

CHAPTER 10 THE SHAPES OF MOLECULES

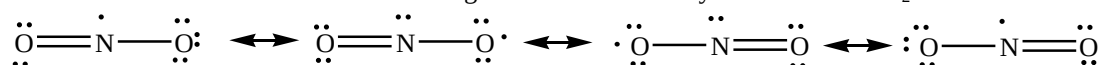
END-OF-CHAPTER PROBLEMS

- 10.1 Plan: To be the central atom in a compound, an atom must be able to simultaneously bond to at least two other atoms.

Solution:

He, F, and H cannot serve as central atoms in a Lewis structure. Helium ($1s^2$) is a noble gas, and as such, it does not need to bond to any other atoms. Hydrogen ($1s^1$) and fluorine ($1s^2 2s^2 2p^5$) only need one electron to complete their valence shells. Thus, they can only bond to one other atom, and they do not have d orbitals available to expand their valence shells.

- 10.2 Resonance must be present any time that a single Lewis structure is inadequate in explaining one or more aspects of a molecule or ion. The two N–O bonds in NO_2 are equivalent in bond length and bond energy; no single Lewis structure can account for this. The following Lewis structures may be drawn for NO_2 :



The average of all of these structures gives equivalent N–O bonds with a bond length that is between N–O and N=O.

- 10.3 Plan: For an element to obey the octet rule it must be surrounded by eight electrons. To determine the number of electrons present, (1) count the individual electrons actually shown adjacent to a particular atom (lone pairs), and (2) add two times the number of bonds to that atom: number of electrons = individual electrons + 2(number of bonds).

Solution:

(a) $0 + 2(4) = 8$; (b) $2 + 2(3) = 8$; (c) $0 + 2(5) = 10$; (d) $2 + 2(3) = 8$; (e) $0 + 2(4) = 8$; (f) $2 + 2(3) = 8$;
(g) $0 + 2(3) = 6$; (h) $8 + 2(0) = 8$. **All the structures obey the octet rule except: c and g.**

- 10.4 For an atom to expand its valence shell, it must have readily available d orbitals. The d orbitals do not become readily available until the third period or below on the periodic table. For the elements in the problem F, S, H, Al, Se, and Cl, the period numbers are 2, 3, 1, 3, 4, and 3, respectively. All of these elements, except those in the first two periods (H and F), can expand their valence shells.

- 10.5 Plan: Count the valence electrons and draw Lewis structures.

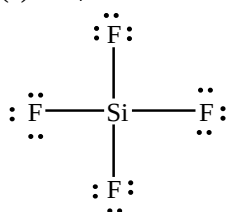
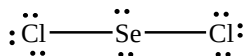
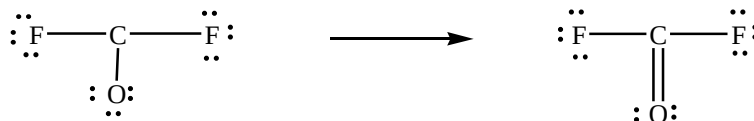
Solution:

Total valence electrons: SiF_4 : $[1 \times \text{Si}(4e^-)] + [4 \times \text{F}(7e^-)] = 32$; SeCl_2 : $[1 \times \text{Se}(6e^-)] + [2 \times \text{Cl}(7e^-)] = 20$;
 COF_2 : $[1 \times \text{C}(4e^-)] + [1 \times \text{O}(6e^-)] + [2 \times \text{F}(7e^-)] = 24$. The Si, Se, and the C are the central atoms, because these are the elements in their respective compounds with the lower group number (in addition, we are told C is central). Place the other atoms around the central atoms and connect each to the central atom with a single bond.

SiF_4 : At this point, eight electrons ($2e^-$ in four Si–F bonds) have been used with $32 - 8 = 24$ remaining; the remaining electrons are placed around the fluorine atoms (three pairs each). All atoms have an octet.

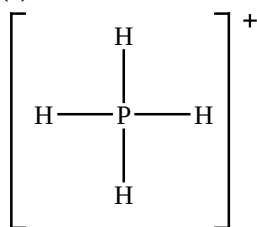
SeCl_2 : The two bonds use $4e^-$ ($2e^-$ in two Se–Cl bonds) leaving $20 - 4 = 16e^-$. These $16e^-$ are used to complete the octets on Se and the Cl atoms.

COF_2 : The three bonds to the C use $6e^-$ ($2e^-$ in three bonds) leaving $24 - 6 = 18e^-$. These $18e^-$ are distributed to the surrounding atoms first to complete their octets. After the $18e^-$ are used, the central C is two electrons short of an octet. Forming a double bond to the O (change a lone pair on O to a bonding pair on C) completes the C octet.

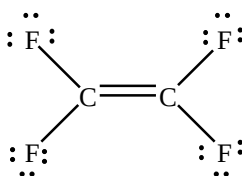
(a) SiF_4 (b) SeCl_2 (c) COF_2 

- 10.6 Total valence electrons: PH_4^+ has 8; C_2F_4 has 36; and SbH_3 has 8. Ignoring H, the atom in the lower group number is central: P, C, and Sb. Added proof: H and F are never central. The two central C atoms must be adjacent. Place all the other atoms around the central atom. Split the F atoms so that each C gets two. Connect all the atoms with single bonds. This uses all the electrons in PH_4^+ , and gives P an octet. The H atoms need no additional electrons. The C atoms have six electrons each, but can achieve an octet by forming a double bond. Splitting the twenty-four remaining electrons in C_2F_4 into twelve pairs and giving three pairs to each F leaves each F with an octet. The last two electrons in SbH_3 end as a lone pair on the Sb, and complete its octet.

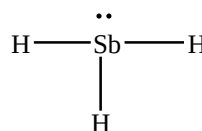
(a)



(b)



(c)



- 10.7 Plan: Count the valence electrons and draw Lewis structures.

Solution:

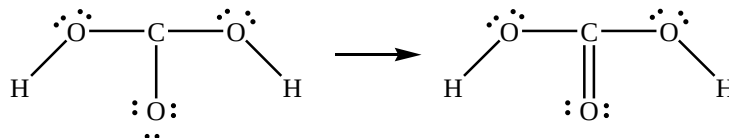
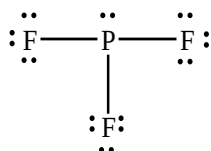
a) PF_3 : $[1 \times \text{P}(5e^-)] + [3 \times \text{F}(7e^-)] = 26$ valence electrons. P is the central atom. Draw single bonds from P to the three F atoms, using $2e^- \times 3 \text{ bonds} = 6e^-$. Remaining e^- : $26 - 6 = 20e^-$. Distribute the $20e^-$ around the P and F atoms to complete their octets.

b) H_2CO_3 : $[2 \times \text{H}(1e^-)] + [1 \times \text{C}(4e^-)] + 3 \times \text{O}(6e^-)] = 24$ valence electrons. C is the central atom with the H atoms attached to the O atoms. Place appropriate single bonds between all atoms using $2e^- \times 5 \text{ bonds} = 10e^-$ so that $24 - 10 = 14e^-$ remain. Use these $14e^-$ to complete the octets of the O atoms (the H atoms already have their two electrons). After the $14e^-$ are used, the central C is two electrons short of an octet. Forming a double bond to the O that does not have an H bonded to it (change a lone pair on O to a bonding pair on C) completes the C octet.

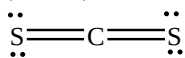
c) CS_2 : $[1 \times \text{C}(4e^-)] + [2 \times \text{S}(6e^-)] = 16$ valence electrons. C is the central atom. Draw single bonds from C to the two S atoms, using $2e^- \times 2 \text{ bonds} = 4e^-$. Remaining e^- : $16 - 4 = 12e^-$. Use these $12e^-$ to complete the octets of the surrounding S atoms; this leaves C four electrons short of an octet. Form a double bond from each S to the C by changing a lone pair on each S to a bonding pair on C.

a) PF_3 (26 valence e^-)

b) H_2CO_3 (24 valence e^-)

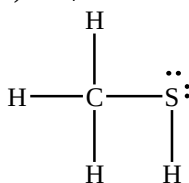


c) CS₂ (16 valence e⁻)

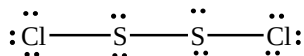


10.8 The C and S atoms are central. The S in part a) is attached to an H and the C. All atoms are attached with single bonds and the remaining electrons are divided into lone pairs. All the atoms, except H, have octets.

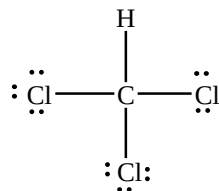
a) CH₄S



b) S₂Cl₂



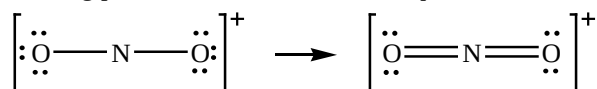
c) CHCl₃



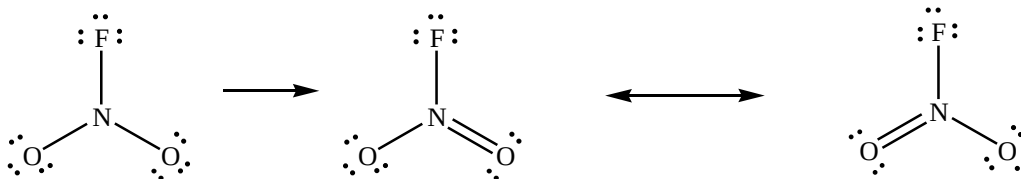
10.9 Plan: The problem asks for resonance structures, so there must be more than one answer for each part.

Solution:

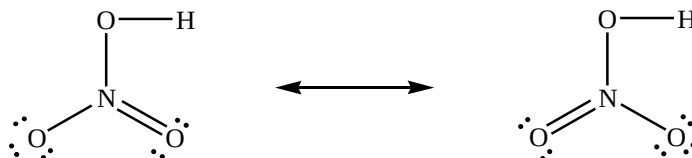
a) NO₂⁺ has [1 x N(5e⁻)] + [2 x O(6e⁻)] - 1e⁻ (+ charge) = 16 valence electrons. Draw a single bond from N to each O, using 2e⁻ x 2 bonds = 4e⁻; 16 - 4 = 12e⁻ remain. Distribute these 12e⁻ to the O atoms to complete their octets. This leaves N 4e⁻ short of an octet. Form a double bond from each O to the N by changing a lone pair on each O to a bonding pair on N. No resonance is required as all atoms can achieve an octet with double bonds.



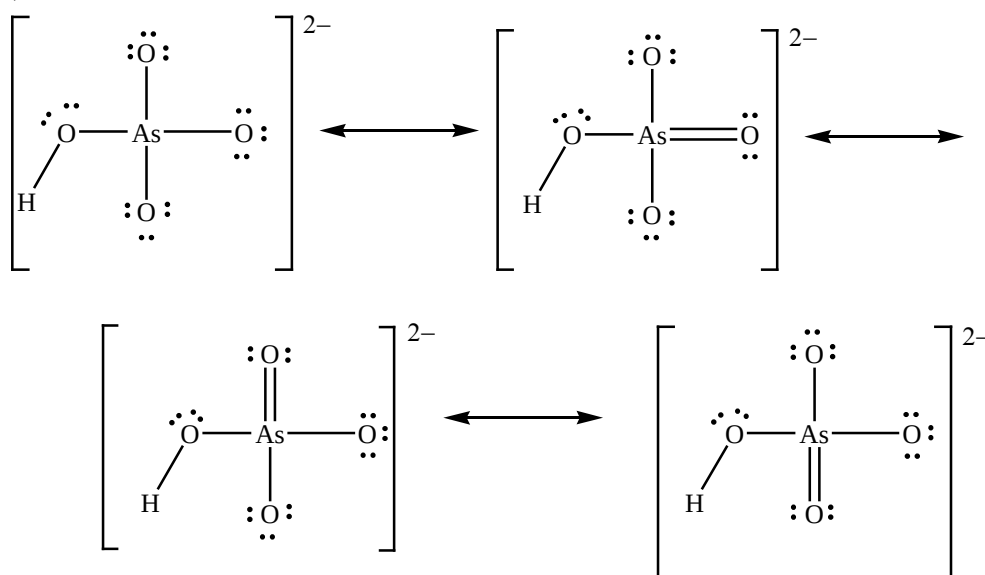
b) NO₂F has [1 x N(5e⁻)] + [2 x O(6e⁻)] + [1 x F(7e⁻)] = 24 valence electrons. Draw a single bond from N to each surrounding atom, using 2e⁻ x 3 bonds = 6e⁻; 24 - 6 = 18e⁻ remain. Distribute these 18e⁻ to the O and F atoms to complete their octets. This leaves N 2e⁻ short of an octet. Form a double bond from either O to the N by changing a lone pair on O to a bonding pair on N. There are two resonance structures since a lone pair from either of the two O atoms can be moved to a bonding pair with N:



10.10 a)



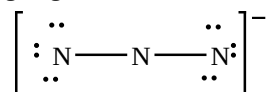
b)



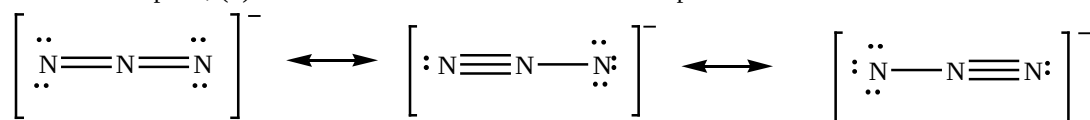
10.11 Plan: Count the valence electrons and draw Lewis structures. Additional structures are needed to show resonance.

Solution:

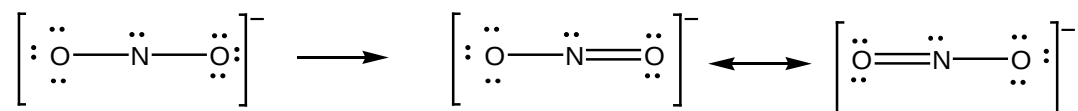
a) N_3^- has $[3 \times \text{N}(5e^-)] + [1 e^- (\text{from charge})] = 16$ valence electrons. Place a single bond between the nitrogen atoms. This uses $2e^- \times 2 \text{ bonds} = 4$ electrons, leaving $16 - 4 = 12$ electrons (6 pairs). Giving three pairs on each end nitrogen gives them an octet, but leaves the central N with only four electrons as shown below:



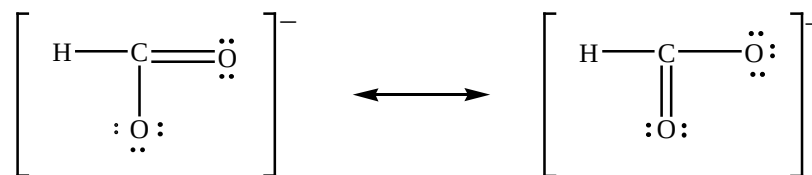
The central N needs four electrons. There are three options to do this: (1) each of the end N atoms could form a double bond to the central N by sharing one of its pairs; (2) one of the end N atoms could form a triple bond by sharing two of its lone pairs; (3) the other end N atom could form the triple bond instead.



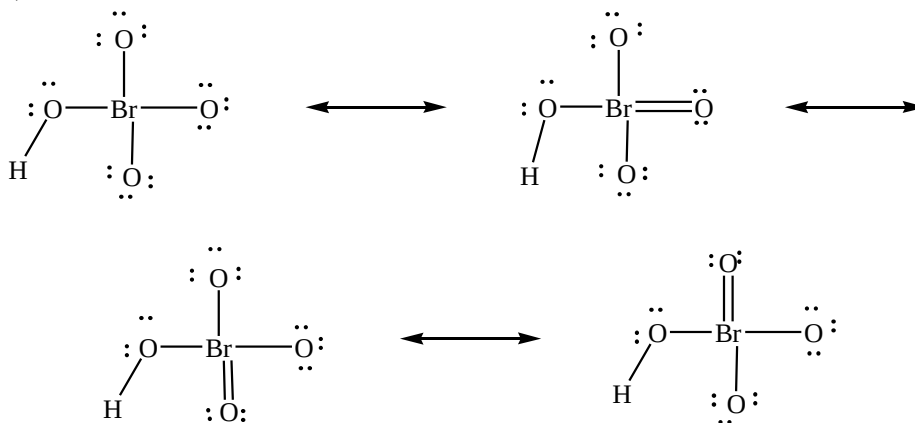
b) NO_2^- has $[1 \times \text{N}(5e^-)] + [2 \times \text{O}(6e^-)] + [1 e^- (\text{from charge})] = 18$ valence electrons. The nitrogen should be the central atom with each of the oxygen atoms attached to it by a single bond ($2e^- \times 2 \text{ bonds} = 4$ electrons). This leaves $18 - 4 = 14$ electrons (seven pairs). If three pairs are given to each O and one pair is given to the N, then both O atoms have an octet, but the N atom only has six. To complete an octet the N atom needs to gain a pair of electrons from one O atom or the other (form a double bond). The resonance structures are:



10.12 a) HCO_2^- has 18 valence electrons.



