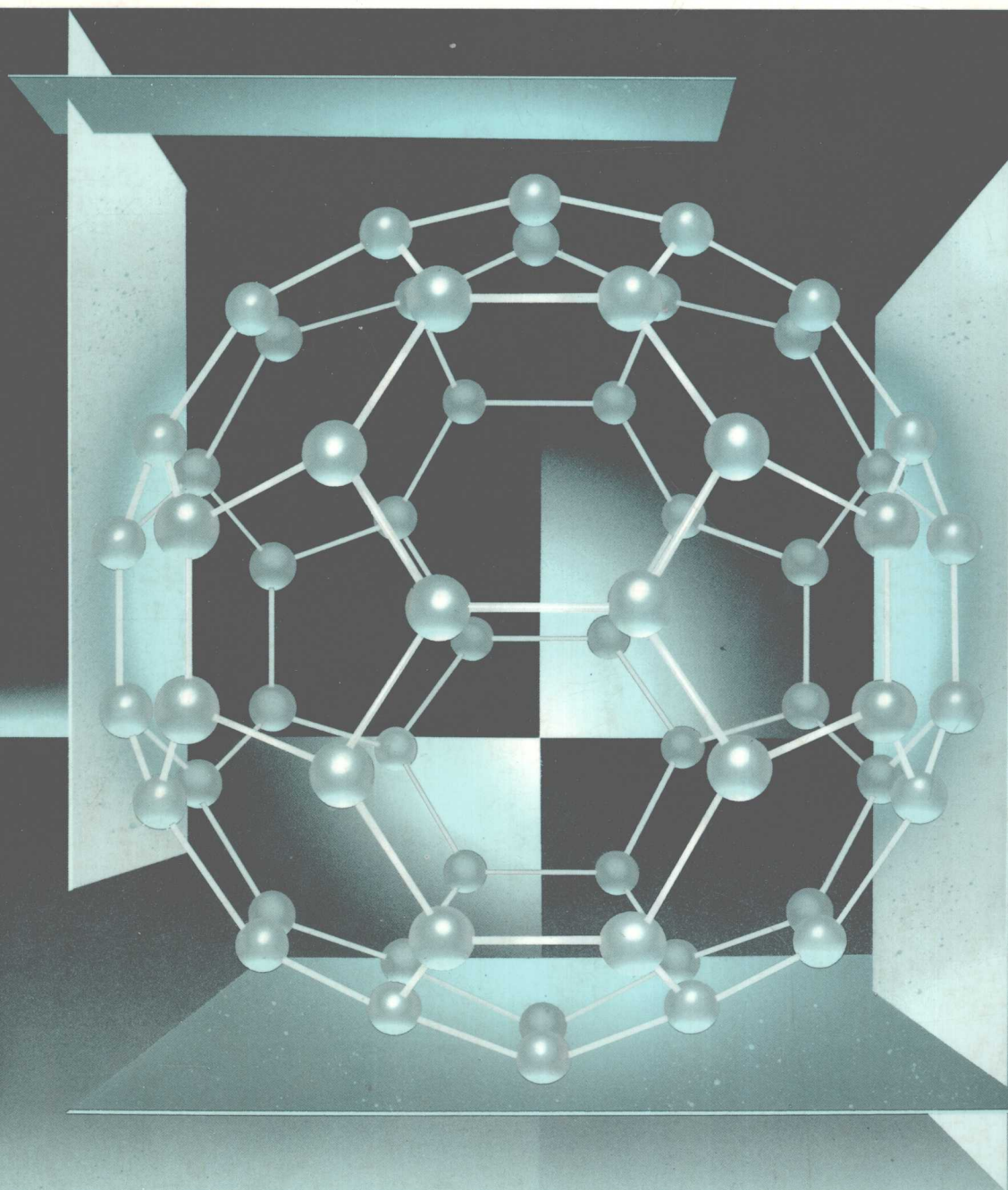


STUDY GUIDE AND SOLUTIONS MANUAL TO ACCOMPANY

ORGANIC CHEMISTRY

THIRD EDITION



FRANCIS A. CAREY
ROBERT C. ATKINS

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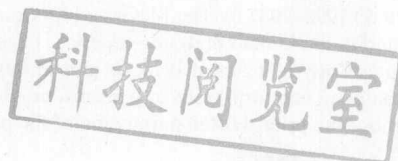
Third Edition

