CHAPTER 10
CHEMICAL BONDING I: BASIC CONCEPTS

PRACTICE EXAMPLES

1A  (E) 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.

\[
\text{Mg, Ge, K, Ne}
\]

1B  (E) 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.

\[
\text{Sn, Br, Tl, S}
\]

2A  (E) 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\(^{2-}\).

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

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

\[
\text{Mg} - 2 e^- \rightarrow [\text{Mg}]^{2+} \quad \text{N} + 3e^- \rightarrow [\text{N}]^{3-} \quad \text{Lewis Structure: [Mg]^{2+}[:N:]^3-[Mg]^{2+}}
\]

2B  (E) 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\(_2\).

\[
\text{Ca} - 2 e^- \rightarrow [\text{Ca}]^{2+} \quad \text{I} + e^- \rightarrow [\text{I}]^- \quad \text{Lewis Structure: [I]^-[Ca]^{2+}[I]^-}
\]

(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.

\[
\text{Ba} - 2 e^- \rightarrow [\text{Ba}]^{2+} \quad \text{S} + 2e^- \rightarrow [\text{S}]^{2-} \quad \text{Lewis Structure: [Ba]^{2+}[S]^{2-}}
\]

(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\(_2\)O.

\[
\text{Li} - 1 e^- \rightarrow [\text{Li}]^+ \quad \text{O} + 2e^- \rightarrow [\text{O}]^{2-} \quad \text{Lewis Structure:[Li]^+[O]^{2-}[Li]^+}
\]
3A (M) In the Br₂ 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 CH₄, 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 (M) The Lewis structure for NΙ₃ is similar to that of NH₃. 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 N₂H₄ 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 C₂H₆, 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 (E) 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 (E) 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 (E) 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 (E) The electrostatic potential map that corresponds to CH$_3$OH 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$_3$SH. 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 (M) (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. :S $\equiv$ C $\equiv$ 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. :S $\equiv$ C $\equiv$ 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 $\equiv$ C $\equiv$ 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 $\equiv$ 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.

\[
:O \equiv C (-:Cl:)_2 \rightarrow :O = C (-:Cl:)_2
\]

6B (a) :O:
\[
\begin{array}{c}
H\equiv C\equiv O\equiv H
\end{array}
\]

(b) H:O:
\[
\begin{array}{c}
H\equiv C\equiv C\equiv H
\end{array}
\]
7A (E)  
(a) A plausible Lewis structure for the nitrosonium cation, NO+, is drawn below:

\[
\begin{array}{c}
\cdot N \equiv O^+ \\
\end{array}
\]

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 \( \text{N}_2\text{H}_5^+ \) is given below:

\[
\begin{array}{cc}
\text{H} & \text{H} \\
\text{H} \equiv \text{N} \equiv \text{N}^+ \\
\text{H} & \text{H}
\end{array}
\]

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 \( \text{O}^{2-} \) is shown below.

\[
\begin{array}{c}
\cdot \cdot O^{2-}
\end{array}
\]

7B (M)  
(a) The most likely Lewis structure for BF\(_4^-\) is drawn below:

\[
\begin{array}{c}
\cdot \cdot \cdot \\
\cdot B \equiv F \\
\cdot \cdot \cdot
\end{array}
\]

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\(_3\)OH\(^+\), the hydroxylammonium ion, has been provided below:

\[
\begin{array}{ccc}
\text{H} & \equiv \text{N} \equiv \text{O}^+ \\
\text{H} & \text{H}
\end{array}
\]

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.

\[ \begin{align*}
\text{Structure 1} & : \text{N} \equiv \text{C} \equiv \text{O}^\ominus \\
\text{Structure 2} & : \text{N} \equiv \text{C} \equiv \text{O}^\oplus \\
\text{Structure 3} & : \text{N} \equiv \text{C} \equiv \text{O}^\ominus
\end{align*} \]

8A (M) 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: \( \text{N} \equiv \text{O} \equiv \text{Cl} \). 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.

\[ \begin{align*}
\text{Oxygen is moved closer to a complete octet by placing the remaining pair of electrons on oxygen as a lone pair.}
\end{align*} \]

\[ \begin{align*}
\text{The valence shell for the oxygen atom can then be closed by forming a double bond between the nitrogen atom and the oxygen atom.}
\end{align*} \]

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."
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 NH₂CN 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.

\[
\text{H} - \text{N} - \text{C} - \text{N} \\
\text{H}
\]

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 NH₂ group. The octet for the NH₂ nitrogen is completed by giving it a lone pair of electrons.

\[
\text{H} - \overset{\cdot}{\text{N}} - \text{C} - \text{N} \\
\text{H}
\]

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:

\[
\text{H} - \overset{\cdot}{\text{N}} - \text{C} - \overset{\cdot}{\text{N}}: \\
\text{H} \\
(\text{Structure 1})
\]

\[
\text{H} - \overset{\cdot}{\text{N}} - \text{C} - \overset{\cdot}{\text{N}}: \\
\text{H} \\
(\text{Structure 2})
\]

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.

\[
\text{H} - \overset{\cdot}{\text{N}} - \text{C} = \text{N}: \\
\text{H} \\
\text{Structure 3}
\]

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.

\[
\text{H} - \overset{\cdot}{\text{N}} = \text{C} = \overset{\cdot}{\text{N}}: \\
\text{H} \\
\text{Structure 4}
\]

The resulting structure has a formal charge of 1- on the terminal nitrogen atom and a 1+ formal charge on the NH₂ 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.

\[ \text{H} \quad \text{N} \quad \text{=: N = C =} \quad \text{2-} \quad \text{H} \]

9A (D) 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:

\[ \text{S} \quad \text{O} \quad \text{O} \]

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 $\pi$-bond, we end up generating the resonance contributor (A) shown below:

\[ \text{O} \quad \text{= S = O} \quad \text{(A)} \]

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 $\pi$-bond, resulting in conversion of a sulfur-oxygen single bond into a sulfur-oxygen double bond:

\[ \text{O} \quad \text{= S = O} \quad \text{(B)} \]

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 (D) 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: 

\[
\begin{array}{c}
\text{O} \\
\text{O} - \text{N} - \text{O} \\
\text{O} \\
\end{array} + 18 \text{ e}^-
\]

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 $\pi$-bond, we end up generating resonance contributor (A):

\[
\begin{array}{c}
\text{O} \\
\text{O} \text{N} \text{O} \\
\text{O} \\
\end{array} \quad (A)
\]

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 $\pi$-bond with the nitrogen atom, we end up generating resonance contributor (C), also shown below.

\[
\begin{array}{c}
\text{O} \\
\text{O} \text{N} \text{O} \\
\text{O} \\
\end{array} \quad (B) \quad \begin{array}{c}
\text{O} \\
\text{O} \text{N} \text{O} \\
\text{O} \\
\end{array} \quad (C)
\]

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)): 

\[
\begin{array}{c}
\text{O} \\
\text{O} \text{N} \text{O} \\
\text{O} \\
\end{array} \quad \text{Resonance Hybrid}
\]
These three resonance forms give bond lengths that are comparable to nitrogen- nitrogen double bonds.

10A  (E) The Lewis structure of \( \text{NCl}_3 \) 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.

\[
\text{Cl} \quad \text{N} \quad \text{Cl}
\]

10B  (E) The Lewis structure of \( \text{POCl}_3 \) 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.

\[
\text{Cl} \quad \text{O} \quad \text{Cl}
\]

11A  (E) 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. \( |S = C = O| \). We can draw other resonance forms, however, the molecular geometry is unaffected.

11B  (E) N is the central atom. \( |\text{N} \equiv \text{N} \equiv \text{O}| \) 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 \( \text{N}_2\text{O} \) molecule is linear. We can draw other resonance forms, however, the molecular geometry is unaffected.

12A  (E) 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.

\[
\text{H} \quad \text{C} \quad \text{O} \quad \text{H}
\]

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 \( \sim 109.5^\circ \), 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 (M) 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 $O-C-O$ bond angle and the $O-C-C$ bond angles all are very close to 120°.

13A (M) 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.

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

13B (M) Lewis structures of the four molecules are drawn below and we can consider the three $C-H$ bonds and the one $C-C$ bond to be nonpolar. The three $C-Cl$ bonds are tetrahedrally oriented.

If there were a fourth $C-Cl$ 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 $NH_4$, where three tetrahedrally-oriented $N-H$ polar bonds are not balanced by a fourth, and for $CH_2Cl_2$, where two tetrahedrally oriented $C-Cl$ 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 (M) The Lewis structure of CH$_3$Br has all single bonds. From Table 10.2, the length of a C—H bond is 110 pm. The length of a C—Br bond is not given in the table. A reasonable value is the average of the C—C and Br—Br bond lengths.

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

14B (E) 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: \(\text{S} – \text{C} \equiv \text{N}\) where there is a formal negative charge on the sulfur atom. This molecule is linear according to VSEPR theory.

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

$$\text{2 H—H} + \text{O=O} \rightarrow \text{H—O—H}$$

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 kJ/mol - 1856 kJ/mol = -486 kJ/mol

15B (M) The chemical equation, with Lewis structures, is:

$$\frac{1}{2} \text{N≡N} + \frac{3}{2} \text{H—H} \rightarrow \text{H—N—H}$$

Energy required to break bonds = \(\frac{1}{2} \text{N≡N} + \frac{3}{2} \text{H—H}\)

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

Energy realized by forming bonds = 3 N—H = 3 × 389 kJ/mol = 1.17 × 10^3 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, \(\Delta H_f = -4 \times 10^1 \text{ kJ/mol}\) of NH$_3$ (Appendix D value is \(\Delta H_f = -46.11 \text{ kJ/mol}\) NH$_3$)

16A (M) The reaction below, \(\text{CH}_3(\text{C}=\text{O})\text{CH}_3(\text{g}) + \text{H}_2(\text{g}) \rightarrow \left(\text{CH}_3\right)_2\text{CH(OH)}(\text{g})\)

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:
\[ \Delta H_{\text{rxn}} = \Delta H(\text{bond breakage}) + \Delta H(\text{bond formation}) \]
\[ \Delta H_{\text{rxn}} = \left[ (1 \times 736) + (1 \times 436) \right] + \left[ (1 \times -360) + (1 \times -414) + (1 \times -464) \right] \]
\[ \Delta H_{\text{rxn}} = -66 \text{ kJ/mol} \]
Therefore, the reaction is exothermic.

\[ \text{16B (E)} \]
First we will double the chemical equation, and represent it in terms of Lewis structures:
\[ 2 \text{H} = \underset{\text{O}}{\text{O}} - \underset{\text{H}}{\text{H}} + \underset{\text{Cl}}{\text{Cl}} - \underset{\text{Cl}}{\text{Cl}} \rightarrow \underset{\text{O}}{\text{O}} = \underset{\text{O}}{\text{O}} + 4 \text{H} = \underset{\text{Cl}}{\text{Cl}} : \]
Energy required to break bonds = \[ 2 \text{Cl} - \text{Cl} + 4 \text{H} - \text{O} \]
= \[ (2 \times 243 \text{ kJ/mol}) + (4 \times 464 \text{ kJ/mol}) = 2342 \text{ kJ/mol} \]
Energy realized by forming bonds = \[ 1 \text{O} = \text{O} + 4 \times \text{H} - \text{Cl} \]
= \[ 498 \text{ kJ/mol} + (4 \times 431 \text{ kJ/mol}) = 2222 \text{ kJ/mol} \]
\[ \Delta H = \frac{1}{2} (2342 \text{ kJ/mol} - 2222 \text{ kJ/mol}) = +60 \text{ kJ/mol} \; \text{The reaction is endothermic}. \]

**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 \( \text{Be|} \) and \( \text{Be:} \).

---

**INTEGRATIVE EXAMPLE**

**A. (M)** The reaction is as follows: \( \text{PCl}_3 + \text{Cl}_2 \rightarrow \text{PCl}_5 \)
\[ \Delta H_{\text{rxn}} = \sum \Delta H_{\text{prod}} - \sum \Delta H_{\text{react}} \]
\[ \Delta H_{\text{rxn}} = (-374.9) - (-287.0 + 0) = -87.9 \text{ kJ/mol} \]
To determine the P–Cl bond energy, we must first deduce the Cl–Cl bond energy:
\( 2\text{Cl} \rightarrow \text{Cl}_2 \ \Delta H_{\text{rxn}} = 0 - 2(121.7) = -243 \text{ kJ/mol} \), which is in reasonable agreement with Table 10-3.
Using the above information, we can determine the P–Cl bond energy:
\[ \Delta H_{\text{rxn}} = \Delta H(\text{bond breakage}) + \Delta H(\text{bond formation}) \]
\[ \Delta H_{\text{rxn}} = 1 \text{Cl} - \text{Cl} \ (\text{broken}) + 2 \text{P} - \text{Cl} \ (\text{formed}) \]
\[ -87.9 = 243 + 2 \text{P} - \text{Cl} \]
\[ \text{P} - \text{Cl} = -165.5 \text{ kJ/mol} \]
The Lewis structures of PCl₃ and PCl₅ 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. (M)
(a) The structures are shown below, with appropriate geometries:

\[ \sum \text{BE}(\text{H}_2\text{NCOH}) = 2(\text{N} - \text{H}) + 1(\text{N} - \text{C}) + 1(\text{C} = \text{O}) + 1(\text{C} - \text{H}) \]
\[ = 2(389) + 305 + 736 + 414 = 2233 \text{ kJ/mol} \]

\[ \sum \text{BE}(\text{H}_2\text{C} = \text{N} - \text{OH}) = 2(\text{C} - \text{H}) + 1(\text{C} = \text{N}) + 1(\text{N} - \text{O}) + 1(\text{O} - \text{H}) \]
\[ = 2(414) + 615 + 222 + 464 = 2129 \text{ kJ/mol} \]

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. (E)
   (a) :Kr:    (b) :Ge:    (c) :N:    (d) :Ga:    (e) :As:    (f) :Rb:

2. (E)
   (a) [H:\ ]\^-   (b) [Sn:]^2+   (c) [K]^-   (d) [Br:]^-   (e) [Se:]^2-   (f) [Se]^{3+}

