Recall that the carbon atom of carbon dioxide bears a partial positive charge because of the electron-attracting power of its attached oxygens. When hydroxide ion (the Lewis base) bonds to this positively polarized carbon, a pair of electrons in the carbon–oxygen double bond leaves carbon to become an unshared pair of oxygen.

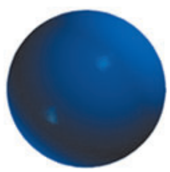
Lewis bases use an unshared pair to form a bond to some other atom and are also referred to as **nucleophiles** ("nucleus seekers"). Conversely, Lewis acids are **electrophiles** ("electron seekers"). We will use these terms hundreds of times throughout the remaining chapters.

Examine the table of contents. What chapters include terms related to *"nucleophile"* or *"electrophile"* in their title?

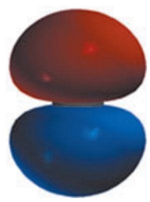
1.18 SUMMARY

This chapter sets the stage for all of the others by reminding us that the relationship between structure and properties is what chemistry is all about. It begins with a review of Lewis structures, moves to a discussion of the Arrhenius, Brønsted–Lowry, and Lewis pictures of acids and bases, and the effects of structure on acidity and basicity.

Section 1.1 A review of some fundamental knowledge about atoms and electrons leads to a discussion of **wave functions, orbitals,** and the **electron configurations** of atoms. Neutral atoms have as many electrons as the number of protons in the nucleus. These electrons occupy orbitals in order of increasing energy, with no more than two electrons in any one orbital. The most frequently encountered atomic orbitals in this text are *s* orbitals (spherically symmetrical) and *p* orbitals ("dumbbell"-shaped).



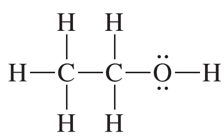
Boundary surface of a carbon 2*s* orbital



Boundary surface of a carbon 2*p* orbital

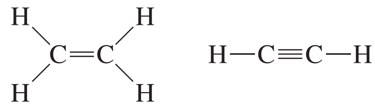
Section 1.2 An **ionic bond** is the force of electrostatic attraction between two oppositely charged ions. Atoms at the upper right of the periodic table, especially fluorine and oxygen, tend to gain electrons to form anions. Elements toward the left of the periodic table, especially metals such as sodium, tend to lose electrons to form cations. Ionic bonds in which carbon is the cation or anion are rare.

Section 1.3 The most common kind of bonding involving carbon is **covalent bonding.** A covalent bond is the sharing of a pair of electrons between two atoms. **Lewis structures** are written on the basis of the **octet rule,** which limits second-row elements to no more than eight electrons in their valence shells. In most of its compounds, carbon has four bonds.



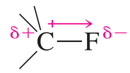
Each carbon has four bonds in ethyl alcohol;
oxygen and each carbon are surrounded by eight electrons.

Section 1.4 Many organic compounds have **double** or **triple bonds** to carbon. Four electrons are involved in a double bond; six in a triple bond.



Ethylene has a carbon–carbon double bond; acetylene has a carbon–carbon triple bond.

Section 1.5 When two atoms that differ in **electronegativity** are covalently bonded, the electrons in the bond are drawn toward the more electronegative element.

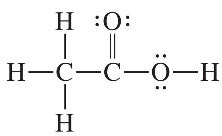


The electrons in a carbon–fluorine bond are drawn away from carbon, toward fluorine.

Section 1.6 Counting electrons and assessing charge distribution in molecules is essential to understanding how structure affects properties. A particular atom in a Lewis structure may be neutral, positively charged, or negatively charged. The **formal charge** of an atom in the Lewis structure of a molecule can be calculated by comparing its electron count with that of the neutral atom itself.

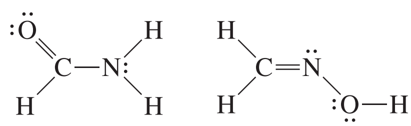
$$\begin{aligned}\text{Formal charge} = {} & (\text{number of electrons in neutral atom}) \\ & - (\text{number of electrons in unshared pairs}) \\ & - \tfrac{1}{2}(\text{number of electrons in covalent bonds})\end{aligned}$$

Section 1.7 Table 1.4 in this section sets forth the procedure to be followed in writing Lewis structures for organic molecules. It begins with experimentally determined information: the **molecular formula** and the **constitution** (order in which the atoms are connected).



