Chapter 8

Bonding: General Concepts

What is a "Chemical Bond"?

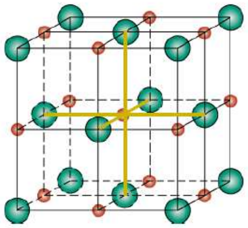
A "strong" attractive force between atoms

How strong is "strong"?

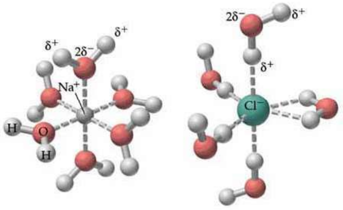
- Strong enough to stop the "bonded" atoms from moving away completely when agitated by thermal motion
- Strong enough to compete with attractions to <u>other</u> atoms

An attraction is not much of a bond if it cannot compete with other forces, regardless of how strong it is.

To be a "bond", it needs to be the dominant force between the atoms.



An atom can be bonded to more than one atom at the same time, but each bond <u>remains intact</u> over time.
Na$^+$ is bonded to 6 Cl$^-$ ions (and each Cl$^-$ to 6 Na$^+$) in a NaCl crystal.



In solution, the force between Na$^+$ and Cl$^-$ is overwhelmed by the forces between the ions and the water molecules, and there is no "bond" between Na$^+$ and Cl$^-$. They diffuse away from each other.

Any attractive force represents a lowered energy (more stability), whether it is a bond or not.

So, it's definitely true that:
Atoms in a bond have lower energy compared with the same atoms separated from each other.

It may not be the strongest, lowest-energy bond an atom could make, but each atom has lower energy than when it is alone.

While we used ions to introduce the concept of bonding, and what distinguishes it from ordinary attraction, it's only one of the possible modes of bonding.

A useful way to classify chemical bonds

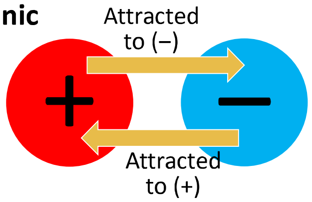
Ionic

- Due to the electrostatic attraction between a cation (+) and an anion (–).
- No sharing of electrons

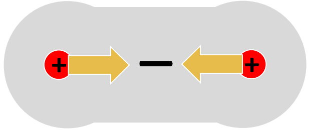
Covalent

- Due to the attraction of the nuclei of two atoms to a higher density of electrons between them (therefore "shared" by both atoms.)

Ionic



Covalent



Each nucleus attracted to extra electron density

What about intermediate cases?

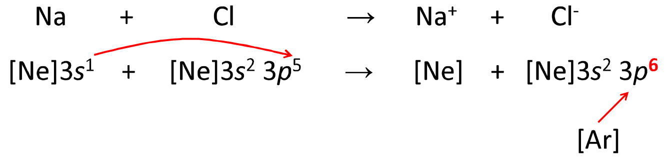
- Most bonds actually fall somewhere in between
- Still , classifying bonds as "ionic" or "covalent" is very useful

We will not consider other kinds of bonding that cannot be easily understood in terms of these two modes 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.



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

$$[\mathrm{Ne}]3s^1 + [\mathrm{Ne}]3s^2\,3p^5 \rightarrow [\mathrm{Ne}] + [\mathrm{Ne}]3s^2\,3p^6$$

[Ar]

But:

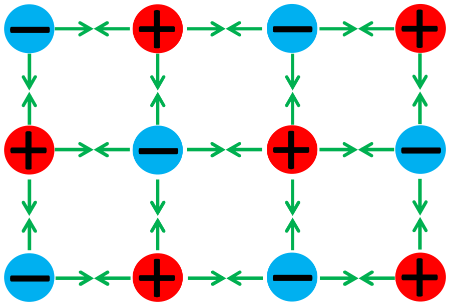
The ionic bond doesn't need to be formed as a result of a direct transfer of an electron between two atoms.

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.

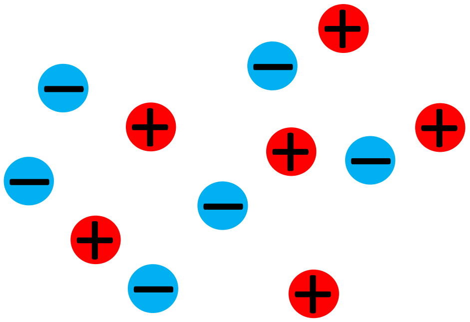
They lead to "ionic compounds".

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

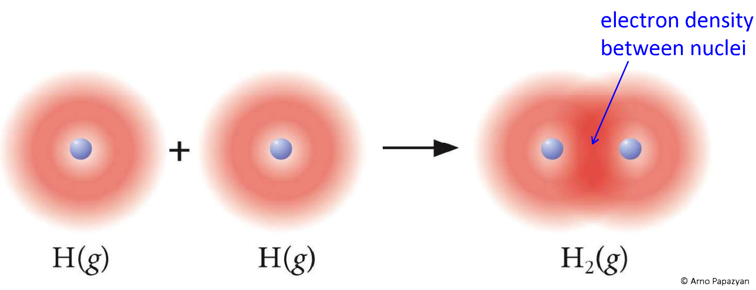
Another way two atoms can be more stable together than apart is by offering the valence electrons the chance to spend more time between the nuclei.

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.

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.



If the atoms are pressed closer, the electrons would be squeezed out and the nuclei would repel each other, making the system less stable.

If the atoms are farther than the "bond length", potential energy of the electrons are higher.

The energy it takes to pull the atoms from "bond length" to completely apart is called "bond dissociation energy".

Polar covalent bonds and Electronegativity

We learned earlier that some elements "like" electrons more than others, as indicated by their larger ionization energy or electron affinity.

- It costs more to remove an electron from them
- More energy is released when an electron is added to 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.

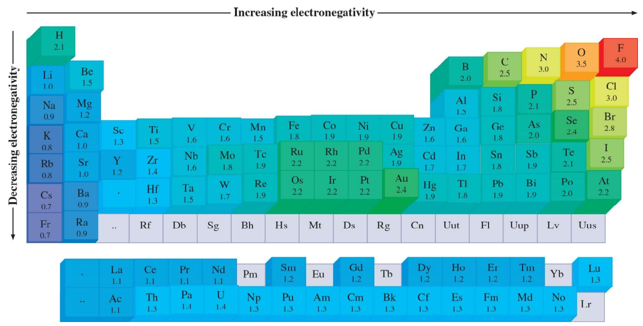
The tendency of a **bonded atom** to <u>attract electrons</u> towards itself is called **"electronegativity"**.

One intuitive way to define electronegativity for an element is to average the ionization energy and electron affinity (which measure how much it "likes" electrons)

- and then scale the set of numbers obtained for all elements appropriately.

That is different from how Linus Pauling* defined it, but that's ok; there are many ways to define the idea of electronegativity mathematically.

*Linus Pauling was a famous Nobel laurate chemist



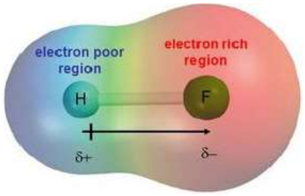
Not surprisingly, electronegativity increases from left to right and from bottom to top in the periodic table, following the **same trend as ionization energy and electron affinity**.

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

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"

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".

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 covalent bonds.

