11

Lewis Structures and the VSEPR Method

*When our views are sufficiently extended as
to enable us to reason with precision concern-
ing the proportions of elemental atoms, we
shall find the arithmetical relation will not
be sufficient to explain their mutual action
and we shall be obliged to acquire a
geometrical conception of their relative
arrangement in all three dimensions. . . .
When the number of particles (combined
with one particle) exists in the proportion of
4/1, stable equilibrium may take place if
the four particles are situated at the angles
of the four equilateral triangles composing a
regular tetrahedron. . . . It is perhaps too
much to hope that the geometrical arrange-
ment of primary particles will ever be
perfectly known.*
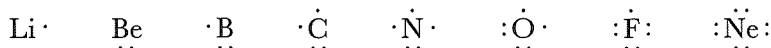
W. H. Wollaston (1808)

In this chapter we shall look at a simple method of representing covalent bonding using Lewis structures. We shall write Lewis structures for familiar molecules and ions and interpret them in terms of electron-pair sharing and the completion of noble-gas valence shells. After we explain oxidation number in terms of the inequality of electron-pair sharing by atoms with different electronegativities, we shall go on to correlate the acidities of certain molecules with the electronic structure of a central atom. And we shall conclude the chapter by showing how the valence-shell electron-pair repulsion (VSEPR) method can be used to predict molecular shape.

11-1 LEWIS STRUCTURES

Electron-dot formulas for chemical compounds were developed by G. N. Lewis, in 1916, as an attempt to comprehend covalent bonding. Our understanding of bonding rests on firmer ground now, but the dot formulas are still a convenient notation. Each valence electron (i.e., an electron in the outermost s and p orbitals) is represented by a dot placed beside the chemical symbol:

H ·   He:

In modern terminology, each of the four compass points of the symbol represents one of the s, p_x, p_y, and p_z atomic orbitals. For example, atoms of the second-period elements are written as

$$\text{Li} \cdot \qquad \text{Be} \qquad \cdot \text{B} \qquad \cdot \overset{\cdot}{\text{C}} \qquad \cdot \overset{\cdot}{\text{N}} \cdot \qquad :\overset{\cdot}{\text{O}} \cdot \qquad :\overset{\cdot}{\text{F}}: \qquad :\overset{\cdot\cdot}{\text{Ne}}:$$

The loss and gain of electrons in the formation of ions can be illustrated by the formation of sodium chloride from sodium and chlorine atoms:

$$\text{Na} \cdot + :\overset{\cdot}{\underset{\cdot\cdot}{\text{Cl}}}: \rightarrow \text{Na}^+ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}:^-$$
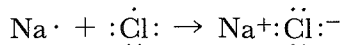
Each ion in sodium chloride has the outer electronic configuration of a noble gas: The sodium ion has the configuration of Ne, and the chloride ion has the configuration of Ar. This transfer of an electron occurs because Cl is more electronegative than Na (3.16 for Cl versus 0.93 for Na). What happens in HI, in which the electronegativities are nearly equal (2.20 and 2.66, respectively)?

According to Lewis' theory of covalence, each atom completes a noble-gas configuration, not by transferring but by *sharing* an electron:

$$\text{H} \cdot + \cdot \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{I}}}: \rightarrow \text{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{I}}}:$$
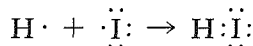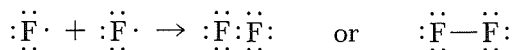
The H atom now has two electrons in its outer valence orbital, as in He, and I has eight electrons, as in Xe. Lewis set forth this principle: *Atoms form bonds by losing, gaining, or sharing enough electrons to achieve the outer electronic configurations of noble gases.* The type of bond, ionic or covalent, depends on whether electrons are transferred or shared. The combining capacities of atoms are a consequence of the proportions in which they must associate to achieve noble-gas configurations. Lewis' theory explains bond type and the pattern of connections of atoms within a molecule. However, it is not able to explain the geometry of molecules.

The Lewis theory made bonding between like atoms, as it occurs in H_2, F_2, or N_2, understandable for the first time. Two hydrogen atoms share their electrons to provide each atom with the He closed-shell structure:

$$\text{H} \cdot + \text{H} \cdot \rightarrow \text{H} : \text{H} \qquad \text{or} \qquad \text{H} \text{—} \text{H}$$
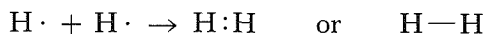
A straight-line bond symbol is often used, as here, in the special sense of a symbol for a Lewis electron-pair bond. Two fluorine atoms share one pair of electrons; thus, each F atom has the Ne structure:

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}} \cdot + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}} \cdot \rightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}: \qquad \text{or} \qquad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}} \text{—} \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}:$$
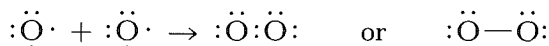
The unshared pairs of electrons on F are called **lone pairs**; we now would interpret them as spin-paired electrons in atomic orbitals that are not involved in bonding. The bond energy, the energy required to break the diatomic molecule into two infinitely separated atoms, is 432 kJ mole^{-1}

for H_2 and only 139 kJ mole^{-1} for F_2. Part of this relative instability of the F_2 molecule may arise from electrostatic repulsion between lone pairs of electrons on the two F atoms.

The H_2 and F_2 molecules are representative of many molecules in which electron-pair bonds are formed such that each atom achieves a closed-shell configuration. Hydrogen needs two electrons to achieve a closed shell, filling the $1s$ valence orbital. Each atom in the second period requires eight electrons (an **octet**) to achieve a closed shell, because the $2s$ and $2p$ orbitals can accommodate a total of eight electrons ($2s^2 2p^6$). This requirement is known as the **octet rule**. In the example of the F_2 molecule, after bonding each F atom has eight electrons associated with it.
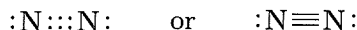
Multiple Bonds

If we try to construct O_2 as we did F_2, we end with unpaired electrons and only seven electrons in the neighborhood of each O atom:

$$:\ddot{\text{O}}\cdot \ + \ :\dot{\ddot{\text{O}}}\cdot \ \rightarrow \ :\dot{\ddot{\text{O}}}:\dot{\ddot{\text{O}}}: \qquad \text{or} \qquad :\dot{\ddot{\text{O}}}\text{—}\dot{\ddot{\text{O}}}:$$

This defect can be eliminated by assuming that the oxygen atoms share *two* pairs of electrons (without regard to the geometry of the process):

$$:\ddot{\text{O}}::\ddot{\text{O}}: \qquad \text{or} \qquad :\ddot{\text{O}}{=}\ddot{\text{O}}:$$
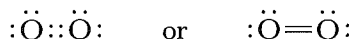
Thus, there is a **double bond** between two oxygen atoms. A **triple bond** must be assumed in N_2 to give each nitrogen atom a noble-gas configuration:

$$:\text{N}:::\text{N}: \qquad \text{or} \qquad :\text{N}{\equiv}\text{N}:$$

This concept of multiple bonds is not all imagination; bond energies and bond lengths both support the idea of a single bond in F_2, a double bond in O_2, and a triple bond in N_2:

	N_2	O_2	F_2
Bond energy (kJ mole^{-1})	942	494	139
Bond length (Å)	1.10	1.21	1.42

A molecule such as N_2, with a triple bond between two atoms, is said to have a **bond order** of three. (The bond order is the number of electron-pair bonds.) The oxygen molecule has a bond order of two, and the F_2 molecule has a bond order of one. The higher the bond order, the more tightly held the atoms, the greater the bond energy, and the shorter the bond.

An interesting problem arises in the Lewis structural formulation of the common air-pollutant molecule, nitric oxide (NO). A closed-shell configuration cannot be constructed for NO because it has an odd number of valence electrons. Nitric oxide has 11 valence electrons, 5 valence electrons originally associated with the nitrogen atom and 6 electrons originally associated with the oxygen atom. Thus either N or O will "own" only
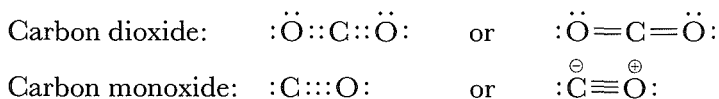
7 electrons in the NO molecule. We choose N because it is less electro-negative than O. Therefore the best structure for NO is

$$:\overset{\cdot}{N}=\underset{\cdot\cdot}{O}:$$
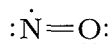
Lewis structures for molecules such as NO, which have an odd number of electrons, cannot have closed shells associated with each atom. At least one atom, nitrogen in the NO example, is left with an **open shell**.

Formal Charges

Carbon dioxide is easy to represent using Lewis structures, but carbon monoxide raises a problem. Each O needs two electrons to achieve the stable eight-electron (octet) structure; thus it should share two electron pairs with C. Yet the carbon atom needs four electrons and should share four pairs. The only satisfactory Lewis structure for CO is obtained by letting three pairs be shared, and by distributing the other four valence electrons in such a way as to complete an eight-electron shell around each atom.

Carbon dioxide: $:\overset{\cdot\cdot}{O}::C::\overset{\cdot\cdot}{O}:$ or $:\overset{\cdot\cdot}{O}=C=\overset{\cdot\cdot}{O}:$

Carbon monoxide: $:C:::O:$ or $:\overset{\ominus}{C}\equiv\overset{\oplus}{O}:$

Carbon monoxide is isoelectronic with N_2, so we might expect the hypothesis of a triple bond in CO to be completely satisfactory. (We can imagine some hypothetical "Schrödinger's Demon" making a molecule of carbon monoxide from a molecule of N_2 by removing a proton from one nitrogen nucleus and adding it to the other.) Nevertheless, the triple-bond hypothesis for CO does present a problem. If we assume that each shared electron pair is shared equally between atoms, then carbon has three of the six electrons from the triple bond, plus the two in the lone pair. It has five electrons but a nuclear charge that will counterbalance only four of them. Similarly, oxygen has five valence electrons but a nuclear charge designed for six. Therefore, carbon has a **formal charge** of -1, and oxygen has a formal charge of $+1$. This statement does not mean that these charges are fully present; it indicates only that the demands of bonding lead to a non-uniform distribution of charge. The formal charges in the case of CO are indicated by $C^\ominus$ and $O^\oplus$ (in the Lewis structure shown).

When calculating the formal charge on the atoms in a molecule, we assign to each atom one electron for each covalent electron-pair bond that it makes, plus all of its lone-pair electrons. The formal charge on the atom is then the charge that it would have if it were an isolated ion with the same number of valence electrons:

$$\text{Formal charge} = Z - (N_{bonds} + N_{nonbonding})$$

Here Z is the atomic number, N_{bonds} is the number of covalent electron-pair bonds that the atom makes with other atoms, and $N_{nonbonding}$ is the total number of electrons the atom has that are not involved in covalent

bonds. You should verify for yourself that in every uncharged molecule discussed so far in this section (except CO) the formal charge on each atom is zero.

Example 1

Write an acceptable Lewis structure for the cyanide molecule (CN).

Solution

A closed-shell configuration cannot be constructed for CN because it has an odd number of valence electrons. The CN molecule has nine valence electrons, four valence electrons associated with the carbon atom and five valence electrons associated with the nitrogen atom. Thus either C or N will "own" only seven electrons in the CN molecule. We choose C because it is less electronegative than N. Therefore the better Lewis structure for CN is

$$\cdot C \equiv N:$$

The alternative structure,

$$:\overset{\ominus}{C} \equiv \overset{\oplus}{N} \cdot$$
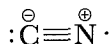
results in formal charges on both C and N atoms. *Such a formal-charge separation should be avoided, if possible, for bonds involving atoms of about the same electronegativity.* Because of the octet rule, a formal-charge separation for CO could not be avoided. For CN, however, it can, and $\cdot C \equiv N:$ is clearly the better Lewis structure for the molecule.