3. (E)
   (a) \[ \begin{array}{c}
         * * \\
         \text{F} \equiv \text{Cl} \\
   \end{array} \]
   (b) \[ \begin{array}{c}
         * * \\
         \text{I} \equiv \text{I} \\
   \end{array} \]
   (c) \[ \begin{array}{c}
         * * \\
         \text{F} \equiv \text{F} \\
   \end{array} \]
   (d) \[ \begin{array}{c}
         * * \\
         \text{N} \equiv \text{F} \\
   \end{array} \]
   (e) \[ \begin{array}{c}
         * * \\
         \text{F} \equiv \text{Te} \equiv \text{F} \\
   \end{array} \]

4. (E) For simplicity, the 3 lone pairs on halogens are not shown in the structures below. Add 6 electrons per halogen atom.
   (a) \[ \begin{array}{c}
         * * \\
         \text{O} \equiv \text{C} \equiv \text{S} \\
   \end{array} \]
   (b) \[ \begin{array}{c}
         * * \\
         \text{H} \equiv \text{C} \equiv \text{C} \equiv \text{H} \\
   \end{array} \]
   (c) \[ \begin{array}{c}
         * * \\
         \text{F} \equiv \text{C} \equiv \text{O} \\
   \end{array} \]
   (d) \[ \begin{array}{c}
         * * \\
         \text{Cl} \equiv \text{S} \equiv \text{O} \\
   \end{array} \]
   (e) \[ \begin{array}{c}
         * * \\
         \text{H} \equiv \text{C} \equiv \text{C} \equiv \text{H} \\
   \end{array} \]
5. (E)

(a) $\text{Cs}^{+} : \text{Br}^{-}$, CsBr, cesium bromide

(b) $\text{H} - \text{Sb} - \text{H}$, hydrogen antimonide or trihydrogen antimonide

(c) $\text{Cl}^{-} - \text{B} - \text{Cl}^{-}$, BCl$_3$, boron trichloride

(d) $\text{Cs}^{+} : \text{Cl}^{-}$, CsCl, cesium chloride

(e) $\text{Li}^{+} : \text{O}^{2-}$, Li$_2$O, lithium oxide

(f) $\text{I}^{-} - \text{Cl}^{-}$, ICl, iodine monochloride

6. (M) AlCl$_3$, SiF$_6^{2-}$, SO$_3$, PO$_4^{3-}$, and ClO$_2$ do not follow the octet rule. For simplicity, where possible, the 3 lone pairs on halogens are not shown in the structures below.

\[
\begin{align*}
\text{Cl} & \quad \text{Al} & \quad \text{Cl} \\
\text{Cl} & \\
\end{align*}
\]

\[
\begin{align*}
\text{F} & \quad \text{Si} & \quad \text{F} \\
\text{F} & \quad \text{F} & \\
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{O} & \quad \text{Cl} \quad \text{O} \\
\text{O} & \quad \text{O} & \\
\end{align*}
\]

7. (M)

NH$_3$ $\quad 5 + (3 \times 1) = 8 \text{ v.e.} = 4 \text{ pairs}$  
BF$_3$ $\quad 3 + (3 \times 7) = 24 \text{ v.e.} = 12 \text{ pairs}$

SF$_6$ $\quad 6 + (6 \times 7) = 48 \text{ v.e.} = 24 \text{ pairs}$  
SO$_3$ $\quad 6 + (3 \times 6) = 24 \text{ v.e.} = 12 \text{ pairs}$

NH$_4^+$ $\quad 5 + (4 \times 1) - 1 = 8 \text{ v.e.} = 4 \text{ pairs}$  
SO$_4^{2-}$ $\quad 6 + (4 \times 6) + 2 = 32 \text{ v.e.} = 16 \text{ pairs}$

NO$_2$ $\quad 5 + (2 \times 6) = 17 \text{ v.e.} = 8.5 \text{ pairs}$

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.
8. (M)
(a) In order to construct an H$_3$ molecule, one H would have to bridge the other two. This would place 3 electrons around the central H atom, which is more than the stable pair found around H in most Lewis structures. As well, one bond would be the normal 2 e$^-$ bond and the other would be a one electron bond, which is beyond Lewis theory (i.e., H–H$^-$–H).

(b) In HHe there would be three electrons between the two atoms, or three electrons around the He atom, one of which would be a nonbonding electron. Neither of these is a particularly stable situation.

(c) He$_2$ would have either a double bond between two He atoms and thus four electrons around each He atom, or three electrons around each He atom (2 e$^-$ in a bond and an unpaired electron on each atom). Neither situation achieves the electron configuration of a noble gas.

(d) H$_3$O has an expanded octet (9 electrons) on oxygen; expanded octets are not possible for elements in the second period. Other structures place a multiple bond between O and H. Both situations are unstable.

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

![Lewis structure of H–H–N–O–H]

(b) Here, Ca–O$^-$ is improperly written as a covalent Lewis structure. CaO is actually an ionic compound. [Ca]$^{2+}$[O]$^{2-}$ is a more plausible Lewis structure for CaO.

10. (E)
(a) :O–Cl–O$^-$ has 20 valence electrons, whereas the molecule ClO$_2$ has 19 valence electrons. This is a proper Lewis structure for the chlorite ion, although the brackets and the minus charge are missing. A plausible Lewis structure for the molecule ClO$_2$ is :O–Cl–O$^-$:

![Lewis structure of ClO$_2$]

(b) [C≡N]$^-$ has only six electrons around the C atom and two too few overall. [C≡N]$^-$ is a more plausible Lewis structure for the cyanide ion.
11. (M) The answer is (c), hypochlorite ion. The flaws with the other answers are as follows:

(a) \(\text{O}=={\text{C}}^{\ominus}\) - does not have an octet of electrons around C.

(b) \([\text{C}=={\text{C}}^{\ominus}]^{-}\) 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.

12. (M)

(a) Mg—\(\text{O}^{\ominus}\) is incorrectly written as a covalent structure. One expects an ionic Lewis structure, namely \([\text{Mg}]^{2+}[\text{O}^{2-}]^{-}\).

(b) \([\text{O}=={\text{N}}]^{2+}\) has too many valence electrons—8.5 electron pairs or 17 valence electrons—it should have \((2 \times 6) + 5 - 1 = 16\) valence electrons or 8 electron pairs. A plausible Lewis structure is \([\text{O}=={\text{N}}=={\text{O}}]^{2+}\), which has 1+ formal charge on N and 0 formal charge of zero on each oxygen.

(c) \([\text{Cl}]^{+}[\text{O}^{2-}]^{+}[\text{Cl}]^{+}\) is written as an ionic structure, even though we expect a covalent structure between nonmetallic atoms. A more plausible structure is \(\text{Cl}=={\text{O}}==\text{Cl}^{+}\).

(d) In the structure \([\text{S}=={\text{C}}^{\ominus}]\) neither S nor C possesses an octet of electrons. In addition, there are only 7 pairs of valence electrons in this structure or 14 valence electrons. There should be \(6 + 4 + 5 + 1 = 16\) valence electrons, or 8 electron pairs. Two structures are possible. \(\text{S}=={\text{C}}==\text{N}^{+}\) has a formal charge of 1- on N and is preferred over \(\text{S}=={\text{C}}==\text{N}^{+}\), with its formal charge of 1- on S, which is less electronegative than N.

**Ionic Bonding**

13. (E)

(a) \([\text{Cl}]^{+}[\text{Ca}]^{2+}[\text{Cl}]^{-}\) (b) \([\text{Ba}]^{2+}[\text{S}]^{2-}\) (c) \([\text{Li}]^{+}[\text{O}]^{2-}[\text{Li}]^{+}\) (d) \([\text{Na}]^{+}[\text{F}]^{-}\)
14. (E) The Lewis symbols are H\textsuperscript{-} for the hydride ion, N\textsuperscript{3-} for the nitride ion.

   (a) [Li]\textsuperscript{+} [H\textsuperscript{-}]
   Lithium hydride
   (b) [H\textsuperscript{-}]\textsuperscript{+} [Ca\textsuperscript{2+}] [H\textsuperscript{-}]
   Calcium hydride
   (c) Mg\textsuperscript{2+} [N\textsuperscript{3-}]
   Magnesium nitride

15. (E)

   (a) [Li]\textsuperscript{+} [S\textsuperscript{2-}] [Li\textsuperscript{+}] : Li\textsubscript{2}S
   (b) [Na\textsuperscript{+}] [F\textsuperscript{-}] : NaF
   (c) [I\textsuperscript{-}] [Ca\textsuperscript{2+}] [I\textsuperscript{-}] : CaI\textsubscript{2}
   (d) [Cl\textsuperscript{-}] [Sc\textsuperscript{3+}] [Cl\textsuperscript{-}] : ScCl\textsubscript{3}

16. (M)

   (a) Al\textsuperscript{3+} 3 [O\ldots H]
   (b) Ca\textsuperscript{2+} 2 [C\equiv N : ]
   (c) + [\text{H} \text{H} \text{H} \text{NH}_3] \text{F}^{-}
   (d) K\textsuperscript{+} [\text{O} \text{Cl} \text{O}]
   (e) 3 Ba\textsuperscript{2+} 2 [\text{O} \text{O} \text{O}]

\[ 401 \]
Formal Charge

17. (M) computations for:

(a) no. valence e\(^{-}\) = 1
   - no. lone-pair e\(^{-}\) = 0
   - ½ no. bond-pair e\(^{-}\) = -1

\[
\begin{array}{ccc}
\text{H—} & \text{—C} & \equiv \equiv \text{C} \\
1 & 4 & 4 \\
-0 & -0 & -2 \\
-1 & -4 & -3 \\
0 & 0 & -1
\end{array}
\]

(b) computations for:

\[
\begin{array}{ccc}
\text{=O—O(\times2)} & \text{C} \\
6 & 6 & 4 \\
-4 & -6 & -0 \\
-2 & -1 & 4 \\
-0 & -1 & 0
\end{array}
\]

(c) computations for:

\[
\begin{array}{ccc}
\text{—H(\times7)} & \text{side C(\times2)} & \text{central C} \\
1 & 4 & 4 \\
-0 & -0 & -0 \\
-1 & -4 & -3 \\
0 & 0 & +1
\end{array}
\]

18. (M) The formal charge on each I is 0,

(a) computed as follows:

\[
\begin{array}{ccc}
\text{no. valence e\(^{-}\)} & = 7 \\
-\text{no. lone-pair e\(^{-}\)} & = -6 \\
-\frac{1}{2} \text{ no. bond-pair e\(^{-}\)} & = -1 \\
\text{formal charge} & = 0
\end{array}
\]

(b) computations for:

\[
\begin{array}{ccc}
\text{=O} & \text{=S—} \\
6 & 6 & 6 \\
-4 & -6 & -2 \\
-2 & -1 & -3 \\
0 & -1 & +1
\end{array}
\]

(c) computations for:

\[
\begin{array}{ccc}
\text{=O} & \text{=N—} \\
6 & 6 & 5 \\
-4 & -6 & -1 \\
-2 & -1 & -3 \\
0 & -1 & +1
\end{array}
\]

19. (M) 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, O₃. 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.

20. (M) The most common instance in which formal charge is not kept to a minimum occurs in the case of ionic compounds. For example, in Mg—O the formal charge on Mg is 1+ and on O it is 1-, while in the ionic version [Mg]²⁺ [O]²⁻, formal charges are 2+ and 2-, respectively.

Additionally, in some resonance hybrids, formal charge is not minimized. In order to have bond lengths agree with experimental results, it may not be acceptable to create multiple bonds. Yet a third instance is when double bonds are created to lower formal charge, particularly when this results in the octet rule being violated. For instance, all the Cl—O bonds in ClO₄⁻ are best represented using single bonds. Although including some double bonds would minimize formal charges, the resulting structure is less desirable because the octet for Cl has been exceeded and this requires the input of additional energy.

21. (E) FC = # valence e⁻ in free atom – number lone-pair e⁻ – ½ # bond pair e⁻
(a) Central O in O₃: 6 – 2 – 3 = +1
(b) Al in AlH₄⁻: 3 – 0 – 4 = –1
(c) Cl in ClO₃⁻: 7 – 2 – 5 = 0
(d) Si in SiF₆²⁻: 4 – 0 – 6 = –2
(e) Cl in ClF₃: 7 – 4 – 3 = 0

22. (M)
(a) H₂NOH is favored because same charges don’t reside adjacent to each other.

(b) S=C=S is favored, because FC on everything is zero.
(c) F–N=O is favored.

\[
\begin{array}{c}
\text{N} \\
\text{F} \\
\text{O}
\end{array}
\]

\[
\begin{array}{c}
\text{F} \\
\text{N} \\
\text{O}
\end{array}
\]

(d) OS\textsubscript{Cl\textsubscript{2}} is favored. Even though the formal charges of all elements on both OS\textsubscript{Cl\textsubscript{2}} and OCl\textsubscript{2}S are zero, OS\textsubscript{Cl\textsubscript{2}} represents a much more realistic structure because the O and Cl atoms are in their normal bonding configuration.

(e) F\textsubscript{3}SN is favored.

