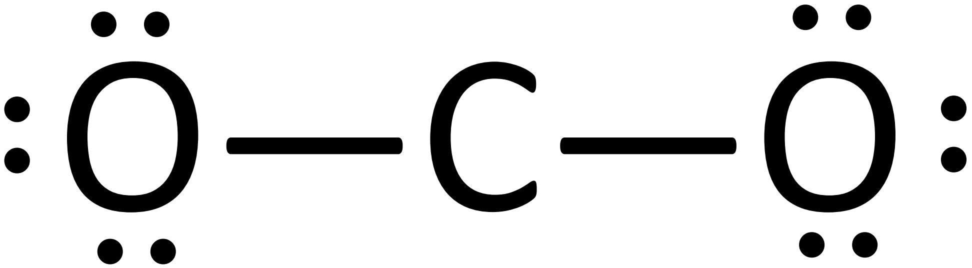


Example: CO_2

electron budget: (2)(6) + (1)(4) = **16** **(8 pairs)**

2 pairs used for 2 bonds.

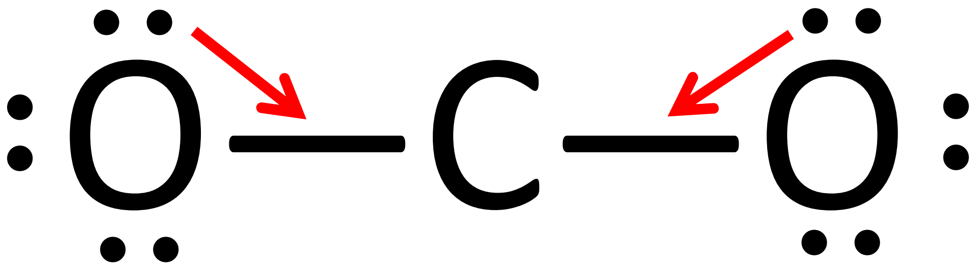
6 pairs remaining

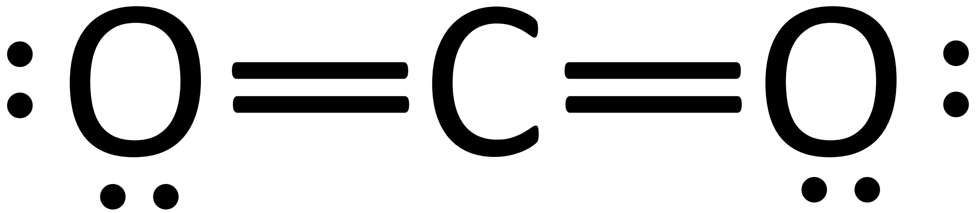


<u>Steps 4 & 5</u>: If central atom needs more pairs, turn lone pairs on peripheral atoms into extra bonds w/ central atom

- Keep bonding as symmetric as possible

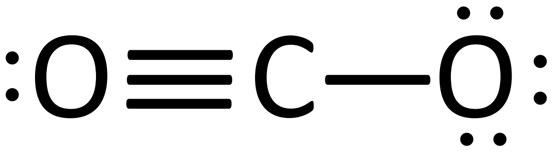
Continuing with CO_2





Now C also has an octet!

Avoid



It’s not symmetric

“Rules of thumb” for Lewis structures

- If the molecular formula contains a single atom of an element (and there is only one such element in the formula) it is safe to designate it as “central atom”

  e.g. NH_3, H_2O, CO_2

- If there are single atoms of more than one element,
  - the “more metallic” one is likely the central atom

    e.g. $COCl_2$, HCN, CFClBrI

  - if still ambiguous, the element that is in the middle of the formula is a good candidate for being the central atom (not guaranteed)

- If the chemical formula is written symmetrically, the skeletal structure is likely symmetric. The atoms in the middle are “central” (more than one “central” atom is possible) and will be treated as such separately.

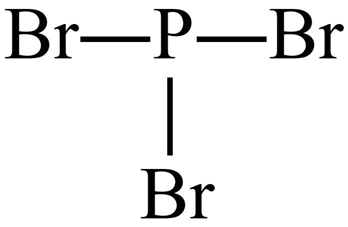
“Rules of thumb” for Lewis structures (continued)

- Hydrogen is never the central atom
- Hydrogen only makes single bonds
- Hydrogen never has a lone pair
- Halogens only make single bonds as peripheral atoms
- Carbon almost never has lone pairs (except in CO and CN^-)

Example: Lewis structure for PBr_3

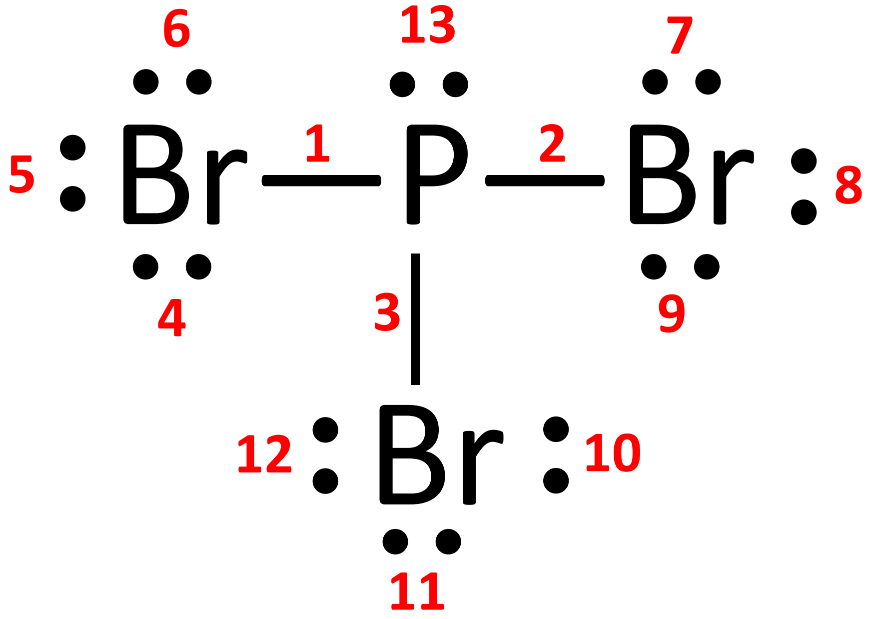
No. of valence e^- = $(1)\underset{\text{P}}{(5)} + (3)\underset{\text{Br}}{(7)} = \mathbf{26}$ (**13** pairs)

Skeleton structure:



- Only one P atom versus three Br atoms.
- P is the central atom

- Skeletal bonds consume 3 pairs.
- Use the remaining 10 pairs to complete the octet(s) with lone pairs



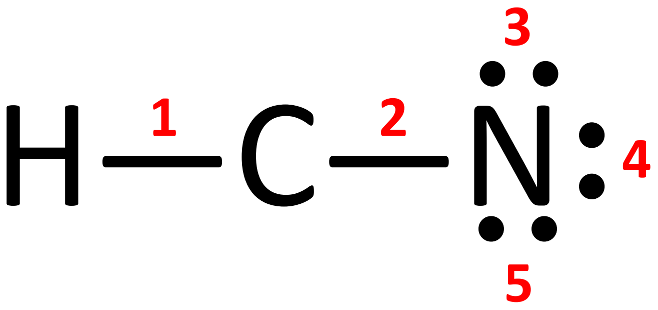
Example: Lewis structure for HCN

No. of valence e^- = $\underset{H}{(1)(1)} + \underset{C}{(1)(4)} + \underset{N}{(1)(5)}$ = **10** (**5** pairs)

