Skills to Develop

- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Identify the oxidation states of atoms in Lewis structures

Previously, we discussed how to write Lewis structures for molecules and polyatomic ions. In some cases, however, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable. But first, let's introduce a concept we will refer back to frequently for the rest of this term: electronegativity.

Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called electronegativity. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Figure \(\PageIndex{1}\) shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling. In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO₂ do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

![Figure \(\PageIndex{1}\): The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table.](image-url)
Calculating Formal Charge

The formal charge of an atom in a molecule is the \textit{hypothetical charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms}. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

\[
\text{formal charge} = \# \text{ valence shell electrons (free atom)} - \# \text{ lone pair electrons} - \frac{1}{2} \# \text{ bonding electrons}
\]

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

We must remember that the formal charge calculated for an atom is not the \textit{actual} charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Example \(\PageIndex{1}\): Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the \textit{interhalogen ion} \(\ce{ICl4-}\).

\textbf{Solution}

\textit{We divide the bonding electron pairs equally for all} \(\ce{I–Cl}\) \textit{bonds}:

\textit{We assign lone pairs of electrons to their atoms. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.}

\textit{Subtract this number from the number of valence electrons for the neutral atom:}

\begin{itemize}
  \item I: \(7 - 8 = -1\)
  \item Cl: \(7 - 7 = 0\)
\end{itemize}

The sum of the formal charges of all the atoms equals \(-1\), which is identical to the charge of the ion \((-1)\).
Calculate the formal charge for each atom in the carbon monoxide molecule:

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

**Answer**

C −1, O +1

Example \( \PageIndex{2} \): Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule \( \text{BrCl}_3 \).

**Solution**

*Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:*

\[ \text{Cl} \equiv \text{Br} \equiv \text{Cl} \]

*Assign the lone pairs to their atom. Now each Cl atom has seven electrons and the Br atom has seven electrons.*

*Subtract this number from the number of valence electrons for the neutral atom. This gives the formal charge:*

- Br: 7 − 7 = 0
- Cl: 7 − 7 = 0

All atoms in \( \text{BrCl}_3 \) have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

**Exercise \( \PageIndex{2} \)**

Determine the formal charge for each atom in \( \text{NCl}_3 \).

**Answer**

N: 0; all three Cl atoms: 0

\[ \text{Cl} \equiv \text{N} \equiv \text{Cl} \]
Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its molecular structure. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion.

Predicting Molecular Structure Guidelines

1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

To see how these guidelines apply, let us consider some possible structures for carbon dioxide, \(\ce{CO2}\). We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand why this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:
Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: \( \ce{CNS^-} \), \( \ce{NCS^-} \), or \( \ce{CSN^-} \). The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:

Note that the sum of the formal charges in each case is equal to the charge of the ion (–1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

Example \( \PageIndex{3} \)): Using Formal Charge to Determine Molecular Structure

Nitrous oxide, \( \ce{N_2O} \), commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?

\[
\begin{align*}
\text{Structure} & : \text{N} \equiv \text{N} \equiv \text{O} & \text{Structure} & : \text{N} \equiv \text{O} \equiv \text{N} \\
\text{Formal charge} & -1 \ 0 \ 0 & \text{Formal charge} & -1 \ +2 \ -1
\end{align*}
\]

The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:

\[
\begin{align*}
\text{Structure} & : \text{N} \equiv \text{N} \equiv \text{O} \\
\text{Formal charge} & -1 \ +1 \ 0
\end{align*}
\]

The number of atoms with formal charges are minimized (Guideline 2), and there is no formal charge larger than one (Guideline 2). This is again consistent with the preference for having the less electronegative atom in the central position.

Exercise \( \PageIndex{3} \))

Which is the most likely molecular structure for the nitrite (\( \ce{NO_2^-} \)) ion?

\[
\begin{align*}
\text{Structure} & : \text{N} \equiv \text{O} \equiv \text{O} & \text{Structure} & : \text{O} \equiv \text{N} \equiv \text{O}
\end{align*}
\]
**Oxidation Numbers**

We have also discussed electronegativity, which gives rise to polarity in bonds and molecules. Thus, sometimes it is helpful for us to define another somewhat artificial device - invented by chemists, not by molecules - which enables us to keep track of electrons in complicated reactions where electrons rearrange into new bonds.

