

# COVALENT BONDING AND ELECTRON PAIR SHARING

Version 1.1: 2004/11/22 14:45:53.470 US/Central

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## Abstract

## Covalent Bonding and Electron Pair Sharing

### 1 Foundation

We begin with our understanding of the relationship between chemical behavior and atomic structure. That is, we assume the Periodic Law that the chemical and physical properties of the elements are periodic functions of atomic number. We further assume the structure of the atom as a massive, positively charged nucleus, whose size is much smaller than that of the atom as a whole, surrounded by a vast open space in which move negatively charged electrons. These electrons can be effectively partitioned into a core and a valence shell, and it is only the electrons in the valence shell which are significant to the chemical properties of the atom. The number of valence electrons in each atom is equal to the group number of that element in the Periodic Table.

### 2 Goals

The atomic molecular theory is extremely useful in explaining what it means to form a compound its component elements. That is, a compound consists of identical molecules, each comprised of the atoms of the component elements in a simple whole number ratio. However, the atomic molecular theory also opens up a wide range of new questions. We would like to know what atomic properties determine the number of atoms of each type which combine to form stable compounds. Why are some combinations observed and other combinations not observed? Some elements with very dissimilar atomic masses (for example, iodine and chlorine) form very similar chemical compounds, but other elements with very similar atomic masses (for example, oxygen and nitrogen) form very dissimilar compounds. What factors are responsible for the bonding properties of the elements in a similar group? In general, we need to know what forces hold atoms together in forming a molecule.

We have developed a detail understanding of the structure of the atom. Our task now is to apply this understanding to develop a similar level of detail about how atoms bond together to form molecules.

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### 3 Observation 1: Valence and the Periodic Table

To begin our analysis of chemical bonding, we define the **valence** of an atom by its tendencies to form molecules. The inert gases do not tend to combine with any other atoms. We thus assign their valence as 0, meaning that these atoms tend to form 0 bonds. Each halogen prefers to form molecules by combining with a single hydrogen atom ( e.g.  $HF$ ,  $HCl$ ). We thus assign their valence as 1, also taking hydrogen to also have a valence of 1. What we mean by a valence of 1 is that these atoms prefer to bind to only one other atom. The valence of oxygen, sulfur, etc. is assigned as 2, since two hydrogens are required to satisfy bonding needs of these atoms. Nitrogen, phosphorus, etc. have a valence of 3, and carbon and silicon have a valence of 4. This concept also applies to elements just following the inert gases. Lithium, sodium, potassium, and rubidium bind with a single halogen atom. Therefore, they also have a valence of 1. Correspondingly, it is not surprising to find that, for example, the combination of two potassium atoms with a single oxygen atom forms a stable molecule, since oxygen's valence of 2 is satisfied by the two alkali atoms, each with valence 1. We can proceed in this manner to assign a valence to each element, by simply determining the number of atoms to which this element's atoms prefer to bind.

In doing so, we discover that the periodic table is a representation of the valences of the elements: elements in the same group all share a common valence. The inert gases with a valence of 0 sit to one side of the table. Each inert gas is immediately preceded in the table by one of the halogens: fluorine precedes neon, chlorine precedes argon, bromine precedes krypton, and iodine precedes xenon. And each halogen has a valence of one. This "one step away, valence of one" pattern can be extended. The elements just prior to the halogens (oxygen, sulfur, selenium, tellurium) are each two steps away from the inert gases in the table, and each of these elements has a valence of two ( e.g.  $H_2O$ ,  $H_2S$ ). The elements just preceding these (nitrogen, phosphorus, antimony, arsenic) have valences of three ( e.g.  $NH_3$ ,  $PH_3$ ), and the elements before that (carbon and silicon most notably) have valences of four ( $CH_4$ ,  $SiH_4$ ). The two groups of elements immediately after the inert gases, the alkali metals and the alkaline earths, have valences of one and two, respectively. Hence, for many elements in the periodic table, the valence of its atoms can be predicted from the number of steps the element is away from the nearest inert gas in the table. This systemization is quite remarkable and is very useful for remembering what molecules may be easily formed by a particular element.