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STUDY GUIDE AND SOLUTIONS MANUAL TO ACCOMPANY ORGANIC CHEMISTRY

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PREFACE

It is our hope that in writing this Study Guide and Solutions Manual we will be able to assist the student in making the study of organic chemistry a more meaningful and worthwhile experience. To achieve maximum effectiveness, a study guide should be more than just an answer book. What we have written was designed with a larger goal in mind.

The Study Guide and Solutions Manual contains detailed solutions to all the problems in the text. Learning how to solve a problem is, in our view, more important than merely knowing the correct answer. To that end we have included solutions sufficiently detailed to provide the student with the steps leading to the solution of each problem.

In addition, each chapter includes summaries headed "Important Terms and Concepts" and/or "Important Reactions." These are intended to provide brief overviews of the major points and topics presented in each chapter of the text. At the conclusion of each chapter is a "Self-Test," designed to test the student's mastery of the material.

The completion of this guide was made possible with the help of numerous people who contributed their time and talent. Our thanks and appreciation also go to the many users of the second edition who have provided us with helpful suggestions, comments, and corrections. We also wish to acknowledge the assistance and understanding of Jennifer Speer, Karen J. Allanson, and David Damstra of McGraw-Hill. Last, we thank our wives and families for their understanding of the long hours invested in this work.

Francis A. Carey
Robert C. Atkins

TO THE STUDENT

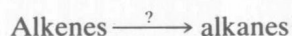
Before beginning the study of organic chemistry, a few words about “how to do it” are in order. You’ve probably heard that organic chemistry is difficult; there’s no denying that. It need not be overwhelming, though, when approached with the right frame of mind and with sustained effort.

First of all you should realize that organic chemistry tends to “build” on itself. That is, once you have learned a reaction or concept, you will find it being used again and again later on. In this way it is quite different from general chemistry, which tends to be much more compartmentalized. In organic chemistry you will continually find previously learned material cropping up and being used to explain and to help you understand new topics. Often, for example, you will see the preparation of one class of compounds using reactions of other classes of compounds studied earlier in the year.

How to keep track of everything? It might be possible to memorize every bit of information presented to you, but you would still lack a fundamental understanding of the subject. It is far better to *generalize* as much as possible.

You will find that the early chapters of the text will emphasize concepts of *reaction theory*. These will be used, as the various classes of organic molecules are presented, to describe *mechanisms* of organic reactions. A relatively few fundamental mechanisms suffice to describe almost every reaction you will encounter. Once learned and understood, these mechanisms provide a valuable means of categorizing the reactions of organic molecules.

There will be numerous facts to learn in the course of the year, however. For example, chemical reagents necessary to carry out specific reactions must be learned. You might find a study aid known as *flash cards* to be helpful. These take many forms, but one idea is to use 3×5 cards. As an example of how the cards might be used, consider the reduction of alkenes (compounds with carbon-carbon double bonds) to alkanes (compounds containing only carbon-carbon single bonds). The front of the card might look like this:



On the reverse of the card would be found the reagents necessary for this reaction:

H₂, Pt or Pd catalyst

The card can actually be studied in two ways. You may ask yourself: What reagents will convert alkenes into alkanes? Or, using the back of the card: What chemical reaction is carried out with hydrogen and a platinum or palladium catalyst? This is by no means the only way to use the cards—be creative! Just making up the cards will help you to study.

While study aids such as flash cards will prove helpful, there is only one way to truly master the subject matter in organic chemistry—*work out problems!* The more you work, the more you will learn. Almost certainly the grade you will receive will be a reflection of your ability to solve problems. Don't just think over the problems, either; write them out as if you were handing them in to be graded. Also, be careful of how you use the Study Guide. The solutions contained in this book have been intended to provide explanations to help you understand the problem. Be sure to write out *your* solution to the problem first, and only then look it up to see if what you have done is correct.

