

Electronic Properties of Atoms and Molecules

The buildup of orbital electronic structure guided by the Pauli principle shows clearly the simple basis for the periodic behavior of the elements. Generally, atoms with the same outer-orbital structure appear in the same column (group) of the periodic table. For example, atoms of the noble gas elements all have completely filled ns and np orbitals (closed-shell configurations). Metal atoms have very few electrons in the outermost s and p orbitals, thus they have a tendency to lose these electrons to achieve stable, closed-shell configurations. In contrast, the outer-orbital structures of nonmetals equal or exceed the s^2p^2 (halfway to s^2p^6) configuration. Nonmetal atoms sometimes gain electrons to achieve stable, closed-shell configurations.

The first-row transition metals are the elements scandium through zinc. These ten elements are the first to have orbital structures involving d electrons. From experience we know that the outer s and p electrons are the principal determinants of the chemical properties of atoms. Thus addition of the ten electrons to the $3d$ level does not alter grossly the chemical properties of these elements. The result is a "long period" of transition elements, all with similar properties.

2-1 LEWIS STRUCTURES FOR ATOMS

For all but a few atoms it is tedious to write the complete orbital electronic structure. It also is unnecessary because only the outer electrons are important in chemical reactions. We call the chemically important or outer electrons the *valence electrons*. The valence electrons of an atom are the electrons in the s and p orbitals beyond the closed-shell configurations. For example, in lithium the two $1s$ electrons are bound tightly to the nucleus of charge $+3$. Like the two electrons in helium, they are chemically unreactive. Thus we say that the valence electronic structure of lithium is $2s^1$, or $\text{Li}\cdot$, in which the symbol Li represents the lithium nucleus and the two $1s$ electrons. The shorthand "dot" structure is called a *Lewis structure*, after G. N. Lewis. The Lewis notation vastly simplifies writing atomic structures.

Valence-orbital structures are so important in chemistry that all serious students should learn them for the main group elements. The learning task is made easy because the valence electronic structures are periodic. For example, oxygen, sulfur, and selenium atoms have the same valence structure ns^2np^4 . Using sulfur as an example we write the Lewis formula for these atoms as $\cdot\ddot{\text{S}}\cdot$. If we know the valence electronic structure of atomic nitrogen is $\cdot\ddot{\text{N}}\cdot$, then we can write the Lewis formula for atomic phosphorus as $\cdot\ddot{\text{P}}\cdot$, because phosphorus is below nitrogen in the periodic table.

Now consider the Lewis structures for chlorine and chloride ion. The closed-shell structure before chlorine is the neon structure, $1s^22s^22p^6$, and chlorine has seven electrons in addition to this closed-shell configuration. Thus