Next we discover that there is a pattern to the valences: for elements in groups 4 through 8 ( e.g. carbon through neon), the valence of each atom *plus* the number of electrons in the valence shell in that atom always equals *eight*. For examples, carbon has a valence of 4 and has 4 valence electrons, nitrogen has a valence of 3 and has 5 valence electrons, and oxygen has a valence of 2 and has 6 valence electrons. Hydrogen is an important special case with a single valence electron and a valence of 1. Interestingly, for each of these atoms, the number of bonds the atom forms is equal to the number of vacancies in its valence shell.

To account for this pattern, we develop a model assuming that each atom attempts to bond to other atoms so as to completely fill its valence shell with electrons. For elements in groups 4 through 8, this means that each atom attempts to complete an "octet" of valence shell electrons. (Why atoms should behave this way is a question unanswered by this model.) Consider, for example, the combination of hydrogen and chlorine to form hydrogen chloride,  $HCl$ . The chlorine atom has seven valence electrons and seeks to add a single electron to complete an octet. Hence, chlorine has a valence of 1. Either hydrogen or chlorine could satisfy its valence by "taking" an electron from the other atom, but this would leave the second atom now needing two electrons to complete its valence shell. The only way for both atoms to complete their valence shells simultaneously is to *share* two electrons. Each atom donates a single electron to the electron pair which is shared. It is this sharing of electrons

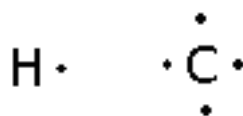


Figure 1

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that we refer to as a chemical bond, or more specifically, as a **covalent bond**, so named because the bond acts to satisfy the valence of both atoms. The two atoms are thus held together by the need to share the electron pair.

#### 4 Observation 2: Compounds of Carbon and Hydrogen

Many of the most important chemical fuels are compounds composed entirely of carbon and hydrogen, *i.e.* hydrocarbons. The smallest of these is methane  $CH_4$ , a primary component of household natural gas. Other simple common fuels include ethane  $C_2H_6$ , propane  $C_3H_8$ , butane  $C_4H_{10}$ , pentane  $C_5H_{12}$ , hexane  $C_6H_{14}$ , heptane  $C_7H_{16}$ , and octane  $C_8H_{18}$ . It is interesting to note that there is a consistency in these molecular formulae: in each case, the number of hydrogen atoms is two more than twice the number of carbon atoms, so that each compound has a molecular formula like  $C_nH_{2n+2}$ . This suggests that there are strong similarities in the valences of the atoms involved which should be understandable in terms of our valence shell electron pair sharing model. In each molecule, the carbon atoms must be directly bonded together, since they cannot be joined together with a hydrogen atom. In the easiest example of ethane, the two carbon atoms are bonded together, and each carbon atom is in turn bonded to three hydrogen atoms. Thus, in this case, it is relatively apparent that the valence of each carbon atom is 4, just as in methane, since each is bonded to four other atoms. Therefore, by sharing an electron pair with each of the four atoms to which it is bonded, each carbon atom has a valence shell of eight electrons.

In most other cases, it is not so trivial to determine which atoms are bonded to which, as there may be multiple possibilities which satisfy all atomic valences. Nor is it trivial, as the number of atoms and electrons increases, to determine whether each atom has an octet of electrons in its valence shell. We need a system of electron accounting which permits us to see these features more clearly. To this end, we adopt a standard notation for each atom which displays the number of valence electrons in the unbonded atom explicitly. In this notation, carbon and hydrogen look like Figure 1, representing the single valence electron in hydrogen and the four valence electrons in carbon.

Using this notation, it is now relatively easy to represent the shared electron pairs and the carbon atom valence shell octets in methane and ethane. Linking bonded atoms together and pairing the valence shell electrons from each gives Figure 2.