One concern frequently expressed by students is that they feel they understand the material but don't do as well as expected on tests. One way to overcome this is to "test" yourself. Each chapter in the Study Guide has a self-test at the end. Work the problems in these tests *without* looking up how to solve them in the text. You'll find it is much harder this way, but it is also a closer approximation to what will be expected of you while taking a test in class.

Success in organic chemistry depends on skills in analytical reasoning. Many of the problems you will be asked to solve require you to proceed through a series of logical steps to the correct answer. Most of the individual concepts of organic chemistry are fairly simple; stringing them together in a coherent fashion is where the challenge lies. By doing exercises conscientiously you should see a significant increase in your overall reasoning ability. Enhancement of their analytical powers is just one fringe benefit enjoyed by those students who attack the course rather than simply attend it.

Gaining a mastery of organic chemistry is hard work. It is hoped that the hints and suggestions outlined here will be helpful to you and that you will find your efforts rewarded with a knowledge and understanding of an important area of science.

Francis A. Carey
Robert C. Atkins

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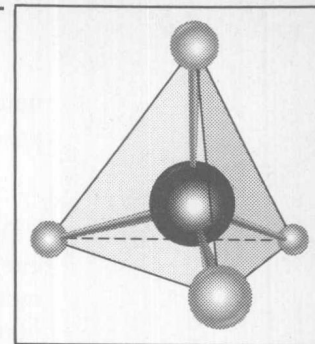
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CHAPTER 1

CHEMICAL BONDING



IMPORTANT TERMS AND CONCEPTS

Atoms, Electrons, and Orbitals (Sec. 1.1) The electronic organization (configuration) of all atoms may be specified by describing the *occupied orbitals* on the atom. An *orbital* is the region of space in which there is a high probability of finding an electron.

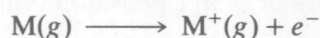
By using *quantum numbers*, each orbital may be completely described. The first shell contains only the 1s orbital; the second shell contains the 2s orbital and three 2p orbitals. The s orbitals are spherical; the p orbitals are orthogonal to each other, and are described as being “dumbbell-shaped.” They are designated $2p_x$, $2p_y$, and $2p_z$, respectively.

According to the *Pauli exclusion principle*, no two electrons may have the same set of quantum numbers. Since the first three quantum numbers describe the orbital and the fourth quantum number, known as *spin*, may take only one of two possible values ($+\frac{1}{2}$ or $-\frac{1}{2}$), a maximum of two electrons may exist in the same orbital.

Hund’s rule states that when electrons enter orbitals of equal energy (for example, the three 2p orbitals), they do so with parallel spin in separate orbitals.

The *valence electrons* of an atom are the outermost electrons, and are the ones most likely to be involved in chemical reactions. The maximum number of electrons in the *valence shell* of any second-row element is 8. Elements that possess eight electrons in their valence shell are said to have a complete *octet* of electrons.

Ionic Bonds (Sec. 1.2) The gain or loss of one or more electrons by a neutral atom results in formation of *ions*. Ions that are positively charged resulting from the loss of one or more electrons are called *cations*. The energy required to completely remove an electron from the highest-energy occupied orbital of an atom is called the *ionization energy*. Ionization is an *endothermic* process, and the ionization energy describes the enthalpy change for the reaction



The general trend is for ionization energy to increase going from left to right across the periodic table.

The negative ions formed when an atom gains one or more electrons are called *anions*. The *exothermic* process, that is, the energy liberated when an electron is added to a

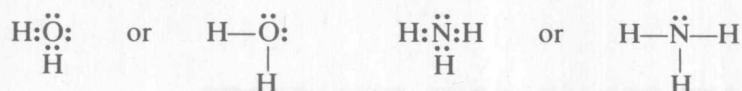
neutral atom is called the *electron affinity*. Electron affinity is the energy change for the process



Ionic bonds form between a metal and a nonmetal, that is, a species of low ionization energy and one of high electron affinity. The transfer of one or more electrons from the metal to the nonmetal gives rise to ions of opposite charge. An *ionic*, or *electrostatic*, *bond* results from the coulombic attraction of the oppositely charged ions for each other.

