1.6: LEWIS STRUCTURES AND FORMAL CHARGES (REVIEW)

Learning Objective

Draw, interpret, and convert between Lewis (Kekule), Condensed, and Bond-line Structures

Note: The review of general chemistry in sections 1.3 - 1.6 is integrated into the above Learning Objective for organic chemistry in sections 1.7 and 1.8.

Lewis Structures

Lewis structures, also known as Lewis-dot diagrams, show the bonding relationship between atoms of a molecule and the lone pairs of electrons in a molecule. While it can be helpful initially to write the individual shared electrons, this approach quickly becomes awkward.

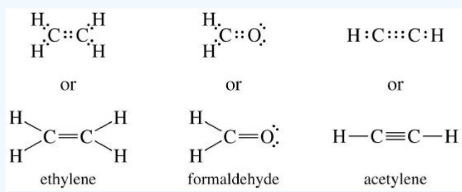
A single line is used to represent one pair of shared electrons. Line representations are only used for shared electrons. Lone pair (unshared) electrons are still shown as individual electrons. Double and triple bonds can also be communicated with lines as shown below.

2 shared electrons form a single bond shown as ':' or '–'

4 shared electrons form a double bond shown as '::' or '='

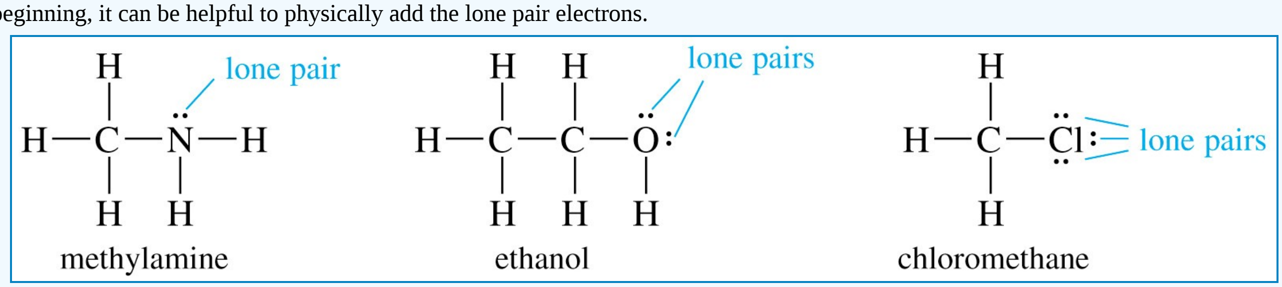
6 shared electrons form at triple bond shown as ':::' or $HC\equiv CH$

Unshared electrons are also called 'Lone Pairs' and are shown as ':'



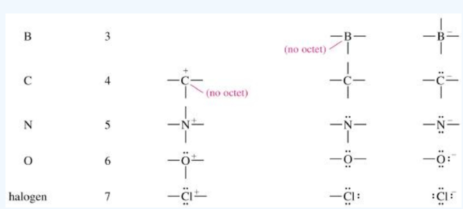
Drawing Lone Pairs

Since the lone pair electrons are often NOT shown in chemical structures, it is important to mentally add the lone pairs. In the beginning, it can be helpful to physically add the lone pair electrons.



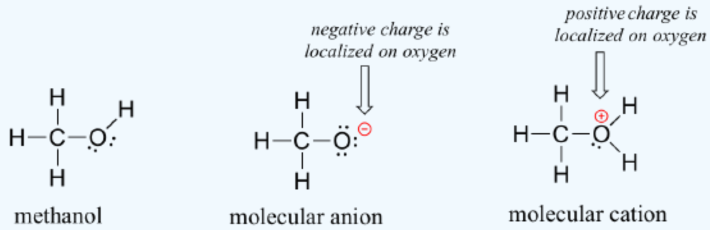
Bonding Patterns

For organic chemistry, the common bonding patterns of carbon, oxygen, and nitrogen have useful applications when evaluating chemical structures and reactivity.