Electronegativity Difference ↑

Bond Polarity ↑

Example

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

Electronegativity differences:

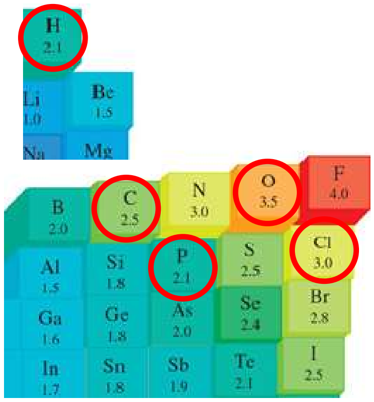
P—H 2.1 – 2.1 = 0

H—O 3.5 – 2.1 = 1.4

C—Cl 3.0 – 2.5 = 0.5

Bond polarities:

P—H < C—Cl < H—O



To compare the polarities of bonds

- We don't always need the exact electronegativity values
- We don't need the exact values of electronegativity differences
- We can use the relative locations in the periodic table
- The farther the two elements are from each other in the direction from the top-right corner (high electronegativity) of the periodic table to the bottom left (low electronegatiovity), the more polar the bond will be

P is to the left of Cl

⇨ Lower EN than Cl

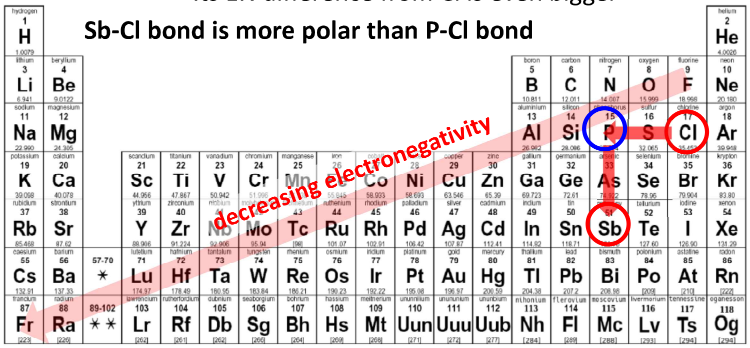
Sb is as far to the left of Cl as P is

But it is also lower

⇨ Its EN is even lower than that of P

⇨ Its EN difference from Cl is even bigger

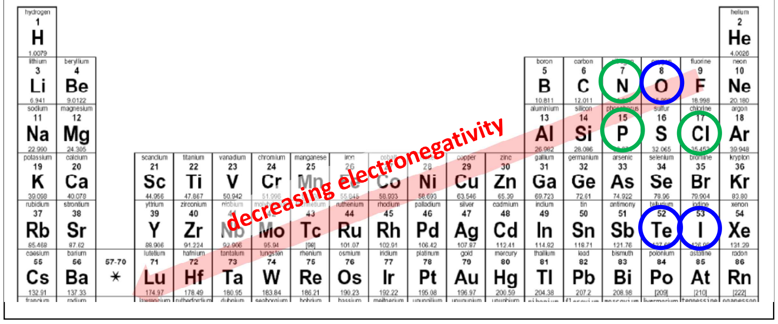
Sb-Cl bond is more polar than P-Cl bond



When we are using just the periodic table, we will avoid cases when the relative electronegativities are ambiguous.

N being higher than P in the periodic table makes its EN go up, and be closer to that of Cl.

But O is so much higher (both in position and electronegativity) than Te that EN difference between O and I is greater than between Te and I (O is a lot more electronegative than I)



In cases when it's too difficult to use the periodic table to compare electronegativities, we can use a table of electronegativities.

- But be aware that there is no precise relationship between electronegativity difference and bond polarity
- Even equal electronegativities can go with a nontrivial bond polarity
- Purely quantum mechanical factors can be as important as electronegativity difference

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Pick the more polar bond:

O—F 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.

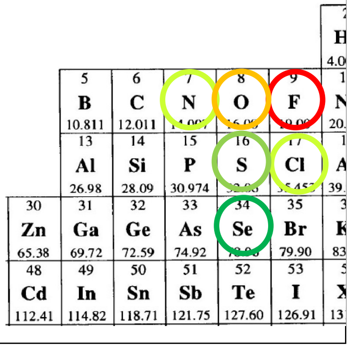
S—Cl Se—Cl

S is less electronegative than Cl.

Se is below S in the samegroup,

so it has even lower EN.

Se and Cl have a larger EN difference.



Polarization creates a "dipole moment"

- Larger the separated charges, larger the dipole moment
- Farther the separation, larger the dipole moment

We use an arrow to represent a dipole moment.

- Tail of the arrow at the positive center of charge.
- Point to the negative charge center

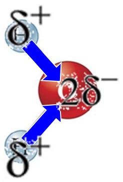
"Chemist's dipole"

Unfortunately the opposite of the convention used in Physics, or by whomever does any actual calculations with dipoles 😏

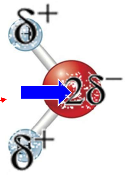
Bond polarity and molecular polarity

- A molecule cannot be polar without polar bonds
- But the presence of polar bonds doesn't guarantee that the molecule is polar because bond dipoles can cancel out
- If the bond dipoles of the polar bonds cancel then the molecule is non-polar. Otherwise it's polar.

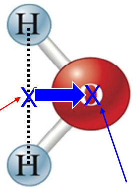
Water molecule has a net dipole moment



Bond dipoles don't cancel, and add up to a net molecular dipole



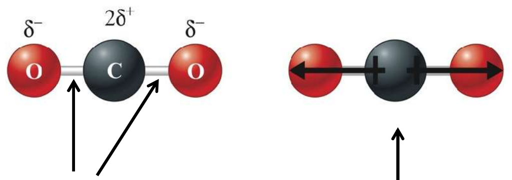
Put another way:
Average locations of the δ⁻ and δ⁺ charges do not coincide.



Average location of (+) charges

Average location of (-) charges

CO_2 has no net dipole moment because its bond dipoles cancel each other



Polar bonds

but nonpolar molecule

- Average locations of the δ⁻ and δ⁺ charges coincide.
- If the molecule was bent like the water molecule, they wouldn't coincide, and the molecule would be polar

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Polar Molecules, Non-polar Molecules

- In practice, if a molecule's dipole moment is "small enough" it would be called "nonpolar"

But

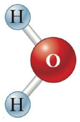
- For our purposes, we will call a molecule "nonpolar" only if its dipole moment is exactly zero
  - It's impractical to calculate the molecular dipole moment at this stage
  - But we can determine if the dipole moment is zero or not
- And we will call a molecule "polar" if its dipole moment is nonzero (no matter how small)

Molecular polarity and symmetry

A simple way to judge polarity:

Symmetric ⇒ Non-polar

Asymmetric (lopsided) ⇒ Polar



We learned that larger electronegativity difference between bonded atoms leads to more polarity in the bond

- If bond polarity is high enough, then the bond is "ionic"
- If not declared "ionic", we will call the bond "polar covalent" as long as there is an electronegativity difference between the bonded atoms

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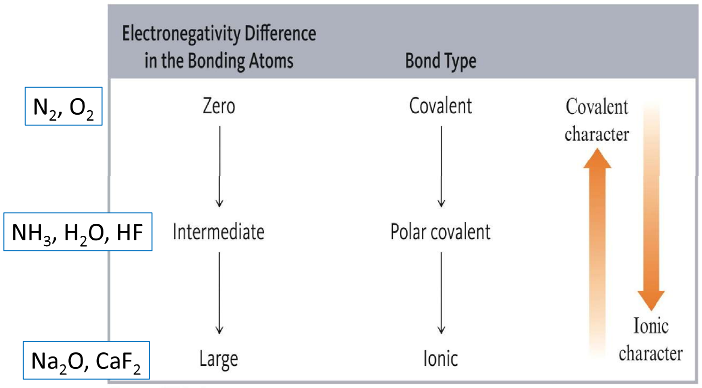
Electronegativity and Bond Type



	Electronegativity Difference in the Bonding Atoms	Bond Type	
N_2, O_2	Zero	Covalent	Covalent character
NH_3, H_2O, HF	Intermediate	Polar covalent	
Na_2O, CaF_2	Large	Ionic	Ionic character

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- 100% covalent bond is possible

  In <u>any diatomic molecule</u>, atoms share the bond electrons equally

- Even the largest electronegativity difference <u>cannot</u> give a 100% ionic bond

  CsF is less than 75% ionic

Simple general rule for binary compounds:

nonmetal-nonmetal bond: **Covalent**
Never ionic

metal-nonmetal bond*: **Ionic**

** In some cases it may be polar <u>covalent</u>*
But then we will be told that we have a <u>molecule</u>

Practice:

Arrange the following bonds from most to least polar:

a) N–F O–F C–F
b) C–F N–O Si–F
c) Cl–Cl B–Cl S–Cl

Practice:

Which of the following bonds in a binary compound would be the least polar yet still be considered polar covalent?

Mg–O C–O O–O Si–O [✓ N–O]

To be considered polar covalent, unequal sharing of electrons must still occur.
We choose the bond with the least difference in electronegativity, but still with some unequal sharing of electrons.

Practice:

Which of the following bonds would be the most polar without being considered ionic?

Mg–O C–O O–O [✓ Si–O] N–O

To not be considered ionic, the bond needs to be between two nonmetals.
The most polar bond between the nonmetals occurs with the bond that has the greatest difference in electronegativity.