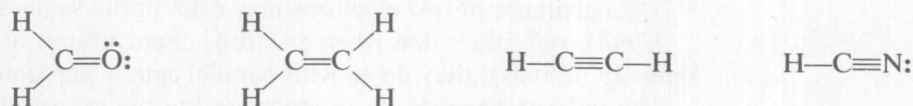
Covalent Bonds (Sec. 1.3) When nonmetals bond together, the forces which hold the atoms together result from *shared electron pair bonds*, or *covalent bonds*. A discrete unit or collection of atoms held together by covalent bonds is known as a *molecule*.

The most popular method for representing the structure of a molecule is with a *Lewis structure*, or “electron dot” formula. Each valence electron in an atom is represented by a dot, and the dots are paired to form covalent bonds in the molecule. The number of valence electrons supplied by a main group element is equal to the group number. Thus carbon has four valence electrons and oxygen has six. Not all the valence electrons on every element are *shared*, that is, part of a covalent bond. They may also exist as *unshared pairs* in an atom of the molecule. Note in the following examples that each pair of dots may be replaced by a line, representing a *single bond* between two atoms.



For elements in the second row of the periodic table, there must be eight electrons in the outer shell of the atom in a stable compound; that is, the *octet* of the atom must be satisfied.

Multiple Bonding (Sec. 1.4) More than one pair of electrons may be shared between two atoms in a molecule. A *double bond* results when two electron pairs (four electrons) are shared; a *triple bond* results from sharing three electron pairs (six electrons). Remember that the octet of a second-row element must not be exceeded when writing Lewis structures. This can become especially important when writing formulas which involve multiple bonds. Some examples include:



Polar Covalent Bonds and Electronegativity (Sec. 1.5) *Electronegativity* is a measure of the tendency of an atom to draw electron density away from another atom to which it is bonded and toward itself. When two atoms of different electronegativity are bonded together, the more electronegative atom will attract electrons, while the less electronegative (or more *electropositive*) atom will donate electrons. The resulting unequal distribution of electron charge, or *dipole*, gives rise to a covalent bond that is *polarized*; such a bond is referred to as a *polar covalent bond*.

Formal Charge (Sec. 1.6) The charge value assigned to an atom in a covalent molecule is the *formal charge* present on that atom. It may be computed as follows:

$$\text{Formal charge} = (\text{group number}) - (\text{electron count})$$

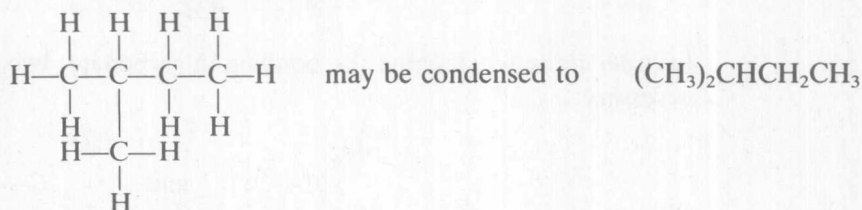
where electron count is the sum of the number of bonds (half the number of shared electrons) and the number of unshared electrons.

Certain commonly encountered examples are worth noting:

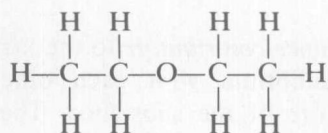
1. Tetravalent N is positive, e.g., NH_4^+ , $\text{N}^+(\text{CH}_3)_4$
2. Trivalent O is positive, e.g., $\text{H}-\overset{+}{\underset{\text{H}}{\text{O}}}-\text{H}$, $\text{CH}_3-\overset{+}{\underset{\text{CH}_3}{\text{O}}}-\text{CH}_3$
3. Univalent O is negative, e.g., $\text{H}-\ddot{\text{O}}:^-$, $\text{CH}_3-\ddot{\text{O}}:^-$

Note that in all these cases the octet of each atom other than H has been satisfied.