Lewis structures for molecules such as CN and NO, which have an odd number of electrons, cannot have closed shells associated with each atom. At least one atom, carbon in the CN example, is left with an open shell. As a consequence of this open-shell structure in CN, two molecules of CN combine to form the dimer $(CN)_2$, which is called *cyanogen*. The driving force for this reaction is readily seen to be the formation of a new carbon–carbon bond without any significant weakening of the carbon–nitrogen triple bond:

$$\cdot C \equiv N: + \cdot C \equiv N: \rightarrow :N \equiv C - C \equiv N:$$
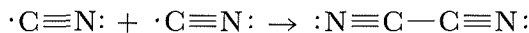
The odd electron in CN is unpaired. The presence of one or more unpaired electrons in an atom or molecule gives rise to a physical property known as *paramagnetism*, which we shall discuss in the next chapter. Experiments show that the paramagnetism of the CN molecule is in accord with the presence of one unpaired electron, as the Lewis structure predicts. However, not all paramagnetic molecules are easily explained by Lewis structures. A multiple-bonded molecule with particularly vexing magnetic

properties (for Lewis' structural theory) is O_2, which is known to have two unpaired electrons in its ground state and to be paramagnetic. An unusual structure such as

$$:\overset{.}{O}\!\!\equiv\!\!\overset{.}{O}: \quad \text{or} \quad :\overset{..}{O}\!\!-\!\!\overset{..}{O}:$$
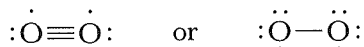
would be required to explain this magnetic behavior. However, the observed bond length and bond energy of O_2 are completely consistent with the simple double-bond structure,

$$:\overset{..}{O}\!\!=\!\!\overset{..}{O}:$$
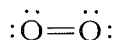
as we have already shown. We will see in Chapter 12 that the molecular orbital theory provides a satisfactory explanation of both the paramagnetism and the bond properties of the oxygen molecule.

Example 2

Write an acceptable Lewis structure for $MgCl_2$.

Solution

A magnesium atom has a low electronegativity and atomic chlorine has a high electronegativity; thus magnesium chloride requires a structure showing ionic bonds. One electron is transferred from the magnesium atom to each of the chlorine atoms in $MgCl_2$. The correct structure indicates the charges:

$$[:\overset{..}{\underset{..}{Cl}}:^-][Mg^{2+}][:\overset{..}{\underset{..}{Cl}}:^-]$$
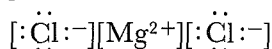
Some Polyatomic Molecules

The Lewis structures of methane (CH_4), ammonia (NH_3), and water (H_2O) are

methane   ammonia   water
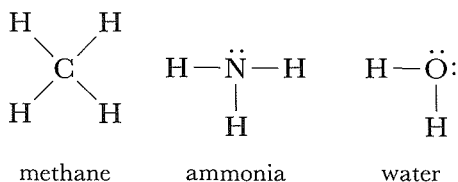
These three molecules are isoelectronic; they have the same number of electrons. The eight valence electrons around the central atom illustrate the octet rule. In CH_4 all eight electrons are involved in bond pairs, whereas the other molecules contain lone electron pairs. Ammonia

has three bond pairs and one lone pair, and water has two bond pairs and two lone pairs.

The usefulness of the octet rule is that it allows us to predict which molecules will be stable under ordinary conditions of temperature and pressure. For example, all the following carbon hydrides are known:

$$CH \qquad CH_2 \qquad CH_3 \qquad CH_4$$

However, only CH_4 obeys the octet rule and is stable under ordinary conditions.

The simple hydrocarbons ethylene and acetylene illustrate multiple bonding; ethane is shown for comparison:

$$
\begin{array}{ccc}
\text{H:C:C:H} & \text{C::C} & \text{H:C:::C:H}
\end{array}
$$

ethane	ethylene	acetylene
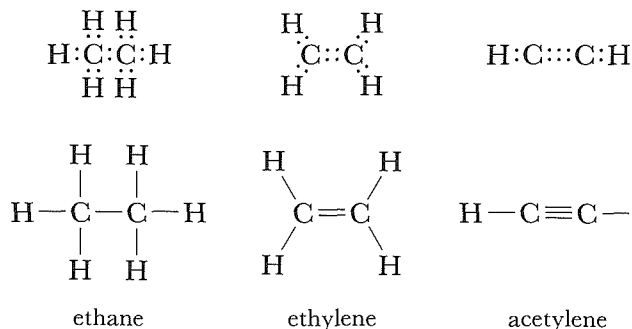
The lone-electron-pair notation is useful when atoms other than C and H are involved:

|		
methyl alcohol	acetic acid	ethylamine
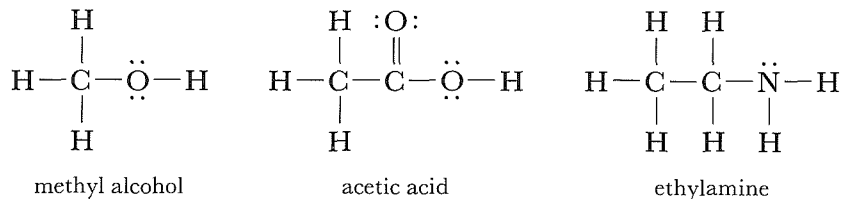
The Ammonium Chloride Molecule

The ammonium chloride molecule, NH_4Cl, contains NH_4^+ and Cl^- ions. The Lewis structures for the nitrogen atom and for each hydrogen atom are

$$:\overset{\cdot}{N}\cdot \qquad H\cdot$$

However, the NH_4^+ ion has one positive charge, which means that it has lost one of its nine electrons. Since all the hydrogen atoms in the ion are equivalent, we give the nitrogen atom the positive charge,

$$\cdot\overset{\cdot}{\underset{\cdot}{N}}\cdot +$$

and write

$$\left[\begin{array}{c} H \\ | \\ H-\overset{\oplus}{N}-H \\ | \\ H \end{array}\right]^{+}$$
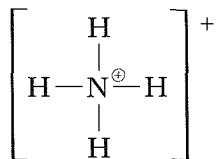
Thus the correct Lewis structure for the NH_4^+ ion has four single bonds and no unshared electrons. Notice that the ammonium ion is isoelectronic with methane. A formal charge of $+1$ is assigned to the nitrogen atom.

Now, we assign the electron that was removed from NH_4 (to give NH_4^+) to the chlorine atom, to give the ion-pair structure for the ammonium chloride molecule:
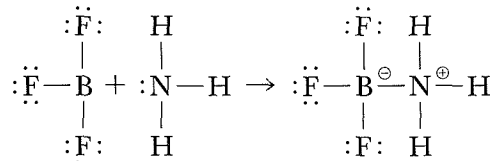
$$\left[\begin{array}{c} H \\ | \\ H-\overset{\oplus}{N}-H \\ | \\ H \end{array}\right]^{+} \qquad [:\overset{..}{\underset{..}{Cl}}:]^{-}$$
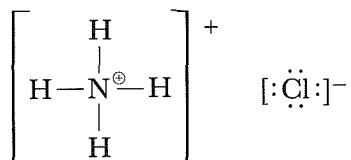
In summary, the nitrogen–hydrogen bonds in NH_4^+ are covalent but have some ionic character, whereas the NH_4^+ ion is attached to Cl^- by an ionic bond.

Lewis Acids and Bases

The BF_3 molecule is represented by the Lewis structure

$$:\overset{..}{\underset{..}{F}}-B-\overset{..}{\underset{..}{F}}:$$
$$|$$
$$:\overset{..}{\underset{..}{F}}:$$
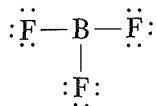
It is unusual because it does not have four electron pairs around the B atom. It reacts with ammonia to form the addition compound BF_3NH_3 as follows:

$$:\overset{..}{\underset{..}{F}}: \quad H \qquad\qquad :\overset{..}{\underset{..}{F}}: \quad H$$
$$| \qquad | \qquad\qquad\qquad | \qquad |$$
$$:\overset{..}{\underset{..}{F}}-B + :N-H \rightarrow :\overset{..}{\underset{..}{F}}-\overset{\ominus}{B}-\overset{\oplus}{N}-H$$
$$| \qquad | \qquad\qquad\qquad | \qquad |$$
$$:\overset{..}{\underset{..}{F}}: \quad H \qquad\qquad :\overset{..}{\underset{..}{F}}: \quad H$$

In this compound, nitrogen, with a lone pair, donates both the electrons of the covalent bond. Such a donor–acceptor bond is sometimes called a **coordinate covalent bond**; however, the distinction is pointless, because once the bond is formed it is like any other covalent bond.

The compound BF_3NH_3 is isoelectronic with CF_3CH_3, and differs from it only by the formal charges that are assigned to the central atoms. The charge is zero for each atom in the carbon compound. But if you work out the formal assignment of charge for the boron compound, you can see

that B has a formal charge of -1, and N, of $+1$. Since formal charges arise from the way in which electrons are distributed in a molecule or ion, the total formal charge of all the atoms must be equal to the total charge on the ion, or zero for a neutral molecule.

A compound such as BF_3, which can accept an electron pair, is called a **Lewis acid**, and an electron-pair donor is a **Lewis base**. This terminology, like that of Brønsted, is an extension of the simple Arrhenius acid–base theory. By the Arrhenius theory, an acid is a substance that produces hydrogen ions or protons in aqueous solution, and a base is a substance that produces hydroxide ions. Brønsted's terminology is more general: An acid is any substance that can donate protons, and a base is a substance that can accept them. To illustrate the differences in the three definitions, consider the neutralization of HCl and NaOH,

$$HCl + NaOH \rightarrow H_2O + NaCl$$
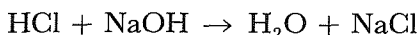
In terms of the species present in aqueous solution, the reaction should be written as

$$H_3O^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + 2H_2O$$

To Arrhenius, HCl is the acid, and NaOH is the base. To Brønsted, H_3O^+ is the acid, and the hydroxide ion (OH^-) is the base since it is the species that combines with the proton. To Lewis, the proton is the acid, because it will combine with the lone pair on the hydroxide ion; the hydroxide ion is the electron-pair donor and hence the base:
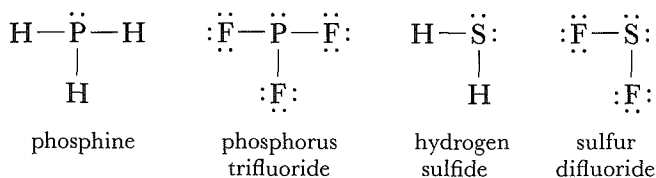
$$H^+ + :\overset{..}{\underset{..}{O}}-H^- \rightarrow H-\overset{..}{\underset{..}{O}}-H$$
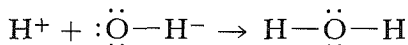
The Brønsted and Lewis theories are both applicable to nonaqueous solutions, whereas Arrhenius' theory is not. Both Brønsted's and Lewis' theories will be useful later. These more general definitions of acids and bases are helpful because they include compounds that do not contain hydrogen, and which we might not recognize as having properties of acids with Arrhenius' theory. For example, because it is an electron acceptor, BF_3 will often catalyze organic reactions that are also catalyzed by protons.

Bonding to Heavier Atoms

The octet rule is extremely valuable as a guide in writing Lewis structural formulas. For second-row nonmetallic elements (B, C, N, O, F), exceptions to the rule are very rare. It is easy to explain why this is so. Atoms of the second-row elements have stable $2s$ and $2p$ orbitals, and the "magic number" of 8 corresponds to the closed valence-orbital configuration $2s^2 2p^6$. Adding more electrons to such a configuration is impossible, because the next atomic orbital available to a second-row element is the high-energy $3s$ orbital.

Beyond the second row in the periodic table the octet rule is not obeyed with such satisfying regularity. However, it remains a useful rule,

as illustrated by molecules such as PH_3, PF_3, H_2S, and SF_2.

$$H-\overset{\cdot\cdot}{P}-H \qquad :\overset{\cdot\cdot}{\underset{}{F}}-\overset{\cdot\cdot}{\underset{}{P}}-\overset{\cdot\cdot}{\underset{}{F}}: \qquad H-\overset{\cdot\cdot}{\underset{}{S}}: \qquad :\overset{\cdot\cdot}{\underset{}{F}}-\overset{\cdot\cdot}{\underset{}{S}}:$$

H	:F:	H	:F:

| phosphine | phosphorus trifluoride | hydrogen sulfide | sulfur difluoride |

Atoms of the heavier elements often do not obey the octet rule. Some of them show a surprising ability to bind more atoms (or associate with more electron pairs) than would be predicted from the octet rule. For example, phosphorus and sulfur form the compounds PF_5 and SF_6, respectively. Lewis structures for these compounds use all the valence electrons of the heavy element in bonding:

| phosphorus pentafluoride | sulfur hexafluoride |
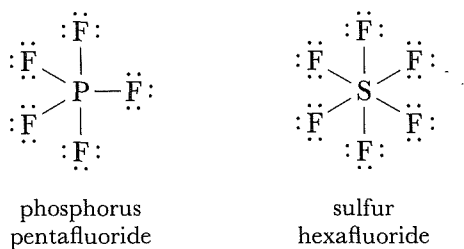
That phosphorus shares 10 electrons and sulfur shares 12 electrons obviously violates the octet rule. The theory of atomic structure helps us see why the violation has occurred. The noble gas in the third row with phosphorus and sulfur is argon. The argon electronic structure fills the $3s$ and $3p$ orbitals, but leaves the five $3d$ orbitals vacant. If some of these $3d$ orbitals are used for electron-pair sharing, extra bonds are possible. The atomic theory thus provides an explanation of the enhanced bonding versatility of elements in the third row and beyond.