FORMAL CHARGES

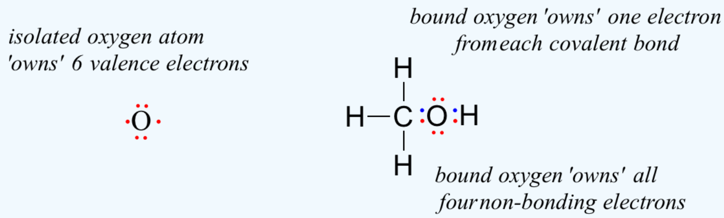
Organic molecules can also have positive or negative charges associated with them. During chemical reactions, it is common to have charge reactant, intermediates, and/or products. Recognizing and distinguishing between neutral and charged bonding patterns will be helpful in learning reaction mechanisms. Consider the Lewis structure of methanol, CH_3OH (methanol is the so-called 'wood alcohol' that unscrupulous bootleggers sometimes sold during the prohibition days in the 1920's, often causing the people who drank it to go blind). Methanol itself is a neutral molecule, but can lose a proton to become a molecular anion (CH_3O^-), or gain a proton to become a molecular cation ($CH_3OH_2^{+}$).



The molecular anion and cation have overall charges of -1 and +1, respectively. But we can be more specific than that - we can also state for each molecular ion that a **formal charge** is located specifically on the oxygen atom, rather than on the carbon or any of the hydrogen atoms.

Figuring out the formal charge on different atoms of a molecule is a straightforward process - it's simply a matter of adding up valence electrons.

A unbound oxygen atom has 6 valence electrons. When it is bound as part of a methanol molecule, however, an oxygen atom is surrounded by 8 valence electrons: 4 nonbonding electrons (two 'lone pairs') and 2 electrons in each of its two covalent bonds (one to carbon, one to hydrogen). In the formal charge convention, we say that the oxygen 'owns' all 4 nonbonding electrons. However, it only 'owns' one electron from each of the two covalent bonds, because covalent bonds involve the sharing of electrons between atoms. Therefore, the oxygen atom in methanol owns 2 + 2 + (½ x 4) = 6 valence electrons.



The formal charge on an atom is calculated as the number of valence electrons owned by the isolated atom minus the number of valence electrons owned by the bound atom in the molecule:

Determining formal charge on an atom

formal charge =

(number of valence electrons owned by the isolated atom)

- (number of valence electrons owned by the bound atom)

or . . .

formal charge =

(number of valence electrons owned by the isolated atom)

- (number of non-bonding electrons on the bound atom)

- (½ the number of bonding electrons on the bound atom)

Using this formula for the oxygen atom of methanol, we have:

formal charge on oxygen =

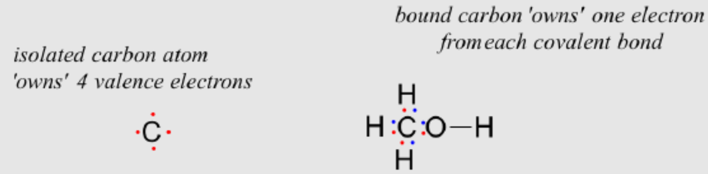
(6 valence electrons on isolated atom)

- (4 non-bonding electrons)

- (½ x 4 bonding electrons)

= 6 - 4 - 2 = **0**. Thus, oxygen in methanol has a formal charge of zero (in other words, it has *no formal charge*).

How about the carbon atom in methanol? An isolated carbon owns 4 valence electrons. The bound carbon in methanol owns (½ x 8) = 4 valence electrons:



formal charge on carbon =

(4 valence electron on isolated atom)

- (0 nonbonding electrons)

- (½ x 8 bonding electrons)

= 4 - 0 - 4 = **0**. So the formal charge on carbon is zero.

For each of the hydrogens in methanol, we also get a formal charge of zero:

formal charge on hydrogen =

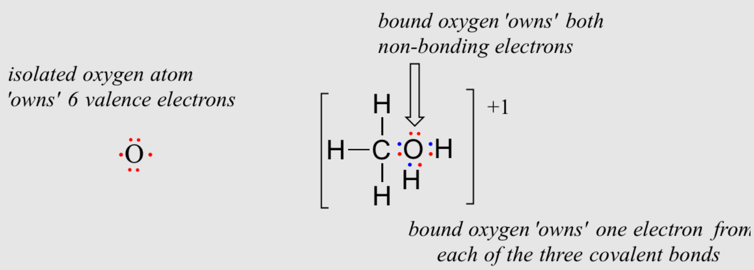
(1 valence electron on isolated atom)

- (0 nonbonding electrons)

- (½ x 2 bonding electrons)

= 1 - 0 - 1 = **0**

Now, let's look at the cationic form of methanol, $CH_3OH_2^+$. The bonding picture has not changed for carbon or for any of the hydrogen atoms, so we will focus on the oxygen atom.