Electron Configurations in Stable Compounds

Considering only compounds of <u>main-group elements</u>:

Covalent bond:

- Shared electrons fill up the valence shells of <u>both</u> atoms.
- Both atoms achieve the electron configuration of the <u>next</u> noble gas.

Ionic bond:

- The valence shell of the **nonmetal** achieves the electron configuration of the <u>next</u> *noble gas.*
- The valence shell of the **metal** is emptied, and it achieves the electron configuration of the <u>previous</u> *noble gas.*

In other words:

For <u>main group elements</u> (i.e. elements in the leftmost 2 and rightmost 6 columns of the periodic table; i.e. outside of transition block), <u>bond formation</u> almost always does this:

Attain the electron configuration of the <u>closest noble gas</u>.

This is true both for ionic and covalent bonds.

Bond lengths and bond strengths

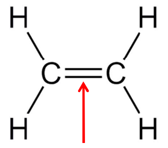
Many factors contribute to bond strength, or whether a bond forms at all, but:

- <u>All else being equal</u>, <u>shorter</u> bond length goes with <u>stronger</u> bond
- Both for covalent and ionic bonds, the sizes of the atoms (or ions) making the bond limit how short the bond can be.
  - Therefore how strong the bond can be
- When the bond is made by large atoms (or ions):
  - ➢Shared electrons can't be very close to the nuclei
  - ➢Ions can't get close to each other

Bond lengths, strengths, and multiple covalent bonding

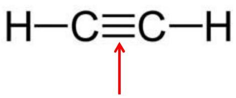
Just as we can have an ionic bond between multiply charged cations and anions (e.g. MgO where we have Mg^{2+} and O^{2-}, or AlN where we have Al^{3+} and N^{3-}), we can have multiple covalent bonds between two atoms.

Covalent bonds are shown as lines between atoms, and 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

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Bond lengths, strengths, and multiple covalent bonding

For a bond between a given pair of atoms:

Single	<	Double	<	Triple
weakest				strongest

which is intuitive.

But we also have:

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.

We will come back to covalent bonding later.

But first, we will study ionic bonding in more detail

Isoelectronic Series

A series of ions/atoms containing the same number of electrons.

For example:

O^{2-}, F^{-}, Ne, Na^{+}, Mg^{2+}, Al^{3+}

Consider what happens to the number of electrons when we form the ions above, and how they would compare with Ne.

Now think of other isoelectronic series. Write a few of them.

Practice:

Choose an alkali metal, an alkaline earth metal, a noble gas, and a halogen so that they constitute an isoelectronic series when the metals and halogen are written as their most stable ions.

- What is the electron configuration for each species?
- Determine the number of electrons for each species.
- Determine the number of protons for each species.

One example could be:
Cl^{-}, Ar, K^{+}, Ca^{2+}

- The electron configuration for each species is $1s^2 2s^2 2p^6 3s^2 3p^6$.
- The number of electrons for each species is 18.
- Cl^{-} has 17 protons, Ar has 18 protons, K^{+} has 19 protons, Ca^{2+} has 20 protons

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Why think about isoelectronic series?

Same number and configuration of electrons

Increasing number of protons (increasing nuclear charge)

We can easily guess how their sizes vary!

For example:

	O^{2-}	F^{-}	Ne	Na^{+}	Mg^{2+}	Al^{3+}	all have 10 electrons
Z:	8	9	10	11	12	13	

Increasing nuclear charge →

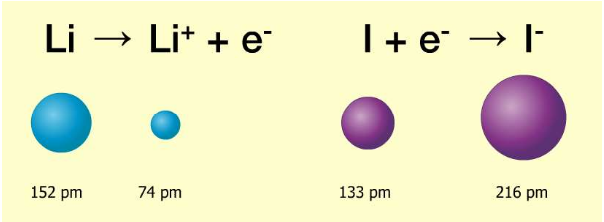
Decreasing radius →

We will be considering the energetics of ionic bonds and ionic compounds for a while here, and ion sizes are important in that regard, as we indicated earlier.

So, understanding isoelectronic series helps.

But we need to study the periodic trends of ionic radii more directly as well.

Ionic Radii



Cations are smaller than the parent atom

- because the valence shell is lost

Anions are larger than the parent atom

- because the extra electron-electron repulsion makes the valence shell puff up

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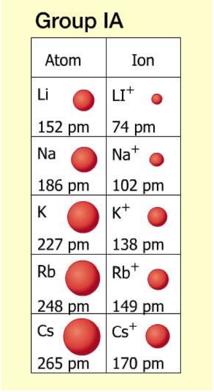
Ionic Radii



Group IA

Atom	Ion
Li 152 pm	Li^{+} 74 pm
Na 186 pm	Na^{+} 102 pm
K 227 pm	K^{+} 138 pm
Rb 248 pm	Rb^{+} 149 pm
Cs 265 pm	Cs^{+} 170 pm

- Ionic radius increases as we go down in a group,
  - — Just like the atomic radius for the neutral atoms of elements
- Each period has one more shell than the previous one, making the ion larger than the one above it in the same group
  - — Just like the atomic radius for the neutral atoms of elements

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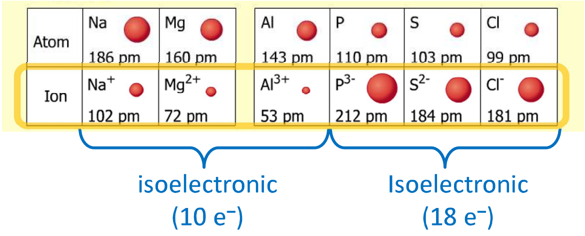
Ionic Radii

Period 3



Atom	Na 186 pm	Mg 160 pm	Al 143 pm	P 110 pm	S 103 pm	Cl 99 pm
Ion	Na^{+} 102 pm	Mg^{2+} 72 pm	Al^{3+} 53 pm	P^{3-} 212 pm	S^{2-} 184 pm	Cl^{-} 181 pm

Considering cations and anions **separately**:

- Ionic radius decreases across a period
- There is a big jump in ionic radius between the last metal cation in the period and the first non-metal anion

Changes in energy when an ionic compound is made

- If we bring cations and anions together into a lattice, the electrostatic attraction between (+) and (-) charges leads to a “favorable” (i.e. low energy) configuration.
  This releases energy from the system.
- That change in the energy of the system is called:
  “lattice energy”

Strength of ionic attractions in the crystal

A measure of ionic bond strength

The conceptual process involving lattice energy

Initial state:

Ions (already formed) **infinitely separated** ← i.e. in the gas phase

$E_{initial} = 0$ ← Zero, because ions can’t sense one another

Final state:

Ions in the actual crystal lattice

E_{final} = Lattice Energy ← A large negative energy

$\Delta E = E_{final} - E_{initial}$

= (Lattice Energy) – 0

= Lattice Energy

+/- attraction leads to low energy, going lower from zero means a large negative value

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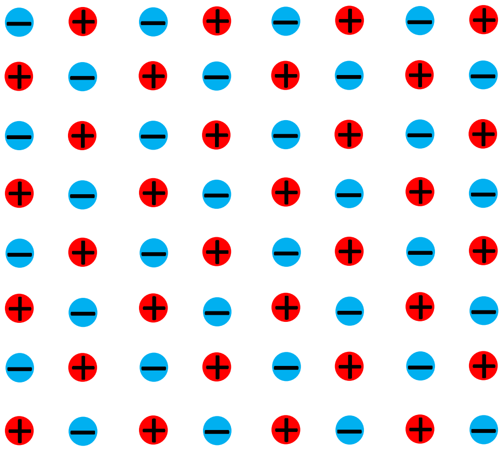
Cations and anions are brought from “infinite separation” (i.e. gas phase) to their positions in the crystal lattice



Lattice Energy

The change in energy that takes place when separated gaseous ions are packed together to form an ionic solid.

$$\text{Lattice energy} = k\left(\frac{Q_1 Q_2}{r}\right)$$

k = proportionality constant*

Q_1 = cation charge Q_2 = anion charge

r = shortest distance between the centers of cations and anions

We will only use this formula as a guide to **compare** the lattice energy (L.E.) of different ionic compounds

* k depends on the crystal type, but we can ignore its variation for the kinds of comparisons we will make

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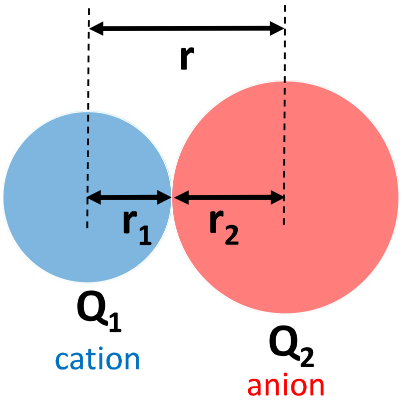
$$r \approx r_{cation} + r_{anion}$$



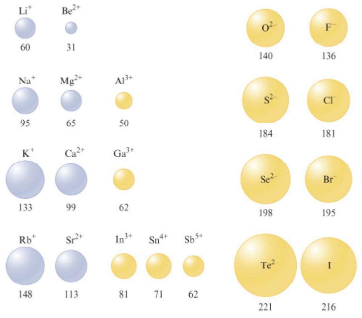
$$k\left(\frac{Q_1 Q_2}{r}\right)$$

$r \approx r_{cation} + r_{anion}$

We can compare r for different ionic compounds, if we know the ionic radii

For given value of $(Q_1 \cdot Q_2)$

We can guess which crystal has the higher lattice energy



We often don’t need the exact ionic radii.

