5.2.2: Covalent Bonds and the Periodic Table

Learning Objectives

- Predict the number of covalent bonds formed based on the elements involved and their position on the periodic table.
- Describe the important exceptions to the octet rule.

Diatomic molecules such as hydrogen (H_2), chlorine (Cl_2), fluorine (F_2), etc. containing covalent bonds between two of the same type of atom are only a few examples of the vast number of molecules that can form. Two different atoms can also share electrons and form covalent bonds. For example, water, (H_2O), has two covalent bonds between a single oxygen atom and two hydrogen atoms. Ammonia, (NH_3, is a central nitrogen atom bonded to three hydrogen atoms. Methane, (CH_4, is a single carbon atom covalently bonded to four hydrogen atoms. In these examples the central atoms form different numbers of bonds to hydrogen atoms in order to complete their valence subshell and form octets.

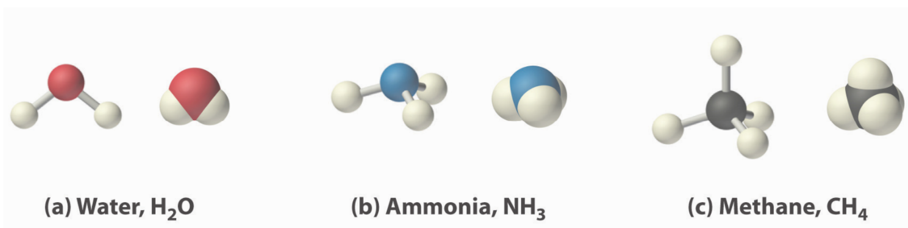
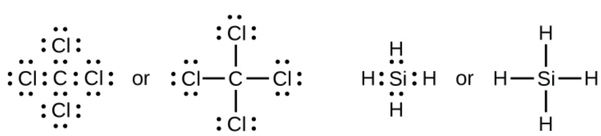


Figure 5.2.2.4: 3D molecule examples. From left to right: water molecule, ammonia molecule, and methane molecule

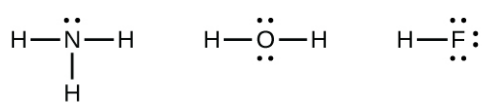
How Many Covalent Bonds Are Formed?

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule and only needs to form one bond. The transition elements and inner transition elements also do not follow the octet rule since they have d and f electrons involved in their valence shells.



carbon tetrachloride silane

Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



ammonia Water hydrogen fluoride

The number of electrons required to obtain an octet determines the number of covalent bonds an atom can form. This is summarized in the table below. In each case, the sum of the number of bonds and the number of lone pairs is 4, which is equivalent to eight (octet) electrons.

Table showing 4 different atoms, each of their number of bonds, and each of their number of lone pairs.

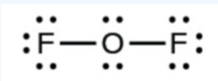
Atom (Group number)	Number of Bonds	Number of Lone Pairs
Carbon (Group 14)	4	0

Atom (Group number)	Number of Bonds	Number of Lone Pairs
Nitrogen (Group 15)	3	1
Oxygen (Group 16)	2	2
Fluorine (Group 17)	1	3

Because hydrogen only needs two electrons to fill its valence shell, it follows the *duet rule*. Hydrogen only needs to form one bond to complete a duet of electrons. This is the reason why H is always a terminal atom and never a central atom.

Example 5.2.2.1

Examine the Lewis structure of OF_2 below. Count the number of bonds formed by each element. Based on the element's location in the periodic table, does it correspond to the expected number of bonds shown in Table 4.1? Does the Lewis structure below follow the octet rule?

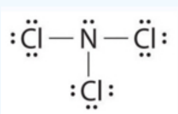


Solution

Yes. F (group 7A) forms one bond and O (group 6A) forms 2 bonds. Each atom is surrounded by 8 electrons. This structure satisfies the octet rule.