Recall that each shared pair of electrons represents a chemical bond. These are examples of what are called **Lewis structures**, after G.N. Lewis who first invented this notation. These structures reveal, at a glance, which atoms are bonded to which, *i.e.* the structural formula of the molecule. We can also easily count the number of valence shell electrons around each atom in the bonded molecule. Consistent with our model of the octet rule, each carbon atom has eight valence electrons and each hydrogen has two in the molecule.

In a larger hydrocarbon, the structural formula of the molecule is generally not predictable from the number of carbon atoms and the number of hydrogen atoms, so the





Figure 4

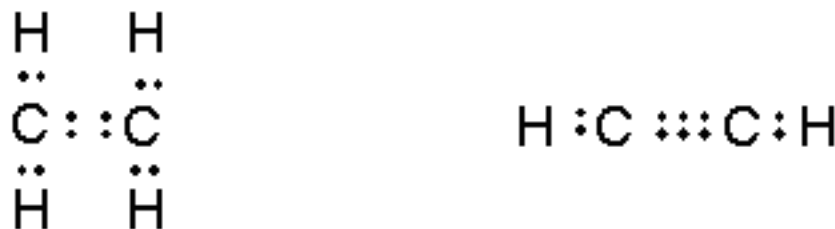


Figure 5

By simply arranging the electrons so that the carbon atoms share a single pair of electrons, we wind up with rather unsatisfying Lewis structures for ethene and acetylene, shown here (Figure 4).

Note that, in these structures, neither carbon atom has a complete octet of valence shell electrons. Moreover, these structures indicate that the carbon-carbon bonds in ethane, ethene, and acetylene should be very similar, since in each case a single pair of electrons is shared by the two carbons. However, these bonds are observed to be chemically and physically very different. First, we can compare the energy required to break each bond (the **bond energy** or **bond strength**). We find that the carbon-carbon bond energy is 347 kJ in  $C_2H_6$ , 589 kJ in  $C_2H_4$ , and 962 kJ in  $C_2H_2$ . Second, it is possible to observe the distance between the two carbon atoms, which is referred to as the **bond length**. It is found that carbon-carbon bond length is 154 pm in  $C_2H_6$ , 134 pm in  $C_2H_4$ , and 120 pm in  $C_2H_2$ . (1picometer = 1pm =  $10^{-12}m$ ). These observations reveal clearly that the bonding between the carbon atoms in these three molecules must be very different.

Note that the bond in ethene is about one and a half times as strong as the bond in ethane; this suggests that the two unpaired and unshared electrons in the ethene structure above are also paired and shared as a second bond between the two carbon atoms. Similarly, since the bond in acetylene is about two and a half times stronger than the bond in ethane, we can imagine that this results from the sharing of three pairs of electrons between the two carbon atoms. These assumptions produce the Lewis structures here (Figure 5).

These structures appear sensible from two regards. First, the trend in carbon-carbon bond strengths can be understood as arising from the increasing number of shared pairs of electrons. Second, each carbon atom has a complete octet of electrons. We refer to the

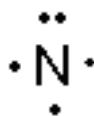


Figure 6

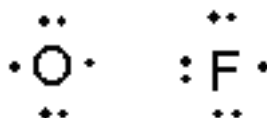


Figure 7

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two pairs of shared electrons in ethene as a **double bond** and the three shared pairs in acetylene as a **triple bond**.

We thus extend our model of valence shell electron pair sharing to conclude that carbon atoms can bond by sharing one, two, or three pairs of electrons as needed to complete an octet of electrons, and that the strength of the bond is greater when more pairs of electrons are shared. Moreover, the data above tell us that the carbon-carbon bond in acetylene is shorter than that in ethene, which is shorter than that in ethane. We conclude that triple bonds are shorter than double bonds which are shorter than single bonds.