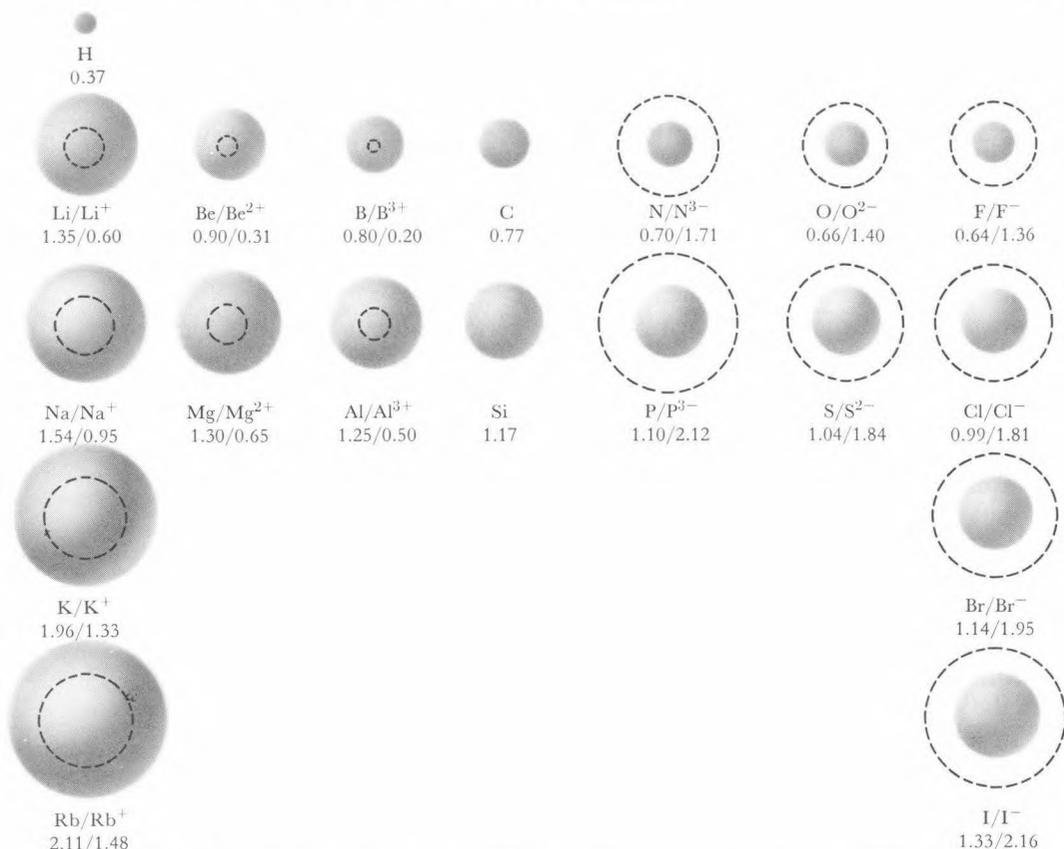
the Lewis atomic structure for chlorine has seven dots, $:\ddot{\text{Cl}}:$, in which Cl represents the nucleus and the $1s^2 2s^2 2p^6$ electrons. When one electron is added to a chlorine atom to produce a chloride ion there are eight valence electrons, thereby giving the closed-shell configuration. The chloride ion has the structure $:\ddot{\text{Cl}}:^-$, which shows the charge of -1 .

2-2 EFFECTIVE ATOMIC RADII IN MOLECULES

Now we turn our attention to the relationship between atomic properties and valence-orbital structures. First we will consider the effective radius of an atom in a molecule. The *effective atomic radius* of an atom is defined as one half the distance between two nuclei of the element that are held together by a purely covalent single bond. (A covalent bond is a pair of electrons shared between two atoms.) For example, the separation of the two protons in the hydrogen molecule, H_2 , is 0.74 \AA . Thus we assign each hydrogen atom in the H_2 molecule an atomic radius of 0.37 \AA . The distance between lithium nuclei in Li_2 is 2.67 \AA . Thus the atomic radius of lithium is approximately 1.34 \AA . The average effective radii of atoms of a selection of representative elements shown in the periodic-table arrangement of Figure 2-1 were determined from experimentally observed bond distances in many molecules. The atomic radius in most cases is compared with the size of the appropriate closed-shell positive or negative ion.

In terms of orbital structure the explanation of the shrinkage of atomic radii across a given row (or period) in Figure 2-1 is as follows. In any given period electrons are added to s and p orbitals, which are not able to shield each other effectively from the increasing positive nuclear charge. Thus an increase in the positive charge of the nucleus results in an increase in the effective nuclear charge, Z_{eff} , thereby decreasing the effective atomic radius. This is the reason why a beryllium atom, for example, is smaller than a lithium atom.

