

CHAPTER 8: Bonding: General Concepts

8.1 Types of Chemical Bonds

Ionic Bonding

Oppositely charged ions are attracted to each other by a strong electrostatic force

$$E = 2.31 \times 10^{-19} \text{ J nm} \times \frac{Q_1 Q_2}{r}$$

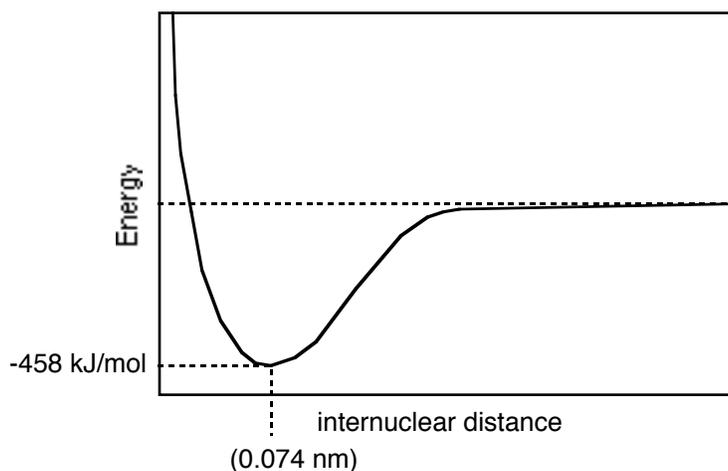
where Q is the ionic charge in atomic units and r is the distance between ions in nm

Covalent Bonding

When two atoms approach each other, the result of the interaction depends on the relative strength of the following forces:

- the attraction one nucleus has for the electrons of the other atom, and vice versa,
- the repulsion between the electrons on each atom,
- the repulsion between nuclei.

Under the proper conditions, a balance may be achieved where the electron clouds of the atoms actually penetrate each other, forming an overlap of electron density and a sharing of electrons between the two overlapped atoms. This sharing of electrons is called a covalent bond.



Consider $\text{H} + \text{H} \rightarrow \text{H}_2$

reference energy = energy of 2 separated H atoms = 0

As atoms approach, there are 4 forces

1 - electron-electron repulsion between the 2 H 1s electrons

2 - electron-proton attraction between each H 1s electron and the opposite nucleus (2 attractive forces)

3 - proton-proton repulsion

At a distance of 0.074 nm, these forces are in balance, and the net energy is 458 kJ/mol lower than the energy of two separated H atoms; i.e., it would require 458 kJ/mol to separate the H atoms.

In this bonded state, the electron density is concentrated in the volume of space directly between the two bonded nuclei.

In a bond such as the sigma bond in H-H, where the two bonded atoms are the same, the attractive force between the shared pair of electrons and each nucleus is the same, and the pair is shared equally between the two nuclei. When the two nuclei are not the same, as in HCl, often, one nucleus will have a stronger attraction for the shared pair than the other, pulling it closer to itself at the expense of the weaker atom. This

unequal attraction results in a polar covalent bond. The stronger atom has an overabundance of electron density, lending it a small (partial) negative charge, while the weaker atom, with less than its share of electron density, acquires a partial positive charge. The bond is now a dipole, the magnitude of which depends on the size of the partial charges and their separation.

8.2 Electronegativity

Electronegativity is the attraction an atom has for a shared pair of electrons. The polarity of a bond can be judged from the difference in electronegativity between the two bonded atoms. The values of electronegativity range from a high of 4.0 for F to a low of 0.7 for Cs. The trend of variation is the same as for electron affinity: electronegativity increases from lower left to upper right.

When two elements have the same electronegativity, the shared pair is equally attracted to both nuclei and the resulting bond is nonpolar. When one atom is more electronegative, the shared pair is more strongly attracted to the more electronegative atom and the resulting bond is polar. As the difference in electronegativity increases, so do the partial positive and negative charges on the atoms, until the charges approach unity. When this condition occurs, the bond is more appropriately described as an ionic bond. Since the transition from nonpolar to ionic is gradual, a difference in electronegativity of 2.0 is arbitrarily chosen to be the minimum difference responsible for an ionic bond. A bond between nonmetals, or between metalloids and nonmetals, is covalent regardless of the electronegativity difference.

