Chapter 8: Bonding

Section 8.1: Lewis Dot Symbols

The Lewis electron dot symbol is named after Gilbert Lewis. In the Lewis dot symbol, the element symbol represents the nucleus and the inner electrons.

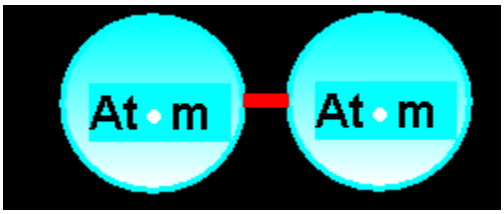
The surrounding dots represent the valence electrons. The valence electrons are the outermost electrons used in making a chemical bond between atoms to form stable molecules or ions. The valence electrons are described for the main group elements.

Group	# valence electrons (# dots)	electron config. for valence shell	Example of Lewis Dot structure
I (1)	1	ns^1	•H •Li •K •Na
II (2)	2	ns^2	•Be• •Mg• •Ca•
XIII (13)	3	ns^2np^1	•B•
XIV (14)	4	ns^2np^2	•C• •Si• •Ge•
XV(15)	5	ns^2np^3	•N• •P•
XVI (16)	6	ns^2np^4	•O• •S•
XVII (17)	7	ns^2np^5	•F• •Cl•

In this section, review the DVD to look at the 3D animations of the Lewis Dot Symbols for main group elements.

Section 8.2: Chemical Bonds

A chemical bond is a link between atoms in molecules or ions, represented by an imaginary line drawn from the nucleus of one atom to the nucleus of the other.



A chemical bond forms when the atoms are arranged in such that they have lower energy in that arrangement than when considered separately.

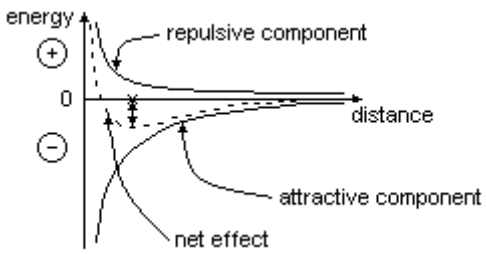
The energy terms involved are:

1. The net potential energy that results from the attractions and repulsions between the charged particles.
2. The kinetic energy due to the motion of the electrons.

Consider a H_2 molecule:
When two individual atoms (H atoms, for instance) are very far from each other, they do not interact with one another. This is so, because the interaction between charges (e^- of one atom w/ protons of the other atom and vice-versa) decreases with increasing distance.

$$\text{energy} \longrightarrow E \propto \frac{Q_1 Q_2}{R} \quad \begin{matrix} \longleftarrow \text{charges} \\ \longleftarrow \text{distance} \end{matrix}$$

As the atoms get closer to each other, they start to feel some attraction toward each other (energy is no longer zero, it becomes negative). Eventually, a distance between atoms is reached where the two atoms reach the most stable state (energy of interaction is most negative). This amount of energy is called the "bond energy". The bond energy is also called "bond enthalpy". In this situation, the distance between atoms is called the bond length. If the atoms get even closer to each other, the arrangement is no longer as stable. This is because the repulsions between electron clouds become significant (interaction energy is less negative).



Repulsive component: e^- of one atom w/ e^- of other atom, proton of one atom w/ proton of other atom. Attractive component: e^- of one atom w/ protons of the other atom. Net effect: sum of attractive and repulsive components.

Section 8.3: Ionic Bonds

The bonding forces that result from the electrostatic attractions of the oppositely charged ions result in the formation of an ionic bond.

Consider NaCl:
In the formation of NaCl, an electron is transferred from the sodium atom to the chlorine atom to form Na^+ and Cl^- ions.