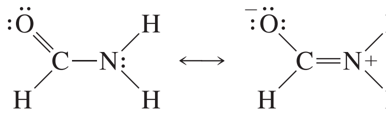
The Lewis structure of acetic acid

Section 1.8 Different compounds that have the same molecular formula are called **isomers.** If they are different because their atoms are connected in a different order, they are called **constitutional isomers.**



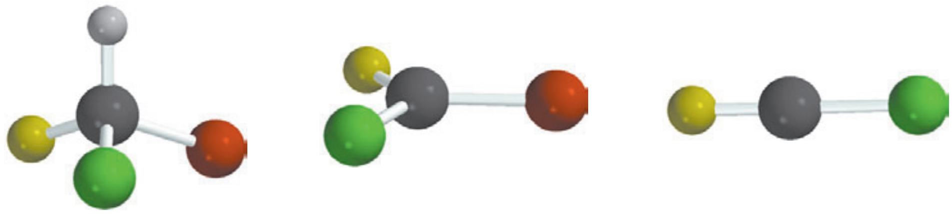
Formamide (*left*) and formaldoxime (*right*) are constitutional isomers; both have the same molecular formula (CH_3NO), but the atoms are connected in a different order.

Section 1.9 Many molecules can be represented by two or more Lewis structures that differ only in the placement of electrons. In such cases the electrons are delocalized, and the real electron distribution is a hybrid of the contributing Lewis structures, each of which is called a **resonance** form. The rules for resonance are summarized in Table 1.5.



Two Lewis structures (resonance forms) of formamide; the atoms are connected in the same order, but the arrangment of the electrons is different.

Section 1.10 The shapes of molecules can often be predicted on the basis of **valence shell electron-pair repulsions.** A tetrahedral arrangement gives the maximum separation of four electron pairs (*left*); a trigonal planar arrangement is best for three electron pairs (*center*), and a linear arrangement for two electron pairs (*right*).



Section 1.11 Knowing the shape of a molecule and the polarity of its various bonds allows the presence or absence of a **molecular dipole moment** and its direction to be predicted.

Both water and carbon dioxide have polar bonds, but water is a polar molecule and carbon dioxide is not.

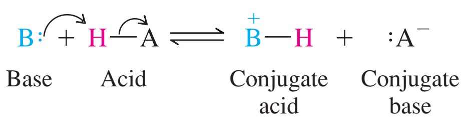
Section 1.12 According to the **Arrhenius** definitions, an acid ionizes in water to produce protons (H^+) and a base produces hydroxide ions (HO^-). The strength of an acid is given by its equilibrium constant K_a for ionization in aqueous solution:

$$K_a = \frac{[H^+][:A^-]}{[HA]}$$

or more conveniently by its pK_a:

$$pK_a = -\log_{10} K_a$$

Section 1.13 According to the **Brønsted–Lowry** definitions, an acid is a proton donor and a base is a proton acceptor.



The Brønsted–Lowry approach to acids and bases is more generally useful than the Arrhenius approach.

Section 1.14 **Basicity constants** are not necessary in the Brønsted–Lowry approach. Basicity is measured according to the pK_a of the conjugate acid. The weaker the conjugate acid, the stronger the base.

Section 1.15 The strength of an acid depends on the atom to which the proton is bonded. The two main factors are the strength of the H—X bond and the electronegativity of X. Bond strength is more important for atoms in the same group of the periodic table, electronegativity is more important for atoms in the same row. Electronegative atoms elsewhere in the molecule can increase the acidity by **inductive effects.**

Electron-delocalization in the conjugate base, usually expressed via resonance between Lewis structures, increases acidity.

Section 1.16 The position of equilibrium in an acid–base reaction lies to the side of the weaker acid.

$$\text{Stronger acid} + \text{Stronger base} \overset{K>1}{\rightleftharpoons} \text{Weaker acid} + \text{Weaker base}$$

This is a very useful relationship. You should practice writing equations according to the Brønsted–Lowry definitions of acids and bases and familiarize yourself with Table 1.7 which gives the pK_a's of various Brønsted acids.

Section 1.17 The Lewis definitions of acids and bases provide for a more general view of acid–base reactions than either the Arrhenius or Brønsted–Lowry picture. A **Lewis acid** is an electron-pair acceptor. A **Lewis base** is an electron-pair donor. The Lewis approach incorporates the Brønsted–Lowry approach as a subcategory in which the atom that accepts the electron pair in the Lewis acid is a proton.

PROBLEMS

1.33 Each of the following species will be encountered at some point in this text. They all have the same number of electrons binding the same number of atoms and the same arrangement of bonds; they are *isoelectronic*. Specify which atoms, if any, bear a formal charge in the Lewis structure given and the net charge for each species.

(a) $:N\equiv N:$
(b) $:C\equiv N:$
(c) $:C\equiv C:$
(d) $:N\equiv O:$
(e) $:C\equiv O:$

1.34 You will meet all the following isoelectronic species in this text. Repeat the previous problem for these three structures.

(a) $:\ddot{O}=C=\ddot{O}:$ (b) $:\ddot{N}=N=\ddot{N}:$ (c) $:\ddot{O}=N=\underset{..}{O}:$

1.35 All the following compounds are characterized by ionic bonding between a group I metal cation and a tetrahedral anion. Write an appropriate Lewis structure for each anion, remembering to specify formal charges where they exist.

(a) $NaBF_4$
(b) $LiAIH_4$
(c) K_2SO_4
(d) Na_3PO_4