Lewis Structures and Resonance

52. a. $\text{POCl}_3$ has $5 + 6 + 3(7) = 32$ valence electrons.

\[
\text{Skeletal structure} \quad \text{Lewis structure}
\]

$\text{SO}_4^{2-}$ has $6 + 4(6) + 2 = 32$ valence electrons.

\[
\begin{bmatrix}
: & : & : \\
\vdots & \vdots & \vdots \\
: & : & : \\
\end{bmatrix}^{2-}
\]

Note: A negatively charged ion will have additional electrons to those that come from the valence shell of the atoms.

XeO$_4$, $8 + 4(6) = 32$ e$^-$

PO$_4^{3-}$, $5 + 4(6) + 3 = 32$ e$^-$

$\text{ClO}_4^{-}$ has $7 + 4(6) + 1 = 32$ valence electrons.

\[
\begin{bmatrix}
: & : & : \\
\vdots & \vdots & \vdots \\
: & : & : \\
\end{bmatrix}^{-}
\]

Note: All these species have the same number of atoms and the same number of valence electrons. They also have the same Lewis structure.
b. \( \text{NF}_2 \) has \( 5 + 3(7) = 26 \) valence electrons. \( \text{SO}_2^2^- \), \( 6 + 3(6) + 2 = 26 \) e\(^-\)

\[
\begin{align*}
\text{F} & \quad \text{N} & \quad \text{F} \\
\text{F} & \quad \text{N} & \quad \text{F} \\
\text{Skeletal structure} & \quad \text{Lewis structure} & \quad \left[ \begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\end{array} \right]^{2^-}
\end{align*}
\]

\( \text{PO}_3^{3^-} \), \( 5 + 3(6) + 3 = 26 \) e\(^-\)

\[
\left[ \begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\end{array} \right]^{3^-}
\]

\( \text{ClO}_2^- \), \( 7 + 3(6) + 1 = 26 \) e\(^-\)

\[
\left[ \begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{O} \\
\end{array} \right]^{-}
\]

*Note:* Species with the same number of atoms and valence electrons have similar Lewis structures.

c. \( \text{ClO}_2^- \) has \( 7 + 2(6) + 1 = 20 \) valence electrons.

\[
\begin{align*}
\text{O} & \quad \text{Cl} & \quad \text{O} \\
\text{Skeletal structure} & \quad \text{Lewis structure} & \quad \left[ \begin{array}{c}
\text{O} \\
\text{O} \\
\end{array} \right]^-
\end{align*}
\]

\( \text{SCl}_2 \), \( 6 + 2(7) = 20 \) e\(^-\)

\[
\text{S} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Skeletal structure} & \quad \text{Lewis structure} & \quad \left[ \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\end{array} \right]^{-}
\]

*Note:* Species with the same number of atoms and valence electrons have similar Lewis structures.

54. a. \( \text{NO}_2^- \) has \( 5 + 2(6) + 1 = 18 \) valence electrons. The skeletal structure is: \( \text{O} - \text{N} - \text{O} \)

To get an octet about the nitrogen and only use 18 e\(^-\), we must form a double bond to one of the oxygen atoms.

\[
\left[ \begin{array}{c}
\text{O} \\
\text{N} \\
\text{O} \\
\end{array} \right]^+ \quad \xrightarrow{\text{resonance}} \quad \left[ \begin{array}{c}
\text{O} \\
\text{N} \\
\text{O} \\
\end{array} \right]^+
\]

Because there is no reason to have the double bond to a particular oxygen atom, we can draw two resonance structures. Each Lewis structure uses the correct number of electrons and satisfies the octet rule, so each is a valid Lewis structure. Resonance structures occur when you have multiple bonds that can be in various positions. We say the actual structure is an average of these two resonance structures.
\[ \text{NO}_3^- \text{ has } 5 + 3(6) + 1 = 24 \text{ valence electrons. We can draw three resonance structures for } \text{NO}_3^-, \text{ with the double bond rotating between the three oxygen atoms.} \]

\[ \begin{array}{cccc}
\text{N} & \text{O} & \text{N} \\
\text{O} & \text{N} & \text{O} \\
\text{O} & \text{N} & \text{O} \\
\end{array} \]

\[ \text{N}_2\text{O}_4 \text{ has } 2(5) + 4(6) = 34 \text{ valence electrons. We can draw four resonance structures for } \text{N}_2\text{O}_4. \]

\[ \begin{array}{ccc}
\text{N} & \text{N} & \text{O} \\
\text{O} & \text{N} & \text{O} \\
\text{O} & \text{N} & \text{O} \\
\text{O} & \text{N} & \text{O} \\
\end{array} \]