This happens because the sodium atom has low ionization energy and the chlorine atom has a high electron affinity. Hence, the formation of these ions leads to the lowest possible energy. The attraction for the extra electron by the chlorine atom and the strong mutual attractions of the oppositely charged ions, Na^+ and Cl^- are the driving forces for the formation of NaCl. Solid NaCl is a material with a melting point of 800 deg.C. Ionic bonding occurs in ionic compounds.

Ionic compounds are formed when an atom which can readily lose electrons,

$$\text{For example : } Na \longrightarrow Na^+ + e^-$$

reacts with an atom that has high electron affinity,

$$\text{For example : } Cl + e^- \longrightarrow Cl^-$$

Thus, an ionic compound results when a metal reacts with a non-metal. The energy of interaction between a pair of ions can be calculated using Coulomb's law. The mathematical expression for Coulomb's law is:

$$E = 2.31 \times 10^{-19}\ \text{J.nm}\left(\frac{Q_1 Q_2}{r}\right)$$

E = Energy in Joules, J

Q_1 and Q_2 = the ion electric charges in electron units

r = distance between the ions in nm

Example: Calculate the ionic energy per pair of ions in NaCl, if the distance between the centers of ions is 0.276 nm.

$$E = 2.31 \times 10^{-19}\ \text{J.nm}\left[\frac{(+1)(-1)}{0.276\ \text{nm}}\right] = -8.37 \times 10^{-19}\ \text{J}$$

The negative sign indicates that the ion pair has lower energy than the separated ions.

Section 8.4: Covalent Bonds

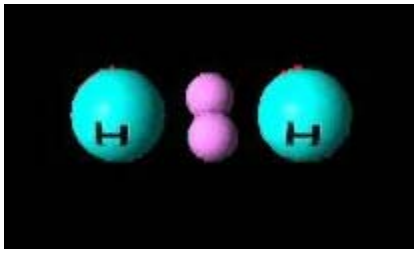
Typically, non-metals do not form cations because they have very large ionization energies. Lewis proposed that a covalent bond is a pair of electrons shared between two atoms. At ordinary temperatures most non-metals exist as molecules.

For example: Hydrogen, oxygen and nitrogen exist as H_2, O_2 and N_2, respectively.

Why do these elements exist as H_2, O_2 and N_2?

The answer involves the understanding of Lewis dot symbols for these elements.

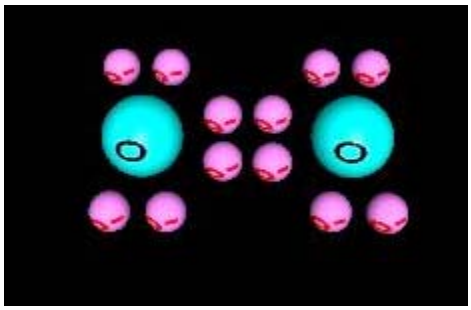
Consider H_2: H–H or H**:**H. Each hydrogen atom has one electron.



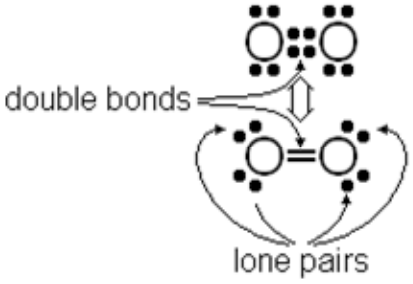
Here, the two electrons are shared by each hydrogen atom. H is in period n = 1. The noble element in that period is He, which has two electrons. Thus, by forming a covalent bond between two hydrogen atoms, the H_2 molecule becomes stable. Hence, there is one bond between two H atoms. And it takes <u>two</u> electrons to make a chemical bond.

Consider O_2: valence shell n = 2 $2s^2 2p^4 \Rightarrow$ 6 valence e^-

Each oxygen atom has six valence electrons. When the two oxygen atoms come close together to form a stable molecule, they adopt the following structure.



Here, four electrons are shared by each oxygen atom. O is in period 2. The noble element in that period is Ne. Ne has 8 valence electrons. Thus, by forming two covalent bonds between two oxygen atoms, the O_2 molecule becomes stable.