EXAMPLE: Classify the following bonds as nonpolar, polar, or ionic:

- a) H-F b) Na-F c) C-S d) C-H

SOLUTION: a) The difference in electronegativity between F and H is $4.0 - 2.1 = 1.9$, so the bond is polar.
 b) The difference is $4.0 - 0.9 = 3.1$, so the bond is ionic.
 c) Both electronegativities are 2.5, so the bond is nonpolar.
 d) The difference is $2.5 - 2.1 = 0.4$, so the bond is very slightly polar.

Electronegativity increases across a row and up a column. (see fig. 8.3, pg. 353)

8.3 Bond Polarity and Dipole Moments

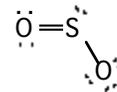
The polarity of a bond is measured by its dipole moment, which is a vector quantity with a magnitude equal to the charge times the distance of charge separation and a direction pointing from the partially positive end (the less electronegative atom) to the partially negative end (the more electronegative atom). The dipole moment of a molecule is the vector sum of the dipole moments of the individual bonds. If a molecule has a nonzero dipole moment, the molecule is polar; otherwise, it is nonpolar. The polarity or nonpolarity of a molecule can be determined by examining the polarity of each bond and the geometry of the molecule. If none of the bonds in the molecule is polar, then the molecule is nonpolar. If any of the bonds are polar, then the polarity depends on the geometry of the molecule.

EXAMPLE: Which of the following molecules is polar? $\text{H}-\text{C}\equiv\text{N}:$ $:\ddot{\text{O}}=\ddot{\text{S}}-\ddot{\text{O}}:$ $:\ddot{\text{O}}=\text{C}=\ddot{\text{O}}:$

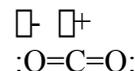
SOLUTION: a) HCN is linear. The difference in electronegativity between H and C is 0.4, pointing toward C (toward the N end of the molecule). The C-N dipole vector also points toward the N end of the molecule. These vectors add to yield a nonzero dipole moment, so the molecule is polar.



b) Each S-O bond is polar, with the dipole moment vector pointing toward O. The molecule is bent, so the vectors add to yield a smaller vector pointing between the S-O bonds. The molecule is polar.



c) The C-O bonds are polar, but they point 180° apart, because the molecule is bent. The vector sum is 0, so the molecule is nonpolar.



8.4 Ions: Electron Configurations and Sizes

Metal atoms tend to lose all valence electrons to form cations

Nonmetal atoms tend to gain enough electrons to fill the outer s and p subshells

cations and anions combine in a ratio that allows for the positive and negative charges to cancel

Ionic radius: cations are smaller than parent atom (see fig. 8.7, pg. 361)

anions are larger than parent atom

in an isoelectronic series, size decreases with Z



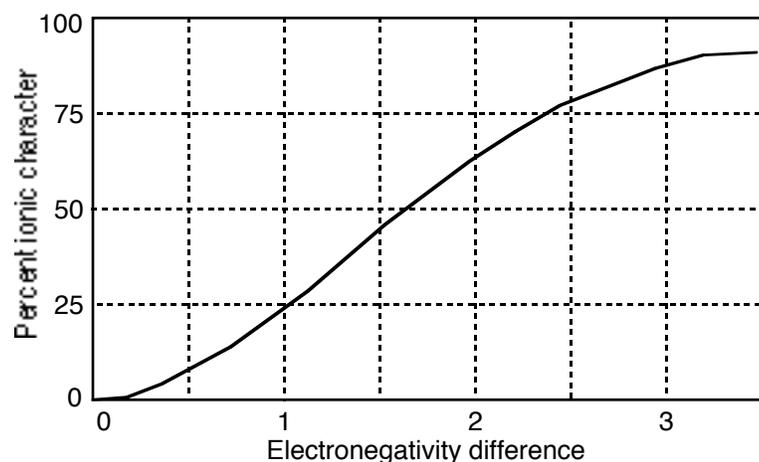
8.5 Formation of Binary Ionic Compounds

Lattice energy - ΔE when separated gaseous ions are packed together to form an ionic solid.

