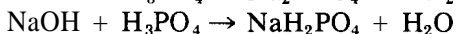are actually replaced. For example, with H_3PO_4 and NaOH, three different reactions are possible:

$$3 \text{ NaOH} + H_3PO_4 \rightarrow Na_3PO_4 \; + 3 \; H_2O$$
$$2 \text{ NaOH} + H_3PO_4 \rightarrow Na_2HPO_4 + 2 \; H_2O$$
$$\text{NaOH} + H_3PO_4 \rightarrow NaH_2PO_4 + H_2O$$
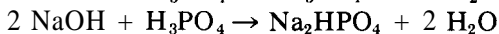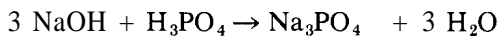
Each of these reactions is possible, and each equation is balanced. Obviously, we need different names for the three different kinds of sodium phosphate salts. Of the several ways to accomplish this, the most highly recommended and unequivocal is to include as part of the name the number of H^+ ions that have *not* been replaced in salt formation. In the example above we would have

Na_3PO_4	sodium phosphate
Na_2HPO_4	sodium monohydrogen phosphate
NaH_2PO_4	sodium dihydrogen phosphate

If the acid contains only two H^+, then only two different salts are possible; they are most acceptably named by the method just described. However, another traditional method that will probably continue in use for many years is to use the prefix *bi-* for the salt of the acid with just half of the hydrogen atoms replaced, as illustrated for the sodium bisulfate that is produced by the reaction

$$\text{NaOH} + H_2SO_4 \rightarrow NaHSO_4 + H_2O$$
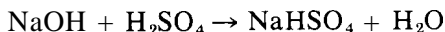
BINARY COMPOUNDS NOT DERIVED FROM ACIDS

The atoms listed in this section may combine with many metals to form binary compounds (compounds made up of two elements) that are saltlike in nature, but are not derived from acids. For purposes of naming, it is convenient to assign negative charges to these atoms. Except in the names of the oxides, the suffixes *-ous* and *-ic* are not used with metals forming compounds in this group. The names of all these compounds end in *-ide*. Only the metal oxides of this group are common.

$H\sim$	LiH	lithium hydride
O^{2-}	FeO	ferrous oxide (Fe_2O_3 ferric oxide)
N^{3-}	Sn_3N_4	tin nitride
P^{3-}	Ba_3P_2	barium phosphide
As^{3-}	Na_3As	sodium arsenide
$C^{4"}$	Al_4C_3	aluminum carbide
Si^{4-}	Mg_2Si	magnesium silicide

BINARY COMPOUNDS COMPOSED OF TWO NONMETALS

Allowing for a bit of quibbling one way or the other, there are only 20 nonmetal-lic elements. Of these 20 elements, six are so unreactive that until recently they were thought never to combine with other elements. If, for practical consid-erations, we eliminate these six elements and hydrogen (which we've already dealt with in various forms above), this leaves just 13 nonmetallic elements (B, C, N, O, F, Si, P, S, Cl, Se, Br, Te, I) that can combine with each other. These nonmetallic binary compounds are designated by the names of the two elements followed by the ending *-ide*. Before the name of the second element there is a prefix to indicate how many atoms of it are in the molecule. Unfortunately, this is not usually done for the first element. The following are examples of some common compounds of this type:

CO	carbon monoxide	SO_3	sulfur trioxide
CO_2	carbon dioxide	CCl_4	carbon tetrachloride
Cl_2O	chlorine monoxide	PF_5	phosphorus pentafluoride
ClO_2	chlorine dioxide	SF_6	sulfur hexafluoride
Cl_2O_7	chlorine heptoxide	N_2O_4	nitrogen tetroxide

PROBLEMS A

Name the following compounds (proper spelling is required).

