CHAPTER 10
CHEMICAL BONDING I: BASIC CONCEPTS

PRACTICE EXAMPLES

1A Mg is in group 2(2A), and thus has 2 valence electrons and 2 dots in its Lewis symbol. Ge is in group 14(4A), and thus has 4 valence electrons and 4 dots in its Lewis symbol. K is in group 1(1A), and thus has 1 valence electron and 1 dot in its Lewis symbol. Ne is in group 18(8A), and thus has 8 valence electrons and 8 dots in its Lewis symbol.

$$\cdot\,\text{Mg}\cdot \qquad \cdot\overset{\cdot}{\underset{\cdot}{\text{Ge}}}\cdot \qquad \text{K}\cdot \qquad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Ne}}}:$$

1B Sn is in Family 4A, and thus has 4 electrons and 4 dots in its Lewis symbol. Br is in Family 7A with 7 valence electrons. Adding an electron produces an ion with 8 valence electrons. Tl is in Family 3A with 3 valence electrons. Removing an electron produces a cation with 2 valence electrons.
S is in Family 6A with 6 valence electrons. Adding 2 electrons produces an anion with 8 valence electrons.

$$\cdot\overset{\cdot}{\underset{\cdot}{\text{Sn}}}\cdot \qquad [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Br}}}:]^- \qquad [\cdot\text{Tl}\cdot]^+ \qquad [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{S}}}:]^{2-}$$

2A The Lewis structures for the cation, the anion, and the compound follows the explanation.

(a) Na loses one electron to form Na^+, while S gains two to form S^{2-}.

$\text{Na}\cdot -1\ e^- \rightarrow [\ \text{Na}]^+$ $\quad \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{S}}}\cdot + 2e^- \rightarrow [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{S}}}:]^{2-}$ Lewis Structure: $[\text{Na}]^+[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{S}}}:]^{2-}[\text{Na}]^+$

(b) Mg loses two electrons to form Mg^{2+}, while N gains three to form N^{3-}.

$\cdot\,\text{Mg}\cdot -2\ e^- \rightarrow [\ \text{Mg}]^{2+}$ $\quad \cdot\overset{\cdot}{\underset{\cdot\cdot}{\text{N}}}\cdot + 3\,e^- \rightarrow [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}:]^{3-}$

Lewis Structure: $[\text{Mg}]^{2+}[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}:]^{3-}[\text{Mg}]^{2+}[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}:]^{3-}[\text{Mg}]^{2+}$

2B Below each explanation are the Lewis structures for the cation, the anion, and the compound.

(a) In order to acquire a noble-gas electron configuration, Ca loses two electrons, and I gains one, forming the ions Ca^{2+} and I^-. The formula of the compound is CaI_2.

$\cdot\,\text{Ca}\cdot -2\ e^- \rightarrow [\ \text{Ca}]^{2+}$ $\quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{I}}}\cdot + e^- \rightarrow [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{I}}}:]^-$ Lewis Structure: $[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{I}}}:]^-[\text{Ca}]^{2+}[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{I}}}:]^-$

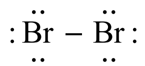
(b) Ba loses two electrons and S gains two to acquire a noble-gas electron configuration, forming the ions Ba^{2+} and S^{2-}. The formula of the compound is BaS.

$\cdot\,\text{Ba}\cdot -2\ e^- \rightarrow [\ \text{Ba}]^{2+}$ $\quad \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{S}}}\cdot + 2e^- \rightarrow [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{S}}}:]^{2-}$ Lewis Structure: $[\text{Ba}]^{2+}[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{S}}}:]^{2-}$

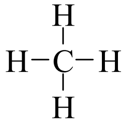
(c) Each Li loses one electron and each O gains two to attain a noble-gas electron configuration, producing the ions Li^+ and O^{2-}. The formula of the compound is Li_2O.

$\cdot\,\text{Li}\ \text{-1}\ e^- \rightarrow [\ \text{Li}]^+$ $\quad \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}\cdot + 2e^- \rightarrow [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}:]^{2-}$ Lewis Structure: $[\text{Li}]^+[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}:]^{2-}[\text{Li}]^+$

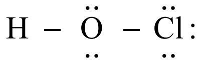
3A In the Br_2 molecule, the two Br atoms are joined by a single covalent bond. This bonding arrangement gives each Br atom a closed valence shell configuration that is equivalent to that for a Kr atom.



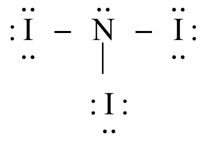
In CH_4, the carbon atom is covalently bonded to four hydrogen atoms. This arrangement gives the carbon atom a valence shell octet and each H atom a valence shell duet.



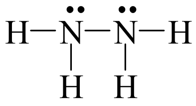
In HOCl, the hydrogen and chlorine atoms are attached to the central oxygen atom through single covalent bonds. This bonding arrangement provides each atom in the molecule with a closed valence shell.



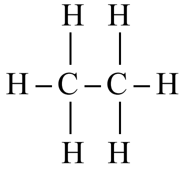
3B The Lewis structure for NI_3 is similar to that of NH_3. The central nitrogen atom is attached to each iodine atom by a single covalent bond. All of the atoms in this structure get a closed valence shell.



The Lewis diagram for N_2H_4 has each nitrogen with one lone pair of electrons, two covalent bonds to hydrogen atoms, and one covalent bond to the other nitrogen atom. With this arrangement, the nitrogen atoms complete their octets while the hydrogen atoms complete their duets.



In the Lewis structure for C_2H_6, each carbon atom shares four pairs of electrons with three hydrogen atoms and the other carbon atom. With this arrangement, the carbon atoms complete their octets while the hydrogen atoms complete their duets.



4A The bond with the most ionic character is the one in which the two bonded atoms are the most different in their electronegativities. We find electronegativities in Figure 10-6 and calculate ΔEN for each bond.

Electronegativities:	H = 2.1	Br = 2.8	N = 3.0	O= 3.5	P = 2.1	Cl = 3.0
Bonds :	H—Br	N—H	N—O	P—Cl		
ΔEN values :	0.7	0.9	0.5	0.9		

Therefore, the N—H and P—Cl bonds are the most polar of the four bonds cited.

4B The most polar bond is the one with the greatest electronegativity difference.

Electronegativities:	C = 2.5	S = 2.5	P = 2.1	O = 3.5	F = 4.0
Bonds:	C — S	C — P	P — O	O — F	
ΔEN values:	0.0	0.4	1.4	0.5	

Therefore, the P — O bond is the most polar of the four bonds cited.

5A The electrostatic potential map that corresponds to IF is the one with the most red in it. This suggests polarization in the molecule. Specifically, the red region signifies a build-up of negative charge that one would expect with the very electronegative fluorine. The other electrostatic potential map corresponds to IBr. The electronegativities are similar, resulting in a relatively non-polar molecule (i.e., little in the way of charge build-up in the molecule).

5B The electrostatic potential map that corresponds to CH_3OH is the one with the most red in it. This suggests polarization in the molecule. Specifically, the red region signifies a build-up of negative charge that one would expect with the very electronegative oxygen atom. The other electrostatic potential map corresponds to CH_3SH. The carbon and sulfur electronegativities are similar, resulting in a relatively non-polar molecule (i.e., little in the way of charge build-up in the molecule).

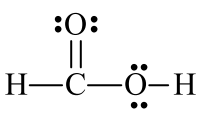
6A **(a)** C has 4 valence electrons and each S has 6 valence electrons: $4+(2\times 6)=16$ valence electrons or 8 pairs of valence electrons. We place C between two S, and use two electron pairs to hold the molecule together, one between C and each S. We complete the octet on each S with three electron pairs for each S. This uses up six more electron pairs, for a total of eight electron pairs used. $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}} - C - \underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}:$ But C does not have an octet. We correct this situation by moving one lone pair from each S into a bonding position between C and S. $:\overset{\cdot\cdot}{S} = C = \overset{\cdot\cdot}{S}:$

(b) C has 4 valence electrons, N has 5 valence electrons and hydrogen has 1 valence electron: Total number of valence electrons = 4 + 5 + 1 = 10 valence electrons or 5 pairs of valence electrons. We place C between H and N, and use two electron pairs to hold the molecule together, one between C and N, as well as one between C and H. We complete the octet on N using three lone pairs. This uses up all five valence electron pairs ($H- C -\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}:$). But C does not yet have an octet. We correct this situation by moving two lone pairs from N into bonding position between C and N. $H-C\equiv N:$

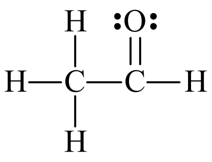
(c) C has 4 valence electrons, each Cl has 7 valence electrons, and oxygen has 6 valence electrons: Thus, the total number of valence electrons = 4 + 2(7) + 6 = 24 valence electrons or 12 pairs of valence electrons. We choose C as the central atom, and use three electron pairs to hold the molecule together, one between C and O, as well as one between C and each Cl. We complete the octet on Cl and O using three lone pairs. This uses all twelve electron pairs. But C does not have an octet. We correct this situation by moving one lone pair from O into a bonding position between C and O.

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} - C(-\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:)_2 \rightarrow :\overset{\cdot\cdot}{O} = C(-\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:)_2$$

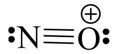
6B **(a)**



(b)

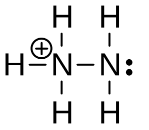


7A **(a)** A plausible Lewis structure for the nitrosonium cation, NO^+, is drawn below:



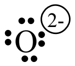
The nitrogen atom is triply bonded to the oxygen atom and both atoms in the structure possess a lone pair of electrons. This gives each atom an octet and a positive formal charge appears on the oxygen atom.

(b) A plausible Lewis structure for $N_2H_5^+$ is given below:

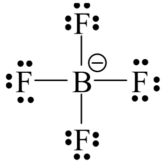


The two nitrogen atoms have each achieved an octet. The right hand side N atom is surrounded by three bonding pairs and one lone pair of electrons, while the left hand side N atom is surrounded by four bonding pairs of electrons. Each hydrogen atom has completed its duet by sharing a pair of electrons with a nitrogen atom. A formal 1+ charge has been assigned to the left hand side nitrogen atom because it is bonded to four atoms (one more than its usual number) in this structure.

(c) In order to achieve a noble gas configuration, oxygen gains two electrons, forming the stable dianion. The Lewis structure for O^{2-} is shown below.

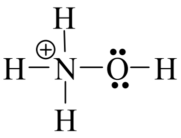


7B **(a)** The most likely Lewis structure for BF_4^- is drawn below:



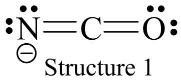
Four bonding pairs of electrons surround the central boron atom in this structure. This arrangement gives the boron atom a complete octet and a formal charge of -1. By virtue of being surrounded by three lone pairs and one bonding electron pair, each fluorine achieves a full octet.

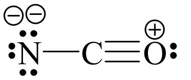
(b) A plausible Lewis structural form for NH_3OH^+, the hydroxylammonium ion, has been provided below:

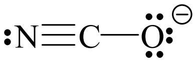


By sharing bonding electron pairs with three hydrogen atoms and the oxygen atom, the nitrogen atom acquires a full octet and a formal charge of 1+. The oxygen atom shares one bonding electron pair with the nitrogen and a second bonding pair with a hydrogen atom.

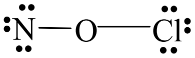
(c) Three plausible resonance structures can be drawn for the isocyanate ion, NCO^-. The nitrogen contributes five electrons, the carbon four, oxygen six, and one more electron is added to account for the negative charge, giving a total of 16 electrons or eight pairs of electrons. In the first resonance contributor, structure 1 below, the carbon atom is joined to the nitrogen and oxygen atoms by two double bonds, thereby creating an octet for carbon. To complete the octet of nitrogen and oxygen, each atom is given a lone pair of electrons. Since nitrogen is sharing just two bonding pairs of electrons in this structure, it must be assigned a formal charge of 1-. In structure 2, the carbon atom is again surrounded by four bonding pairs of electrons, but this time, the carbon atom forms a triple bond with oxygen and just a single bond with nitrogen. The octet for the nitrogen atom is closed with three lone pairs of electrons, while that for oxygen is closed with one lone pair of electrons. This bonding arrangement necessitates giving nitrogen a formal charge of 2- and the oxygen atom a formal charge of 1+. In structure 3, which is the dominant contributor because it has a negative formal charge on oxygen (the most electronegative element in the anion), the carbon achieves a full octet by forming a triple bond with the nitrogen atom and a single bond with the oxygen atom. The octet for oxygen is closed with three lone pairs of electrons, while that for nitrogen is closed with one lone pair of electrons.