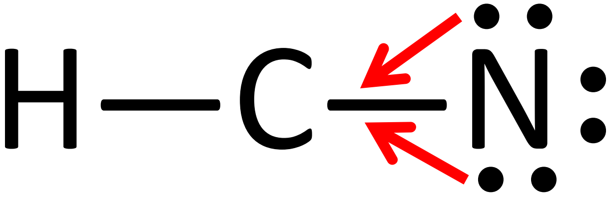
Skeleton structure: H—C—N

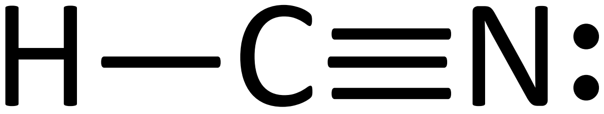
- H is never central
- C is in the middle of the formula
- C is “more metallic” than N

- Skeletal bonds consume 2 pairs.
- Use the remaining 3 pairs to complete the octet(s) with lone pairs



- Complete the octet of C by turning two lone pairs of N into two extra bonds to C

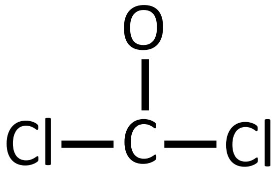




Example: Lewis structure for $COCl_2$

No. of valence $e^- = \underset{\text{C}}{(1)(4)} + \underset{\text{O}}{(1)(6)} + \underset{\text{Cl}}{(2)(7)} = \mathbf{24}$ (**12** pairs)

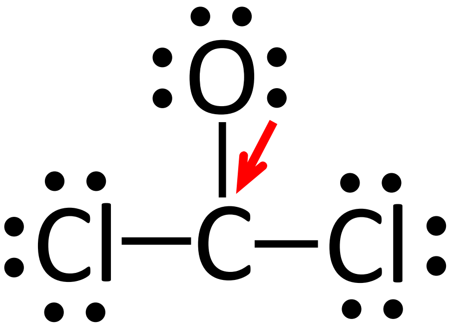
Skeleton structure:



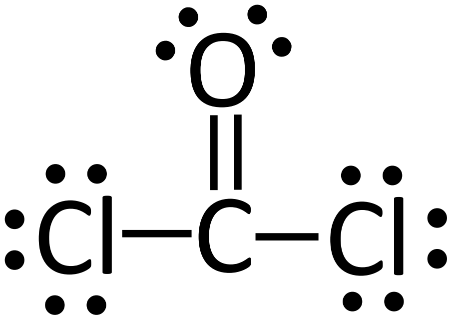
$$\text{Cl}-\overset{\displaystyle\text{O}\atop\displaystyle|}{\text{C}}-\text{Cl}$$

- Only one C atom
- C is “more metallic” than O
- C is the central atom

- Skeletal bonds consume 3 pairs.
- Use the remaining 9 pairs to complete the octet(s) with lone pairs



- Complete the octet of C by turning a lone pair of O into an extra bond to C
  - Cl (a halogen) doesn’t make a double bond as a peripheral atom



Practice:
Check your solution on next page

CO_2

$SeOF_2$

NO_2^-

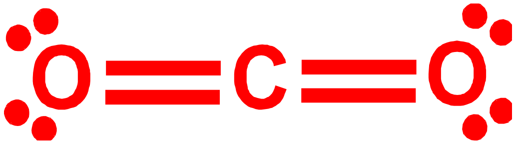
H_3PO_4

SO_3

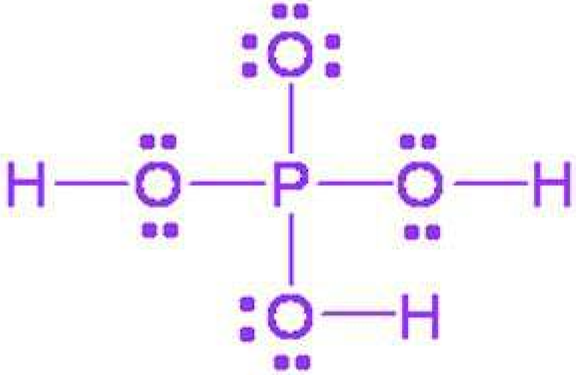
P_2H_4

Practice –Lewis Structures

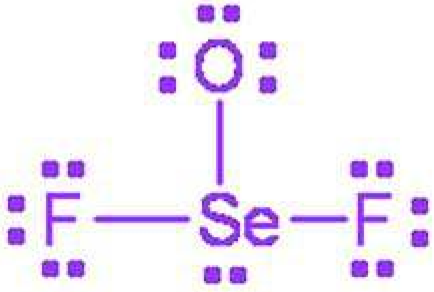
CO_2



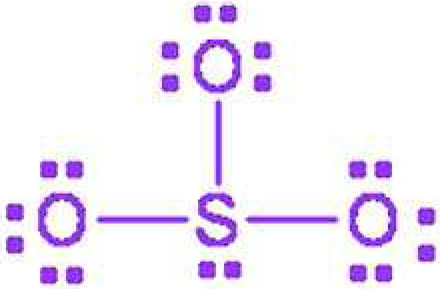
H_3PO_4



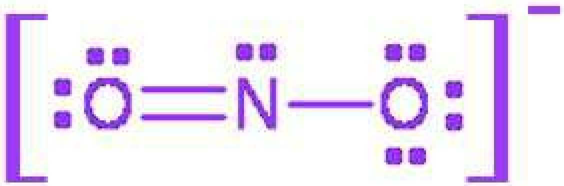
$SeOF_2$



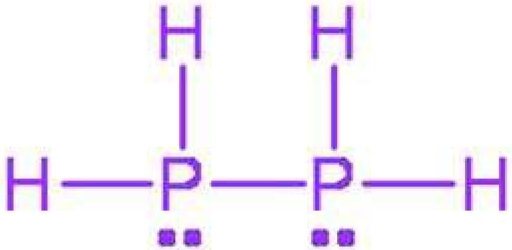
SO_3^{2-}



NO_2^-



P_2H_4

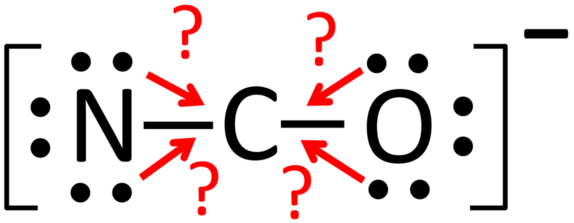


Example: Lewis structure for the cyanate ion, NCO^-

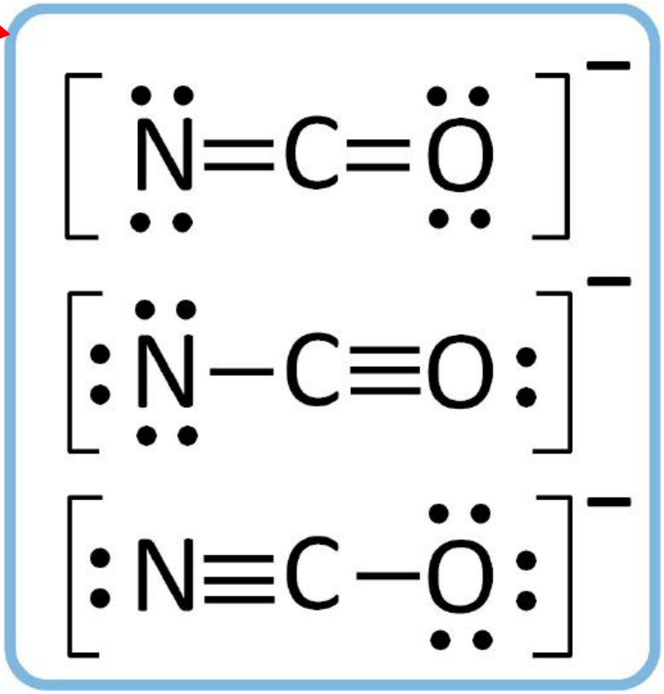
No. of valence e^- = (1)(5) + (1)(4) + (1)(6) –(-1) = **16** (**8** pairs)

Skeleton structure: N—C—O

Lewis structures of ions are shown in square brackets



When we apply the usual method, we can use different lone pairs and obtain multiple, "valid" Lewis structures: **Resonance structures**



But they are not equally favorable.

