

Resonance Structures

- For ozone, we can draw two Lewis structures that are *energetically equivalent* to each other, that have the same types of bonds and formal charges.
- The actual molecule is an *average* of structures **2** and **3**, which are called **resonance structures**.
 - Structure **1** is also a resonance structure of **2** and **3**, but since it has more formal charges, and does not satisfy the octet rule, it is a higher-energy structure, and does not contribute as much to our overall picture of the molecule.
 - In these structures, one of the electron pairs (and hence the negative charge) is “spread out” or *delocalized* over the whole molecule. In contrast, the lone pairs on the oxygen in water are *localized* — i.e., they’re stuck in one place. Resonance delocalization stabilizes a molecule by spreading out charges, and often occurs when lone pairs (or positive charges) are located next to double bonds.

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Resonance Structures

- Structures **2** and **3** are somewhat “fictional” in that they imply that there are “real” double bonds and single bonds in ozone.
 - In reality, ozone has two oxygen-oxygen bonds which are equal in length, and are halfway between the lengths of typical O—O and O=O bonds — effectively, there are two “one-and-a-half” bonds in ozone.
 - The real molecule does *not* alternate back and forth between these two structures; it is a *hybrid* of these two forms.
- As a general rule, when it’s possible to make a double bond in more than one location, and the resulting structures are energetically equivalent to each other, each separate structure must be shown, separated from each other by resonance arrows.

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Examples: Resonance Structures

- Draw all reasonable resonance structures for the following molecules and ions. Identify the most stable (lowest energy) and least stable (highest energy) resonance structures, or whether they are equal in energy. For all atoms, write the formal charge if it is not zero.
 - CO_3^{2-} (carbonate ion)

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Multi-Center Molecules

- Molecules with more than one central atoms are drawn similarly to the ones above. The octet rule and formal charges can be used as a guideline in many cases to decide in which order to connect atoms.

Examples: Multi-Center Molecules

- Draw Lewis structures for the following multi-center molecules. For all atoms, write the formal charge if it is not zero.
 - C_2H_6
 - C_2H_4
 - $\text{CH}_3\text{CH}_2\text{OH}$

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Exceptions to the Octet Rule

- Electron deficient** species, such as beryllium (Be) and boron (B), can have fewer than eight electrons around them, but have zero formal charge.
- Free radicals** (or just **radicals**, or **odd-electron molecules**) contain an odd number of valence electrons. Radicals always have an unpaired electron, and are paramagnetic. These species are usually unstable, and are extremely reactive.
- Expanded octets** are found on atoms that have more than eight electrons around them. Nonmetals from period 3 or higher, such as sulfur and phosphorus, can get around the octet rule by shoving “extra” electrons into empty *d* orbitals.
 - Period 2 elements **CANNOT** have more than 8 electrons!

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Examples: Violations of the Octet Rule

- Draw Lewis structures for the following compounds. In most cases, the central atom violates the octet rule. For all atoms, write the formal charge if it is not zero.
 - BF_3
 - NO (nitrogen monoxide, or nitric oxide)
 - PCl_5
 - SF_6
 - SF_4
 - XeF_4
 - H_2SO_4 (S is the central atom; each H is bonded to a different O)

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The Shapes of Molecules: The VSEPR Model

The Shapes of Molecules: The VSEPR Model

- Drawing a Lewis structure is the first steps towards predicting the three-dimensional shape of a molecule.
 - A molecule's shape strongly affects its physical properties and the way it interacts with other molecules (Chapter 8, 11).
 - Molecular shape plays an important role in the way that biological molecules (proteins, enzymes, DNA, etc.) interact with each other.
- The approximate shape of a molecule can be predicted using the **Valence-Shell Electron-Pair Repulsion (VSEPR) model**, which depicts electrons in bonds and lone pairs as "electron groups" that repel one another and stay as far apart as possible.

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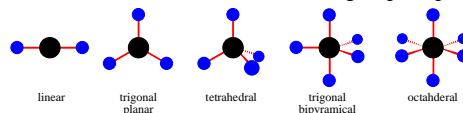
The VSEPR Model

1. Draw the Lewis structure for the molecule and count the number of electron groups surrounding the central atom. An **electron group** is:
 - a single, double or triple bond (multiple bonds count as one electron group)
 - a lone pair
 - an unpaired electron
2. Predict the arrangement of electron groups around each atom by assuming that the groups are oriented in space as far away from one another as possible.
3. The shapes of larger molecules having more than one central are a composite of the shapes of the atoms within the molecule, each of which can be predicted using the VSEPR model.

