

V25.0109: Honors Chemistry I (Honors)

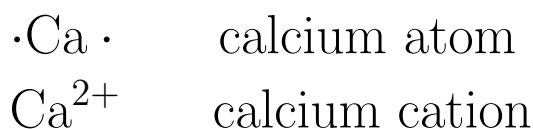
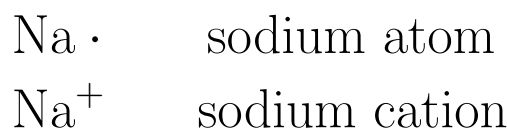
Notes for Lecture 11

I. IONIC BONDING

According to our crude, conceptual definition, chemical bonds can form either by electron transfer between atoms or by sharing of electrons. The former case constitutes a kind of bond known as an *ionic bond*. The reason for this is that if one atom transfer electrons to another, the donor is left with a net positive charge, while the acceptor is left with a net negative charge. According to Coulomb's law, these charged species should attract each other, and this attraction is what stabilizes the bond.

When atoms lose or gain electrons, they become what are called *ions*. Loss of electrons leaves an atom with a net positive charge, and the atom is called a *cation*. Gain of electrons leaves an atom with a net negative charge, and the atom is called an *anion*.

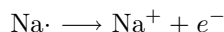
Some examples are:



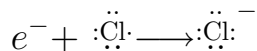
Special stability results when an atom, by losing or gaining electrons has as many valence electrons as a noble gas atom. In this case, we say that an atom or ion has a completed octet. Na^+ has as many electrons as Ne, which explains why it loses only 1 electron, while Ca^{2+} also has as many electrons as Ne, but since it is a Group II, element, it must lose 2 electrons to achieve an octet configuration.

The basic assumption of the Lewis model is that atoms will tend to form chemical bonds in order to complete their valence shells and achieve completed octets (or doublets in the case of H and He). This is known as the *octet rule*.

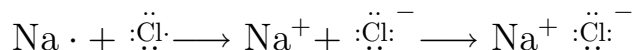
Consider the loss of an electron by sodium:



By losing the electron, Na achieves octet stability, since Na^+ is isoelectronic with Ne. Similarly, chlorine favors gaining an electron:

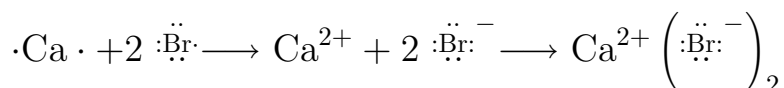


Thus, Na can donate an electron, which Cl can accept and an ionic bond can form between them. This is expressed chemically as



which is a molecule of sodium chloride.

Atoms that can lose two electrons, such as Calcium, can form molecules with two chemical bonds:



In transition metal atoms and in many heavier elements, the octet rule does not apply.

Examples:

Cu^+ ion has 10 valence electrons – copper(I) ion.

Cu^{2+} ion has 9 valence electrons – copper(II) ion.

Fe^{2+} ion has 6 valence electrons – iron(II) ion.

Fe^{3+} ion has 5 valence electrons – iron(III) ion.

These atoms have multiple valencies, hence the roman numeral, which is used to distinguish between the different ions. The roman numeral is taken to be equal to the charge on the ion. The reason for the large number of valence electrons has to do with the unfilled *d* orbitals of these atoms (to be discussed in chapters 15 and 16) next semester.

There are several polyatomic cations and anions that are important and will be encountered later. They are:

NH_4^+ – ammonium ion.

H_3O^+ – hydronium ion (important in acidic solutions).

CO_3^- – carbonate ion.

NO_2^- – nitrite ion.

NO_3^- – nitrate ion.

ClO_4^- – perchlorate ion (forms interesting compounds with the ammonium and hydronium ions).

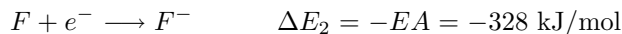
OH^- – hydroxyl ion (important in basic solutions).

II. ENERGETICS OF IONIC BONDING

Consider the KF molecule. K has a low ionization energy and can act as an electron donor according to the reaction:



F has a high electron affinity and can accept an electron according to the reaction:



so that $EA = 328 \text{ kJ/mol}$. The total energy to form K^+ and F^- far away from each other is just the sum of ΔE_1 and ΔE_2 :

$$\Delta E_{\text{tot}} = \Delta E_1 + \Delta E_2 = IE_1 - EA = 91 \text{ kJ/mol}$$

which implies that there is an energy cost associated with the formation of these two ions. How, then, can the ionic bond form if there is an energy cost?