Perhaps the most important consequence of the use of d orbitals is the formation of an important series of oxyacids. The best-known examples are phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4), and perchloric acid ($HClO_4$). It is possible to write a Lewis structure for sulfuric acid that obeys the octet rule:
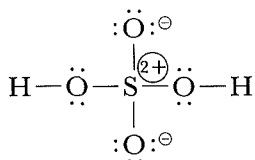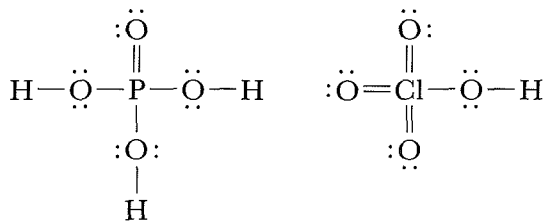
However, examination of this structure reveals that a formal charge of $+2$ is on the sulfur atom. Development of a large positive formal charge on an

electronegative nonmetal atom is not very reasonable. The formal charge can be removed if we write two sulfur–oxygen double bonds, thereby allowing the sulfur atom to share 12 electrons:

$$
\text{H}-\overset{..}{\underset{..}{\text{O}}}-\overset{\overset{\displaystyle :\text{O}:}{\|}}{\underset{\underset{\displaystyle :\text{O}:}{\|}}{\text{S}}}-\overset{..}{\underset{..}{\text{O}}}-\text{H}
$$
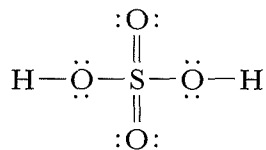
sulfuric acid

Similar Lewis structures can be written for other oxyacids:

$$
\text{H}-\overset{..}{\underset{..}{\text{O}}}-\overset{\overset{\displaystyle :\overset{..}{\text{O}}}{\|}}{\underset{\underset{\displaystyle :\overset{..}{\text{O}}:}{|}}{\text{P}}}-\overset{..}{\underset{..}{\text{O}}}-\text{H} \qquad :\overset{..}{\text{O}}=\overset{\overset{\displaystyle \overset{..}{\text{O}}:}{\|}}{\underset{\underset{\displaystyle :\underset{..}{\text{O}}}{\|}}{\text{Cl}}}-\overset{..}{\underset{..}{\text{O}}}-\text{H}
$$

$$
\underset{\displaystyle \text{H}}{|}
$$

phosphoric acid   perchloric acid

Resonance Structures

There are molecules and ions for which more than one satisfactory Lewis structure can be drawn. For example, the nitrite ion, NO_2^-, can be formulated as either

$$
\overset{\overset{\displaystyle ..}{\text{N}}}{\diagup\quad\diagdown} \\
:\text{O}\qquad :\overset{..}{\text{O}}:^{\ominus} \qquad\text{or}\qquad {}^{\ominus}:\overset{..}{\text{O}}:\quad\overset{..}{\text{O}}:
$$
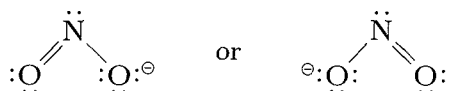
In either case the octet rule is satisfied. If either of these structures were the "correct" one, the ion would have two distinguishable nitrogen–oxygen bonds, one single and one double. Double bonds are shorter than single bonds, but structural studies of NO_2^- show that the two nitrogen–oxygen bonds are indistinguishable.

Consideration of NO_2^- and many other molecules and ions shows that our simple scheme for counting electrons and assigning them to the valence shells of atoms as bonds or unshared pairs is not entirely satisfactory. Fortunately, the simple model may be altered fairly easily to fit many of the awkward cases. The problem with NO_2^- is that the ion is actually more symmetrical than either one of the Lewis electronic structures that we wrote. However, if we took photographs of the two structures shown previously and superimposed the pictures, we would obtain a new structure having the same symmetry as the molecule. The photographic superimposition method is the same as writing a structure such as
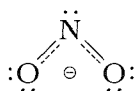
This structure would imply, "NO_2^- is a symmetrical ion, having partial double-bond character in each of the nitrogen–oxygen bonds." For some purposes the structure tells us enough. However, keeping track of the electrons in such a structure requires some rather special notation. What we actually do most of the time in such situations is to write two or more Lewis structures, which we call **resonance structures**, and connect them with a symbol that means: "Superimpose these structures to get a reasonable representation of the molecule." Applied to NO_2^- the structures are
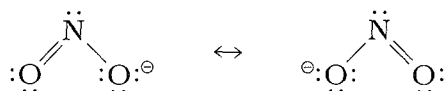
The double-headed arrow is the symbol for superimposition. It should not be confused with the symbol consisting of two arrows pointing in opposite directions, ⇌, which indicates that a reversible chemical reaction is occurring. The double-headed arrow does not imply that a molecule or ion flips back and forth between two structures. Instead, it tells us that the electronic formula of NO_2^- is a hybrid of the two resonance structures. When two or more resonance structures can be drawn for a molecule or ion, the electronic formula for the species is considered to be a **resonance hybrid** of these structures.

When we consider the benzene molecule, C_6H_6, which has six carbon atoms arranged in a ring, we can draw two equally satisfactory structures:
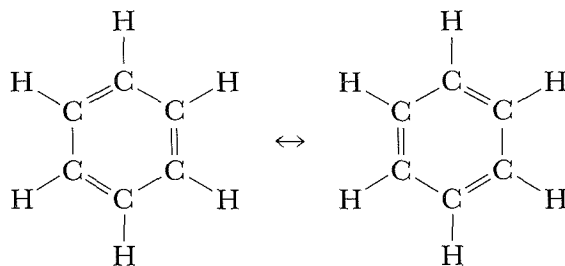

Both resonance structures show the ring to be composed of alternating single and double bonds. However, structural studies reveal that all the carbon–carbon bond distances are equal, as would be expected for a resonance hybrid of the two structures. The full symmetry of the molecule can also be indicated by a single structure with a special dashed-line notation:
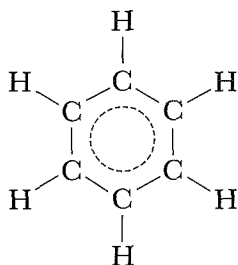
Resonance structures are required in many cases other than those in which they are demanded by symmetry. For example, compare two well-known anions, nitrate (NO_3^-) and nitroamide (^-O_2NNH). Because nitrate has three equivalent nitrogen–oxygen bonds, we write a set of three equivalent resonance structures, and say that the correct formula is a resonance hybrid:
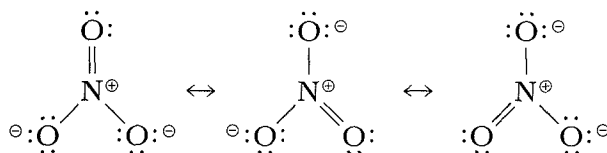

For the nitroamide ion we can write two equivalent structures (I and II), plus a third (III) that is not equivalent to the other two:
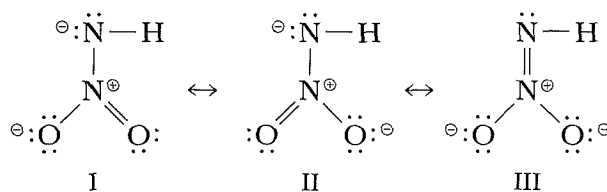
Common sense tells us that all three structures should contribute to our description of the ion. Since the structures are not equivalent, the resonance symbol no longer means, "Mix these structures equally in your thinking." It merely means, "Mix them." Therefore no quantitative implications are intended by the double-headed arrow. When we become semiquantitative in our description we state that structure III "contributes" more to the resonance hybrid of the nitroamide ion than either of the equivalent structures I and II because III places both formal negative charges on the oxygen atoms.

The last of the polyatomic molecules we will discuss is the anion obtained by removing the two protons in sulfuric acid, the sulfate ion, SO_4^{2-}. As in the case of H_2SO_4, an octet-rule structure with only single bonds can be written by assigning three lone pairs to each oxygen atom:

$$:\ddot{O}:^{\ominus}$$
$$|$$
$$^{\ominus}:\ddot{O}-S\overset{(2+)}{=}\ddot{O}:^{\ominus}$$
$$|$$
$$:\ddot{O}:^{\ominus}$$
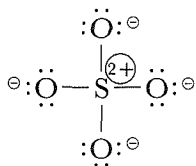
However, if we consider the large positive formal charge on the sulfur atom we conclude that this is not a particularly appropriate structure. A much better representation of the bonding in SO_4^{2-} removes the $+2$ formal charge on the central sulfur atom by forming two sulfur–oxygen double bonds.

There are six equivalent structures with two sulfur–oxygen double bonds and two sulfur–oxygen single bonds. Thus we represent the bonding in SO_4^{2-} as a resonance hybrid of the following six equivalent structures:
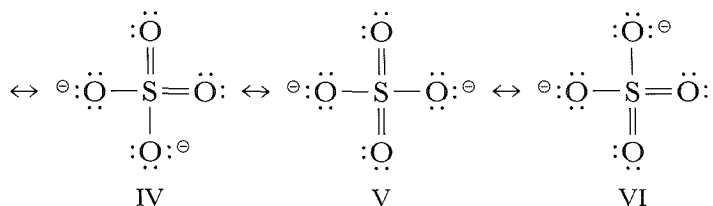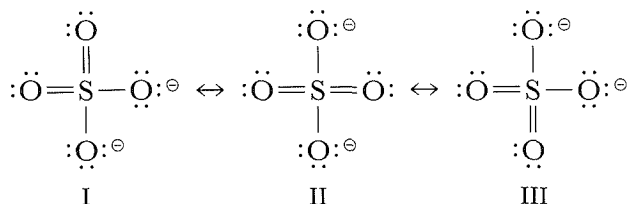
The resonance hybrid of the six equivalent structures (I–VI) of SO_4^{2-} would have an average sulfur–oxygen bond order of $1\frac{1}{2}$. In accord with this model of partial double-bond character is the fact that the observed sulfur–oxygen bond length in SO_4^{2-} (1.49 Å) is 0.21 Å shorter than the standard sulfur–oxygen single-bond length of 1.70 Å, which is obtained by adding the atomic radii of sulfur (1.04 Å) and oxygen (0.66 Å) (see Figure 9-5).

Example 3

Write Lewis structures for SO_2 and SO_3. Can you write a Lewis structure for SO_3 in which all three sulfur–oxygen bonds are equivalent? What is the formal charge on S then?
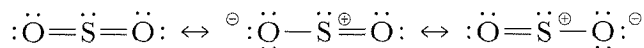
Solution   An SO_2 structure with equivalent bonds is

$$:\ddot{O}=\ddot{S}=\ddot{O}:$$
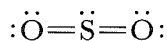
This SO_2 structure is satisfactory in that both sulfur–oxygen bonds are equivalent and there is no formal charge on the sulfur atom; however, it places 10 valence electrons around the S atom. But we already have seen in SO_4^{2-} that as many as 12 valence electrons can be placed around a central sulfur atom. If we insist on no more than 8 electrons around each atom, we cannot draw a single Lewis structure with equivalent bonds for SO_2. However, we can draw two Lewis structures for SO_2 in which one sulfur–oxygen bond is single and one is double, and in which there is a formal-charge separation. An adequate representation of SO_2 would be a resonance hybrid of these two structures:

$$^{\ominus}:\ddot{O}-\ddot{S}\overset{\oplus}{=}O: \leftrightarrow :\ddot{O}=\ddot{S}\overset{\oplus}{-}\ddot{O}:^{\ominus}$$
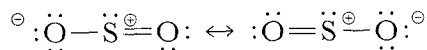
If we had to choose a single structure to represent SO_2, it would be $:O=S=O:$, because the sulfur–oxygen bonds are equivalent and there is no formal-charge separation. A better representation would be a resonance hybrid of this structure and the two others,

$$:\ddot{O}=\ddot{S}=\ddot{O}: \leftrightarrow {}^{\ominus}:\ddot{O}-\ddot{S}\overset{\oplus}{=}\ddot{O}: \leftrightarrow :\ddot{O}=\ddot{S}\overset{\oplus}{-}\ddot{O}:^{\ominus}$$

This is because the observed sulfur–oxygen bond length in SO_2 is a bit longer than expected for a double bond.

