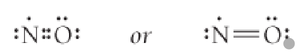
Pearson

5.5: Exceptions to the Octet Rule: Odd-Electron Species, Incomplete Octets, and Expanded Octets

The octet rule in the Lewis model has some exceptions, which we examine in this section. They include (1) *odd-electron species*, molecules or ions with an odd number of electrons; (2) *incomplete octets*, molecules or ions with *fewer than eight electrons* around an atom; and (3) *expanded octets*, molecules or ions with *more than eight electrons* around an atom.

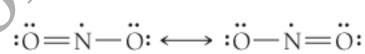
Odd-Electron Species

Molecules and ions with an odd number of electrons in their Lewis structures are **free radicals** (or simply *radicals*). For example, nitrogen monoxide—a pollutant found in motor vehicle exhaust—has 11 electrons. If we try to write a Lewis structure for nitrogen monoxide, we can't achieve octets for both atoms:



> The unpaired electron in nitrogen monoxide is put on the nitrogen rather than the oxygen in order to minimize formal charges.

The nitrogen atom does not have an octet, so this Lewis structure does not satisfy the octet rule. Yet, nitrogen monoxide exists, especially in polluted air. Why? As with any simple theory, the Lewis model is not sophisticated enough to handle every single case. We can't write good Lewis structures for free radicals; nevertheless, some of these molecules exist in nature. It is a testament to the Lewis model, however, that *relatively few* such molecules exist and that, in general, they tend to be somewhat unstable and reactive. NO, for example, reacts with oxygen in the air to form NO_2, another odd-electron molecule represented with the following 17-electron resonance structures:

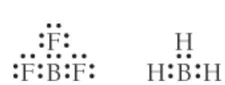


In turn, NO_2 reacts with water to form nitric acid (a component of acid rain) and also reacts with other atmospheric pollutants to form peroxyacetylnitrate (PAN), an active component of photochemical smog. For free radicals, such as NO and NO_2, we simply write the best Lewis structure that we can.

Conceptual Connection 5.3 Odd-Electron Species

Incomplete Octets

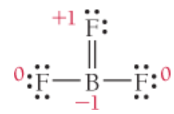
Another significant exception to the octet rule involves those elements that tend to form *incomplete octets*. The most important of these is boron, which forms compounds with only six electrons, rather than eight. For example, BF_3 and BH_3 lack an octet for B:



> Beryllium compounds, such as BeH_2, also have incomplete octets.

You might be wondering why we don't just form double bonds to increase the number of electrons around B. For BH_3, of course, we can't because there are no additional electrons to move into the bonding region. For BF_3, however, we could attempt to give B an octet by moving a lone pair from an F atom into the bonding region with B:

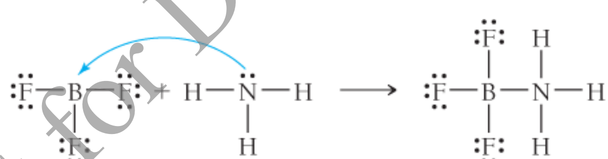
This Lewis structure has octets for all atoms, including boron. However, when we assign formal charges to this structure, we get a negative formal charge on B and a positive formal charge on F:



The positive formal charge on fluorine—the most electronegative element in the periodic table—makes this an unfavorable structure. This leaves us with some questions. Do we complete the octet on B at the expense of giving fluorine a positive formal charge? Or do we leave B without an octet in order to avoid the positive formal charge on fluorine?

The answers to these kinds of questions are not always clear because we are pushing the limits of the Lewis model. In the case of boron, we usually accept the incomplete octet as the better Lewis structure. However, doing so does not rule out the possibility that the Lewis structure with the double bond might be a minor contributing resonance structure. The ultimate answers to these kinds of questions must be determined from experiments. Experimental measurements of the B—F bond length in BF_3 suggest that the bond may be slightly shorter than expected for a single B—F bond, indicating that it may indeed have a small amount of double-bond character.