Structural Formulas (Sec. 1.7) The Lewis notation is the most widely used method for representing the structural formulas of organic molecules. *Condensed structural formulas* may be used. For example:



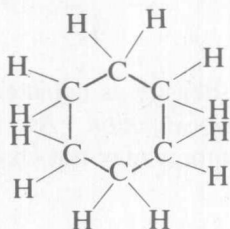
may be condensed to $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$



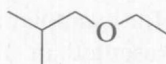
may be condensed to



Bond-line, or “stick,” formulas are often used to represent complex structures in which the carbons and hydrogens are omitted:

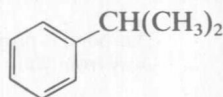


may be written as



is the same as $(\text{CH}_3)_2\text{CHCH}_2\text{OCH}_2\text{CH}_3$

Condensed and bond-line formulas may be combined, as in

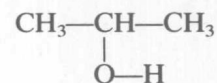


Some simple rules are worth remembering:

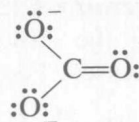
- | | |
|-----------|--|
| Hydrogen: | Forms only one bond |
| Carbon: | Normally has four bonds in a neutral molecule |
| Oxygen: | Has two bonds in a neutral molecule and two unshared electron pairs |
| Nitrogen: | Has three bonds in a neutral molecule and one unshared electron pair |

Constitutional Isomers (Sec. 1.8) Different compounds that have the same molecular formula are *isomers* of each other. *Constitutional isomers*, also known as *structural isomers*, differ in the order of their atomic connections. For example, the following

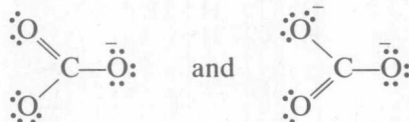
structures each have the formula C_3H_8O , yet they represent different substances:



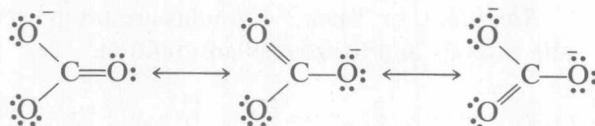
Resonance (Sec. 1.9) For certain chemical substances, the bonding picture depicted by a single Lewis structure does not fully describe the electronic structure of the substance. For example, the three C—O bonds in the carbonate ion, CO_3^{2-} , are equivalent. Yet the following Lewis structure suggests two oxygen atoms connected by single bonds and a third oxygen atom attached by a double bond:



In order to better describe the bonding in carbonate, two additional Lewis structures are necessary:

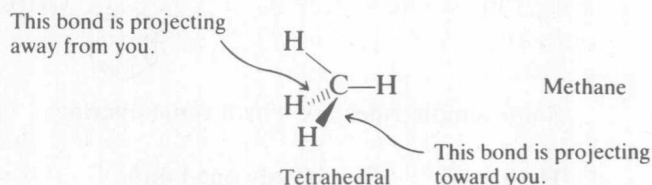


The three structures shown are *resonance contributors* to the “true” bonding picture of carbonate ion. They are *not* in equilibrium with each other, but all contribute simultaneously to the electronic structure of the substance. The true bonding picture could be thought of as a *resonance hybrid* to which each of the individual *resonance structures* contributes. A double-headed arrow is used to indicate resonance, as follows:



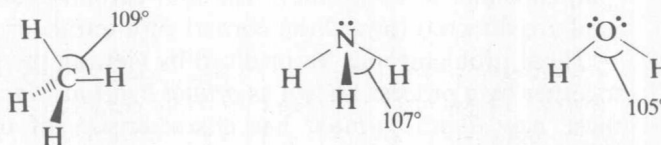
The smearing of electron density as depicted by the preceding resonance structures is an example of *electron delocalization*. An important rule to remember in writing resonance structures is that atoms may not change position—only electrons may differ in their location.