The SO_3 molecule involves more difficulties. There are two Lewis structures in which all three sulfur–oxygen bonds are equivalent:
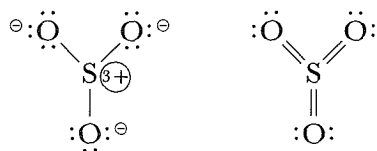
The first structure places a formal charge of $+3$ on S and has only three electron pairs around the central atom. This structure may be rejected. The second structure avoids formal charges, but at the expense of surrounding the S atom with six electron pairs. Three equivalent resonance structures can be drawn with an octet of electrons around S, but they all give S a $+2$ formal charge:
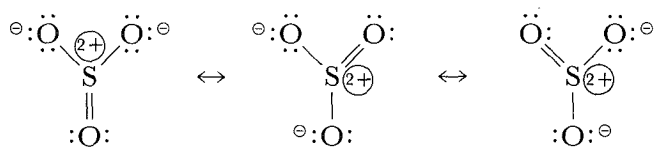
Three additional equivalent resonance structures place a $+1$ formal charge on S:
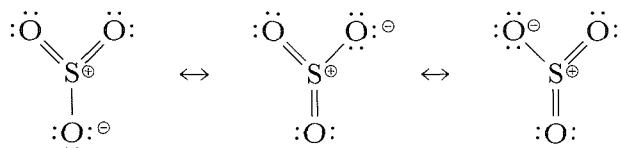
The x-ray and spectroscopic data available reveal that all three bonds in SO_3 are identical, and that their length is shorter than that expected for a single bond but longer than for a double bond. Therefore, we cannot describe the actual molecule accurately with any one Lewis structure, and our failure illustrates the inadequacy of such a simple bond model. We can compromise and say that the structure of the SO_3 molecule is a resonance hybrid of the all-double-bonded structure with a little of the other six structures as well.

The Meaning of Oxidation Numbers

Chlorine is found in a series of oxyanions, ClO^-, ClO_2^-, ClO_3^-, and ClO_4^-, that illustrate its entire range of positive oxidation states. The chloride ion has the Ar noble-gas structure with four pairs of valence electrons. The four oxyanions can be thought of as the products of the reaction of this Cl^- ion as a Lewis base with one to four oxygen atoms, which act as electron-pair acceptors and Lewis acids. Following are the four reactions and the oxidation number of Cl in each oxyanion:
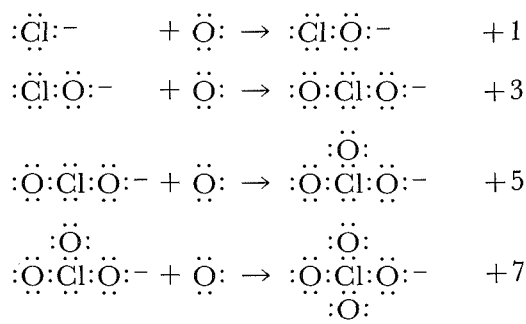
There are no chlorine oxyanions with more than four oxygens because there are no more valence electron pairs on Cl^-.

The formal charge on each atom is determined by assigning one electron in a bond to each participating atom. In contrast, the oxidation number is found by assigning *both* electrons in a bond to the more electronegative of the two atoms. (This is the meaning of Rule 5 in Section 10-1.) Thus the

oxidation number is the charge that the atom would have if it were an isolated ion with the assigned number of electrons:

$$\text{Oxidation number} = Z - (N_{\text{assigned}} + N_{\text{nonbonding}})$$

Here Z is the atomic number, N_{assigned} is the total number of electrons in bonds between the given atom and atoms that are *less* electronegative than it is, and $N_{\text{nonbonding}}$ is the total number of electrons possessed by the atom that are *not* involved in covalent bonds. In calculating oxidation numbers, we always pretend that both electrons in a bond belong to the more electronegative of two bonded atoms. Fluorine, the most electronegative element, always has an oxidation number of -1. Oxygen always has an oxidation number of -2, except in peroxides and compounds of fluorine. In the Cl oxyanions, since Cl has an electronegativity of 3.16, and O, of 3.44, both electrons in a bond are assigned to oxygen. In Cl^-, chlorine has a net charge of -1 and an oxidation number of -1. In ClO^-, chlorine has six assigned electrons and an oxidation number of $+1$, since the bonding electron pair has been assigned to oxygen because of oxygen's greater electronegativity. In ClO_4^-, all four electron pairs have been "abducted" by the more electronegative oxygen atoms, and Cl has an oxidation number of $+7$, *as if* it really had lost all seven of its valence electrons. Oxidation numbers are couched in the language of electron loss and gain. What they really measure, however, is the extent of combination of an atom with other atoms more electronegative than itself.

Example 4

What are the formal charges on Cl in the Lewis structures given previously for ClO^-, ClO_2^-, ClO_3^-, and ClO_4^-? Can better Lewis structures be written for these ions? What are they? Do these new structures change the oxidation numbers of Cl in each case?
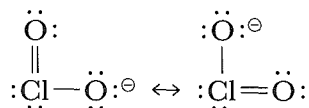
Solution
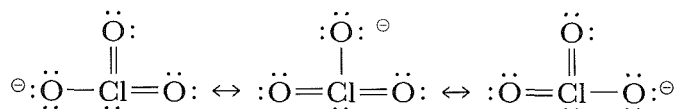
The formal charges on Cl are as follows:
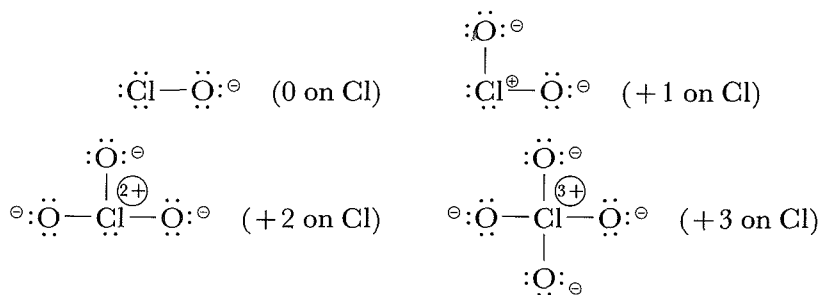
In every ion but ClO^-, a formal positive charge is present on Cl. Better
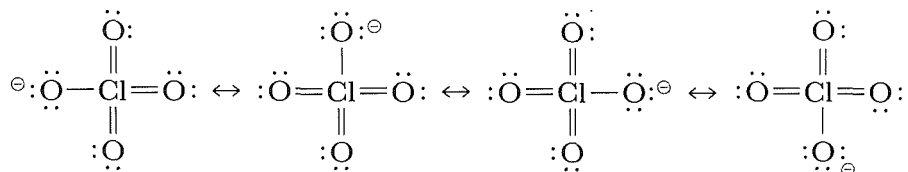
Lewis structures can be written for each ion, in which the formal charge is reduced to zero on Cl. These structures involve Cl=O: bonds, and will result in more than eight electrons around the Cl; this larger number of electrons is acceptable for a third-period atom (see the previous discussion of SO_4^{2-}). Thus we have

$$
\begin{array}{ccc}
\ddot{\text{O}}: & & :\ddot{\text{O}}:^{\ominus} \\
\parallel & & | \\
:\ddot{\text{C}}\text{l}\!-\!\ddot{\text{O}}:^{\ominus} & \leftrightarrow & :\ddot{\text{C}}\text{l}\!=\!\ddot{\text{O}}:
\end{array}
$$

two equivalent resonance structures, each with zero formal charge on Cl; both chlorine–oxygen bonds are equivalent. Next, we have

$$
\begin{array}{ccccc}
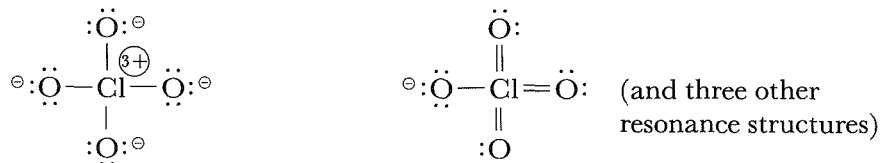\ddot{\text{O}}: & & :\ddot{\text{O}}:^{\ominus} & & \ddot{\text{O}}: \\
\parallel & & | & & \parallel \\
^{\ominus}:\ddot{\text{O}}\!-\!\ddot{\text{C}}\text{l}\!=\!\ddot{\text{O}}: & \leftrightarrow & :\ddot{\text{O}}\!=\!\ddot{\text{C}}\text{l}\!=\!\ddot{\text{O}}: & \leftrightarrow & :\ddot{\text{O}}\!=\!\ddot{\text{C}}\text{l}\!-\!\ddot{\text{O}}:^{\ominus}
\end{array}
$$

three equivalent resonance structures, each with zero formal charge on Cl; all three chlorine–oxygen bonds are equivalent. And,

$$
\begin{array}{ccccccc}
\ddot{\text{O}}: & & :\ddot{\text{O}}:^{\ominus} & & \ddot{\text{O}}: & & \ddot{\text{O}}: \\
\parallel & & | & & \parallel & & \parallel \\
^{\ominus}:\ddot{\text{O}}\!-\!\text{Cl}\!=\!\ddot{\text{O}}: & \leftrightarrow & :\ddot{\text{O}}\!=\!\text{Cl}\!=\!\ddot{\text{O}}: & \leftrightarrow & :\ddot{\text{O}}\!=\!\text{Cl}\!-\!\ddot{\text{O}}:^{\ominus} & \leftrightarrow & :\ddot{\text{O}}\!=\!\text{Cl}\!=\!\text{O}: \\
\parallel & & \parallel & & \parallel & & | \\
:\ddot{\text{O}} & & :\ddot{\text{O}} & & :\ddot{\text{O}} & & :\ddot{\text{O}}:_{\ominus}
\end{array}
$$

four equivalent resonance structures, each with zero formal charge on Cl; all four chlorine–oxygen bonds are equivalent.