23. (M) We begin by counting the total number of valence electrons that must appear in the Lewis structure of the ion CO\textsubscript{2}H\textsuperscript{+}: 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\textsuperscript{+} 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\textsubscript{2}\textsuperscript{+}, we come up with the following structures:

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array}
\]  \quad \text{(A)} \quad \text{\textsuperscript{@}}

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array}
\]  \quad \text{(B)} \quad \text{\textsuperscript{@}}

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array}
\]  \quad \text{(C)} \quad \text{\textsuperscript{@}}

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.
24.  (M) The intention of this question is to make the student aware of the fact that on occasion, one can obtain a better Lewis structure "from the standpoint of formal charge minimization" by using chain-like structures rather than the expected compact, symmetrical structures. The two linear Lewis structures for the ClO₄⁻ (I) and (II) and a compact structure (III) are shown below:

![Lewis Structures](image)

All of these structures have the required 32 valence electrons. Structure I has only one formal charge, 1- on the terminal oxygen atom. Structure II has a total of three formal charges, 1- on each of the terminal oxygen atoms and 1+ on the central chlorine atom. The compact structure, structure III, has formal charges on all of the atoms, 1- on all oxygen atoms and a formal charge of 3+ on the central chlorine atom. From the standpoint of minimizing formal charge, structure I would be deemed the most appropriate. Nevertheless, structure III is the one that is actually adopted by the ClO₄⁻ ion, despite the fact that better minimization is achieved with the linear structure. By using an expanded valence shell with 14 electrons for the central atom, as in structure IV below, one can achieve the same minimum set of formal charges as in structure I:

![Expanded Valence Shell](image)

The chlorine atom presumably uses available 3d orbitals to accommodate the six additional electrons in its valence shell. Structure IV would appear to be the best structure yet, because it has the minimum number of formal charges and is close to the true shape seen in the ClO₄⁻ ion. In light of recent quantum mechanical calculations, however, many chemists now believe that d-orbital involvement in expanded octets should only be invoked when there is no way to avoid them, as in PCl₅ or SF₆. This means that whenever possible, octet structures should be used, even though at times they afford unsettlingly large formal charges. Thus, structure III is now considered by most chemists as being superior to structure IV.

**Lewis Structures**

25.  (E)  

(a) 

(b) 

(c)
26. (E) The total number of valence electrons is $(2 \times 7) + (2 \times 6) = 26$ valence electrons, or 13 pairs of valence electrons. It is unlikely to have F as a central atom; that would require an expanded octet on F. The most plausible structure is:

\[ \cdot\cdot\cdot\cdot\cdotS\cdot\cdot\cdot\cdot\cdotF\cdot\cdot\cdot\cdot\cdot\]

27. (M)

(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:

\[
\begin{array}{c}
\text{O} \\
\text{S} \\
\text{O}
\end{array}
\]

(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:

\[ \text{NO}_2^- \leftrightarrow \text{NO}_2^- \]

(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:

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O}
\end{array}
\]

(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

\[ \cdot\cdot\cdot\cdot\cdotH\cdot\cdot\cdot\cdot\cdotO\cdot\cdot\cdot\cdot\cdot \]
28. (M) Each of the cations has an empty valence shell as the result of ionization. The main task is to determine the Lewis structure of each anion.

(a) The total number of valence electrons in OH\(^{-}\) is \(6+1+1=8\), or 4 electron pairs. A plausible Lewis structure for barium hydroxide is \([\text{Ba}^{2+}[\text{O}\equiv\text{H}^-]\
\]

(b) The total number of valence electrons in NO\(_2\)\(^{-}\) is \(5+(2\times6)+1=18\), or 9 electron pairs. A plausible Lewis structure for sodium nitrite is \([\text{Na}^+[[\text{N}=\text{O}^-] \leftrightarrow [\text{Na}^+[[\text{O}=\text{N}^-\text{O}]]\]

(c) The total number of valence electrons in IO\(_3\)\(^{-}\) is \(7+(3\times6)+1=26\), or 13 electron pairs. A plausible Lewis structure for magnesium iodate is

\[
\begin{array}{c}
\text{[Mg]}^2+\text{[O]}^2-\text{[O]}^2-\text{[O]}^2
\end{array}
\]

(d) The total number of valence electrons in SO\(_4\)\(^{2-}\) is \(6+(4\times6)+2=32\), or 16 electron pairs. A plausible structure for aluminum sulfate is \([\text{SO}_4]^{2-}\text{[Al]}^3\text{[SO}_4]^{2-}\text{[Al]}^3\text{[SO}_4]^{2-}\). Because of the ability of S to expand its octet, SO\(_4\)\(^{2-}\) has several resonance forms, a few of which are:

\[
\begin{array}{c}
\text{[O]}^\ominus\text{[O]}^\ominus\text{[O]}^\ominus\text{[O]}^\ominus
\end{array}
\]

The first structure, without S expanded octet, is preferred.

29. (M) In CH\(_2\)CHCHCHO there are \((4\times4)+(6\times1)+6=28\) valence electrons, or 14 electron pairs. We expect that the carbon atoms bond to each other. A plausible Lewis structure is:

\[
\begin{array}{c}
\text{H} & \text{H} & \text{H} & \text{O} \\
\hline
\text{H} & \text{C} \equiv & \text{C} & \equiv & \text{C} & \equiv & \text{H} \\
\text{H}
\end{array}
\]

30. (E) In C\(_3\)O\(_2\) there are \((3\times4)+(2\times6)=24\) valence electrons or 12 valence electron pairs. A plausible Lewis structure follows: \(\text{O}=\text{C}=\text{C}=\text{O}\).
31. (E) (a) \( :O:\) 
\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H}
\end{array}
\]

32. (E) (a) \( :O:\) 
\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{H}
\end{array}
\]

33. (E) (a) \( :O:\) 
\[
\begin{array}{c}
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array}
\]

34. (E) (a) 
\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{H}
\end{array}
\]

(b) 
\[
\begin{array}{c}
\text{Cl} \\
\text{C} \\
\text{C} \\
\text{N} \\
\text{H}
\end{array}
\]

35. (M) (a) Group 16
\[
\begin{array}{c}
\text{S} \\
\text{S}
\end{array}
\]
\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]

(b) Group 16 except oxygen
\[
\begin{array}{c}
\text{O} \\
\text{S} \\
\text{O}
\end{array}
\]

(c) Group 17 except fluorine
\[
\begin{array}{c}
\text{O} \\
\text{Cl} \\
\text{O}
\end{array}
\]

(d) Group 13
\[
\begin{array}{c}
\text{H} \\
\text{B} \\
\text{H}
\end{array}
\]
36. (M) (a) Group 14

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O}
\end{array}
\]

(b) Group 16 except oxygen

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{O}
\end{array}
\]

(c) Group 17 except fluorine

\[
\begin{array}{c}
\text{O} \\
\text{S} \\
\text{O} \\
\text{O} \\
\text{H}
\end{array}
\]

(d) Group 13

\[
\begin{array}{c}
\text{O} \\
\text{Si} \\
\text{O} \\
\text{O}
\end{array}
\]

37. (M) 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:

\[\text{C—H} \prec \text{Br—H} \prec \text{F—H} \prec \text{Na—Cl} \prec \text{K—F}\]

The actual electronegativity differences follow:

\[
\begin{array}{cccccc}
\text{C} & \text{Br} & \text{F} & \text{Na} & \text{K} \\
(2.5) & (2.8) & (4.0) & (0.9) & (0.8) \\
\Delta \text{EN} & = 0.4 & = 0.7 & = 1.9 & = 2.1 & = 3.2
\end{array}
\]

38. (M) (a) \(\text{F}_2\) cannot possess a dipole moment, since both of the atoms in the diatomic molecule are the same. This means that there is no electronegativity difference between atoms, and hence no polarity in the F—F bond.

(b) \(\tilde{\text{O}}\equiv\tilde{\text{N}}\tilde{\text{O}}\): Each nitrogen-to-oxygen bond in this molecule is polarized toward oxygen, the more electronegative element. The molecule is of the \(\text{AX}_2\text{E}\) category and hence is bent. Therefore the two bond dipoles do not cancel, and the molecule is polar.
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(c) Although each B—F bond is polarized toward F in this trigonal planar AX₃ molecule, these bond dipoles cancel. The molecule is nonpolar.

(d) H—Br: The H—Br bond is polar toward Br, and this molecule is polar as well.

(e) The H—C bonds are not polar, but the C—Cl bonds are, toward Cl. The molecular shape is tetrahedral (AX₄) and thus these two C—Cl dipoles do not cancel each other; the molecule is polar.

(f) Although each Si—F bond is polarized toward F, in this tetrahedral AX₄ molecule these bond dipoles oppose and cancel each other. As a result, the molecule is nonpolar.

(g) O=C=S: In this linear molecule, the two bonds from carbon both are polarized away from carbon. But the C=O bond is more polar than the C=S bond, and hence the molecule is polar.

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

(a) S(2.5)—H(2.1)  \(\Delta EN = 0.4\)  %ionic = 4%
(b) O(3.5)—Cl(3.0)  \(\Delta EN = 0.5\)  %ionic = 5%
(c) Al(1.5)—O(3.5)  \(\Delta EN = 2.0\)  %ionic = 60%
(d) As(2.0)—O(3.5)  \(\Delta EN = 1.5\)  %ionic = 33%

40. (D)

Plot of Electronegativity vs Atomic Number

The property of electronegativity does indeed conform to the periodic law. Each of the “low points” corresponds to an alkali metal, and the end of each trend corresponds to a halogen. This is not unexpected and follows the general trend of increasing \(Z_{eff}\) from left to right, across the periodic table.
41. (M) 
\[
\delta = \frac{\mu}{d} = \frac{0.8881 \times 3.34 \times 10^{-30} \text{ C} \cdot \text{m/D}}{162.8 \times 10^{-12} \text{ m}} \times \frac{1 \text{ e}}{1.602 \times 10^{-19} \text{ C}} = 0.114e, \text{ towards F.}
\]
\[
\delta = \frac{\mu}{d} = \frac{8.547 \times 3.34 \times 10^{-30} \text{ C} \cdot \text{m/D}}{227.0 \times 10^{-12} \text{ m}} \times \frac{1 \text{ e}}{1.602 \times 10^{-19} \text{ C}} = 0.785e, \text{ towards F.}
\]
\[
\delta = \frac{\mu}{d} = \frac{4.3210 \times 3.34 \times 10^{-30} \text{ C} \cdot \text{m/D}}{183.3 \times 10^{-12} \text{ m}} \times \frac{1 \text{ e}}{1.602 \times 10^{-19} \text{ C}} = 0.491e, \text{ towards O.}
\]
\[
\delta = \frac{\mu}{d} = \frac{7.954 \times 3.34 \times 10^{-30} \text{ C} \cdot \text{m/D}}{194.0 \times 10^{-12} \text{ m}} \times \frac{1 \text{ e}}{1.602 \times 10^{-19} \text{ C}} = 0.855e, \text{ towards O.}
\]

42. (M) 
\[
\delta = \frac{\mu}{d} = \frac{1.66 \times 3.34 \times 10^{-30} \text{ C} \cdot \text{m/D}}{98.0 \times 10^{-12} \text{ m}} \times \frac{1 \text{ e}}{1.602 \times 10^{-19} \text{ C}} = 0.353e, \text{ towards O.}
\]
\[
\delta = \frac{\mu}{d} = \frac{1.46 \times 3.34 \times 10^{-30} \text{ C} \cdot \text{m/D}}{131.1 \times 10^{-12} \text{ m}} \times \frac{1 \text{ e}}{1.602 \times 10^{-19} \text{ C}} = 0.232e, \text{ towards C.}
\]
\[
\delta = \frac{\mu}{d} = \frac{117.5 \times 3.34 \times 10^{-30} \text{ C} \cdot \text{m/D}}{1.45 \times 10^{-12} \text{ m}} \times \frac{1 \text{ e}}{1.602 \times 10^{-19} \text{ C}} = 0.257e, \text{ towards N.}
\]
\[
\delta = \frac{\mu}{d} = \frac{1.96 \times 3.34 \times 10^{-30} \text{ C} \cdot \text{m/D}}{194.4 \times 10^{-12} \text{ m}} \times \frac{1 \text{ e}}{1.602 \times 10^{-19} \text{ C}} = 0.210e, \text{ towards S.}
\]

43. (M) 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.
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44. (M) HOCl, HOF, and FOCl have similar structural features, however, they differ in terms of their electron density maps. O, Cl, and F have similar electronegativities, thus FOCl should be fairly neutral (mostly yellow coloration), in terms of the electrostatic potential map. Thus, the molecule on the far right is FOCl. In the molecule HOF, the H atom will be very electropositive (blue coloring), owing to the presence of the very electronegative O and F atoms. Therefore, the molecule on the far right is HOF. This means that HOCl is the center molecule, which, as expected, should have a relatively electropositive H atom (blue coloring, however, not as blue as in the case of HOF).

45. (M) The molecular formulas for the compounds are SF₄ and SiF₄. SiF₄ 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 SiF₄. SF₄ 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.

46. (M) The molecular formulas are ClF₃ and PF₃. Since P is more electropositive than Cl, we can easily argue that the right hand representation in which the central atom has a greater positive charge associated with it (blue coloration) is PF₃. As well, the molecular geometries are different. PF₃ is expected to be trigonal pyramidal while ClF₃ is T-shaped. It is relatively clear that the molecular geometries of the two molecules are different in the electrostatic potential maps. Thus the representation on the left, which is nearly planar, is that for ClF₃, while the non-planar map on the right is that for PF₃.

Resonance

47. (E) In NO₂⁻, the total number of valence electrons is 1+ 5 + (2 × 6) = 18 valence electrons, or 9 electron pairs. N is the central atom. The two resonance forms are shown below:

\[
\text{ONO} \leftrightarrow \text{ONO} \nonumber
\]

48. (M) The only one of the four species that requires resonance forms to correctly describe the intramolecular bonding is CO₃²⁻. Resonance forms of equal energy cannot be generated for the other species. All four Lewis structures are drawn below.

(a) In CO₂, there are \(4 + (2 \times 6) = 16\) valence electrons, or 8 electron pairs. \(\overset{\cdot}{\overset{\cdot}{\text{O}}} = \overset{\cdot}{C} = \overset{\cdot}{O}\)

(b) In OCl⁻, there are \(6 + 7 + 1 = 14\) valence electrons, or 7 electron pairs, \(\overset{\cdot}{\overset{\cdot}{\text{O}}} = \overset{\cdot}{C} = \overset{\cdot}{\text{Cl}}\)
(c) In $\text{CO}_3^{2-}$, there are $4 + (3 \times 6) + 2 = 24$ valence electrons, or 12 electron pairs (see below).

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\end{align*}
\]

(d) In $\text{OH}^-$, there are $6 + 1 + 1 = 8$ valence electrons, or 4 electron pairs.