Molecular Shapes (Sec. 1.10) The most important geometric shape in organic chemistry is the *tetrahedron*. Methane, for example, is described as a *tetrahedral molecule*. The three-dimensionality may be represented in a structural drawing by using a *solid wedge* to depict a bond projecting from the paper toward you, a *dashed wedge* to depict one receding from the paper, and a simple line to depict a bond in the plane of the paper.



The *valence-shell electron pair repulsion (VSEPR) theory* provides a method of explaining molecular shapes. The fundamental idea is that electron pairs, both bonded and nonbonded, will orient themselves as far away from each other as possible around the central atom in a molecule. The geometry of the electron pairs on an atom having two pairs is linear. The geometry of the electron pairs on an atom having three is trigonal planar, and four, tetrahedral. The electron pairs in multiple bonds are treated together.

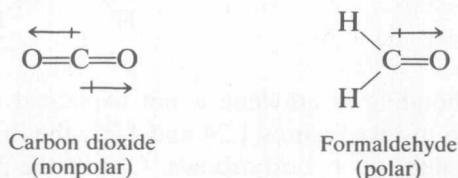
The *shape* of a molecule is determined by the positions of its atoms. Thus ammonia is pyramidal and water bent, although the electron pairs in both molecules exist in a tetrahedral geometry.



In addition to the tetrahedral shape that was shown for methane, the two shapes most commonly encountered in organic chemistry are *linear* and *trigonal planar*:



Molecular Dipole Moments (Sec. 1.11) Only for a diatomic molecule (such as HF) can it be stated with certainty that a polar bond will give rise to a polar molecule. *Molecular polarity* is shape-dependent; that is, the dipoles of the individual polar bonds may cancel the effect of each other, depending on the shape of the molecule. For example, CO₂, which is linear, is a nonpolar molecule, although each carbon-oxygen bond is polar. On the other hand, formaldehyde, H₂CO, is polar; there is no cancellation of the dipole of the CO bond.



Molecular Orbitals (Sec. 1.12) In this chapter the concept of sharing electrons between atoms to form covalent bonds was presented. A more detailed description of these bonds is provided by viewing the orbitals on individual atoms as overlapping and interacting with each other. These regions of interaction are known as *molecular orbitals* (MOs).

Constructive interference, or *in-phase* overlap, of two individual atomic orbitals gives rise to what is called a *bonding molecular orbital*. An electron in a bonding MO is of lower energy than one in the atomic orbitals from which the MO is formed. The result is an *attractive force* between the two atoms.

The subtractive interaction between two atomic orbitals gives rise to an *antibonding molecular orbital*. An electron in an antibonding MO is of higher energy than one in the atomic orbitals from which the antibonding MO arises, resulting in a *repulsion* of the two atoms. When the number of electrons in bonding MOs exceeds the number in antibonding MOs, the net force between the two atoms is attractive, resulting in formation of a stable molecule.

The bonding MOs formed by the overlap of atomic orbitals have the region of highest electron density concentrated between the two nuclei. The electron distribution is symmetric around the internuclear axis. A molecular orbital having this characteristic is known as a σ (*sigma*) orbital. Two nuclei bonded by electrons in a σ orbital are said to be connected by a σ bond.

Bonding in Methane (Sec. 1.13) While the bonding of an organic compound such as methane may be viewed as a collection of molecular orbitals as described in the previous section, most organic chemists prefer to use a bonding description based on the Lewis model, in which covalent bonds are viewed as localized between pairs of atoms.

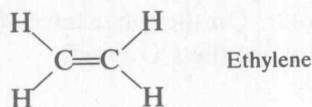
The ground-state electronic configuration of carbon ($1s^2, 2s^2, 2p^2$) is poorly suited for covalent bonding and for explaining the observed facts regarding carbon compounds. This configuration provides only two orbital vacancies, and these are in p orbitals situated perpendicular to each other. The four carbon-hydrogen bonds of methane are equivalent and are directed toward the corners of a tetrahedron (a *tetrahedral* arrangement).

These problems may be resolved by viewing the ground-state atomic orbitals as mixing together by a process known as *orbital hybridization* to form a new set of orbitals. Each of these new *hybrid orbitals* has characteristics of the ground-state atomic orbitals from which they are derived.