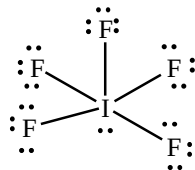
b) HBrO_4 has 32 valence electrons.



10.13 **Plan:** Initially, the method used in the preceding problems may be used to establish a Lewis structure. The total of the formal charges must equal the charge on an ion or be equal to 0 for a compound. The formal charge only needs to be calculated once for a set of identical atoms. Formal charge (FC) = no. of valence electrons – [no. of unshared valence electrons + $\frac{1}{2}$ no. of shared valence electrons].

Solution:

a) IF_5 has $[1 \times \text{I}(7e^-)] + [5 \times \text{F}(7e^-)] = 42$ valence electrons. The presence of five F atoms around the central I means that the I atom will have a minimum of ten electrons; thus, this is an exception to the octet rule. The five I–F bonds use $2e^- \times 5 \text{ bonds} = 10$ electrons leaving $42 - 10 = 32$ electrons (16 pairs). Each F needs three pairs to complete an octet. The five F atoms use fifteen of the sixteen pairs, so there is one pair left for the central I. This gives:



Calculating formal charges:

FC = no. of valence electrons – [no. of unshared valence electrons + $\frac{1}{2}$ no. of shared valence electrons].

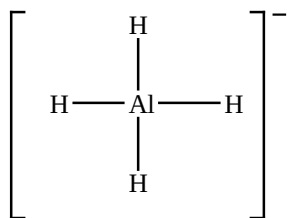
For iodine: $\text{FC}_\text{I} = 7 - [2 + \frac{1}{2}(10)] = 0$

For each fluorine: $\text{FC}_\text{F} = 7 - [6 + \frac{1}{2}(2)] = 0$

Total formal charge = 0 = charge on the compound.

b) AlH_4^- has $[1 \times \text{Al}(3e^-)] + [4 \times \text{H}(1e^-)] + [1e^- \text{ (from charge)}] = 8$ valence electrons.

The four Al–H bonds use all the electrons and Al has an octet.

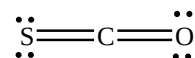


FC = no. of valence electrons – [no. of unshared valence electrons + $\frac{1}{2}$ no. of shared valence electrons].

For aluminum: $\text{FC}_\text{Al} = 3 - [0 + \frac{1}{2}(8)] = -1$

For each hydrogen: $\text{FC}_\text{H} = 1 - [0 + \frac{1}{2}(2)] = 0$

10.14 a) OCS has sixteen valence electrons.

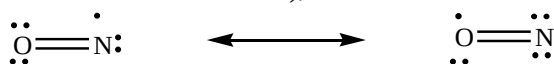


$\text{FC}_\text{S} = 6 - [4 + \frac{1}{2}(4)] = 0$

$\text{FC}_\text{C} = 4 - [0 + \frac{1}{2}(8)] = 0$

$\text{FC}_\text{O} = 6 - [4 + \frac{1}{2}(4)] = 0$

b) NO (has eleven valence electrons); the odd number means there will be an exception to the octet rule.



$$\text{FC}_{\text{O}} = 6 - [4 + \frac{1}{2}(4)] = 0$$

$$\text{FC}_{\text{O}} = 6 - [3 + \frac{1}{2}(4)] = +1$$

$$\text{FC}_{\text{N}} = 5 - [3 + \frac{1}{2}(4)] = 0$$

$$\text{FC}_{\text{N}} = 5 - [4 + \frac{1}{2}(4)] = -1$$

The first resonance structure has a better distribution of formal charges.

10.15 Plan: The general procedure is similar to the preceding problems, plus the oxidation number determination.

Solution:

a) BrO_3^- has $[1 \times \text{Br}(7e^-)] + 3 \times \text{O}(6e^-)] + [1e^- \text{ (from charge)}] = 26$ valence electrons.

Placing the O atoms around the central Br and forming three Br–O bonds uses $2e^- \times 3 \text{ bonds} = 6$ electrons and leaves $26 - 6 = 20$ electrons (ten pairs). Placing three pairs on each O ($3 \times 3 = 9$ total pairs) leaves one pair for the Br and yields structure I below. In structure I, all the atoms have a complete octet. Calculating formal charges:

$$\text{FC}_{\text{Br}} = 7 - [2 + \frac{1}{2}(6)] = +2$$

$$\text{FC}_{\text{O}} = 6 - [6 + \frac{1}{2}(2)] = -1$$

The FC_{O} is acceptable, but FC_{Br} is larger than is usually acceptable. Forming a double bond between any one of the O atoms gives structure II. Calculating formal charges:

$$\text{FC}_{\text{Br}} = 7 - [2 + \frac{1}{2}(8)] = +1$$

$$\text{FC}_{\text{O}} = 6 - [6 + \frac{1}{2}(2)] = -1$$

$$\text{FC}_{\text{O}} = 6 - [4 + \frac{1}{2}(4)] = 0$$

(Double bonded O)

The FC_{Br} can be improved further by forming a second double bond to one of the other O atoms (structure III).

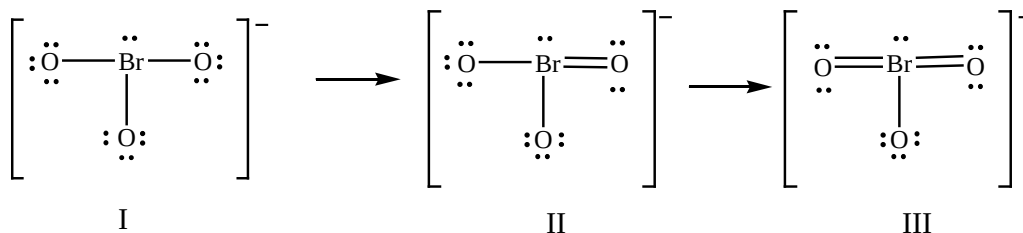
$$\text{FC}_{\text{Br}} = 7 - [2 + \frac{1}{2}(10)] = 0$$

$$\text{FC}_{\text{O}} = 6 - [6 + \frac{1}{2}(2)] = -1$$

$$\text{FC}_{\text{O}} = 6 - [4 + \frac{1}{2}(4)] = 0$$

(Double bonded O atoms)

Structure III has the most reasonable distribution of formal charges.



The oxidation numbers (O.N.) are: $\text{O.N.}_{\text{Br}} = +5$ and $\text{O.N.}_{\text{O}} = -2$.

$$\begin{array}{cc} -6 & \\ +5 & -2 \end{array}$$

Check: The total formal charge equals the charge on the ion (-1).



b) SO_3^{2-} has $[1 \times \text{S}(6e^-)] + [3 \times \text{O}(6e^-)] + [2e^- \text{ (from charge)}] = 26$ valence electrons.

Placing the O atoms around the central S and forming three S–O bonds uses $2e^- \times 3 \text{ bonds} = 6$ electrons and leaves $26 - 6 = 20$ electrons (ten pairs). Placing three pairs on each O ($3 \times 3 = 9$ total pairs) leaves one pair for the S and yields structure I below. In structure I all the atoms have a complete octet. Calculating formal charges:

$$\text{FC}_{\text{S}} = 6 - [2 + \frac{1}{2}(6)] = +1;$$

$$\text{FC}_{\text{O}} = 6 - [6 + \frac{1}{2}(2)] = -1$$

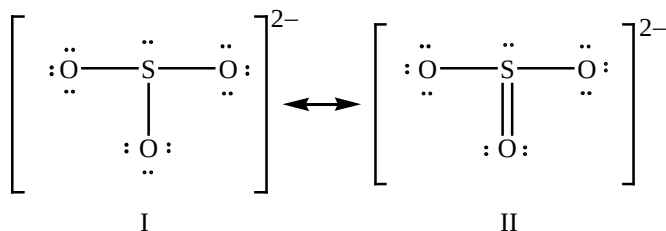
The FC_{O} is acceptable, but FC_{S} is larger than is usually acceptable. Forming a double bond between any one of the O atoms (structure II) gives:

$$\text{FC}_{\text{S}} = 6 - [2 + \frac{1}{2}(8)] = 0$$

$$\text{FC}_{\text{O}} = 6 - [6 + \frac{1}{2}(2)] = -1$$

$$\text{FC}_{\text{O}} = 6 - [4 + \frac{1}{2}(4)] = 0$$

(Double bonded O)



Structure II has the more reasonable distribution of formal charges.

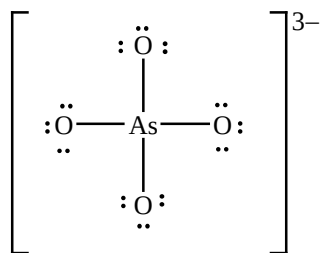
$$\begin{array}{cc} -6 & \\ +4 & -2 \end{array}$$

The oxidation numbers (O.N.) are: $\text{O.N.}_{\text{S}} = +4$ and $\text{O.N.}_{\text{O}} = -2$.



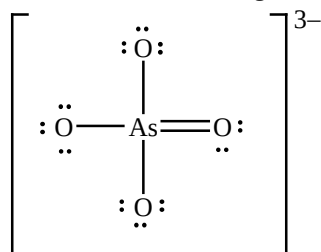
Check: The total formal charge equals the charge on the ion (-2).

- 10.16 a) AsO_4^{3-} has 32 valence electrons. See structure I.
 $\text{FC}_{\text{As}} = 5 - [0 + \frac{1}{2}(8)] = +1$ $\text{FC}_{\text{O}} = 6 - [6 + \frac{1}{2}(2)] = -1$
 Net formal charge $(+1 - 4) = -3$ The octet rule is followed by all atoms.



I

For more reasonable formal charges, move a lone pair from an O to a bonded pair on As (structure II):



II

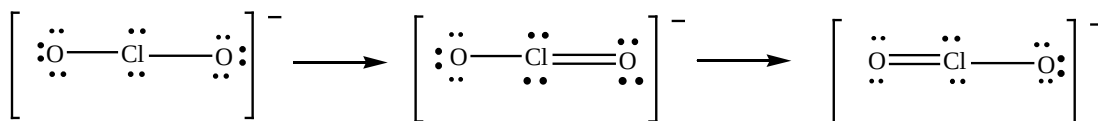
$\text{FC}_{\text{As}} = 5 - [0 + \frac{1}{2}(10)] = 0$ $\text{FC}_{\text{O}(\text{single bond})} = 6 - [6 + \frac{1}{2}(2)] = -1$ $\text{FC}_{\text{O}(\text{double bond})} = 6 - [4 + \frac{1}{2}(4)] = 0$
 Net formal charge: $(0 + 3(-1)) + 0 = -3$ Improved formal charge distribution

O.N.: O -2 each $\times 4 = -8$ total; As +5

b) ClO_2^- has 20 valence electrons. For structure I in which all atoms have an octet:

$\text{FC}_{\text{Cl}} = 7 - [4 + \frac{1}{2}(4)] = +1$ $\text{FC}_{\text{O}} = 6 - [6 + \frac{1}{2}(2)] = -1$

For more reasonable formal charges, see structure II:



I

II

Formal charges in structure II:

$\text{FC}_{\text{Cl}} = 7 - [4 + \frac{1}{2}(6)] = 0$

$\text{FC}_{\text{O}(\text{double bond})} = 6 - [4 + \frac{1}{2}(4)] = 0$

$\text{FC}_{\text{O}(\text{single bond})} = 6 - [6 - \frac{1}{2}(2)] = -1$

O.N.: O -2 each $\times 2 = -4$ total; Cl +3

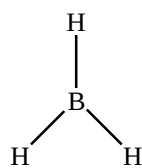
- 10.17 Plan: The octet rule states that when atoms bond, they share electrons to attain a filled outer shell of eight electrons. If an atom has fewer than eight electrons, it is electron deficient; if an atom has more than eight electrons around it, the atom has an expanded octet.

Solution:

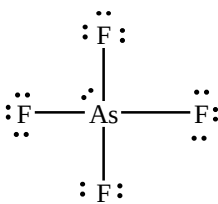
a) BH_3 has $[1 \times \text{B}(3e^-)] + [3 \times \text{H}(1e^-)] = 6$ valence electrons. These are used in three B-H bonds. The B has six electrons instead of an octet; this molecule is **electron deficient**.

b) AsF_4^- has $[1 \times \text{As}(5e^-)] + [4 \times \text{F}(7e^-)] + [1e^- \text{ (from charge)}] = 34$ valence electrons. Four As-F bonds use eight electrons leaving $34 - 8 = 26$ electrons (13 pairs). Each F needs three pairs to complete its octet and the remaining pair goes to the As. The As has an **expanded octet** with ten electrons. The F cannot expand its octet.

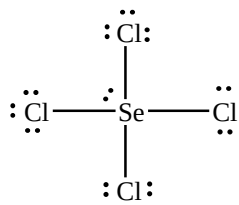
c) SeCl_4 has $[1 \times \text{Se}(6e^-)] + 4 \times \text{Cl}(7e^-) = 34$ valence electrons. The SeCl_4 is isoelectronic (has the same electron structure) as AsF_4^- , and so its Lewis structure looks the same. Se has an **expanded octet** of ten electrons.



(a)

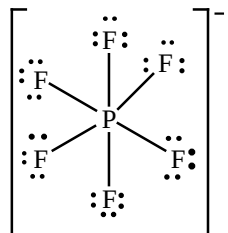


(b)

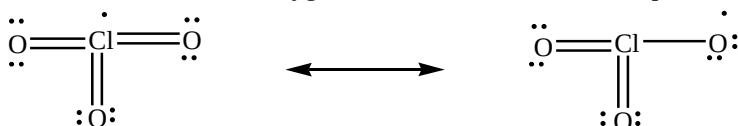


(c)

10.18 a) PF_6^- has 48 valence electrons. P has an **expanded octet** of 12 e^- .

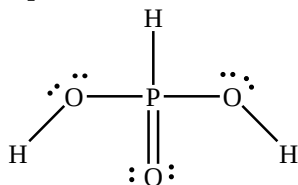


b) ClO_3 has twenty-five valence electrons. The odd number means that there will be an exception. This is a radical: the chlorine or one of the oxygen atoms will lack an e^- to complete its octet.



There are two additional resonance structures where the other O atoms are the ones lacking the octet. The FC predicts that Cl will end with the odd electron.

c) H_3PO_3 has twenty-six valence electrons. To balance the formal charges; the O lacking an H will form a double bond to the P. This compound is an exception in that one of the H atoms is attached to the central P. P has an **expanded octet** of 10 e^- .



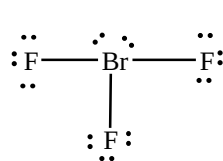
10.19 Plan: The octet rule states that when atoms bond, they share electrons to attain a filled outer shell of eight electrons. If an atom has fewer than eight electrons, it is electron deficient; if an atom has more than eight electrons around it, the atom has an expanded octet.

Solution:

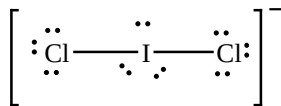
a) BrF_3 has $[1 \times \text{Br}(7e^-)] + [3 \times \text{F}(7e^-)] = 28$ valence electrons. Placing a single bond between Br and each F uses $2e^- \times 3 \text{ bonds} = 6e^-$, leaving $28 - 6 = 22$ electrons (eleven pairs). After the F atoms complete their octets with three pairs each, the Br gets the last two lone pairs. The Br has an **expanded octet** of ten electrons.

b) ICl_2^- has $[1 \times \text{I}(7e^-)] + [2 \times \text{Cl}(7e^-)] + [1e^- (\text{from charge})] = 22$ valence electrons. Placing a single bond between I and each Cl uses $2e^- \times 2 \text{ bond} = 4e^-$, leaving $22 - 4 = 18$ electrons (nine pairs). After the Cl atoms complete their octets with three pairs each, the iodine finishes with the last three lone pairs. The iodine has an **expanded octet** of ten electrons.