Just knowing the trends is enough.

For comparing lattice energies:

- Ionic charges Q_1 and Q_2 are more important than r.
- First check which compound has larger/smaller $Q_1 \cdot Q_2$
- **r** becomes important only for a given value of $Q_1 \cdot Q_2$

More important than r

$$k\left(\frac{\boxed{Q_1Q_2}}{r}\right)$$

important only when $Q_1 \cdot Q_2$ is the same for both compounds

---

Practice

Which compound has larger lattice energy, CaO or CaS?

For both compounds $Q_1 \cdot Q_2 = (+2)(-2) = -4$

So we focus on the relative values of r

So we consider the ionic radii

The cation (Ca^{2+}) is the same for both compounds

So we compare the radii of O^{2-} and S^{2-}

O^{2-} is smaller than S^{2-}

$r_{CaO} < r_{CaS}$

Therefore:

CaO has larger lattice energy

Practice

Which compound has larger lattice energy, Na_2O or MgO?

$Q_1 \cdot Q_2$ is different for the two compounds

$Q_1 \cdot Q_2$ (for Na_2O) = $(+1)(-2) = -2$

$Q_1 \cdot Q_2$ (for MgO) = $(+2)(-2) = -4$

So, we don't worry about the ionic sizes because

$|Q_1 \cdot Q_2|_{MgO} \neq |Q_1 \cdot Q_2|_{Na2O}$

$|Q_1 \cdot Q_2|_{MgO} > |Q_1 \cdot Q_2|_{Na2O}$

Therefore:

MgO has larger lattice energy

So far, we have just compared lattice energies …

But there is a way to calculate lattice energies without using the formula $k\left(\frac{Q_1Q_2}{r}\right)$

We can use Hess's Law ….

"Born-Haber Cycle"

The formation reaction of a binary ionic compound from **solid metal** and the **nonmetal element** is deconstructed into little steps.

- The last of these steps involves lattice energy.
- We normally know the ΔE (or ΔH, the two are close enough for our purposes) for the overall formation reaction and all the steps except for **lattice energy**
- We can then solve for the lattice energy

Steps in the formation of an ionic solid from elements

Sublimation of the solid metal

$M(s) \rightarrow M(g)$ [endothermic]

Ionization of the metal atoms

$M(g) \rightarrow M^+(g) + e^-$ [endothermic]

Dissociation of the nonmetal

$\frac{1}{2} X_2(g) \rightarrow X(g)$ [endothermic]

Creation of nonmetal anions in the gas phase

$X(g) + e^- \rightarrow X^-(g)$ [usually exothermic]

Creation of the solid ionic compound from gas-phase ions

$M^+(g) + X^-(g) \rightarrow MX(s)$ [very exothermic]

Lattice energy

Born-Haber cycle for the formation of LiF

Process	**Energy Change** (kJ)
$Li(s) \rightarrow Li(g)$	161
$Li(g) \rightarrow Li^+(g) + e^-$	520
$\frac{1}{2}F_2(g) \rightarrow F(g)$	77
$F(g) + e^- \rightarrow F^-(g)$	−328
$Li^+(g) + F^-(g) \rightarrow LiF(s)$	Lattice energy (LE)
Overall: $Li(s) + \frac{1}{2}F_2(g) \rightarrow LiF(s)$	−617 kJ (per mole of LiF)

161 + 520. + 77 + (-328) + **LE** = -617

LE = -1047 kJ

<u>“Sublimation of the solid metal”</u>

can instead be called “Formation reaction of M(*g*)”

$M(s) \longrightarrow M(g) \qquad \Delta H = \Delta H_{f,M(g)}$

<u>“Dissociation of the nonmetal”</u>

(also the formation reaction of X(g))

$\frac{1}{2} X_2(g) \longrightarrow X(g) \qquad \Delta H = \Delta H_{f,X(g)}$

can instead be given in the form of:

Bond dissociation of X_2

$X_2(g) \longrightarrow 2X(g) \qquad \Delta H = D_{X\text{-}X}$

Bond Enthalpies (Bond Energies)

“Bond Energy” and “Bond ethalpy” often used interchangeably

It’s the energy needed to **break** a bond

Also known as “<u>bond **dissociation** energy</u>”

To <u>**break**</u> bonds:

Energy must be *added* to the system

Endothermic

To <u>**form**</u> bonds:

energy is *released*

Exothermic

A small bond enthalpy (BE) means:

- The bond is relatively weak.
- The bond released little energy when formed.
- The atoms forming the bond did not reduce their energy much.
- The atoms are relatively high in energy.

A large bond enthalpy (BE) means:

- The bond is relatively strong.
- The bond released a lot of energy when formed.
- The atoms forming the bond reduced their energy by a lot.
- The atoms are relatively low in energy.

If a reaction breaks weak bonds (small BE) and forms strong bonds (large BE):

- The energy released by forming strong bonds is larger than the energy needed to break the weak bonds.
- There will be a net energy release as a result.
- **Exothermic** reaction.

If a reaction breaks strong bonds (large BE) and forms weak bonds (small BE):

- The energy released by forming weak bonds is less than the energy needed to break the strong bonds.
- There will be a net energy absorption as a result.
- **Endothermic** reaction.

Calculating Δ*H* from Bond Enthalpies

$$\Delta H_{rxn} = \left(\begin{array}{c}\text{Sum of}\\ \text{broken}\\ \text{bonds' BEs}\end{array}\right) - \left(\begin{array}{c}\text{Sum of}\\ \text{formed}\\ \text{bonds' BEs}\end{array}\right)$$

$$\Delta H_{rxn} = \begin{pmatrix}\text{Sum of}\\ \text{broken}\\ \text{bonds' BEs}\end{pmatrix} - \begin{pmatrix}\text{Sum of}\\ \text{formed}\\ \text{bonds' BEs}\end{pmatrix}$$

This is **approximate** when we use a **table of "generic" BE values** for a particular type of bond (e.g. C—C, C=C, C—O, C=O, etc.)

- For example the C=O bond would have a different BE in CO_2 versus in an organic molecule.
- Its exact BE would depend on the order in which bonds are broken in a molecule.
  - Knowing the exact BE of a particular bond, independent of other bonds in the molecule is impossible
- **BE has to be an "average" value**, so it's **not exact** for any given compound.

$$\Delta H_{rxn} = \begin{pmatrix}\text{Sum of}\\ \text{broken}\\ \text{bonds' BEs}\end{pmatrix} - \begin{pmatrix}\text{Sum of}\\ \text{formed}\\ \text{bonds' BEs}\end{pmatrix}$$

Also note that this relationship is only applicable to gas phase reactions.

Solvent's interaction with the entire molecule complicates things

---

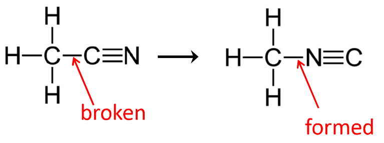
- Figuring out the bonds broken and the bonds formed can be an error-prone process
- Instead, we can simply sum over **all** the bonds in the reactants and do the same for products. Bonds that remain intact during the reaction will appear in both sums and will cancel out
- More numbers to add, but less attention is required, less error-prone

$$\Delta H_{rxn} = \begin{pmatrix}\text{Sum of}\\ \text{bond BEs in}\\ \text{reactants}\end{pmatrix} - \begin{pmatrix}\text{Sum of}\\ \text{bond BEs in}\\ \text{products}\end{pmatrix}$$

Caution: This subtraction is in the opposite order compared with the formula for obtaining ΔH_{rxn} from ΔH_f values.