The answer lies in Coulomb's law, which states that if K^+ and F^- are brought near each other, there is an attraction of opposite charges. Since the charge on K^+ is e and the charge on F^- is $-e$, if the bond length of KF is R_e , the attractive energy between them due to Coulomb's law is

$$\Delta E_{\text{Coul}} = -\frac{e^2}{4\pi\epsilon_0 R_e}$$

which is negative and tends to lower the total energy and stabilize the bond.

Let us estimate the energy needed to form the KF bond from neutral atoms, given the above information. The total energy needed to form the ionic bond should be

$$\Delta E_{\text{f}} \approx -\frac{e^2}{4\pi\epsilon_0 R_e} - EA + IE_1$$

where the first term is the energy gained due to the Coulomb attraction, and the second and third terms constitute the energy needed to transfer the electron from K to F to form ions. Substituting in the numbers:

$$\begin{aligned} IE_1 &= 419 \text{ kJ/mol} \\ EA &= 328 \text{ kJ/mol} \\ R_e &= 2.17 \text{ \AA} = 2.17 \times 10^{-10} \text{ m} \\ e &= 1.602 \times 10^{-19} \text{ C} \end{aligned}$$

gives

$$\Delta E_{\text{f}} \approx -\frac{(1.602 \times 10^{-19} \text{ C})^2}{4\pi(8.854 \times 10^{-12} \text{ C}^2\text{J}^{-1}\text{m}^{-1})(2.17 \times 10^{-10} \text{ m})} \times 6.022 \times 10^{23} \text{ mol}^{-1} + 9.1 \times 10^4 \text{ J/mol}$$

gives the result $-5.49 \times 10^5 \text{ J/mol}$ or -549 kJ/mol . The fact that the energy is negative tells us that the bond is stabilized by the Coulomb attraction. The energy needed to dissociate the bond into neutral species K and F is just

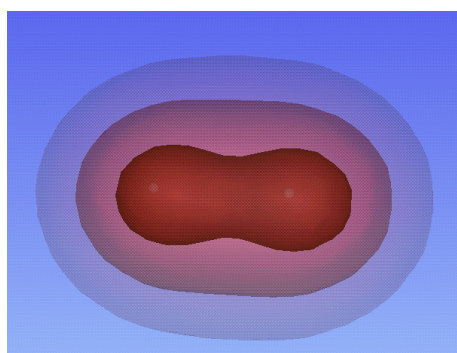
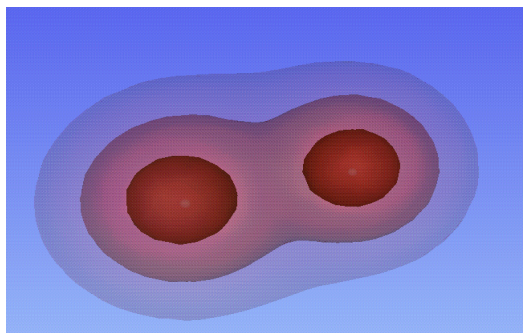
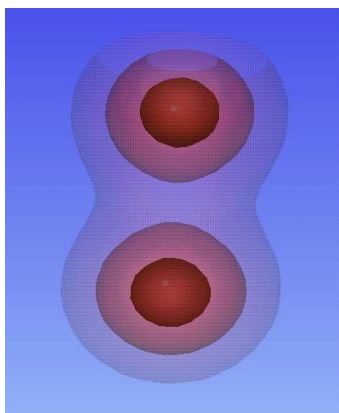
$$\Delta E_{\text{d}} = -\Delta E_{\text{f}}$$

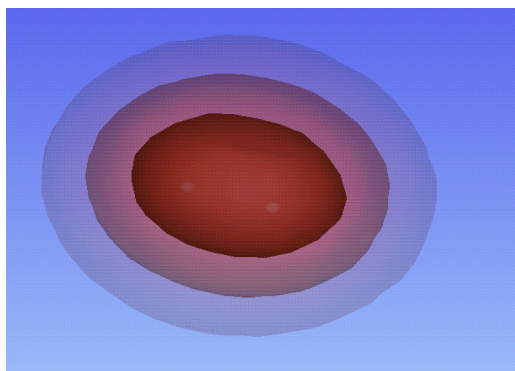
which is 549 kJ/mol . This is the energy needed to overcome the Coulomb attraction and transfer an electron from F^- to K^+ to form neutral species.