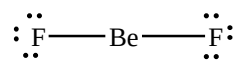
c) BeF_2 has $[1 \times \text{Be}(2e^-)] + [2 \times \text{F}(7e^-)] = 16$ valence electrons. Placing a single bond between Be and each of the F atoms uses $2e^- \times 2 \text{ bonds} = 4e^-$, leaving $16 - 4 = 12$ electrons (six pairs). The F atoms complete their octets with three pairs each, and there are no electrons left for the Be. Formal charges work against the formation of double bonds. Be, with only four electrons, is **electron deficient**.



a)

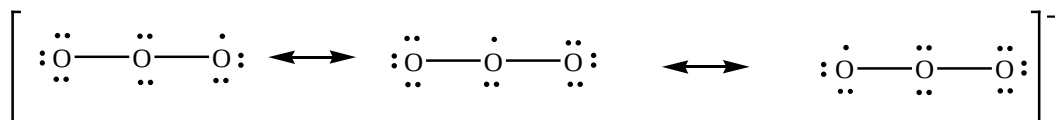


b)



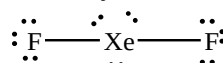
c)

- 10.20 a) O_3^- has nineteen valence electrons (note the odd number). There are several resonance structures possible; only one is necessary for the answer. One of the O atoms has the odd electron (seven total).



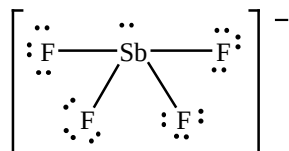
- b) XeF_2 has twenty-two valence electrons.

Xe has an **expanded octet** of $10e^-$.



- c) SbF_4^- has thirty-four valence electrons.

Sb has an **expanded octet** of $10e^-$.



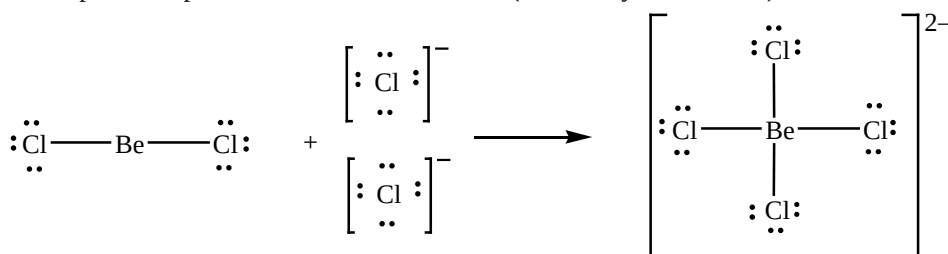
- 10.21 Plan: Draw Lewis structures for the reactants and products.

Solution:

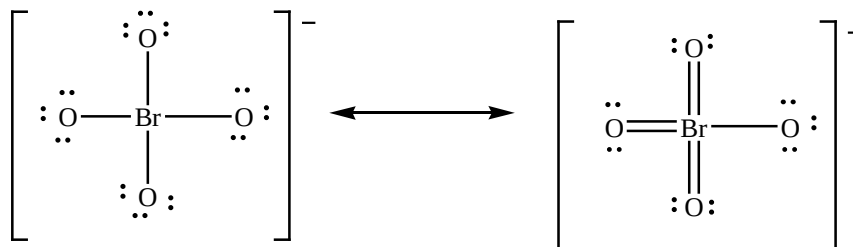
Beryllium chloride has the formula BeCl_2 . BeCl_2 has $[1 \times \text{Be}(2e^-)] + [2 \times \text{Cl}(7e^-)] = 16$ valence electrons. Four of these electrons are used to place a single bond between Be and each of the Cl atoms, leaving $16 - 4 = 12$ electrons (six pairs). These six pairs are used to complete the octets of the Cl atoms, but Be does not have an octet – it is electron deficient.

Chloride ion has the formula Cl^- with an octet of electrons.

BeCl_4^{2-} has $[1 \times \text{Be}(2e^-)] + [4 \times \text{Cl}(7e^-)] + [2e^- \text{ (from charge)}] = 32$ valence electrons. Eight of these electrons are used to place a single bond between Be and each Cl atom, leaving $32 - 8 = 24$ electrons (twelve pairs). These twelve pairs complete the octet of the Cl atoms (Be already has an octet).



- 10.22 Draw a Lewis structure. If the formal charges are not ideal, a second structure may be needed. BrO_4^- has thirty-two valence electrons.



In the structure on the left, all atoms have octets. The formal charges are:

$$\text{FC}_{\text{Br}} = 7 - [0 + \frac{1}{2}(8)] = +3$$

$$\text{FC}_{\text{O}} = 6 - [6 + \frac{1}{2}(2)] = -1$$

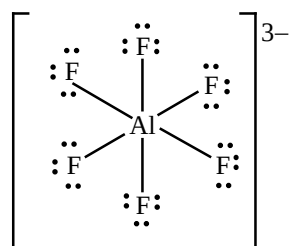
The structure on the right expands the valence shell of the Br to give more favorable formal charges.

$$\text{FC}_{\text{Br}} = 7 - [0 + \frac{1}{2}(14)] = 0$$

$$\text{FC}_{\text{O}(\text{single bonded})} = 6 - [6 + \frac{1}{2}(2)] = -1$$

$$\text{FC}_{\text{O}(\text{double bonded})} = 6 - [4 + \frac{1}{2}(4)] = 0$$

- 10.23 Count the total valence electrons and draw a Lewis structure. AlF_6^{3-} has forty-eight valence electrons.



- 10.24 Plan: Use the structures in the text to determine the formal charges.

Formal charge (FC) = no. of valence electrons – [no. of unshared valence electrons + $\frac{1}{2}$ no. of shared valence electrons].

Solution:

$$\text{Structure A: } \text{FC}_{\text{C}} = 4 - [0 + \frac{1}{2}(8)] = 0; \text{FC}_{\text{O}} = 6 - [4 + \frac{1}{2}(4)] = 0; \text{FC}_{\text{Cl}} = 7 - [6 + \frac{1}{2}(2)] = 0$$

Total FC = 0

$$\text{Structure B: } \text{FC}_{\text{C}} = 4 - [0 + \frac{1}{2}(8)] = 0; \text{FC}_{\text{O}} = 6 - [6 + \frac{1}{2}(2)] = -1;$$

$$\text{FC}_{\text{Cl}(\text{double bonded})} = 7 - [4 + \frac{1}{2}(4)] = +1; \text{FC}_{\text{Cl}(\text{single bonded})} = 7 - [6 + \frac{1}{2}(2)] = 0$$

Total FC = 0

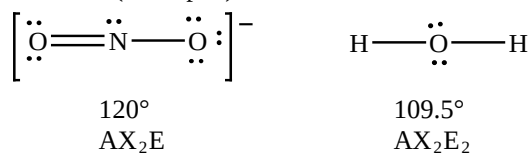
$$\text{Structure C: } \text{FC}_{\text{C}} = 4 - [0 + \frac{1}{2}(8)] = 0; \text{FC}_{\text{O}} = 6 - [6 + \frac{1}{2}(2)] = -1;$$

$$\text{FC}_{\text{Cl}(\text{double bonded})} = 7 - [4 + \frac{1}{2}(4)] = +1; \text{FC}_{\text{Cl}(\text{single bonded})} = 7 - [6 + \frac{1}{2}(2)] = 0$$

Total FC = 0

Structure A has the most reasonable set of formal charges.

- 10.25 Determine the total number of valence electrons present. Next, draw a Lewis structure. Finally, use VSEPR or valence bond theory to predict the shape.
- 10.26 The molecular shape and the electron-group arrangement are the same when there are no lone pairs on the central atom.
- 10.27 A bent (V-shaped) molecule will have the stoichiometry AX_2 , so only AX_2E_n geometries result in a bent molecule. The presence of one or two lone pairs in the **three and four electron-group arrangements** can produce a bent (V-shaped) molecule as either AX_2E or AX_2E_2 . Examples are: NO_2^- and H_2O .



- 10.28 Plan: Examine a list of all possible structures, and choose the ones with four electron groups since the tetrahedral electron-group arrangement has four electron groups.

Solution:

Tetrahedral	AX_4
Trigonal pyramidal	AX_3E
Bent or V shaped	AX_2E_2

- 10.29 a) **A**, which has a square planar molecular geometry, has the most electron pairs. There are four shared pairs and two unshared pairs for a total of six pairs of electrons. The six electron pairs are arranged in an octahedral arrangement with the four bonds in a square planar geometry. B and C have five electron pairs and D has four electron pairs.

b) **A** has the most unshared pairs around the central atom with two unshared pairs. B has only one unshared pair on the central atom and C and D have no unshared pairs on the central atom.

c) **C and D** have only shared pairs around the central atom.

- 10.30 The number of electron pairs governs the overall arrangement of the electrons. The superposition of the atoms on this arrangement gives rise to the molecular shape. The actual molecular shape reflects the positions of the atoms, not the positions of electron pairs.

- 10.31 Plan: Begin with the basic structures and redraw them.

Solution:

a) A molecule that is V shaped has two bonds and generally has either one (AX_2E) or two (AX_2E_2) lone electron pairs.

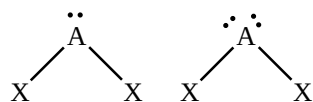
b) A trigonal planar molecule follows the formula AX_3 with three bonds and no lone electron pairs.

c) A trigonal bipyramidal molecule contains five bonding pairs (single bonds) and no lone pairs (AX_5).

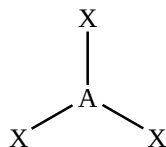
d) A T-shaped molecule has three bonding groups and two lone pairs (AX_3E_2).

e) A trigonal pyramidal molecule follows the formula AX_3E with three bonding pairs and one lone pair.

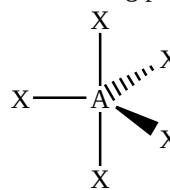
f) A square pyramidal molecule shape follows the formula AX_5E with five bonding pairs and one lone pair.



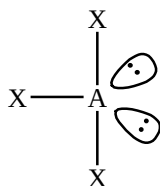
(a)



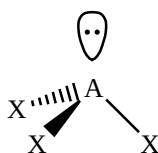
(b)



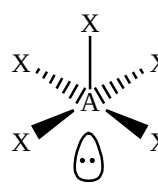
(c)



(d)



(e)



(f)

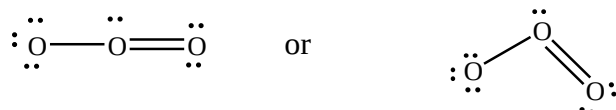
- 10.32 Determine the geometry from the lone pairs and the number of groups attached to the central atom.

a) AX_3E	tetrahedral	109.5°	smaller
b) AX_2	linear	180°	none
c) AX_3	trigonal planar	120°	none
d) AX_2E_2	tetrahedral	109.5°	smaller
e) AX_2	linear	180°	none
f) AX_4E	trigonal bipyramidal	$180^\circ, 120^\circ, 90^\circ$	smaller

10.33 Plan: First, draw a Lewis structure, and then apply VSEPR.

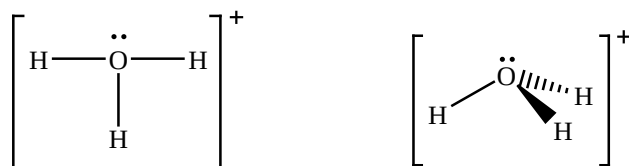
Solution:

a) O_3 : The molecule has $[3 \times \text{O}(6e^-)] = 18$ valence electrons. Four electrons are used to place single bonds between the oxygen atoms, leaving $18 - 4 = 14e^-$ (seven pairs). Six pairs are required to give the end oxygen atoms an octet; the last pair is distributed to the central oxygen, leaving this atom two electrons short of an octet. Form a double bond from one of the end O atoms to the central O by changing a lone pair on the end O to a bonding pair on the central O. This gives the following Lewis structure:



There are three electron groups around the central O, one of which is a lone pair. This gives a **trigonal planar** electron-group arrangement (AX_2E), a **bent** molecular shape, and an ideal bond angle of 120° .

b) H_3O^+ : This ion has $[3 \times \text{H}(1e^-)] + [1 \times \text{O}(6e^-)] - [1e^- \text{ (due to + charge)}] = \text{eight valence electrons}$. Six electrons are used to place a single bond between O and each H, leaving $8 - 6 = 2e^-$ (one pair). Distribute this pair to the O atom, giving it an octet (the H atoms only get two electrons). This gives the following Lewis structure:



There are four electron groups around the O, one of which is a lone pair. This gives a **tetrahedral** electron-group arrangement (AX_3E), a **trigonal pyramidal** molecular shape, and an ideal bond angle of 109.5° .

c) NF_3 : The molecule has $[1 \times \text{N}(5e^-)] + [3 \times \text{F}(7e^-)] = 26$ valence electrons. Six electrons are used to place a single bond between N and each F, leaving $26 - 6 = 20e^-$ (ten pairs). These ten pairs are distributed to all of the F atoms and the N atoms to give each atom an octet. This gives the following Lewis structure:

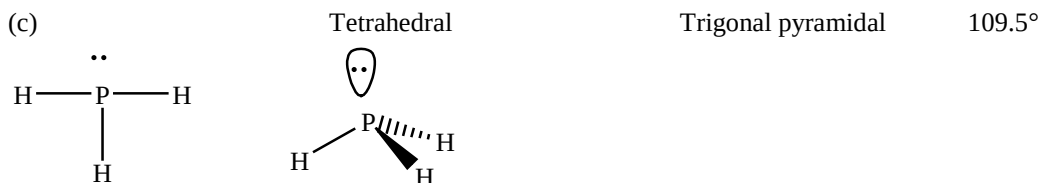


There are four electron groups around the N, one of which is a lone pair. This gives a **tetrahedral** electron-group arrangement (AX_3E), a **trigonal pyramidal** molecular shape, and an ideal bond angle of 109.5° .

10.34	Lewis structure	Electron-group arrangement	Molecular shape	Ideal bond angle
(a)	$\left[\begin{array}{c} \text{:}\ddot{\text{O}}\text{---}\ddot{\text{S}}\text{=}\ddot{\text{O}}\text{:} \\ \\ \text{:}\ddot{\text{O}}\text{:} \end{array} \right]^{2-}$	Tetrahedral	Tetrahedral	109.5°
(b)	$\left[\text{:}\ddot{\text{O}}\text{---}\ddot{\text{N}}\text{=}\ddot{\text{O}}\text{:} \right]^-$	Trigonal planar	Bent	120°

In addition, there are other resonance forms.

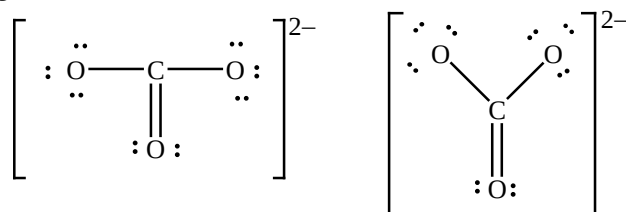
In addition, there are other resonance forms.



10.35 Plan: First, draw a Lewis structure, and then apply VSEPR.

Solution:

(a) CO_3^{2-} : This ion has $[1 \times \text{C}(4e^-)] + [3 \times \text{O}(6e^-)] + [2e^- \text{ (from charge)}] = 24$ valence electrons. Six electrons are used to place single bonds between C and each O atom, leaving $24 - 6 = 18 e^-$ (nine pairs). These nine pairs are used to complete the octets of the three O atoms, leaving C two electrons short of an octet. Form a double bond from one of the O atoms to C by changing a lone pair on an O to a bonding pair on C. This gives the following Lewis structure:



There are two additional resonance forms. There are three groups of electrons around the C, none of which are lone pairs. This gives a **trigonal planar** electron-group arrangement (AX_3), a **trigonal planar** molecular shape, and an ideal bond angle of 120° .