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Electron-Group Shape vs. Molecular Shape

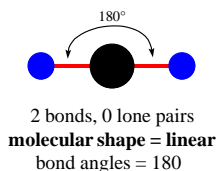
- The **electron-group shape** of a species considers the placement of the bonds **and** the lone pairs that are on the central atom (for example, CH_4 , NH_3 , and H_2O all have four electron group on the central atom). There are five basic electron group shapes:



- The **molecular shape** of a species considers only the placement of the atoms that are on the central atom. Each of the basic electron-group shapes has a number of variations for the molecular shape, depending on whether the electron groups are in bonds or lone pairs.

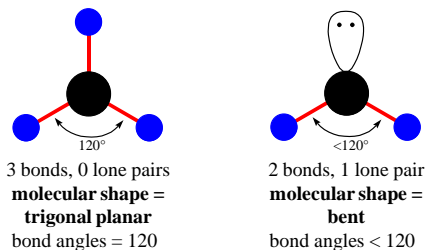
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Two Electron Groups — Linear



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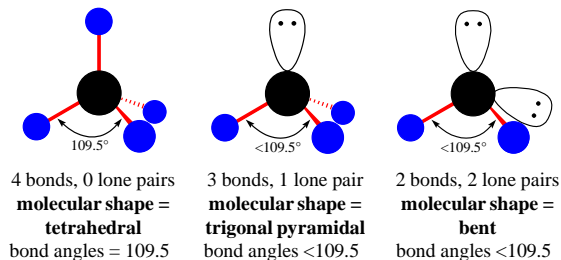
Three Electron Groups — Trigonal Planar



Lone pairs take up more room than covalent bonds; this causes the other atoms to be squashed together slightly, decreasing the bond angles by a few degrees.

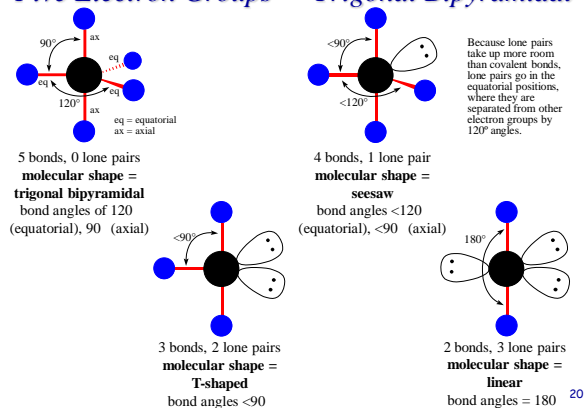
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Four Electron Groups — Tetrahedral



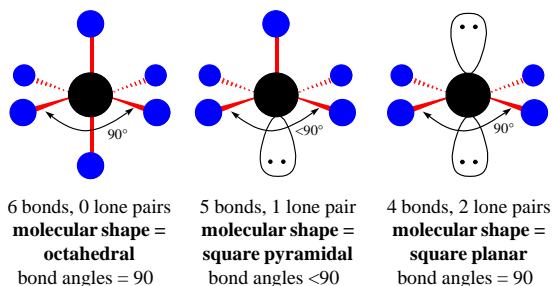
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Five Electron Groups — Trigonal Bipyramidal



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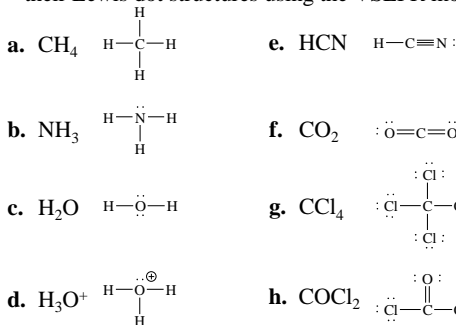
Six Electron Groups — Octahedral



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Examples: Predicting Shapes of Molecules

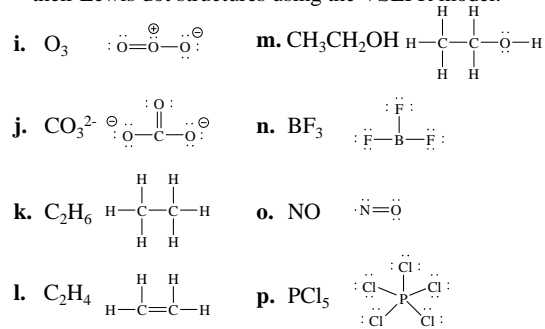
5. Predict the shapes of the following molecules from their Lewis dot structures using the VSEPR model.