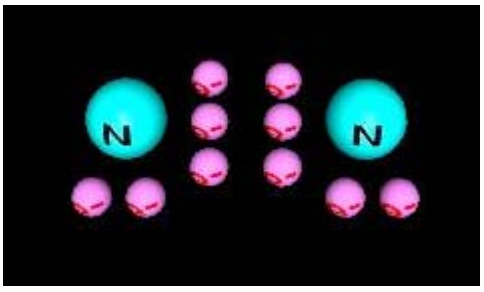


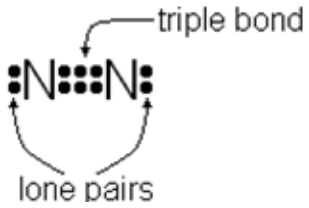
In the O_2 molecule each oxygen atom is surrounded by 8 electrons (octet rule).

Hence, there are two bonds between two O-atoms. These two bonds are called the "double bond" between the O-atoms in the O_2 molecule.

Consider N_2: valence shell n=2 $2s^2 2p^3 \Rightarrow$ 5 valence e^-

Each nitrogen atom has five valence electrons. When the two nitrogen atoms come close together to form a stable molecule, they adopt the following structure.





In the N_2 molecule each nitrogen atom is surrounded by 8 electrons (octet rule).

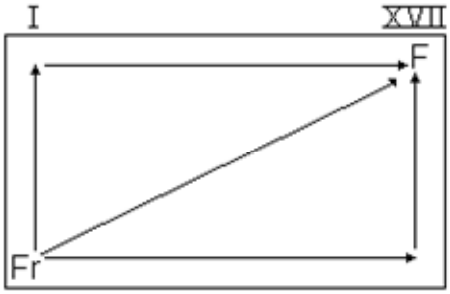
Here, six electrons are shared by each nitrogen atom. N is in period 2. The noble element in that period is Ne. Ne has 8 valence electrons. Thus, by forming three covalent bonds between two nitrogen atoms, the N_2 molecule becomes stable. Hence, there are three bonds between two N-atoms. These three bonds are called the "triple bond" between the two N-atoms in the N_2 molecule.

Section 8.5: Electronegativity

Electronegativity is the ability of an atom to attract the electron pair (bonding pair) to itself when forming a covalent bond. The greater the electronegativity of an atom, the greater its affinity for electrons. Electronegativities are described for main group elements. **In a group, the electronegativity decreases from top to bottom**. **In a period, the electronegativity increases from left to right**.

In a bond, A–B, where the electronegativities of A and B are the same, the bonding electron pair is equally shared among A and B.

Ignoring the group 18 elements (noble elements, which rarely form bonds), the trend in electronegativity is given by:



Electronegativity increases (↑) in the direction given by the arrows.
F is the most electronegative.
Fr is the least electronegative.

When the difference in electronegativity between two atoms is very large (a metal and a non-metal), the resulting bond is ionic (non-metal completely takes away the bonding electron pair, as in Na^+Cl^-, Cs^+F^-). If the difference in electronegativity is small (two non-metals), then a covalent bond results (i.e. C–O, C–Cl, C–H).

Section 8.6: Writing Lewis Structures

The following steps should help you in writing the Lewis structures.

Step 1. In a molecule or ion count the number of valence electrons.

In a molecule, simply add the valence electrons of the atoms present.

For example:

H_2O # of valence electrons = $(2 \times 1) + (1 \times 6) = 8\ e^-$

CCl_4 # of valence electrons = $(1 \times 4) + (4 \times 7) = 32\ e^-$

In a polyatomic cation, subtract the number of electrons based on the charge of the cation.

For example:

NH_4^+ # of valence electrons = $(1 \times 5) + (4 \times 1) - 1 = 8\ e^-$

In a polyatomic anion, add the number of electrons based on the charge of the anion.