This estimated dissociation energy is in qualitative agreement with the experimental value of 498 kJ/mol . However, it can never be quantitative agreement because the energy really needs to be computed using the rules of quantum mechanics, with a proper accounting of the electronic wave functions in the bond.

III. COVALENT BONDING AND LEWIS STRUCTURES

Covalent bonds involve the sharing of electrons between two atoms. What do “shared” electrons actually look like? Below are shown electron density plots of an H_2 molecule at four different separations between the atoms. The sequence shows how the electron density changes as the two atoms are brought closer together, until they reach their true bond length (fourth panel).



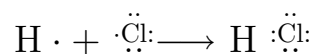


It is clear that as the atoms approach each other, electron density becomes decreasingly localized over each atom individually and increasingly *delocalized* over the entire molecule.

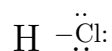
The shared pair of electrons in H_2 would be represented by the following Lewis dot structure:



In this Lewis structure, each H atom has a stable doublet of electrons as a result of sharing. As another example, consider the formation of the molecule HCl:



where Cl has a stable octet as a result of sharing, and H has a stable doublet. A shared pair of electrons is sometimes represented in Lewis structure by a straight line:



The unshared electrons are called *lone pairs* and do not participate in the covalent bond between the two atoms.

Several other examples are given below:

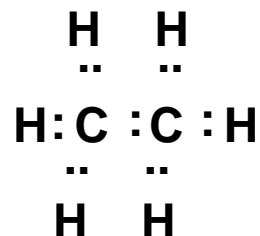
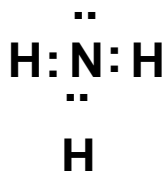
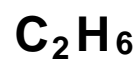
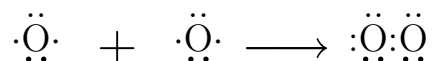


FIG. 1.

Clearly, these diagrams do not represent actual molecular geometries. In each diagram, each hydrogen has a stable doublet, while all other atoms have octets.

What does a lone pair look like? Again, we show an electron density plot for a water molecule below:

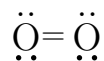
Consider, next, the molecule O_2 . Since O has 6 valence electrons, if we try allowing for one shared pair, we would end up with the following Lewis structure:



Now the oxygen on the right does not have an octet. The way to rectify this is to allow a second shared pair:



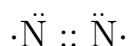
Considering all shared electrons, each oxygen has an octet. The sharing of two pairs of electrons gives rise to a *double bond*, of which this is a particular example. Another way to represent it is:



What about the molecule N_2 . N has 5 valence electrons, so if we try to include only 1 shared pair, the Lewis structure looks like:



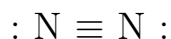
which only gives each atom 6 electrons. A double bond gives rise to:



which is only 7 electrons to each. However, sharing three pairs of electrons leads to the structure:



This is an example of a *triple bond*, which can be represented as



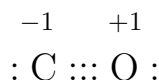
IV. FORMAL CHARGES

Up to now, we have assumed that electrons are equally shared between the two atoms in a covalent bond. While it is true for *homonuclear diatomic* (in which the two atoms are the same species), there is no experimental basis for

the assumption that this holds for a *heteronuclear* diatomic (in which the two atoms are different). To see what the consequence of this assumption is, consider the molecule CO, whose Lewis structure is easily shown to be



If the shared electrons are divided equally between the C and O atoms, then C has a total of 5 electrons (including its lone pair) and O has a total of 5 electrons (including its lone pair). Normally, C has 4 valence electrons and O has 6. Thus, *formally*, C has an extra electron, giving it a *formal charge* of -1. Oxygen formally has one electron too few, giving it a formal charge of +1. Formal charges are included in Lewis structures near the appropriate atoms:



Generally, the formal charge is given by:

$$\text{Formal charge} = \text{Group number} - \text{number of electrons in lone pairs} - \frac{1}{2}(\text{number of electrons in bonds})$$

Formal charges can be used to distinguish between several possible Lewis structures. Generally, the Lewis structure with the smallest formal charges on individual atoms will be the correct one.