$\text{Li(s)} \rightarrow \text{Li(g)}$	$\Delta E = \text{sublimation}$	161 kJ
$\text{Li(g)} \rightarrow \text{Li}^+(\text{g}) + \text{e}^-$	$\Delta E = \text{ionization energy}$	520 kJ
$1/2 \text{F}_2(\text{g}) \rightarrow \text{F}(\text{g})$	$\Delta E = \text{dissociation}$	77 kJ
$\text{F}(\text{g}) + \text{e}^- \rightarrow \text{F}^-(\text{g})$	$\Delta E = \text{electron affinity}$	-328 kJ
$\text{Li}^+(\text{g}) + \text{F}^-(\text{g}) \rightarrow \text{LiF(s)}$	$\Delta E = \text{lattice energy}$	-1047 kJ
$\text{Li(s)} + 1/2 \text{F}_2(\text{g}) \rightarrow \text{LiF(s)}$	$\Delta E = \text{energy of formation}$	-617 kJ

ionic bonds form because of the lattice energy released when oppositely charged ions form a 3-d crystal lattice.

8.6 Partial Ionic Character of Covalent Bonds



$\Delta EN = 1.7$ corresponds to 50% ionic character

For a bond A–B, as ΔEN varies from 0 to 3.5, the bond goes from nonpolar covalent ($\Delta EN = 0$) to polar covalent ($\Delta EN > 0, < 1.7$) to ionic (50% ionic character, $\Delta EN > 1.7$).

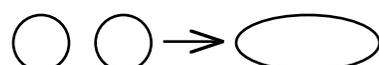
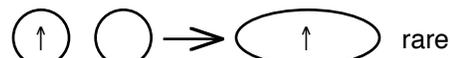
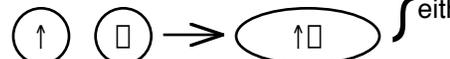
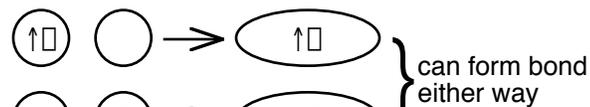
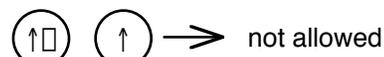
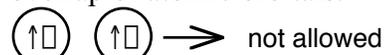
Generally can assume that compounds between metals and nonmetals, or compounds which include polyatomic ions, are ionic, and compounds between nonmetals are covalent.

8.7 The Covalent Chemical Bond: A Model

8.8 Covalent Bond Energies and Chemical Reactions

8.9 The Localized Electron Bonding Model

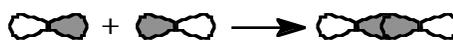
Localized Electron bonding model (LE): covalent bonds are described as the sharing of electron pairs through overlap of atomic orbitals.



Valence Bond theory - atoms form bonds by overlapping orbitals to share electrons.

there is a maximum of 2 electrons per overlap (Pauli Exclusion Principle)

can also form a bond by overlapping p orbitals



According to the model, there are two ways that orbitals can overlap to form bonds:

sigma (σ) bond

a head-on overlap of orbitals. Electron density is concentrated along the axis of the bond (an imaginary line connecting the two bonded atoms) and is greatest directly between the two bonded nuclei, resulting in the lowest possible electron energy. Because sigma bonds are symmetrical around the bond axis, they are free to rotate about this axis. Only one sigma bond can exist between any two atoms.

pi (π) bond



a side to side overlap of p orbitals. Electron density along the bond axis is zero, with twin maxima of electron density above and below the bond axis. This is a weaker bond because the electron density is zero directly between the two bonded nuclei. A pi bond cannot occur unless a sigma bond is already present.