For example:

ClO^- # of valence electrons = $(1 \times 7) + (1 \times 6) + 1 = 14\ e^-$

Step 2. From the chemical formula of the molecule or ion, select the central atom.

The central atom is the least electronegative atom in a molecule or ion. If there are hydrogen atoms in a molecule or ion, <u>do not</u> select hydrogen as the central atom.

For example:

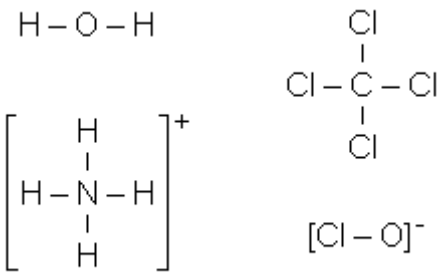
$H_2O \rightarrow$ O is the central atom

$CCl_4 \rightarrow$ C is the central atom

$NH_4^+ \rightarrow$ N is the central atom

$OCl^- \rightarrow$ Cl is the central atom

Step 3. Write the central atom and draw a skeleton structure.

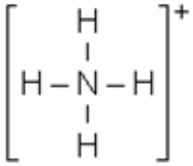


Step 4. For each bond in a molecule or ion, subtract 2 electrons from the total number of valence electrons.

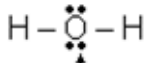
H_2O	$8 - 4 = 4\ e^-$
CCl_4	$32 - 8 = 24\ e^-$
NH_4^+	$8 - 8 = 0\ e^-$
OCl^-	$14 - 2 = 12\ e^-$

This is the number of electrons that are available for non-bonding electron pairs (lone pairs) and for multiple bonds.

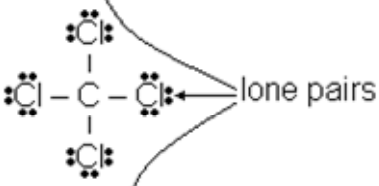
Step 5. Determine the number of electrons needed to complete the octet rule around each atom (duet for H).



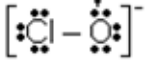
Needs O e^-. N already satisfies the octet rule as it is surrounded by 4 bonds (8 e^-).



Needs 4 e^- (2 x 2 or 2 pairs).



Needs 24 e^- (4 x 6 or 3 pairs per Cl atom).



Needs 12 e^- (6 for Cl, 6 for C).

Step 6. If the number of electrons determined in Step 4 is not sufficient to provide all atoms with octets, there must be one or more multiple bonds.

(This is not the case with any of the above examples.)

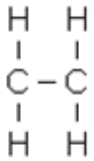
Section 8.7 - 8.8: Writing Lewis Structures for Molecules with Multiple Bonds

For Example: Consider C_2H_4

Step 1. In a molecule or ion count the number of valence electrons.
In C_2H_4, there are 12 valence e^- i.e. (2 x 4) + (4 x 1)

Step 2. From the chemical formula of the molecule or ion, select the central atom.
In C_2H_4 select carbon as the central atom.

Step 3. Write the central atom and draw a skeleton structure.

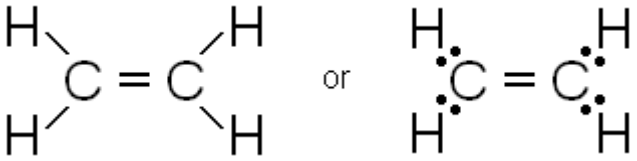


Requires 10 electrons (5 (single bonds) x 2 (# of electrons/bond))

Step 4. For each bond in a molecule or ion, subtract 2 electrons from the total number of valence electrons.
There will be 12 -10 = 2 e^- left to complete the structure satisfying the octet rule around each C.

Step 5. Determine the number of electrons needed to complete the octet rule around each atom (duet for H).
We need 4 e^- to place two lone pairs, one on each carbon. This cannot be done since we have only 2 e^- left (step 4).