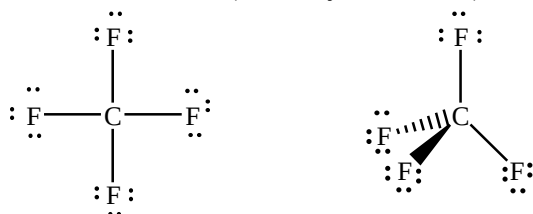
(b) SO_2 : This molecule has $[1 \times \text{S}(6e^-)] + [2 \times \text{O}(6e^-)] = 18$ valence electrons. Four electrons are used to place a single bond between S and each O atom, leaving $18 - 4 = 14e^-$ (seven pairs). Six pairs are needed to complete the octets of the O atoms, leaving a pair of electrons for S. S needs one more pair to complete its octet. Form a double bond from one of the end O atoms to the S by changing a lone pair on the O to a bonding pair on the S. This gives the following Lewis structure:



There are three groups of electrons around the C, one of which is a lone pair.

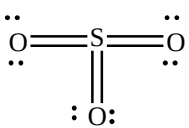
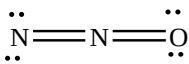
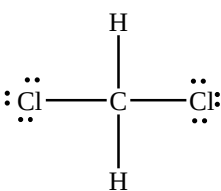
This gives a **trigonal planar** electron-group arrangement (AX_2E), a **bent (V-shaped)** molecular shape, and an ideal bond angle of 120° .

(c) CF_4 : This molecule has $[1 \times \text{C}(4e^-)] + [4 \times \text{F}(7e^-)] = 32$ valence electrons. Eight electrons are used to place a single bond between C and each F, leaving $32 - 8 = 24 e^-$ (twelve pairs). Use these twelve pairs to complete the octets of the F atoms (C already has an octet). This gives the following Lewis structure:



There are four groups of electrons around the C, none of which is a lone pair.

This gives a **tetrahedral** electron-group arrangement (AX_4), a **tetrahedral** molecular shape, and an ideal bond angle of 109.5° .

10.36	Lewis structure	Electron-group arrangement	Molecular shape	Ideal bond angle
		Trigonal planar	Trigonal planar	120°
		Linear	Linear	180°
		Tetrahedral	Tetrahedral	109.5°

10.37 Plan: Examine the structure shown, and then apply VSEPR.

Solution:

a) This structure shows three electron groups with three bonds around the central atom.

There appears to be no distortion of the bond angles so the shape is **trigonal planar**, the classification is **AX₃**, with an ideal bond angle of **120°**.

b) This structure shows three electron groups with three bonds around the central atom.

The bonds are distorted down indicating the presence of a lone pair. The shape of the molecule is **trigonal pyramidal** and the classification is **AX₃E**, with an ideal bond angle of **109.5°**.

c) This structure shows five electron groups with five bonds around the central atom.

There appears to be no distortion of the bond angles so the shape is **trigonal bipyramidal** and the classification is **AX₅**, with ideal bond angles of **90°** and **120°**.

10.38 a) This structure shows five electron groups with five bonds around the central atom.

There appears to be no distortion of the bond angles so the shape is **square pyramidal** (in reality square pyramidal structures have a slight distortion of the bond angles because there is a lone pair across from the atom at the apex of the pyramid). The classification is **AX₅E**, with an ideal bond angle of **90°**.

b) This structure shows three electron groups with three bonds around the central atom.

There appears to be no distortion of the bond angles so the shape is **T shaped** (in reality T shaped structures have a slight distortion of the bond angles to the apical bonds because there are two equatorial lone pairs). The classification is **AX₃E₂**, with an ideal bond angle of **90°**.

c) This structure shows four electron groups with four bonds around the central atom.

There appears to be no distortion of the bond angles so the shape is **tetrahedral** and the classification is **AX₄**, with an ideal bond angle of **109.5°**.

10.39 Plan: The Lewis structures must be drawn, and VSEPR applied to the structures. Lone pairs on the central atom generally result in a deviation of the ideal bond angle.

Solution:

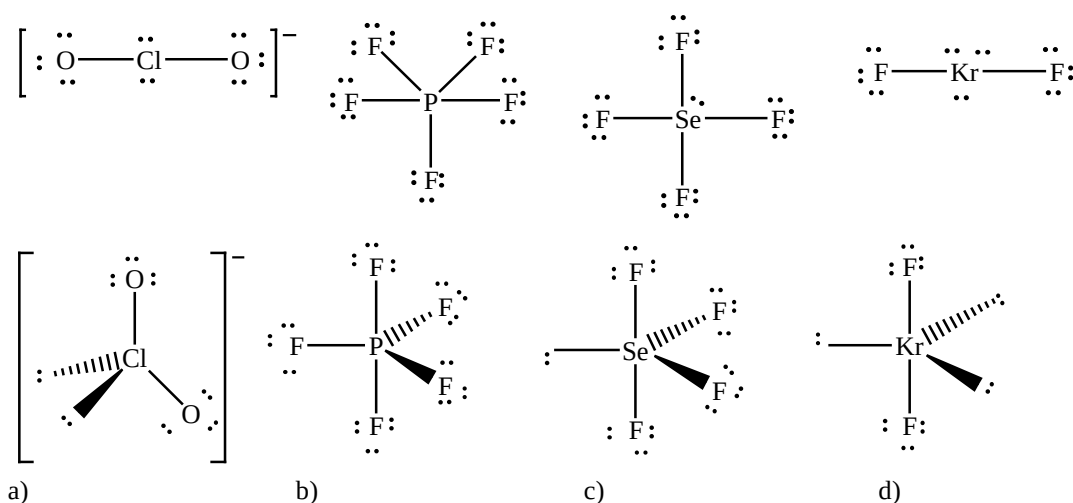
a) The ClO_2^- ion has $[1 \times \text{Cl}(7e^-)] + [2 \times \text{O}(6e^-)] + [1e^- \text{ (from charge)}] = 20$ valence electrons. Four electrons are used to place a single bond between the Cl and each O, leaving $20 - 4 = 16$ electrons (eight pairs). All eight pairs are used to complete the octets of the Cl and O atoms. There are two bonds (to the O atoms) and two lone pairs on the Cl for a total of four electron groups (**AX₂E₂**). The structure is based on a tetrahedral electron-group arrangement with an ideal bond angle of **109.5°**. The shape is **bent** (or V shaped). The presence of the lone pairs will cause the remaining angles to be **less than 109.5°**.

b) The PF_5 molecule has $[1 \times \text{P}(5e^-)] + [5 \times \text{F}(7e^-)] = 40$ valence electrons. Ten electrons are used to place single bonds between P and each F atom, leaving $40 - 10 = 30e^-$ (fifteen pairs). The fifteen pairs are used to complete the octets of the F atoms. There are five bonds to the P and no lone pairs (**AX₅**). The electron-group

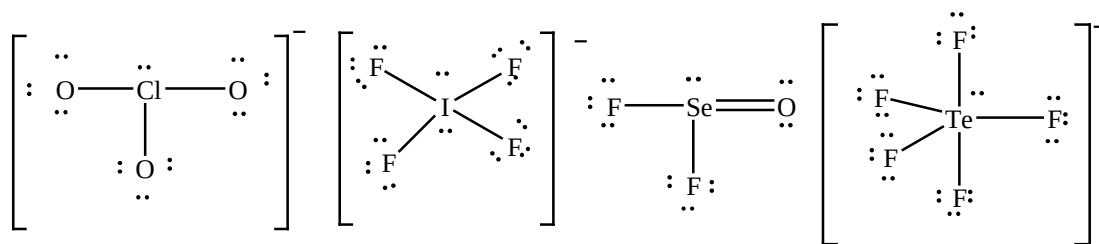
arrangement and the shape is **trigonal bipyramidal**. The ideal bond angles are **90° and 120°**. The absence of lone pairs means the **angles are ideal**.

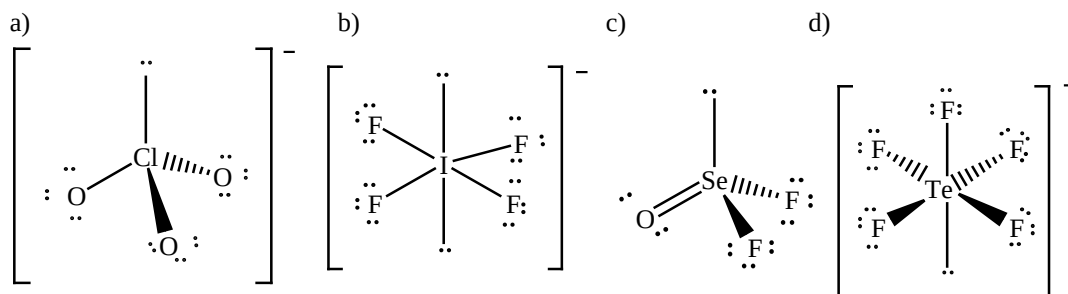
c) The SeF_4 molecule has $[1 \times \text{Se}(6e^-)] + [4 \times \text{F}(7e^-)] = 34$ valence electrons. Eight electrons are used to place single bonds between Se and each F atom, leaving $34 - 8 = 26e^-$ (thirteen pairs). Twelve pairs are used to complete the octets of the F atoms which leaves one pair of electrons. This pair is placed on the central Se atom. There are four bonds to the Se which also has a lone pair (AX_4E). The structure is based on a trigonal bipyramidal structure with ideal angles of **90° and 120°**. The shape is **seesaw**. The presence of the lone pairs means the angles are **less than ideal**.

d) The KrF_2 molecule has $[1 \times \text{Kr}(8e^-)] + [2 \times \text{F}(7e^-)] = 22$ valence electrons. Four electrons are used to place a single bond between the Kr atom and each F atom, leaving $22 - 4 = 18e^-$ (nine pairs). Six pairs are used to complete the octets of the F atoms. The remaining three pairs of electrons are placed on the Kr atom. The Kr is the central atom. There are two bonds to the Kr and three lone pairs (AX_2E_3). The structure is based on a trigonal bipyramidal structure with ideal angles of 90° and 120°. The shape is **linear**. The placement of the F atoms makes their ideal bond angle to be $2 \times 90^\circ = 180^\circ$. The placement of the lone pairs is such that they cancel each other's repulsion, thus the actual **bond angle is ideal**.



- 10.40
- a) The ClO_3^- ion has twenty-six valence electrons. The Cl is the central atom. There are three bonds (to the O atoms) and one lone pair on the Cl (AX_3E). The shape is **trigonal pyramidal**. The structure is based on a tetrahedral electron-group arrangement with an ideal bond angle of **109.5°**. The presence of the lone pair will cause the remaining angles to be **less than 109.5°**.
- b) The IF_4^- ion has thirty-six valence electrons. The I is the central atom. There are four bonds to the I and two lone pairs (AX_4E_2). The shape is **square planar**. The structure is based on an octahedral electron-group arrangement with ideal bond angles of **90°**. The repulsion from the two lone pairs cancels so the **angles are ideal**.
- c) The SeOF_2 molecule has twenty-six valence electrons. The Se is the central atom. There are three bonds to the Se which also has a lone pair (AX_3E). The shape is **trigonal pyramidal**. The structure is based on a tetrahedral structure with ideal angles of **109.5°**. The presence of the lone pair means the angles are **less than ideal**.
- d) The TeF_5^- ion has forty-two valence electrons. The Te is the central atom. There are five bonds to the Te which also has one lone pair (AX_5E). The shape is **square pyramidal**. The structure is based on an octahedral with ideal angles of **90°**. The presence of the lone pair means the angles are **less than ideal**.

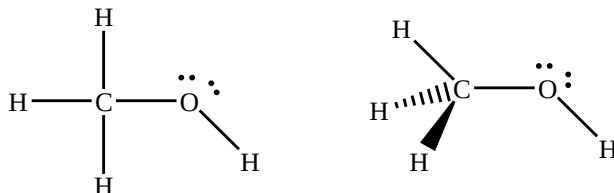




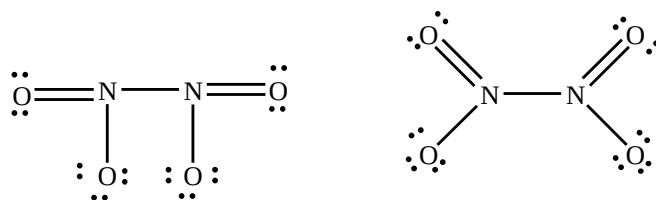
10.41 Plan: The Lewis structures must be drawn, and VSEPR applied to the structures.

Solution:

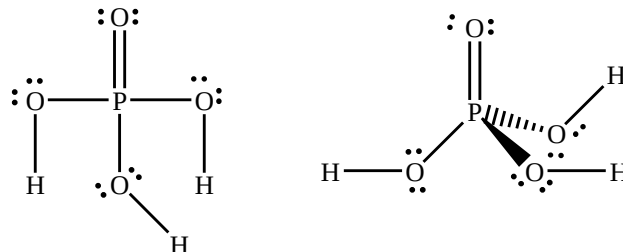
a) CH_3OH : This molecule has $[1 \times \text{C}(4e^-)] + [4 \times \text{H}(1e^-)] + [1 \times \text{O}(6e^-)] =$ fourteen valence electrons. In the CH_3OH molecule, both carbon and oxygen serve as central atoms. (H can never be central.) Use eight electrons to place a single bond between the C and the O atom and three of the H atoms and another two electrons to place a single bond between the O and the last H atom. This leaves $14 - 10 = 4 e^-$ (two pairs). Use these two pairs to complete the octet of the O atom. C already has an octet and each H only gets two electrons. The carbon has four bonds and no lone pairs (AX_4), so it is **tetrahedral** with **no deviation** (no lone pairs) from the ideal angle of 109.5° . The oxygen has two bonds and two lone pairs (AX_2E_2), so it is **V shaped** or **bent** with the angles **less than the ideal** angle of 109.5° .



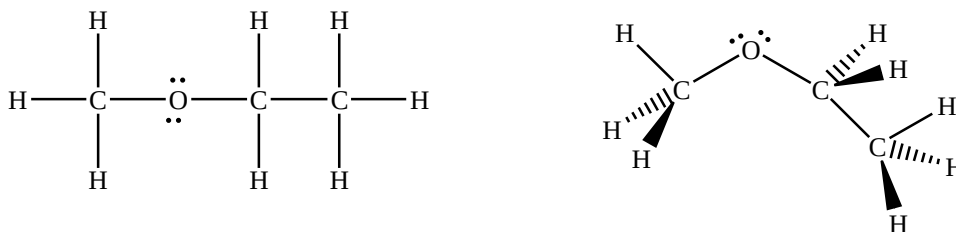
b) N_2O_4 : This molecule has $[2 \times \text{N}(5e^-)] + [4 \times \text{O}(6e^-)] = 34$ valence electrons. Use ten electrons to place a single bond between the two N atoms and between each N and two of the O atoms. This leaves $34 - 10 = 24e^-$ (twelve pairs). Use the twelve pairs to complete the octets of the oxygen atoms. Neither N atom has an octet, however. Form a double bond from one O atom to one N atom by changing a lone pair on the O to a bonding pair on the N. Do this for the other N atom as well. In the N_2O_4 molecule, both nitrogen atoms serve as central atoms. This is the arrangement given in the problem. Both nitrogen atoms are equivalent with three groups and no lone pairs (AX_3), so the arrangement is **trigonal planar** with **no deviation** (no lone pairs) from the ideal angle of 120° . The same results arise from the other resonance structures.



10.42 a) In the H_3PO_4 molecule the P and each of the O atoms with an H attached serve as central atoms. The P has four groups and no lone pairs (AX_4), so it is **tetrahedral** with **no deviation** from the ideal angle of 109.5° . The H bearing O atoms have two bonds and two lone pairs (AX_2E_2), so the arrangement is **V shaped** or **bent** with angles **less than the ideal** value of 109.5° .



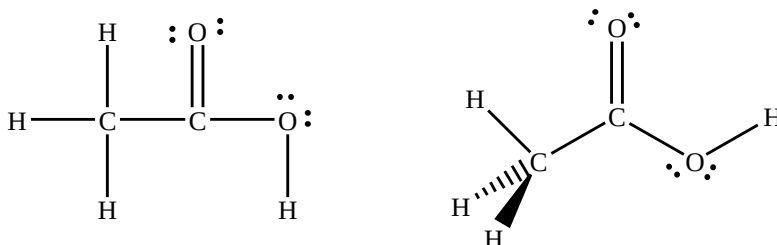
b) In the $\text{CH}_3\text{OCH}_2\text{CH}_3$ molecule, all atoms except the hydrogen atoms serve as central atoms. All the carbons have four bonds and no lone pairs (AX_4), so they are tetrahedral with no deviation from the ideal bond angle of 109.5° . The oxygen has two bonds and two lone pairs (AX_2E_2), so the arrangement is **V shaped** or **bent** with angles **less than the ideal** value of 109.5° .