49. (M) Bond length data from Table 10.2 follow:

- $\text{N} \equiv \text{N} = 109.8$ pm
- $\text{N} = \text{N} = 123$ pm
- $\text{N} \equiv \text{O} = 145$ pm
- $\text{N} = \text{O} = 120$ pm
- $\text{N} \equiv \text{O} = 136$ pm

The experimental N—N bond length of 113 pm approximates that of the N≡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).

50. (M) We begin by drawing all three valid resonance forms of $\text{HNO}_3$ and then analyzing their distributions of formal charge to determine which is the most plausible.

In all three structures, the formal charges of N and H are the same:

- For an oxygen that forms two bonds (either 2 single or one double), f.c. = 6 - 2 - (2 × 2) = 0
- For an oxygen that forms only one bond, f.c. = 6 - 1 - (3 × 2) = -1
- For the oxygen that forms three bonds (a single and a double), f.c. = 6 - 3 - (1 × 2) = +1

Thus, structures (a) and (b) are equivalent in their distributions of formal charges, zero on all atoms except 1+ on N and 1- on one O. These are degenerate resonance forms (i.e., they are of equal energy). Structure (c) is quite different, with formal charges of 1- on two O's, and 1+ on the other, and a formal charge of 1+ on N. Structure (c) is thus the least plausible, because of the adjacent like charges.
51. (M)

(a) Both structures are equivalent.

\[
\begin{align*}
\text{A} & : 
\begin{array}{c}
0 \\
\text{H} & - & \text{C} & - & \text{O} \\
\end{array} \\
\text{B} & : 
\begin{array}{c}
0 \\
\text{H} & - & \text{C} & = & \text{O} \\
\end{array}
\end{align*}
\]

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

\[
\begin{align*}
\text{A} & : 
\begin{array}{c}
0 \\
\text{H} & - & \text{O} & - & \text{C} & - & \text{O} \\
\end{array} \\
\text{B} & : 
\begin{array}{c}
+1 \\
\text{H} & - & \text{O} & = & \text{C} & - & \text{O} \\
\end{array} \\
\text{C} & : 
\begin{array}{c}
0 \\
\text{H} & - & \text{O} & - & \text{C} & = & \text{O} \\
\end{array}
\end{align*}
\]

(c) Structure B is more important.

\[
\begin{align*}
\text{A} & : 
\begin{array}{c}
+2 \\
\text{F} & \rightarrow & \text{S} & = & \text{O} \\
\end{array} \\
\text{B} & : 
\begin{array}{c}
+1 \\
\text{F} & \rightarrow & \text{S} & = & \text{O} \\
\end{array} \\
\text{C} & : 
\begin{array}{c}
0 \\
\text{F} & \rightarrow & \text{S} & = & \text{O} \\
\end{array}
\end{align*}
\]

(d) Structure A is more important.

\[
\begin{align*}
\text{A} & : 
\begin{array}{c}
0 \\
\text{N} & - & \text{N} & = & \text{O} \\
\end{array} \\
\text{B} & : 
\begin{array}{c}
-1 \\
\text{N} & - & \text{N} & = & \text{O} \\
\end{array} \\
\text{C} & : 
\begin{array}{c}
-1 \\
\text{N} & - & \text{N} & = & \text{O} \\
\end{array}
\end{align*}
\]
52. (M)

(a) Structures A and B are equivalent and most important.

(b) Structure A is the most important.

(c) Both structures are equivalent.

(d) All structures are equivalent.
Odd-electron species

53. (M)
   (a) CH₃ 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.

   \(\text{CH}_3\)

   \(\begin{array}{c}
   \text{H} \\
   \text{C} \\
   \text{H}
   \end{array}\)

   (b) ClO₂ 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:

   \(\text{ClO}_2\)

   \(\begin{array}{c}
   \ddot{\text{O}} \\
   \text{Cl} \\
   \ddot{\text{O}}
   \end{array}\)

   (c) NO₃ 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.

54. (M)
   (a) C₂H₅ has a total of \((5 \times 1) + (2 \times 4) = 13\) valence electrons or 6 electron pairs and a lone electron on C. A plausible Lewis structure is given to the right.

   \(\text{C}_2\text{H}_5\)

   \(\begin{array}{c}
   \text{H} \\
   \text{H} \\
   \text{C} \\
   \text{C} \\
   \text{H}
   \end{array}\)

   (b) HO₂ has a total of \((2 \times 6) + 1 = 13\) valence electrons or 6 electron pairs (2 bonding and 4 non-bonding) and a lone electron on O. A plausible Lewis structure is given to the right.

   \(\text{HO}_2\)

   \(\begin{array}{c}
   \ddot{\text{O}} \\
   \text{H} \\
   \ddot{\text{O}}
   \end{array}\)

   (c) ClO has a total of \(7 + 6 = 13\) valence electrons or 6 electron pairs (1 bonding and 5 non-bonding) and a lone electron on either Cl or O. A plausible Lewis structure is given to the right.

   \(\text{ClO}\)

55. (E) 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) NO₃ \(5 + (3 \times 6) = 23\) valence electrons paramagnetic

   (d) SO₃ \(6 + (3 \times 6) = 24\) valence electrons diamagnetic

   (e) SO₃²⁻ \(6 + (3 \times 6) + 2 = 26\) valence electrons diamagnetic

   (f) HO₂ \(1 + (2 \times 6) = 13\) valence electrons paramagnetic
56. **(D)** In NO₂, there are \(5 + (2 \times 6) = 17\) valence electrons, 8 electron pairs and a lone electron. N is the central atom and it carries the lone electron. A plausible Lewis structure is (A) which has a formal charge of 1+ on N and 1- on the single-bonded O. Another Lewis structure, with zero formal charge on each atom, is (B). The major difference is that one of the oxygen atoms carries the lone electron. In both cases, due to the unpaired electron we expect NO₂ to be paramagnetic. We would expect a bond to form between two NO₂ molecules as a result of the pairing of the lone unpaired electrons in the NO₂ molecules. If the second Lewis structure for NO₂ is used, the one with zero formal charge on each atom and the lone electron on oxygen, a plausible structure for N₂O₄ is (C). If the first Lewis structure for NO₂ where there are formal charges and a lone electron on nitrogen is used to form a bond between molecules, a plausible Lewis structure containing a N—N bond results (D). Resonance structures can be drawn for this second version of N₂O₄. A N—N bond is observed experimentally in N₂O₄. In either structure, the product N₂O₄ has all electrons paired up in bonding and non-bonding lone pairs; the molecule is expected to be (and is) diamagnetic. Lewis structures for (A) – (D) are shown below.

\[
\begin{align*}
\text{(A)} & \quad \vdots \cdot \overset{\alpha}{\text{N}}=\overset{\alpha}{\text{O}} \\
\text{(B)} & \quad \vdots \cdot \overset{\alpha}{\text{O}}=\overset{\alpha}{\text{N}}=\overset{\alpha}{\text{O}} \\
\text{(C)} & \quad \vdots \cdot \overset{\beta}{\text{O}}=\overset{\beta}{\text{N}}=\overset{\beta}{\text{O}} \\
\text{(D)} & \quad \vdots \cdot \overset{\beta}{\text{O}}=\overset{\beta}{\text{N}}=\overset{\beta}{\text{O}}
\end{align*}
\]

**Expanded Octets**

57. **(M)** In PO₄³⁻: \(5 + (4 \times 6) + 3 = 32\) valence electrons or 16 electron pairs. An expanded octet is not needed.

In PI₃: \(5 + (3 \times 7) = 26\) valence electrons or 13 electron pairs. An expanded octet is not needed.

In ICl₃: \(7 + (3 \times 7) = 28\) valence electrons or 14 electron pairs. An expanded octet is necessary.

In OSCl₂: \(6 + 6 + (2 \times 7) = 26\) valence electrons or 13 electron pairs. An expanded octet is not needed.
In SF₄: \(6 + (4 \times 7) = 34\) valence electrons or 17 electron pairs. An expanded octet is necessary.

In ClO₄⁻: \(7 + (4 \times 6) + 1 = 32\) valence electrons or 16 electron pairs. An expanded octet is not needed.

58. (M) Let us draw the Lewis structure of H₂CSF₂. The molecule has \((2 \times 1) + 4 + 6 + (4 \times 7) = 40\) valence electrons, or 20 electron pairs. With only single bonds and all octets complete, there is a 1− formal charge on C and 1+ on S, as in the left structure below. The right structure below avoids an undesirable separation of charge by creating a carbon-to-sulfur double bond (charge separation requires the input of energy).

The bond can be described either as a single bond with ionic contributions or a double bond in which the formal charges are eliminated.

**Molecular Shapes**

59. (M) The AXₐEₘ 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) Dinitrogen is linear; two points define a line.

(b) Hydrogen cyanide is linear. The molecule belongs to the AX₂ category, and these species are linear.

(c) NH₄⁺ is tetrahedral. The ion is of the AX₄ type, which has a tetrahedral electron-group geometry and a tetrahedral shape.

(d) NO₃⁻ is trigonal planar. The ion is of the AX₃ 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 AX₂E type, which has a trigonal planar electron-group geometry and a bent shape.
60. (M) The $AX_E^n$ designations that are cited below are to be found in Table 11.1 of the text, along with a sketch and a picture of a model of each type of structure.

(a) PCl$_3$ is a trigonal pyramid. The molecule is of the $AX_E^3$ type, and has a tetrahedral electron-group geometry and a trigonal pyramid shape.

(b) SO$_4^{2-}$ has a tetrahedral shape. The ion is of the type $AX_4$, and has a tetrahedral electron-group geometry and a tetrahedral shape. The other resonance forms of the sulfate ion have the same shape.

(c) SOCl$_2$ has a trigonal pyramidal shape. This molecule is of the $AX_E^3$ type and has a tetrahedral electron-group geometry and a trigonal pyramidal shape.

(d) SO$_3$ has a trigonal planar shape. The molecule is of the $AX_3$ type, with a trigonal planar electron-group geometry and molecular shape. The other resonance contributors have the same shape.

(e) BrF$_4^+$ has a distorted see-saw shape. The molecule is of the $AX_E^4$ type, with a trigonal bipyramid electron-group geometry and a see-saw molecular shape.

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

(a) H$_2$S tetrahedral electron-group geometry, bent (angular) molecular geometry

(b) N$_2$O$_4$ trigonal planar electron-group geometry around each N, (planar molecule)

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

(d) SbCl$_6^-$ octahedral electron-group geometry, octahedral geometry

(e) BF$_3^-$ tetrahedral electron-group geometry, tetrahedral molecular geometry
62. (M) In each case, a plausible Lewis structure is given first, followed by the $AX_nE_m$ notation for each species followed by the electron-group geometry and, finally, the molecular geometry.

(a) CO  linear electron-group geometry, linear molecular geometry

(b) SiCl$_4$  tetrahedral electron-group geometry, tetrahedral molecular geometry

(c) PH$_3$  tetrahedral electron-group geometry, trigonal pyramidal molecular geometry

(d) ICl$_3$  trigonal bipyramidal electron-group geometry, T- shape molecular geometry

(e) SbCl$_5$  electron-group geometry and molecular geometry, trigonal bipyramidal

(f) SO$_2$  trigonal planar electron-group geometry, bent molecular geometry

(g) AlF$_6^{3-}$  octahedral electron-group geometry, octahedral geometry
63. (M) 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$_3$E 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.

64. (E) We can predict shapes by first of all drawing the Lewis structures for the species. Thus, SO$_3^{2-}$ and NI$_3$ both have the same shape.

65. (M) (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. O = C = O This is a molecule of type AX$_2$. CO$_2$ has a linear electron-shape geometry and a linear shape.

(b) In Cl$_2$CO 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.
66. (M) Lewis structures enable us to determine molecular shapes.

(a) \( \text{N}_2\text{O}_4 \) has \( (2 \times 5) + (4 \times 6) = 34 \) valence electrons, or 17 electron pairs. There are three atoms bound to each N in \( \text{N}_2\text{O}_4 \), making the molecule triangular planar around each N. The entire molecule does not have to be planar, however, since there is free rotation around the \( \text{N} — \text{N} \) bond.

(b) \( \text{C}_2\text{N}_2 \) has \( (2 \times 4) + (2 \times 5) = 18 \) valence electrons, or 9 electron pairs. There are two atoms attached to each C, requiring a linear geometry. The entire molecule is linear.

(c) \( \text{C}_2\text{H}_6 \) has \( (2 \times 4) + (6 \times 1) = 14 \) valence electrons, or 7 electron pairs. There are four atoms attached to each C. The molecular geometry around each C is tetrahedral, as shown in the sketch above.

(d) \( \text{CH}_3\text{OCH}_3 \) has 6 more valence electrons than \( \text{C}_2\text{H}_6 = 20 \) valence e\(^-\) or 10 electron pairs. Around the central O, the electron-group geometry is tetrahedral. With two of the electron groups being lone pairs, the molecular geometry around the central atom is bent.

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

(a) In \( \text{ClO}_4^- \) 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.
Chapter 10: Chemical Bonding I: Basic Concepts

(b) In $\text{S}_2\text{O}_3^{2-}$ 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 $\text{PF}_6^-$ 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 $\text{I}_3^-$ 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.

68. (D)

(a) In $\text{OSF}_2$, there are a total of $6 + 6 + (2 \times 7) = 26$ valence electrons, or 13 electron pairs. $\text{S}$ is the central atom. A plausible Lewis structure is shown to the right. This molecule is of the type $\text{AX}_3\text{E}_1$. It has a tetrahedral electron-group geometry and a trigonal pyramidal shape.

(b) In $\text{OSF}_2^2$, there are a total of $(2 \times 6) + 6 + (2 \times 7) = 32$ valence electrons, or 16 electron pairs. $\text{S}$ is the central atom. One plausible Lewis structure is shown to the right. The molecule is of the $\text{AX}_4$ type. It has a tetrahedral electron-group geometry and a tetrahedral shape. The structure with all single bonds is preferred because it avoids an expanded octet.

(c) In $\text{SF}_5^-$, there are $6 + (5 \times 7) + 1 = 42$ valence electrons, or 21 electron pairs. A plausible Lewis structure is shown to the right. The ion is of the $\text{AX}_3\text{E}$ type. It has an octahedral electron-group geometry and a square pyramidal molecular shape.