Structure 1

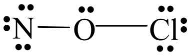

Structure 2


Structure 3

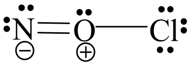
<u>8A</u> The total number of valence electrons in NOCl is 18 (5 from nitrogen, 6 from oxygen and 7 from chlorine). Four electrons are used to covalently link the central oxygen atom to the terminal chlorine and nitrogen atoms in the skeletal structure: N—O—Cl. Next, we need to distribute the remaining electrons to achieve a noble gas electron configuration for each atom. Since four electrons were used to form the two covalent single bonds, fourteen electrons remain to be distributed. By convention, the valence shells for the terminal atoms are filled first. If we follow this convention, we can close the valence shells for both the nitrogen and the chlorine atoms with twelve electrons.



Oxygen is moved closer to a complete octet by placing the remaining pair of electrons on oxygen as a lone pair.

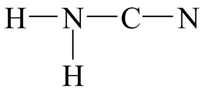


The valence shell for the oxygen atom can then be closed by forming a double bond between the nitrogen atom and the oxygen atom.

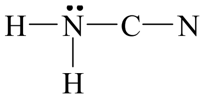


This structure obeys the requirement that all of the atoms end up with a filled valence shell, but is much poorer than the one derived in Example 10-8 because it has a positive formal charge on oxygen, which is the most electronegative atom in the molecule. In other words, this structure can be rejected on the grounds that it does not conform to the third rule for determining plausibility of a Lewis structure based on formal charges, which states that "negative formal charges should appear on the most electronegative atom, while any positive formal charge should appear on the least electronegative atom."

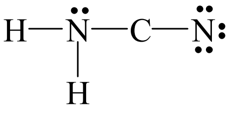
8B There are a total of sixteen valence electrons in the cyanamide molecule (five from each nitrogen atom, four from carbon and one electron from each hydrogen atom). The formula has been written as NH_2CN to remind us that carbon, the most electropositive *p*-block element in the compound, should be selected as the central atom in the skeletal structure.

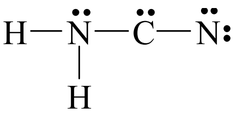


To construct this skeletal structure we use 8 electrons. Eight electrons remain to be added to the structure. Note: each hydrogen atom at this stage has achieved a duet by forming a covalent bond with the nitrogen atom in the NH_2 group. The octet for the NH_2 nitrogen is completed by giving it a lone pair of electrons.

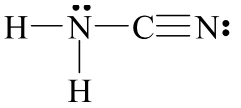


The remaining six electrons can then be given to the terminal nitrogen atom, affording structure 1, shown below. Alternatively, four electrons can be assigned to the terminal nitrogen atom and the last two electrons can be given to the central carbon atom, to produce structure 2 below:

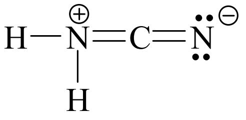

(Structure 1)


(Structure 2)

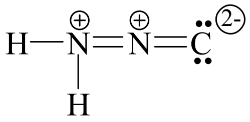
The octet for the carbon atom in structure 1 can be completed by converting two lone pairs of electrons on the terminal nitrogen atom into two more covalent bonds to the central carbon atom.


Structure 3

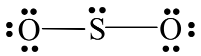
Each atom in structure 3 has a closed-shell electron configuration and a formal charge of zero. We can complete the octet for the carbon and nitrogen atoms in structure 1 by converting a lone pair of electrons on each nitrogen atom into a covalent bond to the central carbon atom.


Structure 4

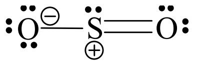
The resulting structure has a formal charge of 1- on the terminal nitrogen atom and a 1+ formal charge on the NH_2 nitrogen atom. Although structures 3 and 4 both satisfy the octet and duet rules, structure 3 is the better of the two structures because it has no formal charges. A third structure which obeys the octet rule (depicted below), can be rejected on the grounds that it has formal charges of the same type (two 1+ formal charges) on adjacent atoms, as well as negative formal charges on carbon, which is not the most electronegative element in the molecule.



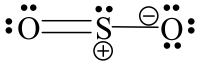
9A The skeletal structure for SO_2 has two terminal oxygen atoms bonded to a central sulfur atom. Sulfur has been selected as the central atom by virtue of its being the most electropositive atom in the molecule. It turns out that two different Lewis structures of identical energy can be derived from the skeletal structure described above. First we determine that SO_2 has 18 valence electrons (6 from each atom). Four of the valence electrons must be used to covalently bond the three atoms together. The remaining 14 electrons are used to close the valence shell of each atom. Twelve electrons are used to give the terminal oxygen atoms a closed shell. The remaining two electrons (14 -12 = 2) are placed on the sulfur atom, affording the structure depicted below:



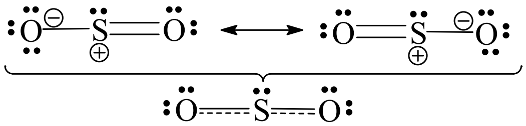
At this stage, the valence shells for the two oxygen atoms are closed, but the sulfur atom is two electrons short of a complete octet. If we complete the octet for sulfur by converting a lone pair of electrons on the right hand side oxygen atom into a sulfur-to-oxygen π-bond, we end up generating the resonance contributor (A) shown below:

 (A)

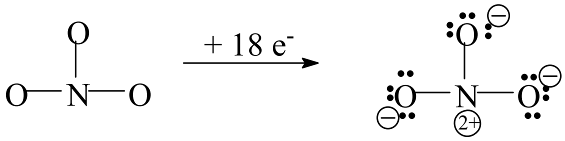
Notice that the structure has a positive formal charge on the sulfur atom (most electropositive element) and a negative formal charge on the left-hand oxygen atom. Remember that oxygen is more electronegative than sulfur, so these charges are plausible. The second completely equivalent contributor, (B), is produced by converting a lone pair on the left-most oxygen atom in the structure into a π-bond, resulting in conversion of a sulfur-oxygen single bond into a sulfur-oxygen double bond:

 (B)

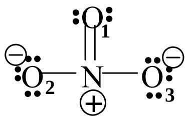
Neither structure is consistent with the observation that the two S-O bond lengths in SO_2 are equal, and in fact, the true Lewis structure for SO_2 is neither (A) nor (B), but rather an equal blend of the two individual contributors called the resonance hybrid (see below).



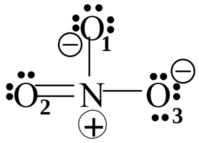
9B The skeletal structure for the NO_3^- ion has three terminal oxygen atoms bonded to a central nitrogen atom. Nitrogen has been chosen as the central atom by virtue of being the most electropositive atom in the ion. It turns out that three contributing resonance structures of identical energy can be derived from the skeletal structure described here. We begin the process of generating these three structures by counting the total number of valence electrons in the NO_3^- anion. The nitrogen atom contributes five electrons, each oxygen contributes six electrons, and an additional electron must be added to account for the 1-charge on the ion. In total, we must account for 24 electrons. Six electrons are used to draw single covalent bonds between the nitrogen atom and three oxygen atoms. The remaining 18 electrons are used to complete the octet for the three terminal oxygen atoms:

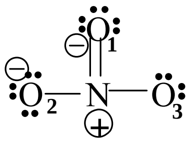


At this stage the valence shells for the oxygen atoms are filled, but the nitrogen atom is two electrons short of a complete octet. If we complete the octet for nitrogen by converting a lone pair on O_1 into a nitrogen-to-oxygen π-bond, we end up generating resonance contributor (A):

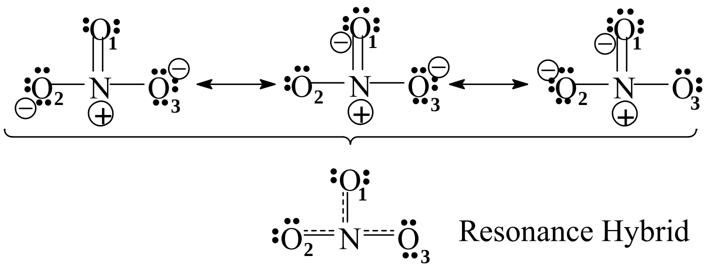

(A)

Notice the structure has a 1+ formal charge on the nitrogen atom and a 1- on two of the oxygen atoms (O_2 and O_3). These formal charges are quite reasonable energetically. The second and third equivalent structures are generated similarly; by moving a lone pair from O_2 to form a nitrogen to oxygen (O_2) double bond, we end up generating resonance contributor (B), shown below. Likewise, by converting a lone pair from oxygen (O_3) into a π-bond with the nitrogen atom, we end up generating resonance contributor (C), also shown below.


(B)

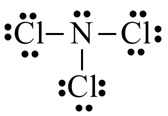

(C)

None of these individual structures ((A), (B), or (C)) correctly represents the actual bonding in the nitrate anion. The actual structure, called the resonance hybrid, is the equally weighted average of all three structures (i.e. 1/3(A) + 1/3(B) + 1/3(C)):

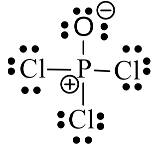

Resonance Hybrid

These three resonance forms give bond lengths that are comparable to nitrogen- nitrogen double bonds.

10A The Lewis structure of NCl_3 has three Cl atoms bonded to N and one lone pair attached to N. These four electron groups around N produce a tetrahedral electron-group geometry. The fact that one of the electron groups is a lone pair means that the molecular geometry is trigonal pyramidal.



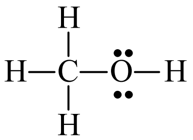
10B The Lewis structure of $POCl_3$ has three single P-Cl bonds and one P-O bond. These four electron groups around P produce a tetrahedral electron-group geometry. No lone pairs are attached to P and thus the molecular geometry is tetrahedral.



11A The Lewis structure of COS has one S doubly-bonded to C and an O doubly-bonded to C. There are no lone pairs attached to C. The electron-group and molecular geometries are the same: linear. $|\overline{S}=C=\overline{O}|$. We can draw other resonance forms, however, the molecular geometry is unaffected.

11B N is the central atom. $|N\equiv N—\overline{\underline{O}}\,|$ This gives an octet on each atom, a formal charge of 1+ on the central N, and a 1– on the O atom. There are two bonding pairs of electrons and no lone pairs on the central N atom. The N_2O molecule is linear. We can draw other resonance forms, however, the molecular geometry is unaffected.

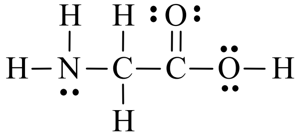
12A In the Lewis structure of methanol, each H atom contributes 1 valence electron, the C atom contributes 4, and the O atom contributes 6, for a total of $(4\times 1)+4+6=14$ valence electrons, or 7 electron pairs. 4 electron pairs are used to connect the H atoms to the C and the O, 1 electron pair is used to connect C to O, and the remaining 2 electron pairs are lone pairs on O, completing its octet.



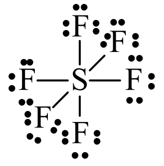
The resulting molecule has two central atoms. Around the C there are four bonding pairs, resulting in a tetrahedral electron-group geometry and molecular geometry. The H—C—H bond angles are ~109.5º, as are the H—C—O bond angles. Around the O there are two bonding pairs of electrons and two lone pairs, resulting in a tetrahedral electron-group geometry and a bent molecular shape around the O atom, with a $C—O—H$ bond angle of slightly less than 109.5°.