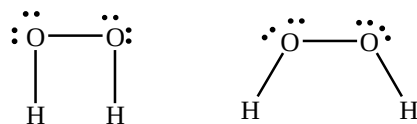
10.43 **Plan:** The Lewis structures must be drawn, and VSEPR applied to the structures.

Solution:

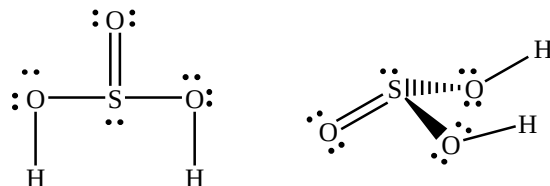
a) CH_3COOH has $[2 \times \text{C}(4e^-)] + [4 \times \text{H}(1e^-)] + [2 \times \text{O}(6e^-)] =$ twenty-four valence electrons. Use fourteen electrons to place a single bond between all of the atoms. This leaves $24 - 14 = 10 e^-$ (five pairs). Use these five pairs to complete the octets of the O atoms; the C atom bonded to the H atoms has an octet but the other C atom does not have a complete octet. Form a double bond from the O atom (not bonded to H) to the C by changing a lone pair on the O to a bonding pair on the C. In the CH_3COOH molecule, the carbons and the O with H attached serve as central atoms. The carbon bonded to the H atoms has four groups and no lone pairs (AX_4), so it is **tetrahedral** with **no deviation** from the ideal angle of 109.5° . The carbon bonded to the O atoms has three groups and no lone pairs (AX_3), so it is **trigonal planar** with **no deviation** from the ideal angle of 120° . The H bearing O has two bonds and two lone pairs (AX_2E_2), so the arrangement is **V shaped** or **bent** with an angle **less than the ideal** value of 109.5° .



b) H_2O_2 has $[2 \times \text{H}(1e^-)] + [2 \times \text{O}(6e^-)] =$ fourteen valence electrons. Use six electrons to place single bonds between the O atoms and between each O atom and an H atom. This leaves $14 - 6 = 8 e^-$ (four pairs). Use these four pairs to complete the octets of the O atoms. In the H_2O_2 molecule, both oxygen atoms serve as central atoms. Both O atoms have two bonds and two lone pairs (AX_2E_2), so they are **V shaped** or **bent** with angles **less than the ideal** value of 109.5° .

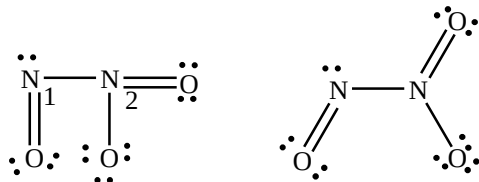


10.44 a) In the H_2SO_3 molecule, the S and the O atoms with an H attached serve as central atoms. The S has three groups and one lone pair (AX_3E), so it is **trigonal pyramidal** with angles **less than** the ideal angle of 109.5° . The H bearing O atoms each have two bonds and two lone pairs (AX_2E_2), so the arrangement is **V shaped** or **bent** with an angle **less than the ideal** value of 109.5° .



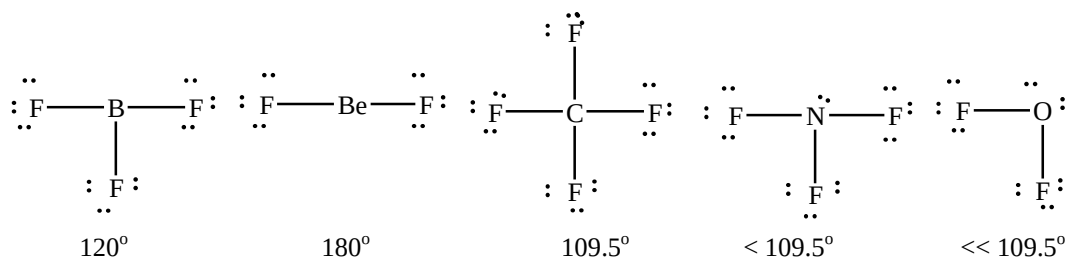
b) The N_2O_3 molecule has the structure indicated in the problem with the N atoms serving as central atoms. The nitrogen labeled N_1 has two groups and a lone pair (AX_2E), so it is **V shaped** or **bent** with angles **less than the**

ideal value of 120° . The nitrogen labeled N_2 has three bonds and no lone pairs (AX_3), so it is **trigonal planar** with **no deviation** from the ideal angle of 120° .



- 10.45 Plan: First, draw a Lewis structure, and then apply VSEPR. The presence of lone pairs on the central atom generally results in a smaller than ideal bond angle.

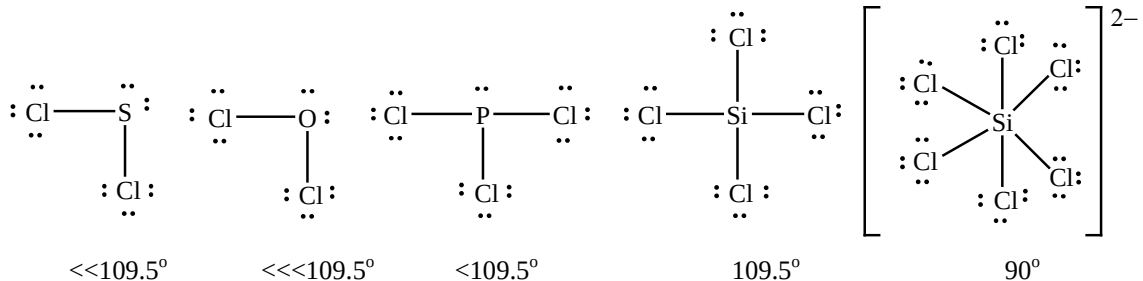
Solution:



Bond angles: $OF_2 < NF_3 < CF_4 < BF_3 < BeF_2$

BeF_2 is an AX_2 type molecule, so the angle is the ideal 180° . BF_3 is an AX_3 molecule, so the angle is the ideal 120° . CF_4 , NF_3 , and OF_2 all have tetrahedral electron-group arrangements of the following types: AX_4 , AX_3E , AX_2E_2 , respectively. The ideal tetrahedral bond angle is 109.5° , which is present in CF_4 . The one lone pair in NF_3 and OF_2 decreases the angle a little. The two lone pairs in OF_2 decrease the angle even more.

- 10.46



Bond angles: $SiCl_4 > PCl_3 > SCl_2 > OCl_2 > SiCl_6^{2-}$

All the species except $SiCl_6^{2-}$ are based on a tetrahedral electron-group arrangement. $SiCl_6^{2-}$ has an octahedral electron arrangement with an ideal angle of 90° . The tetrahedral arrangement has an ideal bond angle of 109.5° , which is present in AX_4 species like $SiCl_4$. The ideal tetrahedral bond angle is reduced slightly by the lone pair in AX_3E species such as PCl_3 . A greater reduction in the ideal tetrahedral bond angle is present in AX_2E_2 species such as SCl_2 and OCl_2 with two lone pairs. The angle is reduced less around the larger S atom.

- 10.47 Plan: The ideal bond angles depend on the electron-group arrangement. Deviations depend on lone pairs.

Solution:

a) The C and N have three groups, so they are **ideally 120°** , and the O has four groups, so **ideally the angle is 109.5°** . The N and O have lone pairs, so the **angles are less than ideal**.

b) All central atoms have four pairs, so ideally all the angles are **109.5°** . The lone pairs on the O **reduce** this value.

c) The B has three groups (no lone pairs) leading to an **ideal bond angle of 120°** . All the O atoms have four pairs (**ideally 109.5°**), two of which are lone, and **reduce the angle**.

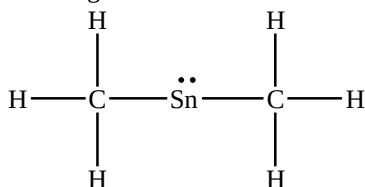
- 10.48 a) The N has three groups, no lone pairs, so the angle is **ideal**, and equal to **120°** . The O, attached to the H, has four groups (**ideally 109.5°**); the lone pairs **reduce the bond angle from ideal**.

b) The C, attached to the O, has three groups and no lone pairs so the angle will be the **ideal 120°**. The remaining C has four groups, and with no lone pairs the angle will be ideal and equal to **109.5°**.
 c) The C with three groups will have angles that are **ideal (120°)**. The O, with the H attached, has four groups. The presence of four groups gives an **ideal angle of 109.5°**, which is **reduced** by the lone pairs.

10.49

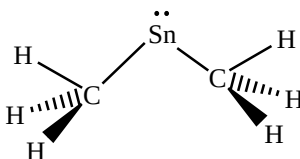
a) Type: AX₂E

Ideal angle: 120°



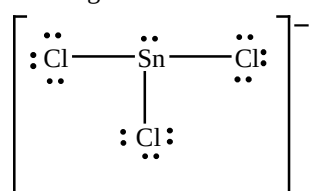
Shape: bent

Actual angle: <120° (because of the lone pair)



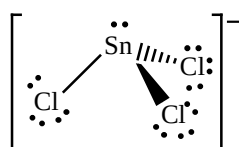
b) Type: AX₃E

Ideal angle: 109.5°



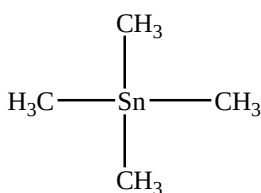
Shape: trigonal pyramidal

Actual angle: <109.5° (because of the lone pair)



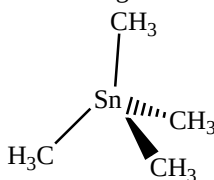
c) Type: AX₄

Ideal angle: 109.5°



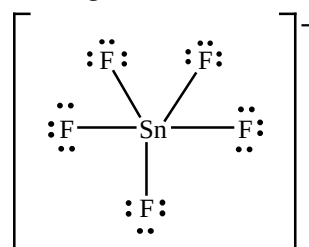
Shape: tetrahedral

Actual angle: 109.5° (there are no lone pairs)



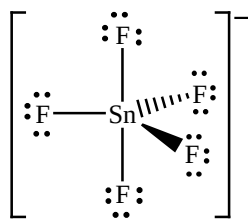
d) Type: AX₅

Ideal angles: 120° and 90°



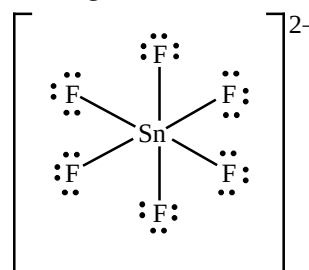
Shape: trigonal pyramidal

Actual angle: 120° and 90° (there are no lone pairs)



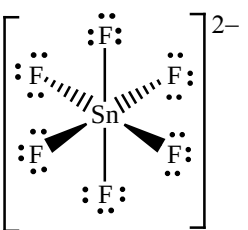
e) Type: AX₆

Ideal angles: 90°



Shape: octahedral

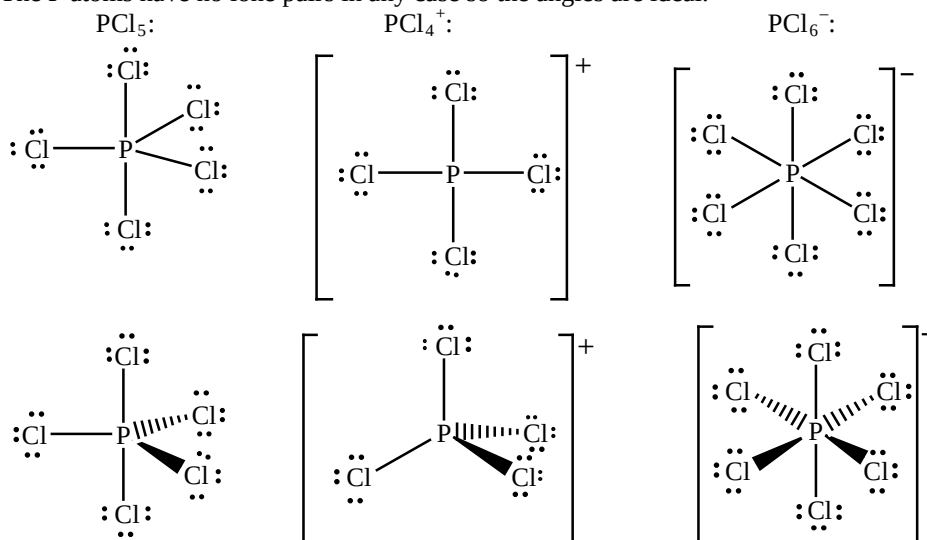
Actual angle: 90° (there are no lone pairs)



10.50 Plan: The Lewis structures are needed to predict the ideal bond angles.

Solution:

The P atoms have no lone pairs in any case so the angles are ideal.



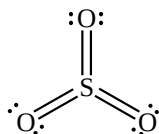
The original PCl_5 is AX_5 , so the shape is trigonal bipyramidal, and the angles are 120° and 90° .

The PCl_4^+ is AX_4 , so the shape is tetrahedral, and the angles are 109.5° .

The PCl_6^- is AX_6 , so the shape is octahedral, and the angles are 90° .

Half the PCl_5 (trigonal bipyramidal, 120° and 90°) become tetrahedral PCl_4^+ (tetrahedral, 109.5°), and the other half become octahedral PCl_6^- (octahedral, 90°).

10.51 Molecules are polar if they have polar bonds that are not arranged to cancel each other. If the polar covalent bonds are arranged in such a way as to cancel each other, the molecule will be nonpolar. An example of a molecule with polar covalent bonds that is not polar is SO_3 . The trigonal planar shape causes the three polar S–O bonds to cancel.



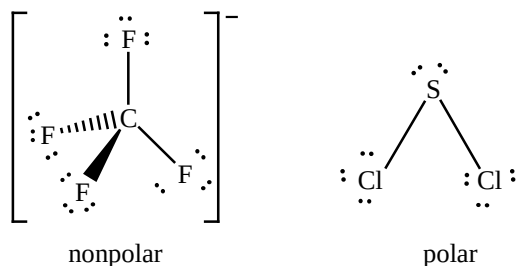
10.52 Plan: To determine if a bond is polar, determine the electronegativity difference of the atoms participating in the bond. The greater the electronegativity difference, the more polar the bond. To determine if a molecule is polar (has a dipole moment), it must have polar bonds, and a certain shape determined by VSEPR.

Solution:

a)Molecule	Bond	Electronegativities	Electronegativity difference
SCl_2	S–Cl	S = 2.5 Cl = 3.0	$3.0 - 2.5 = 0.5$
F_2	F–F	F = 4.0 F = 4.0	$4.0 - 4.0 = 0.0$
CS_2	C–S	C = 2.5 S = 2.5	$2.5 - 2.5 = 0.0$
CF_4	C–F	C = 2.5 F = 4.0	$4.0 - 2.5 = 1.5$
BrCl	Br–Cl	Br = 2.8 Cl = 3.0	$3.0 - 2.8 = 0.2$

The polarities of the bonds increase in the order: $\text{F–F} = \text{C–S} < \text{Br–Cl} < \text{S–Cl} < \text{C–F}$. Thus, CF_4 has the most polar bonds.

b) The F_2 and CS_2 cannot be polar since they do not have polar bonds. CF_4 is an AX_4 molecule, so it is tetrahedral with the four polar C–F bonds arranged to cancel each other giving an overall nonpolar molecule. **BrCl has a dipole moment** since there are no other bonds to cancel the polar Br–Cl bond. **SCl_2 has a dipole moment** (is polar) because it is a bent molecule, AX_2E_2 , and the electron density in both S–Cl bonds is pulled towards the more electronegative chlorine atoms.