### 5 Observation 3: Compounds of Nitrogen, Oxygen, and the Halogens

Many compounds composed primarily of carbon and hydrogen also contain some oxygen or nitrogen, or one or more of the halogens. We thus seek to extend our understanding of bonding and stability by developing Lewis structures involving these atoms. Recall that a nitrogen atom has a valence of 3 and has five valence electrons. In our notation, we could draw a structure in which each of the five electrons appears separately in a ring, similar to what we drew for C. However, this would imply that a nitrogen atom would generally form five bonds to pair its five valence electrons. Since the valence is actually 3, our notation should reflect this. One possibility looks like this (Figure 6).

Note that this structure leaves three of the valence electrons "unpaired" and thus ready to join in a shared electron pair. The remaining two valence electrons are "paired," and this notation implies that they therefore are not generally available for sharing in a covalent bond. This notation is consistent with the available data, *i.e.* five valence electrons and a valence of 3. Pairing the two non-bonding electrons seems reasonable in analogy to the fact that electrons are paired in forming covalent bonds.

Analogous structures can be drawn for oxygen, as well as for fluorine and the other halogens, as shown here (Figure 7).

With this notation in hand, we can now analyze structures for molecules including nitrogen, oxygen, and the halogens. The hydrides are the easiest, shown here (Figure 8).

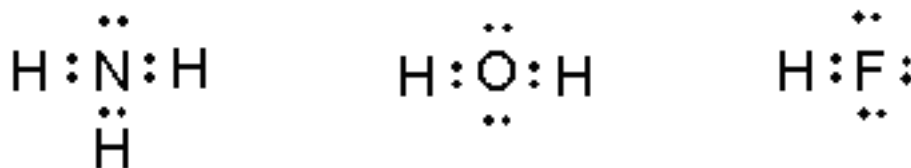


Figure 8

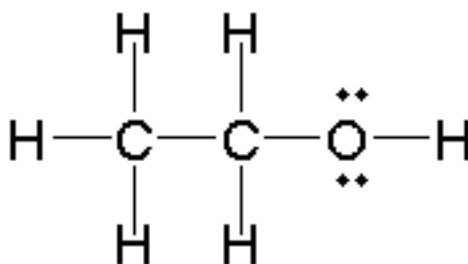


Figure 9

Note that the octet rule is clearly obeyed for oxygen, nitrogen, and the halogens.

At this point, it becomes very helpful to adopt one new convention: a pair of bonded electrons will now be more easily represented in our Lewis structures by a straight line, rather than two dots. Double bonds and triple bonds are represented by double and triple straight lines between atoms. We will continue to show non-bonded electron pairs explicitly.

As before, when analyzing Lewis structures for larger molecules, we must already know which atoms are bonded to which. For example, two very different compounds, ethanol and dimethyl ether, both have molecular formula  $C_2H_6O$ . In ethanol, the two carbon atoms are bonded together and the oxygen atom is attached to one of the two carbons; the hydrogens are arranged to complete the valences of the carbons and the oxygen shown here (Figure 9).

This Lewis structure reveals not only that each carbon and oxygen atom has a completed octet of valence shell electrons but also that, in the stable molecule, there are four non-bonded electrons on the oxygen atom. Ethanol is an example of an **alcohol**. Alcohols can be easily recognized in Lewis structures by the C-O-H group. The Lewis structures of all alcohols obey the octet rule.

In dimethyl ether, the two carbons are each bonded to the oxygen, in the middle, shown here (Figure 10).

**Ethers** can be recognized in Lewis structures by the C-O-C arrangement. Note that, in both ethanol and dimethyl ether, the octet rule is obeyed for all carbon and oxygen atoms. Therefore, it is not usually possible to predict the structural formula of a molecule from Lewis structures. We must know the molecular structure prior to determining the Lewis

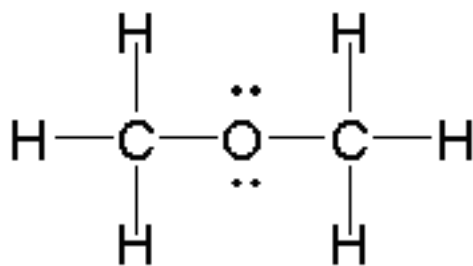


Figure 10

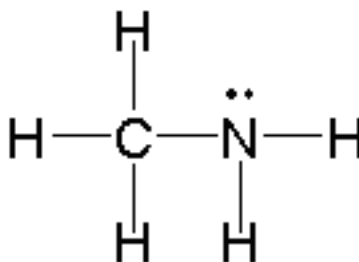


Figure 11

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structure.