b. \[ \text{OCN}^- \text{ has } 6 + 4 + 5 + 1 = 16 \text{ valence electrons. We can draw three resonance structures for } \text{OCN}^-. \]

\[ \begin{array}{cccc}
\text{O} & \text{C} & \equiv & \text{N} \\
\text{C} & \equiv & \text{N} & \equiv \\
\text{N} & \equiv & \text{C} & \equiv \\
\end{array} \]

\[ \text{SCN}^- \text{ has } 6 + 4 + 5 + 1 = 16 \text{ valence electrons. Three resonance structures can be drawn.} \]

\[ \begin{array}{cccc}
\text{S} & \equiv & \text{C} & \equiv \\
\text{C} & \equiv & \text{N} & \equiv \\
\text{N} & \equiv & \text{C} & \equiv \\
\end{array} \]

\[ \text{N}_3^- \text{ has } 3(5) + 1 = 16 \text{ valence electrons. As with OCN}^- \text{ and SCN}^-, \text{ three different resonance structures can be drawn.} \]

\[ \begin{array}{cccc}
\text{N} & \equiv & \text{N} & \equiv \\
\text{N} & \equiv & \text{N} & \equiv \\
\text{N} & \equiv & \text{N} & \equiv \\
\end{array} \]
72. For $SO_4^{2-}$, $ClO_4^-$, $PO_4^{3-}$, and $ClO_5^-$, only one of the possible resonance structures is drawn.

a. Must have five bonds to P to minimize formal charge of P. The best choice is to form a double bond to O since this will give O a formal charge of zero and single bonds to Cl for the same reason.

b. Must form six bonds to S to minimize formal charge of S.

\[ \begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{Cl} \\
\text{Cl}
\end{array} \quad P, \text{ FC} = 0 \quad \begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{Cl} \\
\text{Cl}
\end{array} \quad S, \text{ FC} = 0
\]

\[ \begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{Cl} \\
\text{Cl}
\end{array} \quad \text{Cl, FC} = 0 \quad \begin{array}{c}
\text{O} \\
\text{P} \\
\text{O} \\
\text{O}
\end{array} \quad \text{P, FC} = 0
\]

c. Must form seven bonds to Cl to minimize formal charge.

d. Must form five bonds to P to minimize formal charge.

\[ \begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{Cl} \\
\text{Cl}
\end{array} \quad \text{Cl, FC} = 0 \quad \begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{Cl} \\
\text{Cl}
\end{array} \quad \text{Cl, FC} = 0
\]

e. \quad f. \quad \begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{Cl} \\
\text{Cl}
\end{array} \quad \text{S, FC} = 0 \quad \begin{array}{c}
\text{Xe} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array} \quad \text{Xe, FC} = 0
\]

g. \quad \begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{Cl} \\
\text{Cl}
\end{array} \quad \text{Cl, FC} = 0
\]

h. We can't. The following structure has a zero formal charge for N:

\[ \begin{array}{c}
\text{N} \\
\text{O} \\
\text{O}
\end{array} \quad \text{N, FC} = 0
\]

but N does not expand its octet. We wouldn't expect this resonance form to exist.

74. $OCN^-$ has $6 + 4 + 5 + 1 = 16$ valence electrons.

\[ \begin{array}{c}
\text{O} \\
\text{C} \\
\text{N}
\end{array} \quad \text{OCN}^- \quad \begin{array}{c}
\text{O} \\
\text{C} \\
\text{N}
\end{array} \quad \text{OCN}^- \quad \begin{array}{c}
\text{O} \\
\text{C} \\
\text{N}
\end{array} \quad \text{OCN}^- 
\]

<table>
<thead>
<tr>
<th>Formal charge</th>
<th>0</th>
<th>0</th>
<th>-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formal charge</td>
<td>-1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Formal charge</td>
<td>+1</td>
<td>0</td>
<td>-2</td>
</tr>
</tbody>
</table>
Only the first two resonance structures should be important. The third places a positive formal charge on the most electronegative atom in the ion and a -2 formal charge on N.

\[
\text{CNO}^-:
\]

\[
\begin{array}{c}
\text{Formal charge} \\
-2 & +1 & 0 \\
\end{array}
\]

\[
\begin{array}{c}
-1 & +1 & -1 \\
-3 & +1 & +1 \\
\end{array}
\]

All the resonance structures for fulminate (CNO\(^-\)) involve greater formal charges than in cyanate (OCN\(^-\)), making fulminate more reactive (less stable).