Example

Predict ΔH for the following reaction in the gas phase:



	Bond Enthalpy (kJ/mol)
C–H	413
C–N	305
C–C	347
C ≡ N	891

ΔH = [347] – [305] = **42 kJ** (BE of broken bond) – (BE of formed bond)

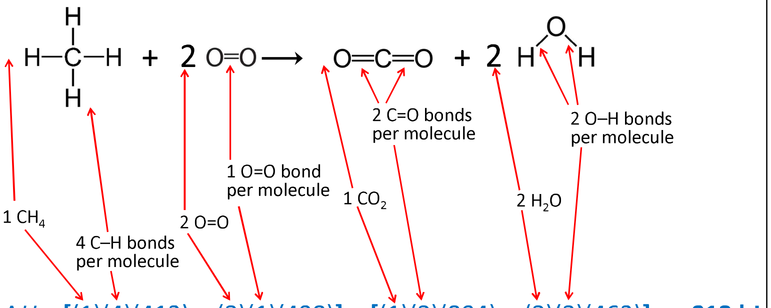
Or, if we don't want to spot the broken and formed bonds, we can subtract the sum of all BEs in reactants from the sum of all BEs in products

ΔH = [3(413) + 347 + 891] – [3(413) + 305 + 891] = **42 kJ**

Example

	Bond Enthalpy (kJ/mol)
C–H	413
O=O	498
C=O	804
O–H	463

Predict ΔH for the following gas-phase reaction:



$$\Delta H = [(1)(4)\underset{\text{C–H}}{(413)} + (2)(1)\underset{\text{O=O}}{(498)}] - [(1)(2)\underset{\text{C=O}}{(804)} + (2)(2)\underset{\text{O–H}}{(463)}] = \mathbf{-812\ kJ}$$

Modeling Bonding

- The reality of what keeps atoms in compounds together is complex.
- But it would be wasteful, impractical, and to solve the quantum mechanical equations every time we ask a question about molecules.
- The complexity can be reduced by using models that are good enough to be useful and simple enough to think about compounds and molecules in an intuitive, tangible way.

Localized Electron Model

In this model:

- A molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms.
- But we still consider the electrons as contributing to the valence shell of individual atoms, rather than to the entire molecule (or the polyatomic ion)

Basically a fancy name for constructing Lewis Structures to understand and predict covalent bonding and associated electron distribution.

Localized Electron Model does three things:

1. Description of valence electron arrangement (Lewis structure).
   Only 2-dimensional description here.
2. Description of atomic orbital types used by atoms to share electrons or hold lone pairs.
   What happens to atomic orbitals when they form bonds
3. Prediction of geometry (via the VSEPR model)
   3-Dimensional description of molecular structure
   - ➢ *We will see it at the end of this chapter*

Lewis Structures

A simple and surprisingly powerful way to do "quantum chemistry" for molecules and polyatomic ions

Uses the "**Octet Rule**":

Each atom in a covalently bonded entity "wants":

8 electrons (an "octet") in its valence shell

(except for H, which always gets 2 electrons)

Octet rule is applied through electron **pairs**

Valence electron <u>pairs</u> making octets everywhere

- Each atom has 4 pairs of electrons, making an "octet"
  - ➢ Hydrogen attains only one pair (a "duet")
- Each bond is a pair of electrons ("bonding pair")
- Non-bonding electrons also form pairs ("lone pair")
- Exceptions to the "octet rule" exist, and can be handled

<u>General steps for writing Lewis structures:</u>

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.
6. Admire your work. You just did "quantum chemistry" in a very quick way that is unfairly powerful!

A couple of terms to clarify

<u>"Central atom"</u>

- The atom at the center of the molecule or ion
- In some cases there may be more than one "central atom", and we treat each one the same way
- They may violate the octet rule

<u>"Peripheral atoms"</u>

- Atoms bonded to the central atom
- They don't violate octet rule

Step 1: Calculate the number of valence electrons

- Sum up the valence electrons brought by each atom
- Subtract the charge (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

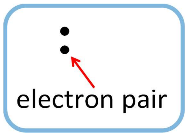
H—O—H   H is never central

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



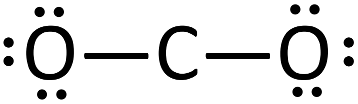
- By putting enough lone pairs on each atom
- Start with peripheral atoms
- Put remaining (if any) pairs on the central atom

Example: CO_2

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

2 pairs used for 2 bonds.

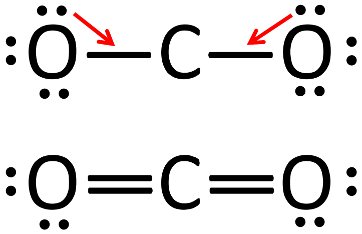
6 pairs remaining



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

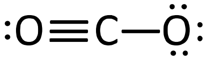
- Keep bonding as symmetric as possible

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
↑ central ↑ central ↑ central

"Rules of thumb" for Lewis structures

If there are single atoms of more than one element,

- the "more metallic" one is likely the central atom

e.g. $COCl_2$ — ↑ central (more "metallic" than O)
HCN — ↑ central (more "metallic" than N)
CFClBrI — ↑ central (more "metallic" than halogens)

Carbon is often the central atom when it occurs in the molecule or the ion, since it is the most "metallic" of the common nonmetals

"Rules of thumb" for Lewis structures

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.

Even if the formula isn't written symmetrically, symmetric structures are often favored in nature.

First see if you can draw a symmetric skeletal structure before attempting asymmetric ones.

"Rules of thumb" for Lewis structures

- 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^-)
- Carbon never violates the octet rule
  - It may have an incomplete octet in a reactive cation or a radical, but you should give it an incomplete octet only if absolutely must

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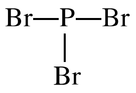
Example: Lewis structure for PBr_3

No. of valence e^- = (1)(5) + (3)(7) = **26** (**13** pairs)

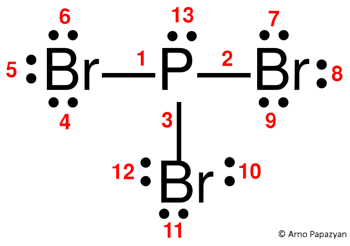
P Br

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

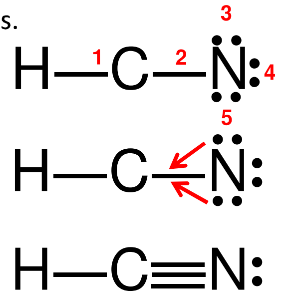
No. of valence e^- = (1)(1) + (1)(4) + (1)(5) = **10** (**5** pairs)

H C N

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 here 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

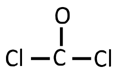


Example: Lewis structure for $COCl_2$

No. of valence e^- = (1)(4) + (1)(6) + (2)(7) = **24** (**12** pairs)

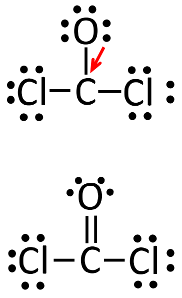
C O Cl

Skeleton structure:



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

- Skeletal bonds here 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

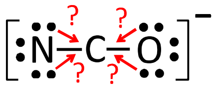


Example: Lewis structure for the cyanate ion, NCO^-

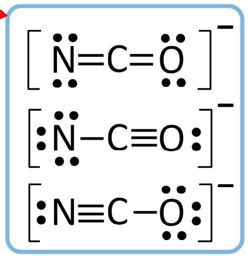
No. of valence e^- = (1)(5) + (1)(4) + (1)(6) –(-1) = **16** (**8** pairs)

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.