Each structure contributes to the actual structure, depending on how "favorable" it is.

If one is much more favorable than others, we use it as the "real" Lewis structure.

The favorable Lewis structure is normally found using "formal charges" (skipped here).

Lewis structures with different distributions of the extra bond(s) are called “resonance structures”.

Deciding which “resonance structure” best describes the bonding in the actual molecule is typically done using “formal charges”, which we will not study here.

But we will look at equivalent resonance structures that we sometimes get for a given molecule, differing only in the placement of the double-bond(s).

- When writing Lewis structures for some molecules, such as SO_2, we can write more than one good Lewis structure.
- Begin with the skeletal structure:

$$\mathrm{O} - \mathrm{S} - \mathrm{O}$$

- Sum the valence electrons.

$$(\#\ \text{valence } e^- \text{ in S}) + 2(\#\ \text{valance } e^- \text{ in O})$$

$$6\ e^- + 2(6\ e^-) = 18\ e^-$$

Resonance: Equivalent Lewis Structures for the Same Molecule

- Next, we place two electrons between each pair of atoms:

O:S:O (4 of 18 electrons used)

and then distribute the remaining electrons, first to terminal atoms:


$:\overset{..}{\underset{..}{O}}:S:\overset{..}{\underset{..}{O}}:$ (16 of 18 electrons used)

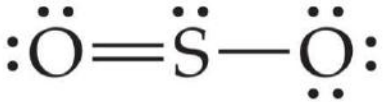
and finally to the central atom.


$:\overset{..}{\underset{..}{O}}:\overset{..}{S}:\overset{..}{\underset{..}{O}}:$ (18 of 18 electrons used)

- Since the central atom lacks an octet, move one lone pair from an oxygen atom into the bonding region to form a double bond, giving all of the atoms octets.

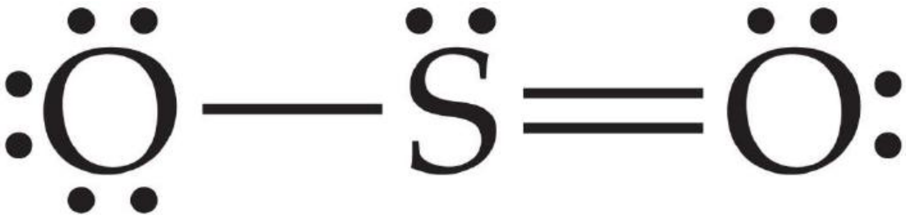

$:\overset{..}{O}::\overset{..}{S}:\overset{..}{\underset{..}{O}}:$

or


$:\overset{..}{O}=\overset{..}{S}-\overset{..}{\underset{..}{O}}:$

Resonance: Equivalent Lewis Structures for the Same Molecule

- We could have formed the double bond with the other oxygen atom.



- The two structures are equally correct as Lewis structures.
- We find that the molecule exists in nature as an **average** of the two Lewis structures and neither one alone represents reality.

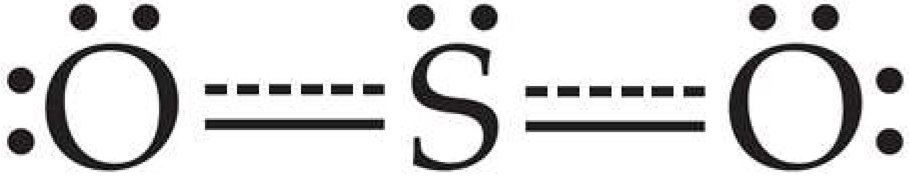
Resonance: Equivalent Lewis Structures for the Same Molecule

- *Either* one of the two Lewis structures for SO_2 would predict that SO_2 would contain two different kinds of bonds (one double bond and one single bond).
- When we examine SO_2 in nature, we find that both of the bonds are equivalent and intermediate in strength and length between a double bond and single bond.

Resonance: Equivalent Lewis Structures for the Same Molecule

- In nature, we find that the bonds in SO_2 are equivalent.
- We account for this in Lewis theory by representing the molecule with both structures, called **resonance structures**, with a double-headed arrow between them.

- The true structure of SO_2 is intermediate between these two resonance structures.



The extra bond is distributed between two structural S-O bonds.

- The electrons in the extra bond are "delocalized"

Each S-O bond is 1.5 bond (more than single, less than double bond)

Resonance: Equivalent Lewis Structures for the Same Molecule

A molecule with more than one equivalent Lewis structure (i.e. “resonance structure”) exists as an average of these structures because the average is more stable than the individual resonance structures.

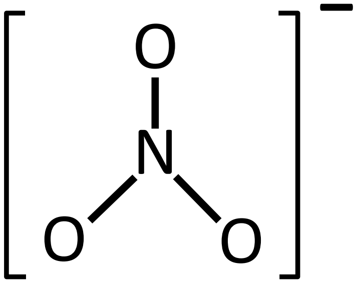
In that case, the molecule (or ion) is said to have **“resonance”**, and is stabilized by “resonance”, or **“delocalization”** of the electrons in the extra bonds being spread over more than two atoms.

Another example of resonance and delocalized bonding

Consider the nitrate ion, NO_3^-

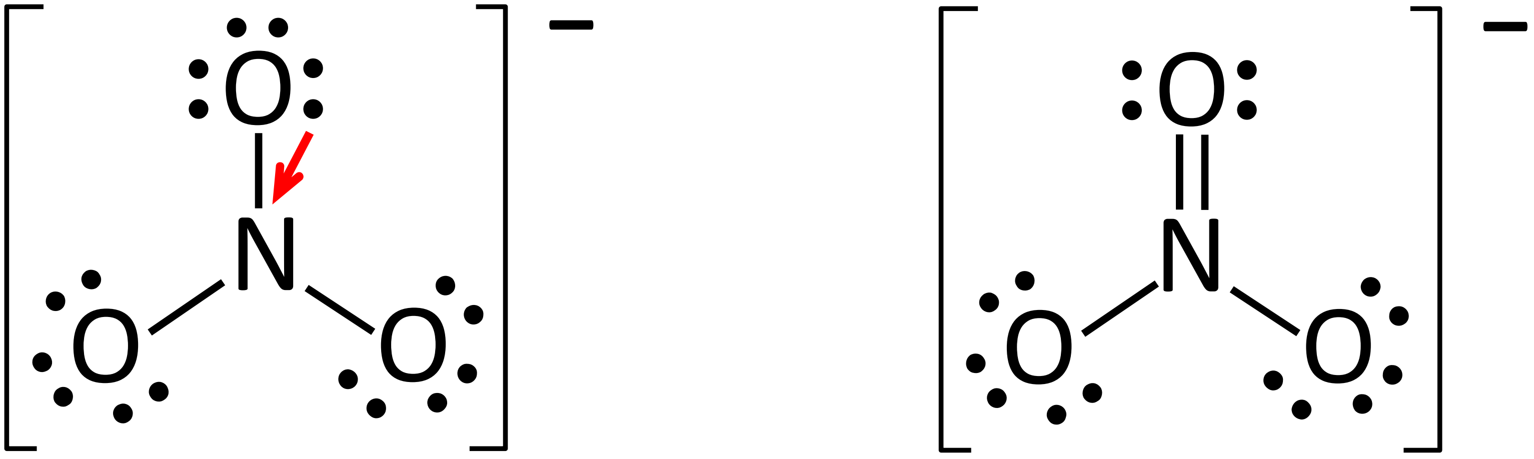
No. of valence e^- = (1)(5) + (3)(6) –(-1) = **24** (**12** pairs)

Skeleton structure:



- Only one N atom
- N is the central atom

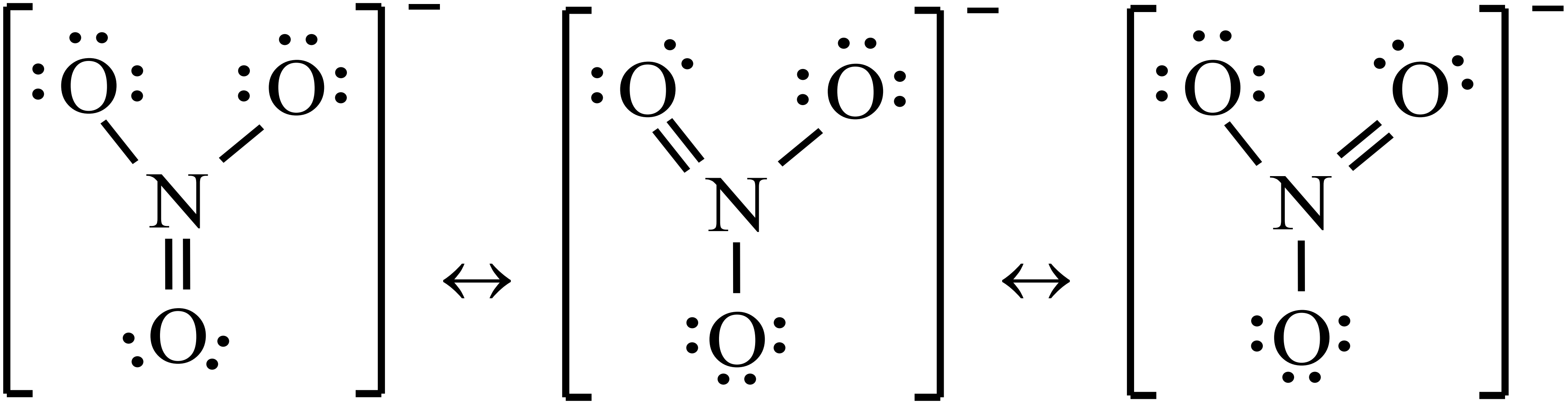
When we distribute the electron pairs as usual, we get:



But is there any reason one oxygen is more appropriate than the other two oxygens to make the double bond? **No**

Remember that Lewis structures with different distributions of the extra bond(s) are called “resonance structures”

Sometimes alternative Lewis structures are equivalent



No single oxygen is “special” and has no reason to be entitled to the double-bond.

Each structure has 2 N-O single bonds and 1 N=O double bond

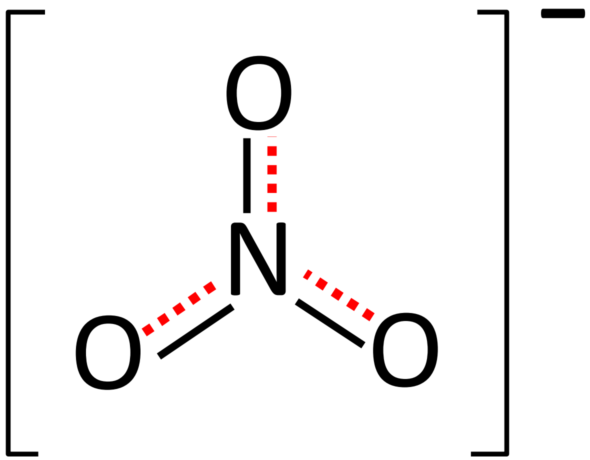
But the double bond is with a different O in each.

When the resonance structures are equivalent, they become important. They imply that:

- The electrons of the extra bond(s) cannot “decide” which bond distribution is best
- The electrons in the extra bonds(s) get distributed, i.e. “delocalized”
- So those electrons partially add to the bonding of more than one skeletal bond.
- The extra bonding they bring to each skeletal connection is only partial

Actual structure is an average of the resonance structures.

The electrons in the extra bond are **delocalized.**



The “moving” extra bond is taking the place of a lone pair on the oxygen it moved to, and the lone pair also delocalizes.

But it’s harder to show.

So we often don’t show lone pairs when we show delocalized bonds

- One extra bond is spread over 3 skeletal bonds
- It adds 1/3 bond to each bond
- Each N—O bond is 1+1/3 = 1.33 bond
- Slightly stronger and shorter than a single bond
- But not quite a double bond

Exceptions to the octet rule — less than an octet

“Early” members of the second period (Be, B) and Al in the third period violate the octet rule.

Yes, Be and Al, even if they are metals, can form covalent bonds under the right circumstances.

Be is satisfied with 2 electron pairs (4 electrons)

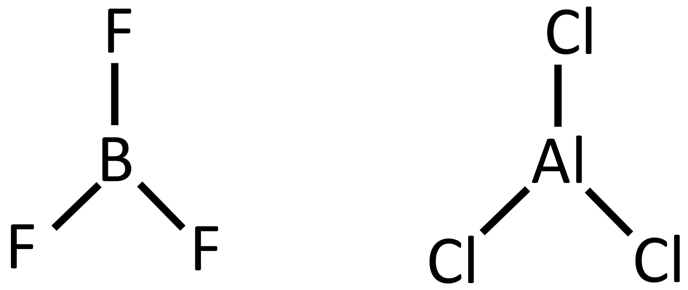
B and Al are satisfied with 3 electron pairs (6 electrons)

When we draw the Lewis structures of molecules containing these elements, we don’t complete their octets.

Instead, we stop at 2 pairs for Be, and 3 pairs for B and Al.

Cl — Be — Cl

2 bonds; no lone pairs



3 bonds; no lone pairs

Exceptions to the octet rule –– exceeding the octet

We won’t deal with those cases in this course

“Bond order”, “bond length”, and “bond strength”

We have seen and considered multiple bonds, and their relative strengths and lengths.

We have even seen partial extra bonds be added onto skeletal bonds, leading to bonds that were more than a simple, single bond, but not quite a double bond either.

We did not yet define a quantity describing this “**degree of bonding**”.

We call that “**bond order**”.

“Bond order”, “bond length”, and “bond strength”

Bond order:

1 for a single bond

2 for a double bond

3 for a triple bond

It can be fractional if there are delocalized bonds, e.g. 1.33, 1.5 etc. as we have seen in the nitrate ion NO_3^-

Bond strength goes up with Bond Order:

Single < Double < Triple

weakest strongest

For a given pair of atoms

Bond length goes down with Bond Order:

Single < Double < Triple

longest shortest

For a given pair of atoms

Note:

We can’t easily compare a C=O double bond with a C—C single bond because the pair of atoms making the bonds are not the same.

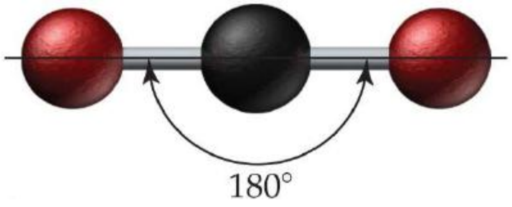
Predicting the Shapes of Molecules

- Lewis theory, in combination with **valence shell electron pair repulsion (VSEPR) theory**, can be used to predict the shapes of molecules.
- VSEPR theory is based on the idea that **electron groups**—lone pairs, single bonds, or multiple bonds—repel each other.
  - So it’s more like “valence shell electron group repulsion”
  - VSEGR?
- This repulsion between the negative charges of electron groups on the central atom determines the geometry of the molecule.

- Predict the shape of CO_2, which has the Lewis structure:

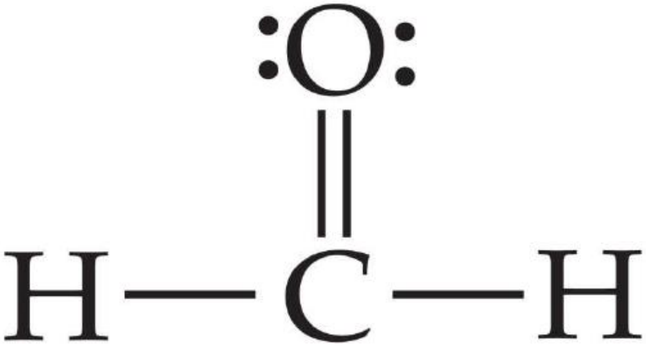
$$:\ddot{O}=C=\ddot{O}:$$

- The geometry of CO_2 is determined by the repulsion between the ***two*** electron groups (the two double bonds) on the central carbon atom. These two electron groups get as far away from each other as possible, resulting in a bond angle of 180° and a **linear** geometry for CO_2.