1. $Ca(OH)_2$
2. Ag_3PO_4
3. $AgSCN$
4. $MgC_8H_4O_4$
5. $(NH_4)_2SO_4$
6. ZnS
7. $Cd(CN)_2$
8. $Ba(IO_3)_2$
9. $CuSO_3$
10. CuI
11. $Fe(NO_3)_3$

12. FeC_2O_4
13. Hg_2Cl_2
14. $MnCO_3$
15. $Mn(OH)_3$
16. $Ni(ClO)_2$
17. $CrAsO_4$
18. $SnBr_4$
19. CrF_2
20. $Pb(MnO_4)_2$
21. Na_4SiO_4
22. Bi_2O_5

23. $Al(ClO_4)_3$
24. $Hg(C_2H_3O_2)_2$
25. $CsClO_3$
26. $Sr(IO)_2$
27. Rb_3AsO_3
28. Be_3N_2
29. $Ca(HCO_3)_2$
30. $Sb(NO_3)_3$
31. PCl_3
32. $Bi(OCN)_3$
33. $Al_2(S_2O_3)_3$

Without consulting a text, give the formulas for the following compounds.

34. aluminum bromate

35. mercurous phosphate

36. bismuth(III) oxide

37. strontium bicarbonate

38. aurous iodide

39. chromium(III) iodate

40. manganous hydroxide

41. lithium arsenide

42. arsenic(III) sulfate

43. stannic chloride

44. nickelous periodate

45. chlorine heptoxide

46. silver oxalate

47. chromium(II) borate

48. antimonous sulfide

49. aluminum acetate

50. calcium oxalate

51. sodium chlorite

52. tin(II) azide

53. mercury(II) cyanide

54. ammonium sulfite

55. cobalt(II) permanganate

56. plumbous carbonate

57. zinc phosphide

58. cupric silicate

59. barium hypoiodite

60. Given that selenium (Se) is similar in properties to sulfur (S), and that francium (Fr) is similar to sodium (Na), write the formulas for the following compounds.
    (a) zinc selenide
    (b) francium phosphate
    (c) cobalt(II) selenite
    (d) selenium dioxide
    (e) francium selenate
    (f) selenium hexafluoride
    (g) francium hydride

61. Write balanced chemical equations for the following reactions.
    (a) beryllium hydroxide + thiocyanic acid
    (b) periodic acid + antimonic hydroxide
    (c) mercurous hydroxide + acetic acid
    (d) arsenious acid + chromous hydroxide
    (e) eerie hydroxide + boric acid
    (f) hydrazoic acid + ferrous hydroxide
    (g) lithium hydroxide + hypobromous acid

PROBLEMS B

Name the following compounds (proper spelling is required).

62. Ag_3PO_4

63. $CoCl_3$

64. $Be(NO_2)_2$

65. $Fe(MnO_4)_3$

66. NH_4NO_2

67. Al_2S_3

68. $Zn(IO_4)_2$

69. $Pb_3(BO_3)_2$

70. $As(CN)_3$

71. $Ni_3(AsO_3)_2$

72. I_2O_7

73. Ba_2Si

74. $AuHSO_3$

75. $Ba(BrO)_2$

76. CaH_2

77. N_2O_5

78. Sb_2S_3

79. MgC_2O_4

80. ICl   83. Ca_3P_2 86. $CrBr_2$

81. Rb_4SiO_4 84. MnO_2 87. $BaCrO_4$

82. SF_6 85. $Cu(C_2H_3O_2)_2$ 88. $Cd(SCN)_2$

Without consulting a text, give the formulas for the following compounds.

89. potassium oxalate   102. iron(III) bromate

90. cupric arsenate   103. arsenic(V) perchlorate

91. bismuthous carbonate   104. magnesium monohydrogen borate

92. manganese(III) oxide   105. boron trifluoride

93. mercurous sulfate   106. strontium silicate

94. nitrogen tri-iodide   107. beryllium hydroxide

95. cobalt(II) borate   108. stannic oxide

96. cesium hypoiodite   109. gold(III) fluoride

97. boron nitride   110. ferric chromate

98. cadmium dichromate   111. iodine pentoxide

99. ammonium acetate   112. lithium thiocyanate

100. zinc cyanide   113. silver thiosulfate

101. tin(II) phosphate   114. antimonic permanganate

115. Given that astatine (At) is similar in properties to chlorine (Cl), and that
     gallium (Ga) is similar to aluminum (Al), write the formulas for the following
     compounds.
     (a) potassium astatate   (d) hydrastatic acid
     (b) barium astatide   (e) gallium thiocyanate
     (c) gallium sulfate   (f) gallium hypoastatite