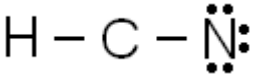
Step 6. If the number of electrons determined in Step 4 is not sufficient to provide all atoms with octets, there must be one or more multiple bonds.
The 2 e^- (calculated in step 4) can be placed as an extra bond between the 2 carbon atoms. Doing this ensures that the octet rule is obeyed by each carbon.



Note: The example below is not covered in the DVD.

Consider HCN: # of valence e^- = 10 e^- (1 + 4 + 5)

10 e^- - 4 e^- = 6 e^-



Octet rule is fulfilled for N, but not C.
4 e^- missing on C can be filled by 2 double bonds or 1 single bond and 1 triple bond. H cannot have a double bond, so 1 single and 1 triple bond is the only solution.

In Section 8.8, practice the Interactive Problems on writing Lewis Structures.

Sections 8.9 - 8.10: Writing Lewis Resonance Structures

Resonance structures have the same relative placement of atoms, but different locations of bonding and lone pairs of electrons.

For example: Write the Lewis structure of SO_2

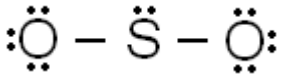
Step 1. In a molecule or ion count the number of valence electrons.
Thus, in SO_2 there are 18 valence e^- i.e. 6 + (2 x 6).

Step 2. From the chemical formula of the molecule or ion, select the central atom.
S is the least electronegative, so it is the central atom.

Step 3. Write the central atom and draw a skeleton structure.

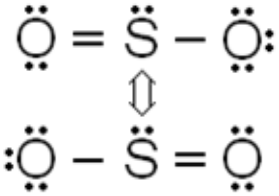
Step 4. For each bond in a molecule or ion, subtract 2 electrons from the total number of valence electrons.
18 – (2 x 2) = 14 e^- (7 lone pairs)

Step 5. Determine the number of electrons needed to complete the octet rule around each atom (duet for H).



16 electrons would be needed if there are only single bonds, meaning that there are two extra electrons needed. The octet rule for S can be fulfilled by adding a double bond. Electrons that make a bond are called bonding electrons. Remember, it takes two electrons to make a bond.

Electrons represented as dots around the atoms are called **lone pairs** of electrons.



Resonance forms differ only in the distribution of electrons,
not in the distribution of atoms

In Section 8.10, practice the Interactive Problem.

Sections 8.11 - 8.12: Formal Charges

Certain molecules and polyatomic ions often have more than one Lewis structure, all of which obey the rules for writing Lewis structures.

The question is which of the many possible Lewis structures describes the actual bonding in a molecule or ion? The answer involves calculating the **formal charge** of each atom (except hydrogen) in a molecule or ion.

The formal charge of an atom in a molecule or ion is the difference between the number of valence electrons on the free atom and the sum of the unshared electrons and one-half the number of shared electrons. Mathematically, this is expressed as:

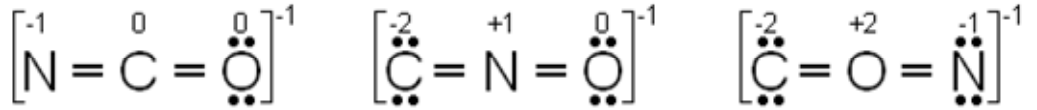
$$F = V - \left(U + \frac{S}{2} \right)$$

Here, F = formal charge of an atom
V = valence electrons
U = unshared electrons
S = shared electrons

Structures with the lowest formal charges are likely to be of the lowest energy.

The molecules discussed here are different than those discussed in the DVD.

Example: consider the cyanate ion, NCO^-.