Ethanol and dimethyl ether are examples of **isomers**, molecules with the same molecular formula but different structural formulae. In general, isomers have rather different chemical and physical properties arising from their differences in molecular structures.

A group of compounds called **amines** contain hydrogen, carbon, and nitrogen. The simplest amine is methyl amine, whose Lewis structure is here (Figure 11).

"Halogenated" hydrocarbons have been used extensively as refrigerants in air conditioning systems and refrigerators. These are the notorious "chlorofluorocarbons" or "CFCs" which have been implicated in the destruction of stratospheric ozone. Two of the more important CFCs include Freon 11,  $CFCl_3$ , and Freon 114,  $C_2F_4Cl_2$ , for which we can easily construct appropriate Lewis structures, shown here (Figure 12).

Finally, Lewis structures account for the stability of the diatomic form of the elemental halogens,  $F_2$ ,  $Cl_2$ ,  $Br_2$ , and  $I_2$ . The single example of  $F_2$  is sufficient, shown here (Figure 13).

We can conclude from these examples that molecules containing oxygen, nitrogen, and the halogens are expected to be stable when these atoms all have octets of electrons in their valence shells. The Lewis structure of each molecule reveals this character explicitly.

On the other hand, there are many examples of common molecules with apparently unusual valences, including: carbon dioxide  $CO_2$ , in which the carbon is bonded to only two atoms and each oxygen is only bonded to one; formaldehyde  $H_2CO$ ; and hydrogen

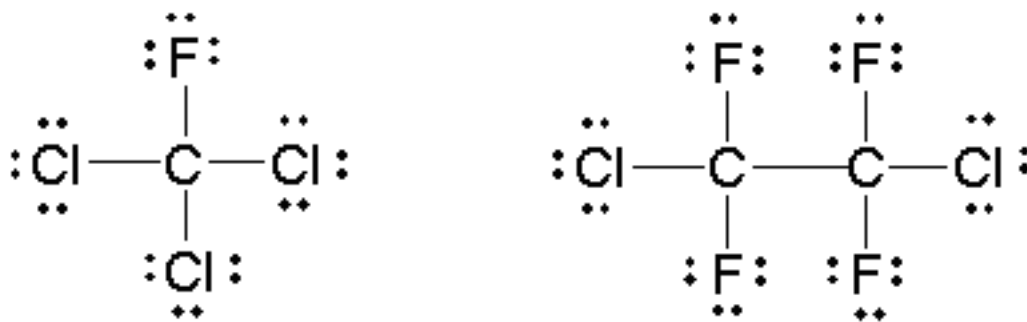


Figure 12

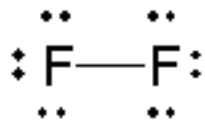


Figure 13

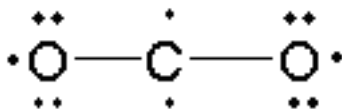


Figure 14

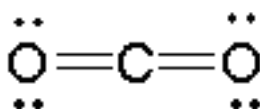


Figure 15

cyanide  $HCN$ . Perhaps most conspicuously, we have yet to understand the bonding in two very important elemental diatomic molecules,  $O_2$  and  $N_2$ , each of which has fewer atoms than the valence of either atom.