116. Write balanced chemical equations for the following reactions.
     (a) hydrosulfuric acid + zinc hydroxide
     (b) ferric hydroxide + permanganic acid
     (c) oxalic acid + plumbous hydroxide
     (d) aluminum hydroxide + carbonic acid
     (e) bromic acid + cupric hydroxide
     (f) auric hydroxide + dichromic acid
     (g) sulfamic acid + strontium hydroxide

Sizes and Shapes of Molecules

A knowledge of molecular shapes and sizes is important to an understanding of chemical reactions. The shape of a molecule (and the bond types it possesses) has important implications for the manner in which it enters into chemical reactions. The shape and size of molecules also influence their packing in the crystalline state.

When atoms combine to produce molecules, they often do so in accord with the *octet rule*. Your text undoubtedly contains a fairly detailed discussion of the octet rule. In essence, it may be described as the tendency for an atom to lose, gain, or share electrons in order to achieve an s^2p^6 configuration in the outermost shell. The simplest atoms (H, Li, Be, and so on) tend to achieve a $1s^2$ configuration, according to what might be called the duet rule.

In Chapter 8, we emphasize the loss and gain of electrons, leading to the formation of electrically charged ions, such as Na^+ and Cl~. When electrons are *shared,* a molecule is formed, and the atoms are connected by a *covalent bond*. In this chapter we emphasize the approximate shapes, interatomic distances, and bond energies of molecules and molecular ions that are held together by covalent bonds.

COVALENT BOND ENERGIES

The strengths of the bonds that hold the atoms together in a molecule can be determined in a variety of ways: for example, by direct calorimetric measure-

ment, by dissociation equilibrium measurements, by absorption spectrum measurements, or by mass spectrometry.

We define *bond energy* as the energy change (ΔH) for the chemical process in which one mole of a given bond is broken, when both the reactants and the products are in the hypothetical ideal-gas state of 1 atm and 25°C. For a diatomic molecule, the bond energy is identical to the energy required to dissociate *the gaseous* molecule into its respective *gaseous* atoms. For the dissociation of Cl_2 gas this corresponds to the reaction

$$Cl_{2(g)} \rightleftarrows 2\ Cl_{(g)}$$
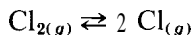
for which the Cl–Cl bond energy is 58.0 kcal. We say that $\Delta H_{Cl-Cl} = 58.0$ kcal.

For a polyatomic molecule of the type AB_n, which possesses n A-B bonds, our definition of bond energy implies that each bond is the same, and that it corresponds to $\frac{1}{n}$ of the total energy required to dissociate the gaseous AB_n molecule into A + n B gaseous atoms. This is a useful definition except when studying the detailed steps of a chemical reaction. For example, the total binding energy in a CH_4 molecule is 397 kcal/mole and, by our definition of bond energy, the C-H bond energy = 397/4 = 99.3 kcal. Extensive, complicated, and detailed studies have shown, however, that each H atom is not equally easily removed from carbon in this molecule; it is estimated that the individual bond energies are 104 kcal for CH_3–H, 106 kcal for CH_2–H, 106 kcal for CH-H, and 81 kcal for C-H, with a total of 397 kcal. In most cases, such detailed information is not available; neither is it normally needed except in discussion of the individual steps involved in chemical reactions.

The atoms of some elements (such as C, N, and O) are able to share more than one pair of electrons between them, to form single, double, or triple bonds—depending on whether one, two, or three pairs of electrons are shared. In general, the bonding energy increases and the internuclear distance decreases as the number of bonds between a pair of atoms increases.

By studying the experimentally determined bond energies of hundreds of compounds, researchers have uncovered some useful generalizations, such as the following.

1. A single bond between two *identical* atoms has about the same strength (ΔH_{A-A}) in any molecule in which it occurs. Because the atoms are identical, the bond is purely covalent.