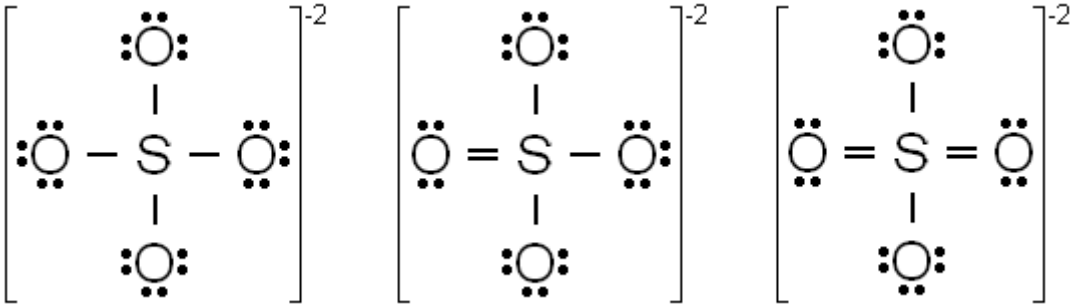
N: $5-(4+\frac{1}{2}(4))=-1$ C: $4-(4+\frac{1}{2}(4))=-2$ C: $4-(4+\frac{1}{2}(4))=-2$

C: $4-(0+\frac{1}{2}(8))=0$ N: $5-(0+\frac{1}{2}(8))=+1$ O: $6-(0+\frac{1}{2}(8))=+2$

O: $6-(4+\frac{1}{2}(4))=0$ O: $6-(4+\frac{1}{2}(4))=0$ N: $5-(4+\frac{1}{2}(4))=-1$

Most stable form of NCO^-.

Example: Consider the sulfate ion, SO_4^{-2}



$S_{FC}=6-(0+\frac{1}{2}(4))=+2$ $S_{FC}=6-(0+\frac{1}{2}(10))=+1$ $S_{FC}=6-(0+\frac{1}{2}(12))=0$

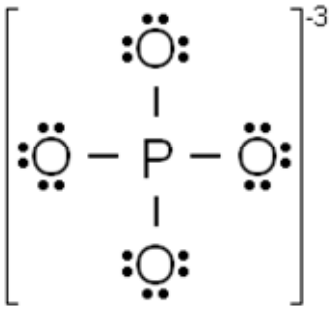
$O_{FC}=6-(6+\frac{1}{2}(2))=-1$

$O_{FC}=6-(4+\frac{1}{2}(4))=0$

The resonance structure with two double bonds is the favored form of the sulfate ion because it has the smallest possible formal charges.

Example: Phosphate ion, PO_4^{-3}

P:	5 e^-	32 e^-
4O:	24 e^-	
-3	3 e^-	



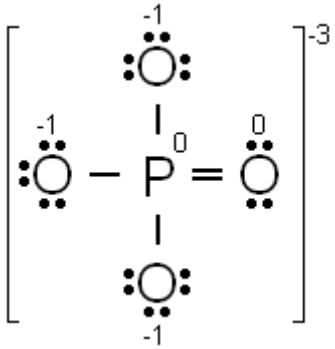
8 e^- for 4 P–O bonds (24 e^- left).
Need 24 e^- for lone pairs on O atoms.

One might think that this is the structure for PO_4^{-3}.

The formal charge on P in the above structure is : $5 - (0 + \frac{1}{2}(8)) = +1$

The formal charge for each O above is : $6 - (6 + \frac{1}{2}(2)) = -1$

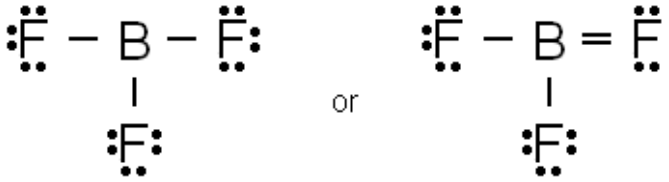
P has empty d-orbitals (3d). Hence, as shall be discussed in the next section, it does not need to satisfy the octet rule.



The formal charge on P in the above structure is : $5 - (0 + \frac{1}{2}(10)) = 0$

Consider boron trifluoride, BF_3.
Boron in boron trifluoride does not need to follow the octet rule as will be discussed in the next section. Hence, the Lewis dot structure of boron trifluoride can be drawn either with three bonds or four bonds from the central B atom. BF_3 has 24 valence electrons.