<u>We will learn to find the favorable Lewis structure later (using "formal charges").</u>

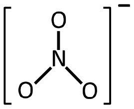
Lewis structures with different distributions of the extra bond(s) are called “resonance structures”

Delocalized Bonding

Consider the nitrate ion, NO_3^-

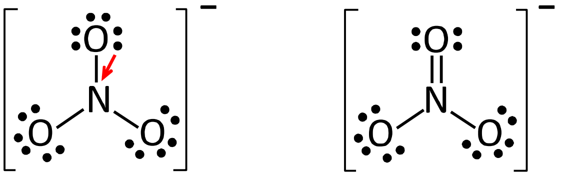
No. of valence e^- = (1)(5) + (3)(6) –(-1) = **24** (**12** pairs)

Skeleton structure:



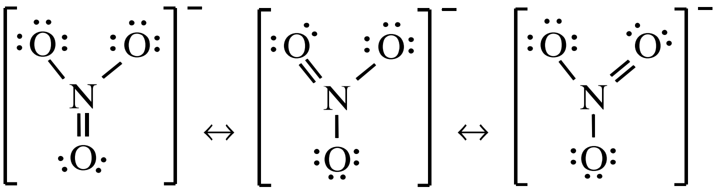
- Only one N atom
- N is the central atom

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**

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”
- Those electrons add to the bonding of more than one skeletal bond.
- The extra bonding they bring to each skeletal connection is only partial

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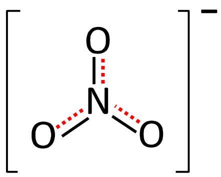
Actual structure is an <u>average</u> of the resonance structures.

The electrons in the extra bond are <u>**delocalized.**</u>



The “moving” bond is taking the place of a lone pair, which must also delocalize.

But it’s harder to show.

So we 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

Formal Charge

The charge an atom **would** have **if** electrons in bonds were shared **equally**.

Electronegativities are completely ignored.
(Exact opposite of the pretense in assigning oxidation numbers where each atom’s electronegativity was exaggerated as if each atom in a compound was an ion)

Formal charge is due to the **electron surplus or deficit** compared with the number of valence electrons in the non-bonded atom.

Even though formal charges aren't completely "real", they do have enough reality to give good guidance on the local charges of a covalent entity (molecule or a polyatomic ion).

They can explain the polarity of a bond you would expect to be nonpolar, or the non-polarity of a bond you would expect to be polar.

They are useful in developing intuition on the reaction mechanisms.

For example, if an atom has a positive formal charge, it may be "vulnerable to an attack" by an electron-rich reactant.

In calculating formal charges, we assume:

- Both electrons of a lone pair of an atom belong to that atom.
- Only one electron of a bond belongs to the atom.

Formal charges must add up to the net charge of the species.

Formal Charge = No. of valence e^- – number of e^- assigned to the atom

Formal Charge = No. of valence e^- – number of non-bonding e^- – number of bonds

(1 e^- per bond)

Formal Charge = Main Group # – 2 × number of lone pairs – number of bonds

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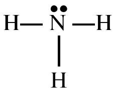
Formal Charge = Main Group # – 2 × number of lone pairs – number of bonds



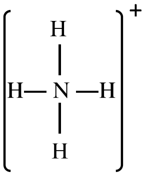
Formal charge of H = 1 – 0 – 1 = 0

Formal charge of N = 5 – 2 – 3 = 0

no. of valence e^-

no. of nonbonding e^-

1 e^- per bond



Formal charge of H = 1 – 0 – 1 = 0

Formal charge of N = 5 – 0 – 4 = +1

no. of valence e^-

no. of nonbonding e^-

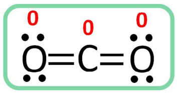
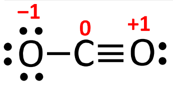
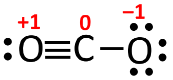
1 e^- per bond

Formal charges can be used to evaluate <u>nonequivalent</u> resonance structures.

In the preferred resonance structure:

- Formal charges should be as close to zero as possible.
- Formal charges match the atom's electronegativity
  (–) formal charge on the more electronegative atom
  (+) formal charge on the less electronegative atom

Let's go back to the non-equivalent resonance structures of CO_2

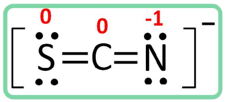
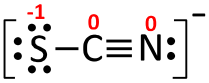
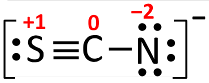
	Formal Charges		
	O	C	O
Most favorable Lewis structure  ✓ Smallest possible charges (all zero)	6-(2)(2)-2 = 0	4-(0)(2)-4 = 0	6-(2)(2)-2 = 0
 Total magnitude of charges is not minimized Also an O with a (+) charge	6-(3)(2)-1 = –1	4-(0)(2)-4 = 0	6-(1)(2)-3 = +1
 Total magnitude of charges is not minimized Also an O with a (+) charge	6-(1)(2)-3 = +1	4-(0)(2)-4 = 0	6-(3)(2)-1 = –1

Non-equivalent resonance structures of SCN^-

We will skip the derivation of the resonance structures.

As the annoying phrase in textbooks goes: "left as an exercise for the reader" 😉

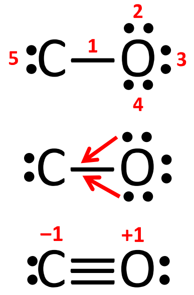
Formal Charges

	S	C	N
Most favorable Lewis structure  Smallest possible charge And (-) charge is on the most electronegative atom ✓	6-(2)(2)-2 = **0**	4-(0)(2)-4 = **0**	5-(2)(2)-2 = **−1**
 (-) charge is not on the most electronegative atom	6-(3)(2)-1 = **−1**	4-(0)(2)-4 = **0**	5-(1)(2)-3 = **0**
 Total magnitude of charges is not minimized	6-(1)(2)-3 = **+1**	4-(0)(2)-4 = **0**	5-(3)(2)-1 = **−2**

Sometimes unfavorable formal charges are the only option
Example: Lewis structure for carbon monoxide, CO

No. of valence e⁻ = (1)(4) + (1)(6) = **10** (**5** pairs)

C O



Formal charge of C = 4 – (1)(2) – (3) = −1

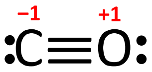
Formal charge of O = 6 – (1)(2) – (3) = +1

The only structure that satisfies the octet rule, but …

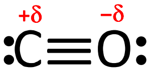
(-) charge is on the less electronegative atom

(+) charge is on the more electronegative atom

Formal charges explain why CO is actually a nonpolar molecule



Cancels the effect of electronegativity difference between C and O



CO bond in the actual CO molecule has practically zero polarity!

A shortcut for Formal Charges

- **If <u>not</u> violating the octet rule**

$$\text{Formal Charge} = \boxed{\text{number of bonds}} - \boxed{\text{number of bonds needed to complete octet}}$$

<u>Number of bonds needed to complete the octet</u>

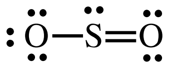
F, Cl, Br, I	(Group 7A)	8 – 7 = **1**
O, S, Se, Te	(Group 6A)	8 – 6 = **2**
N, P, As	(Group 5A)	8 – 5 = **3**
C, Si	(Group 4A)	8 – 4 = **4**

# of bonds it "normally" makes

With each covalent bond, the atom uses one more electron from another atom to complete its octet. So the numbers are the same as the magnitudes of the charge of the anion the element normally makes.

If you find it difficult to understand or remember the "usual number of bonds" for a given element, the shortcut is probably not useful for you , and you can ignore it.

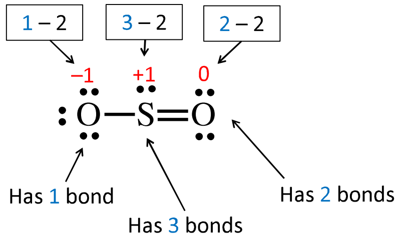
Shortcut for Formal Charges – an example



S is <u>not</u> violating the octet rule, so we can use the shortcut

Oxygen (Group 6A) normally makes 2 bonds

Sulfur (Group 6A) normally makes 2 bonds

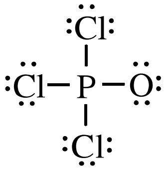


Consider the Lewis structure for $POCl_3$. Assign the formal charge for each atom in the molecule.

P: 5 – 4 – 0 = +1

O: 6 – 6 – 1 = –1

Cl: 7 – 6 – 1 = 0



Seeing that the octet rule is not violated (we only need to check the central atom), we could also use the shortcut for formal charges.

P: 4-3 = +1
O: 1-2 = -1
Cl: 1-1 = 0

If you visually get used to the usual number of bonds an element makes, you can basically "see" the formal charge by the number of bonds.