(d) In $\text{ClO}_4^-$, there are a total of $1 + 7 + (4 \times 6) = 32$ valence electrons, or 16 electron pairs. $\text{Cl}$ is the central atom. A plausible Lewis structure is shown to the right. This ion is of the $\text{AX}_4$ type. It has a tetrahedral electron-group geometry and a tetrahedral shape.
(e) In ClO₃⁻, the total number of valence electrons is \(1 + (3 \times 6) + 7 = 26\) valence electrons, or 13 electron pairs. A plausible Lewis structure is shown to the right. The molecule is of the type AX₃E. It has a tetrahedral electron-group geometry and a trigonal pyramidal molecular shape.

**69.** (M) In BF₃⁻, 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 AX₄. It has a tetrahedral electron-group geometry and a tetrahedral shape.

**70.** (M) The molecular geometry is indicated by the VSEPR notation (i.e., AX₃E₂). Formal charge is reduced by moving lone pairs of electrons from the terminal atoms and forming multiple bonds to the central atom. The VSEPR notation is unchanged, however, when formal charge is increased or decreased. For example, consider SO₂:

<table>
<thead>
<tr>
<th>VSEPR notation</th>
<th>AX₂E</th>
<th>AX₂E</th>
<th>AX₂E</th>
</tr>
</thead>
<tbody>
<tr>
<td>shape: bent</td>
<td>shape: bent</td>
<td>shape: bent</td>
<td></td>
</tr>
</tbody>
</table>

**71.** (M) 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.

<table>
<thead>
<tr>
<th>O=C=O</th>
<th>O=N=O</th>
<th>O=O</th>
<th>O=Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>180°</td>
<td>120°</td>
<td>120°</td>
<td>109°</td>
</tr>
</tbody>
</table>

**72.** (M) CO₃²⁻ and NO₃⁻ are trigonal planar, because the central atom has no lone pairs. SO₃²⁻ and ClO₃⁻ are trigonal pyramidal, because the lone pair on the central atom forces a shape change.
### Shapes of Molecules with More Than One Central Atom

75. (E) A maximum of 5 atoms can be in the same plane

76. (E) A maximum of 7 atoms can be in the same plane
77. (E) All angles ~109.5° with the exception of

\[ O_c - C - C \]
\[ O_b = C - C \quad \text{120°} \]
\[ O_b = C - O_c \]

78. (E) All angles ~ 109.5° with the exception of

\[ O_c - C_b - C \]
\[ O_b = C_b - O_c \]
\[ O_b = C_b - C \]
\[ O_a = C_a - C \]
\[ C - C_a - C \]

79. (M) By inspection:

80. (M) By inspection:
Polar Molecules

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

(a) $\text{SO}_2$ has a total of $6 + (2 \times 6) = 18$ valence electrons, or 9 electron pairs. The molecule has two resonance forms. $\text{O} \equiv \overset{\text{S}}{\text{O}} \equiv \overset{\text{O}}{\text{O}} \leftrightarrow \overset{\text{O}}{\text{O}} \equiv \overset{\text{S}}{\text{O}}$. Each of these resonance forms is of the type $\text{AX}_2E$. Thus it has a trigonal planar electron-group geometry and a bent shape. Since each $\text{S}--\text{O}$ bond is polar toward $\text{O}$, and since the bond dipoles do not point in opposite directions, the molecule has a resultant dipole moment, pointing from $\text{S}$ through a point midway between the two $\text{O}$ atoms. Consequently, $\text{SO}_2$ is polar.

(b) $\text{NH}_3$ has a total of $5 + (3 \times 1) = 8$ valence electrons, or 4 electron pairs. $\text{N}$ is the central atom. A plausible Lewis structure is shown to the right. The molecule is of the $\text{AX}_3\text{E}$ type; it has a tetrahedral electron-group geometry and a trigonal pyramidal shape. Each $\text{N}-\text{H}$ bond is polar toward $\text{N}$. 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 $\text{H}$ atoms) through $\text{N}$. Consequently, the molecule is polar.

(c) $\text{H}_2\text{S}$ has a total of $6 + (2 \times 1) = 8$ valence electrons, or 4 electron pairs. $\text{S}$ is the central atom and a plausible Lewis structure is $\text{H}-\overset{\text{S}}{\text{H}}$. This molecule is of the $\text{AX}_2\text{E}_2$ type; it has a tetrahedral electron-group geometry and a bent shape. Each $\text{H}--\text{S}$ bond is polar toward $\text{S}$. Since the bonds do not symmetrically oppose each other, the molecule has a net dipole moment, pointing from $\text{S}$ to a point midway between the two $\text{H}$ atoms. $\text{H}_2\text{S}$ is polar.

(d) $\text{C}_2\text{H}_4$ consists of atoms that all have about the same electronegativities. Of course, the $\text{C}--\text{C}$ bond is not polar and essentially neither are the $\text{C}--\text{H}$ bonds. The molecule is planar. Thus, the entire molecule is nonpolar.

(e) $\text{SF}_6$ has a total of $6 + (6 \times 7) = 48$ valence electrons, or 24 electron pairs. $\text{S}$ is the central atom. All atoms have zero formal charge in the Lewis structure. This molecule is of the $\text{AX}_6$ type. It has an octahedral electron-group geometry and an octahedral shape. Even though each $\text{S}--\text{F}$ bond is polar toward $\text{F}$, the bonds symmetrically oppose each other, resulting in a molecule that is nonpolar.

(f) $\text{CH}_2\text{Cl}_2$ 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 ($\text{C}--\text{Cl}$) do not cancel the effect of each other.
82.  (D)  
(a) HCN is a linear molecule, which can be derived from its Lewis structure $\text{H—C≡N}$. The $\text{C≡N}$ bond is strongly polar toward N, while the $\text{H—C}$ bond is generally considered to be nonpolar. Thus, the molecule has a dipole moment, pointed from C toward N.

(b) $\text{SO}_3$ is a trigonal planar molecule, which can be derived from its Lewis structure. Each sulfur-oxygen bond is polar from S to O, but the three bonds are equally polar and are pointed in symmetrical opposition so that they cancel. The $\text{SO}_3$ molecule has a dipole moment of zero.

(c) $\text{CS}_2$ is a linear molecule, which can be derived from its Lewis structure $\text{S= C =S}$. Each carbon-sulfur bond is polar from C to S, but the two bonds are equally polar and are pointed in opposition to each other so that they cancel. The $\text{CS}_2$ molecule has a dipole moment of zero.

(d) $\text{OCS}$ also is a linear molecule. Its Lewis structure is $\text{O = C =S}$. But the carbon-oxygen bond is more polar than the carbon-sulfur bond. Although both bond dipoles point from the central atom to the bonded atom, these two bond dipoles are unequal in strength. Thus, the molecule is polar in the direction from C to O.

(e) $\text{SOCl}_2$ is a trigonal pyramidal molecule. Its Lewis structure is shown to the right. The lone pair is at one corner of the tetrahedron. Each bond in the molecule is polar, with the dipole moments pointing away from the central atom. The sulfur-chlorine bond is less polar than the sulfur-oxygen bond, and this makes the molecule polar. The dipole moment of the molecule points from the sulfur atom to the base of the trigonal pyramid, not toward the center of the base but slightly toward the O apex of that base.

(f) SiF$_4$ is a tetrahedral molecule, with the following Lewis structure. Each Si — F bond is polar, with its negative end away from the central atom toward F in each case. These four Si — F bond dipoles oppose each other and thus cancel. SiF$_4$, as a result, has no dipole moment.

(g) POF$_3$ is a tetrahedral molecule. A valid Lewis structure is shown to the right. All four bonds are polar, with their dipole moments pointing away from the central atom. The P — F bond polarity is greater than that of the P — O bond. Thus, POF$_3$ is a polar molecule with its dipole moment pointing away from the P toward the center of the triangle formed by the three F atoms.
83. (M) In H₂O₂, 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: \(\text{H} - \overline{\text{O}} - \overline{\text{O}} - \text{H}\). 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.

84. (M)
(a) FNO has a total of \(7 + 5 + 6 = 18\) valence electrons, or 9 electron pairs. N is the central atom. A plausible Lewis structure is \(\text{F} - \overline{\text{N}} = \overline{\text{O}}\). The formal charge on each atom in this structure is zero.
(b) FNO is of the \(\text{AX}_2\text{E}\) type. It has a trigonal planar electron-group geometry and a bent shape.
(c) The N—F bond is polar toward F and the N—O bond is polar toward O. In FNO, these two bond dipoles point in the same general direction, producing a polar molecule. In FNO₂, however, the additional N—O bond dipole partially opposes the polarity of the other two bond dipoles, resulting in a smaller net dipole moment.

Bond Lengths

85. (E) The answer is c. Br₂ possess the longest bond. Single bonds are generally longer than multiple bonds. Of the two molecules with single bonds, Br₂ is expected to have longer bonds than BrCl, since Br is larger than Cl.

(a) \(\overline{\text{O}} = \overline{\text{O}}\)  
(b) |\(\overline{\text{N}} = \overline{\text{N}}\)|  
(c) |\(\overline{\text{Br}} - \overline{\text{Br}}\)|  
(d) |\(\overline{\text{Br}} - \overline{\text{Cl}}\)|

86. (M) The bond lengths predicted will be larger than the actual bond lengths. This is because we do not take into account polarity of the bond. In the case of the I-Cl bond, the electronegativity difference is small, thus the predicted bond length should be close to the experimental value. In the case of the C-F bond, the electronegativity difference is quite large, thus it is expected that the actual bond length will be shorter than the one predicted.

(a) I—Cl bond length \(= \left(\frac{\text{[I—I bond length] + (Cl—Cl bond length)]}}{2}\right)\) 
\(= \left[\frac{266 \text{ pm} + 199 \text{ pm}}{2}\right] = 233 \text{ pm} \) (literature 232 pm)

(b) C — F bond length \(= \left(\frac{\text{[C—C bond length] + (F—F bond length)]}}{2}\right)\) 
\(= \left[\frac{154 \text{ pm} + 143 \text{ pm}}{2}\right] = 149 \text{ pm} \) (literature 135 pm)
87. (M) 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 = \(\frac{[\text{I—I bond length} + \text{(Cl—Cl bond length)}]}{2}\) = \(\frac{266 \text{ pm} + 199 \text{ pm}}{2} = 233 \text{ pm}\)

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

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

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

88. (M) First we need to draw the Lewis structure of each of the compounds cited, so that we can determine the order, and hence the relative length, of each O-to-O bond.

(a) In \(\text{H}_2\text{O}_2\), there are \((2 \times 1) + (2 \times 6) = 14\) valence electrons or 7 electron pairs. A plausible Lewis structure is \(\text{H}—\overset{=}{\text{O}}—\overset{=}{\text{O}}—\text{H}\).

(b) In \(\text{O}_2\), the total number of valence electrons is \((2 \times 6 =) 12\) valence electrons, or 6 electron pairs. A plausible Lewis structure is \(\overset{=}{\text{O}}—\overset{=}{\text{O}}\).

(c) In \(\text{O}_3\), the total number of valence electrons is \((3 \times 6) = 18\) valence electrons, or 9 electron pairs. A plausible Lewis structure is \(\overset{=}{\text{O}}—\overset{=}{\text{O}}—\overset{=}{\text{O}}\) (two most stable resonance contributors).

Thus, \(\text{O}_2\) should have the shortest O-to-O bond, because the O atoms are joined via a double bond. The single O—O bond in \(\text{H}_2\text{O}_2\) should be longest.

89. (E) 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 = \(\frac{145 + 143}{2} = 144 \text{ pm}\).

90. (M) In \(\text{H}_2\text{NOH}\), there are \((3 \times 1) + 5 + 6 = 14\) valence electrons total, or 7 electron pairs. N and O are the two central atoms. A plausible Lewis structure has zero formal charge on each atom. The N—H bond lengths are 100 pm, the O—H bond is 97 pm long, and the N—O bond is 136 pm in length. All values are taken from Table 10.2. All bond angles approximate the tetrahedral bond angle of 109.5º, but are expected to be somewhat smaller, perhaps by 2º to 4º each.
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91. (E) The reaction \( \text{O}_2(g) \rightarrow 2 \text{O}(g) \) 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.

92. (M) The net result of this reaction involves breaking one mole of \( \text{C}—\text{H} \) bonds (which requires 414 kJ) and forming one mole of \( \text{H}—\text{I} \) bonds (which produces 297 kJ). Thus, this reaction is endothermic (i.e., a net infusion of energy is necessary).

(b) The net result of this reaction involves breaking one mole of \( \text{H}—\text{H} \) bonds (which requires 436 kJ) and one mole of \( \text{I}—\text{I} \) bonds (which requires 151 kJ), along with forming two moles of \( \text{H}—\text{I} \) bonds (which produces \( 2 \times 297 = 594 \) kJ). Thus, this reaction is exothermic (just barely, mind you).

93. (M) The reaction in terms of Lewis structures is:

Analysis of the Lewis structures of products and reactants indicates that a \( \text{C}—\text{H} \) bond and a \( \text{Cl}—\text{Cl} \) bond are broken, and a \( \text{C}—\text{Cl} \) and a \( \text{H}—\text{Cl} \) bond are formed.

