Solutions to Additional Bonding Problems

1. For the following examples, the valence electron count is placed in parentheses after the empirical formula and only the resonance structures that satisfy the octet rule are given.

\[
H_2C=NH \quad (12)
\]

\[
C_6H_6 \quad (30)
\]

\[
H_2CCO \quad (16)
\]

\[
HN_3 \quad (16)
\]

2. \(H_2CNH\) -- Only 1 resonance structure: the formal charges on all the atoms = 0.

\(C_6H_6\) -- 2 possible resonance structures: the formal charges on all the atoms = 0. The actual structure is an equal mixture of the 2 resonance structures.
Since (a) involves no separation of formal charges, it makes a much larger contribution to the actual structure of HC(O)NH$_2$ than does (b).

Since structure (c) involves (i) separating larger formal charges of opposite sign and (ii) placing like formal charges at a small separation corresponding to the NºN bond length, it will make a much smaller contribution than either (a) or (b). Structure (a) involves separating +1 and –1 formal charges to an N=N distance; structure (b) involves separating +1 and –1 formal charges to an N–N distance. Since the N=N distance (a double bond) is considerably shorter than the N–N distance (a single bond) we expect resonance structure (a) to make a larger contribution to the actual structure of HN$_3$ than does resonance structure (b).

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**Diagrams:**

(a) \[ \text{HC(O)NH}_2 \]

(b) \[ \text{HN}_3 \]

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**Contributions**

(a) \( \gg \) (b)

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**Resonance structures for HN$_3$:**

(a) \[ \text{HN}_3 \]

(b) \[ \text{HN}_3 \]

(c) \[ \text{HN}_3 \]

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**Bond Angles:**

- \( \times \text{ClOCl} = 109.5^\circ \)
- \( \times \text{HPH} = 109.5^\circ \)
- \( \Delta \text{FAsF} = 109.5^\circ \)
- \( \Delta \text{FBrF} = 90^\circ \)
4. SCl₂: The central atom is S. The number of valence electrons = 6 (from S) + 14 (7 from each Cl) = 20. Trial structure: \( \text{Cl} - \tilde{\text{S}} - \text{Cl} \): uses 20 electrons. There are 4 electron pairs around S. Since there are two Cl atoms there must be 2 bonding pairs of electrons and 2 non-bonding pairs. By VSEPR theory, the electron pair geometry will be tetrahedral. However, \( \text{Cl} - \tilde{\text{S}} - \text{Cl} \) will be somewhat less than 109.5° because of the larger size of the non-bonding pairs. Recall, non-bonding–bonding pair repulsion > bonding pair–bonding pair repulsion. This result is consistent with the experimental bond angle of 100.3°.

5. NO₂⁺: No. of valence of electrons = 2 (6) + 5 – 1 (for the positive charge) = 16. Trial structure: \( \tilde{\text{O}} - \tilde{\text{N}} - \tilde{\text{O}} \): uses 20 electrons. Introduce 1 triple bond or 2 double bonds. Possible resonance structures are:
In (a) there are 4 pairs of valence electrons around the central atom N. Since the N=O bonds are double bonds there are only 2 electron groups around the central atom. The bonding pairs geometry around N is linear. All electron groups are bonding so the molecular geometry is linear.

In NO₂, there are 9 valence electrons around N. The main resonance structure is

\[
\overset{\ddots}{\mathrm{O}} \quad \overset{\ddots}{\mathrm{N}} \quad \overset{\ddots}{\mathrm{O}}
\]

Thus, there are 4 pairs of electrons and one odd electron around N but only 3 groups. The idealized electron group geometry is trigonal planar.

\[
\overset{\ddots}{\mathrm{O}} \quad \overset{\ddots}{\mathrm{N}} \quad \overset{\ddots}{\mathrm{O}}
\]

The actual O–N–O angle will increase somewhat to a value >120°.