V. GENERAL RULES FOR DRAWING LEWIS STRUCTURE

The following is a list of rules that can be used to determine the Lewis structure of a molecule:

1. Count up the total number of valence electrons. First add up the group numbers of all atoms in the molecule. If the molecule is an anion, add one electron for each unit of charge on the anion. If it is a cation, subtract one electron for each unit of charge on the cation.
2. Calculate the total number of electrons that would be needed for each atom to have an octet (or doublet for H).
3. Subtract the result of step 1 from the result of step 2. This is the total number of shared or bonding electrons.
4. Assign two bonding electrons to each bond.
5. If bonding electrons remain, assign them in pairs making some of the bonds double or triple bonds. (Usually, only C, N, O, and S can form double bonds, and only C and N can form triple bonds). There may be more than one way to do this. Keep all possible structures that result.
6. Assign remaining electrons as lone pairs, giving octets to all atoms except H.
7. Determine the formal charges and put them next to the appropriate atoms. (A formal charge of 0 need not be written explicitly). Check that the formal charges add up to the total charge on the molecule/ion. Do this for all structures obtained in step 5. The structure with the smallest formal charges should be considered as the preferred structure.

Example: Ethylene (C_2H_4).

Step 1: Total valence electrons = $2 \times 4 + 4 = 12$

Step 2: Total electrons needed for octets/doublets = $2 \times 8 + 4 \times 2 = 24$

Step 3: Total shared/bonding electrons = $24 - 12 = 12$. Total electrons in lone pairs = $12 - 12 = 0$.

Step 4:

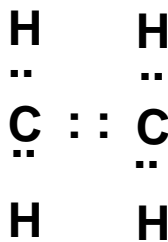
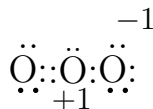


FIG. 2.

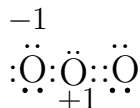
Note that, in order to use up all of the bonding electrons, the C=C double bond is necessary. For this case, all of the formal charges work out to be 0, which is shown straightforwardly.

VI. RESONANT STRUCTURES

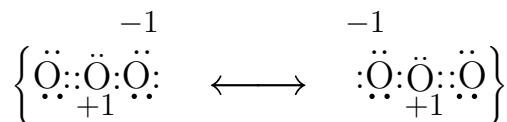
Sometimes more than one viable Lewis structure is possible. Consider the ozone O_3 molecule, whose possible Lewis structures are:



and



From these, one would predict that the two bond OO bond lengths are different. However, experimentally, they are known to be the same, so it seems that the octet rule is breaking down. A “bogus” fix to this problem is to define something called *resonant* structures. In a resonant structure, the molecule is said to exist in a hybrid state between the two. In a sense, the molecule is both structures at once. The resonant structure is represented as:



VII. BREAKDOWN OF THE OCTET RULE

Given the crudeness of the octet rule, it should not be surprising that there are cases for which it does not work. Below, some of examples of octet rule breakdown are described:

- Step 1:** Total valence electrons = $6 + 6 \times 7 = 48$
Step 2: Total electrons needed for octets = $7 \times 8 = 56$
Step 3: Total shared/bonding electrons = $56 - 48 = 8$.

Now we have a problem because we have 6 bonds but only 8 electrons to put in them. If each bond is to receive a pair of electrons, we would need 12 shared electrons rather than 8.

The solution to this problem is to allow for more bonding electrons. Extra bonding electrons are assigned to the central atom, S in this case, which can accommodate an *expanded valence shell* due to its relatively high atomic number. Now, step 2 becomes:

- Step 2:** Total electrons needed for 6 octets + one 12-tet = 60.
Step 3: Total shared/bonding electrons = $60 - 48 = 12$.
Step 4:

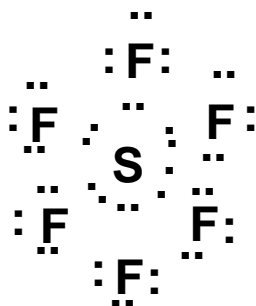


FIG. 5.

This example suggests that step 6 of the usual Lewis structure rules should be replaced by

- 6'. Assign lone pairs to the terminal atoms to give them octets. If any electrons remain, assign them to the central atoms as lone pairs.

Rule 5 now becomes irrelevant.

