Unit 1, Lesson 09: Variations on Covalent Bonding, Exceptions to the Octet Rule

A. Insufficient electrons to complete a stable octet: boron and beryllium

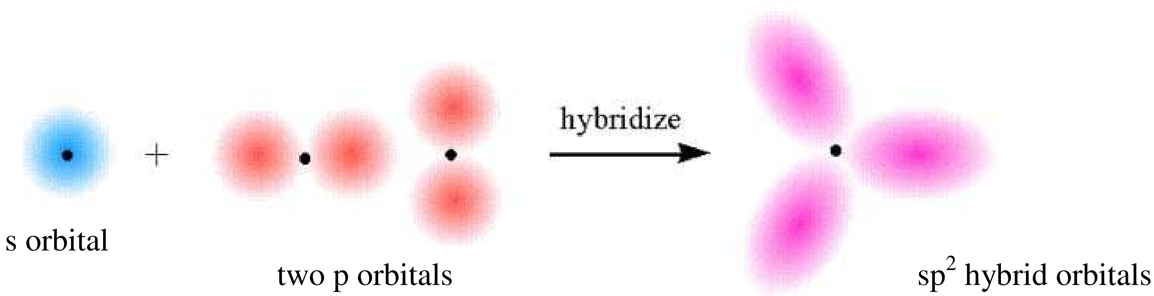
1. Boron:

According to boron's ***predicted*** orbital diagram, it has one unpaired electron, so it should form one bond.

1s²	2s²	2p¹		
↑↓	↑↓	↑		

However, experimentally we find that boron forms 3 bonds so it must have three half-filled orbitals.

Boron's three valence electrons "hybridize". That is, they spread out equally around the atom with one electron in each of three equivalent orbitals. This is a lower energy electron arrangement. Because the three "new" orbitals are a blending of one "s" and two "p" orbitals, they are called "sp^2" hybrid orbitals.

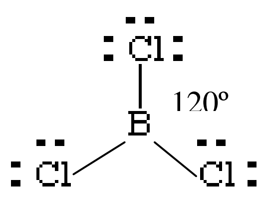


Boron's actual electron configuration is:

1s²	2sp²		
↑↓	↑	↑	↑

Because boron has three unpaired valence electrons (sp^2 hybrids), it forms three bonds. Because it is a very small atom, boron forms stable compounds with only six shared electrons instead of a full octet.

eg. BCl_3 (boron trichloride)



2. Beryllium:

According to beryllium's ***predicted*** orbital diagram, it has no unpaired electrons, so it should not form any bonds.

1s²	2s²	2p		
↑↓	↑↓			

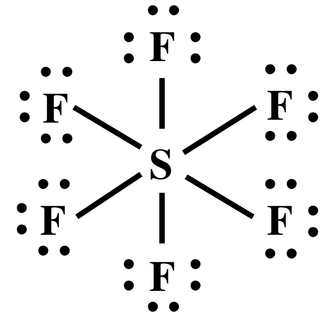
However, experimentally we find that boron forms 2 bonds so it must have two half-filled orbitals.

Beryllium's two $2s^2$ electrons also "hybridize". That is, they spread out equally around the atom with one electron in each of two equivalent orbitals. This is a lower energy electron arrangement. Because the two "new" orbitals are a blending of one "s" and one "p" orbital, they are called "sp^1" hybrid orbitals.

So, beryllium has two unpaired valence electrons (sp^1 hybrids) and forms two bonds. Because beryllium is a very small atom, it forms stable molecules with only four shared electrons instead of a full octet.

eg. $BeCl_2$ (beryllium dichloride)

B. Expansion of the Valence Level



eg. Sulfur can form several compounds with six bonds, for example SF_6 (sulfur hexafluoride). However, according to its electron configuration ($1s^22s^22p^63s^23p^4$) sulfur should only form 2 bonds, so how is this possible? The best explanation seems to be that all six valence electrons hybridize and spread out equally around the nucleus. By hybridizing, all six electrons become available for bonding. This is called an "expanded valence energy level".