BF_3



$B_{FC} = 3 - (0 + \frac{1}{2}(6)) = 0$

$F_{FC} = 7 - (6 + \frac{1}{2}(2)) = 0$

$B_{FC} = 3 - (0 + \frac{1}{2}(8)) = -1$

$F_{FC} = 7 - (6 + \frac{1}{2}(2)) = 0$ (single)

$F_{FC} = 7 - (4 + \frac{1}{2}(4)) = +1$ (double)

Hence, the most favorable Lewis dot structure is that showing three single bonds.

Note the following rules which apply for the determination of formal charges:

- For molecules, the sum of the formal charges must add up to zero since molecules are electrically neutral species.
- For cations, the sum of formal charges equals the positive charge of the cation.
- For anions, the sum of formal charges equals the negative charge of the anion.
- For neutral molecules, the Lewis structure in which the formal charges are zero for all atoms is preferred to one in which there are non-zero formal charges.
- For ions, Lewis structures with small formal charges are preferred.
- For Lewis structures with similar distribution of formal charges, the most preferred structure is the one in which the negative formal charges are placed on the more electronegative atoms (outer atoms since the central atom is the least electronegative).

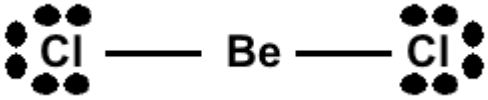
In Section 8.12, practice the Interactive Problem.

Section 8.13: Exceptions to the Octet Rule

Incomplete Octets:

In some molecules and ions, the number of electrons surrounding the central atom is less than eight. Such atoms have an **incomplete octet**.

For example: Consider the Lewis dot structure of $BeCl_2$



Both Cl atoms satisfy the octet rule.
Be violates the octet rule.
In fact, Be has an incomplete octet.

The most important elements which often have an incomplete octet when forming molecules are Be, B and Al. Be may be surrounded by 4 valence electrons, while B and Al may be surrounded by 6 valence electrons.

Radicals:

Molecules containing an **odd number of valence electrons** violate the octet rule.

For example: Consider the Lewis dot structure of nitrogen monoxide (also known as nitric oxide) NO.

The total number of valence electrons in NO is 11.
For such molecules, it is impossible to write Lewis structures in which all atoms obey the octet rule. The Lewis dot structure giving both atoms a formal charge of zero is:

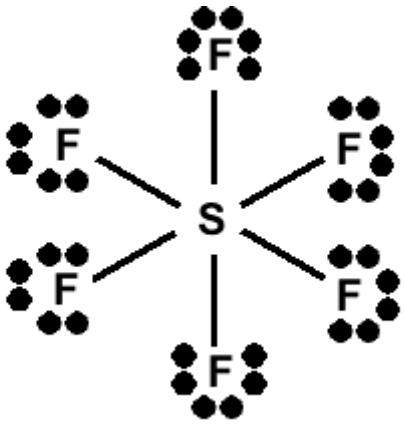
Nitrogen is the central atom, as it is less electronegative than oxygen. It is always the central atom that violates the octet rule. NO is an example of what one calls a radical. **Radicals** are compounds with one or more unpaired electrons.

Expanded Octet:

The largest number of molecules to violate the octet rule consists of a central atom surrounded by more than four pairs of valence electrons. These are called **expanded octets**.

For example: Consider the Lewis dot structure of SF_6

The total number of valence electrons is 48.
The Lewis dot structure giving both atoms a formal charge of zero is:



Each fluorine atoms satisfy the octet rule. However, the central sulfur atom has 12 electrons, which is called an expanded octet.

Elements which can have expanded octets in molecules include:

In period 3: P, S, Cl
In period 4: As, Se, Br
In period 5: Sb, Te, I, Xe

Note that elements in periods n = 3, 4, 5, 6 or 7 do not need to follow the octet rule because they can accept electrons in their empty d-orbitals to form more than four bonds.

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