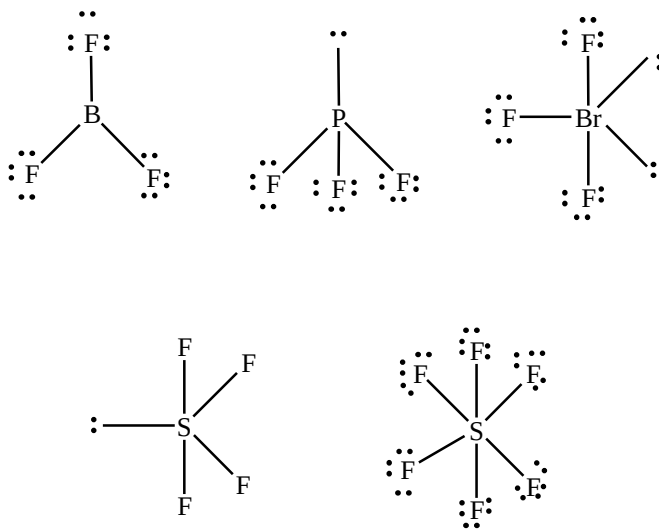


10.53 a) The greater the difference in electronegativity the more polar the bond:

Molecule	Bond	Electronegativities	Electronegativity difference
BF ₃	B–F	B = 2.0 F = 4.0	4.0 – 2.0 = 2.0
PF ₃	P–F	P = 2.1 F = 4.0	4.0 – 2.1 = 1.9
BrF ₃	Br–F	Br = 2.8 F = 4.0	4.0 – 2.8 = 1.2
SF ₄	S–F	S = 2.5 F = 4.0	4.0 – 2.5 = 1.5
SF ₆	S–F	S = 2.5 Cl = 4.0	4.0 – 2.5 = 1.5

The polarities of the bonds are increasing in the order: Br–F < S–F < P–F < B–F. Thus, **BF₃** has the most polar bonds.

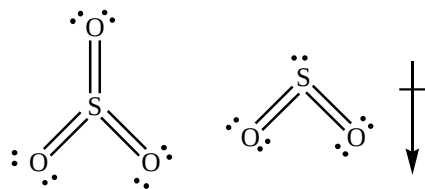
b) All the molecules meet the requirement of having polar bonds. The arrangement of the bonds must be considered in each case. BF₃ is trigonal planar, AX₃, so it is nonpolar because the polarities of the bonds cancel. **PF₃ has a dipole moment** (is polar) because it has a trigonal pyramidal geometry, AX₃E. **BrF₃ has a dipole moment** because it has a T-shaped geometry, AX₃E₂. **SF₄ has a dipole moment** because it has a see-saw geometry, AX₄E. SF₆ is nonpolar because it is octahedral, AX₆, and the bonds are arranged so they cancel.



10.54 Plan: If only two atoms are involved, only an electronegativity difference is needed. The greater the difference in electronegativity, the more polar the bond. If there are more than two atoms, the molecular geometry must be determined.

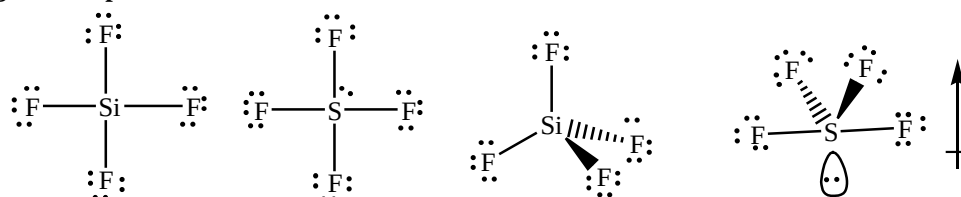
Solution:

a) All the bonds are polar covalent. The SO₃ molecule is trigonal planar, AX₃, so the bond dipoles cancel leading to a nonpolar molecule (no dipole moment). The SO₂ molecule is bent, AX₂E, so the polar bonds result in electron density being pulled towards one side of the molecule. **SO₂ has a greater dipole moment** because it is the only one of the pair that is polar.



b) ICl and IF are polar, as are all diatomic molecules composed of atoms with differing electronegativities. The electronegativity difference for ICl ($3.0 - 2.5 = 0.5$) is less than that for IF ($4.0 - 2.5 = 1.5$). The greater difference means that **IF has a greater dipole moment**.

c) All the bonds are polar covalent. The SiF_4 molecule is nonpolar (has no dipole moment) because the bonds are arranged tetrahedrally, AX_4 . SF_4 is AX_4E , so it has a see-saw shape, where the bond dipoles do not cancel. **SF_4 has the greater dipole moment**.



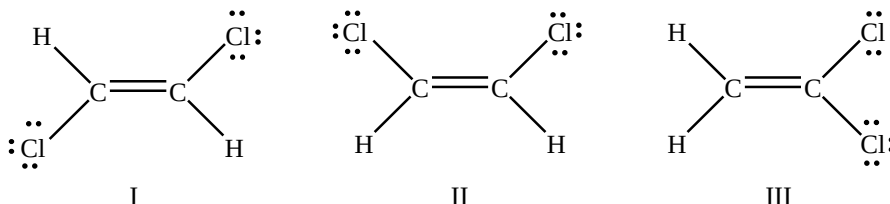
d) H_2O and H_2S have the same basic structure. They are both bent molecules, AX_2E_2 , and as such, they are polar. The electronegativity difference in H_2O ($3.5 - 2.1 = 1.4$) is greater than the electronegativity difference in H_2S ($2.5 - 2.1 = 0.4$) so **H_2O has a greater dipole moment**.

- 10.55 a) All the bonds are polar covalent. Both the molecules are bent (SO_2 and ClO_2 are AX_2E_2). The difference in electronegativity is greater in SO_2 than in ClO_2 so **SO_2 has a greater dipole moment**.
 b) HBr and HCl are polar, as are all diatomic molecules composed of atoms with differing electronegativities. The electronegativity difference for HBr is less than that for HCl. The greater difference means that **HCl has a greater dipole moment**.
 c) All the bonds are polar covalent. The BeCl_2 molecule is nonpolar (has no dipole moment) because the bonds are arranged linearly, AX_2 . SCl_2 is AX_2E_2 , so it has a bent shape, where the bond dipoles do not cancel. **SCl_2 has the greater dipole moment**.
 d) All the bonds are polar covalent. AsF_5 is AX_5 , so it is trigonal bipyramidal and nonpolar. AsF_3 is AX_3E , so it is trigonal pyramidal and polar. **AsF_3 has a greater dipole moment**.

- 10.56 Plan: Draw Lewis structures, and then apply VSEPR. A molecule has a dipole moment if polar bonds do not cancel.

Solution:

$\text{C}_2\text{H}_2\text{Cl}_2$ has $[2 \times \text{C}(4e^-)] + [2 \times \text{H}(1e^-)] + [2 \times \text{Cl}(7e^-)] = 24$ valence electrons. The two carbon atoms are bonded to each other. The H atoms and Cl atoms are bonded to the C atoms. Use ten electrons to place a single bond between all of the atoms. This leaves $24 - 10 = 14e^-$ (seven pairs). Use these seven pairs to complete the octets of the Cl atoms and one of the C atoms; the other C atom does not have a complete octet. Form a double bond between the carbon atoms by changing the lone pair on one C atom to a bonding pair. There are three possible structures for the compound $\text{C}_2\text{H}_2\text{Cl}_2$:



The presence of the double bond prevents rotation about the $\text{C}=\text{C}$ bond, so the structures are “fixed.” The $\text{C}-\text{Cl}$ bonds are more polar than the $\text{C}-\text{H}$ bonds, so the key to predicting the polarity is the positioning of the $\text{C}-\text{Cl}$ bonds. Structure I has the $\text{C}-\text{Cl}$ bonds arranged so that they cancel leaving I as a nonpolar molecule. Both II and III have $\text{C}-\text{Cl}$ bonds on the same side so the bonds work together making both molecules polar. Both I and II will react with H_2 to give a compound with a Cl attached to each C (same product). Structure III will react with H_2 to

give a compound with two Cl atoms on one C and none on the other (different product). **Structure I must be X** as it is the only one that is nonpolar (has no dipole moment). **Structure II must be Z** because it is polar and gives the same product as compound X. This means that **Structure III must be the remaining compound, Y**. **Compound Y (III) has a dipole moment.**

- 10.57 Plan: The Lewis structures are needed to do this problem. A single bond (bond order = 1) is weaker and longer than a double bond (bond order = 2) which is weaker and longer than a triple bond (bond order = 3). To find the heat of reaction, add the energy required to break all the bonds in the reactants to the energy released to form all bonds in the product. Remember to use a negative sign for the energy of the bonds formed since bond formation is exothermic. The bond energy values are found in Table 9.2.

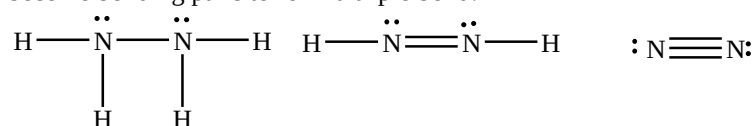
Solution:

a) The H atoms cannot be central, and they are evenly distributed on the N atoms.

N_2H_4 has $[2 \times N(5e^-)] + [4 \times H(1e^-)]$ = fourteen valence electrons, ten of which are used in the bonds between the atoms. The remaining two pairs are used to complete the octets of the N atoms.

N_2H_2 has $[2 \times N(5e^-)] + (2 \times H(1e^-))$ = twelve valence electrons, six of which are used in the bonds between the atoms. The remaining three pairs of electrons are not enough to complete the octets of both N atoms, so one lone pair is moved to a bonding pair between the N atoms.

N_2 has $[2 \times N(5e^-)]$ = ten valence electrons, two of which are used to place a single bond between the two N atoms. Since only four pairs of electrons remain and six pairs are required to complete the octets, two lone pairs become bonding pairs to form a triple bond.



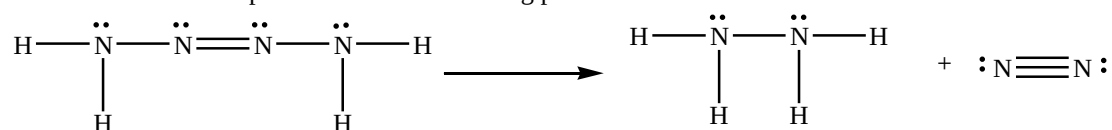
Hydrazine

Diazene

Nitrogen

The **single (bond order = 1) N–N bond is weaker and longer** than any of the others are. The **triple bond (bond order = 3) is stronger and shorter** than any of the others. The **double bond (bond order = 2) has an intermediate strength and length**.

b) N_4H_4 has $[4 \times N(5e^-)] + [4 \times H(1e^-)]$ = twenty-four valence electrons, fourteen of which are used for single bonds between the atoms. When the remaining five pairs are distributed to complete the octets, one N atom lacks two electrons. A lone pair is moved to a bonding pair for a double bond.



Reactant bonds broken:

$$4 \text{ N-H} = 4 \text{ mol } (391 \text{ kJ/mol}) = 1564 \text{ kJ}$$

$$2 \text{ N-N} = 2 \text{ mol } (160 \text{ kJ/mol}) = 320 \text{ kJ}$$

$$1 \text{ N=N} = 1 \text{ mol } (418 \text{ kJ/mol}) = 418 \text{ kJ}$$

$$\Sigma \Delta H_{\text{bonds broken}}^{\circ} = 2302 \text{ kJ}$$

Product bonds formed:

$$4 \text{ N-H} = 4 \text{ mol } (-391 \text{ kJ/mol}) = -1564 \text{ kJ}$$

$$1 \text{ N-N} = 1 \text{ mol } (-160 \text{ kJ/mol}) = -160 \text{ kJ}$$

$$1 \text{ N}\equiv\text{N} = 1 \text{ mol } (-945 \text{ kJ/mol}) = -945 \text{ kJ}$$

$$\Sigma \Delta H_{\text{bonds formed}}^{\circ} = -2669 \text{ kJ}$$

$$\Delta H_{\text{rxn}}^{\circ} = \Sigma \Delta H_{\text{bonds broken}}^{\circ} + \Sigma \Delta H_{\text{bonds formed}}^{\circ} = 2302 \text{ kJ} + (-2669 \text{ kJ}) = -367 \text{ kJ}$$

- 10.58 a) SiF_4 with its thirty-two valence electrons is an AX_4 molecule and has a tetrahedral molecular shape. SiF_5^- with its forty valence electrons is an AX_5 ion and has a trigonal bipyramidal molecular shape. **B** best represents the change in molecular shape from tetrahedral to trigonal bipyramidal.
b) **SiF_4 : tetrahedral, AX_4 ; SiF_5^- : trigonal bipyramidal, AX_5 .**

- 10.59 Draw Lewis structures, and then determine the formal charges.
The atom sequence may be ONF, NOF, or NFO. F is never central so the structure cannot be NFO.
NOF $\ddot{\text{O}}=\ddot{\text{N}}-\ddot{\text{F}}:$ $\ddot{\text{N}}=\ddot{\text{O}}-\ddot{\text{F}}:$

$$\text{FC}_{\text{O}} = +6 - (4 + 1/2(4)) = 0$$

$$\text{FC}_{\text{O}} = +6 - (2 + 1/2(6)) = +1$$

$$\text{FC}_{\text{N}} = +5 - (2 + 1/2(6)) = 0$$

$$\text{FC}_{\text{N}} = +5 - (4 + 1/2(4)) = -1$$

$$\text{FC}_{\text{F}} = +7 - (6 + 1/2(2)) = 0$$

$$\text{FC}_{\text{F}} = +7 - (6 + 1/2(2)) = 0$$

Thus, the structure on the left is the correct structure.

- 10.60 **Plan:** Use the Lewis structures shown in the text. The equation for formal charge (FC) is
FC = no. of valence electrons – [no. of unshared valence electrons + ½ no. of shared valence electrons].

Solution:

a) Formal charges for Al_2Cl_6 :

$$\text{FC}_{\text{Al}} = 3 - [0 + 1/2(8)] = -1$$

$$\text{FC}_{\text{Cl, ends}} = 7 - [6 + 1/2(2)] = 0$$

$$\text{FC}_{\text{Cl, bridging}} = 7 - [4 + 1/2(4)] = +1$$

(Check: Formal charges add to zero, the charge on the compound.)

Formal charges for I_2Cl_6 :

$$\text{FC}_{\text{I}} = 7 - [4 + 1/2(8)] = -1$$

$$\text{FC}_{\text{Cl, ends}} = 7 - [6 + 1/2(2)] = 0$$

$$\text{FC}_{\text{Cl, bridging}} = 7 - [4 + 1/2(4)] = +1$$

(Check: Formal charges add to zero, the charge on the compound.)

b) The aluminum atoms have no lone pairs and are AX_4 , so they are tetrahedral. The two tetrahedral Al atoms cannot give a planar structure. The iodine atoms in I_2Cl_6 have two lone pairs each and are AX_4E_2 so they are square planar. Placing the square planar I atoms adjacent can give a planar molecule.

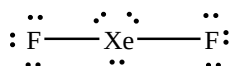
- 10.61 The Lewis structure for each is required.

Compound

Lewis structure

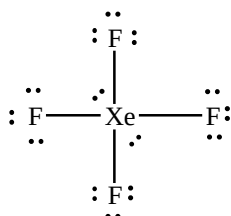
Molecular geometry

XeF_2



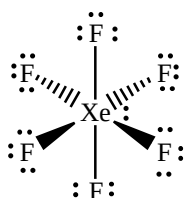
Linear (AX_2E_3)

XeF_4



Square planar (AX_4E_2)

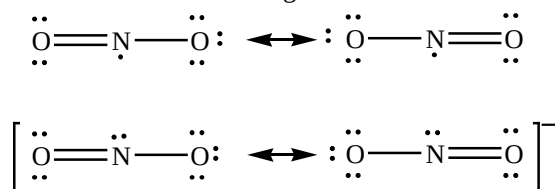
XeF_6



Distorted octahedral (AX_6E)

- 10.62 a) SO_3 is an AX_3 molecule and has a trigonal planar shape. SO_3^{2-} is an AX_3E species and has a trigonal pyramidal molecular shape. C best illustrates the change in molecular shape from trigonal planar to trigonal pyramidal.
b) **Yes**, there is a change in polarity during the reaction as the nonpolar SO_3 molecule becomes the polar SO_3^{2-} ion.

- 10.63 From the Lewis structures, both are AX_2E which has an ideal bond angle of 120° . But the “lone pair” on N in NO_2 is only half a pair, so it only exerts “half” the repulsion. This allows the bond angle to open to a larger than normal bond angle. The “complete” lone pair in NO_2^- , like other lone pairs, forces the bonding pairs together to give a smaller than normal bond angle.



- 10.64 $Xe(g) + 3F_2(g) \rightarrow XeF_6(g)$

$$\Delta H_{\text{rxn}}^\circ = \Sigma \Delta H_{\text{bonds broken}}^\circ + \Sigma \Delta H_{\text{bonds formed}}^\circ$$

The three F-F bonds must be broken, and six Xe-F bonds are formed.