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Examples: Predicting Shapes of Molecules

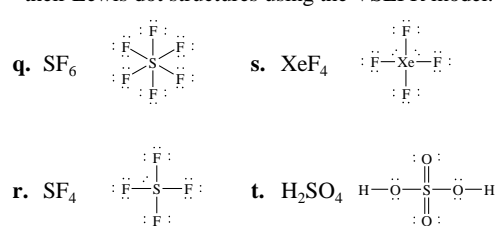
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Examples: Predicting Shapes of Molecules

5. Predict the shapes of the following molecules from their Lewis dot structures using the VSEPR model.



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Molecular Shape and Polarity

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Electronegativity

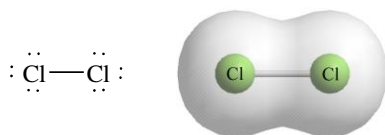
- **Electronegativity** is a measure of the ability of an atom in a molecule to attract shared electrons in a covalent bond.
- Electronegativity increases from bottom to top within a group and from left to right across a period:

H																	He
2.20																	n.a.
Li	Be											B	C	N	O	F	Ne
0.98	1.57											2.04	2.55	3.04	3.44	3.98	n.a.
Na	Mg											Al	Si	P	S	Cl	Ar
0.93	1.31											1.61	1.90	2.19	2.58	3.16	n.a.
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Cu	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.82	1.00	1.36	1.54	1.63	1.66	1.55	1.83	1.88	1.91	1.90	1.65	1.81	2.01	2.18	2.55	2.96	3.00
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0.82	0.95	1.22	1.33	1.60	2.16	1.90	2.20	2.28	2.20	1.93	1.69	1.78	1.96	2.05	2.10	2.66	2.60
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0.79	0.89	1.10	1.30	1.50	2.36	1.90	2.20	2.20	2.28	2.54	2.00	1.62	2.33	2.02	2.00	2.20	n.a.
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	—	Uuq	—	—	—	—
0.70	0.89	1.10	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	—	n.a.	—	—	—	—

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Nonpolar Covalent Bonds

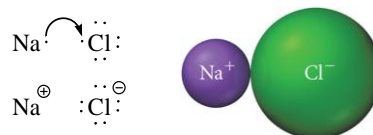
- When two atoms of the same electronegativity share electrons, the electrons are shared *equally*, and the bond is a **nonpolar covalent bond** — there is a *symmetrical* distribution of electrons between the bonded atoms.
 - When two Cl atoms are joined by a covalent bond, the electrons spend just as much time close to one Cl as they do to the other; the resulting molecule is nonpolar (indicated by the symmetrical electron cloud shown below):



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Ionic Bonds

- When two atoms have an electronegativity difference of greater than 2.0 units, the bond is an **ionic bond** — one atom takes the electrons *away* from the other atom, producing cations and anions instead of a covalent bond.
 - For example Na has an electronegativity of 0.93, and Cl is 3.16, a difference of 2.23 units. The Cl atom takes an electron away from the Na, producing a fully ionic bond:



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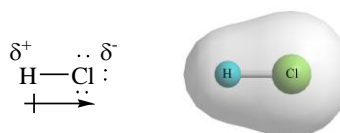
Polar Covalent Bonds

- When two bonded atoms have an electronegativity difference between 0.4 and 2.0 units, the electrons are shared *unequally*, and the bond is a **polar covalent bond** — there is an *unsymmetrical* distribution of electrons between the bonded atoms, because one atom in the bond is “pulling” on the shared electrons harder than the other, but not hard enough to take the electrons completely away.
- The more electronegative atom has a **partial negative charge** (δ^-), because the electrons are pulled slightly towards that atom, and the less electronegative atom has a **partial positive charge** (δ^+), because the electrons are partly (but not completely) pulled away from that atom.