Energy required to break bonds: \( \text{C}—\text{H} + \text{Cl}—\text{Cl} = 414 + 243 = 657 \text{ kJ/mol} \)

Energy realized by forming bonds: \( \text{C}—\text{Cl} + \text{H}—\text{Cl} = 339 + 431 = 770 \text{ kJ/mol} \)

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

94. (M) The reaction in terms of Lewis structures is:

The net result is the breakage of an \( \text{O}—\text{O} \) bond (142 kJ/mol) and the formation of an \( \text{N}—\text{O} \) bond (222 kJ/mol). \( \Delta H = 142 \text{ kJ/mol} - 222 \text{ kJ/mol} = -80 \text{ kJ/mol} \)

95. (M) 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) \( \frac{1}{2}(\text{O}—\text{O}) + \frac{1}{2}(\text{H}—\text{H}) \rightarrow \text{O}—\text{H} \)

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

Bonds formed: \( \text{O}—\text{H} = 464 \text{ kJ} \)

\( \Delta H^\circ = 467 \text{ kJ} - 464 \text{ kJ} = 3 \text{ kJ/mol} \)

If the \( \text{O}—\text{H} \) bond dissociation energy of 428.0 kJ/mol from Figure 10-16 is used, \( \Delta H_f^\circ = 39 \text{ kJ/mol} \).
(b) \[ |N≡N| + 2 \text{H–H} \rightarrow H–\overline{N}–\overline{N}–\text{H} \]

Bonds broken = N ≡ N + 2 H — H = 946 kJ + 2 × 436 kJ = 1818 kJ
Bonds formed = N—N + 4 N—H = 163 kJ + 4 × 389 kJ = 1719 kJ
\[ \Delta H_f^\circ = 1818 \text{ kJ} - 1719 \text{ kJ} = 99 \text{ kJ} \]

96. (M) The reaction of Example 10-15 is \[ \text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g}) \]
\[ \Delta H_{\text{rxn}} = -113 \text{ kJ} \]. In Appendix D are the following values:
\[ \Delta H_f^\circ[\text{CH}_4(\text{g})] = -74.81 \text{ kJ}, \Delta H_f^\circ[\text{HCl}(\text{g})] = -92.31 \text{ kJ}, \Delta H_f^\circ[\text{Cl}_2(\text{g})] = 0 \]
Thus, we have
\[ \Delta H_{\text{rxn}} = \Delta H_f^\circ[\text{CH}_3\text{Cl}(\text{g})] + \Delta H_f^\circ[\text{HCl}(\text{g})] - \Delta H_f^\circ[\text{CH}_4(\text{g})] - \Delta H_f^\circ[\text{Cl}_2(\text{g})] \]
\[ -113 \text{ kJ} = -74.81 \text{ kJ} - (-74.81 \text{ kJ}) - (0.00) \]
\[ \Delta H_f^\circ[\text{CH}_3\text{Cl}(\text{g})] = -113 \text{ kJ} + 92.31 \text{ kJ} - 74.81 \text{ kJ} = -96 \text{ kJ} \]

97. (M) 
\[ \text{H--C≡C--H} + \text{H–H} \rightarrow \text{C≡C--H} \]

<table>
<thead>
<tr>
<th>Bonds broken</th>
<th>Energy change</th>
<th>Bonds formed</th>
<th>Energy change</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mol C≡C</td>
<td>1 × 837 kJ</td>
<td>1 mol C=C</td>
<td>1 × -611 kJ</td>
</tr>
<tr>
<td>1 mol H—H</td>
<td>1 × 436 kJ</td>
<td>2 mol C-H</td>
<td>2 × -414 kJ</td>
</tr>
</tbody>
</table>

Energy required to break bonds: +1273 kJ
Energy obtained upon bond formation: -1439 kJ
Overall energy change = 1273 kJ - 1439 kJ = -166 kJ/mol = \[ \Delta H_{\text{rxn}}^\circ \]

98. (M) First we must determine the value of \( \Delta H \) for reaction (2).
(1) \[ \text{C(s)} \rightarrow \text{C(g)} \quad \Delta H^\circ = 717 \text{ kJ/mol} \]
(2) \[ \text{C(g)} + 2 \text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) \quad \Delta H^\circ = ? \]

Net: \[ \text{C(s)} + 2 \text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) \quad \Delta H_f^\circ = -75 \text{ kJ/mol} \]
717 kJ + 75 kJ = -75 kJ or \[ \Delta H_f^\circ = -75 \text{ kJ} - 717 \text{ kJ} = -792 \text{ kJ} \]
To determine the energy of a C—H bond, we need to analyze reaction (2) in some detail.
In this reaction, 2 H—H bonds are broken and 4 C—H bonds are formed, resulting in the production of 792 kJ/mol.
Chapter 10: Chemical Bonding I: Basic Concepts

\[-792 \text{ kJ/mol} = \text{energy of broken bonds} - \text{energy of formed bonds}\]
\[= (2 \times 436 \text{ kJ/mol}) - (4 \times \text{C—H})\]

\[4 \times \text{C—H} = 792 \text{ kJ/mol} + (2 \times 436 \text{ kJ/mol}) = 1664 \text{ kJ/mol}\]

\[\text{C—H} = 1662 \div 4 = 416 \text{ kJ/mol} \text{ (compares favorably to the literature value of 414 kJ/mol)}\]

99. (M)

\[
\begin{array}{c}
\text{[} \begin{array}{c}
\text{O} \\
\text{N} \\
\text{O}
\end{array} \end{array} + \begin{array}{c}
\text{O} \\
\rightarrow
\end{array} \begin{array}{c}
\text{N=O} \\
\text{+ O=O}
\end{array}
\end{array}
\]

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

Using the calculated \(\Delta H_f\), we can calculate the \(\text{O\text{---N}}\) bond energy:

\[\Delta H_f = -(2 \times (\text{O:::N}) + 0) - (590 + 498) = -192.1\]

\(\text{O\text{---N}} = 448 \text{ kJ/mol}, \text{ which is between the values for N=O and N–O.}\)

100. (M)

\[
\begin{array}{c}
\text{[} \begin{array}{c}
\text{O} \\
\text{O} \\
\text{O}
\end{array} \end{array} + \begin{array}{c}
\text{O} \\
\rightarrow
\end{array} \begin{array}{c}
\text{2 O=O}
\end{array}
\end{array}
\]

\[\Delta H_f = -394 \text{ kJ}\]

\[\Delta H_f = 2(\text{O ::: O}) - 2(498) = -394 \text{ kJ/mol}\]

\(\text{O\text{---O}} = (-394 + 996) / 2 = 301 \text{ kJ/mol}, \text{ which is an intermediate value between O=O and O–O bond energies.}\)

**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. (M) 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

\[\Sigma(\text{bond energies}) = \Delta H = -744 \text{ kJ/mol reaction}\]
102. (M)
(a) There is at least one instance in which one atom must bear a formal charge—a polyatomic ion. In these cases, formal charges must be invoked to ensure that there be no more than one unpaired electron in the structure.

(b) Since three points define a plane, stating that a triatomic molecule is planar is just stating a reiteration of a fundamental tenet of geometry. In fact, it is misleading, for some triatomic molecules are actually linear. HCN is one example of a linear triatomic molecule, as is CO₂. Of course, some molecules with more than three atoms are also planar; two examples are XeF₄ and H₂C=CH₂.

(c) This statement is incorrect because in some molecules that contain polar bonds, the bonds are so oriented in space that there is no resulting molecular dipole moment. Examples of such molecules are CO₂, BeCl₃, CCl₄, PCl₅, and SF₆.

103. (M) First we determine the empirical formula of the compound, based on 100 g of compound.

\[
\text{amount } S = 47.5 \text{ g } S \times \frac{1 \text{ mol } S}{32.07 \text{ g } S} = 1.48 \text{ mol } S
\]

\[
\text{amount } Cl = 52.5 \text{ g } Cl \times \frac{1 \text{ mol } Cl}{35.45 \text{ g } Cl} = 1.48 \text{ mol } Cl
\]

The empirical formula of the compound is SCl. It has 6 + 7 = 13 valence electrons. A plausible, yet unsatisfactory, Lewis structure is \(\text{S} \equiv \text{Cl}\). Although there is zero formal charge on each atom in this structure, there is not an octet of electrons around sulfur. On the other hand, in S₂Cl₂ there is an octet of electrons around each atom. Thus a more plausible Lewis structure is \(\text{S} \equiv \text{S} \equiv \text{Cl} \equiv \text{Cl}\).

104. (M)

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

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

Because three moles of C weigh 36.0 g and four moles weigh 48.0 g, this hydrocarbon is C₃H₆.

A possible Lewis structure is \(\text{H} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{H}\).

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).

\[
\text{H} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{H}
\]

\[
\text{H} \text{H} \text{H} \text{H}
\]
105. (D) First we determine the empirical formula of this C, H compound.

\[
\text{amount } C \text{ = 4.04 g } \text{ CO}_2 \times \frac{1 \text{ mol } \text{ CO}_2}{44.01 \text{ g } \text{ CO}_2} \times \frac{1 \text{ mol } C}{1 \text{ mol } \text{ CO}_2} = 0.0.0918 \text{ mol } C + 0.0918 \rightarrow 1.00 \text{ mol } C
\]

\[
\text{amount } C = 1.24 \text{ g } \text{ H}_2\text{O} \times \frac{1 \text{ mol } \text{ H}_2\text{O}}{18.02 \text{ g } \text{ H}_2\text{O}} = 0.138 \text{ mol } \text{ H} + 0.0918 \rightarrow 1.50 \text{ mol } \text{ H}
\]

empirical formula = C$_2$H$_3$ possible molecular formula = C$_4$H$_6$

Lewis structure

\[
\text{H} \overline{\text{C}} \equiv \text{C} \cdot \text{H}
\]

There are several other isomers that share this molecular formula.

106. (M) The two isomers are \[\text{H} \equiv \text{C} \equiv \text{C} \equiv \text{H} \text{ and } \text{H} \equiv \text{C} \equiv \text{C} \equiv \text{H}\].

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≡C—H chain is linear, but the H$_3$C— molecular geometry is tetrahedral.

107. (M) There are three valid resonance forms for the N$_3^-$ ion; all three are shown below:

\[\Theta \text{N} \equiv \text{N} \equiv \text{N} \Theta \quad \text{2} \quad \text{3} \]

The best resonance form is the one with the lowest formal charge (all N have octets). Thus, resonance form 1 is the greatest contributor (probably the only contributor). The bond length give (116 pm) has a bond order between 2.0 (123 pm) and 3.0 (110 pm). This deviation from a bond order of 2 (double bond) can be explained by the formal charges in the ion which gives the bonds within the ion some partial ionic character.

108. (M) Because \[\Delta H^\circ_1 [\text{NO}(g)] = +90.25 \text{ kJ/mol}, \text{ thus } \frac{1}{2} \text{N}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{NO}(g)\]

has a \[\Delta H_{\text{rxn}} = 90.25 \text{ kJ/mol}. \quad \Delta H_{\text{rxn}} = \Delta H(\text{N = O}) - \frac{1}{2} \Delta H(\text{N = N}) - \frac{1}{2} \Delta H(\text{O = O})\]

The heat of reaction will be the algebraic sum of bonds broken (N$_2$ and O$_2$) and bonds formed (NO). Note that bond breaking requires energy, while bond making releases energy.

\[+90.25 \text{ kJ} = -\Delta H(\text{N = O}) - \left(\frac{946 \text{ kJ}}{2}\right) - \left(\frac{498 \text{ kJ}}{2}\right)\]

\[\Delta H(\text{N = O}) = (90.25 + 473 + 249) \text{ kJ/mol} = +632 \text{ kJ/mol}\]
109. (M) The HN$_3$ molecule has \(1 + (3 \times 5) = 16\) valence electrons, or 8 pairs. Average bond lengths are 136 pm for N\(\equiv\)N, 123 pm for N=\(\equiv\)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 \(\text{H} - \overline{\text{N}} = \overline{\text{N}} = \text{N}\). The three N’s lie on a line, with a 120° H\(\equiv\)N\(\equiv\)N bond angle:

\[
\text{H} - \overline{\text{N}} = \overline{\text{N}} = \text{N}
\]

Another valid resonance form is \(\text{H} - \overline{\text{N}} = \overline{\text{N}} = \text{N}\) which would have one N-N separation consistent with a nitrogen-nitrogen triple bond. It would also predict a tetrahedral H\(\equiv\)N\(\equiv\)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\(\equiv\)N\(\equiv\)N bond angle.

110. (D) For N$_5^+$ the number of valence electrons is \((5\times5)-1 = 24\). There are four possible Lewis structures with formal charges that are not excessive (<±2).

\[
\begin{align*}
\text{Structure 1} & : \text{N} \equiv \overline{\text{N}} = \overline{\text{N}} = \overline{\text{N}} = \text{N} \\
\text{Structure 2} & : \text{N} \equiv \overline{\text{N}} = \overline{\text{N}} = \text{N} \equiv \text{N} \\
\text{Structure 3} & : \text{N} \equiv \overline{\text{N}} - \overline{\text{N}} = \text{N} = \text{N} \\
\text{Structure 4} & : \text{N} \equiv \overline{\text{N}} - \overline{\text{N}} = \text{N} \equiv \text{N}
\end{align*}
\]

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.)