2. A strictly covalent bond between two *different* atoms (A and B) is about the same strength as the average of the bond strengths that would be observed if each atom were bonded to another like itself. That is,

$$\Delta H_{A-B} = \tfrac{1}{2}[\Delta H_{A-A} + \Delta H_{B-B}] \qquad (9\text{-}1)$$

TABLE 9-1
Covalent Bond Radii and Energies, and Electronegativities

Element	Radius (A)	Bond energy ΔH_{A-A} (kcal/mole)	Electronegativity (e) of element
H—H	0.30	104.2	2.1
B—B	0.88	62.7	2.0
C—C	0.772	83.1	2.5
C=C	0.667	147	
C≡C	0.603	**194**	
Si—Si	1.17	42.2	1.8
Si=Si	1.07		
Ge—Ge	1.22	37.6	1.8
Sn—Sn	1.40	34.2	1.8
N—N	0.70	38.4	3.0
N=N	0.60	100	
N≡N	0.55	226.2	
P—P	1.10	51.3	2.1
P=P	1.00	117	
As—As	1.21	32.1	2.0
Sb—Sb	1.41	30.2	1.9
Bi—Bi	1.52	25	1.9
O—O	0.66	33.2	3.5
O=O	0.55		
S—S	1.04	50.9	2.5
S=S	0.94		
Se—Se	1.17	44.0	2.4
Se=Se	1.07		
Te—Te	1.37	33.0	2.1
F—F	0.64	36.6	4.0
Cl—Cl	0.99	58.0	3.0
Br—Br	1.14	46.1	2.8
I—I	1.33	36.1	2.5

These two generalizations mean that to each element there can be assigned a "covalent bond energy" (ΔH_{A-A}), which can be used to estimate the strength of a bond between any two atoms that form a strictly covalent bond. Table 9-1 lists a few of these covalent bond energy assignments. Carbon and iodine form a purely covalent bond so, by our second generalization, its approximate bond energy would be

$$\Delta H_{C-I} = \tfrac{1}{2}[\Delta H_{C-C} + \Delta H_{I-I}]$$
$$= \tfrac{1}{2}[83.1 + 36.1] = 59.6 \text{ kcal}$$

ELECTRONEGATIVITY

Unfortunately, as in so many sharing processes, the pair of electrons in a covalent bond often is not shared equally by the two atoms. The atom with the greater electron affinity will hold the pair closer to its nucleus, with the result that its end of the bond (and its end of the molecule) will be somewhat more negatively charged than the other end. When this happens, we say that the bond is partially ionic and, because opposite charges attract each other, this partially ionic bond will be stronger than it would have been with equal sharing.

Linus Pauling made a careful study of a tremendous number of partially ionic covalent bonds and came to the conclusion that, as a measure of its electron affinity, each element could be assigned an *electronegativity value* (e) that would make it possible to estimate the energy of these bonds. To calculate the approximate bond energy ($\triangle H_{A-B}$) between the atoms A and B, his formula requires knowledge of the A-A bond energy ($\triangle H_{A-A}$), the B-B bond energy ($\triangle H_{B-B}$), and the electronegativities of A and B (ϵ_A and ϵ_B). Table 9-1 lists some electronegativity values along with covalent bond energies. Pauling's finding, which we might call generalization #3, is the following

3 The energy of a partially ionic covalent bond between two atoms (A and B) is equal to the energy expected from a strictly covalent bond between the two atoms *plus* an amount of energy related to the square of the difference in their electronegativities. In equation form, Pauling's formula (with units in kcal) is

$$\triangle H_{A\ B} = \tfrac{1}{2}[\triangle H_{A-A} + \triangle H_{B-B}] + 23\ 06(\epsilon_A - \epsilon_B)^2 \qquad (9\text{-}2)$$

You can see that, if A and B have equal electronegativities, then $\triangle H_{A\ B}$ is simply the average of the two covalent bond energies. The greater the difference in electronegativities, the greater the percentage of ionic character and the stronger the bond. If the difference in electronegativity becomes too great, the bond is essentially ionic, and the atoms are held together by electrostatic forces as in an ionic crystal, the concept of a molecule disappears.