The better Lewis structures do *not* change the oxidation-number assignments. In each, *all* bonding electrons are assigned to the more electronegative atom, which is oxygen. So, for perchlorate (ClO_4^-), for example, we make the following comparison:

$$
\begin{array}{cc}
:\ddot{\text{O}}:^{\ominus} & \ddot{\text{O}}: \\
| {\scriptstyle(3+)} & \parallel \\
^{\ominus}:\ddot{\text{O}}\!-\!\text{Cl}\!-\!\ddot{\text{O}}:^{\ominus} & ^{\ominus}:\ddot{\text{O}}\!-\!\text{Cl}\!=\!\ddot{\text{O}}: \quad\text{(and three other} \\
| & \parallel \qquad\qquad \text{resonance structures)} \\
:\ddot{\text{O}}:^{\ominus} & :\ddot{\text{O}}
\end{array}
$$

Lewis structure with large formal-charge separation (poor); formal charge on Cl = +3; oxidation number of Cl obtained by assigning all four bonding pairs to O, as if the bonds were all ionic; oxidation number of Cl = +7

Lewis structure with zero formal charge on Cl (better); oxidation number of Cl obtained by assigning all seven bonding pairs to O, as if the bonds were all ionic; oxidation number of Cl = +7

11-2 ACIDITY OF OXYACIDS

The simple Lewis model of bonding, with all its defects, does give us a physical understanding of the relative acidity of compounds that contain a central atom bonded to oxygen atoms alone, or to the oxygen atoms in hydroxide ion and water. Oxides of nonmetals dissolve in water to form acids. For example,

$$SO_3 + H_2O \rightarrow H_2SO_4$$

(Sulfuric acid is not prepared this way commercially, however.) In such oxyacids the protons are bound to oxygen:

$$\ddot{O}:$$
$$\|$$
$$:\ddot{O}=S-\ddot{O}-H$$
$$|$$
$$:O:$$
$$|$$
$$H$$
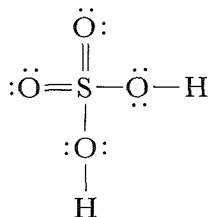
Consider a series of compounds containing hydroxide groups bound to positive ions ranging from Na^+ to Cl^{7+}: $NaOH$, $Mg(OH)_2$, $Al(OH)_3$, $Si(OH)_4$, $OP(OH)_3$ or H_3PO_4, $O_2S(OH)_2$ or H_2SO_4, and O_3ClOH or $HClO_4$. Now consider the bonds in the structure

$$M \overset{1}{-} O \overset{2}{-} H$$
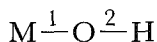
in which M is the central atom. If the bond breaks at position 1 to form M^+ and OH^-, the compound is basic. If it breaks at position 2 to form $M-O^-$ and H^+, the compound is acidic. For the preceding series of compounds, Na^+OH^- is an ionic compound that is very soluble in water; thus, OH^- and Na^+ are separated easily. The smaller, more highly charged Mg^{2+} ion binds more tightly to OH^-, thereby making magnesium hydroxide, $Mg(OH)_2$, less soluble than $NaOH$ and a weaker base. Aluminum hydroxide is virtually insoluble in water, but loses OH^- to strong acids and H^+ to strong bases:

$$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$$
$$Al(OH)_3 + OH^- \rightarrow AlO(OH)_2^- + H_2O$$
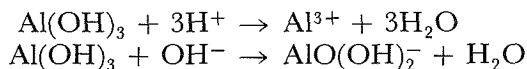
As we have seen, a compound such as aluminum hydroxide, which is able to react either as a base with an acid, or as an acid with a base, is called **amphoteric**. Hydrogen species such as HCO_3^- that can either lose a proton (giving CO_3^{2-}) or gain a proton (forming H_2CO_3) are called **amphiprotic**.

The exact formula of the ion represented by $AlO(OH)_2^-$ is uncertain. Recent work has shown that the hydrated aluminum ion is $Al(H_2O)_6^{3+}$. Removal of three protons from this would give neutral, insoluble $Al(OH)_3(H_2O)_3$, which could then lose another proton and form

$Al(OH)_4(H_2O)_2^-$. This formula probably most nearly represents the actual situation.

Silicic acid, $Si(OH)_4$, easily gives up water molecules to form SiO_2. It is a weak acid and reacts with NaOH. However, it does not react with HCl; thus, the compound is not amphoteric:

$$Si(OH)_4 + 2NaOH \rightarrow Na_2SiO_3 + 3H_2O$$
$$Si(OH)_4 + HCl \rightarrow \text{no reaction}$$
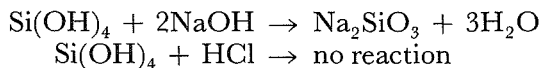
The compounds H_3PO_4, H_2SO_4, and $HClO_4$ become progressively more acidic; $HClO_4$ is the strongest oxyacid known. It appears that the oxygen–hydrogen bonds in this series become easier to break as the oxidation number of the central atom increases. However, HNO_3, in which N is in the $+5$ oxidation state, is a much stronger acid than $Te(OH)_6$, in which Te is in the $+6$ oxidation state. A better correlation can be made between acidity of oxyacids and the formal charge on the central atom, provided all Lewis structures are written to be consistent with the octet rule. With this provision, the formal charges on the central atoms in several oxyacids are
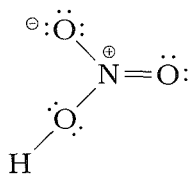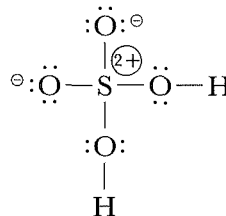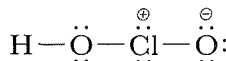

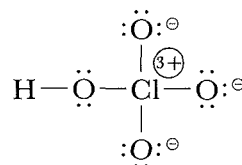Formal charge: N = +1   Formal charge: S = +2
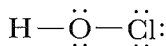
Formal charge: Cl = 0   Formal charge: Cl = +1   Formal charge: Cl = +3

In general, acidity increases with increasing formal charge on the central atom. The higher the formal positive charge on a central atom, the more the central atom will attract electrons from attached oxygen atoms. This results in a weakening of the oxygen–hydrogen bond, thereby allowing easier removal of the H^+ and therefore an increase in acid strength. The effect of formal charge on acidity for similar species is shown by the data in Table 11-1; a small increase in negative charge on an atom to which a proton is attached enormously decreases the acidity of the species.

There is another, simpler correlation between the acidity of oxyacids and their structures. Acidity increases as the number of oxygen atoms
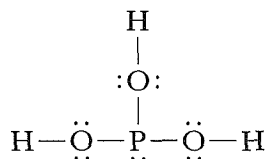
Table 11-1		
Effect of Formal Charge on Acid Strength		
Substance	**Formal charge on O, N, S**	**pK**
H_3O^+	+1	−1.75
H_2O	0	+15.7
OH^-	−1	25
NH_4^+	+1	9.25
NH_3	0	35
H_2S	0	7.04
HS^-	−1	11.96

without hydrogen atoms attached increases. Table 11-2 shows such a correlation in which the pK's of oxyacids are clearly functions of n in the formula $XO_n(OH)_m$ and are much less influenced by the value of m.

The correlations of acidity with structure are approximate but have led to interesting discoveries. For instance, the pK of H_3PO_3 is 1.8 for the first hydrogen ionization. A chemist would instinctively write the structure as

$$\begin{array}{c} \text{H} \\ | \\ :\!\text{O}\!: \\ | \\ \text{H}-\overset{..}{\underset{..}{\text{O}}}-\text{P}-\overset{..}{\underset{..}{\text{O}}}-\text{H} \end{array}$$

for this acid, which would suggest a pK of about 7 to 9 (see the "very weak" group in Table 11-2). However, the pK_1 of 1.8 suggests that phosphorus has one oxygen bound to it, which is not bound to a hydrogen atom. Structural studies show that only two protons can be ionized and that the third proton is attached to phosphorus. Thus, the structure of H_3PO_3 should be written as

$$\begin{array}{c} :\!\overset{..}{\text{O}}\; \\ \| \\ \text{H}-\overset{..}{\underset{..}{\text{O}}}-\text{P}-\overset{..}{\underset{..}{\text{O}}}-\text{H} \\ | \\ \text{H} \end{array}$$
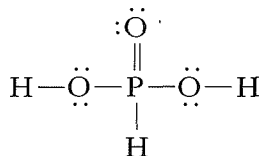
This structure is clearly consistent with the correlation in Table 11-2.

Example 5

Would you expect perchloric acid, $HClO_4$, to be stronger than nitric acid, HNO_3? Why?
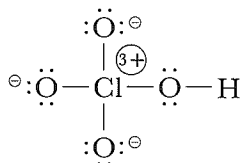
Table 11-2

pK Values for Inorganic Oxyacids[a]

X(OH)$_m$ (very weak)		XO(OH)$_m$ (weak)		XO$_2$(OH)$_m$ (strong)		XO$_3$(OH)$_m$ (very strong)	
Cl(OH)	7.5	ClO(OH)	2.0	ClO$_2$(OH)	(−3)	ClO$_3$OH	(−8)
Br(OH)	8.7	NO(OH)	3.4	NO$_2$(OH)	−1.4	MnO$_3$(OH)	(−8)
I(OH)	10.6	IO(OH)	1.6	IO$_2$(OH)	0.8		
B(OH)$_3$	9.2	SO(OH)$_2$	1.8	SO$_2$(OH)$_2$	(−3)		
Sb(OH)$_3$	11.0	SeO(OH)$_2$	2.5	SeO$_2$(OH)$_2$	(−3)		
Si(OH)$_4$	9.7	TeO(OH)$_2$	2.5				
Ge(OH)$_4$	8.6	CO(OH)$_2$	6.4				
Te(OH)$_6$	7.7	PO(OH)$_3$	2.1				
As(OH)$_3$	9.2	AsO(OH)$_3$	2.3				
		HPO(OH)$_2$	1.8				
		H$_2$PO(OH)	2.0				

[a]Values given within parentheses are estimated values.

Solution

The Lewis structure of HClO$_4$ that places exactly eight electrons around Cl is

$$:\ddot{O}:^{\ominus}$$
$$|\;^{(3+)}$$
$$^{\ominus}:\ddot{O}-Cl-\ddot{O}-H$$
$$|$$
$$:\underset{..}{O}:^{\ominus}$$

The formal charge on Cl is $+3$. The related structure for HNO$_3$,

$$^{\ominus}:\ddot{O}:$$
$$\backslash\;^{\oplus}$$
$$N=\ddot{O}:$$
$$/$$
$$\underset{..}{O}.$$
$$H^{/}$$
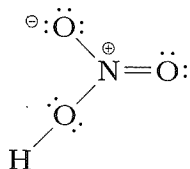
places a $+1$ formal charge on N. Thus we would expect HClO$_4$ to be a stronger acid than HNO$_3$ (which it is; see Table 11-2). Since both acids have the same number of −OH groups (one each), the oxidation-number method also predicts the relative acidities correctly. The oxidation number of Cl in HClO$_4$ is $+7$, which is greater than the $+5$ for N in HNO$_3$. Finally, the number of oxygen atoms without hydrogen atoms attached to the central atom is greater for HClO$_4$ than for HNO$_3$ ($n = 3$ for HClO$_4$; $n = 2$ for HNO$_3$), again suggesting that HClO$_4$ is the stronger acid.

11-3   THE VSEPR METHOD
AND MOLECULAR GEOMETRY

Up to this point we have been concerned mainly with identifying the bonds and lone pairs in the Lewis structures of molecules and ions. But we can say much more about the structure of a molecule than is implied by its Lewis diagram. Molecules and complex ions have shapes (geometries), and it is this aspect of structure that we shall discuss next.

Molecules have all sorts of geometrical structures. For example, the ground-state molecular geometry of CO_2 is linear, whereas that of OCl_2 is angular (bent); BF_3 is trigonal planar, NF_3 is trigonal pyramidal, and ClF_3
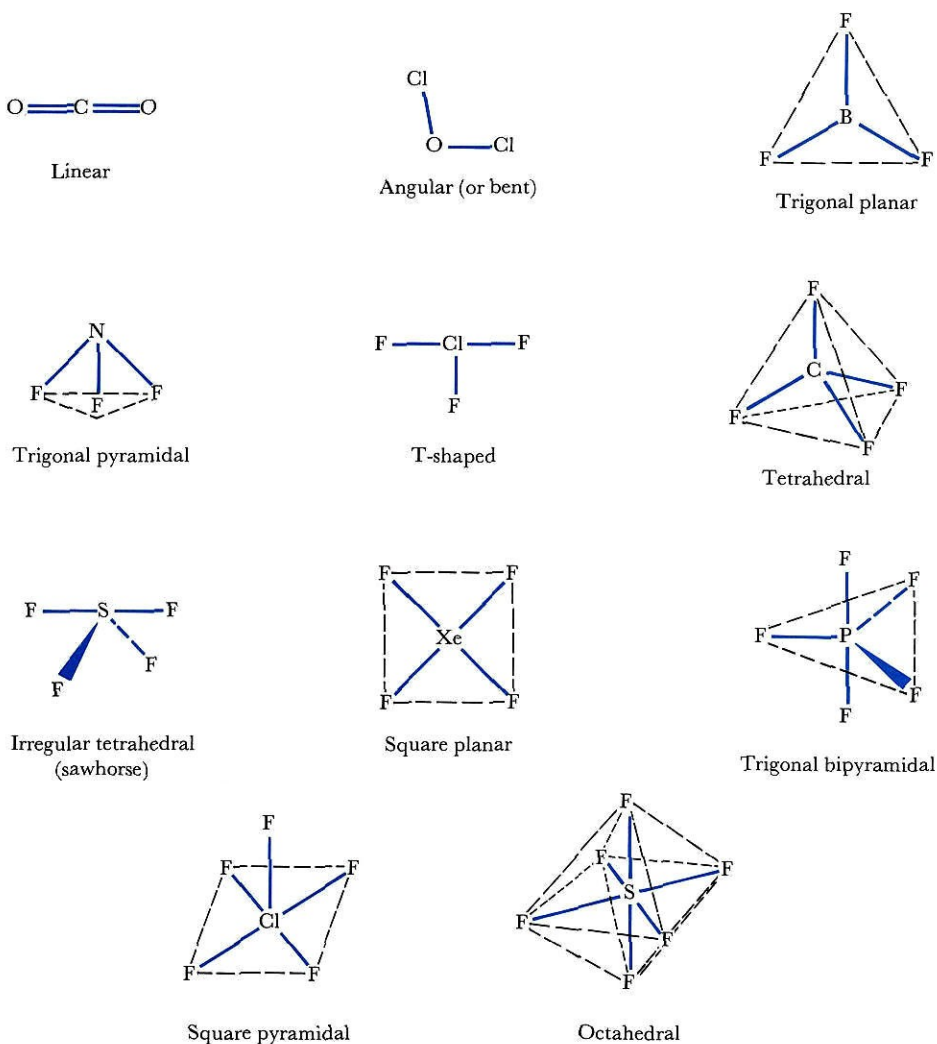
Figure 11-1

Some common
molecular
geometries.