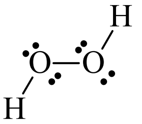
12B The Lewis structure is drawn below. With four electron groups surrounding each, the electron-group geometries of N, the central C, and the right-hand O are all tetrahedral. The $H—N—H$ bond angle and the $H—N—C$ bond angles are almost the tetrahedral angle of 109.5°, made a bit smaller by the lone pair. The $H—C—N$ angles, the $H—C—H$ angle and the H—C—C angles all are very close to 109.5°. The $C—O—H$

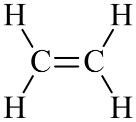
bond angle is made somewhat smaller than 109.5° by the presence of two lone pairs on O. Three electron groups surround the right-hand C, making its electron-group and molecular geometries trigonal planar. The $\mathrm{O—C—O}$ bond angle and the $\mathrm{O—C—C}$ bond angles all are very close to 120°.



13A Lewis structures of the three molecules are drawn below. Around the S in the SF_6 molecule are six bonding pairs of electrons, and no lone pairs. The molecule is octahedral; each of the S-F bond moments is cancelled by one on the other side of the molecule.

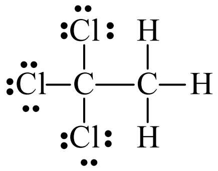


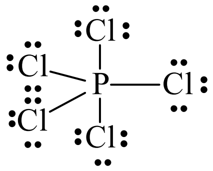


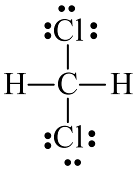


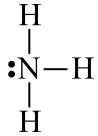
SF_6 is nonpolar. In H_2O_2, the molecular geometry around each O atom is bent; the bond moments do not cancel. H_2O_2 is polar. Around each C in C_2H_4 are three bonding pairs of electrons; the molecule is planar around each C and planar overall. The polarity of each $—CH_2$ group is cancelled by the polarity of the other $H_2C—$ group. C_2H_2 is nonpolar.

13B Lewis structures of the four molecules are drawn below and we can consider the three $\mathrm{C—H}$ bonds and the one $\mathrm{C—C}$ bond to be nonpolar. The three $\mathrm{C—Cl}$ bonds are tetrahedrally oriented.





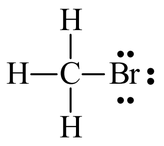




If there were a fourth $\mathrm{C—Cl}$ bond on the left-hand C, the bond dipoles would cancel out, producing a nonpolar molecule. Since it is not there, the molecule is polar. A similar argument is made for NH_3, where three tetrahedrally-oriented $\mathrm{N—H}$ polar bonds are not balanced by a fourth, and for CH_2Cl_2, where two tetrahedrally oriented $\mathrm{C—Cl}$ bonds are not balanced by two others. This leaves PCl_5 as the only nonpolar species; it is a highly symmetrical molecule in which individual bond dipoles cancel out.

14A The Lewis structure of CH_3Br has all single bonds. From Table 10.2, the length of a $\mathrm{C—H}$ bond is 110 pm. The length of a $\mathrm{C—Br}$ bond is not given in the table. A reasonable value is the average of the $\mathrm{C—C}$ and $\mathrm{Br—Br}$ bond lengths.

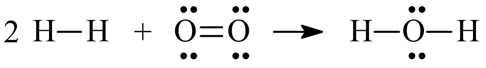
$$\text{C—Br} = \frac{\text{C—C} + \text{Br—Br}}{2} = \frac{154\text{ pm} + 228\text{ pm}}{2} = 191\text{ pm}$$



$H_3C{-}\ddot{\underset{\cdot\cdot}{Br}}{:}$

14B In Table 10.2, the C=N bond length is 128 pm, while the C≡N bond length is 116 pm. The observed C—N bond length of 115 pm is much closer to a carbon-nitrogen triple bond. This can be explained by using the following Lewis structure: $|\overline{\underline{S}} - C \equiv N|$ where there is a formal negative charge on the sulfur atom. This molecule is linear according to VSEPR theory.

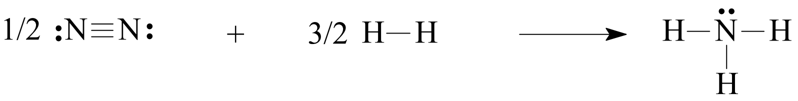
15A We first draw Lewis structures for all of the molecules involved in the reaction.



$$2\ \text{H—H} + \ddot{\underset{\cdot\cdot}{O}}{=}\ddot{\underset{\cdot\cdot}{O}} \longrightarrow \text{H—}\ddot{\underset{\cdot\cdot}{O}}\text{—H}$$

Break 1 O=O + 2H—H = 498 kJ/mol + (2 × 436 kJ/mol) = 1370 kJ/mol absorbed
Form 4H—O = (4 × 464 kJ/mol) = 1856 kJ/mol given off
Enthalpy change $= 1370\text{ kJ/mol} - 1856\text{ kJ/mol} = -486\text{ kJ/mol}$

15B The chemical equation, with Lewis structures, is:



$$1/2\ {:}N{\equiv}N{:} \quad + \quad 3/2\ \text{H—H} \longrightarrow \text{H—}\ddot{\underset{|}{N}}\text{—H}$$

Energy required to break bonds $= \frac{1}{2}\text{N} \equiv \text{N} + \frac{3}{2}\text{H — H}$

$= (0.5 \times 946\text{ kJ/mol}) + (1.5 \times 436\text{ kJ/mol}) = 1.13 \times 10^3\text{ kJ/mol}$

Energy realized by forming bonds $= 3\text{ N — H} = 3 \times 389\text{ kJ/mol} = 1.17 \times 10^3\text{ kJ/mol}$

$\Delta H = 1.13 \times 10^3\text{ kJ/mol} - 1.17 \times 10^3\text{ kJ/mol} = -4 \times 10^1\text{ kJ/mol of } NH_3$.

Thus, $\Delta H_f = -4 \times 10^1\text{ kJ/mol } NH_3$ (Appendix D value is $\Delta H_f = -46.11\text{ kJ/mol } NH_3$)

16A The reaction below,

$CH_3(C{=}O)CH_3(g) + H_2(g) \rightarrow (CH_3)_2CH(OH)(g)$

Involves the following bond breakages and formations:
Broken: 1 C=O bond (736 kJ/mol)
Broken: 1 H–H bond (436 kJ/mol)
Formed: 1 C–O bond (360 kJ/mol)
Formed: 1 C–H bond (414 kJ/mol)
Formed: 1 O–H bond (464 kJ/mol)

Therefore, the energy of the reaction is:

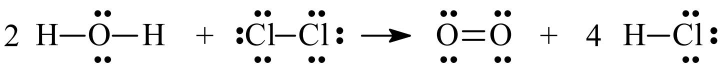
$\Delta H_{rxn} = \Delta H(\text{bond breakage}) + \Delta H(\text{bond formation})$

$\Delta H_{rxn} = [(1 \times 736) + (1 \times 436)] + [(1 \times -360) + (1 \times -414) + (1 \times -464)]$

$\Delta H_{rxn} = -66\text{ kJ/mol}$

Therefore, the reaction is exothermic.

16B First we will double the chemical equation, and represent it in terms of Lewis structures:



$$2\ H{-}\ddot{\underset{\cdot\cdot}{O}}{-}H + :\ddot{\underset{\cdot\cdot}{Cl}}{-}\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow \ddot{\underset{\cdot\cdot}{O}}{=}\ddot{\underset{\cdot\cdot}{O}} + 4\ H{-}\ddot{\underset{\cdot\cdot}{Cl}}:$$

$$\text{Energy required to break bonds} = 2\ \text{Cl}—\text{Cl} + 4\text{H}—\text{O}$$
$$= (2\times 243\ \text{kJ/mol}) + (4\times 464\ \text{kJ/mol}) = 2342\ \text{kJ/mol}$$

$$\text{Energy realized by forming bonds} = 1\ \text{O}=\text{O} + 4 \times \text{H}—\text{Cl}$$
$$= 498\ \text{kJ/mol} + (4\times 431\ \text{kJ/mol}) = 2222\ \text{kJ/mol}$$

$\Delta H = \frac{1}{2}(2342\ \text{kJ / mol} - 2222\ \text{kJ / mol}) = +60\ \text{kJ / mol}$; The reaction is endothermic.

Important Note: In this and subsequent chapters, a lone pair of electrons in a Lewis structure can be shown as a line or a pair of dots. Thus, the Lewis structure of Be is both Be| and Be:.

INTEGRATIVE EXAMPLE

A. The reaction is as follows: $PCl_3 + Cl_2 \rightarrow PCl_5$

$\Delta H_{rxn} = \sum \Delta H_{prod} - \sum \Delta H_{react}$

$\Delta H_{rxn} = (-374.9) - (-287.0 + 0) = -87.9\ \text{kJ/mol}$

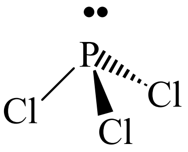
To determine the P–Cl bond energy, we must first deduce the Cl–Cl bond energy:

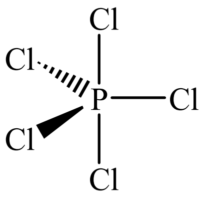
$2Cl \rightarrow Cl_2$ ΔH_{rxn} = 0 – 2(121.7) = -243 kJ/mol, which is in reasonable agreement with Table 10-3.

Using the above information, we can determine the P–Cl bond energy:

$$\Delta H_{rxn} = \Delta H(\text{bond breakage}) + \Delta H(\text{bond formation})$$
$$\Delta H_{rxn} = 1\ \text{Cl}-\text{Cl (broken)} + 2\ \text{P}-\text{Cl (formed)}$$
$$-87.9 = 243 + 2\ \text{P}-\text{Cl}$$
$$\text{P}-\text{Cl} = -165.5\ \text{kJ/mol}$$

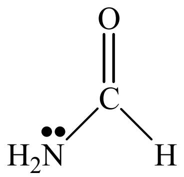
The Lewis structures of PCl_3 and PCl_5 are shown below.



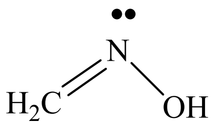


Since the geometries of the two molecules differ, the orbital overlap between P and the surrounding Cl atoms will be different and therefore the P–Cl bonds in these two compounds will also be slightly different.

B. **(a)** The structures are shown below, with appropriate geometries:



Formamide



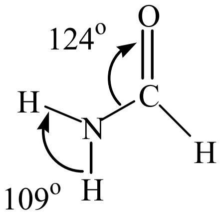
Formaldoxime

$$\sum \mathrm{BE}(\mathrm{H_2NCOH}) = 2(\mathrm{N-H}) + 1(\mathrm{N-C}) + 1(\mathrm{C=O}) + 1(\mathrm{C-H})$$
$$= 2(389) + 305 + 736 + 414 = 2233 \text{ kJ/mol}$$

$$\sum \mathrm{BE}(\mathrm{H_2C=N-OH}) = 2(\mathrm{C-H}) + 1(\mathrm{C=N}) + 1(\mathrm{N-O}) + 1(\mathrm{O-H})$$
$$= 2(414) + 615 + 222 + 464 = 2129 \text{ kJ / mol}$$

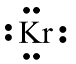
Since BE of formamide is greater than that of formaldoxime, it is more stable, and its conversion endothermic.

(b) The experiment shows that the geometry around C is trigonal planar, and around N is trigonal pyramidal.

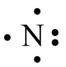


EXERCISES

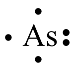
Lewis Theory

1. **(a)**


(b)


(c)


(d)


(e)


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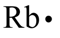
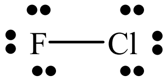


3.