Pi bonding allows for the existence of multiple bonds, in which more than one pair of electrons are shared between the same two atoms. In a Lewis structure, shared pairs are represented by lines connecting the bonded atoms.

single bond (—) - a lone sigma bond, 1 shared pair of electrons

double bond (=) - one sigma bond and one pi bond, 2 shared pairs

triple bond (≡) - one sigma bond and two pi bonds, 3 shared pairs

8.10 Lewis Structures

The Octet Rule

The driving force behind the formation of covalent bonds is the lowering of electronic energy that occurs when a shared pair of electrons can get close to two nuclei at the same time. Breaking this bond involves pulling electrons away from nuclei, so it involves the expenditure of an amount of energy on the order of the ionization energy for the elements involved. When we recall that the nonmetals have the highest ionization energies, it is no surprise that the nonmetals form the strongest covalent bonds.

In order to form a bond, overlap must occur between the orbitals of the bonding atoms. Just as for atoms, the Pauli exclusion principle demands that there be no more than two electrons per orbital, which, since the shared electrons "belong" to both overlapped orbitals, means that there can be no more than two electrons total in the two overlapping orbitals. This arrangement can happen by:

- overlapping a full orbital with an empty orbital, or
- overlapping a half-full orbital with a half-full orbital.

With four valence orbitals (one s and three p) each holding two electrons, an upper limit of eight valence electrons is set. It is observed that in the vast majority of covalent compounds, this upper limit is met, that is, that all valence orbitals are filled. This result is to be expected if we view valence vacancies as low energy holes that electrons can fall into.

Octet rule: when forming covalent compounds, atoms tend to gain electrons through sharing until they completely occupy the outer s and p subshells.

Hydrogen, of course, has no outer p subshell, so it obeys the octet rule by gaining one electron through sharing (the "duet rule"). All other elements (except He, which is inert) have both s and p subshells, so, for them, we could restate the octet rule: all elements but hydrogen tend to form bonds until they are surrounded by eight valence electrons.

Element symbol - represents nucleus and all inner shell electrons

Valence electrons are represented as follows;

- | | |
|--|--|
| — shared pair | : lone pair |
| — single bond (□ bond, 1 shared pair) | = double bond (□ bond + π bond, 2 shared pairs) |
| ≡ triple bond (□ bond + 2 π bond, 3 shared pairs) | |

Rules for Drawing Lewis Structures

1. Draw a skeleton of the molecule. The likelihood of an atom being in the center of the molecule increases
 - a) if the atom is further to the left on the chart, or
 - b) if the atom is further down a group on the chart.
2. Count the number of valence electrons and subtract 2 for each bond needed to connect the atoms in the skeleton.
3. Count the number of electrons each atom in the skeleton still needs to acquire an octet (remember that H only needs two, so H will always be finished after step 1).
4. If the number from step 3 is greater than the number from step two, for each pair short, add one bond to the skeleton (thus forming a multiple bond) and subtract two electrons from the total from step 1.
5. Distribute the remaining electrons to give each atom an octet.

When drawing the skeleton, the element furthest from the F corner of the chart is most likely to be central. For molecules with more than one central atom, derive clues from the formula.

N_2H_2 , CO_2 , HCN , CH_3COOH , HF , H_2O , NH_3

EXAMPLE: Draw the Lewis structure for SO_2 .

SOLUTION: S and O are both in the same group, but S is further down in the group, so S must be the central atom, and the skeleton is



The total number of valence electrons is 6 for O and 6 each for the two sulfur atoms, for a total of 18. (Remember that the number of valence electrons for a main group element is equal to the group number.) Subtracting two electrons for each bond in the skeleton leaves 14.



Now, count the number of electrons each atom in the skeleton needs to reach 8. Remember that a shared pair counts twice, once for each atom sharing it.

O - has one pair, needs 6 more electrons.

S - has two pair, needs 4 more electrons.

O - has one pair, needs 6 more electrons.

total needed = 16 more electrons

We need 16 more electrons to give each atom an octet, yet we have only 14 electrons left, so we are one pair short. We make up this deficit by adding another bond, thereby counting another pair twice.



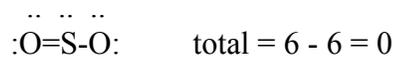
Now distribute the remaining twelve electrons to give each atom an octet. O has two pair and needs 4 more electrons



S has three pair and needs 2 more electrons



O has one pair and needs 6 more electrons



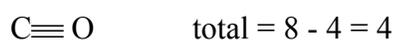
We now have a valid Lewis structure. We have accounted for all 18 valence electrons, and each atom has an octet.

