3.8: Exceptions to the Octet Rule

Returning briefly to classical Lewis diagrams. Consider the diagram shown below for the molecule SF_4. In constructing this diagram, six valence electrons are placed around the sulfur and seven valence electrons are placed around each fluorine. As we attempt to pair these to form covalent bonds, we note that there are “too many” electrons on the sulfur! We clearly cannot form a covalent bond using three electrons, so we *split* one pair, move the single electrons into bonding position and form bonds with the remaining two fluorines. The “extra pair” of electrons just *sits there* on the sulfur and does not participate directly in the bonding.

This is an example of **valence expansion**. In general, elements *below* the second period in the periodic table (S, Se, Te, etc.) will commonly have 10 – 12 electrons in their valence shells. As in SF_4, these electrons are not directly involved in the formation of covalent bonds, but they affect the overall reactivity of the particular molecule.

In general, all molecular compounds containing elements that appear below the second row in the periodic table are capable of valence expansion and you need to be very careful when you are drawing Lewis diagrams for these compounds. As we saw in Section 3.1 for the molecule nitrogen oxide (NO), stable molecules also exist in which atoms are *not* surrounded by an octet of electrons. Another example of this is the molecule BF_3, which is shown in the following example.

✔ Example 3.8.1: Boron Trifluoride

Construct a Lewis diagram for the molecule BF_3.

Solution

Boron has three valence electrons and fluorine has seven. The central atom in our structure will be boron (it is to the *left* of fluorine in the periodic table). Next, we draw the boron (our central atom) with its’ three electrons and place the three fluorines around the boron with the electrons arranged to form the three covalent bonds. Each of the fluorines have a full octet. The boron, however, is only surrounded by six electrons. Because of this, the boron in BF_3 is a powerful *electron acceptor* and forms strong complexes with electrons from other compounds. In Chapter 8 we will see that this property is called Lewis acidity and BF_3 is a very powerful Lewis acid.