Exercise 5.2.2.1

Examine the Lewis structure of NCl_3 below. Count the number of bonds formed by each element. Based on the element's location in the periodic table, does it correspond to the expected number of bonds shown in Table 4.1? Does the Lewis structure below follow the octet rule?



Answer

Both Cl and N form the expected number of bonds. Cl (group 7A) has one bond and 3 lone pairs. The central atom N (group 5A) has 3 bonds and one lone pair. Yes, the Lewis structure of NCl_3 follows the octet rule.

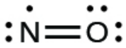
Octet Rule Exceptions

As important and useful as the octet rule is in chemical bonding, there are many covalent molecules with central atoms that do not have eight electrons in their Lewis structures. This does not mean that the octet rule is useless—quite the contrary. As with many rules, there are exceptions, or violations. These molecules fall into three categories:

- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient (diminished octet) molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Expanded octet (hypervalent) molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron molecules

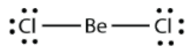
Although they are few, some stable compounds, often called *free radicals*, have an odd number of electrons in their valence shells. With an odd number of electrons, at least one atom in the molecule will have to violate the octet rule. Examples of stable, odd-electron molecules are NO, NO_2, and ClO_2. The Lewis electron dot diagram for NO, a compound produced in internal combustion engines when oxygen and nitrogen react at high temperatures, is as follows:



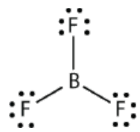
As you can see, the nitrogen and oxygen share four electrons between them. The oxygen atom has an octet of electrons but the nitrogen atom has only seven valence electrons, two electrons in the double bond, one lone pair, and one additional lone electron. Although NO is a stable compound, it is very chemically reactive, as are most other odd-electron compounds.

Electron-deficient molecules

These stable compounds have less than eight electrons around an atom in the molecule, i.e. they have less than an octet. The most common examples are the covalent compounds of beryllium and boron. For example, beryllium can form two covalent bonds, resulting in only four electrons in its valence shell:

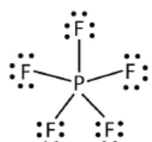


Boron commonly makes only three covalent bonds, resulting in only six valence electrons around the B atom. A well-known example is BF_3:

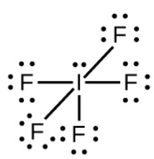


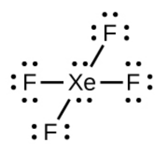
Expanded Octet Molecules

Elements in the second period of the periodic table (*n* = 2) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2*s* and three 2*p* orbitals). Elements in the third and higher periods (*n* ≥ 3) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals in the same shell. Molecules formed from these elements have expanded octets and are sometimes called hypervalent molecules. Phosphorous pentachloride shares five pairs of electrons for a total of ten electrons in the valence shell.



In some expanded octet molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:





Example 5.2.2.2

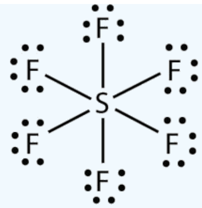
Identify each violation to the octet rule by drawing a Lewis electron dot diagram.

a. ClO
b. SF_6

Solution

1. With one Cl atom and one O atom, this molecule has 6 + 7 = 13 valence electrons, so it is an odd-electron molecule. A Lewis electron dot diagram for this molecule is as follows:

2. In SF_6, the central S atom makes six covalent bonds to the six surrounding F atoms, so it is an expanded valence shell molecule. Its Lewis electron dot diagram is as follows:



? Exercise 5.2.2.2: Xenon Difluoride

Identify the violation to the octet rule in XeF_2 by drawing a Lewis electron dot diagram.

Answer

The Xe atom has an expanded valence shell with more than eight electrons around it.

Concept Review Exercises

1. How is a covalent bond formed between two atoms?
2. How does covalent bonding allow atoms in group 6A to satisfy the octet rule?

Answers

1. Covalent bonds are formed by two atoms sharing electrons.
2. The atoms in group 6A make two covalent bonds.