In NO₂⁻, there are 18 valence electrons: the actual structure is a resonance hybrid (equal mixture of (a) and (b) taken together). For a discussion of the angle consider (a). There are 8 valence electrons around N:

\[
\left[ \overset{\ddots}{\mathrm{O}} \quad \overset{\ddots}{\mathrm{N}} \quad \overset{\ddots}{\mathrm{O}} \right]^{-} \quad \left[ \overset{\ddots}{\mathrm{O}} \quad \overset{\ddots}{\mathrm{N}} \quad \overset{\ddots}{\mathrm{O}} \right]^{-}
\]

There are 4 electron pairs but since there is one double bond there are only 3 electron groups. The idealized electron group geometry is trigonal planar. Strong repulsion between the non-bonding electron pair and the bonding pairs will result in a decrease of the O–N–O angle to a value somewhat smaller than 120°.

6. The first step is to write down all the Lewis structures for CH₃COOH and CH₃COO⁻ which satisfy the octet rule:

CH₃COOH (24 valence electrons). Possible Lewis structures are:

\[
\left[ \overset{\ddots}{\mathrm{H}} \quad \overset{\ddots}{\mathrm{C}} \quad \overset{\ddots}{\mathrm{C}} \quad \overset{\ddots}{\mathrm{O}} \quad \overset{\ddots}{\mathrm{H}} \right] \quad \left[ \overset{\ddots}{\mathrm{H}} \quad \overset{\ddots}{\mathrm{C}} \quad \overset{\ddots}{\mathrm{C}} \quad \overset{\ddots}{\mathrm{O}} \quad \overset{\ddots}{\mathrm{H}} \right]
\]
The relative importance of these structures is (a) >> (b). The CO$_2$ bond is much closer to a CO double bond than it is to a CO single bond. In contrast, the CO$_3$ bond is much closer to a CO single bond than it is to a C – O double bond. The two CO bonds in CH$_3$COOH differ in length.

CH$_3$COO$^-$ (24 valence electrons). Possible Lewis structures are:

(a) 

(b) 

The relative importance of these structures is (a) = (b). Each CO bond in CH$_3$COO$^-$ is 1.5 times the strength of a single CO bond. We expect the two CO bonds to be of the same length and to be shorter than the length of a CO single bond, but longer than the length of a CO double bond.

7. (a) NCO$^-$ (16 valence electrons). Lewis structures which obey the octet rule are:

(a) 

(b) 

(c) 

To compute the formal charges we follow the procedure presented in the text. This procedure leads to the following formal charges in each of the above structures:

\[
\begin{array}{cccc}
0 & 0 & -1 & -1 \\
N & C & O & N \\
C & O & N & O \\
\end{array}
\]

From these formal charges, we see that only structure (c) involves any separation of formal charge; structures (a) and (b) simply involve placing the overall –1 charge of the ion on different atoms. From formal charge considerations, (c) will be the least important of the three resonance structures. From electronegativity considerations, it is energetically preferable to place a negative charge on the more electronegative atom. In this case, this means that a structure in which the –1 charge is placed on O will be preferred over that which has the –1 charge on N. On the basis of formal charge and electronegativity ideas, the relative importance of these structures is: (a) > (b) >> (c).

(b) CNO$^-$ (16 valence electrons). Lewis structures which obey the octet rule are:

(a) 

(b) 

(c)
The formal charges on the atoms in each of these three structures are:

- Structure (a): C -1, N +1, O -1
- Structure (b): C -2, N +1, O 0
- Structure (c): C -3, N +1, O +1

In structure (c) we separate a -3 charge from a +1 charge. Since the energy required to separate formal charges of opposite sign increases as the magnitude of the charges increases and as the separation increases, the energy of resonance structure (c) will be greater than that of either (a) or (b). Similarly, since the energy required to bring formal charges of the same sign together increases as the magnitude of the charges increases and as the separation decreases, the energy of resonance structure (c) will be greater than that of either (a) or (b) and structure (c) will make a smaller contribution to the actual structure. Structure (a) which places a -1 charge on the most electronegative atom (O) and a +1 on N and a -1 on C will be more important than structure (b) which has zero formal charge on O and a -2 charge on C which is not a very electronegative atom. On the basis of formal charge and electronegativity ideas, the relative importance of these structures is: (a) > (b) >> (c).