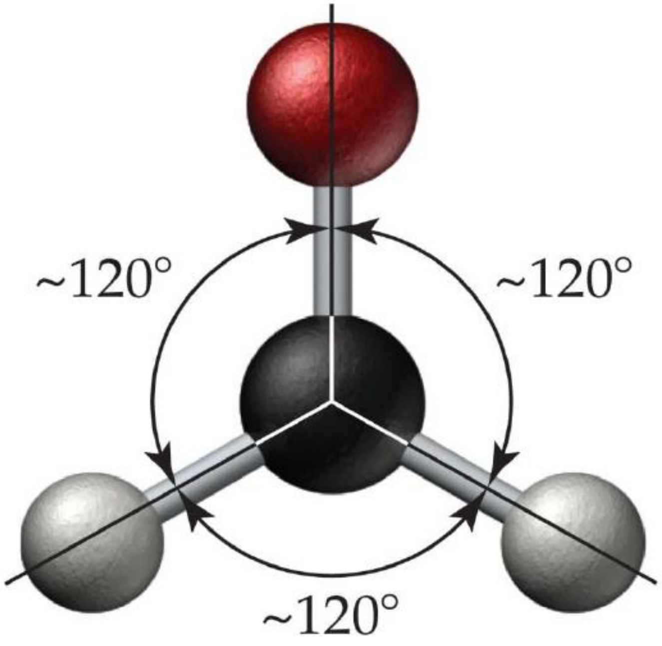


Predicting the Shape of H_2CO

- H_2CO has the Lewis structure:



- This molecule has ***three*** electron groups around the central atom.
- These three electron groups get as far away from each other as possible, resulting in a bond angle of 120° and a **trigonal planar** geometry.

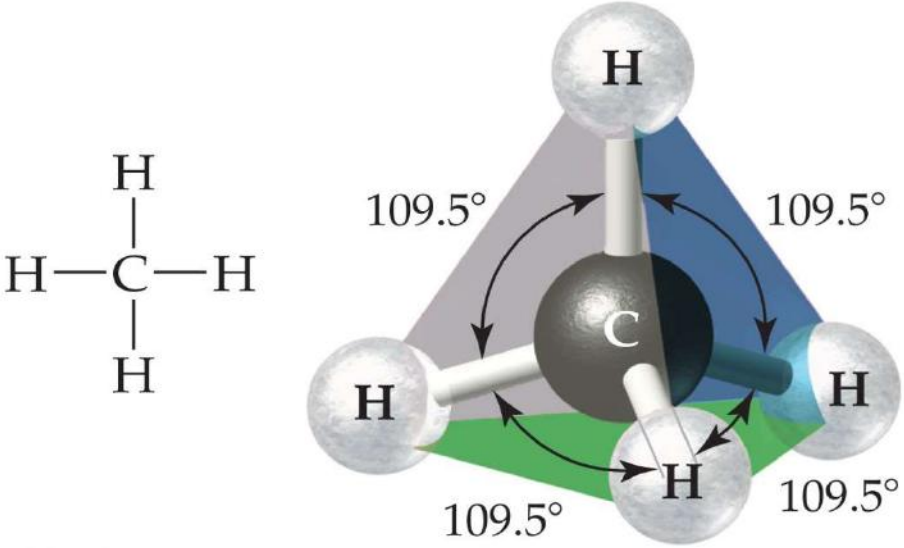


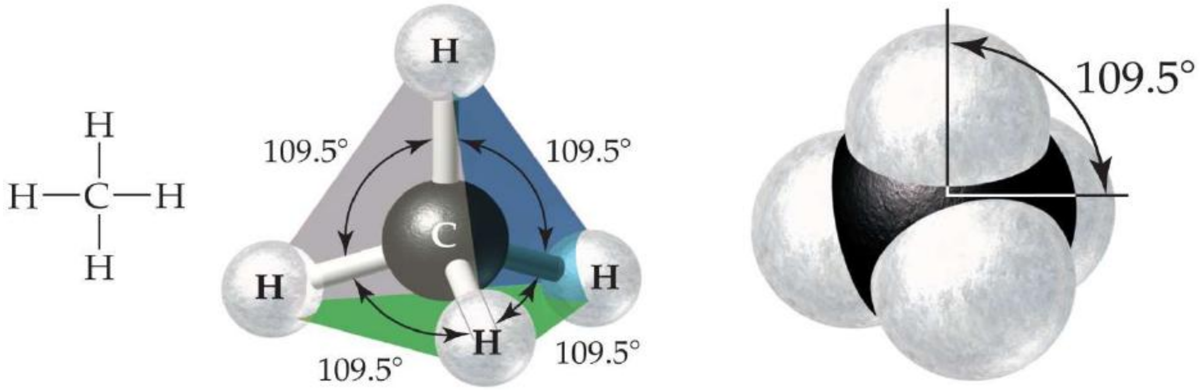
Predicting the Shape of H_2CO

- These angles predicted for H_2CO are approximate. The C═O double bond contains more electron density than do C—H single bonds, resulting in a slightly greater repulsion; thus, the HCH bond angle is actually 116° and the HCO bond angles are actually 122°.

If a molecule has *four* electron groups around the central atom, as does CH_4, it has a **tetrahedral** geometry with bond angles of 109.5°.

A tetrahedron is a geometric shape with four triangular faces.



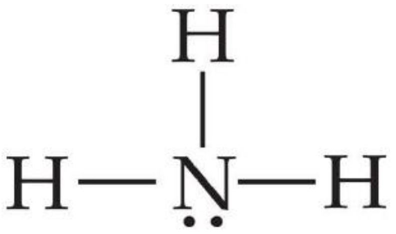


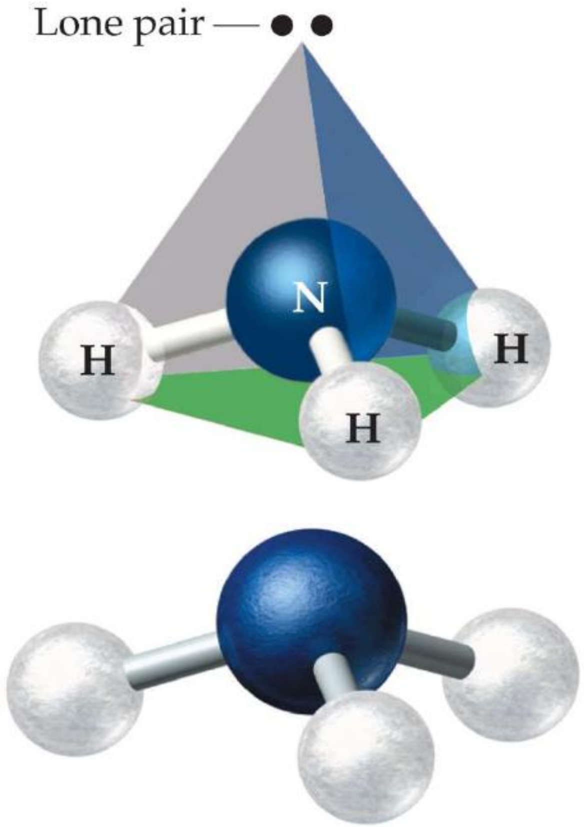
- The **mutual repulsion of the four electron groups** causes the tetrahedral shape—the tetrahedron allows the maximum separation among the four groups.
- When we write the structure of CH_4 on paper, it may seem that the molecule should be square planar, with bond angles of 90°, but it is not planar.
- In three dimensions the four electron groups can get farther away from each other by forming the tetrahedral geometry.