(a)


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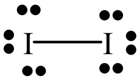

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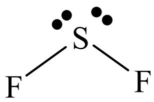
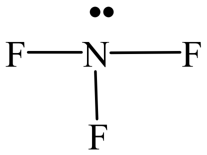
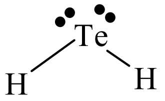
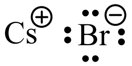


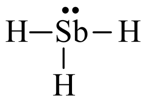
(d)

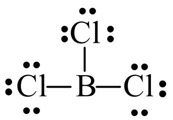


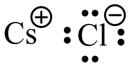
(e)

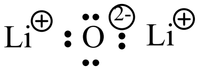


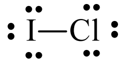
5. **(a)**  CsBr, cesium bromide

(b)  H_3Sb, hydrogen antimonide or trihydrogen antimonide

(c)  BCl_3, boron trichloride

(d)  CsCl, cesium chloride

(e)  Li_2O, lithium oxide

(f)  ICl, iodine monochloride

7. NH_3 $5+(3\times 1)=8$ v.e.$=4$ pairs

BF_3 $3+(3\times 7)=24$ v.e.$=12$ pairs

SF_6 $6+(6\times 7)=48$ v.e.$=24$ pairs

SO_3 $6+(3\times 6)=24$ v.e.$=12$ pairs

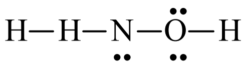
NH_4^+ $5+(4\times 1)-1=8$ v.e.$=4$ pairs

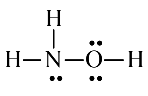
SO_4^{2-} $6+(4\times 6)+2=32$ v.e.$=16$ pairs

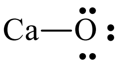
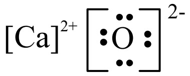
NO_2 $5+(2\times 6)=17$ v.e.$=8.5$ pairs

NO_2 cannot obey the octet rule; there is no way to pair all electrons when the number of electrons is odd.

All of these Lewis structures obey the octet rule except for BF_3, which is electron deficient, and SF_6, which has an expanded octet.

9. **(a)**  has two bonds to (four electrons around) the second hydrogen, and only six electrons around the nitrogen. A better Lewis structure is shown below.



(b) Here,  is improperly written as a covalent Lewis structure. CaO is actually an ionic compound.  is a more plausible Lewis structure for CaO.

11. The answer is (c), hypochlorite ion. The flaws with the other answers are as follows:

(a) $\ominus\!:\!\underset{\cdot\cdot}{\ddot{O}}-\overset{\oplus}{C}=\underset{\cdot\cdot}{\ddot{N}}\ominus$ – does not have an octet of electrons around C.

(b) $[C{=}C\,:\,]^{-}$ does not have an octet around either C. Moreover, it has only 6 valence electrons in total while it should have 10, and finally, the sum of the formal charges on the two carbons doesn't equal the charge on the ion.

(d) The total number of valence electrons in NO is incorrect. No, being an odd-electron species should have 11 valence electrons, not 12.

Ionic Bonding

13. **(a)** $[:\underset{\cdot\cdot}{\ddot{Cl}}:]^{-}[Ca]^{2+}[:\underset{\cdot\cdot}{\ddot{Cl}}:]^{-}$ **(b)** $[Ba]^{2+}[:\underset{\cdot\cdot}{\ddot{S}}:]^{2-}$ **(c)** $[Li]^{+}[:\underset{\cdot\cdot}{\ddot{O}}:]^{2-}[Li]^{+}$ **(d)** $[Na]^{+}[:\underset{\cdot\cdot}{\ddot{F}}:]^{-}$

15. **(a)** $[Li]^{+}[:\underset{\cdot\cdot}{\ddot{S}}:]^{2-}[Li]^{+}$: Li_2S **(b)** $[Na]^{+}[:\underset{\cdot\cdot}{\ddot{F}}:]^{-}$: NaF

(c) $[:\underset{\cdot\cdot}{\ddot{I}}:]^{-}[Ca]^{2+}[:\underset{\cdot\cdot}{\ddot{I}}:]^{-}$: CaI_2 **(d)** $\begin{array}{c}[:\underset{\cdot\cdot}{\ddot{Cl}}:]^{-}\\ [:\underset{\cdot\cdot}{\ddot{Cl}}:]^{-}[Sc]^{3+}[:\underset{\cdot\cdot}{\ddot{Cl}}:]^{-}\end{array}$: $ScCl_3$

Formal Charge

17.

(a)

computations for:	H—	—C≡	≡C
no. valence e^-	1	4	4
- no. lone-pair e^-	–0	–0	–2
$-\frac{1}{2}$ no. bond-pair e^-	–1	–4	–3
formal charge	0	0	–1

(b)

computations for:	=O	—O(×2)	C
no. valence e^-	6	6	4
- no. lone-pair e^-	–4	–6	–0
$-\frac{1}{2}$ no. bond-pair e^-	–2	–1	–4
formal charge	–0	–1	0

(c)

computations for:	—H(×7)	side C(×2)	central C
no. valence e^-	1	4	4
- no. lone-pair e^-	–0	–0	–0
$-\frac{1}{2}$ no. bond-pair e^-	–1	–4	–3
formal charge	0	0	+1

19. There are three features common to formal charge and oxidation state. First, both indicate how the bonding electrons are distributed in the molecule. Second, negative formal charge (in the most plausible Lewis structure) and negative oxidation state are generally assigned to the more electronegative atoms. And third, both numbers are determined by a set of rules, rather than being determined experimentally. Bear in mind, however, that there are also significant differences. For instance, there are cases where atoms of the same type with the same oxidation state have different formal charges, such as oxygen in ozone, O_3. Another is that formal charges are used to decide between alternative Lewis structures, while oxidation state is used in balancing equations and naming compounds. Also, the oxidation state in a compound is invariant, while the formal charge can change. The most significant difference, though, is that whereas the oxidation state of an element in its compounds is usually not zero, its formal charge usually is.

21. FC = # valence e^- in free atom – number lone-pair e^- – ½ # bond pair e^-

(a) Central O in O_3: 6 – 2 – 3 = +1

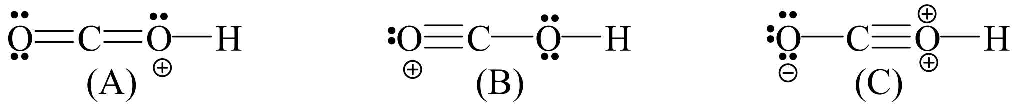
(b) Al in AlH_4^- : 3 – 0 – 4 = –1

(c) Cl in ClO_3^- : 7 – 2 – 5 = 0

(d) Si in SiF_6^{2-} : 4 – 0 – 6 = –2

(e) Cl in ClF_3 : 7 – 4 – 3 = 0

23. We begin by counting the total number of valence electrons that must appear in the Lewis structure of the ion CO_2H^+: one from hydrogen, four from carbon, and six from each of the two oxygen (12 in all from the oxygen atoms). One electron is lost to establish the 1+ charge on the ion. In all, sixteen electrons are in the valence shell of the cation. If the usual rules for constructing valid Lewis structures are applied to HCO_2^+, we come up with the following structures:

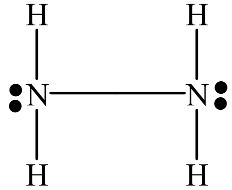


In structure (A), the internal oxygen atom caries the positive charge, while in structure (B), the positive charge is located on the terminal oxygen atom. A third structure can also be drawn, however, due to an unacceptably large charge build-up, this form can be neglected. Thus, in this case of A and B, we cannot use the concept of formal charge to pick one structure over the other because the positive formal charge in both structures is located on the same type of atom, namely, an oxygen atom. In other words, based on formal charge rules alone, we must conclude that structures (A) and (B) are equally plausible.

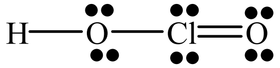
Lewis Structures

25.

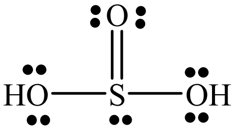
(a)



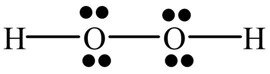
(b)



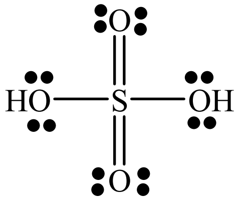
(c)



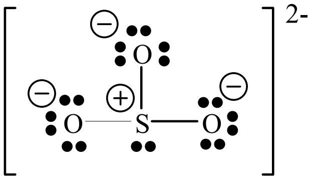
(d)



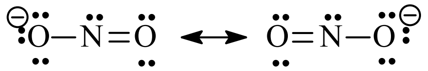
(e)



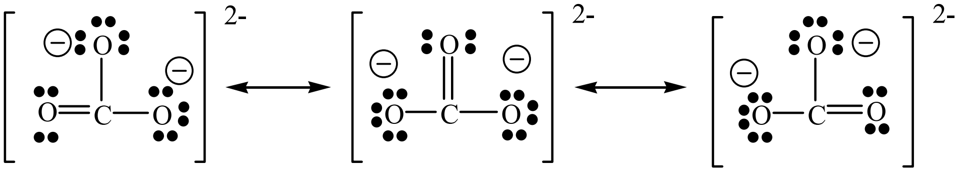
27. **(a)** The total number of valence electrons in SO_3^{2-} is $6+(3\times 6)+2=26$, or 13 electron pairs. A plausible Lewis structure is:

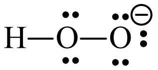


(b) The total number of valence electrons in NO_2^{-} is $5+(2\times 6)+1=18$, or 9 electron pairs. There are two resonance forms for the nitrite ion:

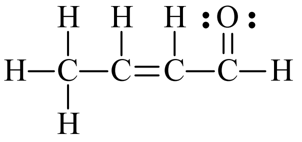


(c) The total number of valence electrons in CO_3^{2-} is $4+(3\times 6)+2=24$, or 12 electron pairs. There are three resonance forms for the carbonate ion:

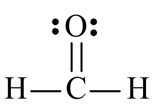


(d) The total number of valence electrons in HO_2^{-} is $1+(2\times 6)+1=14$, or 7 electron pairs. A plausible Lewis structure is 

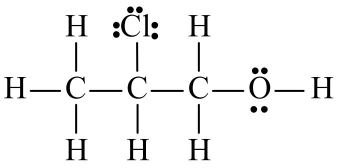
29. In $CH_3CHCHCHO$ there are $(4\times 4)+(6\times 1)+6=28$ valence electrons, or 14 electron pairs. We expect that the carbon atoms bond to each other. A plausible Lewis structure is:



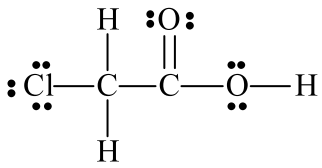
31. **(a)**



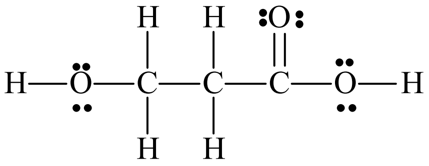
(b)



33. **(a)**

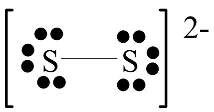


(b)

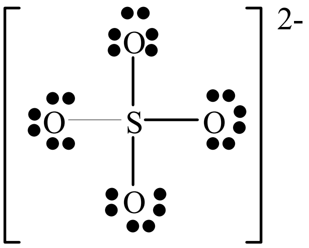


35.