**Additional Exercises**

98. If we can draw resonance forms for the anion after loss of H\(^+\), we can argue that the extra stability of the anion causes the proton to be more readily lost, i.e., makes the compound a better acid.

a.

b.

\[
\begin{array}{c}
\text{CH}_3 & \text{C} & \text{CH} & \text{C} & \text{CH}_3 \\
\text{CH}_3 & \text{C} & \text{CH} & \text{C} & \text{CH}_3 \\
\end{array}
\]

c.

In all three cases, extra resonance forms can be drawn for the anion that are not possible when the H\(^+\) is present, which leads to enhanced stability.
Molecular Structure and Polarity

76. a. \( \text{SeO}_3, 6 + 3(6) = 24 \text{ e}^- \)

\[
\begin{array}{c}
120^\circ \\
\text{Se} \\
120^\circ \\
\text{Se} \\
120^\circ \\
\text{O} \\
\end{array}
\]

\( \text{SeO}_3 \) has a trigonal planar molecular structure with all bond angles equal to \( 120^\circ \). Note that any one of the resonance structures could be used to predict molecular structure and bond angles.

b. \( \text{SeO}_2, 6 + 2(6) = 18 \text{ e}^- \)

\[
\begin{array}{c}
\approx 120^\circ \\
\text{Se} \\
\text{Se} \\
\end{array}
\]

\( \text{SeO}_2 \) has a V-shaped molecular structure. We would expect the bond angle to be approximately \( 120^\circ \) as expected for trigonal planar geometry.

Note: Both \( \text{SeO}_3 \) and \( \text{SeO}_2 \) structures have three effective pairs of electrons about the central atom. All the structures are based on a trigonal planar geometry, but only \( \text{SeO}_3 \) is described as having a trigonal planar structure. Molecular structure always describes the relative positions of the atoms.

c. \( \text{PCl}_3 \) has \( 5 + 3(7) = 26 \) valence electrons. 

d. \( \text{SCl}_2 \) has \( 6 + 2(7) = 20 \) valence electrons

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{P} \\
\end{array}
\]

Trigonal pyramid; all angles are \(<109.5^\circ\).

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

V-shaped; angle is \(<109.5^\circ\).

e. \( \text{SiF}_4 \) has \( 4 + 4(7) = 32 \) valence electrons.

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

Tetrahedral; all angles are \( 109.5^\circ \).

Note: In \( \text{PCl}_3, \text{SCl}_2, \) and \( \text{SiF}_4, \) there are four pairs of electrons about the central atom in each case. All the structures are based on a tetrahedral geometry, but only \( \text{SiF}_4 \) has a tetrahedral structure. We consider only the relative positions of the atoms when describing the molecular structure.
80.  
a. $\text{ICl}_5, 7 + 5(7) = 42 \text{ e}^-$  
b. $\text{XeCl}_4, 8 + 4(7) = 36 \text{ e}^-$  

Square pyramid, $\approx 90^\circ$ bond angles  

Square planar, $90^\circ$ bond angles  

C. $\text{SeCl}_6$ has $6 + 6(7) = 48$ valence electrons.  

Octahedral, $90^\circ$ bond angles

Note: All these species have six pairs of electrons around the central atom. All three structures are based on the octahedron, but only $\text{SeCl}_6$ has an octahedral molecular structure.

Assignment 11 Challenge Problem – Solutions

1. a.  

\[
\text{best (all FC=0)} \quad \leftrightarrow \quad \text{okay} \quad \leftrightarrow \quad \text{okay}
\]

b. bent, with $\angle\text{OSO} < 120^\circ$

2. a.  

\[
\text{best (all FC=0)} \quad \leftrightarrow \quad \text{okay} \quad \leftrightarrow \quad \text{bad (3 of these)}
\]

b. trigonal planar, with $\angle\text{OSO} = 120^\circ$

c. The structure that has all zero formal charges requires supervalent $\text{O}$, which is not possible. The structure that obeys the octet rule has a formal charge of $+2$ on the central $\text{O}$ atom, which is not acceptable.
3. a. 

\[ \begin{align*}
\text{O} & \quad \text{N}^{+1} \quad \text{O}^{-1} \quad \leftrightarrow \quad -1 \quad \text{O} & \quad \text{N}^{+1} \quad \text{O} \\
\text{okay} & \quad \text{okay}
\end{align*} \]

b. bent, with \( \angle \text{ONO} < 120^\circ \)

c. \( \text{NO}_2 \) is a radical in which N has only 7 electrons.

d. Draw and evaluate all reasonable resonance structure(s) for \( \text{NO}_2^+ \).

e. The nitrogen–oxygen bond (BO = 2) within \( \text{NO}_2^+ \) is shorter than the nitrogen–oxygen bond (BO = 1.5) within \( \text{NO}_2 \).