EXAMPLE: Draw the Lewis structure of CO

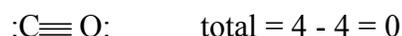
SOLUTION: The skeleton is simply C-O. The total number of valence electrons is 4 (from C) + 6 (from O) = 10, minus 2 for the bond in the skeleton leaves 8.



Both C and O have one pair and need 6 more electrons each, or 12 electrons needed, which is 4 short of the total, so 2 bonds must be added.



Now C and O each have three pair and need 2 electrons each



The following rule is often useful in drawing molecular skeletons or determining where to place extra bonds:

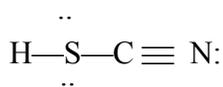
The number of bonds a nonmetal is likely to form is equal to (8 - the group number). Atoms with low electronegativities are more likely to form more than the expected number of bonds; atoms with high electronegativities are more likely to form less than the expected number of bonds.

In the example above, C, which is expected to form (8 - 4) = 4 bonds forms 3 bonds instead, and O, which is expected to form (8 - 6) = 2 bonds, forms 3 bonds instead, in contradiction to the above rule.

EXAMPLE: Draw the Lewis structure of HSCN.

SOLUTION: The skeleton, as the formula implies, is H-S-C-N. The total number of valence electrons is 1+6+4+5=16. The skeleton contains 6 electrons, leaving only 10. The number of electrons needed to give each atom (except H) an octet is 4 (for S) + 4 (for C) + 6 (for N) = 14 electrons needed. We are short 2 pair, so 2 more bonds must be added. To determine where to place them, consider that S would be expected to

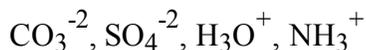
have 2 bonds, C to have 4, and N to have 3. The best Lewis structure should come as close as possible to satisfying these expectations. This can be done by placing both extra bonds between the C and N



Lewis Structures for Polyatomic Ions

For polyatomic ions, follow rules as above, except rule 2

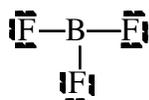
2 add up total # of valence electrons, subtract 2 for each bond in the skeleton, subtract charge from total



8.11 Exceptions to the Octet Rule

Electron-Deficient Molecules: The elements in groups I, II, and III are mostly metals and form ionic compounds; however, boron (a metalloid), aluminum, and beryllium (and occasionally lithium and magnesium) have high enough electronegativities that they will form covalent bonds with some elements. When such compounds form, half-filled orbitals on the metal overlap with half-filled orbitals on the other atom. Since the elements in groups I, II, and III have, at most, 1, 2, or 3 half-filled orbitals (and 3, 2, or 1 empty orbitals, respectively), these elements cannot gain enough electrons to complete an octet. A coordinate covalent bond formed by overlapping an empty orbital with a full orbital on the other atom could complete the octet, but the group I, II, or III elements will always have a lower electronegativity than the nonmetals with which they react, so they are unable to attract this electron density toward themselves (away from the more electronegative atom). All covalent compounds of group I, II, or III elements (except hydrogen) are electron deficient.

Electron deficient compounds - covalent compounds of groups 1, 2, or 3 have few valence electrons and low electronegativities

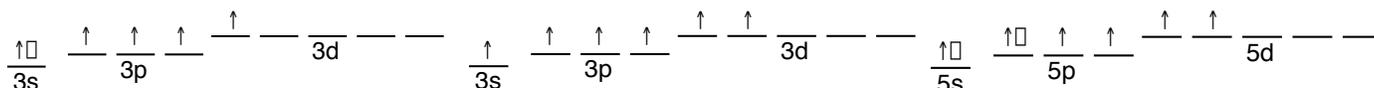
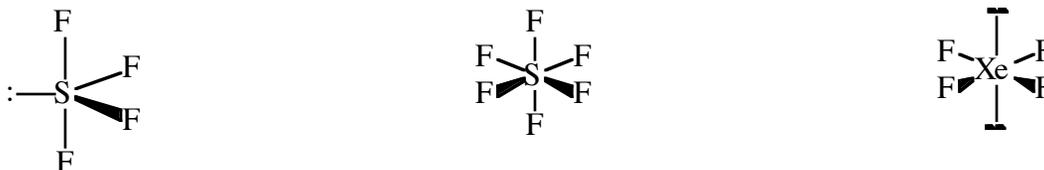