Linear

Angular (or bent)

Trigonal planar

Trigonal pyramidal

T-shaped

Tetrahedral

Irregular tetrahedral
(sawhorse)

Square planar

Trigonal bipyramidal

Square pyramidal

Octahedral

is T-shaped; CF_4 is tetrahedral, SF_4 is irregular tetrahedral (sawhorse), and ClF_4^- is square planar; PF_5 is trigonal bipyramidal but ClF_5 is square pyramidal; and finally, SF_6 is octahedral. These geometrical structures are shown in Figure 11-1.
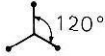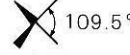
How are we to understand all these geometries? Is there any simple way to predict them (and predict others as well)? The answer to the last question, surprisingly, is that there is—it is a method that was described by N. V. Sidgwick and H. M. Powell in 1940, and extended by R. J. Gillespie and R. S. Nyholm in 1957. This approach is called the **valence-shell electron-pair repulsion (VSEPR) method**; it states that the bonding electron pairs and lone electron pairs of an atom will adopt a spatial arrangement that minimizes electron-pair repulsion around that atom.

Before applying the VSEPR method to molecular systems, let us first consider the most favorable arrangement for n electron pairs circumscribed on a sphere. For values of n from 2 through 6, the predicted arrangement is shown in Figure 11-2. The predicted arrangement for 7 through 12 electron pairs will be discussed later in this section.

To apply the VSEPR method to molecules we simply count the number of lone electron pairs and the number of atoms around the central atom in a polyatomic molecule. We will call the total number of lone pairs of electrons and attached atoms the **steric number**, *SN*. If there are no lone pairs of electrons around the central atom (A) and the *SN* arises only from attached atoms (X), the observed molecular geometry agrees with that shown in Figure 11-2. In each of the examples shown in Table 11-3, the predicted geometry involves separating the bonding electron pairs as much as possible, to minimize electron-pair repulsion. It should be emphasized that multiple bonds between atoms do not alter the predictions of molecular

Table 11-3

Predicted Geometries for Various Molecules

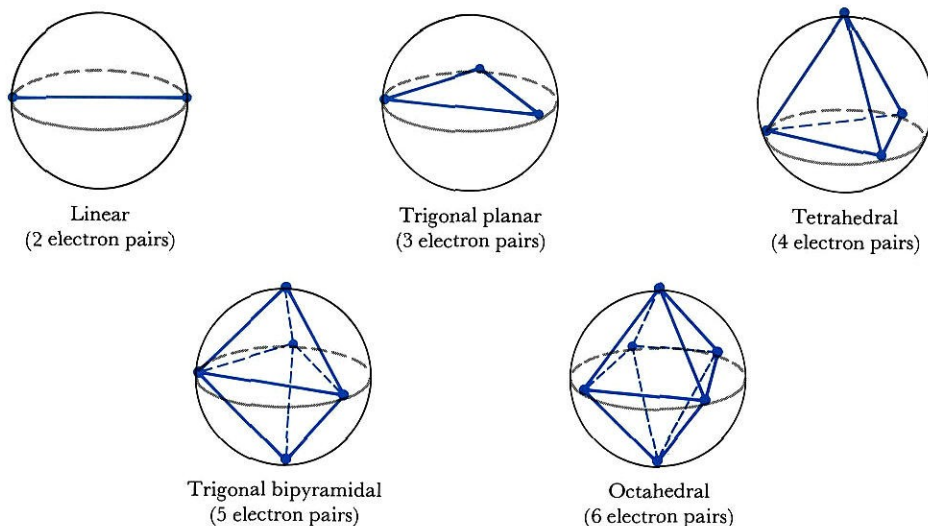| Molecule	Steric number	Predicted geometry		Example
AX_2	2	Linear	180°	CO_2
AX_3	3	Trigonal planar	120°	BF_3
AX_4	4	Tetrahedral	109.5°	CF_4
AX_5	5	Trigonal bipyramidal	90° 120°	PF_5
AX_6	6	Octahedral	90° 90°	SF_6

Figure 11-2   The arrangement of electron pairs on the surface of a sphere so that the distance between electron pairs is maximized.

geometry. For example, beryllium dihydride and carbon dioxide each have $SN = 2$ and are predicted to be linear:
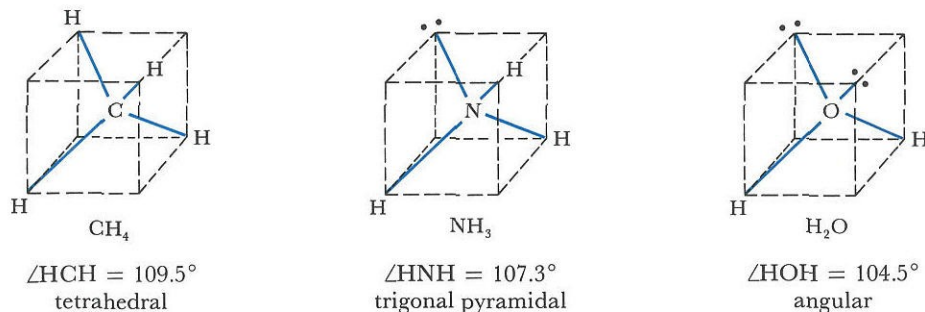
$$\text{H}-\text{Be}-\text{H} \qquad :\ddot{\text{O}}=\text{C}=\ddot{\text{O}}:$$

However, if one of the attached atoms is replaced by a lone pair of electrons, the molecular geometry does change. By *molecular geometry* we mean the positions of the atoms that we can determine experimentally, but not the placement of lone pairs of electrons, which can only be inferred. Thus for AX_3 and AX_2E where X represents an attached atom and E a lone pair of electrons, we obtain the following structures:

trigonal
planar
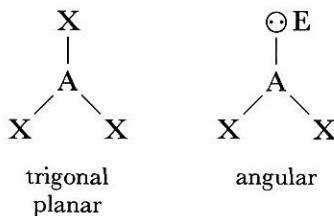
angular

We can predict not only that an AX_2E molecule will be angular but also that the XAX angle will be *less* than 120°. This prediction results from the postulate that lone electron pairs are closer to the central atom and therefore have a repulsive effect larger than that of bonding electron pairs.
   We can apply this same postulate to predict the relative bond angles

in the isoelectronic sequence CH_4, $:NH_3$, and $H_2\ddot{O}:$. Each of these molecules has $SN = 4$. However, in view of the lone-pair/bond-pair repulsions in NH_3 and H_2O, we predict the bond angles in these two molecules to be less than the tetrahedral angle (109.5°). The experimental bond angles agree with these predictions.
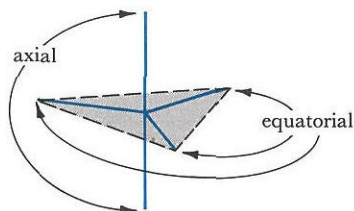

CH_4	NH_3	H_2O
$\angle HCH = 109.5°$	$\angle HNH = 107.3°$	$\angle HOH = 104.5°$
tetrahedral	trigonal pyramidal	angular

Examples of predicted molecular shapes from $SN = 2$ through $SN = 6$ are shown in Figure 11-3.

The structure of a molecule that contains different atoms attached to a central atom exhibits distortions from the idealized structures shown in Figure 11-3. Thus CH_3Cl has HCH angles of 110.5° and ClCH angles of 108.5°, compared to the perfect tetrahedron for which all bond angles are 109.5°. Further examples of these distortions from an idealized geometry are provided by ethylene and formaldehyde. In both molecules the carbon atoms have $SN = 3$, for which the idealized bond angles are 120°. The observed structures are
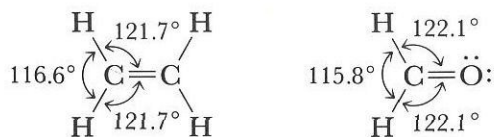
Here one can consider that the two pairs of electrons in a double bond exert more of an electrostatic repulsion than the electron pairs in the single bonds, pushing the C—H bonds slightly together.

The placement of electron pairs for $SN = 5$ deserves special comment. The spatial arrangement for five electron pairs is a trigonal bipyramid, in which there are three equatorial and two axial positions:
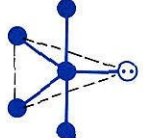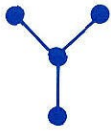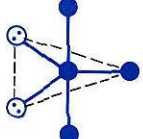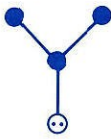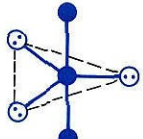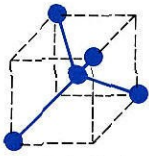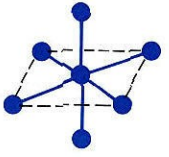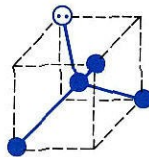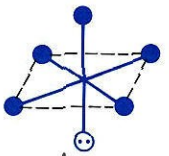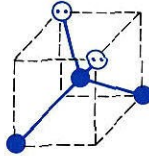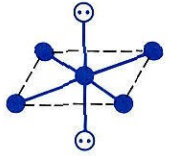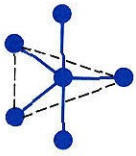
SN	Number of lone pairs	Molecular shape	Example
2	0	linear	BeH_2, CO_2
3	0	trigonal planar	SO_3, BF_3
3	1	angular	SO_2, O_3
4	0	tetrahedral	CH_4, CF_4, SO_4^{2-}
4	1	trigonal pyramidal	NH_3, PF_3, $AsCl_3$
4	2	angular	H_2O, H_2S, SF_2
5	0	trigonal bipyramidal	PF_5, PCl_5, AsF_5

SN	Number of lone pairs	Molecular shape	Example
5	1	sawhorse	SF_4
5	2	T-shaped	ClF_3
5	3	linear	XeF_2, I_3^-, IF_2^-
6	0	octahedral	SF_6, PF_6^-, SiF_6^{2-}
6	1	square pyramidal	IF_5, BrF_3
6	2	square planar	XeF_4, IF_4^-

Figure 11-3   Molecular shapes predicted by the VSEPR method.

The shape of a molecule such as PF_5 must be trigonal bipyramidal because there are no lone pairs surrounding the central phosphorus atom. However, it is not necessary that the axial bond lengths be equal to the equatorial bond lengths. Since each axial bond experiences three 90° repulsions compared to only two 90° repulsions for the equatorial positions, we predict that the axial bonds will be longer than the equatorial bonds (the 90° interactions are much larger than 120° or 180° interactions, because electron-pair repulsions decrease very rapidly as the distance between pairs increases). Experimentally, the axial $P-F$ bond lengths are 1.577 Å, compared to 1.534 Å for the equatorial bond lengths.