Another example is the I_3^- anion. According to the rules:

- Step 1:** Total valence electrons = $7 \times 3 + 1 = 22$
Step 2: Total electrons for octets = $8 \times 3 = 24$
Step 3: Total shared/bonding electrons = $24 - 22 = 2$.

Two electrons is not enough for the two bonds in the I_3^- ion. Thus, one of the iodines will have its valence shell expanded. We need two extra electrons, so step 2 now becomes:

- Step 2:** Total electrons for 2 octets + one 10-tet = 26.
Step 3: Total shared/bonding electrons = $26 - 22 = 4$.

The resulting Lewis structure is:

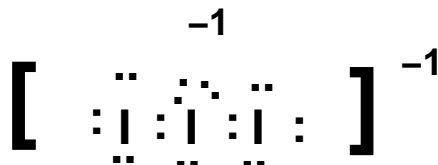


FIG. 6.

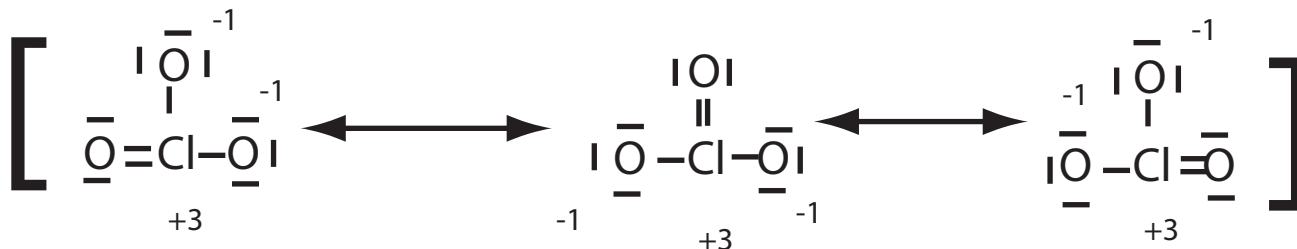
For the next example, consider the ion ClO_3^+ . Now, if we follow the rules of Lewis structures, we would obtain

Step 1: Number of valence electrons = $7 + 6 \times 3 - 1 = 24$.

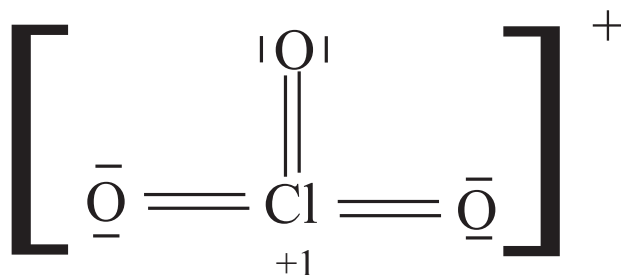
Step 2: Number of electrons for octets = $8 \times 4 = 32$.

Step 3: Number of shared electrons = $32 - 24 = 8$.

The number of lone-pair electrons would be $24 - 8 = 16$. Thus, strictly following these rules, we would have three resonant structures, and we would obtain the Lewis structure shown below.



We might even be able to justify this structure on the basis that Cl^{3+} is isoelectronic to carbon, which can form double bonds. There are discussion boards out there that suggest this to be the correct Lewis structure. However, our first clue that this might not be correct is the fact that +3 is a high formal charge to have on the chlorine. In addition, the cation FO_3^+ exists, but not in the structure shown above with the F as the central atom. A quick check in the literature [see Freceer *et al. Structural Chemistry* **9**, 9 (1998)]. Rather, F interacts with O_3 as if the latter were ozone. This means that something unusual needs to happen for Cl to form bonds to three oxygens. If there were a structure in which Cl had a formal charge of +1, then it would be isoelectronic to sulfur, and as the last example indicates, S can undergo valence shell expansion. Given this, if we allow Cl to expand its valence shell, it could form three double bonds to each of the oxygens, giving overall lower formal charges, and a Lewis structure as shown below:



which is the more likely structure.

VIII. MOLECULAR GEOMETRY AND THE VSEPR THEORY

The problem of determining an accurate molecular geometry is rather complex. Given an arrangement of N atoms with coordinates $\mathbf{r}_1, \dots, \mathbf{r}_N$, the total energy, E , of the assembly is a function of these N coordinate vectors and is determined by the electronic structure:

$$E = E(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

The optimal geometry of the molecule will be determined by those particular values of the coordinates for which the total energy is a minimum. Thus, in principle, one should compute the derivative of the energy function with respect to each coordinate and set all these derivatives equal to 0 (which is how one does a minimization problem):

$$\frac{\partial E}{\partial \mathbf{r}_i} = 0$$

which would lead to a set of $3N$ equations in $3N$ unknowns. The solution of such a problem is extremely difficult and is an active area of research.

