

Review

LEWIS STRUCTURES

INTRODUCTION: Molecular compounds are formed when two or more atoms share valence electrons forming a covalent bond. This results in two types of orbitals; nonbonding orbitals (lone pairs), where the valence electrons are localized to one nuclei, and bonding orbitals, where the valence electrons are shared between two or more nuclei. Lewis dot structures are a convention for drawing molecules that use dots to represent lone electrons and lines to represent electron pairs, with bonds orbitals represented as a line between two atoms.

The postulate that a bond can be represented by a line between two atoms has problems when an orbital involves more than two atoms, like the extended molecular π orbitals involving the overlap of unhybridized atomic p orbitals in structures like benzene. In this case we can draw more than one Lewis dot structure based on the location of the double bonds (defined as a σ and a π bond) and invoke the concept of resonance, where the true structure is the average of all the resonance structures. In the case of Benzene there are two ways you can draw the alternating single and double bonds, and neither of them is correct. You would expect a double bond (bond order =2) to be stronger, and thus shorter than the weaker single bond (bond order = 1) but in Benzene they are all the same, being longer than a double and shorter than a single (bond order of 1.5).

Another shortcoming of Lewis dot structures, and the reason we need to review them, is they cannot account for molecular geometries. The types of intermolecular forces operating between molecules is often determined by their shapes and the first step in determining a molecule's shape is to determine its Lewis dot structure.

OBJECTIVE: Draw Lewis Dot structures

PROCEDURES:

1. Determine total number of available valence electrons.
 - Determine the total number of valence electrons available, each atoms of the representative elements contributes the number of electrons equal to it's group number (IA – VIIA). Note, if there is an odd number of electrons, the structure will be a free radical, which has a lone electron in an orbital. This electron will exist in a nonbonding orbital or a multiple bond.
 - If the compound is an ion, add one electron for each negative charge and subtract one electron for each positive charge
2. Determine structural connectivity.
 - First atom is central atom (unless Hydrogen, which can never be central)
 - If more than 2 types of atoms, set up in order of formula.
 - Organic compounds often contain multiple carbons connected to each other and often result in structural isomers (different ways of connecting the atoms).

3. Draw hypothetical structure with each atom surrounded by 8 electrons in pairs.
 - a. Place two electrons forming a single bond between bonded atoms by drawing a line between the two atoms.
 - b. For each atom not surrounded by an octet of electrons (4 bonds), add lone pairs of electrons (two dots to a lone pair, although I often use a line tangential to the surface of that nuclei's atomic symbol) until all atoms are surrounded by an octet. Note, hydrogen can only have 2 valence electrons.

4. Count the total number of electrons in the hypothetical structure.
 - a. If it is equal to the number of available electrons from step 2, this is the correct Lewis Dot Structure.
 - b. If it is **GREATER** than the number of available electrons from step 2, **go to step 5**.
 - c. If it is **LESS** than the available number of electrons from step 2, **go to step 7**.

5. Determine if any atoms can have less than an octet. **If not, proceed to step 6**, if so, decrease the number of lone pairs around these atoms until the total number of electrons in structure equals the number from step 2.
 - a. Hydrogen always has a duet (one bond – 2 electrons)
 - b. Group IIA can have a quartet (4 electrons)
 - c. Group IIIA can have a sextet (6 electrons)

6. Place multiple bonds into structure by replacing two lone pairs from two adjacent atoms with a bonding pair. Repeat this until the structure has the same number of electrons as determined in step 2.

7. If any atoms have d orbitals available (3rd period or greater), they can have an “expanded octet”, that is more than 8 valence electrons. Add lone pairs to these atoms until the number of electrons equals the number from step 2.

8. **RESONANCE STRUCTURES:** Check to see if additional electron configurations can be drawn by changing the position electrons (but not the connectivity of the atoms). These should have come out in step 6. The best configurations will be the ones where the atoms are assigned the formal charges closest to zero. In the event that no resonance structure has a zero formal charge, assign negative formal charges to the most electronegative elements.

9. **FORMAL CHARGES:** These correlate the electron locations in the molecule to the atom that donates them. The formal charge (FC) for each atom can be determined by the following equation.

$$FC = \text{Group\#} - (\# \text{ lone electrons} + \frac{1}{2} \# \text{ bonding electrons})$$