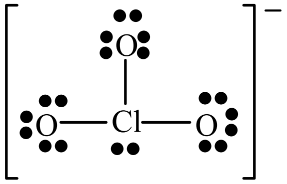
(a) Group 16



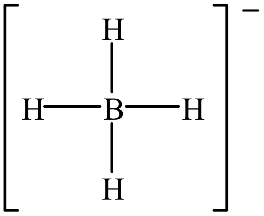
(b) Group 16 except oxygen



(c) Group 17 except fluorine



(d) Group 13



Polar Covalent Bonds and Electrostatic Potential Maps

37. Na — Cl and K — F both possess bonds between a metal and a nonmetal. Thus, they have the largest ionic character, with the ionic character of K — F being greater than that of Na — Cl, both because K is more metallic (closer to the lower left of the periodic table) than Na and because F is more nonmetallic (closer to the upper right) than Cl. The remaining three bonds are covalent bonds to H. Since H and C have about the same electronegativity (a fact you need to memorize), the H — C bond is the most covalent (or the least ionic). Br is somewhat more electronegative than is C, while F is considerably more electronegative than C, making the F — H bond the most polar of the three covalent bonds. Thus, ranked in order of increasing ionic character, these five bonds are:

C — H < Br — H < F — H < Na — Cl < K — F

The actual electronegativity differences follow:

$$\begin{array}{llllll} & \mathrm{C}(2.5)\text{-}\mathrm{H}(2.1) < & \mathrm{Br}(2.8)\text{-}\mathrm{H}(2.1) < & \mathrm{F}(4.0)\text{-}\mathrm{H}(2.1) < & \mathrm{Na}(0.9)\text{-}\mathrm{Cl}(3.0) < & \mathrm{K}(0.8)\text{-}\mathrm{F}(4.0) \\ \Delta\mathrm{EN} & = 0.4 & = 0.7 & = 1.9 & = 2.1 & = 3.2 \end{array}$$

39. The percent ionic character of a bond is based on the difference in electronegativity of its constituent atoms and Figure 10.7.

(a) $\mathrm{S}(2.5)\text{—}\mathrm{H}(2.1)$	**(b)** $\mathrm{O}(3.5)\text{—}\mathrm{Cl}(3.0)$	**(c)** $\mathrm{Al}(1.5)\text{—}\mathrm{O}(3.5)$	**(d)** $\mathrm{As}(2.0)-\mathrm{O}(3.5)$
Δ EN 0.4	0.5	2.0	1.5
%ionic = 4%	= 5 %	=60 %	=33 %

41.

$\mathrm{Cl}\!+\!\!\!\longrightarrow\mathrm{F}$

$$\delta = \frac{\mu}{d} = \frac{0.8881\,\mathrm{D} \times\ 3.34\times10^{-30}\ \mathrm{C\cdot m/D}}{162.8\times10^{-12}\ \mathrm{m}} \times \frac{1e}{1.602\times10^{-19}\ \mathrm{C}} = 0.114e\text{, towards F.}$$

$\mathrm{Rb}\!+\!\!\!\longrightarrow\mathrm{F}$

$$\delta = \frac{\mu}{d} = \frac{8.547\,\mathrm{D} \times\ 3.34\times10^{-30}\ \mathrm{C\cdot m/D}}{227.0\times10^{-12}\ \mathrm{m}} \times \frac{1e}{1.602\times10^{-19}\ \mathrm{C}} = 0.785e\text{, towards F.}$$

$\mathrm{Sn}\!+\!\!\!\longrightarrow\mathrm{O}$

$$\delta = \frac{\mu}{d} = \frac{4.3210\,\mathrm{D} \times\ 3.34\times10^{-30}\ \mathrm{C\cdot m/D}}{183.3\times10^{-12}\ \mathrm{m}} \times \frac{1e}{1.602\times10^{-19}\ \mathrm{C}} = 0.491e\text{, towards O.}$$

$\mathrm{Ba}\!+\!\!\!\longrightarrow\mathrm{O}$

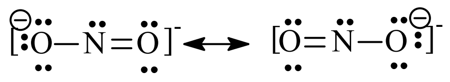
$$\delta = \frac{\mu}{d} = \frac{7.954\,\mathrm{D} \times\ 3.34\times10^{-30}\ \mathrm{C\cdot m/D}}{194.0\times10^{-12}\ \mathrm{m}} \times \frac{1e}{1.602\times10^{-19}\ \mathrm{C}} = 0.855e\text{, towards O.}$$

43. When looking at the electrostatic potential map, we expect similar structures. However, in the case of $F_2C{=}O$, the carbon should be more electropositive than in $H_2C{=}O$ due to the presence of very electronegative fluorine atoms (as opposed to H atoms). Thus, for $F_2C{=}O$, one expects the center of the molecule to appear blue. As well, the electronegative oxygen atom should have less electron density associated with it, thus $H_2C{=}O$ should have a greater amount of red (electron rich) than the corresponding $F_2C{=}O$, again, as a result of the presence of highly electronegative fluorine atoms. $F_2C{=}O$ is represented on the left, while $H_2C{=}O$ is represented on the right.

45. The molecular formulas for the compounds are SF_4 and SiF_4. SiF_4 is a symmetric molecule (tetrahedral). It is expected that the fluorine atoms should have the same electron density (same coloration). Since Si is more electropositive, it should have a greater blue coloration (more positive center). This suggests the electrostatic potential map on the right is for SiF_4. SF_4 is not a symmetric molecule. It has a trigonal bipyramidal electron geometry, where a lone pair occupies an equatorial position. It has a saw-horse or see-saw molecular shape in which the two axial fluorine atoms are nearly 180° to one another, while the two equatorial fluorine atoms are ~120° to one another. Owing to the lone pair in the equatorial position, the equatorial fluorine atoms will not be as electronegative as the axial fluorine atoms. This is certainly the case for the representation on the left.

Resonance

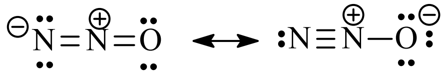
47. In NO_2^-, the total number of valence electrons is $1+5+(2\times 6)=18$ valence electrons, or 9 electron pairs. N is the central atom. The two resonance forms are shown below:



49. Bond length data from Table 10.2 follow:

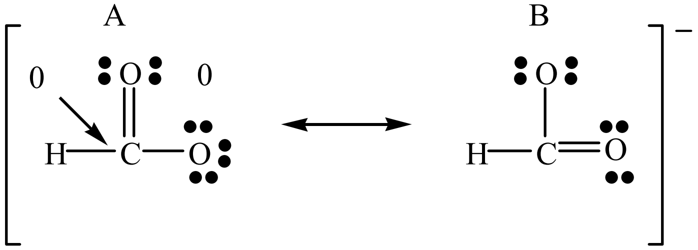
$N\equiv N$ 109.8 pm $N=N$ 123 pm $N—N$ 145 pm $N=O$ 120 pm $N—O$ 136 pm

The experimental $N—N$ bond length of 113 pm approximates that of the $N\equiv N$ triple bond, which appears in structure (a). The experimental $N—O$ bond length of 119 pm approximates that of the N=O double bond, which appears in structure (b). Structure (d) is highly unlikely because it contains no nitrogen-to-nitrogen bonds, and a N—N bond was found experimentally. Structure (c) also is unlikely, because it contains a very long (145 pm) $N—N$ single bond, which does not agree at all well with the experimental N-to-N bond length. The molecule seems best represented as a resonance hybrid of (a) and (b).

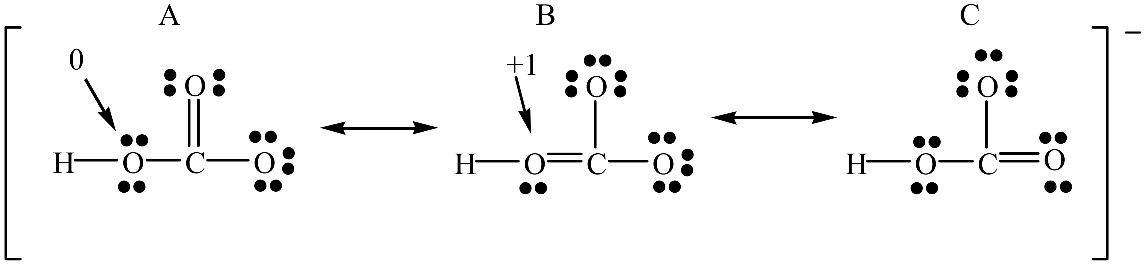


51.

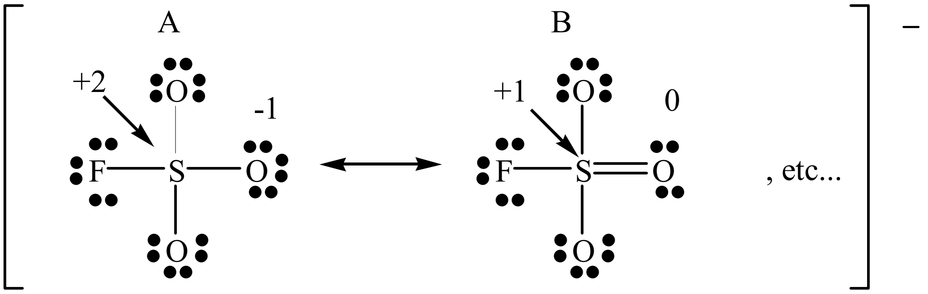
(a) Both structures are equivalent.



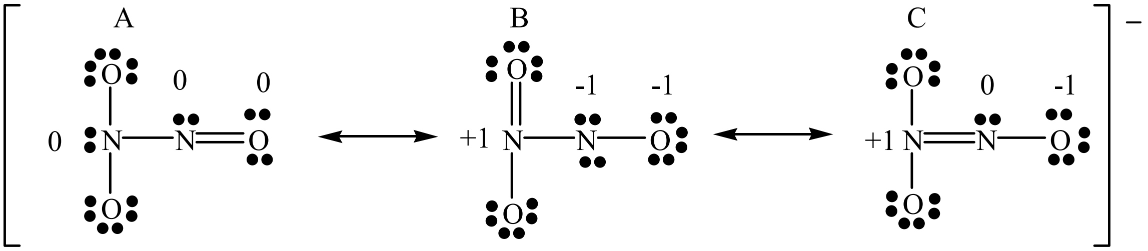
(b) Structures A and C are the most important, and they are equivalent.



(c) Structure B is more important.

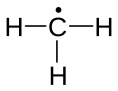


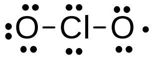
(d) Structure A is more important.



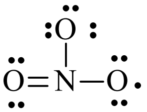
Odd-electron species

53. **(a)** CH_3 has a total of $(3 \times 1) + 4 = 7$ valence electrons, or 3 electron pairs and a lone electron. C is the central atom. A plausible Lewis structure is shown on the right.



(b) ClO_2 has a total of $(2 \times 6) + 7 = 19$ valence electrons, or 9 electron pairs and a lone electron. Cl is the central atom. A plausible Lewis structure is: 

(c) NO_3 has a total of $(3 \times 6) + 5 = 23$ valence electrons, or 11 electron pairs, plus a lone electron. N is the central atom. A plausible Lewis structure is shown to the right. Other resonance forms can also be drawn.



55. Since electrons pair up (if at all possible) in plausible Lewis structures, a species will be paramagnetic if it has an odd number of (valence) electrons.

(a)	OH^-	$6+1+1=8$ valence electrons	diamagnetic
(b)	OH	$6+1=7$ valence electrons	paramagnetic
(c)	NO_3	$5+(3 \times 6)=23$ valence electrons	paramagnetic
(d)	SO_3	$6+(3 \times 6)=24$ valence electrons	diamagnetic
(e)	SO_3^{2-}	$6+(3 \times 6)+2=26$ valence electrons	diamagnetic
(f)	HO_2	$1+(2 \times 6)=13$ valence electrons	paramagnetic

Expanded Octets

57. In PO_4^{3-}: $5+(4\times 6)+3=32$ valence electrons or 16 electron pairs. An expanded octet is not needed.

In PI_3: $5+(3\times 7)=26$ valence electrons or 13 electron pairs. An expanded octet is not needed.

In ICl_3: $7+(3\times 7)=28$ valence electrons or 14 electron pairs. An expanded octet is necessary.

In $OSCl_2$: $6+6+(2\times 7)=26$ valence electrons or 13 electron pairs. An expanded octet is not needed.

In SF_4: $6+(4\times 7)=34$ valence electrons or 17 electron pairs. An expanded octet is necessary.

In ClO_4^-: $7+(4\times 6)+1=32$ valence electrons or 16 electron pairs. An expanded octet is not needed.