8. PbCl₄:

- Number of valence electrons = 4 (for Pb) + 28 (for 4 Cl) = 32 and the Lewis electron dot structure satisfying the octet rule is:

  :Cl:
  \[\begin{array}{c}
  \vdots \\
  \vdots \\
  Cl-\text{Pb}-Cl \\
  \vdots \\
  \vdots \\
  Cl:
  \end{array}\]

Pb is surrounded by 4 pairs of electrons. Since there are no multiple bonds, Pb is surrounded by 4 electron groups. The idealized electron group geometry is tetrahedral. Since all the electron groups are bonding, the observed molecular geometry is tetrahedral.

SbH₃:

- Number of valence electrons = 5 (for Sb) + 3 (or 3 H) = 8 and the Lewis electron dot structure satisfying the octet rule is:

  H---Sb---H
  |      |
  H

Sb is surrounded by 4 pairs of electrons. Since there are no multiple bonds, Sb is surrounded by 4 electron groups. The idealized electron group geometry is tetrahedral. The observed geometry of the molecule is determined by the positions of the atoms. Since the 4 electron groups are not equivalent there will be deviations from this ideal geometry. Such effects will increase the angle between the lone pair and the bonding pair and will, thereby, decrease the angle between two different bonding pairs. These effects will result in < H–Sb–H < 109.5°

SO₂:

- Number of valence electrons = 6 (for S) + 12 (for 2 O) = 18. There are two Lewis
electron dot structures which satisfy the octet rule and the actual structure of \( \text{SO}_2 \) will be an equal mixture of the two resonance structures shown below:

\[
\begin{align*}
\text{S} & \equiv \text{\^S} \equiv \text{\^O} \\
\text{O} & \equiv \text{\^O} \equiv \text{\^S}
\end{align*}
\]

S is surrounded by 3 groups of electrons; 2 of these are bonding electron groups and the third is a non-bonding pair of electrons. The idealized electron group geometry is trigonal planar. Since the 3 electron groups are not equivalent the observed geometry will deviation from this ideal geometry. Such effects will increase the angle between the lone pair and the bonding 3-electron group and will decrease the angle between two different bonding 3-electron groups. These effects will result in \( \angle \text{O} - \text{S} - \text{O} < 120^\circ \).

9. Recall that 1 Debye = 1.0 x 10^{-18} \text{ esu-cm}; it would be preferable to convert this to SI units (C m). In SI units, 1 Debye = 3.338 x 10^{-30} \text{ C m}.

For CsF, \( \mu = 7.88 \text{ D} = 7.88 \times 3.338 \times 10^{-30} \text{ C m} = 26.303 \times 10^{-30} \text{ C m} \).

Since \( \mu = \delta r \), then \( \delta = \mu/r = 26.303 \times 10^{-30} \text{ C m} / 2.55 \times 10^{-10} \text{ m} = 1.032 \times 10^{-19} \text{ C} \)

For a bond that is 100\% ionic, \( \delta = e = 1.602 \times 10^{-19} \text{ C} \)

\% ionic character = \( \frac{1.032 \times 10^{-19} \text{ C}}{1.602 \times 10^{-19} \text{ C}} \times 100\% = 64.4\% \)

10. Here we must examine the electronegativity difference, \( \Delta \text{EN} \), between the bonded atoms. As \( \Delta \text{EN} \) increases the degree of ionic character increases.

HCl (\( \Delta \text{EN} = 0.9 \)); CIF (\( \Delta \text{EN} = 1.0 \)); CCl\(_4\) (\( \Delta \text{EN} = 0.5 \)); KCl (\( \Delta \text{EN} = 2.2 \)); Cl\(_2\) (\( \Delta \text{EN} = 0 \))

Thus, the order of decreasing ionic character is: KCl > CIF > HCl > CCl\(_4\) > Cl\(_2\)

11. To determine the dipole moment for the whole molecule we must examine the magnitude of the bond moments and the geometry of the bond moments. The magnitude of the bond moment is a measure of the degree of polarity of the bond. To determine the polarity of the bond we examine the electronegativity difference of the bonded atoms. For the molecules considered here the order of decreasing polarity of the bonds is:

\( \text{CF} > \text{CCl} > \text{CH} > \text{CBr} \)