Next we consider the SF_4 molecule, which has four bond pairs and one lone pair surrounding the sulfur atom. Where should we place the lone electron pair in SF_4? According to the VSEPR method, the most prohibitive repulsion is lone pair/lone pair, followed in order by lone pair/bond pair and bond pair/bond pair. Therefore, in SF_4 the "worst" repulsion is lone pair/bond pair because there is only one lone pair. If we place the lone pair in one of the equatorial orbitals, it will repel only two bonded pairs at a 90° angle, whereas in an axial orbital it will repel three pairs at 90°:

three 90° interactions
(axial placement of lone pair)

two 90° interactions
(equatorial placement of lone pair)
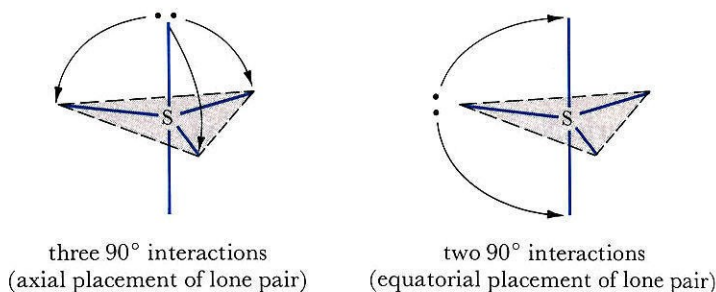
Therefore the VSEPR choice is equatorial placement of the lone electron pair, which results in a smaller number of 90° interactions. Accordingly, we also place the second (e.g., ClF_3) and third (e.g., I_3^-) lone pairs into equatorial orbitals, and predict the shapes shown in Figure 11-3.

The equatorial position of the lone pairs in SF_4 and ClF_3 should result in distortions of the idealized 90° and 120° angles between bonds. Indeed, the experimental geometries indicate the expected distortions:

As our last example in the discussion of $SN = 5$, we consider those molecules in which the attached atoms are not all identical. Examples of such molecules are CH_3PF_4 and SOF_4. In each of these molecules, the

less electronegative groups occupy the equatorial positions and cause distortions from the idealized 90° and 120° angles similar to those caused by lone electron pairs. Thus we find the following structures:

$$\text{CH}_3 \overset{\text{F}}{\underset{\text{F}}{\overset{91.8°}{\underset{122.2°}{\text{P}}}}} \overset{\text{F}}{\underset{\text{F}}{}} \qquad \text{O} \overset{\text{F}}{\underset{\text{F}}{\overset{90.6°}{\underset{124.9°}{\text{S}}}}} \overset{\text{F}}{\underset{\text{F}}{}}$$
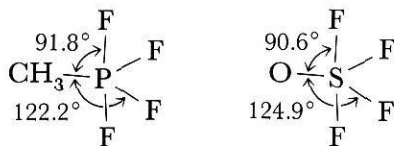
The VSEPR method is easy to use and gives the correct molecular shape for a remarkably large number of molecules. All the predicted shapes in Figure 11-3 are in agreement with experimentally determined molecular structures.

The VSEPR method can be summarized by three simple rules:

1. The electron pairs around a central atom will adopt a spatial arrangement that minimizes electron-pair repulsion.

2. The most prohibitive repulsion is lone pair/lone pair, followed in order by lone pair/bond pair and bond pair/bond pair.

3. Among several structures involving 90° interactions, the most favored structure is the one that results in a smaller number of 90° lone-pair interactions.

Steric Numbers Greater Than Six

The idealized geometries for 7 through 12 electron pairs are shown in Figure 11-4. For any real molecular system there are several different geometries that have nearly the same energy. Thus, the IF_7 molecule ($SN = 7$) has a pentagonal bipyramidal structure rather than the monocapped octahedral structure shown in Figure 11-4a.
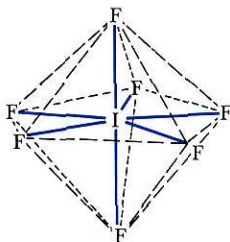
pentagonal bipyramidal structure
of IF_7

Another molecule with $SN = 7$ is XeF_6. Its molecular geometry is predicted to be *irregular octahedral* because of the presence of the lone pair on the xenon atom. The precise structure has not been determined experimentally because the geometry is not static—an intramolecular rearrangement process rapidly interconverts fluorine positions. In agreement
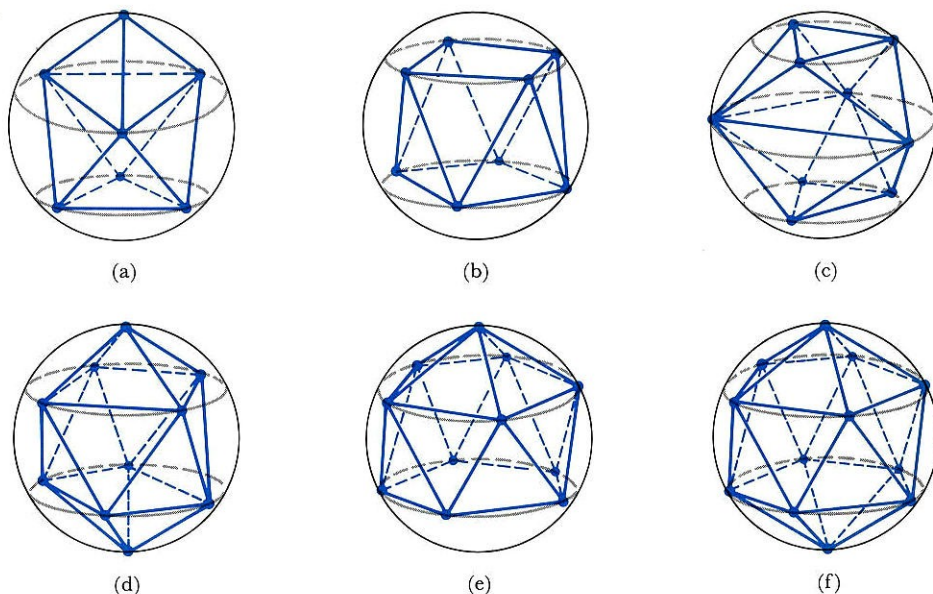
Figure 11-4 Arrangements of 7 through 12 electron pairs on a sphere that maximize their distance apart: (a) 7 pairs—monocapped octahedron; (b) 8 pairs—square antiprism; (c) 9 pairs—tricapped trigonal prism; (d) 10 pairs—bicapped square antiprism; (e) 11 pairs—monocapped pentagonal antiprism; (f) 12 pairs—icosahedron.

with the VSEPR prediction, however, the structure is definitely not regular octahedral.

Examples of species with SN equal to 8 and 9 are TaF_8^{3-} and ReH_9^{2-}. These complex ions have the predicted square antiprismatic and tricapped trigonal prismatic structures, respectively. Steric numbers higher than 9 are rare and will not be discussed here.

Exceptions to the VSEPR Rules

So far we have applied the VSEPR method to predict the molecular shapes of molecules that have all their electrons in pairs. If a molecule has one electron that is unpaired, we cannot predict molecular shape so simply. Consider the isoelectronic series BeH_3^{2-}, BH_3^-, CH_3, and NH_3^+, all of which have the Lewis electron-dot structure

$$H-\overset{\textstyle .}{A}-H$$
$$|$$
$$H$$
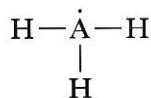
Experimental evidence indicates that NH_3^+ is strictly trigonal planar, whereas CH_3 probably is trigonal planar but may be slightly pyramidal. No experimental evidence exists for BeH_3^{2-} and BH_3^-, but accurate quantum-

	Table 11-4

Bond Angles in Group VA and Group VIA Hydrides

Hydride	Bond angle
NH_3	107.3°
PH_3	93.3°
AsH_3	91.8°
H_2O	104.5°
H_2S	92.2°
H_2Se	91.0°

mechanical calculations predict the degree of distortion from trigonal planar to trigonal pyramidal structures to follow the order $NH_3^+ < CH_3 < BH_3^- < BeH_3^{2-}$.

Other molecules that are not readily understood in terms of the VSEPR rules are the third-, fourth-, and subsequent-row compounds of Groups VA and VIA. The geometries of the hydrides of these compounds are compared to those of the second-row elements in Table 11-4. It is clear that only the second-row compounds exhibit bond angles near the expected tetrahedral angle. The subsequent-row compounds all exhibit bond angles near 90°. A weak explanation of this phenomenon is that because of the larger size of the central atom, there is less bond pair/bond pair repulsion in these compounds, so the bond angles are considerably smaller than the tetrahedral angle (see Chapter 13, Example 1).

Other exceptions to the VSEPR rules are provided by the ions $TeCl_6^{2-}$, $TeBr_6^{2-}$, and $SbBr_6^{3-}$, which are found to be regular octahedral, even though they are all of the AX_6E type and should be distorted just as predicted for XeF_6. This is explained after the fact by noting that the Br and Cl atoms are fairly bulky and consequently that the atom–atom repulsions perhaps dominate over the lone pair/bond pair repulsions.
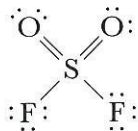
Don't be discouraged by the fact that there are a few exceptions to the VSEPR rules. In most cases they work fine, which is more than can be said for the great majority of chemical "theories"!
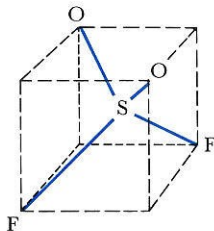
Example 6

Predict the molecular geometry of SO_2F_2 using the VSEPR method.

Solution The Lewis structure of SO_2F_2 is

$$\ddot{\ddot{O}} \qquad \ddot{O}:$$
$$\diagdown \diagup$$
$$S$$
$$\diagup \diagdown$$
$$:\ddot{F}: \qquad \ddot{F}:$$

The *SN* is 4; the structure is tetrahedral:

Example 7

Predict the shape of ClO_2^-.

Solution The Lewis structure of ClO_2^- is

$$\ddot{O}: \qquad\qquad :\ddot{O}:^{\ominus}$$
$$\| \qquad\qquad\qquad |$$
$$:\ddot{Cl}-\ddot{O}:^{\ominus} \leftrightarrow :\ddot{Cl}=\ddot{O}:$$
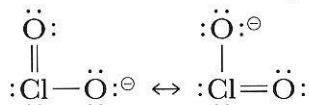
The *SN* is 4. The two O atoms plus the two lone pairs are arranged tetrahedrally around Cl, giving the ClO_2^- ion an *angular* shape:
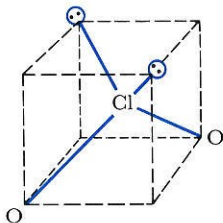
Summary

Lewis structures are the electronic formulas of molecules and complex ions that use lines to indicate **shared electron pairs** (bonds) between atoms and two dots on each atom to indicate a **lone pair** of electrons. For molecules and

complex ions containing only first- and second-period atoms, the best Lewis structures are always ones in which each atom is surrounded by the same number of electrons as in the next noble-gas atom. For H, this is two electrons (one electron pair as in He); for the second-period atoms of non-metallic elements (B, C, N, O, F), this is eight electrons (four electron pairs as in Ne). Because exactly eight electrons complete a closed $2s^2 2p^6$ shell, the rule in drawing Lewis structures is to surround each second-period atom with an octet of electrons. This is known as the **octet rule**

A bond in which two electron pairs are shared between atoms is called a **double bond**; one that involves three shared electron pairs is called a **triple bond.** The **bond order** is the number of shared electron pairs between two atoms. Bond orders of single, double, and triple bonds are 1, 2, and 3, respectively. As the bond order increases between any two atoms, the bond strength increases and the bond length decreases. If an unpaired (or odd) electron is left on an atom in a Lewis structure, the molecule or ion has an **open shell.**

If an atom in a Lewis structure "owns" more or fewer electrons than it does as a free neutral atom, then it possesses a **formal charge**. For the purpose of determining formal charge, each shared electron pair counts as one "owned" electron, and each lone pair counts as two. Thus in the ammonium ion, NH_4^+, N has a formal charge of $+1$ because it owns only four electrons (and it owns five valence electrons in atomic nitrogen, $2s^2 2p^3$). **Isoelectronic** species possess the same number of electrons; CH_4 and NH_4^+ are isoelectronic.

A **Lewis acid** is an electron-pair acceptor (an example is BF_3); a **Lewis base** is an electron-pair donor (an example is $:NH_3$).

If two or more acceptable Lewis structures can be written for a molecule or ion, together they describe the electronic structure of the species. The individual Lewis structures are called **resonance structures** and the "mixed" structure they represent by the notation of a double-headed arrow is called a **resonance hybrid.**

If atoms of different electronegativities are bonded together in a Lewis structure, the **oxidation numbers** are obtained by arbitrarily assigning all bonding electron pairs to the more electronegative partner, as if the structure were ionic. For example, the Lewis structure for CO_2 is

$$:\ddot{O}{=}C{=}\ddot{O}:$$
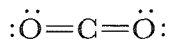
Assigning all the bonding pairs to the oxygens gives

$$:\ddot{\underset{..}{O}}:^{2-} \qquad C^{4+} \qquad :\ddot{\underset{..}{O}}:^{2-}$$
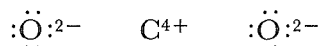
The oxidation number of carbon is $+4$, and the oxidation number of oxygen is -2 in CO_2.