From this brief discussion you can see that more often than not most covalent bonds will be "partially ionic," and most ionic bonds will be "partially covalent." We shall describe a bond as being ionic or covalent according to its predominant characteristic. Some chemists like to say that a bond possesses a certain "percent ionic character." One way of calculating an *approximate* value for this quantity is with the expression

$$\log F_c = -\left(\frac{\epsilon_A - \epsilon_B}{3}\right)^2 \qquad (9\text{-}3)$$

where F_c is the fraction of *covalent* character. The fraction *of ionic* character is $F = 1 - F_c$

PROBLEM:
Calculate approximate values for the bond energy and the percent ionic character
for the C–Cl bond in CCl_4.

SOLUTION:
From Table 9-1 we find

$$\Delta H_{C-C} = 83.1 \text{ kcal/mole}$$
$$\Delta H_{Cl-Cl} = 58.0 \text{ kcal/mole}$$

and

$$\epsilon_C = 2.5$$
$$\epsilon_{Cl} = 3.0$$

With the Pauling equation, we obtain

$$\Delta H_{C-Cl} = \tfrac{1}{2}[83.1 + 58.0] + (23.06 \times 3.0 - 2.5)^2$$
$$= 70.6 + 5.8 = 76.4 \text{ kcal/mole}$$
$$\log F_c = - \left(\frac{3.0 - 2.5}{3}\right)^2 = -0.027778$$
$$F_c = 0.938$$
$$F_I = I - 0.938 = 0.062$$

Percent ionic character = 6.2%

COVALENT BOND RADII

Before considering shape principles, we should take a look at the sizes of
molecules, particularly their internuclear distances. Electron diffraction studies
of molecules in the gas phase are especially useful for the determination of
these distances (and the angles that the atom pairs form with one another). An
interatomic distance is defined as the *average* internuclear distance between
two atoms bonded together. Because these two atoms vibrate, the distance
between them alternately lengthens and shortens in rapid succession but, if the
distance is averaged for a period of time, the atoms appear to be separated by
some fixed distance. A fourth generalization can be made about these
distances.

4. The atoms of a given element always appear to have essentially the
   same radius (R), regardless of the kinds of atoms to which they are
   bound (or their electronegativities). That is, covalent radii are additive,

and the approximate interatomic distance (D) between two atoms (A and B) will be given by

$$D_{A-B} = R_A + R_B$$

PROBLEM:

Calculate the C–Cl distance in the CCl_4 molecule.

SOLUTION:

The interatomic distance is the sum of the covalent radii so, with data from Table 9-1,

$$D_{C-Cl} = R_C + R_{Cl} = 0.77 + 0.99 = 1.76 \text{ A}$$

We have already observed in the preceding problem that the C-Cl bond energy is about 76 4 kcal/mole, and that it possesses about 6% ionic character.

SHAPES OF MOLECULES

To predict the shape of a molecule, we can apply a set of simple principles. Before we outline them, however, you should realize that they have little predictive value when you try to answer the question, "What molecule is formed when two or more particular elements react?" From the same elements, but under differing conditions, it is possible to prepare many different molecules, not just one. Instead, our principles will answer the question, "What is the shape of the molecule with a particular formula?"

The concept of the *central atom* is convenient to use in discussing the shapes of molecules. In a simple molecule, one of the atoms usually is "central" to the whole molecule. For example, in CCl_4 the central atom is C, the one to which all the other atoms are attached.

We shall use the term *ligand* (L) in its broadest sense to refer to those atoms that are attached to the central atom. What we mean by the shape of a molecule or ion is the geometrical arrangement of the ligands about the central atom.

General Predictive Principles

In broad outline, our shape-prediction approach will assume that the valence electrons of the central atom (M) are all spin-paired (that is, their axes are parallel but spinning in opposite directions), and that these pairs of electrons will repel each other in such a way that they occupy positions of minimum repulsion (that is, positions of minimum potential energy). The electron pairs will try to get as far away from each other as they can and still stay in the molecule. The central atom's valence electron pairs will fall into one of two