Predicting the Shapes of Molecules with Lone Pairs on the Central Atom

The NH_3 molecule has four electron groups (one lone pair and three bonding pairs).

- **electron geometry**—the geometrical arrangement of the electron groups—is **tetrahedral**.
- **molecular geometry**—the geometrical arrangement of the atoms—is **trigonal pyramidal.**
- The lone pair is closer to the central atom because it's not attracted to another atom. So it pushes onto the bonding pairs.
  - The actual bond angles in NH_3 are a little smaller than the ideal tetrahedral angles



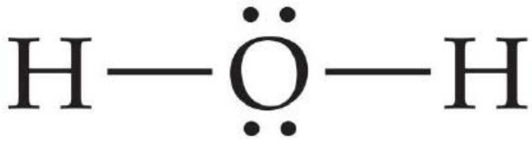


Trigonal pyramidal structure

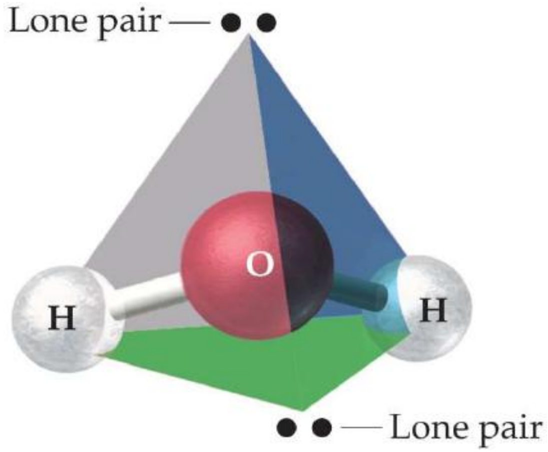
Predicting the Shapes of Molecules with Lone Pairs on the Central Atom

The H_2O molecule has four electron groups (two lone pairs and two bonding pairs).

- **electron geometry**—the geometrical arrangement of the electron groups—is **tetrahedral**.
- **molecular geometry**—the geometrical arrangement of the atoms—is **bent.**
- The lone pairs are closer to the central atom because they are not attracted to another atom, pushing onto the bonding pairs.
  - – The actual bond angle in H_2O is a little smaller than the ideal tetrahedral angle

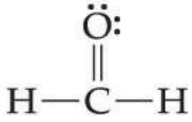
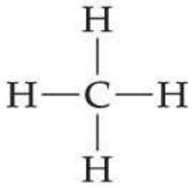
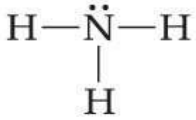


$$H-\underset{\cdot\cdot}{\ddot{O}}-H$$



Bent structure

TABLE 10.1 Electron and Molecular Geometries

Electron Groups*	Bonding Groups	Lone Pairs	Electron Geometry	Angle between Electron Groups**	Molecular Geometry	Example	
2	2	0	linear	180°	linear	$:\ddot{O}=C=\ddot{O}:$	
3	3	0	trigonal planar	120°	trigonal planar	 $\mathrm{H-\overset{\overset{\ddot{O}:}{\|}}{C}-H}$	
3	2	1	trigonal planar	120°	bent	$:\ddot{O}=\ddot{S}-\ddot{\underset{\cdot\cdot}{O}}:$	
4	4	0	tetrahedral	109.5°	tetrahedral	 $\mathrm{H-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-H}$	
4	3	1	tetrahedral	109.5°	trigonal pyramidal	 $\mathrm{H-\underset{\underset{H}{\vert}}{\ddot{N}}-H}$	
4	2	2	tetrahedral	109.5°	bent	$\mathrm{H-\underset{\cdot\cdot}{\ddot{O}}-H}$	

---

* Count only electron groups around the *central* atom. Each of the following is considered one electron group: a lone pair, a single bond, a double bond, and a triple bond.

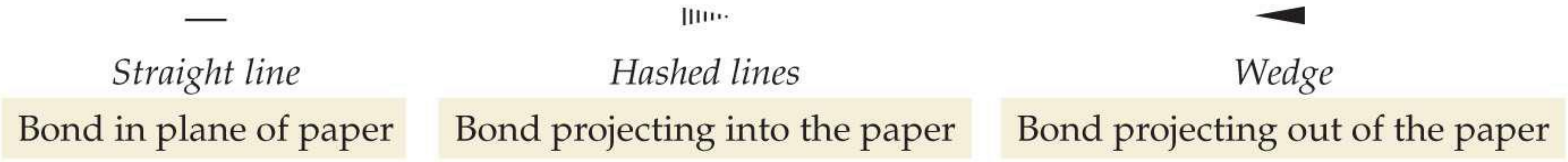
** Angles listed here are idealized. Actual angles in specific molecules may vary by several degrees.

Predicting Geometry Using VSEPR Theory

1. Draw a correct Lewis structure for the molecule.
2. Determine the total number of electron groups around the central atom.
3. Determine the number of bonding groups and the number of lone pairs around the central atom.
4. Refer to the table in the previous slide to determine the electron geometry and molecular geometry.

Representing Molecular Geometries on Paper

Many chemists use this notation for bonds to indicate three-dimensional structures on two-dimensional paper.



Straight line
Bond in plane of paper

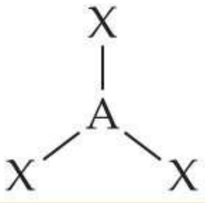
Hashed lines
Bond projecting into the paper

Wedge
Bond projecting out of the paper

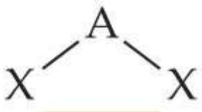
Representing Molecular Geometries on Paper

The major molecular geometries used in this book are shown here using this notation:

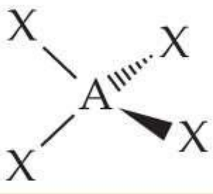
Linear



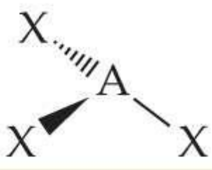
Trigonal planar



Bent



Tetrahedral



Trigonal pyramidal

VSEPR simulation

phet.colorado.edu/sims/html/molecule-shapes/latest/molecule-shapes_en.html

Please use it!
It’s like having molecular models in your digital device

Polar Bonds and Polar Molecules

Just because a molecule has polar bonds, it doesn’t mean it is a polar molecule

Dipole moment is a vector

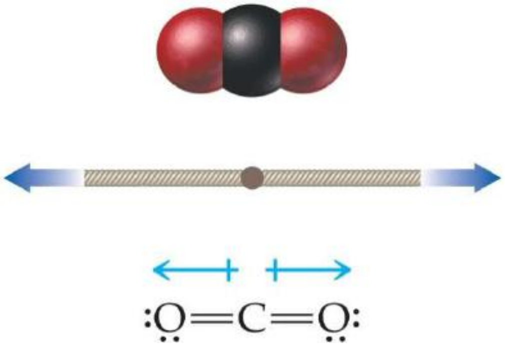
Dipole moment of the molecule is the vector sum of its bond dipoles

If the bond dipoles are equal in magnitude, and placed symmetrically around a center, they would cancel one another and the net dipole moment of the molecule would be zero!

Consider carbon dioxide:

$:\ddot{O}=C=\ddot{O}:$

- Each *bond* is polar because the difference in electronegativity between oxygen and carbon is 1.0.
- CO_2 has a linear geometry, the dipole moment of one bond completely cancels the dipole moment of the other, and the *molecule* is nonpolar.