We can obtain oxidation numbers by arbitrarily assigning the electrons of each covalent bond to the more electronegative atom in the bond. This is in contrast to the **Formal Charge** which divides each bonding pair equally without concern for which atom may be more electronegative. When this division has been done for all bonds, the charge remaining on each atom is said to be its oxidation number. If two like atoms are joined, each atom is assigned half the bonding electrons.

**Example \(\PageIndex{4}\): Oxidation Number**

Determine the oxidation number of each atom in each of the following formulas: (a) \(\text{Cl}_2\); (b) \(\text{CH}_4\); (c) \(\text{NaCl}\); (d) \(\text{OF}_2\); (e) \(\text{H}_2\text{O}_2\).

**Solution:**

In each case we begin by drawing a Lewis diagram:

- In each Lewis diagram, electrons have been color coded to indicate the atom from which they came originally. The boxes enclose electrons assigned to a given atom by the rules for determining oxidation number.

  a) Since the bond in \(\text{Cl}_2\) is purely covalent and the electrons are shared equally, one electron from the bond is assigned to each \(\text{Cl}\), giving the same number of valence electrons (7) as a neutral \(\text{Cl}\) atom. Thus neither atom has lost any electrons, and the oxidation number is 0. This is indicated by writing a 0 above the symbol for chlorine in the formula

  \[
  \overset{0}{\text{Cl}}\,_{\text{2}}
  \]

  b) Since \(\text{C}\) is more electronegative than \(\text{H}\), the pair of electrons in each \(\text{C—H}\) bond is assigned to \(\text{C}\). Therefore each \(\text{H}\) has **lost** the one valence electron it originally had, giving an oxidation number of +1. The \(\text{C}\) atom has **gained** four electrons, giving it a negative charge and hence an oxidation number of – 4:

  \[
  \overset{-4}{\text{C}}\overset{+1}{\text{H}}\,_{\text{4}}
  \]

  c) In \(\text{NaCl}\) each \(\text{Na}\) atom has lost an electron to form an \(\text{Na}^+\) ion, and each \(\text{Cl}\) atom has gained an electron to form \(\text{Cl}^-\). The oxidation numbers therefore correspond to the ionic charges:
d) Since F is more electronegative than O, the bonding pairs are assigned to F in oxygen difluoride (OF₂). The O is left with four valence electrons, and each F has eight. The oxidation numbers are

\[
\overset{+2}{\text{O}} \overset{-1}{\text{F}_2}\]

\[
\overset{+1}{\text{Na}} \overset{-1}{\text{Cl}}\]

e) In Hydrogen peroxide (H₂O₂) the O—H bond pairs are assigned to the more electronegative O’s, but the O—O bond is purely covalent, and the electron pair is divided equally. This gives each O seven electrons, a gain of 1 over the neutral atom. The oxidation numbers are

\[
\overset{+1}{\text{H}_2} \overset{-1}{\text{O}_2}\]

Oxidation numbers are mainly used by chemists to identify and handle a type of chemical reaction called a **redox reaction**, or an **oxidation-reduction reaction**. This type of reaction can be recognized because it involves a **change in oxidation number** of at least one element. We explored this last term. Oxidation numbers can sometimes also be useful in writing Lewis structures, particularly for oxyanions. In the sulfite ion, SO₃²⁻ for example, the oxidation number of sulfur is +4, suggesting that only four sulfur electrons are involved in the bonding. Since sulfur has six valence electrons, we conclude that two electrons are not involved in the bonding, i.e., that there is a **lone pair**. With this clue, a plausible Lewis structure is much easier to draw:

\[
\overset{2-}{\text{O:S:O:}}
\]
Video \(\PageIndex{2}\): A video overview of oxidation numbers and Lewis structures.

**Summary**

In a Lewis structure, formal charges can be assigned to each atom by treating each bond as if one-half of the electrons are assigned to each atom. These hypothetical formal charges are a guide to determining the most appropriate Lewis structure. A structure in which the formal charges are as close to zero as possible is preferred. Oxidation numbers can further be used to help elucidate the correct Lewis structure.

**Key Equations**

- \(\text{formal charge} = \#\text{ valence shell electrons (free atom)} - \#\text{ one pair electrons} - \dfrac{1}{2}\text{\# bonding electrons}\)

**Glossary**

- **formal charge**: charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

- **molecular structure**: arrangement of atoms in a molecule or ion
resonance
situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

resonance forms
two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

resonance hybrid
average of the resonance forms shown by the individual Lewis structures

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