Group 1, 2, 3 elements tend to form (group number) bonds and leave 4 - (group number) empty orbitals. Most frequent with elements toward the top of groups 1, 2, and 3. When drawing Lewis structures, if central atom is a group 1, 2, or 3 element, leave empty orbitals rather than creating π bonds.

Expanded-Shell Compounds: Nonmetals in period 3 and below, and transition metals, can use d orbitals in addition to the valence shell s and p orbitals in forming bonds. For a nonmetal to use d orbitals, valence electrons must be excited from the ground state into the vacant d subshell. This promotion serves to unpair previously paired electrons so that the atom can form more bonds. Since energy is required to excite electrons into the d subshell, nonmetals usually will only form expanded shell compounds when they react with the very reactive elements F, O, and sometimes, Cl.

The transition metals already have electrons in d orbitals, and all covalent transition metal compounds are expanded shell compounds. These compounds often obey an 18-electron rule, rather than the octet rule, because the capacity of the s, p, and d subshells together is 18 electrons.

Expanded Shell compounds - covalent compounds of transition metals and some compounds of period 3, group 5 and greater nonmetals (P - Rn corner of chart). Electrons are promoted from valence s and p orbitals into empty d orbitals in order to form more bonds.



When drawing Lewis structures of expanded shell compounds, any extra electrons go on the central atom.

Odd-Electron Molecules (free radicals): A half-filled orbital usually means that there is a low energy hole into which another electron can fall; this is the basis of the octet rule. In some molecules, however, the low energy hole is shallow enough that the molecule can have a stable existence (sometimes as stable as molecules which obey the octet rule) while still being one electron short of obeying the octet rule. These free radicals are usually more reactive than those molecules which obey the octet rule, and tend to enter into chain reactions (since the products of a reaction involving an odd number of electrons must include at least one free radical).

Odd-Electron Molecules (radicals) (378) - generally, molecules with an odd number of electrons are unstable, but there are some stable compounds of N with an odd electron.



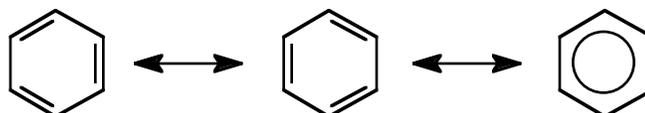
One important property of radicals is that they are reactive. In any reaction between a radical and a non-radical, at least one of the products of the reaction must be another radical, so radical reactions tend to be chain reactions.

8.12 Resonance

Resonance occurs when two or more equally valid Lewis structures can be drawn for the same molecule or ion.



Resonance often occurs when there is an option of placement of π bonds.



FORMAL CHARGE (385)

The formal charge of an atom in a molecule or polyatomic ion is the charge that it would have if it had half of all its shared electrons to itself. It can be calculated by the formula

Formal Charge - the difference between the number of valence electrons on the free atom and the number of valence electrons assigned to the atom in the molecule.

1. lone pairs belong entirely to the atom on which they reside
2. shared pairs are divided equally between the two bonded atoms

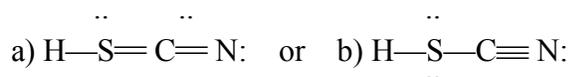
$$\text{formal charge} = (\text{valence electrons}) - (\# \text{ of unshared electrons}) - 1/2(\# \text{ of shared electrons})$$

In a neutral molecule, the sum of all formal charges must be zero. In a polyatomic ion, the sum of all formal charges must be equal to the charge of the ion.

Formal charge is useful for determining which of two or more Lewis structures is correct. Usually, the Lewis structure with the fewest formally charged atoms is correct. Negative charges should reside on the more electronegative atom.