Vector Notation for Dipole Moments

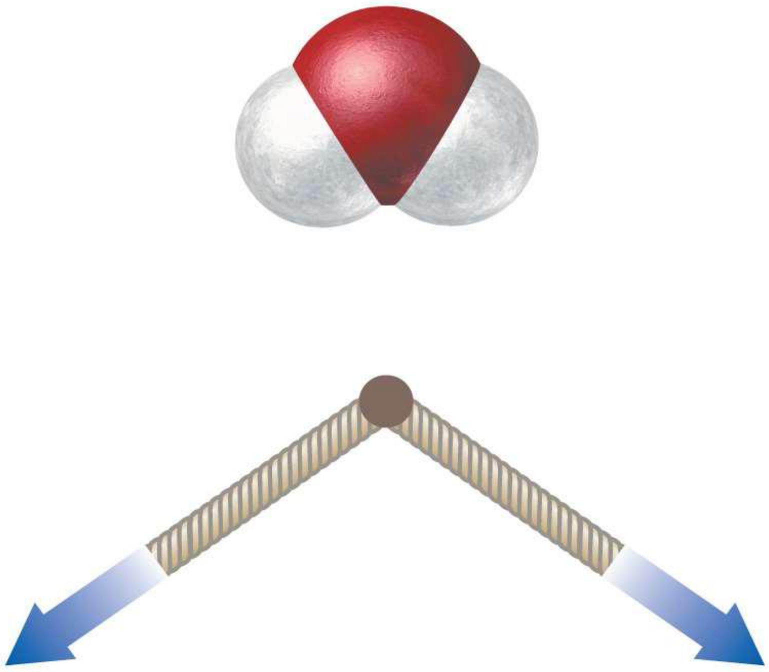
- If the arrows (vectors) point in exactly opposing directions as in carbon dioxide, the dipole moments cancel.
- In the vector representation of a dipole moment, the vector points in the direction of the atom with the partial negative charge.

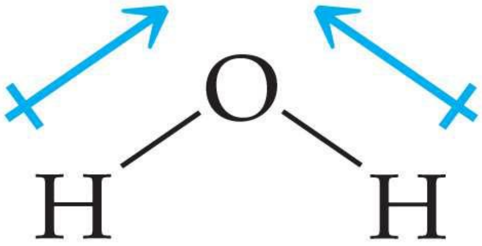
  Note:

  If you find yourself in a physics course, be prepared to reverse this “pictorial” convention of chemists. In physics and physical chemistry, dipole “arrow” goes in the opposite direction.

Consider water (H_2O):

- Each *bond* is polar
- Water has two dipole moments that do not cancel, and the *molecule* is polar.





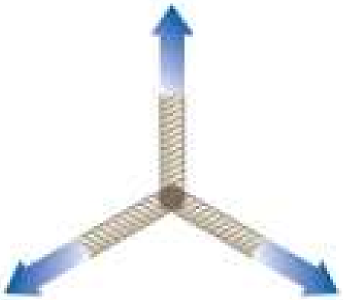
Polar Bonds and Polar Molecules

TABLE 10.3 Common Cases of Adding Dipole Moments to Determine Whether a Molecule Is Polar

Nonpolar

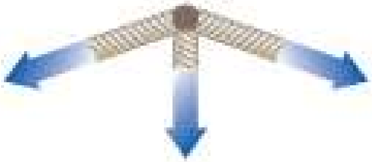
Two identical polar bonds pointing in opposite directions will cancel. The molecule is nonpolar.

Nonpolar



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

Polar

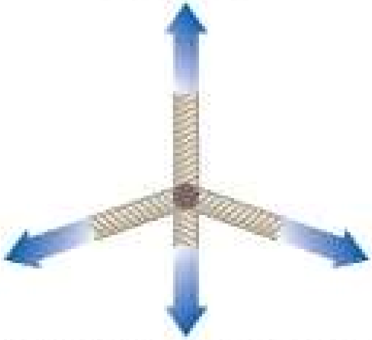


Three polar bonds in a trigonal pyramidal arrangement (109.5°) will not cancel. The molecule is polar.

Polar

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

Nonpolar



Four identical polar bonds in a tetrahedral arrangement (109.5° from each other) will cancel. The molecule is nonpolar.

Note: In all cases where the polar bonds cancel, the bonds are assumed to be identical.
If one or more of the bonds are different than the other(s), the bonds will not cancel and the molecule is polar.

Molecular polarity is ultimately due to breaking of symmetry

If the molecule is asymmetric (lopsided) → polar

If you can tell, by inspection, that the molecule is lopsided, great!

If not, you can still use a couple of shortcuts at this level.

But they should not be relied upon if the central atom exceeds the octet!

Shortcuts to determine molecular polarity

The molecule is polar (asymmetric) if:

- If the central atom has one or more lone pairs

  e.g. H_2O, SO_2

- If there is more than one kind of peripheral atom

  e.g. CH_3Cl, CH_2O, HCN

IMPORTANT:

These shortcuts for polarity are not reliable when the central atom exceeds the octet (will be covered in General Chemistry)

Practice:
Check your solution on next page

CF_4

Find:

- Lewis structure
- Electronic geometry
- Molecular geometry
  - including bond angle(s)
- Indicate polar or non-polar

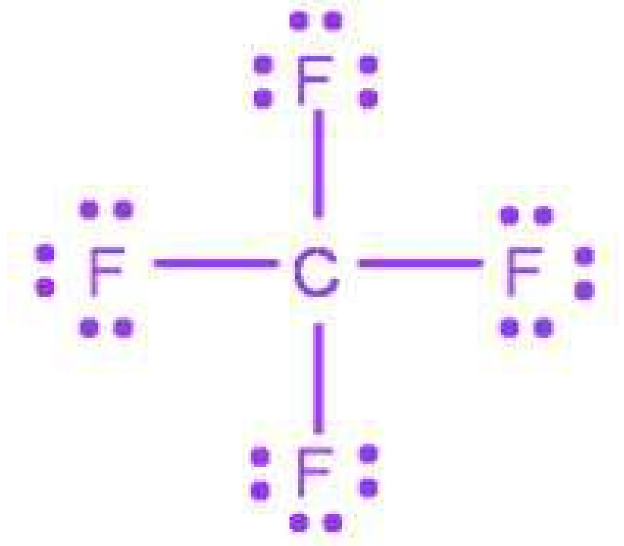
CF_4

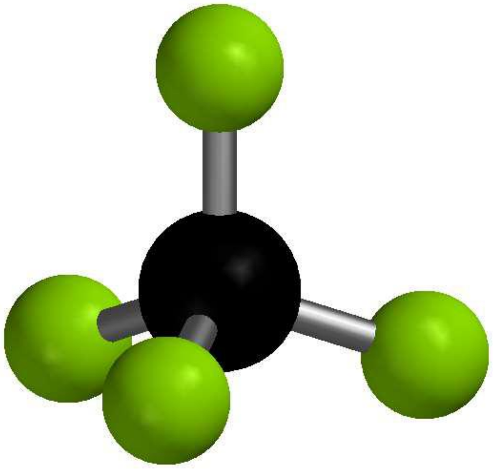
Electronic geometry: Tetrahedral

Molecular geometry: Tetrahedral

bond angles = 109.5°

Polar Bonds but non-polar molecule





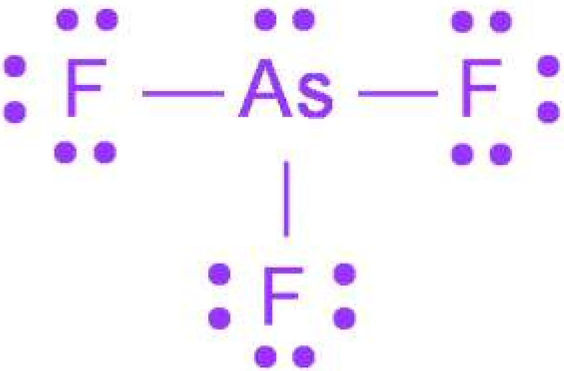
Practice:
Check your solution on next page

AsF_3

Find:

- Lewis structure
- Electronic geometry
- Molecular geometry
  - including bond angle(s)
- Indicate polar or non-polar