BF_3 can complete its octet in another way—via a chemical reaction. The Lewis model predicts that BF_3 might react in ways that would complete its octet, and indeed it does. For example, BF_3 reacts with NH_3 as follows:

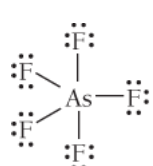


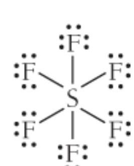
The product has complete octets for all atoms in the structure.

> When nitrogen bonds to boron, the nitrogen atom provides both of the electrons. This kind of bond is a *coordinate covalent bond*, which we will discuss in Chapter 22.

Expanded Octets

Elements in the third row of the periodic table and beyond often exhibit *expanded octets* of up to 12 (and occasionally 14) electrons. Consider the Lewis structures of arsenic pentafluoride and sulfur hexafluoride:

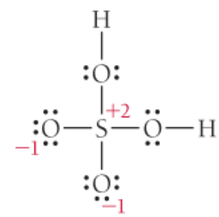




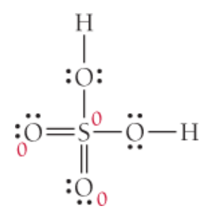
In AsF_5 arsenic has an expanded octet of 10 electrons, and in SF_6 sulfur has an expanded octet of 12 electrons.

In AsF_5 arsenic has an expanded octet of 10 electrons, and in SF_6 sulfur has an expanded octet of 12 electrons. Both of these compounds exist and are stable. Ten- and 12-electron expanded octets are common in third-period elements and beyond. This is because the *d* orbitals in these elements are energetically accessible (they are not much higher in energy than the orbitals occupied by the valence electrons) and can accommodate the extra electrons (see Section 3.3). Expanded octets *never* occur in second-period elements because they do not have energetically accessible *d* orbitals and therefore never exhibit expanded octets.

In some Lewis structures, we must decide whether or not to expand an octet in order to lower formal charge. For example, consider the Lewis structure of H_2SO_4:



Notice that both of the oxygen atoms have a −1 formal charge and that sulfur has a +2 formal charge. While this amount of formal charge is acceptable, especially since the negative formal charge resides on the more electronegative atom, it is possible to eliminate the formal charge by expanding the octet on sulfur:



Which of these two Lewis structures for H_2SO_4 is better? Again, the answer is not straightforward. Experiments show that the sulfur–oxygen bond lengths in the two sulfur–oxygen bonds without the hydrogen atoms are shorter than expected for sulfur–oxygen single bonds, indicating that the Lewis structure with double bonds plays an important role in describing the bonding in H_2SO_4. In general, we expand octets in third-row (or beyond) elements in order to lower formal charge. However, we should *never* expand the octets of second-row elements.

Example 5.8 Writing Lewis Structures for Compounds Having Expanded Octets

Write the Lewis structure for XeF_2.

SOLUTION

Begin by writing the skeletal structure. Since xenon is the less electronegative atom, put it in the central position.

F Xe F

Calculate the total number of electrons for the Lewis structure by summing the number of valence electrons for each atom.

Total number of electrons for Lewis structure = (number of valence e^- in Xe) + 2(number of valence e^- in F)

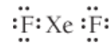
$$= 8 + 2(7)$$
$$= 22$$

Place two bonding electrons between the atoms of each pair of atoms.

F:Xe:F

(4 of 22 electrons used)

Distribute the remaining electrons to give octets to as many atoms as possible, beginning with terminal atoms and finishing with the central atom. Arrange additional electrons around the central atom, giving it an expanded octet of up to 12 electrons.



(16 of 22 electrons used)

(22 of 22 electrons used)

FOR PRACTICE 5.8 Write the Lewis structure for XeF_4.

FOR MORE PRACTICE 5.8 Write the Lewis structure for H_3PO_4. If necessary, expand the octet on any appropriate atoms to lower formal charge.

Interactive Worked Example 5.8 **Writing Lewis Structures for Compounds Having Expanded Octets**

Conceptual Connection 5.4 **Expanded Octets**

Interactive