Fortunately, there exists a simple theory for determining molecular geometries at a qualitative level, which is useful for understanding the basic shapes of molecules. This theory is known as the VSEPR theory, which is an acronym for the **v**alence **s**hell **e**lectron **p**air **r**epulsion **t**heory. It is useful for estimating the shapes of molecules for which there is a central atom bonded to several other atoms surrounding it.

The basic principle of the VSEPR theory is that molecular geometry can be predicted based on the notion that electron pairs in molecules tend to repel each other and achieve a maximum separation from each other. This applies both to bonding electrons as well as lone pairs.

In order to use the VSEPR principle, one needs to compute a number known as the *steric number*. This is given by

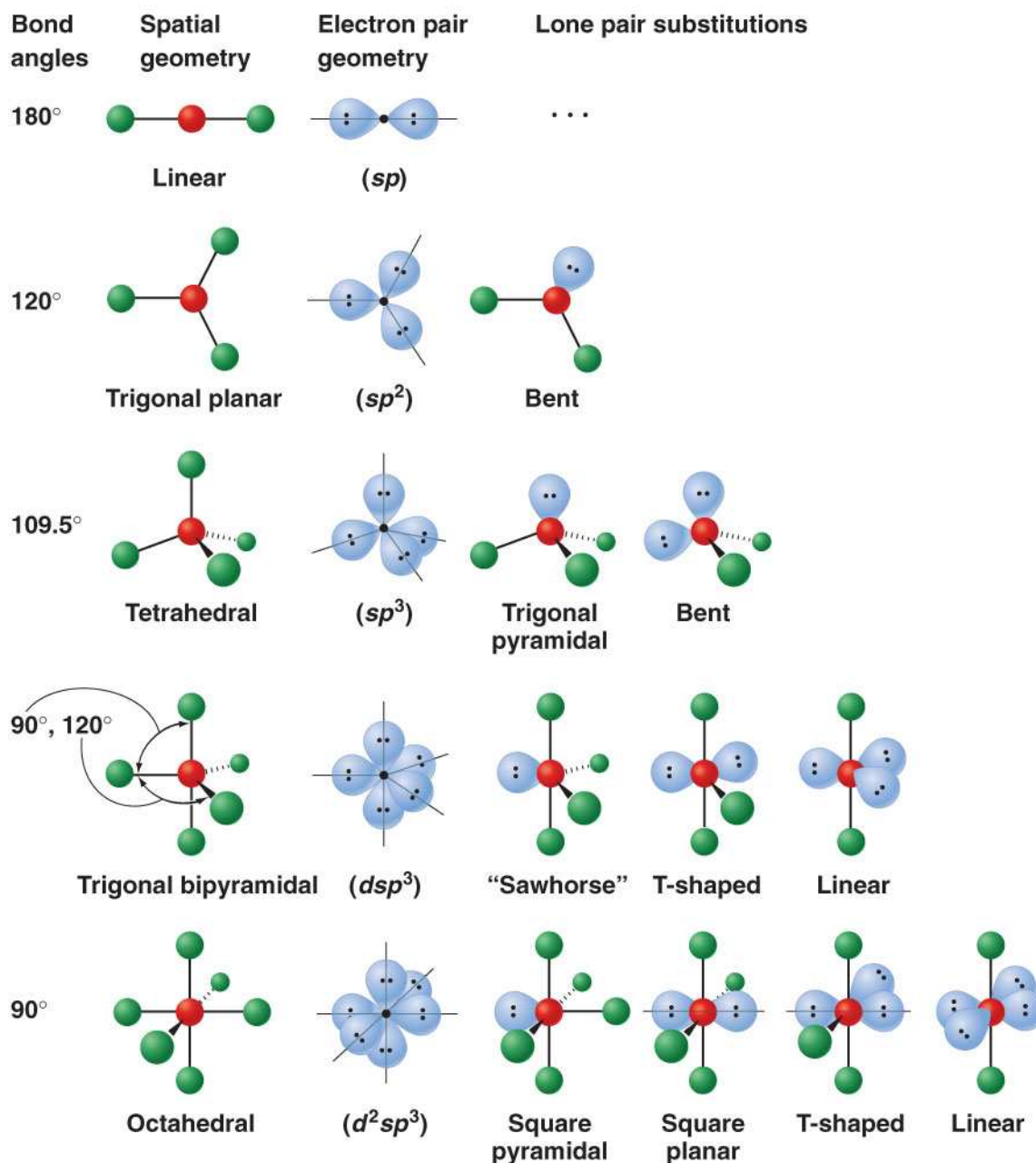
$$SN = (\text{number of atoms bonded to central atom}) + (\text{number of lone pairs on central atom})$$