In the case of methane, mixing the $2s$ orbital of the carbon atom with the three $2p$ orbitals yields four new sp^3 hybrid orbitals. Each C—H σ bond is formed from the overlap of an sp^3 hybrid orbital with a hydrogen $1s$ orbital, as shown in text Figure 1.20. These orbitals are arranged in a tetrahedral fashion around the carbon atom.

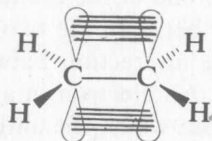
Bonding in Ethane (Sec. 1.14) Bonding in ethane, C_2H_6 , may be explained in a manner similar to that used for methane. The hybrid orbitals from each of two carbons may overlap to form an sp^3-sp^3 σ bond. The carbon-carbon single bond framework of larger organic molecules is constructed of orbital overlaps similar to that in ethane.

sp^2 Hybridization: Bonding in Ethylene. (Sec. 1.15) Ethylene has the structure

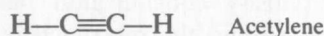


The bonding in ethylene is not explained using the sp^3 orbital hybridization model. As shown in text Figures 1.24 and 1.25, the $2s$ orbital and two $2p$ orbitals mix to yield three equivalent sp^2 hybrid orbitals. One of the $2p$ orbitals remains unhybridized.

The carbon-carbon double bond of an alkene such as ethylene consists of a σ (sigma) component and a π (pi) component. The carbons of the double bond are sp^2 hybridized. The three hybrid orbitals are utilized to form sigma bonds to three atoms, all of which lie in the same plane as the carbon atom. The remaining p orbitals of the double-bonded carbons are parallel to each other, giving rise to a π orbital. The result of this arrangement is that the four atoms attached to the double bond are in one plane. Ethylene is a planar molecule:



sp Hybridization: Bonding in Acetylene (Sec. 1.16) Acetylene has a carbon-carbon triple bond.



The carbons of acetylene are sp hybridized. The $2s$ orbital and one $2p$ orbital of carbon mix to form two equivalent sp hybrid orbitals, as shown in text Figure 1.28. Two p orbitals remain unhybridized in the sp orbital hybridization model. A carbon-carbon triple bond has a σ component resulting from overlap of an sp hybrid orbital from each carbon, and two π components resulting from overlap of the unhybridized p orbitals on each carbon. The bonding of acetylene is shown in text Figure 1.29.

SOLUTIONS TO TEXT PROBLEMS

1.1 Carbon is the element of atomic number 6, and so has a total of six electrons. Two of these electrons are in the 1s level. The four electrons in the 2s and 2p levels (the valence shell) are the valence electrons. Carbon has four valence electrons.

1.2 Electron configurations of elements are derived by applying the following principles:

- The number of electrons in a neutral atom is equal to its atomic number Z .
- The maximum number of electrons in any orbital is 2.
- Electrons are added to orbitals in order of increasing energy, filling the 1s orbital before any electrons occupy the 2s level. The 2s orbital is filled before any of the 2p orbitals, and the 3s orbital is filled before any of the 3p orbitals.
- All the 2p orbitals are of equal energy, and each is singly occupied before any is doubly occupied. The same holds for the 3p orbitals.

With this as background, the electron configuration of the third-row elements is derived as follows [$2p^6 = 2p_x^2 2p_y^2 2p_z^2$]:

Na ($Z = 11$)	$1s^2 2s^2 2p^6 3s^1$
Mg ($Z = 12$)	$1s^2 2s^2 2p^6 3s^2$
Al ($Z = 13$)	$1s^2 2s^2 2p^6 3s^2 3p_x^1$
Si ($Z = 14$)	$1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1$
P ($Z = 15$)	$1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$
S ($Z = 16$)	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$
Cl ($Z = 17$)	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$
Ar ($Z = 18$)	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^2$

1.3 The electron configurations of the designated ions are:

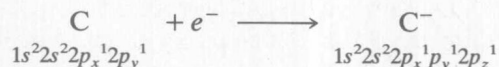
Ion	Z	Number of electrons in ion	Electron configuration of ion
(b) He^+	2	1	$1s^1$
(c) H^-	1	2	$1s^2$
(d) O^-	8	9	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$
(e) F^-	9	10	$1s^2 2s^2 2p^6$
(f) Ca^{2+}	20	18	$1s^2 2s^2 2p^6 3s^2 3p^6$

Those with a noble gas configuration are H^- , F^- , and Ca^{2+} .