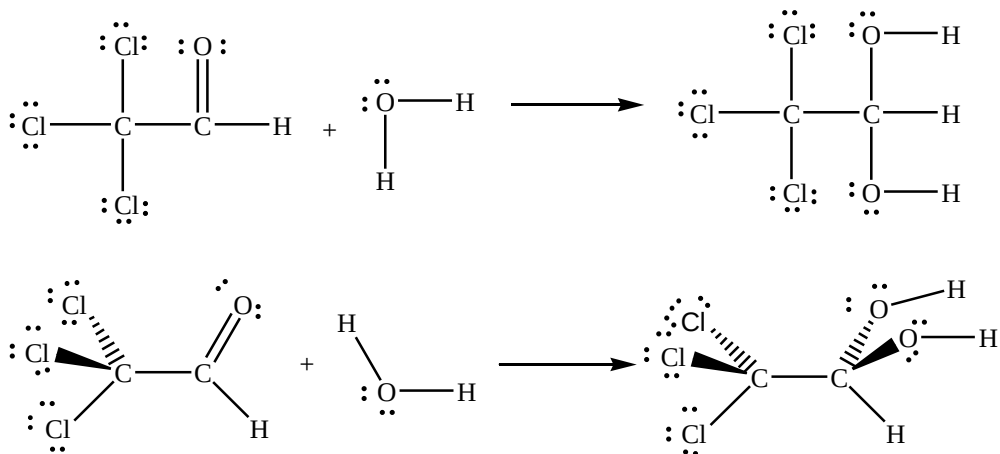
$$\Delta H_{\text{rxn}}^\circ = 3 BE_{\text{F-F}} + 6 BE_{\text{Xe-F}}$$

$$-402 \text{ kJ/mol} = (3 \text{ mol})(159 \text{ kJ/mol}) + (6 \text{ mol})(-BE_{\text{Xe-F}})$$

$$-879 \text{ kJ/mol} = 6 (-BE_{\text{Xe-F}})$$

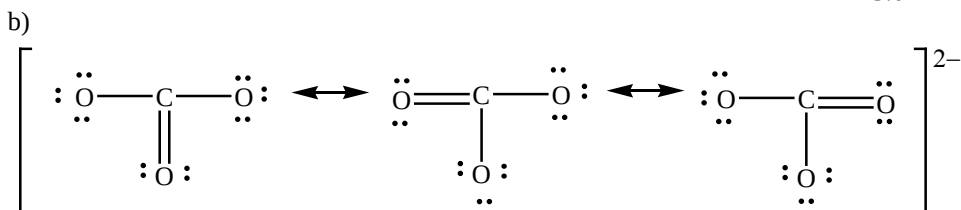
$$146.5 = \mathbf{146 \text{ kJ/mol}} = BE_{\text{Xe-F}}$$

- 10.65

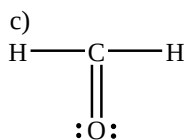


The C with the chlorine atoms attached does not change shape. That C is tetrahedral in both compounds. The other C changes from trigonal planar (AX_3) to tetrahedral (AX_4).

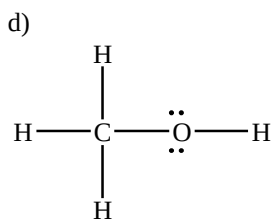
- 10.66 a) $\text{C} \equiv \text{O}:$ Bond order (avg.) 3.0



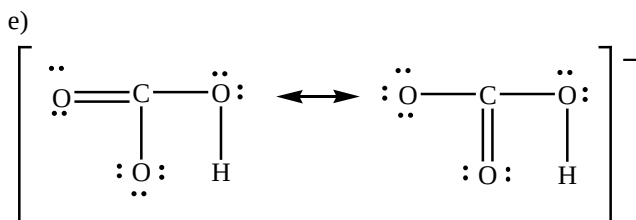
Each C-O bond is a single bond two-thirds of the time and a double bond the rest of the time. The average is $[(1 + 1 + 2)/3] = 4/3 = 1.33$



2.0



1.0

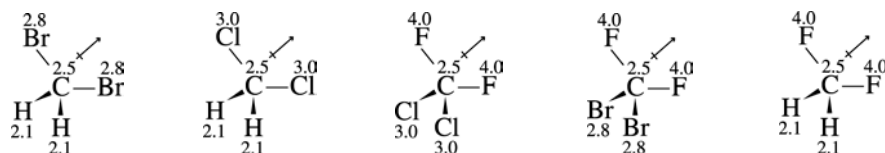


The resonating double bond means the average bond length is $[(1 + 2)/2] = 1.5$

The C–O bond for the O attached to the H does not resonate and remains 1.0

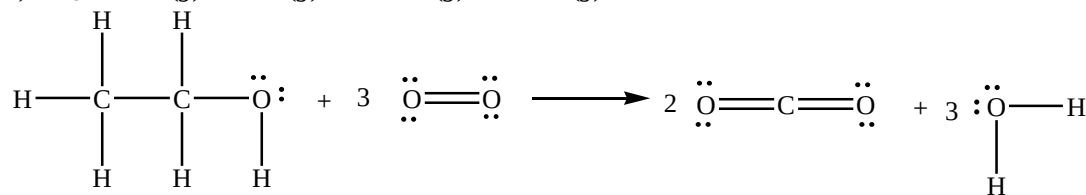
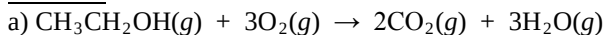
Bond length $\mathbf{a} < \mathbf{c} < \mathbf{e} < \mathbf{b} < \mathbf{d}$ ignoring O attached to H in part e)

Bond strength $\mathbf{d} < \mathbf{b} < \mathbf{e} < \mathbf{c} < \mathbf{a}$



- 10.68 Plan: Ethanol burns (combusts) with O_2 to produce CO_2 and H_2O . To find the heat of reaction in part a), add the energy required to break all the bonds in the reactants to the energy released to form all bonds in the product. Remember to use a negative sign for the energy of the bonds formed since bond formation is exothermic. The bond energy values are found in Table 9.2. The heat of vaporization of ethanol must be included for part b). The enthalpy change in part c) is the sum of the heats of formation of the products minus the sum of the heats of formation of the reactants. The calculation for part d) is the same as in part a).

Solution:



Reactant bonds broken:

$$1 \times \text{C}-\text{C} = (1 \text{ mol})(347 \text{ kJ/mol}) = 347 \text{ kJ}$$

$$5 \times \text{C}-\text{H} = (5 \text{ mol})(413 \text{ kJ/mol}) = 2065 \text{ kJ}$$

$$1 \times \text{C}-\text{O} = (1 \text{ mol})(358 \text{ kJ/mol}) = 358 \text{ kJ}$$

$$1 \times \text{O}-\text{H} = (1 \text{ mol})(467 \text{ kJ/mol}) = 467 \text{ kJ}$$

$$3 \times \text{O}=\text{O} = (3 \text{ mol})(498 \text{ kJ/mol}) = 1494 \text{ kJ}$$

$$\Sigma \Delta H_{\text{bonds broken}}^\circ = 4731 \text{ kJ}$$

Product bonds formed:

$$4 \times \text{C}=\text{O} = (4 \text{ mol})(-799 \text{ kJ/mol}) = -3196 \text{ kJ}$$

$$6 \times \text{O}-\text{H} = (6 \text{ mol})(-467 \text{ kJ/mol}) = -2802 \text{ kJ}$$

$$\Sigma \Delta H_{\text{bonds formed}}^{\circ} = -5998 \text{ kJ}$$

$$\Delta H_{\text{rxn}}^{\circ} = \Sigma \Delta H_{\text{bonds broken}}^{\circ} + \Sigma \Delta H_{\text{bonds formed}}^{\circ} = 4731 \text{ kJ} + (-5998 \text{ kJ}) = -1267 \text{ kJ} \text{ for each mole of ethanol burned}$$

b) If it takes 40.5 kJ/mol to vaporize the ethanol, part of the heat of combustion must be used to convert liquid ethanol to gaseous ethanol. The new value becomes:

$$\Sigma \Delta H_{\text{combustion (liquid)}}^{\circ} = -1267 \text{ kJ} + (1 \text{ mol}) \left[\frac{40.5 \text{ kJ}}{1 \text{ mol}} \right] = -1226.5 = -1226 \text{ kJ per mole of liquid ethanol burned}$$

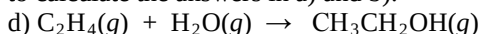
$$\text{c) } \Delta H_{\text{rxn}}^{\circ} = \Sigma m \Delta H_{\text{f}}^{\circ} (\text{products}) - \Sigma n \Delta H_{\text{f}}^{\circ} (\text{reactants})$$

$$\Delta H_{\text{rxn}}^{\circ} = \{2 \Delta H_{\text{f}}^{\circ} [\text{CO}_2(\text{g})] + 3 \Delta H_{\text{f}}^{\circ} [\text{H}_2\text{O}(\text{g})]\} - \{1 \Delta H_{\text{f}}^{\circ} [\text{C}_2\text{H}_5\text{OH}(\text{l})] + 3 \Delta H_{\text{f}}^{\circ} [\text{O}_2(\text{g})]\}$$

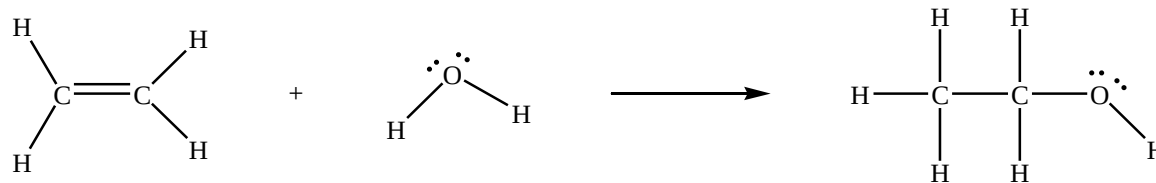
$$= [(2 \text{ mol})(-393.5 \text{ kJ/mol}) + (3 \text{ mol})(-241.826 \text{ kJ/mol})] - [(1 \text{ mol})(-277.63 \text{ kJ/mol}) + 3 \text{ mol}(0 \text{ kJ/mol})]$$

$$= -1234.848 = -1234.8 \text{ kJ}$$

The two answers differ by less than 10 kJ. This is a very good agreement since average bond energies were used to calculate the answers in a) and b).



The Lewis structures for the reaction are:



Reactant bonds broken:

$$1 \times \text{C}=\text{C} = (1 \text{ mol})(614 \text{ kJ/mol}) = 614 \text{ kJ}$$

$$4 \times \text{C}-\text{H} = (4 \text{ mol})(413 \text{ kJ/mol}) = 1652 \text{ kJ}$$

$$2 \times \text{O}-\text{H} = (2 \text{ mol})(467 \text{ kJ/mol}) = 934 \text{ kJ}$$

$$\Sigma \Delta H_{\text{bonds broken}}^{\circ} = 3200 \text{ kJ}$$

Product bonds formed:

$$1 \times \text{C}-\text{C} = (1 \text{ mol})(-347 \text{ kJ/mol}) = -347 \text{ kJ}$$

$$5 \times \text{C}-\text{H} = (5 \text{ mol})(-413 \text{ kJ/mol}) = -2065 \text{ kJ}$$

$$1 \times \text{C}-\text{O} = (1 \text{ mol})(-358 \text{ kJ/mol}) = -358 \text{ kJ}$$

$$1 \times \text{O}-\text{H} = (1 \text{ mol})(-467 \text{ kJ/mol}) = -467 \text{ kJ}$$

$$\Sigma \Delta H_{\text{bonds formed}}^{\circ} = -3237 \text{ kJ}$$

$$\Delta H_{\text{rxn}}^{\circ} = \Sigma \Delta H_{\text{bonds broken}}^{\circ} + \Sigma \Delta H_{\text{bonds formed}}^{\circ} = 3200 \text{ kJ} + (-3237 \text{ kJ}) = -37 \text{ kJ}$$

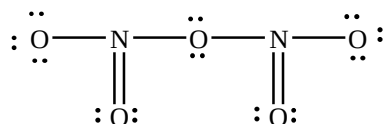
- 10.69 Determine the empirical formula from the percent composition (assuming 100 grams of compound). The empirical formula and the molar mass may then be used to determine the molecular formula. Count the valence electrons in the molecular formula and then construct the Lewis structure. Name the compound from its molecular formula.

$$\text{N} \quad 25.9 \text{ g}/(14.01 \text{ g/mol}) = 1.849 \text{ mol}/1.849 \text{ mol} = 1.00 \quad \text{Only round at the end.}$$

$$\text{O} \quad (100.0 - 25.9) \text{ g}/(16.00 \text{ g/mol}) = 4.631 \text{ mol}/1.849 \text{ mol} = 2.50$$

Doubling the ratios gives N = 2 and O = 5 or N₂O₅ with a molar mass of 108.02 g/mol. Since this is the same as the molar mass given in the problem, the empirical and molecular formulas are both N₂O₅.

This formula has 40 valence electrons, and when drawn with no N-N or O-O bonds one gets the following Lewis structure:



The name of this compound is **dinitrogen pentoxide**.

- 10.70 **Plan:** Determine the empirical formula from the percent composition (assuming 100 g of compound). Use the titration data to determine the mole ratio of acid to the NaOH. This ratio gives the number of acidic H atoms in the formula of the acid. Finally, combine this information to construct the Lewis structure.

Solution:

$$\text{Moles of H} = (2.24 \text{ g H}) \left(\frac{1 \text{ mol}}{1.008 \text{ g H}} \right) = 2.222 \text{ mol H}$$

$$\text{Moles of C} = (26.7 \text{ g C}) \left(\frac{1 \text{ mol}}{12.01 \text{ g C}} \right) = 2.223 \text{ mol C}$$

$$\text{Moles of O} = (71.1 \text{ g O}) \left(\frac{1 \text{ mol}}{16.00 \text{ g O}} \right) = 4.444 \text{ mol O}$$

The preliminary formula is $\text{H}_{2.222}\text{C}_{2.223}\text{O}_{4.444}$.

Dividing all subscripts by the smallest subscript to obtain integer subscripts:

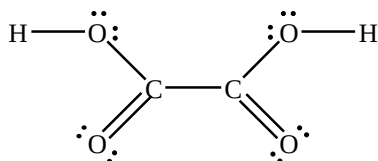
$$\frac{\text{H}_{2.222}}{2.222} \frac{\text{C}_{2.223}}{2.222} \frac{\text{O}_{4.444}}{2.222} = \text{HCO}_2$$

The empirical formula is HCO_2 .

Calculate the amount of NaOH required for the titration:

$$\text{Mmoles of NaOH} = (50.0 \text{ mL}) \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(\frac{0.040 \text{ mol NaOH}}{\text{L}} \right) \left(\frac{1 \text{ mmol}}{0.001 \text{ mol}} \right) = 2.0 \text{ mmol NaOH}$$

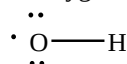
Thus, the ratio is 2.0 mmole base/1.0 mmole acid, or each acid molecule has two hydrogen atoms to react (diprotic). The empirical formula indicates a monoprotic acid, so the formula must be doubled to: $\text{H}_2\text{C}_2\text{O}_4$. $\text{H}_2\text{C}_2\text{O}_4$ has $[2 \times \text{H}(1e^-)] + [2 \times \text{C}(4e^-)] + [4 \times \text{O}(6e^-)] = 34$ valence electrons to be used in the Lewis structure. Fourteen of these electrons are used to bond the atoms with single bonds, leaving $34 - 14 = 20$ electrons or ten pairs of electrons. When these ten pairs of electrons are distributed to the atoms to complete octets, neither C atom has an octet; a lone pair from the oxygen without hydrogen is changed to a bonding pair on C.



- 10.71 **Plan:** Draw the Lewis structure of the OH species. The standard enthalpy of formation is the sum of the energy required to break all the bonds in the reactants and the energy released to form all bonds in the product. Remember to use a negative sign for the energy of the bonds formed since bond formation is exothermic. The bond energy values are found in Table 9.2.