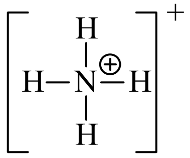
Molecular Shapes

59. The AX_nE_m designations that are cited below are to be found in Table 10.1 of the text, along with a sketch and a picture of a model of each type of structure.

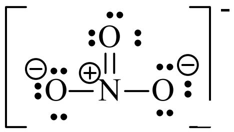
(a) Dinitogen is linear; two points define a line. $:N\equiv N:$

(b) Hydrogen cyanide is linear. The molecule belongs to the AX_2 category, and these species are linear. $H-C\equiv N:$

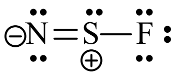
(c) NH_4^+ is tetrahedral. The ion is of the AX_4 type, which has a tetrahedral electron-group geometry and a tetrahedral shape.



(d) NO_3^- is trigonal planar. The ion is of the AX_3 type, which has a trigonal planar electron-group geometry and a trigonal planar shape. The other resonance forms are of the same type.

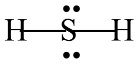


(e) NSF is bent. The molecule is of the AX_2E type, which has a trigonal planar electron-group geometry and a bent shape.

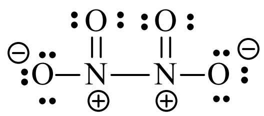


61. We first draw all the Lewis structures. From each, we can deduce the electron-group geometry and the molecular shape.

(a) H_2S tetrahedral electron-group geometry, bent (angular) molecular geometry



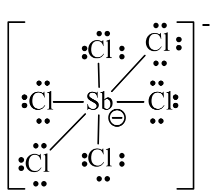
(b) N_2O_4 trigonal planar electron-group geometry around each N, (planar molecule)



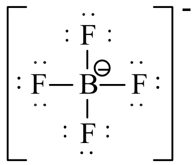
(c) HCN linear electron-group geometry, linear molecular geometry

$H{-}C{\equiv}N{:}$

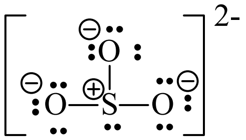
(d) $SbCl_6^-$ octahedral electron-group geometry, octahedral geometry

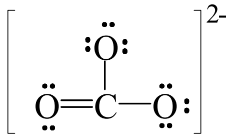


(e) BF_4^- tetrahedral electron-group geometry, tetrahedral molecular geometry



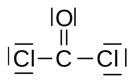
63. A trigonal planar shape requires that three groups and no lone pairs be bonded to the central atom. Thus PF_6^- cannot have a trigonal planar shape, since six atoms are attached to the central atom. In addition, PO_4^{3-} cannot have a trigonal planar shape, since four O atoms are attached to the central P atom. We now draw the Lewis structure of each of the remaining ions, as a first step in predicting their shapes. The SO_3^{2-} ion is of the AX_3E type. It has a tetrahedral electron-group geometry and a trigonal pyramidal shape. The CO_3^{2-} ion is of the AX_3 type, and has a trigonal planar electron-group geometry and a trigonal planar shape.



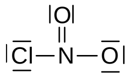


65. **(a)** In CO_2 there are a total of $4+(2\times 6)=16$ valence electrons, or 8 electron pairs. The following Lewis structure is plausible. $\overline{\underline{O}} = C = \overline{\underline{O}}$ This is a molecule of type AX_2. CO_2 has a linear electron-shape geometry and a linear shape.

(b) In Cl_2CO there are a total of $(2\times 7)+4+6=24$ valence electrons, or 12 electron pairs. The molecule can be represented by a Lewis structure with C as the central atom. This molecule is of the AX_3 type. It has a trigonal planar electron-group geometry and molecular shape.

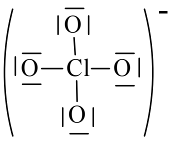


(c) In $ClNO_2$ there are a total of $7+5+(2\times 6)=24$ valence electrons, or 12 electron pairs. N is the central atom. A plausible Lewis structure is shown to the right: This molecule is of the AX_3 type. It has a trigonal planar electron-group geometry and a trigonal planar shape.

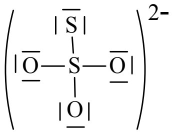


67. First we draw the Lewis structure of each species, then use it to predict the molecular shape. The structures are provided below.

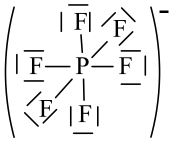
(a) In ClO_4^- there are $7+(4\times 6)+1=32$ valence electrons or 16 electron pairs. A plausible Lewis structure follows. Since there are four atoms and no lone pairs bonded to the central atom, the molecular shape and the electron-group geometry are the same: tetrahedral.



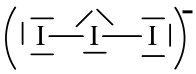
(b) In $S_2O_3^{2-}$ there are $(2\times 6)+(3\times 6)+2=32$ valence electrons or 16 electron pairs. A plausible Lewis structure follows. Since there are four atoms and no lone pairs bonded to the central atom, both the electron-group geometry and molecular shape are tetrahedral.



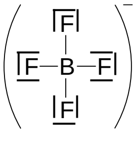
(c) In PF_6^- there are $5+(6\times 7)+1=48$ valence electrons or 24 electron pairs. Since there are six atoms and no lone pairs bonded to the central atom, the electron-group geometry and molecular shape are octahedral.



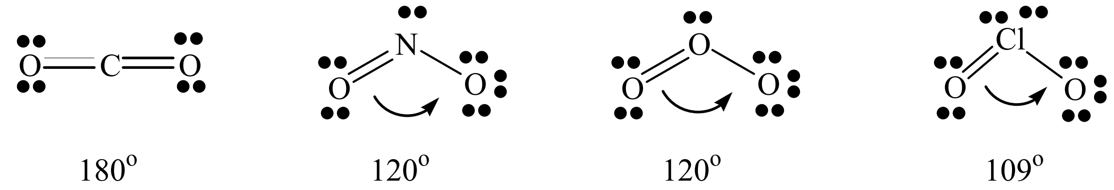
(d) In I_3^- there are $(3\times 7)+1=22$ valence electrons or 11 electron pairs. There are three lone pairs and two atoms bound to the central atom. The electron-group geometry is trigonal bipyramidal, thus, the molecular shape is linear.



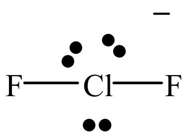
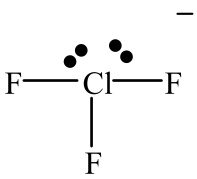
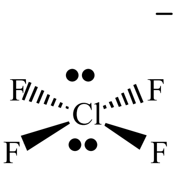
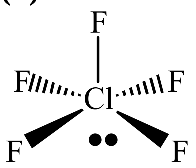
69. In BF_4^-, there are a total of $1+3+(4\times 7)=32$ valence electrons, or 16 electron pairs. A plausible Lewis structure has B as the central atom. This ion is of the type AX_4. It has a tetrahedral electron-group geometry and a tetrahedral shape.



71. Looking at the structures, the molecular angle/shape depends on the number of valence electron pairs on the central atom. The more pairs there are, the more acute the angle becomes.

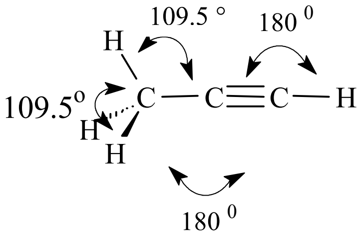


73.

	(a)	**(b)**	**(c)**	**(d)**
				
e^- group geometry	Trigonal Bipyramidal	Trigonal Bipyramidal	Octahedral	Octahedral
Molecular geometry	Linear	T-Shaped	Square Planar	Square Pyramidal

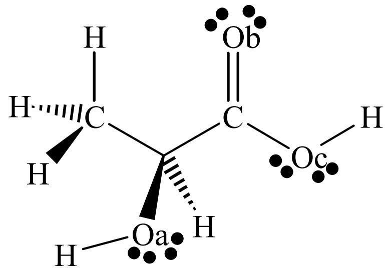
Shapes of Molecules with More Than One Central Atom

75.



A maximum of 5 atoms can be in the same plane

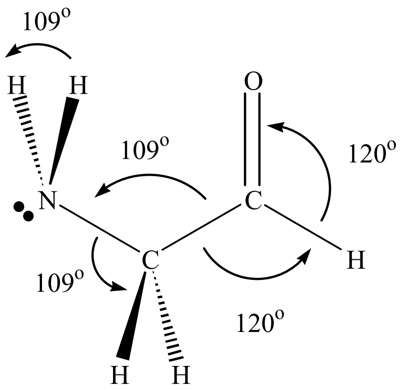
77.



All angles ~109.5° with the exception of

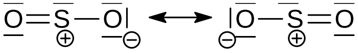
$$\left.\begin{array}{l} O_c - C - C \\ O_b = C - C \\ O_b = C - O_c \end{array}\right\} 120^\circ$$

79.

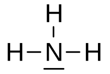


Polar Molecules

81. For each molecule, we first draw the Lewis structure, which we use to predict the shape.

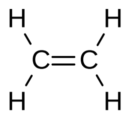
(a) SO_2 has a total of $6+(2\times 6)=18$ valence electrons, or 9 electron pairs. The molecule has two resonance forms.  $O=\underset{\oplus}{S}-\underset{\ominus}{O} \longleftrightarrow \underset{\ominus}{O}-\underset{\oplus}{S}=O$ Each of these resonance forms is of the type AX_2E. Thus it has a trigonal planar electron-group geometry and a bent shape. Since each S—O bond is polar toward O, and since the bond dipoles do not point in opposite directions, the molecule has a resultant dipole moment, pointing from S through a point midway between the two O atoms. Consequently, SO_2 is polar.

(b) NH_3 has a total of $5+(3\times 1)=8$ valence electrons, or 4 electron pairs. N is the central atom. A plausible Lewis structure is shown to the right. The molecule is of the AX_3E type; it has a tetrahedral electron-group geometry and a trigonal pyramidal shape. Each N-H bond is polar toward N. Since the bonds do not symmetrically oppose each other, there is a resultant molecular dipole moment, pointing from the triangular base (formed by the three H atoms) through N. Consequently, the molecule is polar.

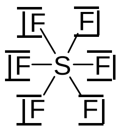

$H-\overset{\displaystyle H}{\underline{N}}-H$

(c) H_2S has a total of $6+(2\times 1)=8$ valence electrons, or 4 electron pairs. S is the central atom and a plausible Lewis structure is $H\text{-}\overline{\underline{S}}\text{-}H$. This molecule is of the AX_2E_2 type; it has a tetrahedral electron-group geometry and a bent shape. Each $H—S$ bond is polar toward S. Since the bonds do not symmetrically oppose each other, the molecule has a net dipole moment, pointing through S from a point midway between the two H atoms. H_2S is polar.

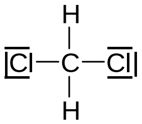
(d) C_2H_4 consists of atoms that all have about the same electronegativities. Of course, the $C—C$ bond is not polar and essentially neither are the $C—H$ bonds. The molecule is planar. Thus, the entire molecule is nonpolar.



(e) SF_6 has a total of $6+(6\times 7)=48$ valence electrons, or 24 electron pairs. S is the central atom. All atoms have zero formal charge in the Lewis structure. This molecule is of the AX_6 type. It has an octahedral electron-group geometry and an octahedral shape. Even though each $S — F$ bond is polar toward F, the bonds symmetrically oppose each other, resulting in a molecule that is nonpolar.



(f) CH_2Cl_2 has a total of $4+(2\times 1)+(2\times 7)=20$ valence electrons, or 10 electron pairs. A plausible Lewis structure is shown to the right. The molecule is tetrahedral and polar, since the two polar bonds $(C — Cl)$ do not cancel the effect of each other.



83. In H_2O_2, there are a total of $(2\times 1)+(2\times 6)=14$ valence electrons, 7 electron pairs. The two O atoms are central atoms. A plausible Lewis structure has zero formal charge on each atom: $H-\overline{\underline{O}}-\overline{\underline{O}}-H$. In the hydrogen peroxide molecule, the $O — O$ bond is non-polar, while the $H — O$ bonds are polar, with the dipole moment pointing toward O. Since the molecule has a resultant dipole moment, it cannot be linear, for, if it were linear the two polar bonds would oppose each other and their polarities would cancel.