111. (M) The carbon-carbon distances of 130 pm are close to those of a C\(\equiv\)C double bond, (134 pm). The carbon-oxygen distances of 120 pm are close to that of a C\(\equiv\)O double bond, 123 pm. In C$_3$O$_2$ there are \(3 \times 4 + 2 \times 6 = 24\) valence electrons or 12 valence electron pairs. The molecule is almost certainly linear. A plausible Lewis structure follows.

\[
\overline{\text{O}} = \text{C} \equiv \text{C} \equiv \text{C} = \overline{\text{O}}
\]
112. (M) In PCl₅ there are $5 + 5 \times 7 = 40$ valence electrons = 20 pairs. The Lewis structures are shown below. Since there are five atoms and no lone pairs attached to the central atom, the electron-group geometry and molecular shape of the molecule are the same, namely, trigonal bipyramidal. In PCl₄⁺ there are $5 + 4 \times 7 - 1 = 32$ valence electrons = 16 pairs. Since there are four atoms and no lone pairs bonded to the central atom, the electron-group geometry and molecular shape of the species are the same, namely, tetrahedral. In PCl₆⁻ there are $5 + 6 \times 7 + 1 = 48$ valence electrons = 24 pairs. Since there are six atoms and no lone pairs bonded to the central atom, the electron-group geometry and molecular shape of the species are the same, namely, octahedral.

$$\text{PCl}_5 \quad \text{PCl}_4^+ \quad \text{PCl}_6^-$$

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

$$\begin{align*}
&\text{N} \equiv \text{N} \quad \text{H} \equiv \text{H} \quad \text{H} \equiv \text{C} \equiv \text{N} \\
&\text{Bonds broken} = \frac{1}{2} \text{N} \equiv \text{N} + \frac{1}{2} \text{H} \equiv \text{H} = \frac{1}{2} \text{(946 kJ + 436 kJ)} = 691 \text{ kJ} \\
&\text{Bonds formed} = \text{H} \equiv \text{C} + \text{C} \equiv \text{N} = 414 \text{ kJ} + 891 \text{ kJ} = 1305 \text{ kJ} \\
&\Delta H = 691 \text{ kJ} - 1305 \text{ kJ} = -614 \text{ kJ} \\
&\text{Then we determine } \Delta H^\circ \text{.} \\
&(a) \quad \text{C(s)} \rightarrow \text{C(g)} \quad \Delta H = 717 \text{ kJ} \\
&(b) \quad \text{C(g)} + \frac{1}{2} \text{N}_2(g) + \frac{1}{2} \text{H}_2(g) \rightarrow \text{HCN(g)} \quad \Delta H = -614 \text{ kJ} \\
&\text{Net: C(s) + } \frac{1}{2} \text{N}_2(g) + \frac{1}{2} \text{H}_2(g) \rightarrow \text{HCN(g)} \quad \Delta H^\circ = +103 \text{ kJ} \\
&\text{This compares favorably to the value of 135.1 kJ/mol given in Appendix D-2.}
\end{align*}$$

114. (M) We analyze the formation reaction for H₂O₂(g) via the use of Lewis structures.

$$\begin{align*}
&\text{H}_2 + \text{O} \equiv \text{O} \rightarrow \text{H} \equiv \text{O} \equiv \text{O} \equiv \text{H} \\
&\text{Bonds broken} = \text{H} \equiv \text{H} + \text{O} \equiv \text{O} \\
&\text{Energy required: 436 kJ + 498 kJ = 934 kJ} \\
&\text{Bonds formed} = 2(\text{H} \equiv \text{O}) + \text{O} \equiv \text{O} \\
&\text{Energy released: 2} \times 464 \text{ kJ} + \text{O} \equiv \text{O} = 928 \text{ kJ} + \text{O} \equiv \text{O} \\
&\Delta H^\circ \text{f} = -136 \text{ kJ} = 934 \text{ kJ} - 928 \text{ kJ} - \text{O} \equiv \text{O} \\
&\text{Bond energy } (\text{O} \equiv \text{O}) = 142 \text{ kJ} \\
&\text{This is the same as the value in Table 10.3.}
\end{align*}$$
115. (D) Ambiguity arises because of uncertainty over (i) bond order between C and S and (ii) the position of the H atoms

116. (M) We first compute the heats of reaction.

\[ \text{CH}_3\text{OH}(g) + \text{H}_2\text{S}(g) \rightarrow \text{CH}_3\text{SH}(g) + \text{H}_2\text{O}(g) \]

\[ \Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{f}[\text{H}_2\text{O}(g)] + \Delta H^\circ_{f}[\text{CH}_3\text{SH}(g)] - \left[ \Delta H^\circ_{f}[\text{CH}_3\text{OH}(g)] + \Delta H^\circ_{f}[\text{H}_2\text{S}(g)] \right] \]

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

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

\[ \Sigma \text{bond energies} = \Delta H^\circ_{\text{rxn}} = -43.4 \text{ kJ} \]

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).
117. (M)

\[
\begin{align*}
\text{Li} & \quad \text{Br} \quad 217 \text{ pm} \quad \mu = 7.268 \text{ D} \quad \Delta \text{EN} = 1.7 \\
\text{Na} & \quad \text{Cl} \quad 236 \text{ pm} \quad \mu = 7.268 \text{ D} \quad \Delta \text{EN} = 2.1
\end{align*}
\]

(a) \[
\begin{align*}
\delta_{\text{Li-Br}} &= \frac{\mu \times 3.34 \times 10^{-30} \text{ CmD}^{-1}}{d} = \frac{7.268 \text{ D} \times 3.34 \times 10^{-30} \text{ CmD}^{-1}}{217 \times 10^{-12} \text{ m}} \approx 1.12 \times 10^{-19} \text{ C (} \approx 70\% \text{ ionic)}
\\
\delta_{\text{Na-Cl}} &= \frac{\mu \times 3.34 \times 10^{-30} \text{ CmD}^{-1}}{d} = \frac{9.001 \text{ D} \times 3.34 \times 10^{-30} \text{ CmD}^{-1}}{236 \times 10^{-12} \text{ m}} \approx 1.27 \times 10^{-19} \text{ C (} \approx 80\% \text{ ionic)}
\end{align*}
\]

(b) Using the $\Delta \text{EN}$ values for each gas phase species and Figure 10-7, we can estimate that Li-Br $\sim 50\%$ ionic and Na-Cl $\sim 70\%$ ionic.

(c) The value for NaCl agrees quite well, however, LiBr does not show as good an agreement. This is probably due to the large lone pairs on Br, the small size of the Li atom (especially relative to the Br atom), and the fact that the Li atom does not have much shielding. As well, bear in mind that these are very loosely associated atoms.

118. (M) IF$_7$ has a pentagonal bipyramidal structure, with the following internal angles:

- 180° angle for F$_a$–I–F$_a$
- 90° angle for F$_a$–I–F$_b$
- 72° angle for F$_b$–I–F$_b$
- I is $sp^3d^2$ (7-electron regions around central atom)
119. (D) Consider the possible resonance forms for each acid (shown below).

Note: All of these carboxylic acids display delocalization of the negative charge across the carboxylate group. Let’s consider each acid in turn, to assess the stability of the anion/acidity of the acid.

Acetic acid
In the case of acetic acid (1A and 1B), the hydrogen atoms do not contribute to the stability of the anion. In fact, one might argue that the hydrogen atoms with an electronegativity of 2.1, donates electron density to the adjacent (α) carbon and thus offsets delocalization of the negative charge on the anion.

Fluoroacetic acid
In the case of fluoroacetic acid (2A and 2B), other than the carboxylate resonance forms, the fluorine atom does not contribute significantly to the stability of the anion by way of resonance. However, fluorine is quite electronegative compared to carbon, resulting in the development of a partial positive charge on the α-carbon. This allows for more extensive delocalization of the negative charge on the anions, which leads to greater stability for the anion.

Cyanoacetic acid
In the case of cyanoacetic acid (3A to 3D), we clearly see the carboxylate resonance delocalization. However, there are resonance forms in the cyano group that result in a formally positively charged carbon (carbocation) being directly bonded to the α-carbon. This will allow for more complete delocalization of negative charge on the anion. There is one problem, however. The resonance forms for the cyano group do not leave the carbon...
atom with the formal positive charge in the cyano group with a complete octet. Although
the cyano group is electron withdrawing, it behaves very much like a very electronegative
halide by virtue of the fact that a very electronegative nitrogen is directly bonded to carbon
in the cyano group. This results in a slightly positive charge on the carbon attached to the
$\alpha$-carbon, resulting in significant delocalization of the negative charge on the anion.

Nitroacetic acid
In the case of nitroacetic acid (4A to 4B), we clearly see the carboxylate resonance
delocalization. However, there are resonance forms in the nitro group that result in the
development of a positive formal charge on the nitrogen atom directly bonded to the $\alpha$-
carbon. This will significantly allow for the delocalization of negative charge on the anion.
Unlike the cyano group, the nitro group has a formal positive charge on nitrogen and
complete octets for all the second row atoms in the acid. Thus, the nitro group will allow
for the most delocalization of the negative charge on the anion, which makes nitroacetic
acid the strongest of the four acids and the nitroacetate ion the most stable conjugate base.

The acids in order of strength should be: nitroacetic $>$ cyanoacetic $>$ fluoroacetic $>$ acetic.

120. (M) For the halogens we have the following data:

<table>
<thead>
<tr>
<th>Atom</th>
<th>Electronegativity</th>
<th>Ionization Energy (kJ/mol)</th>
<th>Electron Affinity (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>4.0</td>
<td>1680</td>
<td>-328</td>
</tr>
<tr>
<td>Cl</td>
<td>3.0</td>
<td>1256</td>
<td>-349</td>
</tr>
<tr>
<td>Br</td>
<td>2.8</td>
<td>1143</td>
<td>-324.6</td>
</tr>
<tr>
<td>I</td>
<td>2.5</td>
<td>1009</td>
<td>-295.2</td>
</tr>
</tbody>
</table>

From the data above and using $\chi = k \times (IE - EA)$ for the halogens, we find the following
values for $k$: F = 0.00199, Cl = 0.00187, Br = 0.00191, I = 0.00192.

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.

$\chi = k \times (IE - EA) = 2.2 = 0.00199(900-EA)$  $EA \sim -260$ kJ/mol

121. (M) Structure (a) has too many electrons, resulting in a molecule with an overall charge of
-2 (each sulfur has a formal charge of -1). Structure (b) has formal charges of +1 on each
sulfur atom and -1 on each Cl atom. Structure (c) has considerable formal charge built up
in this Lewis structure (each sulfur carries a formal charge of -2 and each chlorine carries a
formal charge of +2). Both structures (d) and (e) have no formal charges in the Lewis
structure and may be considered “good” Lewis structures, however, structure (d) has 10
electrons around each sulfur (expanded octet), while in structure (e), all atoms have an
octet. Given this information, structure (e) best represents the molecule, however, one
cannot rule out structure (d) completely based solely on the expanded octet, especially
since S has vacant 3 d orbitals that may be used in expanding its octet. Read Section 10-6:
Expanded Octets.
122. (D) The molecules hydrogen azide, nitrosyl azide and trifluoromethyl azide share some common structural elements. They can be viewed as N$_3^-$ attached to H, NO, and CF$_3$ respectively. There are numerous resonance structures that can be written for these molecules. Some of the resonance forms are better than others for several reasons, including such factors as the lack of a full octet and unacceptably large charge separations. Drawn below are the various resonance forms for the molecules. The Lewis diagrams have been modified to include geometric considerations that are imposed on the molecule by hybridization and the effects of lone pairs.

Let’s consider each molecule in turn.

Hydrogen azide (linear N-N-N):

\[
\begin{align*}
\text{(A) Good resonance forms} & \quad \text{(C) Poor resonance form (charge buildup)} \\
\text{(B) Good resonance forms} & \quad \text{(D) Good resonance forms} \\
\end{align*}
\]

Resonance forms (A) and (B) are the best, owing to low formal charges. (C) is clearly not an important an resonance contributor because it possess two adjacent like charges. Note that the molecule should be bent at the hydrogen bonded nitrogen.

Hydrogen azide(cyclic form):

\[
\begin{align*}
\text{(D) Very strained ring (no formal charges)} & \quad \text{(E) Good resonance forms} \\
\text{(F) Good resonance forms} & \quad \text{(G) Good resonance forms} \\
\end{align*}
\]

Resonance form (D) is clearly favored because all of the atoms have a formal charge of zero. This structural isomer would be highly reactive owing to the very strained ring which imposes internal N-N-N angles that approach ~ 60° and a hybridization scheme that tries to accommodate both 120 or 109.5° angles.

Trifluoromethyl azide:

\[
\begin{align*}
\text{(G) Good resonance forms} & \quad \text{(H) Good resonance forms} \\
\text{(I) Poor resonance form (charge buildup)} & \quad \text{(J) Poor resonance form} \\
\end{align*}
\]

Resonance forms (G) and (H) are the best, owing to low formal charges for the constituent atoms. Structure (I) is clearly not as important a resonance contributor because it contains...
destabilizing adjacent positive charges. The molecule is expected to be very reactive and hence hard to isolate.

Nitrosyl azide

Best resonance forms (small distance between charge separation)

\[
\begin{align*}
\text{Poor resonance forms} & \quad \text{(charge buildup)} \\
\text{Good resonance forms (however, large charge separation)} & \quad \text{(small distance between charge separation)}
\end{align*}
\]

Nitrosyl azide is a bent molecule. Based on the best two Lewis structures, we expect that the molecule is bent at the two leftmost nitrogen atoms (~ 115 ° ± 20 °).

123. (M) Consider each molecule separately:

B\(_2\)F\(_4\): A total of 34 electrons. Neutral molecule. There are no formal charges in the molecule. Free rotation about single bond, with the possibility of all atoms being planar. There are no valid resonance forms.

N\(_2\)O\(_4\): A total of 34 electrons. Neutral molecule with formal charges. Free rotation about single bond, with the possibility of all atoms being planar. There are 3 valid resonance forms.