We first analyze  $CO_2$ , noting that the bond strength of one of the  $CO$  bonds in carbon dioxide is 532 kJ, which is significantly greater than the bond strength of the  $CO$  bond in ethanol, 358 kJ. By analogy to the comparison of bonds strengths in ethane to ethene, we can imagine that this difference in bond strengths results from double bonding in  $CO_2$ . Indeed, a Lewis structure of  $CO_2$  in which only single electron pairs are shared (Figure 14) does not obey the octet rule, but one in which we pair and share the extra electrons reveals that double bonding permits the octet rule to be obeyed (Figure 15).

A comparison of bond lengths is consistent with our reasoning: the single  $CO$  bond in ethanol is 148 pm, whereas the double bond in  $CO_2$  is 116.

Knowing that oxygen atoms can double-bond, we can easily account for the structure of formaldehyde. The strength of the  $CO$  bond in  $H_2CO$  is comparable to that in  $CO_2$ , consistent with the Lewis structure here (Figure 16).

What about nitrogen atoms? We can compare the strength of the  $CN$  bond in  $HCN$ , 880

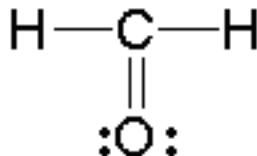


Figure 16

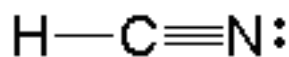


Figure 17

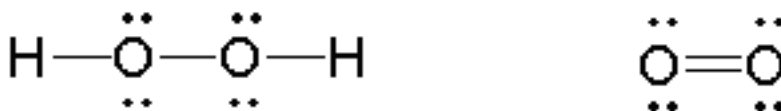


Figure 18

kJ, to that in methyl amine, 290 kJ. This dramatic disparity again suggests the possibility of multiple bonding, and an appropriate Lewis structure for  $HCN$  is shown here (Figure 17).

We can conclude that oxygen and nitrogen atoms, like carbon atoms, are capable of multiple bonding. Furthermore, our observations of oxygen and nitrogen reinforce our earlier deduction that multiple bonds are stronger than single bonds, and their bond lengths are shorter.

As our final examples in this section, we consider molecules in which oxygen atoms are bonded to oxygen atoms. Oxygen-oxygen bonds appear primarily in two types of molecules. The first is simply the oxygen diatomic molecule,  $O_2$ , and the second are the peroxides, typified by hydrogen peroxide,  $H_2O_2$ . In a comparison of bond energies, we find that the strength of the  $OO$  bond in  $O_2$  is 499 kJ whereas the strength of the  $OO$  bond in  $H_2O_2$  is 142 kJ. This is easily understood in a comparison of the Lewis structures of these molecules, showing that the peroxide bond is a single bond, whereas the  $O_2$  bond is a double bond, shown here (Figure 18).

We conclude that an oxygen atom can satisfy its valence of 2 by forming two single bonds or by forming one double bond. In both cases, we can understand the stability of the resulting molecules by in terms of an octet of valence electrons.

## 6 Interpretation of Lewis Structures

Before further developing our model of chemical bonding based on Lewis structures, we pause to consider the interpretation and importance of these structures. It is worth recalling that we have developed our model based on observations of the numbers of bonds formed by individual atoms and the number of valence electrons in each atom. In general, these structures are useful for predicting whether a molecule is expected to be stable under normal conditions. If we cannot draw a Lewis structure in which each carbon, oxygen, nitrogen, or halogen has an octet of valence electrons, then the corresponding molecule probably is not stable. Consideration of bond strengths and bond lengths enhances the model by revealing the presence of double and triple bonds in the Lewis structures of some molecules.

At this point, however, we have observed no information regarding the geometries of

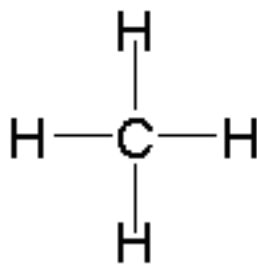


Figure 19



Figure 20

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molecules. For example, we have not considered the angles measured between bonds in molecules. Consequently, the Lewis structure model of chemical bonding does not at this level predict or interpret these bond angles. (This will be considered here<sup>1</sup>.) Therefore, although the Lewis structure of methane is drawn as shown here (Figure 19).