1.4 A positively charged ion is formed when an electron is removed from a neutral atom. The equation representing the ionization of carbon and the electron configurations of the neutral atom and the ion are:



A negatively charged carbon is formed when an electron is added to a carbon atom. The additional electron enters the $2p_z$ orbital.



Neither C^+ nor C^- has a noble gas electron configuration.

- 1.5 Hydrogen has one valence electron and fluorine has seven. The covalent bond in hydrogen fluoride arises by sharing the single electron of hydrogen with the unpaired electron of fluorine.

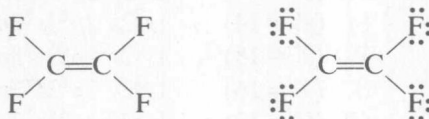
Combine $\text{H}\cdot$ and $\cdot\ddot{\text{F}}:$ to give the Lewis structure for hydrogen fluoride $\text{H}:\ddot{\text{F}}:$

- 1.6 In order to satisfy the Lewis rules, C_2H_6 must have a carbon-carbon bond.

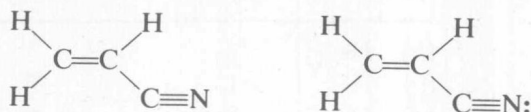
Combine two $\cdot\dot{\text{C}}\cdot$ and six $\text{H}\cdot$ to write the Lewis structure of ethane $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}:\ddot{\text{C}}:\ddot{\text{C}}:\text{H} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$

There are a total of 14 valence electrons distributed as shown. Each carbon is surrounded by eight electrons.

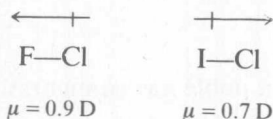
- 1.7 (b) Each carbon contributes four valence electrons and each fluorine contributes seven. Thus, C_2F_4 has 36 valence electrons to be accounted for. The octet rule is satisfied for carbon only if the two carbons are attached by a double bond and there are two fluorines on each carbon. The pattern of connections shown (at left) accounts for 12 electrons. The remaining 24 electrons are divided equally (six each) among the four fluorines. The complete Lewis structure is shown at right.



- (c) Since the problem states that the atoms in $\text{C}_3\text{H}_3\text{N}$ are connected in the order CCCN and all hydrogens are bonded to carbon, the order of attachments can only be as shown (below left) in order to have four bonds to each carbon. Three carbons contribute 12 valence electrons, three hydrogens contribute 3, and nitrogen contributes 5, for a total of 20. The nine bonds indicated in the partial structure account for 18 electrons. Since the octet rule is satisfied for carbon, add the remaining two electrons as an unshared pair on nitrogen (below right).



- 1.8 The direction of a bond dipole is governed by the electronegativity of the atoms involved. Among the halogens the order of electronegativity is $\text{F} > \text{Cl} > \text{Br} > \text{I}$. Therefore fluorine attracts electrons away from chlorine in FCl and chlorine attracts electrons away from iodine in ICl .



Chlorine is the positive end of the dipole in FCl and the negative end in ICl .

- 1.9 (b) Neither phosphorus nor bromine has a formal charge in PBr_3 .

	Valence electrons in neutral atom	Electron count	Formal charge
Phosphorus:	5	$\frac{1}{2}(6) + 2 = 5$	0
Bromine:	7	$\frac{1}{2}(2) + 6 = 7$	0

$$\begin{array}{c} :\ddot{\text{Br}}: \\ | \\ :\ddot{\text{Br}}-\ddot{\text{P}}-\ddot{\text{Br}}: \end{array}$$