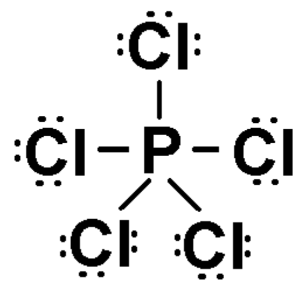
Sulfur: [Ne] $3s^2\,3p^4$

[Ne] [↑↓] [↑↓][↑][↑] hybridizes to [Ne] [↑][↑][↑][↑][↑][↑]

$3s^2$ $3p^4$

- all six of the s and p electrons are involved in bonding, so the central sulfur atom has no lone pairs

eg. Similarly, phosphorus can form compounds with halogens, such as PCl_5 by expanding its valence level. Phosphorus has five valence electrons which hybridize and spread themselves out around the nucleus in an expanded valence energy level. These five unpaired electrons can then form bonds with five other atoms, as shown in the diagram.



Phosphorus: [Ne] $3s^2\,3p^3$

[Ne] [↑↓] [↑][↑][↑] hybridizes to [Ne] [↑][↑][↑][↑][↑]

$3s^2$ $3p^3$

- all five of the s and p electrons are involved in bonding, so the central phosphorus has no lone pairs

Clues that you are dealing with an expanded valence:

- a compound has more than 4 of one type of atom eg. PF_5 or SCl_6
- a halogen has formed more than one bond eg. IF_4 (iodine has formed 4 bonds) or $ClF_4{}^{1+}$
- a Noble gas is involved in bonding eg. XeF_6 or $XeOF_4$

To draw Lewis structures of molecules with insufficient and expanded valence levels, we must modify the "system" we used for bonding by the Octet rule. Both insufficient and expanded valence molecules are exceptions to the octet rule, so a new method is needed.

To draw molecules or ions involving an expanded valence:

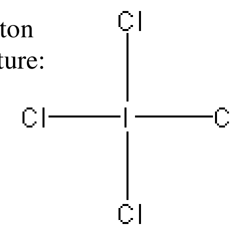
1. Identify the central atom (the atom with the lowest electronegativity).
2. Draw a skeleton structure with an expanded valence shell so that all other atoms are bonded to the central atom. Assume that the bonded atoms form their normal number of bonds, eg. halogens form one bond, oxygen forms two.

ONLY THE CENTRAL ATOM MAY HAVE AN EXPANDED VALENCE.

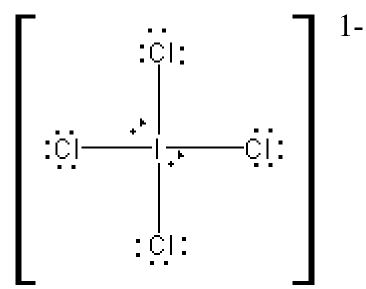
3. Calculate the number of valence electrons that we ***have*** (adjust for charges on ions).
4. Calculate the number of electrons that are found in bonds for the structure you drew in step 2.
5. Subtract the number of electrons in bonds (step 4) from the number of valence electrons we ***have*** (step 3) to determine the number of electrons found in lone pairs.
6. Distribute the electrons found in lone pairs to complete stable octets for the bonded atoms. Any leftover lone pairs are placed on the central atom.
7. For ions, draw them inside square brackets and indicate the ion's charge.

eg. Iodine tetrachloride ion has the molecular formula $\mathbf{IC\ell_4^{1-}}$

skeleton structure:



1. Central atom: iodine
2. Skeleton structure:
3. Valence electrons we ***have***: 7 + (4 x 7) + 1 = 36 total valence electrons
4. Electrons found in bonds: 4 x 2 = 8
5. Electrons found in lone pairs: 36 – 8 = 28 or 14 lone pairs
6. To complete stable octets for the chlorine atoms, we use 12 lone pairs. That leaves 2 lone pairs to be placed on the central iodine atom in an expanded valence
7. Complete the Lewis structure, including square brackets and the charge on the ion.



eg. $\mathbf{C\ell OF_4^{1+}}$

1. Central atom: chlorine
2. Skeleton structure (for Grade 12, it does not matter how you arrange the atoms around the central atom)
3. Valence electrons we ***have***: 7 + 6 + (4 x 7) –1 = 40 total valence e-
4. Electrons found in bonds: 6 x 2 = 12
5. Electrons found in lone pairs: 40 – 12 = 28 or 14 lone pairs
6. To complete stable octets for the oxygen and fluorine atoms, we use all 14 lone pairs. There are no lone pairs to be placed on the chlorine.
7. Complete the Lewis structure, including square brackets and the charge on the ion.