This does *not* imply that methane is a flat molecule, or that the angles between *CH* bonds in methane is 90°. Rather, the structure simply reveals that the carbon atom has a complete octet of valence electrons in a methane molecule, that all bonds are single bonds, and that there are no non-bonding electrons. Similarly, one can write the Lewis structure for a water molecule in two apparently different ways, shown here (Figure 20).

However, it is very important to realize that these two structures are *identical* in the Lewis model, because both show that the oxygen atom has a complete octet of valence electrons, forms two single bonds with hydrogen atoms, and has two pairs of unshared electrons in its valence shell. In the same way, the two structures for Freon 114 shown here (Figure 21) are also *identical*.

These two drawings do not represent different structures or arrangements of the atoms in the bonds.

Finally, we must keep in mind that we have drawn Lewis structures strictly as a convenient tool for our understanding of chemical bonding and molecular stability. It is based on commonly observed trends in valence, bonding, and bond strengths. These structures must not be mistaken as observations themselves, however. As we encounter additional experimental observations, we must be prepared to adapt our Lewis structure model to fit

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<sup>1</sup><http://cnx.rice.edu/content/Case Study 5???/latest/>

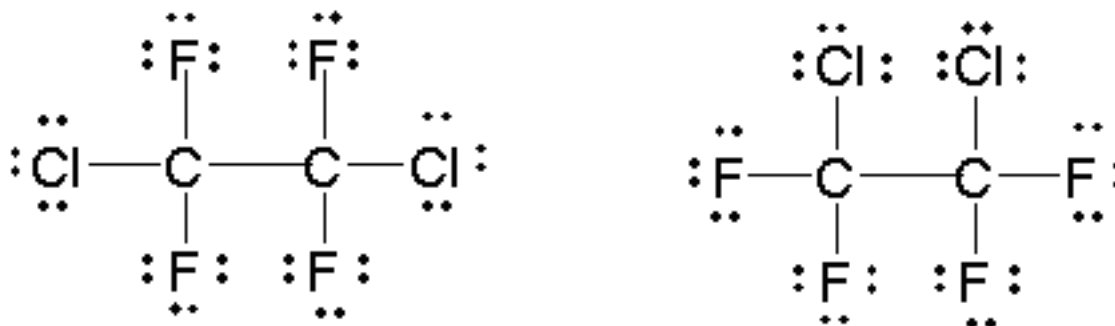


Figure 21

these observations, but we must never adapt our observations to fit the Lewis model.

## 7 Extensions of the Lewis Structure Model

With these thoughts in mind, we turn to a set of molecules which challenge the limits of the Lewis model in describing molecular structures. First, we note that there are a variety of molecules for which atoms clearly must bond in such a way as to have more than eight valence electrons. A conspicuous example is  $SF_6$ , where the sulfur atom is bonded to six F atoms. As such, the S atom must have 12 valence shell electrons to form 6 covalent bonds. Similarly, the phosphorous atom in  $PCl_5$  has 10 valence electrons in 5 covalent bonds, the Cl atom in  $ClF_3$  has 10 valence electrons in 3 covalent bonds and two lone pairs. We also observe the interesting compounds of the noble gas atoms, e.g.  $XeO_3$ , where noble gas atom begins with eight valence electrons even before forming any bonds. In each of these cases, we note that the valence of the atoms S, P, Cl, and Xe are normally 2, 3, 1, and 0, yet more bonds than this are formed. In such cases, it is not possible to draw Lewis structures in which S, P, Cl, and Xe obey the octet rule. We refer to these molecules as "expanded valence" molecules, meaning that the valence of the central atom has expanded beyond the expected octet.

There are also a variety of molecules for which there are too few electrons to provide an octet for every atom. Most notably, Boron and Aluminum, from Group III, display bonding behavior somewhat different than we have seen and thus less predictable from the model we have developed so far. These atoms have three valence shell electrons, so we might predict a valence of 3 on the basis of the octet rule. However, compounds in which boron or aluminum atoms form five bonds are never observed, so we must conclude that simple predictions based on the octet rule are not reliable for Group III.