An **oxyacid** contains the unit $M{-}O{-}H$; that is, it has a hydrogen atom that can be lost as H^+ bonded to an oxygen atom, which in turn is

bonded to a so-called central atom. A molecule or ion of the $M—O—H$ type that can act both as a base (donating OH^- to an acid) and as an acid (donating H^+ to a base) is amphoteric. A species such as HSO_4^- that can either lose or gain a proton (H^+) is amphiprotic:

$$SO_4^{2-} \xleftarrow{-H^+} HSO_4^- \xrightarrow{+H^+} H_2SO_4$$
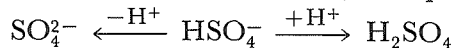
The strengths of oxyacids increase as the formal charge on the central atom increases, provided those charges are determined consistently from Lewis structures in which the octet rule is obeyed. An alternative procedure is to count the number of oxygens attached to M but *not* bound to hydrogens. That is, for the general oxyacid formula $MO_n(OH)_m$, acid strength increases as n increases. Nitric acid, HNO_3, or $NO_2(OH)$, is weaker than perchloric acid, $HClO_4$, or $ClO_3(OH)$.

The valence-shell electron-pair repulsion (VSEPR) method predicts the geometries (shapes) of molecules and complex ions. The main VSEPR rule is that the atoms and lone pairs around a central atom will adopt a spatial arrangement that minimizes electron-pair repulsion. The steric number (SN) is the total number of atoms and lone pairs that are attached to a given central atom. Arrangements that minimize electron-pair repulsions are as follows: $SN = 2$, linear; $SN = 3$, trigonal planar; $SN = 4$, tetrahedral; $SN = 5$, trigonal bipyramidal; and $SN = 6$, octahedral (see Figure 11-2).

Self-Study Questions

1. What experimental evidence is there that O_2 has a bond order of 2, and that N_2 has a bond order of 3?
2. How are N_2, O_2, and F_2 represented by Lewis structures?
3. Which molecule has the greatest bond energy: O_2, F_2, or N_2?
4. Is the HI bond covalent, or ionic?
5. Is the NaCl bond covalent, or ionic?
6. What is meant by an open shell? Name a molecule that has one.
7. How is formal charge defined?
8. Which has a higher $C—C$ bond order, ethylene or acetylene?
9. What is meant by the statement that the ammonium ion and methane are isoelectronic? If they are, then why do they not have similar chemical properties?
10. What combination of boron and hydrogen would be isoelectronic with methane and the ammonium ion? Can you think of any good reasons why such a boron compound might or might not exist?
11. Is the addition compound of BF_3 and NH_3 isoelectronic with any organic compound?
12. How are Lewis acids and bases different from Brønsted acids and bases, and from Arrhenius acids and bases?

13. In the water solution of ammonia,

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$
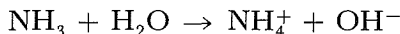
which of the species on the left (or the species that can be derived from them) is the acid and which is the base, according to the definitions of Arrhenius, Brønsted, and Lewis?

14. Why can sulfur bond to six fluorines (in SF_6), whereas oxygen bonds to a maximum of two (in OF_2)?

15. What are resonance structures?

16. What is a resonance hybrid?

17. Why are three resonance structures required to describe the bonding in the nitrate ion, NO_3^-?

18. What is the difference between oxidation number and formal charge? How is each one calculated for an atom in a molecule?

19. Which acid is stronger, $Te(OH)_6$ or H_3PO_4? Why?

20. How does the acidity of an oxyacid depend on the formal charge on the central atom?

21. How does acidity depend on the number of oxygens (without hydrogens) attached to the central atom of an oxyacid?

22. Which is the stronger acid, perchloric ($HClO_4$) or nitric (HNO_3)? Why?

23. What is the VSEPR method? What are the rules used in applying it to predict molecular geometry?

24. What is the steric number (*SN*)? What is the steric number of CO_2? Of SF_4? Of PF_5? Of SF_6?

25. How will six electron pairs arrange themselves to minimize repulsions?

26. What is the geometry of SF_4? Of ClF_3?

27. How does the VSEPR method explain the geometry of XeF_6?

28. Why is the geometry of IF_7 an exception to the VSEPR prediction? What geometry is it predicted to have?

29. What is the geometry of $TeCl_6^{2-}$? Does this agree with the VSEPR prediction? Suggest a reason for the discrepancy.

30. Which are greater, repulsions between two lone pairs or repulsions between two bond pairs? How does this order of repulsions affect the bond angle in H_2O?

Problems

Lewis structures

1. Write Lewis structures for the atoms or ions Na, C, Si, Cl, Ca^{2+}, K^+, Ar, Cl^-, and S^{2-}.

2. What are the Lewis structures for the diatomic molecules or ions O_2, CO, Li_2^+, and CN^-?

3. What are the Lewis structures for Cl_2, N_2, NO, and HCl? Which of these molecules would you expect to be paramagnetic, and why?

4. Write Lewis structures for $BaCl_2$, PH_3, NH_4Cl, HOCl (no H—Cl bond), H_2O, H_2O_2, and NO_2^-.

5. Write Lewis structures for $CaCl_2$, SiH_4, CS_2 (no S—S bond), ClO_2 (chlorine dioxide), ClO_2^- (chlorite ion), and N_2O.

6. Write Lewis structures for BrO_4^-, SiH_4, PCl_4^+, CH_2Cl_2, and BF_4^-.

7. Xenon forms a number of interesting molecules and ions with fluorine and oxygen. Write a Lewis structure for each of the following: XeO_4, XeO_3, XeF_8^{2-}, XeF_6, XeF_4, XeF_2, and XeF^+. Show the placement of formal charges in the Lewis structures. Avoid structures with formal-charge separation, if possible. Using expected trends in effective atomic radii, predict whether the Xe—F bond length in XeF_4 will be longer or shorter than the I—F bond length in the related ion IF_4^-.

8. Nitrogen forms a trifluoride, NF_3, but NF_5 does not exist. For phosphorus both PF_3 and PF_5 are known. Write Lewis structures for NF_3, PF_3, and PF_5. Present possible explanations for the fact that PF_5 is stable, whereas NF_5 is not. In the light of your explanations, which of the following molecules would you expect to be nonexistent: OF_2, OF_4, OF_6, SF_2, SF_4, SF_6? Write Lewis structures and appropriate comments to support your case.

9. Write Lewis structures for CO_2 and SO_2. Are the C—O bonds primarily ionic, or primarily covalent? What shape do you expect for each molecule?

10. The acetylene molecule, HCCH, is linear. Write a Lewis structure for acetylene. Do you expect the C—C bond to be longer in C_2H_2 than in C_2H_4? Compare the energies of the C—C bonds in C_2H_4 and C_2H_2.

11. Iodine forms several oxyanions of the type IO_x^{n-}. Write Lewis structures for IO_3^-, IO_4^-, and IO_6^{5-}. Predict the relative I—O bond lengths in these oxyanions.

12. Write a Lewis structure for S_2. Do you expect the bond energy of S_2 to be larger, or smaller, than that of Cl_2?

13. Write Lewis structures for BF_3 and NO_3^-. Do these molecular species have anything in common?

14. Write Lewis structures for CN^- and CO. The C—O bond length is shorter in CO than it is in CO_2. Explain.

15. Write Lewis structures for the following molecules and ions. Show resonance structures if appropriate. Also indicate in each case whether there are formal charges on one or more atoms.
   a) FBr
   b) S_2
   c) Cl_2
   d) P_2
   e) NCO^-
   f) CNO^-
   g) $BeCl_2$
   h) CS_2
   i) BF_3
   j) SO_3
   k) CO_3^{2-}
   l) CF_4
   m) $SiBr_4$
   n) BF_4^-
   o) NCl_3
   p) PF_3
   q) CH_3^-
   r) SF_2
   s) XeO_3
   t) SO_2
   u) SF_6
   v) Na_2O
   w) ClO_2
   x) N_2F_2
   y) CsF
   z) SrO

16. For each of the following descriptions give the Lewis structure of a known chemical example:
   a) A diatomic molecule with one unpaired electron
   b) A triatomic molecule with two double bonds
   c) A diatomic molecule with formal-charge separation
   d) A diatomic molecule with partial ionic character
   e) An alkaline-earth oxide
   f) A molecule or ion with two equivalent resonance structures
   g) A molecule or ion with three equivalent resonance structures

17. Predict relative N—O bond lengths for NO_2^+, NO_2, and NO_2^-.

18. Borazine has the formula $(BHNH)_3$. The combination of a boron atom and a nitrogen atom is isoelectronic with two carbon atoms and has the same sum of atomic weights. Formulate an acceptable structure for borazine. Can you draw more than one equivalent structure?

Formal charge

19. For the following species, assign formal charges to each of the atoms and indicate the net charge on each species:

$$[:C\equiv N:] \qquad [:\ddot{S}=C=\ddot{N}:]$$
$$[:\ddot{N}=N=\ddot{N}:] \qquad [:\ddot{S}=C=\ddot{O}:]$$
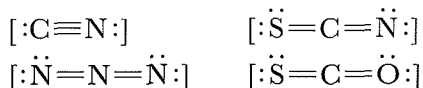
20. In diazomethane (H_2CNN), one nitrogen atom is attached directly to the carbon atom, and the second nitrogen atom is attached to the first. Draw Lewis structures for this molecule in which (a) the two N atoms are joined by a triple bond and (b) the middle N atom forms two double bonds to C and to N. When correctly drawn, each C and N atom should have eight electrons in its valence shell. What is the formal charge on each atom in each of the two structures?

Lewis acids and bases

21. For each of the following reactions, indicate which molecule or ion is the Lewis acid and which is the Lewis base:
    a) $Ag^+ + 2NH_3 \rightarrow Ag(NH_3)_2^+$
    b) $C_2H_3O_2^- + HF \rightarrow HC_2H_3O_2 + F^-$

22. Trimethyl phosphine, $(CH_3)_3P$, reacts with oxygen atoms to give trimethylphosphine oxide, $(CH_3)_3PO$. Is the trimethyl phosphine a Lewis acid or Lewis base in this reaction?

Resonance structures

23. When acetic acid is ionized in solution, the two carbon–oxygen bonds have the same length. Write two resonance structures for the acetate ion that account for this fact.

24. The electronic structure of the thiocyanate ion, NCS^-, can be represented as a hybrid of two resonance structures. Write these two structures and give the carbon–nitrogen and carbon–sulfur bond orders for each structure.

Oxyacids

25. Periodic acid, $(HO)_5IO$, is an oxyacid. Write a Lewis structure for periodic acid. Explain why the I—O bond length (1.78 Å) is shorter than the I—OH bond lengths (1.89 Å).

26. Predict whether $(HO)_5IO$ will be a stronger or weaker acid than $Te(OH)_6$.

VSEPR method

27. Predict the molecular shape of each of the following molecules:
    a) CS_2 f) SiH_4 j) ClO_2
    b) SO_3 g) SF_2 k) IF_5
    c) ICl_3 h) SeF_6 l) OF_2
    d) BF_3 i) PF_3 m) H_2Te
    e) CBr_4

28. What is the geometry around the central atom in each of the following species: CH_4, BF_3, NF_3, ICl_4^-, H_2O?

29. What is the geometry around the central atom in each of the following molecules and ions: BrO_3^-, $CHCl_3$, ClO_4^-, H_2S?

30. Give examples of ions or molecules that have the following structures:

a) $[AB_3]^{2-}$ planar
b) $[AB_3]$ planar
c) $[AB_3]$ pyramidal
d) $[AB_3]^-$ pyramidal
e) $[AB_4]^-$ tetrahedral
f) $[AB_4]^{2-}$ tetrahedral
g) $[AB_2]$ linear
h) $[AB_2]$ bent

31. What is the geometry around each carbon atom in acetic acid,

$$H_3C-\overset{\overset{\textstyle O}{\|}}{C}-OH$$
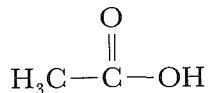
Which carbon–oxygen bond will be longer?

Suggested Reading

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