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)

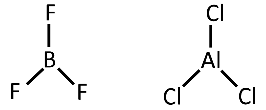
B and Al are satisfied with 3 electron pairs (6 electrons)

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



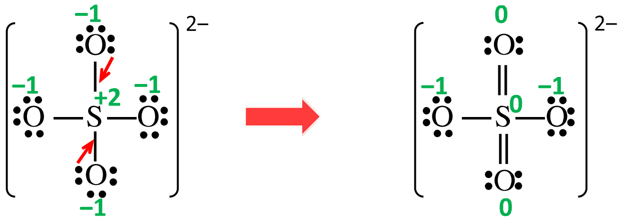
3 bonds; no lone pairs

Octet rule followers and violators (summary):

- C, N, O, and F should always be assumed to obey the octet rule, except in rare cases. But:
  As second-row elements, they never exceed the octet.
- Third-row and heavier elements often do satisfy the octet rule but they can appear to exceed the octet
- Beryllium (Be) tends to have 4 electrons in its covalent compounds. Can have more if both of a bonding pair is brought by another atom.
- Boron (B) and Aluminum (Al) often have only 6 electrons in their covalent compounds. Can have more if both of a bonding pair is brought by another atom.
- **Peripheral atoms never violate the octet rule**

Reducing formal charges in oxyanions by making extra bonds to the central atom

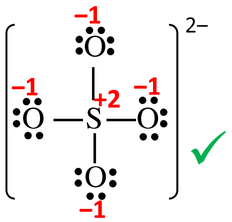
We could draw extra bonds to the central atom, not to satisfy the octet rule, but to violate it in order to reduce formal charges!



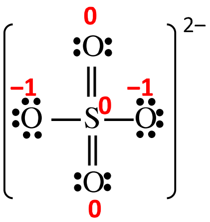
And it's done on paper all the time.

But …

No need to violate the octet rule in oxyanions like SO_4^{2-}



- "Awful" charges
- But there's evidence they are actually closer to reality



- Charges minimized
- **But no evidence they are real**
- But you'll find it drawn this way almost everywhere

¯_(ツ)_/¯

If an oxyanion has 4 oxygens, giving each one a single bond and a -1 formal charge will give you all the predictions you need!

Even though it's pretty standard practice to reduce formal charges in oxyanions by making double bonds to the central atom, **we won't do that**.

Do not violate the octet rule just to reduce formal charges.

It's extra work to do something that has little evidence from nature, and predicts nothing new about the ion.

If an oxyanion has 4 oxygens, giving each one a single bond and a -1 formal charge will give you all the predictions you need!

Shortcut for Number of Lone Pairs on the <u>Central Atom</u>

Works when:

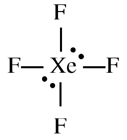
- Peripheral atoms are hydrogens or halogens
- We know all the bonds to the central atom are single

$$\left(\begin{array}{c}\text{Number of}\\ \text{lone pair}\\ \text{electrons on}\\ \text{central atom}\end{array}\right) = \left(\begin{array}{c}\text{No. of val.}\\ \text{electrons}\\ \text{central atom}\\ \text{brings}\end{array}\right) - \left(\begin{array}{c}\text{Number}\\ \text{of bonds}\\ \text{on central}\\ \text{atom}\end{array}\right) - \left(\begin{array}{c}\text{Net}\\ \text{charge}\end{array}\right)$$

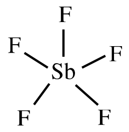
$$\text{No. of lone pairs} = \frac{1}{2}(\text{No. of lone pair electrons})$$

Examples using the shortcut for number of lone pairs on the <u>Central Atom</u>

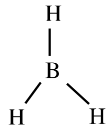
XeF_4 $\quad \text{No. of lone pairs} = \frac{1}{2}(8 - 4 - 0) = 2$



SbF_5 $\quad \text{No. of lone pairs} = \frac{1}{2}(5 - 5 - 0) = 0$



BH_3 $\quad \text{No. of lone pairs} = \frac{1}{2}(3 - 3 - 0) = 0$



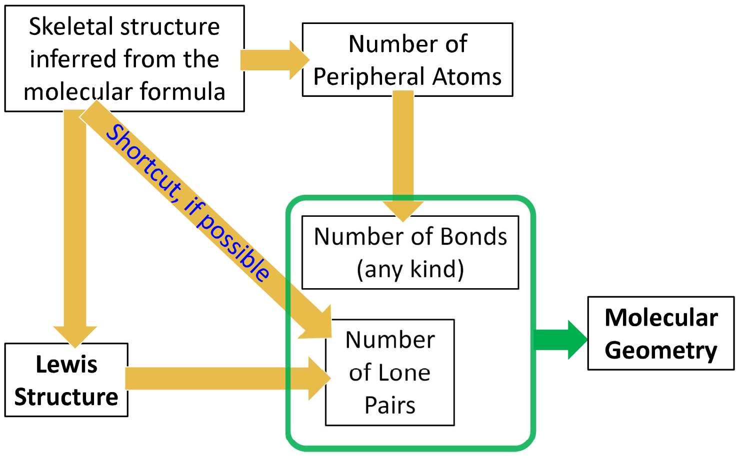
Lewis structures give us a crucial piece of information to help us **deduce the <u>molecular geometry:</u>**

<u>number of lone-pairs</u> on the **<u>central atom</u>**

- Easy enough to tell how many bonds; just count the peripheral atoms
- It's the number of lone pairs on the central atom that is not obvious and we get from Lewis structures

---

A flowchart for finding the molecular geometry



How a Lewis Structure leads to Molecular Geometry: VSEPR Model

"Valence Shell Electron-Pair Repulsion"

- **Predicts the 3-dimensional shape of the molecule**
- The structure around a given atom is determined by minimizing electron pair repulsions.
- Electron groups locate and orient themselves as far apart from one another as possible

---

VSEPR Model

Actually it would be more accurate to call it VSEGR

Valence Shell Electron-**<u>Group</u>** Repulsion?

It's the electron **<u>group</u>** that counts.

A double-bond (2 pairs) or a triple bond (3 pairs) is 1 group.

A lone pair is also one group

Steps to Apply the VSEPR Model

1. Draw the Lewis structure for the molecule.
2. Count the electron groups and arrange them in a way that minimizes repulsion (put the groups as far apart as possible.) You get the geometry of the electron groups.
3. Put the peripheral atoms at the end of bonding groups

   Choose the location of the bonds and lone pairs if necessary.
4. Determine the name of the <u>molecular structure</u> from positions of the <u>atoms</u>.

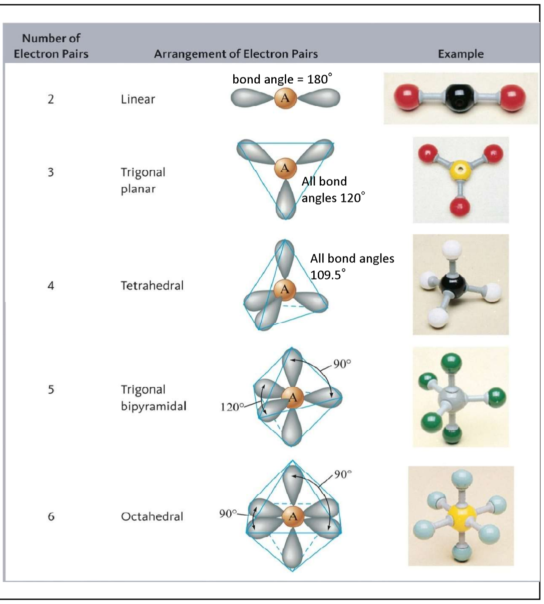
If you find it hard to think in 3D, you can memorize the table(s) at:
https://www.papazyan.org/MolecularGeometry,Polarity,Hybridization.pdf

VSEPR simulation

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

Use it!