The oxygen owns 2 non-bonding electrons and 3 bonding elections, so the formal charge calculations becomes:

formal charge on oxygen =

(6 valence electrons in isolated atom)

- (2 non-bonding electrons)

- (½ x 6 bonding electrons)

= 6 - 2 - 3 = **1**. A formal charge of +1 is located on the oxygen atom.

For methoxide, the anionic form of methanol, the calculation for the oxygen atom is:

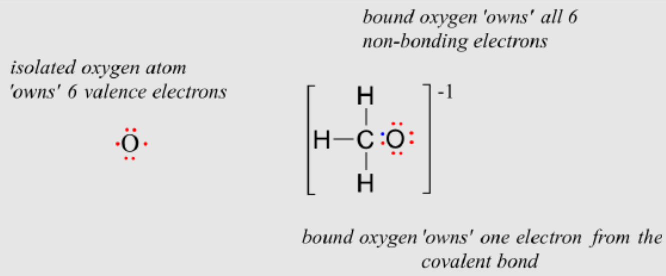
formal charge on oxygen =

(6 valence electrons in isolated atom)

- (6 non-bonding electrons)

- (½ x 2 bonding electrons)

= 6 - 6 - 1 = -**1**. A formal charge of -1 is located on the oxygen atom.

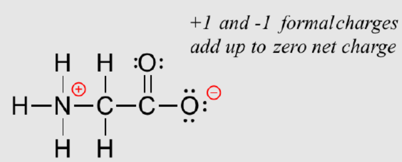


A very important rule to keep in mind is that *the sum of the formal charges on all atoms of a molecule must equal the net charge on the whole molecule.*

When drawing the structures of organic molecules, it is very important to show all non-zero formal charges, being clear about where the charges are located. *A structure that is missing non-zero formal charges is not correctly drawn, and will probably be marked as such on an exam!*

At this point, thinking back to what you learned in general chemistry, you are probably asking “What about dipoles? Doesn’t an oxygen atom in an O-H bond ‘own’ more of the electron density than the hydrogen, because of its greater electronegativity?” This is absolutely correct, and we will be reviewing the concept of bond dipoles later on. For the purpose of calculating formal charges, however, bond dipoles don’t matter - we always consider the two electrons in a bond to be shared equally, even if that is not an accurate reflection of chemical reality. Formal charges are just that - a formality, a method of electron book-keeping that is tied into the Lewis system for drawing the structures of organic compounds and ions. Later, we will see how the concept of formal charge can help us to visualize how organic molecules react.

Finally, don't be lured into thinking that just because the net charge on a structure is zero there are no atoms with formal charges: one atom could have a positive formal charge and another a negative formal charge, and the net charge would still be zero. **Zwitterions,** such as amino acids, have both positive and negative formal charges on different atoms:

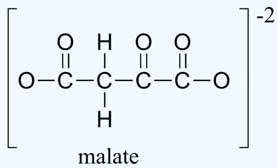


glycine
(an amino acid)

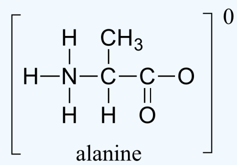
Even though the *net* charge on glycine is zero, it is still neccessary to show the location of the positive and negative formal charges.

Exercise 1.4

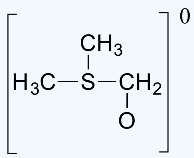
Fill in all missing lone pair electrons and formal charges in the structures below. Assume that all atoms have a complete valence shell of electrons. Net charges are shown outside the brackets.

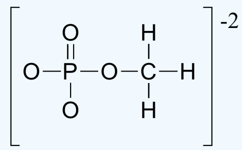
a) 

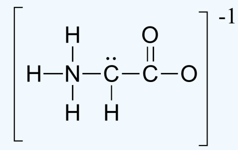
malate

b) 

alanine

c) 

d) 

e) 

Solutions to exercises