The second number can be determined directly from the Lewis structure.

Once the steric number is known, the basic shape of the molecule is given by the following assignment of shapes:

$SN = 2$	linear
$SN = 3$	trigonal planar
$SN = 4$	tetrahedral
$SN = 5$	trigonal bipyramidal
$SN = 6$	octahedral

The basic shapes are shown in the left column of the figure below:



Copyright © 2006 Pearson Education, Inc., Publishing as Benjamin Cummings

FIG. 7. VSEPR shapes

The reason for these assignments will become clear through a study of several examples:

1. CO₂

The Lewis diagram for CO₂ is



Thus, the steric number of the central carbon is

$$SN = 2 + 0 = 2$$

and, according to the assignment table, the shape is linear:



The linear shape can be understood on the basis of the electron repulsion principle: The central carbon is surrounded by two sets of shared electron pairs, which want to achieve a maximum separation between them. The maximum separation they can achieve is at a 180° angle between the pairs, giving rise to the linear configuration.

2. ClO_3^+

The Lewis diagram for this cation is was shown earlier. The steric number of the central chlorine is

$$SN = 3 + 0 = 3$$

and the geometry, according to the table, is trigonal planar:

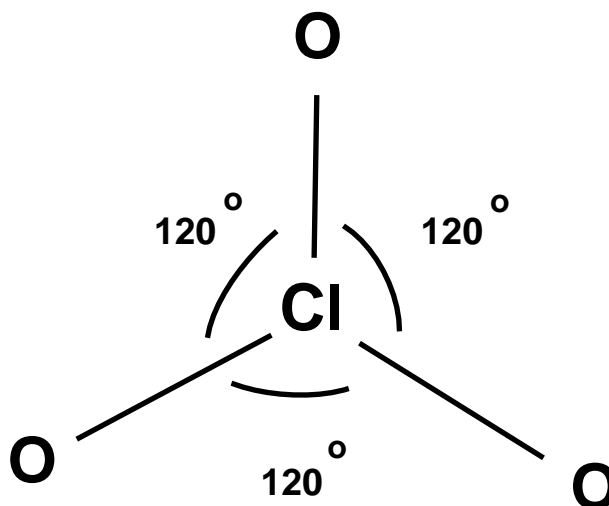
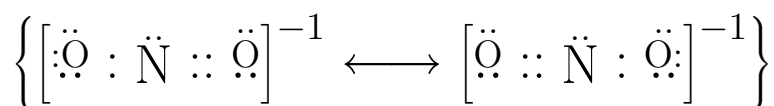


FIG. 8.

Again, this geometry can be seen to achieve a maximum separation between the three pairs of shared electrons around the chlorine.

3. NO_2^-

The Lewis structure for this anion is a resonant form:



The steric number of the nitrogen is

$$SN = 2 + 1 = 3$$

Hence the basic shape should be trigonal planar. However, one of the atoms will be missing from this structure and replaced by the lone pair on the nitrogen. Hence its shape will actually be bent, with a bond angle less than 120° owing to the fact that the lone pair is spatially more delocalized than the bonding pairs. This spatial delocalization of the lone pair causes the bonding pair to be repelled from the lone pair at greater distances than could be achieved by a 120 degree angle, giving rise to the smaller bend angle in the structure:

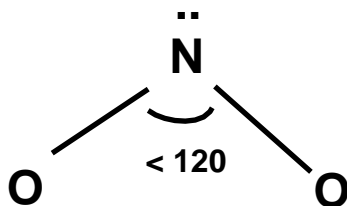


FIG. 9.

Because of the resonant structure, the bond lengths are the same.