

7.2: Exceptions to the Octet Rule

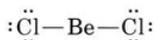
Considering the tremendous variety in properties of elements and compounds in the periodic system, it is asking a great deal to expect a rule as simple as [Lewis' octet theory](#) to be able to predict all formulas or to account for all molecular structures involving [covalent bonds](#). Lewis' theory concentrates on resemblances to noble-gas ns^2np^6 valence octets. Therefore it is most successful in accounting for formulas of compounds of the representative elements, whose distinguishing electrons are also s and p electrons. [The octet rule](#) is much less useful in dealing with compounds of the transition elements or inner transition elements, most of which involve some participation of d or f orbitals in bonding.

Even among the representative elements there are some exceptions to the Lewis theory. These fall mainly into three categories:

1. Some stable molecules simply do not have enough electrons to achieve octets around all atoms. This usually occurs in compounds containing Be or B.
2. Elements in the third period and below can accommodate more than an octet of electrons. Although elements such as Si, P, S, Cl, Br, and I obey the octet rule in many cases, under other circumstances they form more bonds than the rule allows.
3. Free Radicals

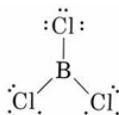
Electron Deficient Species

Good examples of the first type of exception are provided by BeCl_2 and BCl_3 . Beryllium dichloride, BeCl_2 , is a covalent rather than an ionic substance. Solid BeCl_2 has a relatively Complex structure at room temperature, but when it is heated to 750°C , a vapor which consists of separate BeCl_2 molecules is obtained. Since Cl atoms do not readily form multiple bonds, we expect the Be atom to be joined to each Cl atom by a single bond. The structure is



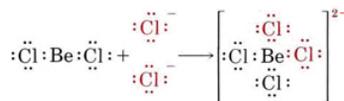
A central Be structure is single bonded to two chlorine atom. The three pairs of unpaired electrons on each chlorine is shown as dots.

Instead of an octet the valence shell of Be contains only *two* electron pairs. Similar arguments can be applied to boron trichloride, BCl_3 , which is a stable gas at room temperature. We are forced to write its structure as



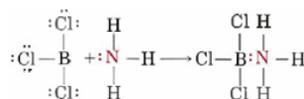
A central B atom is single bonded to three chlorine atoms. The three chlorine atoms are 60° from one another and form a triangular shape with boron in the center. The three pairs of unpaired electrons on chlorine are shown as dots.

in which the valence shell of boron has only three pairs of electrons. Molecules such as BeCl_2 and BCl_3 are referred to as **electron deficient** because some atoms do not have complete octets. Electron-deficient molecules typically react with species containing lone pairs, acquiring octets by formation of coordinate covalent bonds. Thus BeCl_2 reacts with Cl^- ions to form BeCl_4^- ;



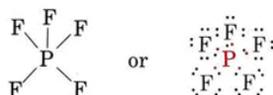
A BeCl_2 molecule reacts with two chlorine anions to give BeCl_4^- with a complete octet set. The overall charge of the molecule is negative 2.

BCl_3 reacts with NH_3 in the following way:



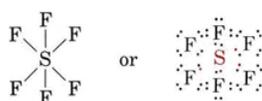
Species with Expanded Octets

Examples of molecules with more than an octet of electrons are phosphorus pentafluoride (PF₅) and sulfur hexafluoride (SF₆). Phosphorus pentafluoride is a gas at room temperature. It consists of PF₅ molecules in which each fluorine atom is bonded to the phosphorus atom. Since each bond corresponds to a shared pair of electrons, the Lewis structure is



P is connected to two equally spaced F atoms below it and three equally spaced F atoms above it. The dot diagram shows that P has a total of ten electrons on its valence.

Instead of an octet the phosphorus atom has 10 electrons in its valence shell. Sulfur hexafluoride (also a gas) consists of SF₆ molecules. Its structure is



Sulfur bonded to six Fluorine that are equally spaced out from one another. The dot diagram shows that sulfur has 12 electrons in its valence shell.

Here the sulfur atom has six electron pairs in its valence shell.

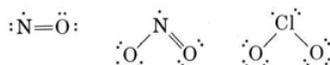
An atom like phosphorus or sulfur which has more than an octet is said to have *expanded its valence shell*. This can only occur when the valence shell has enough orbitals to accommodate the extra electrons. For example, in the case of phosphorus, the valence shell has a principal quantum number $n = 3$. An octet would be $3s^2 3p^6$. However, the $3d$ subshell is also available, and some of the $3d$ orbitals may also be involved in bonding. This permits the extra pair of electrons to occupy the valence ($n = 3$) shell of phosphorus in PF₅.

Expansion of the valence shell is impossible for an atom in the second period because there is no such thing as a $2d$ orbital. The valence ($n = 2$) shell of nitrogen, for example, consists of the $2s$ and $2p$ subshells only. Thus nitrogen can form NF₃ (in which nitrogen has an octet) but not NF₅. Phosphorus, on the other hand, forms both PF₃ and PF₅, the latter involving expansion of the valence shell to include part of the $3d$ subshell.

Free Radicals

The majority of molecules or complex ions discussed in general chemistry courses are demonstrated to have *pairs of electrons*. However, there are a few stable molecules which contain an odd number of electrons. These molecules, called "*free radicals*", contain at least one unpaired electron, a clear violation of the *octet rule*. Free radicals play many important roles a wide range of applied chemistry fields, including biology, medicine, and astrochemistry.

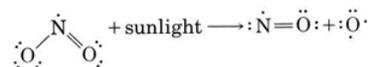
Three well-known examples of such molecules are nitrogen (II) oxide, nitrogen(IV) oxide, and chlorine dioxide. The most plausible *Lewis structures* for these molecules are



The N in nitrogen 2 oxide is double bonded to O, has one pair of unpaired electrons and one unpaired electron in its valence. The Nitrogen in nitrogen 4 oxide has one double bond with O, one single bond with O, and one unpaired electron. The Chlorine in chlorine dioxide is single bonded to two O which leaves one pair of unpaired electrons and one unpaired electrons in its valence.

Free radicals are usually more reactive than the average molecule in which all electrons are paired. In particular they tend to combine with other molecules so that their unpaired electron finds a partner of opposite spin. Since most molecules have all electrons paired, such reactions usually produce a new free radical. This is one reason why automobile emissions which cause even small concentrations of NO and NO₂ to be present in the air can be a serious pollution problem. When one of these free radicals reacts with other automobile emissions, the problem does not go away. Instead a different free radical is produced which is just as

reactive as the one which was consumed. To make matters worse, when sunlight interacts with NO_2 , it produces *two* free radicals for each one destroyed:



In this way a bad problem is made very much worse.

A fourth very interesting example of a free radical is oxygen gas. The Lewis structure for Oxygen usually hides the fact that it is a "*diradical*", containing two unpaired electrons. This is often cited as a *serious flaw in Lewis bond theory*, and was a major impetus for development of [molecular orbital theory](#). We know oxygen is a diradical because of its paramagnetic character, which is easily demonstrated by attraction of oxygen to an external magnet.

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