Bond Lengths

85. The answer is c. Br_2 possess the longest bond. Single bonds are generally longer than multiple bonds. Of the two molecules with single bonds, Br_2 is expected to have longer bonds than BrCl, since Br is larger than Cl.

(a) $\overline{\underline{O}}=\overline{\underline{O}}$ **(b)** $|N\equiv N|$ **(c)** $|\overline{\underline{Br}}—\overline{\underline{Br}}|$ **(d)** $|\overline{\underline{Br}}—\overline{\underline{Cl}}|$

87. A heteronuclear bond length (one between two different atoms) is approximately equal to the average of two homonuclear bond lengths (one between two like atoms) of the same order (both single, both double, or both triple).

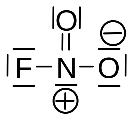
(a) I—Cl bond length $= [(\text{I—I bond length}) + (\text{Cl—Cl bond length})] \div 2$
$= [266\text{ pm} + 199\text{ pm}] \div 2 = 233\text{ pm}$

(b) $O — Cl$ bond length $=\left[(\text{O—O bond length})+(\text{Cl—Cl bond length})\right]\div 2$
$=[145\text{ pm}+199\text{ pm}]\div 2=172\text{ pm}$

(c) $C — F$ bond length $=\left[(\text{C—C bond length})+(\text{F—F bond length})\right]\div 2$
$=[154\text{ pm}+143\text{ pm}]\div 2=149\text{ pm}$

(d) $C — Br$ bond length $=\left[(\text{C—C bond length})+(\text{Br—Br bond length})\right]\div 2$
$=[154\text{ pm}+228\text{ pm}]\div 2=191\text{ pm}$

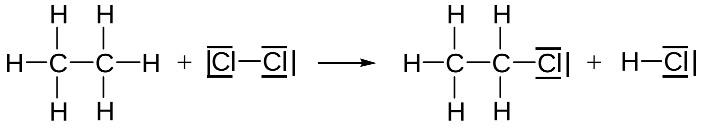
89. The N — F bond is a single bond. Its bond length should be the average of the N — N single bond (145 pm) and the F — F single bond (143 pm). Thus, the average N — F bond length $= (145 + 143) \div 2 = 144$ pm.



Bond Energies

91. The reaction $O_2(g) \rightarrow 2\ O(g)$ is an endothermic reaction since it requires the breaking of the bond between two oxygen atoms without the formation of any new bonds. Since bond breakage is endothermic and the process involves only bond breakage, the entire process must be endothermic.

93.



Analysis of the Lewis structures of products and reactants indicates that a C – H bond and a Cl — Cl bond are broken, and a C — Cl and a H — Cl bond are formed.

$$\text{Energy required to break bonds} = \text{C—H} + \text{Cl—Cl} = 414\ \frac{\text{kJ}}{\text{mol}} + 243\ \frac{\text{kJ}}{\text{mol}} = 657\ \frac{\text{kJ}}{\text{mol}}$$

$$\text{Energy realized by forming bonds} = \text{C—Cl} + \text{H—Cl} = 339\ \frac{\text{kJ}}{\text{mol}} + 431\ \frac{\text{kJ}}{\text{mol}} = 770\ \frac{\text{kJ}}{\text{mol}}$$

$$\Delta H = 657 \text{ kJ/mol} - 770 \text{ kJ/mol} = -113 \text{ kJ/mol}$$

95. In each case we write the formation reaction, but specify reactants and products with their Lewis structures. All species are assumed to be gases.

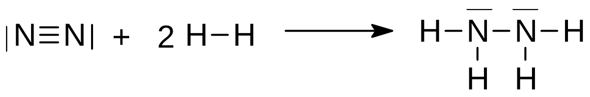
(a) $\frac{1}{2}(\overline{\underline{O}}{=}\overline{\underline{O}}) + \frac{1}{2}(\text{H}-\text{H}) \longrightarrow \bullet\overline{\underline{O}}-\text{H}$

Bonds broken: $\frac{1}{2}\ (\text{O}=\text{O}) + \frac{1}{2}\ (\text{H—H}) = 0.5(498 \text{ kJ} + 436 \text{ kJ}) = 467 \text{ kJ}$

Bonds formed: O—H = 464 kJ $\qquad \Delta H° = 467 \text{ kJ} - 464 \text{ kJ} = 3 \text{ kJ/mol}$

If the O — H bond dissociation energy of 428.0 kJ/mol from Figure 10-16 is used, $\Delta H_f^{\,o} = 39$ kJ / mol.

(b)

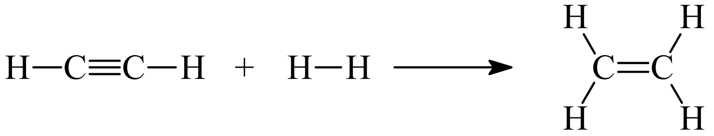


Bonds broken $= \text{N} \equiv \text{N} + 2\,\text{H} — \text{H} = 946 \text{ kJ} + 2 \times 436 \text{ kJ} = 1818 \text{ kJ}$

Bonds formed $= \text{N—N} + 4\ \text{N—H} = 163 \text{ kJ} + 4 \times 389 \text{ kJ} = 1719 \text{ kJ}$

$\Delta H_f^{\,o} = 1818 \text{ kJ} - 1719 \text{ kJ} = 99 \text{ kJ}$

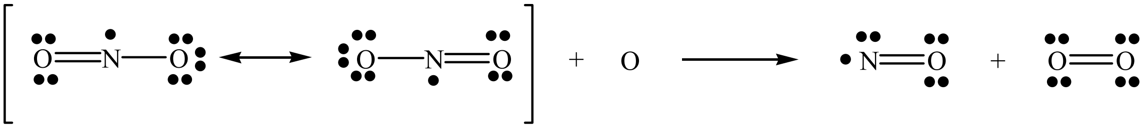
97.



Bonds broken	Energy change	Bonds formed	Energy change
1 mol C≡C	1 × 837 kJ	1 mol C=C	1 × −611 kJ
1 mol H—H	1 × 436 kJ	2 mol C-H	2 × −414 kJ
Energy required to break bonds	+1273 kJ	Energy obtained upon bond formation	-1439 kJ

Overall energy change = 1273 kJ − 1439 kJ = −166 kJ/mol = ΔH°_{rxn}

99.



$$\Delta H_f = (0 + 90.25) - (33.18 + 249.2) = -192.1 \text{ kJ/mol}$$

Using the calculated ΔH_f, we can calculate the $\mathrm{O}\overset{\text{——}}{\text{- - -}}\mathrm{N}$ bond energy:

ΔH_f = -(2×(O:::N) + 0) – (590 + 498) = -192.1

$\mathrm{O}\overset{\text{——}}{\text{- - -}}\mathrm{N}$ = 448 kJ/mol, which is between the values for N=O and N–O.

INTEGRATIVE AND ADVANCED EXERCISES

Important Note: In this and subsequent chapters, a lone pair of electrons in a Lewis structure often is shown as a line rather than a pair of dots. Thus, the Lewis structure of Be is Be| or Be:

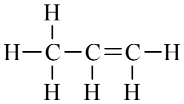
101. Recall that bond breaking is endothermic, while bond making is exothermic.
Break 2 N-O bonds requires 2(631 kJ/mol) = +1262 kJ
Break 5 H-H bonds requires 4(436 kJ/mol) = +2180 kJ
Make 6 N-H bonds yields 5(-389 kJ/mol) = -2334 kJ
Make 4 O-H bonds yields 4(-463 kJ/mol) = -1852 kJ
Σ(bond energies) = ΔH = -744 kJ/mol reaction

104.

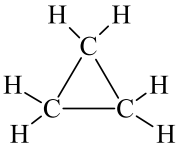
$$\text{amount of gas} = \frac{PV}{RT} = \frac{749 \text{ mmHg} \times \dfrac{1 \text{ atm}}{760 \text{ mmHg}} \times 0.193 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 299.3 \text{ K}} = 0.00774 \text{ mol}$$

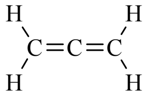
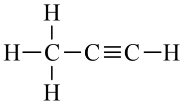
$$\text{M} = \frac{\text{mass}}{\text{amount}} = \frac{0.325 \text{ g}}{0.00774 \text{ mol}} = 42.0 \text{ g/mol}$$

Because three moles of C weigh 36.0 g and four moles weigh 48.0 g, this hydrocarbon is C_3H_6.

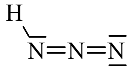
A possible Lewis structure is  $H-\underset{H}{\overset{H}{C}}-\underset{H}{C}=\underset{H}{C}-H$

There is another possible Lewis structure: the three C atoms are arranged in a ring, with two H atoms bonded to each C atom (see below).

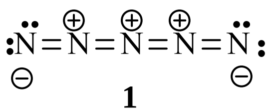
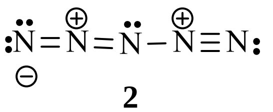


106. The two isomers are  and  $H-\underset{H}{\overset{H}{C}}-C\equiv C-H$

The left-hand isomer is planar around the first and third C atoms, but we cannot predict with VSEPR theory whether the molecule is planar overall; in other words, the two $H-C-H$ planes may be at 90° to each other. (They are, in fact.) In the right-hand isomer, the $C-C\equiv C-H$ chain is linear, but the H_3C- molecular geometry is tetrahedral.

109. The HN_3 molecule has $1+(3\times 5)=16$ valence electrons, or 8 pairs. Average bond lengths are 136 pm for $N-N$, 123 pm for $N=N$, and 110 pm for $N\equiv N$. Thus it seems that one nitrogen-to-nitrogen bond is a double bond, while the other is a triple bond. A plausible Lewis structure is $H-\overline{N}=N=\underline{\overline{N}}$ The three N's lie on a line, with a $120°\ H-N-N$ bond angle: 
Another valid resonance form is $H-\underline{\overline{N}}-N\equiv N|$ which would have one N-N separation consistent with a nitrogen-nitrogen triple bond. It would also predict a tetrahedral H—N—N bond angle of 109.5°. Thus, the resulting resonance hybrid should have a bond angle between 120° and 109.5°, which is in good agreement with the observed 112° $H-N-N$ bond angle.

110. For N_5^+ the number of valence electrons is (5×5)-1 = 24. There are four possible Lewis structures with formal charges that are not excessive (<±2).


1

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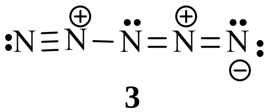
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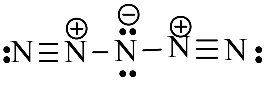

4

Structure **1** has three adjacent atoms possessing formal charges of the same sign. Energetically, this is highly unfavorable. Structure **2** & **3** are similar and highly unsymmetrical but these are energetically more favorable than **1** Structure **4** is probably best of all, as all of the charges are close together with no two adjacent charges of the same sign. If structures **2**, **3,** or **4** are chosen, the central nitrogen has one or two lone pairs. Thus, the structure of N_5^+ will be angular. (Note: an angle of 107.9 ° has been experimentally observed for the angle about the central nitrogen, as well, the bond length of the terminal N-N bonds is very close to that seen in N_2, suggesting a triple bond. This suggests that resonance form **4** best describes the structure of the ion.)