Consider first boron trifluoride,  $BF_3$ . The bonding here (Figure 22) is relatively simple to model with a Lewis structure if we allow each valence shell electron in the boron atom to be shared in a covalent bond with each fluorine atom.

Note that, in this structure, the boron atom has only six valence shell electrons, but the octet rule is obeyed by the fluorine atoms.

We might conclude from this one example that boron atoms obey a sextet rule. However, boron will form a stable ion with hydrogen,  $BH_4^-$ , in which the boron atom does have a complete octet. In addition,  $BF_3$  will react with ammonia  $NH_3$  for form a stable compound,

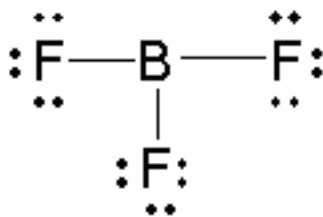


Figure 22

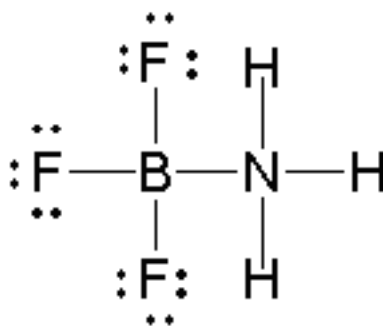


Figure 23

$NH_3BF_3$ , for which a Lewis structure can be drawn in which boron has a complete octet, shown here (Figure 23).

Compounds of aluminum follow similar trends. Aluminum trichloride,  $AlCl_3$ , aluminum hydride,  $AlH_3$ , and aluminum hydroxide,  $Al(OH)_3$ , all indicate a valence of 3 for aluminum, with six valence electrons in the bonded molecule. However, the stability of aluminum hydride ions,  $AlH_4^-$ , indicates that Al can also support an octet of valence shell electrons as well.

We conclude that, although the octet rule can still be of some utility in understanding the chemistry of Boron and Aluminum, the compounds of these elements are less predictable from the octet rule. This should not be disconcerting, however. The octet rule was developed in Section 3 on the basis of the observation that, for elements in Groups IV through VIII, the number of valence electrons plus the most common valence is equal to zero. Elements in Groups I, II, and III do not follow this observation most commonly.

## 8 Resonance Structures

Another interesting challenge for the Lewis model we have developed is the set of molecules for which it is possible to draw more than one structure in agreement with the octet rule. A notable example is the nitric acid molecule,  $HNO_3$ , where all three oxygens are bonded

to the nitrogen. Two structures can be drawn for nitric acid with nitrogen and all three oxygens obeying the octet rule.

In each structure, of the oxygens not bonded to hydrogen, one shares a single bond with nitrogen while the other shares a double bond with nitrogen. These two structures are not identical, unlike the two freon structures in Figure 12, because the atoms are bonded differently in the two structures.

## 9 Review and Discussion Questions

### Exercise 1:

Compounds with formulae of the form  $C_nH_{2n+2}$  are often referred to as "saturated" hydrocarbons. Using Lewis structures, explain how and in what sense these molecules are "saturated."

### Exercise 2:

Molecules with formulae of the form  $C_nH_{2n+1}$  (e.g.  $CH_3$ ,  $C_2H_5$ ) are called "radicals" and are extremely reactive. Using Lewis structures, explain the reactivity of these molecules.

### Exercise 3:

State and explain the experimental evidence and reasoning which shows that multiple bonds are stronger and shorter than single bonds.

### Exercise 4:

Compare  $N_2$  to  $H_4N_2$ . Predict which bond is stronger and explain why.

### Exercise 5:

Explain why the two Lewis structures for Freon 114, shown in Figure 12, are identical. Draw a Lewis structures for an isomer of Freon 114, that is, another molecule with the same molecular formula as Freon 114 but a different structural formula.