C\(_2\)O\(_4\)^{2-}: A total of 34 electrons. Must be the dianion where the formal charges add to the overall charge of the anion. Free rotation about single bond, with the possibility of all atoms being planar. There are 3 valid resonance forms.
124. (M) Shown below is the deprotonation and the expected resonance stabilized enolate product, which has two forms (A and B below). In structure A, the negative charge is on the CH₂ carbon atom and in structure B it is on the oxygen atom. Both of these resonance forms will contribute to the hybrid structure of the anion. Structure A is desirable in that it possess a very strong C = O bond (relative to the weaker C = C bond in B). Structure B has the negative charge on oxygen, the more electronegative atom, which is better able to accommodate the negative charge.

\[
\begin{align*}
\text{H}_2\text{C} & \text{C} \text{C} \text{H} \\
\text{Br} & \text{H} \text{H} \text{H} \\
\text{strong base} & \text{-H}^+ \\
\rightarrow & \\
\text{H}_2\text{C} & \text{C} \text{C} \text{H} \\
\text{H} & \text{H} \text{H} \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{C} & \text{C} \text{C} \text{H} \\
\text{H} & \text{H} \text{H} \text{H} \\
\text{A} & \\
\text{B} &
\end{align*}
\]

125. (M) The anion PBr₄⁻ has 34 electrons. Its electronic geometry is trigonal bypyramidal, while ideally, its molecular geometry is expected to be a see-saw. Since phosphorus is a relatively small atom and bromine is a relatively large atom, significant distortions may exist in the anion such that the bromine atoms distribute themselves more evenly around the phosphorus centre. With extensive delocalization of the phosphorus lone pair over the four bromine atoms, the structure will approach a pure tetrahedron. Even if the lone pair stays localized on the phosphorus, the geometry may well appear to be tetrahedral, albeit distorted (see below).

\[
\begin{align*}
\text{Trigonal} & \text{ bipyramidal} \\
\text{rotate} & \text{45°} \\
\text{remove one} & \text{equatorial lone pair} \\
\text{distorted tetrahedral} & \\
\text{tetrahedral} &
\end{align*}
\]

126. (a) Sulfur in the form of S₈ is not planar, because each sulfur atom in the S₈ ring has a tetrahedral electron group geometry. Below is the drawing of a flat S₈ ring, which is provided to show a simplified Lewis structure, accompanied with the actual shape of the S₈ ring:

\[
\begin{align*}
\text{Simplified Lewis diagram of S₈ ring} & \\
\text{Actual structure} &
\end{align*}
\]
Simplified Lewis diagram of oxidized $S_8$ ring

Actual structure

127. (M)

(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. (M)

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

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

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

(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 H−Cl bond is 20% ionic. These values are in good agreement with each other.
129. (D)

(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 $52.0^\circ$ angle in the figure is one-half of the $104^\circ$ bond angle in water. The length is given as 1.84 D. We can construct a right angled triangle by bisecting the $76.0^\circ$ angle. The right angled triangle has a hypotenuse = O—H bond dipole and the two other angles are $52^\circ$ and $38^\circ$. The side opposite the bisected $76.0^\circ$ angles is $\frac{1}{2} (1.84 \text{ D}) = 0.92 \text{ D}$. We can calculate the bond dipole using: $\sin 38.0^\circ = \frac{0.92 \text{ D}}{\text{O-H bond dipole}} = 0.61566$, hence O—H bond dipole = 1.49 D.

(b) For H$_2$S, we do not know the bond angle. We shall represent this bond angle as $2\alpha$. Using a similar procedure to that described in part (a), above, a diagram can be constructed and the angle $2\alpha$ calculated as follows:

\[
\cos \alpha = \frac{1}{2} \left( \frac{0.93 \text{ D}}{0.67 \text{ D}} \right) = 0.694 \quad \alpha = 46.05^\circ
\]

or $2\alpha = 92.1^\circ$

The H—S—H angle is approximately 92°.

(c)

Molecule and associated individual bond dipoles

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

Geometric Relationship

Mathematical solution: $\sin (\phi) = \frac{0.25 \text{ D}}{1.87 \text{ D}} \quad \phi = 7.6^\circ$

The H-C-Cl bond angle is $(90 + \phi)^\circ = 90^\circ + 7.6^\circ = 97.6^\circ$
130. (D) Step 1 in the alternative approach is similar to the first step in the method used for drawing Lewis structures. The only significant difference is that "electron pairs" rather than the total number of valence electrons are counted in this alternative approach. The second step in the alternative strategy is also similar to the second step for writing Lewis structures. By counting the number of bonding electron pairs in the alternative method, one is effectively working out the number of bonds present in the skeletal structure of the Lewis diagram. In step 3, the number of electron pairs surrounding the central atom is calculated. This is basically the same procedure as completing the octets for the terminal atoms and assigning the remaining electrons to the central atom in the Lewis structure. Finally, in step 4 of the alternative method, the number of lone pair electrons on the central atom is calculated. This number, together with the result from step 3, allows one to establish the VSEPR class. Consequently, both the alternative strategy and the Lewis diagram provide the number of bonding electron pairs and lone pairs on the central atom for the species whose shape is being predicted. Since the shape of the molecule or ion in the VSEPR approach is determined solely by the number and types of electron pairs on the central atom (i.e., the VSEPR class) both methods end up giving the same result.

Included in the "alternative strategy" is the assumption that the central atom does not form double bonds with any of the terminal atoms. This means that in many instances, the central atom does not possess a complete octet. The presence or absence of an octet is, however, of no consequence to the VSEPR method because, according to the tenets of this theory, the shape adopted by the molecule is determined solely by the number and types of electron pairs on the central atom. Examples follow on the next two pages.

(a) PCl$_5$

1. Total e$^-$ pairs = \( \frac{(1 \times 5e^- \text{ from P atom}) + (5 \times 7e^- \text{ from the 5 Cl atoms})}{2} = 20 \text{ pairs of } e^- \)
2. Number of bonding e$^-$ pairs = 6 atoms \( (5\times\text{Cl} + 1\times\text{P}) - 1 = 5 \text{ bonding } e^- \text{ pairs.} \)
3. Number of e$^-$ pairs around the central atom = \( (20(\text{total } e^- \text{ pairs}) - 3\times(5 \text{ terminal Cl}) = 5 \text{ e}^- \text{ pairs around P atom.} \)
4. Number of lone pair e$^-$ = 5 e$^-$ pairs around P → 5 bonding pairs of e$^- = 0$

Thus, according to this alternative approach, PCl$_5$ belongs to the VSEPR class AX$_5$. Molecules of this type adopt a trigonal bipyramidal structure.
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(b) \( \text{NH}_3 \)
1. Total e\(^-\) pairs =
\[
\frac{(1 \times 5e^- \text{ from N atom}) + (3 \times 1 e^- \text{ from the 3 H atoms})}{2} = 4 \text{ pairs of } e^- \\
\]
2. Number of bonding e\(^-\) pairs = 4 atoms \((1 \times N + 3 \times H) - 1 = 3\text{ bonding } e^- \text{ pairs.} \)
3. Number of e\(^-\) pairs around the central atom = 4(total) e\(^-\) pairs \(-\) 0
   = 4 e\(^-\) pairs around N atom.
4. Number of lone pair e\(^-\) = 4 e\(^-\) pairs around N \(-\) 3 bonding pairs of e\(^-\) = 1 lone pair of e\(^-\)

Thus, according to this alternative approach, \( \text{NH}_3 \) belongs to the VSEPR class AX\(_3\)E. Molecules of this type adopt a trigonal pyramidal structure.

(c) \( \text{ClF}_3 \)
1. Total e\(^-\) pairs = \[
\frac{(1 \times 7e^- \text{ from Cl atom}) + (3 \times 7e^- \text{ from the 3 F atoms})}{2} = 14 \text{ e}^- \text{ pairs} \\
\]
2. Number of bonding e\(^-\) pairs = 4 atoms \((1 \times Cl + 3 \times F) - 1 = 3\text{ bonding } e^- \text{ pairs.} \)
3. Number of e\(^-\) pairs around the central atom = 14(total) pairs \(-\) 3\times(3 terminal F atoms)
   = 5 e\(^-\) pairs around Cl atom.
4. Number of lone pair e\(^-\) = 5 e\(^-\) pairs around Cl \(-\) 3 bonding pairs of e\(^-\) = 1 lone pair of e\(^-\)

Thus, according to this alternative approach, \( \text{ClF}_3 \) belongs to the VSEPR class AX\(_3\)E\(_2\). Molecules of this type adopt a T-shaped structure.

(d) \( \text{SO}_2 \)
1. Total e\(^-\) pairs = \[
\frac{(1 \times 6e^- \text{ from S atom}) + (2 \times 6e^- \text{ from the 2 O atoms})}{2} = 9 \text{ e}^- \text{ pairs} \\
\]
2. Number of bonding e\(^-\) pairs = 3 atoms \((1 \times S + 2 \times O) - 1 = 2\text{ bonding } e^- \text{ pairs.} \)
3. Number of e\(^-\) pairs around the central atom = 9(total) pairs \(-\) 3\times(2 terminal O atoms)
   = 3 e\(^-\) pairs around S atom.
4. Number of lone pair e\(^-\) = 3 e\(^-\) pairs around S \(-\) 2 bonding pairs of e\(^-\) = 1 lone pair of e\(^-\)

Thus, according to this alternative approach, \( \text{SO}_2 \) belongs to the VSEPR class AX\(_2\)E. Molecules of this type adopt a bent structure.

(e) \( \text{ClF}_4^- \)
1. Total e\(^-\) pairs = \[
\frac{(1 \times 7e^- \text{ from Cl}) + (4 \times 7e^- \text{ from the 4 F}) + (1e^- \text{ for charge of -1})}{2} = 18 \text{ pairs of } e^- \\
\]
2. Number of bonding e\(^-\) pairs = 5 atoms \((1 \times Cl + 4 \times F) - 1 = 4\text{ bonding } e^- \text{ pairs.} \)
3. Number of e\(^-\) pairs around the central atom = 18(total) pairs \(-\) 3\times(4 terminal F atoms)
   = 6 e\(^-\) pairs around Cl atom.
4. Number of lone pair e\(^-\) = 6 e\(^-\) pairs around Cl \(-\) 4 bonding pairs of e\(^-\) = 2 lone pair of e\(^-\)

Thus, according to this alternative approach, \( \text{ClF}_4^- \) belongs to the VSEPR class AX\(_4\)E\(_2\). Molecules of this type adopt a square planar structure.
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(f) \( \text{PCl}_4^+ \)

1. Total \( e^- \) pairs = \( \frac{(1 \times 5e^- \text{ from P}) + (4 \times 7e^- \text{ from the 4 Cl}) - (1e^- \text{ for } +1 \text{ charge})}{2} \)
   = 16 pairs of \( e^- \)

2. Number of bonding \( e^- \) pairs = 5 atoms \( (4\times \text{Cl} + 1\times \text{P}) - 1 = 4 \) bonding \( e^- \) pairs.

3. Number of \( e^- \) pairs around the central atom = 16 (total) pairs - 3 (4 terminal Cl atoms)
   = 4 \( e^- \) pairs around P atom.

4. Number of lone pair \( e^- \) = 4 \( e^- \) pairs around P - 4 bonding pairs of \( e^- = 0 \)

Thus, according to this alternative approach, \( \text{ClF}_4^+ \) belongs to the VSEPR class AX_4. Molecules of this type adopt a tetrahedral structure.

**SELF-ASSESSMENT EXERCISES**

131. (E)
   
   (a) Valence electrons: Electrons in the outermost shell of an atom which are involved in the bonding
   
   (b) Electronegativity: A measure of atoms competing for electrons with other atoms
   
   (c) Bond dissociation energy: The energy required to break a covalent bond
   
   (d) Double covalent bond: A sharing of two pairs of electrons between two atoms
   
   (e) Coordinate covalent bond: A covalent bond in which one atom contributes both electrons to make a bond

132. (E)
   
   (a) Formal charge: The apparent (but not necessarily actual) charge on an atom derived from the Lewis structure based on the number of valence, shared, and unshared electrons
   
   (b) Resonance: For a given compound, resonance means two or more Lewis structures, which contribute to the final “correct” structure
   
   (c) Expanded valence shell: When an atom in a molecule can accommodate more than 8 electrons in its valence shell (happens usually with p-block atoms in the 3p or higher subshells such as S, P, As, etc., because they can use their empty d subshells for the extra electrons)
   
   (d) Bond energy: The energy released when a bond is formed.

133. (E)
   
   (a) Ionic and covalent bonds: In ionic bonds, there is no sharing of electrons, but rather a complete transfer of electrons from one atom to another. In covalent bonds, there is sharing of a pair (or more) of electrons between two atoms.
   
   (b) Lone-pair and bond-pair electrons: Lone pairs are electron pairs entirely localized on one atom. Bond pairs are pairs of electrons shared between two atoms.
(c) Molecular geometry and electron-group geometry: Molecular geometry only considers arrangement of atoms, and is influenced by the lone pairs. An electron-group geometry ignores the atoms and determines the ultimate geometry using electron pairs only.

(d) Bond dipole and resultant dipole moment: Bond dipole is a measure of the difference in electron densities between two bonded atoms as a result of the difference in their electronegativities. The resultant dipole moment is a measure of the polarity of the molecule derived from individual bond dipoles and the molecular geometry.

(e) Polar molecules and non-polar molecules: Polar molecules have a net dipole moment, whereas non-polar molecules do not.

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

\[ \text{\text{C}}=\text{\text{N}} \]

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

\[ \text{O}==\text{N}==\text{O} \]

Formal charge on O is: \(6 - 4 - 2 = 0\)

136. (E) The answer is (a), SO\(_2\). NO is linear by definition since there are only two atoms. The other molecules have the following structures:

\[ \text{O}==\text{S}==\text{O} \quad \text{O}==\text{C}==\text{O} \quad \text{H}==\text{C}==\text{N} \]

137. (E) The answer is (a), SO\(_3\). The other choices are polar, because: CH\(_2\)Cl\(_2\) 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. (E) The answer is (b), N\(_2\), because one has to break three covalent bonds to dissociate the two N atoms from each other.

139. (E) 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. (M)

(a)

\[ \text{O}==\text{Cl}==\text{O} \]

(b)

\[ \text{F}==\text{P}==\text{F} \]
141. (M) 

<table>
<thead>
<tr>
<th>Group</th>
<th>Bond Length (pm)</th>
<th>Bond Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C−H</td>
<td>110</td>
<td>414</td>
</tr>
<tr>
<td>C=O</td>
<td>120</td>
<td>736</td>
</tr>
<tr>
<td>C−C</td>
<td>154</td>
<td>347</td>
</tr>
<tr>
<td>C−Cl</td>
<td>178</td>
<td>339</td>
</tr>
</tbody>
</table>

142. (E) 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. (E) 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.

144. (E) The structure of the NH₃ 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. (E) A pyramidal geometry is observed when an atom has one lone pair and is bonded to three other atoms (AX₃E). A bent geometry is observed when an atom has two lone pairs and is bonded to two other atoms (AX₂E₂). For both, the bond angles will be approximately (usually smaller than) 109°.

147. (M)

148. (M) The way to approach this concept map is to break it down to three major topics: Lewis dot structures, shape of molecule, and polarity. Lewis dot structures can be divided into simpler subtopics, such as Lewis symbols, the 8-electron rule, and the expanded valence shell. Molecular shape can be divided into molecular geometry and electron-group geometry. Polarity can be described in terms of dipole moment of the molecule, which can itself be described in terms of bond dipole and molecular geometry.