Formal charges occur when a coordinate covalent bond forms. This bond is one in which an empty orbital on one atom overlaps with a full orbital on the other atom. The atom with the empty orbital will usually have the greater electronegativity, and will acquire a negative formal charge.

EXAMPLE: On the basis of formal charge, decide which of the following Lewis structures is correct:



SOLUTION: For structure a, the formal charges are

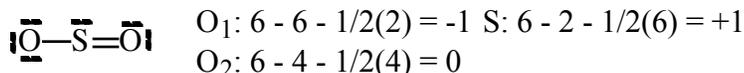
$$\begin{array}{ll} \text{H} & 1 - 0 - 1/2(2) = 0 \\ \text{C} & 4 - 0 - 1/2(8) = 0 \\ \text{S} & 6 - 2 - 1/2(6) = +1 \\ \text{N} & 5 - 4 - 1/2(4) = -1 \end{array}$$

For structure b, the formal charges are

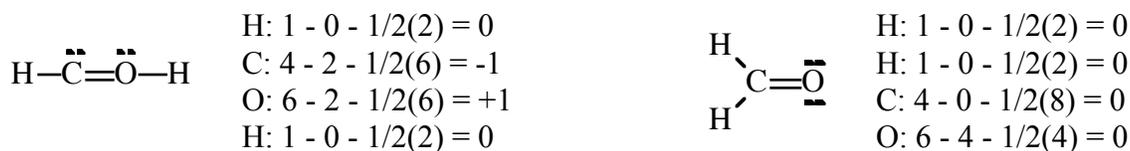
$$\begin{array}{ll} \text{H} & 1 - 0 - 1/2(2) = 0 \\ \text{C} & 4 - 0 - 1/2(8) = 0 \\ \text{S} & 6 - 4 - 1/2(4) = 0 \\ \text{N} & 5 - 2 - 1/2(6) = 0 \end{array}$$

Since structure b has no formally charged atoms, it must be the correct one.

Example: SO_2



Use formal charge to choose between structures:

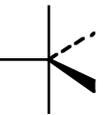


8.13 Molecular Structure: The VSEPR Model

One way of determining molecular geometry is based on the principle that electron pairs repel each other, so when several pairs occupy space around an atom, they should be configured as far apart as possible. This Valence-Shell Electron-Pair Repulsion (VSEPR) theory requires only that the Lewis structure of the molecule be known, and assumes

- 1) both lone pairs and bonding pairs take up space around an atom
- 2) multiple (double and triple) bonds are counted as a single bonding pair
- 3) lone pairs require more space than bonding pairs, so they should be assigned roomier locations and kept as far apart as possible.

The following table shows how the geometry depends on the Lewis structure for molecules with 2 to 6 pairs of electrons around the central atom. The total number of electron pairs (counting multiple bonds as a single pair) is shown in the first column. The general geometry for that number of pairs is shown next. The actual shape is derived from the general geometry depending on how many of the electron pairs are bonding pairs and how many are lone pairs.

# pairs	geometry	bond angles	bonding pairs	lone pairs	type	shape		
2	linear	180°	2	0	AB ₂	linear	BeH ₂	
3	trigonal planar	120°	3	0	AB ₃	trigonal planar	BF ₃	
			2	1	AB ₂ E	bent	SnCl ₂	
4	tetrahedral	109.5°	4	0	AB ₄	tetrahedral	CH ₄	
			3	1	AB ₃ E	pyramidal	NH ₃	
			2	2	AB ₂ E ₂	bent	H ₂ O	
5	trigonal bipyramid	90° 120°	5	0	AB ₅	trigonal bipyramid	PF ₅	
			4	1	AB ₄ E	see-saw	SF ₄	
			3	2	AB ₃ E ₂	T-shape	IF ₃	
			2	3	AB ₂ E ₃	linear	XeF ₂	
6	octahedral	90°	6	0	AB ₆	octahedral	SF ₆	
			5	1	AB ₅ E	square pyramid	BrF ₅	
			4	2	AB ₄ E ₂	square planar	XeF ₄	

Molecules with multiple bonds: count multiple bonds as if they were single bonds in VSEPR.