AsF$_3$



Electronic geometry: Tetrahedral

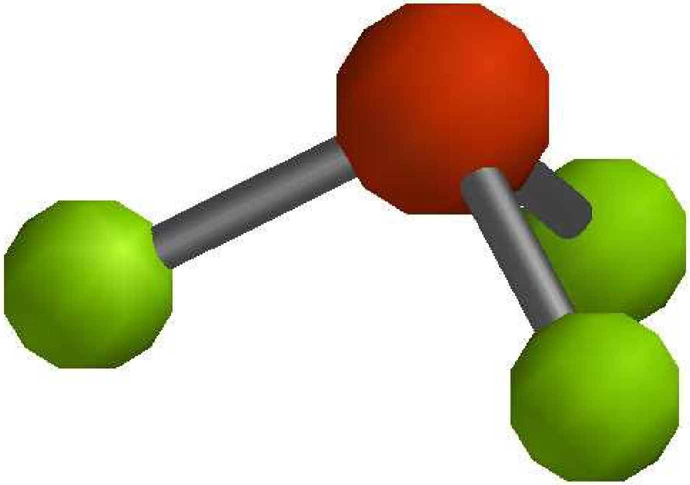
Molecular geometry:Trigonal pyramidal

bond angles = 109.5° (ideal)

< 109.5° (actual)

-- because lone pair takes up more space

Polar molecule



Practice:
Check your solution on next page

BF_3

Find:

- Lewis structure
- Electronic geometry
- Molecular geometry
  - including bond angle(s)
- Indicate polar or non-polar

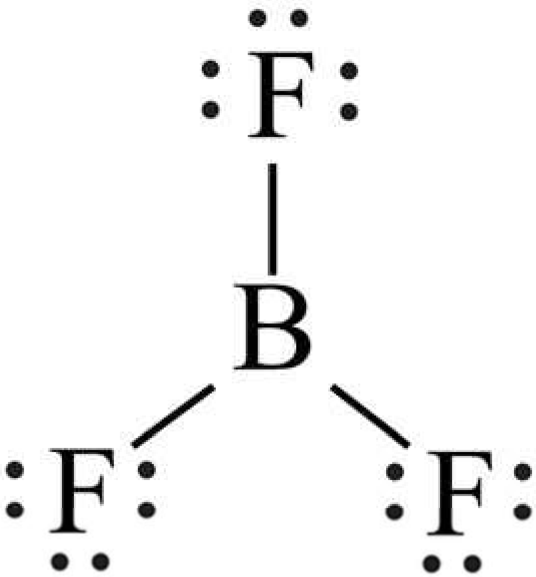
BF_3

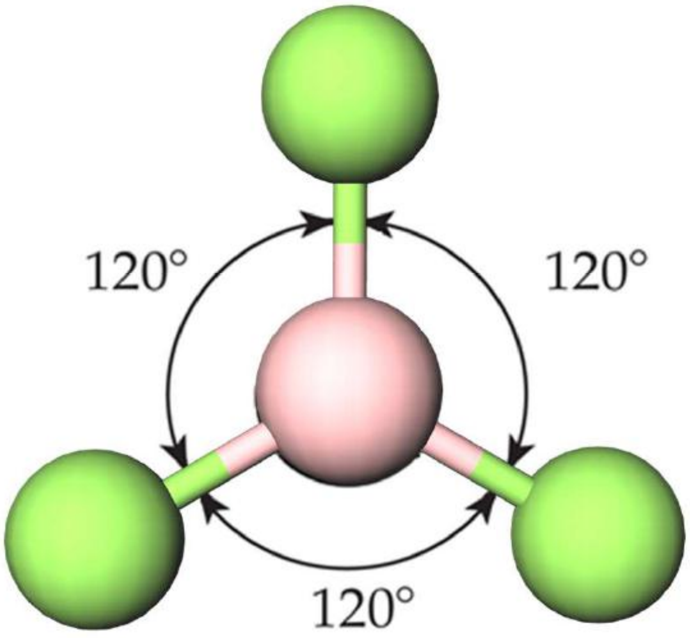
Electronic geometry: Trigonal planar

Molecular geometry: Trigonal planar

bond angles = 120°

Non-polar molecule





Practice:
Check your solution on next page

SO_2

Find:

- Lewis structure
- Electronic geometry
- Molecular geometry
  - including bond angle(s)
- Indicate polar or non-polar

SO_2

Electronic geometry: Trigonal Planar

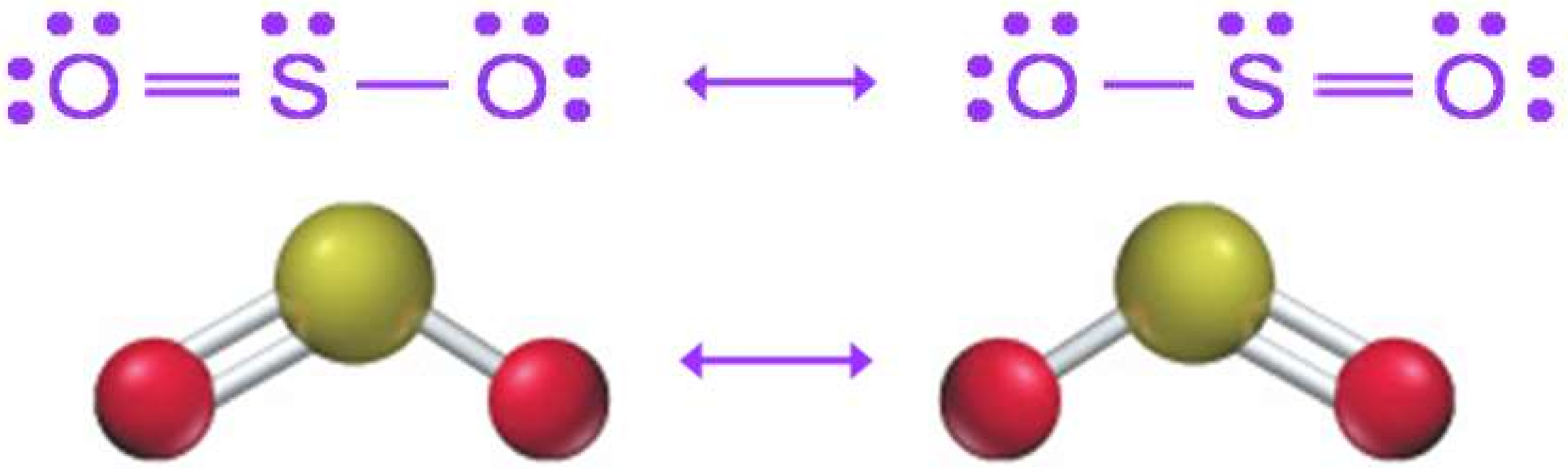
Molecular geometry: Bent

Ideal bond angle = 120°

Actual bond angle < 120°

-- because the lone pair takes up more space

Polar molecule



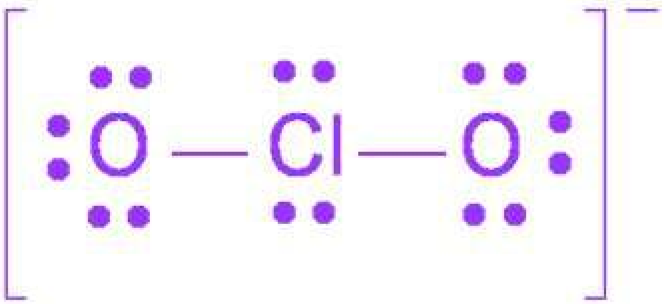
Practice:
Check your solution on next page

ClO_2^-

Find:

- Lewis structure
- Electronic geometry
- Molecular geometry
  - including bond angle(s)
- Indicate symmetric or asymmetric
  - An ion’s charge makes it behave much more polar than even the most polar neutral molecule, regardless of whether the ion has a dipole or not (dissolves in polar liquids, does not dissolve in non-polar liquids, etc) so we are asking about the symmetry instead of polarity

ClO_2^-



Electronic geometry: Tetrahedral

Molecular geometry: Bent

Ideal bond angle = 109.5°

Actual bond angle< 109.5°

-- because the lone pairs take up more space

Asymmetric