Even though each C – H bond in CH\(_4\) and each C – Cl bond in CCl\(_4\) is polar, the tetrahedral structure of CH\(_4\) and CCl\(_4\) results in a complete cancellation of the bond moments. CH\(_4\) and CCl\(_4\) have zero net dipole moment. For the remaining molecules the bond moments will not cancel. A consideration of the bond moments presented above leads to the following order of increasing dipole moments:

\( \text{CCl}_4 = \text{CH}_4 < \text{CH}_3\text{Br} < \text{CH}_3\text{Cl} < \text{CH}_3\text{F} \)
12. Recognize that the ordering of the MO’s for O and F is different from that for B, C, and N.
For O and F the ordering is:
\[ \sigma 2s < \sigma^*2s < \sigma 2p_z < \pi 2p_x, \pi 2p_y < \pi^*2p_x, \pi^*2p_y < \sigma^*2p_z \]

To answer this question, we determine the ground state electron configuration, calculate the
bond order, and then recognize that a molecule with a larger Bond Order will have a greater
bond energy.

(a) \( \text{B}_2 \) (6 valence electrons):
   electron config.: \((\sigma 2s)^2 \ (\sigma^*2s)^2 \ (\pi 2p_x)^1 \ (\pi 2p_y)^1 \)
   Bond Order = 1

   \( \text{B}_2^+ \) (5 valence electrons):
   electron config.: \((\sigma 2s)^2 \ (\sigma^*2s)^2 \ (\pi 2p_x)^1 \)
   Bond Order = 0.5

   \( \text{B}_2 \) will have the greater bond energy

(b) \( \text{O}_2^- \) (11 valence electrons):
   electron configuration: \((\sigma 2s)^2 \ (\sigma^*2s)^2 \ (\sigma 2p_z)^2 \ (\pi 2p_x)^2 \ (\pi 2p_y)^2 \ (\pi^*2p_x)^1 \)
   Bond Order = 2.5

   \( \text{O}_2^- \) (13 valence electrons):
   electron configuration: \((\sigma 2s)^2 \ (\sigma^*2s)^2 \ (\sigma 2p_z)^2 \ (\pi 2p_x)^2 \ (\pi 2p_y)^2 \ (\pi^*2p_x)^2 \ (\pi^*2p_y)^1 \)
   Bond Order = 1.5

   \( \text{O}_2^- \) will have the greater bond energy

(c) \( \text{Be}_2 \) (4 valence electrons):
   electron config.: \((\sigma 2s)^2 \ (\sigma^*2s)^2 \)
   Bond Order = 0

   \( \text{Be}_2^+ \) (3 valence electrons):
   electron config.: \((\sigma 2s)^2 \ (\sigma^*2s)^1 \)
   Bond Order = 0.5

   \( \text{Be}_2^+ \) will have the greater bond energy

(d) & (e): \( \text{F}_2^+ \) (13 valence electrons):
   electron configuration: \((\sigma 2s)^2 \ (\sigma^*2s)^2 \ (\sigma 2p_z)^2 \ (\pi 2p_x)^2 \ (\pi 2p_y)^2 \ (\pi^*2p_x)^1 \)
   Bond Order = 1.5

   \( \text{F}_2 \) (14 valence electrons):
   electron configuration: \((\sigma 2s)^2 \ (\sigma^*2s)^2 \ (\sigma 2p_z)^2 \ (\pi 2p_x)^2 \ (\pi 2p_y)^2 \ (\pi^*2p_x)^2 \ (\pi^*2p_y)^2 \)
   Bond Order = 1.0

   \( \text{F}_2^- \) (15 valence electrons):
   electron config.: \((\sigma 2s)^2 \ (\sigma^*2s)^2 \ (\sigma 2p_z)^2 \ (\pi 2p_x)^2 \ (\pi^*2p_x)^2 \ (\pi^*2p_y)^2 \ (\sigma^*2p_z)^1 \)
   Bond Order = 0.5

   \( \text{F}_2^+ \) will have a greater bond energy than \( \text{F}_2 \)

   \( \text{F}_2 \) will have a greater bond energy than \( \text{F}_2^- \)