Solution:

a) The OH molecule has $[1 \times \text{O}(6e^-)] + [1 \times \text{H}(1e^-)] = 7$ valence electrons to be used in the Lewis structure. Two of these electrons are used to bond the atoms with a single bond, leaving $7 - 2 = 5$ electrons. Those five electrons are given to oxygen. But no atom can have an octet, and one electron is left unpaired. The Lewis structure is:



b) The formation reaction is: $1/2\text{O}_2(g) + 1/2\text{H}_2(g) \rightarrow \text{OH}(g)$. The heat of reaction is:

$$\Delta H_{\text{rxn}}^\circ = \Sigma \Delta H_{\text{bonds broken}}^\circ + \Sigma \Delta H_{\text{bonds formed}}^\circ = 39.0 \text{ kJ}$$

$$[1/2 (\text{BE}_{\text{O=O}}) + 1/2 (\text{BE}_{\text{H-H}})] + [\text{BE}_{\text{O-H}}] = 39.0 \text{ kJ}$$

$$[(1/2 \text{ mol})(498 \text{ kJ/mol}) + (1/2 \text{ mol})(432 \text{ kJ/mol})] + [\text{BE}_{\text{O-H}}] = 39.0 \text{ kJ}$$

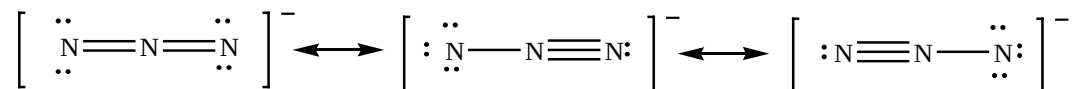
$$465 \text{ kJ} + [\text{BE}_{\text{O-H}}] = 39.0 \text{ kJ}$$

$$\text{BE}_{\text{O-H}} = -426 \text{ kJ or } 426 \text{ kJ}$$

c) The average bond energy (from the bond energy table) is 467 kJ/mol. There are two O–H bonds in water for a total of $2 \times 467 \text{ kJ/mol} = 934 \text{ kJ}$. The answer to part b) accounts for 426 kJ of this, leaving:
 $934 \text{ kJ} - 426 \text{ kJ} = 508 \text{ kJ}$

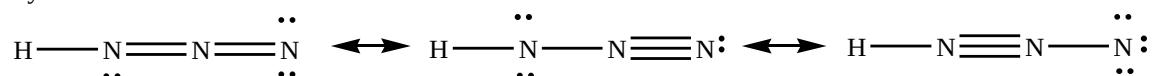
10.72 Both N_3^- and HN_3 have sixteen valence electrons.

Azide ion:



There are three resonance structures for the N_3^- ion. The formal charges in the first structure are, from left to right, -1 , $+1$, and -1 . In the other two Lewis structures the single bonded N has a formal charge of -2 , making both of these less stable than the first structure. The central N is $+1$ and the triple bonded N is 0 . The first resonance structure is more important; the structure should have two equal bonds with a bond order of 2 .

Hydrazoic acid:

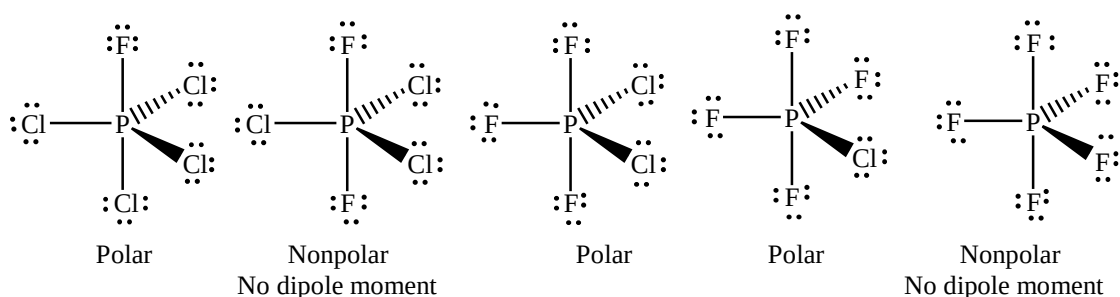


HN_3 also has three resonance structures. The formal charge for the H is 0 in all the structures. In the structure with two double bonds, the formal charges for the N atoms are, left to right: 0 , $+1$, and -1 . The structure where the H is attached to the single bonded N, has N atoms with the following formal charges: -1 , $+1$, and 0 . In the final Lewis structure, the formal charges on the N atoms are: $+1$, $+1$, and -2 . The third structure is clearly not as good as the other two. The first two structures should be averaged to give, starting at the H-end, a bond order of 1.5 then a bond order of 2.5 . Thus, the two bonds are unequal.

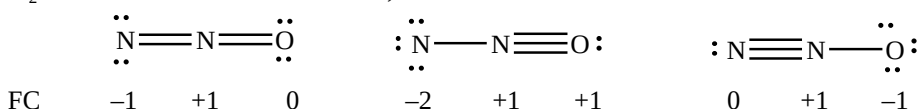
10.73 Plan: The basic Lewis structure will be the same for all species. The Cl atoms are larger than the F atoms. All of the molecules are of the type AX_5 and have trigonal bipyramidal molecular shape. The equatorial positions are in the plane of the triangle and the axial positions above and below the plane of the triangle. In this molecular shape, there is more room in the equatorial positions.

Solution:

- a) The F atoms will occupy the smaller **axial positions** first so that the larger Cl atoms can occupy the equatorial positions which are less crowded.
- b) The molecule containing only F atoms is nonpolar (has no dipole moment), as all the polar bonds would cancel. The molecules with one F or one Cl would be polar since the P–F and P–Cl bonds are not equal in polarity and thus do not cancel each other. The presence of two axial F atoms means that their polarities will cancel (as would the three Cl atoms) giving a nonpolar molecule. The molecule with three F atoms is also polar.

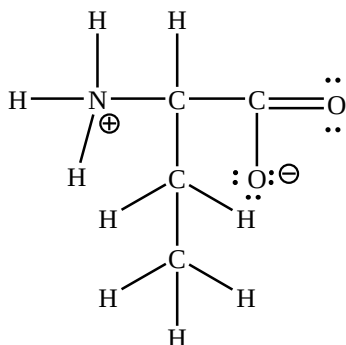


10.74 N_2O has sixteen valence electrons; there are three resonance structures.



The third structure has a more reasonable distribution of formal charges. The third form has a strong triple bond between the N atoms and a weak N–O bond. It is easy to break the N–O bond which is why this compound easily decomposes to support combustion.

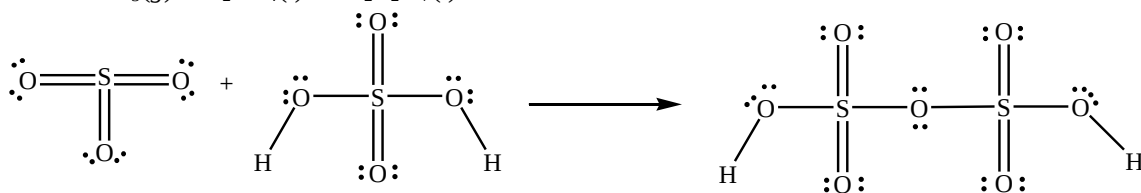
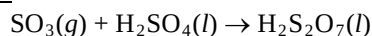
- 10.75 The molecule has forty-two valence electrons. Thirty electrons are already accounted for in the skeleton structure in the bonds. $42 - 30 = 12$ valence electrons remain. If these twelve electrons are given to the two oxygen atoms to complete their octets, the carbon atom that is bonded to the two oxygen atoms does not have an octet. A lone pair from one of the oxygen atoms is changed to a bonding pair on the C. All the atoms have 0 formal charge except the N (FC = +1), and the single bonded O (FC = -1)



- 10.76 a) **Yes**, the black sphere can represent selenium. SeF_4 has thirty-four valence electrons. Eight of these electrons are used in the four Se–F single bonds and twenty-four electrons are used to complete the octets of the F atoms. The remaining electron pair goes to selenium and the molecule is AX_4E . The molecular geometry is the seesaw molecular shape shown.
- b) **Yes**, the black sphere can represent nitrogen if the species is an anion with a -1 charge. The NF_4^- ion has thirty-four valence electrons and would have the seesaw molecular shape as an AX_4E species.
- c) For BrF_4 to have the thirty-four valence electrons needed for this seesaw molecular geometry, the charge of the species must be +1. BrF_4^+ would have $[1 \times \text{Br}(7e^-)] + [4 \times \text{F}(7e^-)] - [1e^- \text{ from } + \text{ charge}] = 34$ valence electrons.

- 10.77 Plan: Draw the Lewis structures. Calculate the heat of reaction using the bond energies in Table 9.2.

Solution:



Reactant bonds broken:

$$5 \times \text{S}=\text{O} = (5 \text{ mol})(552 \text{ kJ/mol}) = 2760 \text{ kJ}$$

$$2 \times \text{S}-\text{O} = (2 \text{ mol})(265 \text{ kJ/mol}) = 530 \text{ kJ}$$

$$2 \times \text{O}-\text{H} = (2 \text{ mol})(467 \text{ kJ/mol}) = 934 \text{ kJ}$$

$$\Sigma \Delta H_{\text{bonds broken}}^\circ = 4224 \text{ kJ}$$

Product bonds formed:

$$4 \times \text{S}=\text{O} = (4 \text{ mol})(-552 \text{ kJ/mol}) = -2208 \text{ kJ}$$

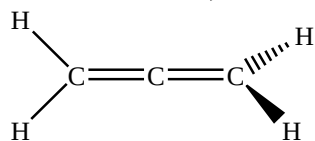
$$4 \times \text{S}-\text{O} = (4 \text{ mol})(-265 \text{ kJ/mol}) = -1060 \text{ kJ}$$

$$2 \times \text{O}-\text{H} = (2 \text{ mol})(-467 \text{ kJ/mol}) = -934 \text{ kJ}$$

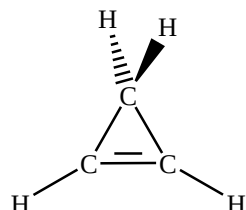
$$\Sigma \Delta H_{\text{bonds formed}}^\circ = -4202 \text{ kJ}$$

$$\Delta H_{\text{rxn}}^\circ = \Sigma \Delta H_{\text{bonds broken}}^\circ + \Sigma \Delta H_{\text{bonds formed}}^\circ = 4224 \text{ kJ} + (-4202 \text{ kJ}) = 22 \text{ kJ}$$

- 10.78 Draw the 2 Lewis structures, and then apply VSEPR to predict the angles.



There are no deviations from the ideal angles. The central carbon is linear (180°). The end C atoms are trigonal planar (120°).

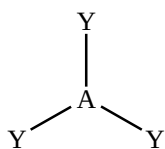


Ideally, the single bonded carbon should be tetrahedral (109.5°), and the double bonded carbons are trigonal planar (120°). The 3-membered ring will approximate an equilateral triangle with 60° angles. The external bonds are probably close to ideal, but the internal bonds are much less.

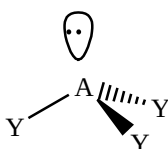
- 10.79 Plan: Pick the VSEPR structures for AY_3 substances. Then determine which are polar.

Solution:

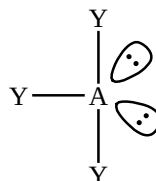
The molecular shapes that have a central atom bonded to three other atoms are trigonal planar, trigonal pyramidal, and T shaped:



a)
three groups
(AX_3)
trigonal planar



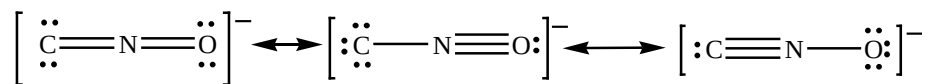
b)
four groups
(AX_3E)
trigonal pyramidal



c)
five groups
(AX_3E_2)
T shaped

Trigonal planar molecules, such as a), are nonpolar, so it cannot be AY_3 . Trigonal pyramidal molecules b) and T-shaped molecules c) are polar, so either could represent AY_3 .

- 10.80 Draw the resonance structures for the fulminate ion, and determine the formal charges:

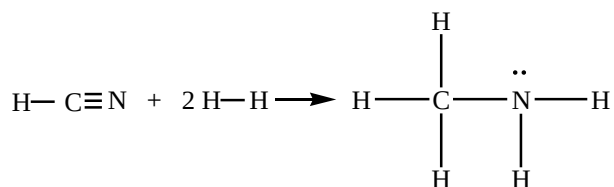


F.C. -2 +1 0 -3 +1 +1 -1 +1 -1

None of the structures has a good distribution of formal charges, thus, none are stable. The best of the choices is the middle structure.

- 10.81 a) Shape A is T shaped (AX_3E_2); Shape B is trigonal planar (AX_3); Shape C is trigonal pyramid (AX_3E). XeF_3^+ , with twenty-eight valence electrons, has two unshared pairs on Xe and is AX_3E_2 and is the T-shaped molecular shape in A. $SbBr_3$, with twenty-six valence electrons, has one unshared pair on Sb; thus it is AX_3E and is the trigonal pyramidal molecular shape in C. $GaCl_3$, with twenty-four valence electrons, has no unshared pairs on Ga; thus it is AX_3 and is the trigonal planar shape in B.
b) Shapes **A and C** are polar.
c) Shape **A**, which is T-shaped, has the most valence electrons (ten) around the central atom.

10.82 The simplified Lewis structures for the reaction are:



Reactant bonds broken:

$$1 \times \text{C}-\text{H} = (1 \text{ mol})(413 \text{ kJ/mol}) = 413 \text{ kJ}$$

$$1 \times \text{C}\equiv\text{N} = (1 \text{ mol})(891 \text{ kJ/mol}) = 891 \text{ kJ}$$

$$2 \times \text{H}-\text{H} = (2 \text{ mol})(432 \text{ kJ/mol}) = 864 \text{ kJ}$$

$$\Sigma \Delta H^\circ_{\text{bonds broken}} = 2168 \text{ kJ}$$

Product bonds formed:

$$3 \times \text{C}-\text{H} = (3 \text{ mol})(-413 \text{ kJ/mol}) = -1239 \text{ kJ}$$

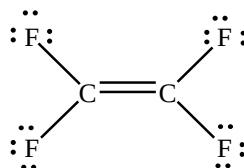
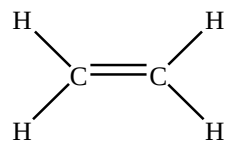
$$1 \times \text{C}-\text{N} = (1 \text{ mol})(-305 \text{ kJ/mol}) = -305 \text{ kJ}$$

$$2 \times \text{N}-\text{H} = (2 \text{ mol})(-391 \text{ kJ/mol}) = -782 \text{ kJ}$$

$$\Sigma \Delta H^\circ_{\text{bonds formed}} = -2326 \text{ kJ}$$

$$\Delta H^\circ_{\text{rxn}} = \Sigma \Delta H^\circ_{\text{bonds broken}} + \Sigma \Delta H^\circ_{\text{bonds formed}} = 2168 \text{ kJ} + (-2326 \text{ kJ}) = -158 \text{ kJ}$$

10.83 a)

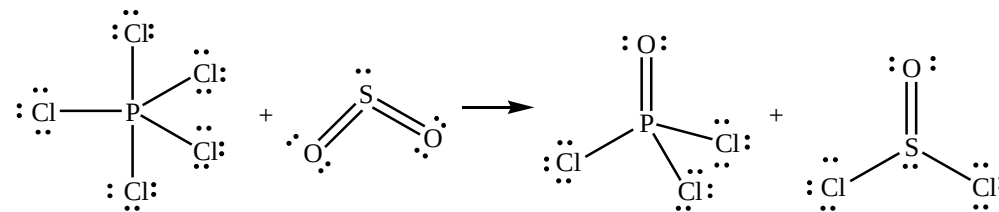
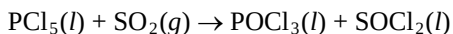


All the carbons are trigonal planar so the ideal angles should all be 120° .

b) The observed angles are slightly less than ideal because the $\text{C}=\text{C}$ bond repels better than the single bonds. The larger F atoms cannot get as close together as the smaller H atoms, so the angles in tetrafluoroethylene are not reduced as much.

10.84 The top portions of the molecules are similar; therefore the top portions will interact with biomolecules in a similar manner.

10.85



PCl_5 : AX_5 **trigonal bipyramidal**

SO_2 : AX_2E **bent**

POCl_3 : AX_4 **tetrahedral**

SOCl_2 : AX_3E **trigonal pyramidal**