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Polar Covalent Bonds

- For example, in the HCl molecule, Cl is more electronegative than H by 0.96 electronegativity units. The shared electrons are pulled slightly closer to the Cl, making that end of the molecule very slightly negative (δ^-), while the H end of the molecule is very slightly positive (δ^+).
- We say that the bond has a **dipole** — the electron cloud is *polarized* towards one end of the molecule:



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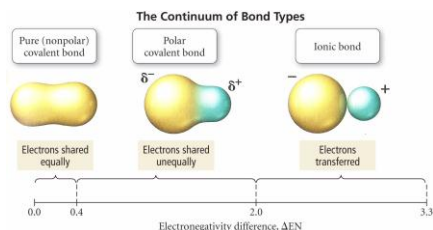
Electronegativity and Bond Polarity

- The degree of polarity in a covalent bond depends on the electronegativity difference, ΔEN , between the two bonded atoms:

ΔEN 0 - 0.4 Nonpolar covalent bond

ΔEN 0.4 - 2.0 Polar covalent bond

$\Delta EN > 2.0$ Ionic bond



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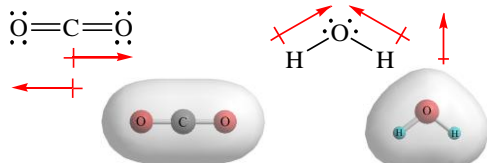
Molecular Shape and Polarity

- In a diatomic molecule (X_2 or XY), there is only one bond: if that bond is polar, the molecule is polar, and if it is nonpolar, the molecule is nonpolar.
- In larger molecules, *both molecular shape and bond polarity determine whether or not the molecule is polar*.
 - A molecule *must* contain polar bonds in order for the molecule to be polar.
 - If the polar bonds in a molecule are aligned exactly opposite to each other, or if they are sufficiently symmetric, the bond polarities cancel out, making the molecule nonpolar. (Polarity is a vector quantity, so both the magnitude and the *direction* must be taken into account.)

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Molecular Shape and Polarity

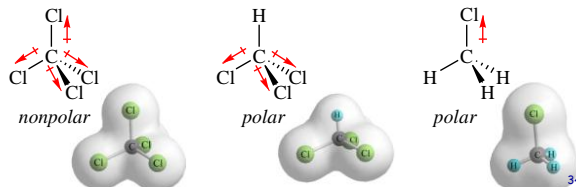
- Carbon dioxide, CO_2 , contains two polar $C=O$ double bonds. However, these polar bonds point 180° away from each other, and the bond polarities cancel out. The molecule is **nonpolar**.
- Water, H_2O , contains two polar bonds $O-H$ bonds. The bonds are at an angle of about 105° , and the bond polarities do *not* cancel out. There is an overall dipole going from the H end of the molecule towards the O end. The molecule is **polar**.



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Molecular Shape and Polarity

- Molecules in which all of the atoms surrounding the central atom are the same tend to be nonpolar if there are no lone pairs on the central atom. If some of the atoms surrounding the central atom are different, however, the molecule may be polar.
- For example, carbon tetrachloride, CCl_4 , is nonpolar, but chloroform, $CHCl_3$, and methyl chloride, CH_3Cl are polar:



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Polarity and Physical Properties

- The polarity of a molecule has a strong effect on its physical properties. Molecules which are more polar have stronger intermolecular forces between them, and have, in general, higher boiling points (as well as other different physical properties).
- For species which have an overall charge, the term "charged" is used instead, since the terms "polar" and "nonpolar" do not really apply to charged species; charged species are, by definition, essentially polar.

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Examples: Predicting Molecular Polarity

6. Draw the most stable possible Lewis structure for each of the following molecules, predict the shape around the central atom, and state whether the molecule is polar or nonpolar (or charged if it is an ion). (For all atoms, write the formal charge if it is not zero.)

- | | | |
|-------------|-----------------|--------------|
| a. CH_4 | h. $COCl_2$ | o. NO |
| b. NH_3 | i. O_3 | p. PCl_5 |
| c. H_2O | j. CO_3^{2-} | q. SF_6 |
| d. H_3O^+ | k. C_2H_6 | r. SF_4 |
| e. HCN | l. C_2H_4 | s. XeF_4 |
| f. CO_2 | m. CH_3CH_2OH | t. H_2SO_4 |
| g. CCl_4 | n. BF_3 | |

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