113. The Lewis structures for the species in reaction (2) follow.

$$|N\equiv N| \quad H-H \quad H-C\equiv N|$$

$$\text{Bonds broken} = \frac{1}{2}\ N\equiv N + \frac{1}{2}\ H-H = \frac{1}{2}\ (946\ \text{kJ} + 436\ \text{kJ}) = 691\ \text{kJ}$$

$$\text{Bonds formed} = H-C + C\equiv N = 414\ \text{kJ} + 891\ \text{kJ} = 1305\ \text{kJ}$$

$$\Delta H = 691\ \text{kJ} - 1305\ \text{kJ} = -614\ \text{kJ}$$

Then we determine ΔH°_f

$$\text{(a)} \quad C(s) \longrightarrow C(g) \qquad \Delta H = +717\ \text{kJ}$$

$$\underline{\text{(b)} \quad C(g) + \tfrac{1}{2}\ N_2(g) + \tfrac{1}{2}\ H_2(g) \longrightarrow HCN(g) \quad \Delta H = -614\ \text{kJ}}$$

$$\text{Net:} \quad C(s) + \tfrac{1}{2}\ N_2(g) + \tfrac{1}{2}H_2(g) \longrightarrow HCN(g) \qquad \Delta H^\circ_f = +103\ \text{kJ}$$

This compares favorably to the value of 135.1 kJ/mol given in Appendix D-2.

116. We first compute the heats of reaction.

$$CH_3OH(g) + H_2S(g) \longrightarrow CH_3SH(g) + H_2O(g)$$

$$\Delta H^\circ_{rxn} = \Delta H^\circ_f[H_2O(g)] + \Delta H^\circ_f[CH_3SH(g)] - [\Delta H^\circ_f[CH_3OH(g)] + \Delta H^\circ_f[H_2S(g)]]$$

$$= -241.8\ \text{kJ} + (-22.9\ \text{kJ}) - [(-200.7\ \text{kJ} - 20.63\ \text{kJ})] = -43.4\ \text{kJ}$$

Breaking of one mole of C-O bond requires (360 kJ) = +360 kJ

Breaking of one mole of H-S bond requires (368 kJ) = + 368 kJ

Breaking of one mole of O-H bond requires (464 kJ) = + 464 kJ

Making of one mole of C-S bond yields = -*x* kJ

Making 2 moles of O-H bonds yields 2(-464 kJ) = -928 kJ

$$\Sigma(\text{bond energies}) = \Delta H^\circ_{rxn} = -43.4\ \text{kJ}$$

Then… 264 -*x* = -43.4 and *x* = 307 kJ, which is the C-S bond energy for the C—S bond in methanethiol (estimate only).

120. For the halogens we have the following data:

Atom	Electronegativity	Ionization Energy (kJ/mol)	Electron Affinity (kJ/mol)
F	4.0	1680	-328
Cl	3.0	1256	-349
Br	2.8	1143	-324.6
I	2.5	1009	-295.2

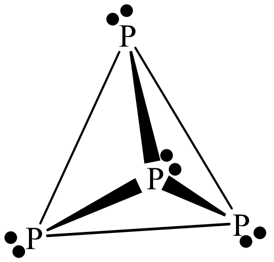
From the data above and using $\chi = k\times(IE - EA)$ for the halogens, we find the following values for k: F = $0.0019\underline{9}$ Cl = $0.0018\underline{7}$ Br = $0.0019\underline{1}$ I = $0.0019\underline{2}$

We shall assume that the value of *k* for astatine is 0.0019. As well, from the data, we can estimate the ionization energy for astatine to be ~900 kJ/mol. The text gives 2.2 as the electronegativity for astatine. We can now estimate a value for the electron affinity of At.

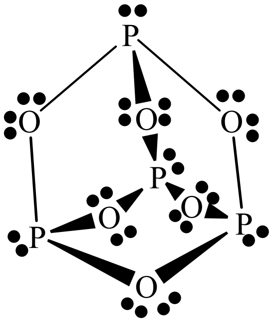
$\chi = k\times(IE - EA) = 2.2 = 0.0019(900\text{-EA})$ $\quad EA \sim -260$ kJ/mol

127.

(a)



(b)



The O atoms in P_4O_6 are surrounded by 4 groups and so the geometry around each O is tetrahedral. Therefore, the P–O–P bond is not linear.

FEATURE PROBLEMS

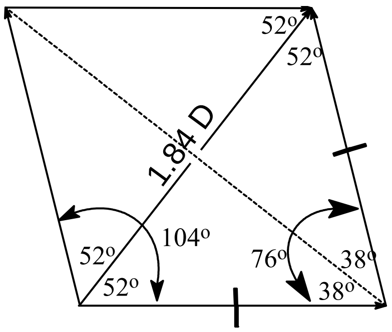
128. **(a)** The average of the $\text{H}—\text{H}$ and $\text{Cl}—\text{Cl}$ bond energies is (436+243) kJ ÷ 2 = 340 kJ/mol. The ionic resonance energy is the difference between this calculated value and the measured value of the $\text{H}—\text{Cl}$ bond energy:

$\text{IRE} = 431 \text{ kJ/mol} - 340 \text{ kJ/mol} = 91 \text{ kJ/mol}$

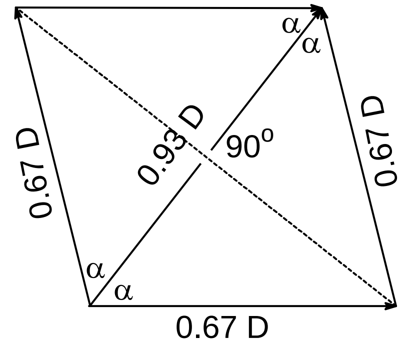
(b) $\Delta\text{EN} = \sqrt{\text{IRE}/96} = \sqrt{91/96} = 0.97$

(c) An electronegativity difference of 0.97 gives about a 23% ionic character, read from Figure 10.7. The result of Example 10-4 is that the $\text{H}—\text{Cl}$ bond is 20% ionic. These values are in good agreement with each other.

129. **(a)** The two bond dipole moments can be added geometrically, by placing the head of one at the tail of the other, as long as we do not change the direction or the length of the moved dipole. The resultant molecular dipole moment is represented by the arrow drawn from the tail of one bond dipole to the head of the other. This is shown in the figure to the right. The 52.0° angle in the figure is one-half of the 104° bond angle in water. The length is given as



1.84 D. We can construct a right angled triangle by bisecting the 76.0° angle. The right angled triangle has a hypotenuse = O — H bond dipole and the two other angles are 52° and 38°. The side opposite the bisected 76.0 ° angles is ½ (1.84 D) = 0.92 D. We can calculate the bond dipole using: $\sin 38.0° = \frac{0.92\,\text{D}}{\text{O-H bond dipole}} =$ 0.61566, hence O—H bond dipole = 1.49 D.



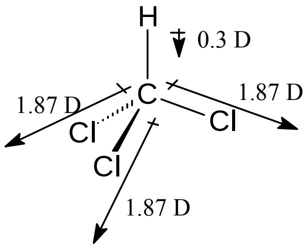
(b) For H_2S, we do not know the bond angle. We shall represent this bond angle as 2α. Using a similar procedure to that described in part (a), above, a diagram can be constructed and the angle 2 α calculated as follows:

$$\cos\alpha = \frac{\frac{1}{2}(0.93\,\text{D})}{0.67\,\text{D}} = 0.694 \quad \alpha = 46.05°$$

or $2\alpha = 92.\underline{1}$ °

The H—S—H angle is approximately 92°.

(c)



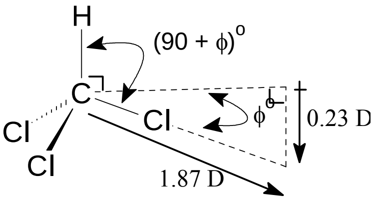
Molecule and associated individual bond dipoles

$\mu_{C-H} + 3(\mu_{C-Cl}) = 1.04$ D

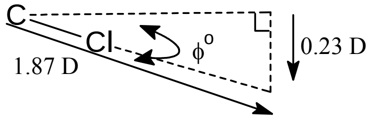
$0.30\text{ D} + 3(x) = 1.04$ D

$x = 0.25\text{ D} = \mu_{C-Cl}$

Relationship between dipole moment(molecular) and bond dipoles(Vector addition)



Geometric Relationship



Mathematical solution: $\sin(\phi) = \frac{0.25\text{ D}}{1.87\text{ D}}$

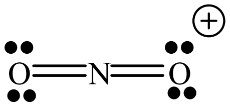
$\phi = 7.6^{\circ}$

The H-C-Cl bond angle is $(90 + \phi)^{\circ} = 90^{\circ} + 7.6^{\circ} = 97.6^{\circ}$

134. The answer is (b). The structure is:

$$[:\text{C}\equiv\text{N}:]^{-}$$

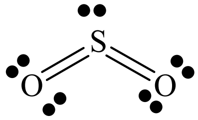
135. The answer is (c). The structure is:

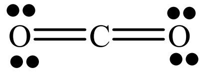


$$\text{O}=\text{N}^{+}=\text{O}$$

Formal charge on O is: 6 – 4 – 2 = 0

136. The answer is (a), SO_2. NO is linear by definition since there are only two atoms. The other molecules have the following structures:





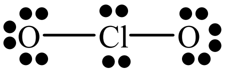
137. The answer is (a), SO_3. The other choices are polar, because: CH_2Cl_2 has a non-uniform field of atoms around the central atom C; NH_3 is trigonal pyramidal and has a lone pair of electrons on N; in FNO, there are three different atoms with different electron affinities.

138. The answer is (b), N_2, because one has to break three covalent bonds to dissociate the two N atoms from each other.

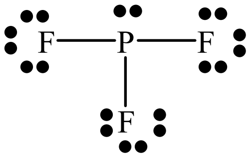
139. The answer is (c), Br_2, because the greater the covalent radii of the two atoms involved, the longer the bond length. Br is the largest atom and therefore, Br–Br bond would be the longest.

140.

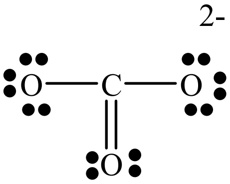
(a)



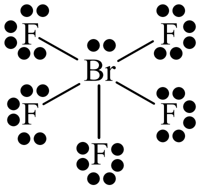
(b)



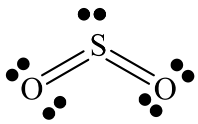
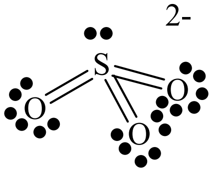
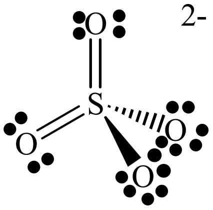
(c)



(d)



141.

	(a)	**(b)**	**(c)**
			
e^- group geometry	Trigonal planar	Tetrahedral	Tetrahedral
Molecular geometry	Bent	Trigonal pyramidal	Tetrahedral

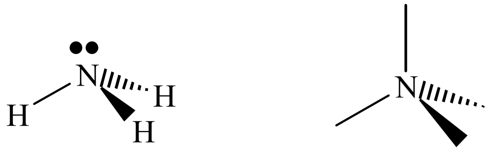
142. Ba and Mg are active metals with a low EN, S is the most electronegative (and non-metallic) as indicated by its location on the periodic table. In comparing Bi and As, Bi has lower EN value, as indicated by its location. Therefore, Bi has the middle position:
Ba < Mg < Bi < As < S

143.

Bond	Bond Energy (kJ/mol)	Bond Length (pm)
C–H	414	110
C=O	736	120
C–C	347	154
C–Cl	339	178

144. VSEPR theory is valence shell electron pair repulsion theory. It is based on the premise that electron pairs assume orientations about an atom to minimize electron pair repulsions.

145. The structure of the NH_3 molecule and the arrangement of electrons is shown below:



As can be seen, there are 4 pairs of electrons around the nitrogen atoms. Three pairs are in the form of covalent bonds with hydrogen atoms, and one is a lone pair. Since there are 4 electron pairs around the central atom, the way to maximize the distance between them is to set up a tetrahedral electron group geometry. However, since there are only three atoms bonding to the central atom, the molecular geometry is trigonal pyramidal.

146. A pyramidal geometry is observed when an atom has one lone pair and is bonded to three other atoms (AX_3E). A bent geometry is observed when an atom has two lone pairs and is bonded to two other atoms (AX_2E_2). For both, the bond angles will be approximately (usually smaller than) 109°.

147.