Minimum Repulsion Arrangements of Electron Groups



Number of Electron Pairs	Arrangement of Electron Pairs		Example
2	Linear	bond angle = 180˚	
3	Trigonal planar	All bond angles 120˚	
4	Tetrahedral	All bond angles 109.5˚	
5	Trigonal bipyramidal	90° 120°	
6	Octahedral	90° 90°	

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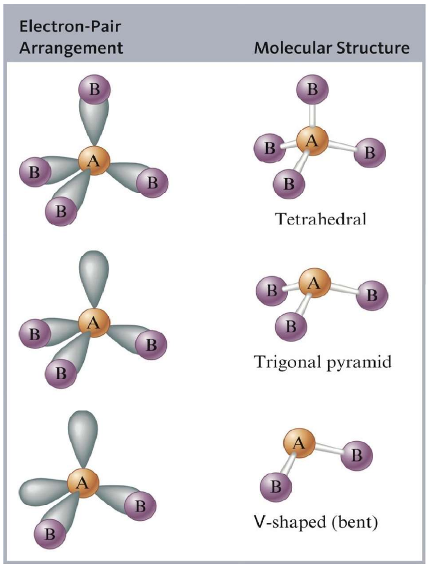
Structures of Molecules With Four Electron Groups Around the Central Atom

- All 4 peripheral positions are equivalent.
- It doesn't matter which bond is replaced with a lone pair.



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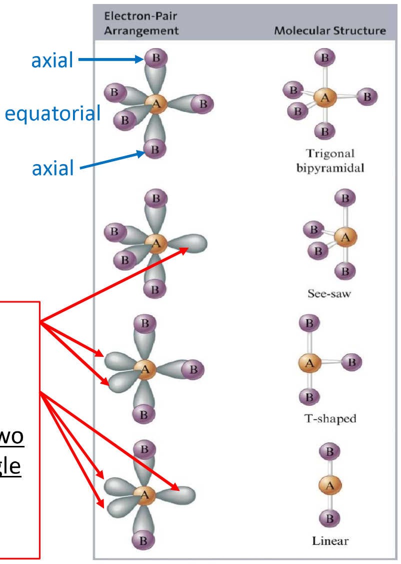
Structures of Molecules With Five Electron Groups Around the Central Atom



Atoms are missing from the equatorial positions

Lone pairs repulse more

Equatorial position has <u>only two</u> *lone-pair* neighbors at <u>90˚ angle</u>

Axial has <u>three</u> *lone-pair* neighbors at <u>90˚ angle</u>

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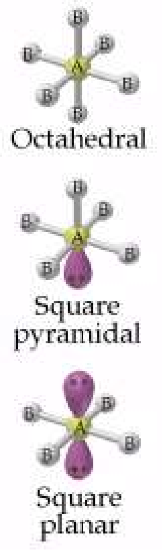
Structures of Molecules With Six Electron Groups Around the Central Atom



All 6 peripheral positions are equivalent.

It doesn't matter which bond is replaced with a lone pair.

Second atom is lost from position across the first lone pair.

That is the only position that avoids a 90˚ angle between lone pairs

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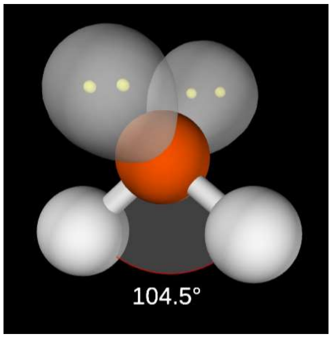
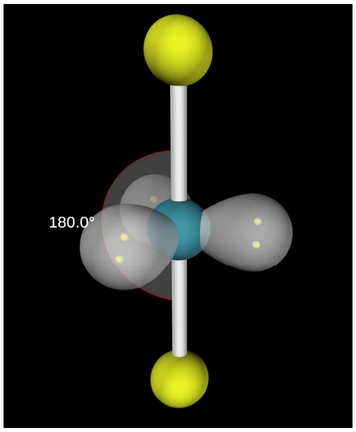
Ideal Bond Angles & Actual Bond Angles

- Lone pairs are "fatter" and closer to the central atom than bonding pairs
- They push the bonds towards one another
- When the push from lone pairs do not cancel one another:
  - Bond angles are smaller than ideal
- If there is only one lone pair, no cancellation possible
  - Bond angles are smaller than ideal
- When lone pairs are symmetrically placed and cancel one another's effects:
  - Bond angles are ideal



- In H_2O the lone pairs press on the O-H bonds <u>asymmetrically</u> (a net push from one side)
- H-O-H bond angle is less than the ideal tetrahedral angle of 109.5°



- In XeF_2 the lone pairs press on the Xe-F bonds <u>symmetrically</u> (no net push from any one side)
- F-Xe-F bond angle is equal to the ideal linear angle of 180°

Practice

Determine the shape for each of the following molecules, and include bond angles:

HCN
PH_3
SF_4

Practice

Determine the shape for each of the following molecules, and include bond angles:

O_3
KrF_4

Polar Molecules, Non-polar Molecules

Remember:

- <u>In practice</u>, if a molecule's dipole moment is "small enough" it would be called "nonpolar"

<u>But</u>

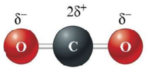
- For our purposes, we will call a molecule "nonpolar" only if its dipole moment is <u>exactly</u> zero
- And we will call a molecule "polar" if its dipole moment is nonzero (no matter how small)

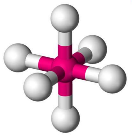
Molecular polarity and symmetry

A simple way to judge polarity:

Symmetric ⇨ Non-polar

Dipole moment is zero

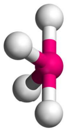




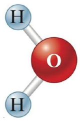
SF_6

Asymmetric (lopsided) ⇨ "Polar"

Dipole moment is nonzero
(but could be tiny)

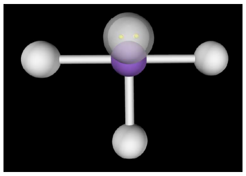


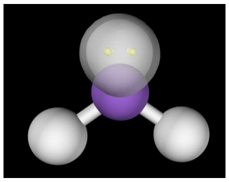
SF_4



How "symmetric" does a molecule need to be in order to be "nonpolar" (have a zero dipole moment) ?

If we see a T-shaped or a V-shaped (bent) molecule, we might perceive it as "pretty symmetric"



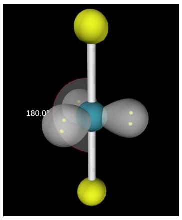


But they are not symmetric enough to be non-polar

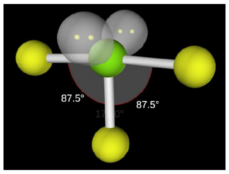
There **is** a trick for figuring out symmetry …

Guessing symmetry from bond-angle distortion

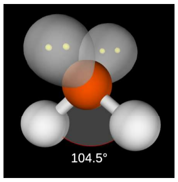
- Imagine the lone pairs as huge, and pushing on the bonds
- Are the lone pairs completely cancelling each other's push?
- If yes, the bond angles remain ideal, and also the molecule is symmetric
- If no, the bond angles get "squished" to be smaller than ideal, and also the molecule is asymmetric



Bond angle = 180° (ideal)
Nonpolar molecule



Bond angle < 90°
Polar molecule



Bond angle < 109.5°
Polar molecule

If all the peripheral atoms are the same, the "bond-angle intuition" works simply:

- If bond angles are ideal ⇨ zero dipole
- If bond angles are not ideal ⇨ nonzero dipole

But please remember:

Polarity is not caused by the non-ideal angles

Both polarity and non-ideal bond angles are caused by asymmetry

---

What if there are no lone pairs, and there are more than one kind of peripheral atoms?

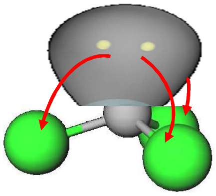
If one or more of the peripheral atoms are different from the rest, treat them as if they are lone pairs and see if they would distort the bond angles.

As with real lone pairs:

- If they would distort the angles, the molecule is asymmetric, therefore polar
- If they would cancel each other's push and the angles would remain ideal, then the molecule is symmetric, therefore nonpolar.

Imagine the tiny hydrogen in $CHCl_3$ as a huge lone pair.

Would it push on the other bonds and reduce the bond angles?



Yes. It would.

Therefore $CHCl_3$ is asymmetric enough to be polar.

Additional online resources on molecular geometry
They are linked under Ch. 8 resources

Two very cool and useful tools:

3D VSEPR simulation
phet.colorado.edu/sims/html/molecule-shapes/latest/molecule-shapes_en.html

Molecular Polarity simulation
phet.colorado.edu/sims/html/molecule-polarity/latest/molecule-polarity_en.html

A table summarizing VSEPR
(plus hybridizations covered in Ch. 9):
www.papazyan.org/MolecularGeometry,Polarity,Hybridization.pdf