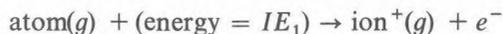
From hydrogen to lithium there is a large increase in effective atomic radius. The reason is that a third electron in a lithium atom is in an orbital that has a much larger effective radius than the hydrogen $1s$ orbital. According to the Pauli principle the third electron in lithium must be in an orbital with a larger principal quantum number, namely the $2s$ orbital. Seven more electrons can be added to the $2s$ and $2p$ orbitals, which have approximately the same radii. However, these electrons do not effectively shield each other from the positive nuclear charge as it increases, and the result is an increase in Z_{eff} and a corresponding decrease in radii in the series lithium ($Z = 3$) through neon ($Z = 10$). After neon additional electrons cannot be accommodated by the $n = 2$ level. Thus an eleventh electron must go into the $n = 3$ level, specifically, into the $3s$ orbital. Since the effective radii increase from the $n = 1$ to $n = 2$ to $n = 3$ valence orbitals, the effective size of an atom also increases with increasing atomic number within each group in the periodic table.

**2-1**

Relative atomic radii of some elements compared with the radii of the appropriate closed-shell ions. Radii are in Å. Solid spheres represent atoms and dashed circles represent ions. Notice that positive ions are smaller than their neutral atoms and negative ions are larger. Why should this be so?

2-3 IONIZATION ENERGIES AND ORBITAL CONFIGURATIONS

As we discussed in Section 1-6, the ionization energy, IE , of an atom is the energy required to remove an electron from the gaseous atom. The first ionization energy, IE_1 , is the energy needed to remove one electron from the neutral gaseous atom to produce a unipositive gaseous ion. The process can be written

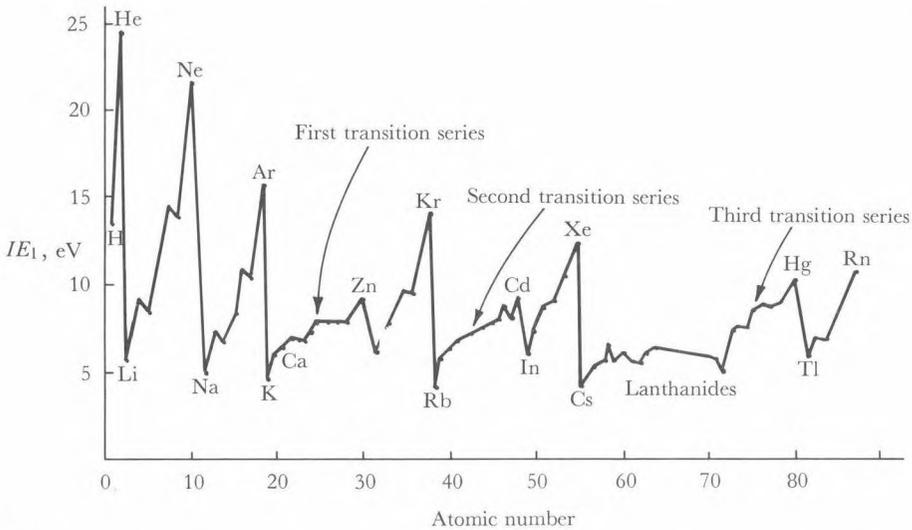
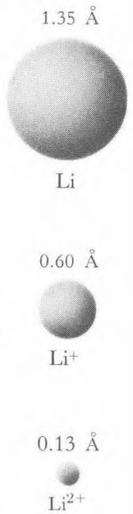


For sodium we write



2-2

Average single-bond atomic radius of the lithium atom compared with the average ionic radius of Li^+ and the calculated Bohr radius of Li^{2+} .

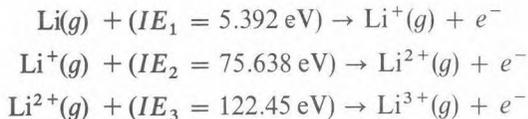


2-3

Variation of atomic ionization energy, in electron volts, with atomic number. Notice that maximum ionization energies in a given row occur for the noble gases and that the ionization energies of the transition elements are similar.

The first ionization energies for most of the elements are listed in Table 2-1, together with their ground-state orbital electronic configurations. For any atom IE_1 is always the smallest ionization energy.

In all atoms but hydrogen further ionizations are possible. For example, the three ionizations for lithium are



The large increase in the order $IE_1 < IE_2 < \dots < IE_n$ is understandable because as electrons are lost the effective nuclear charge, Z_{eff} , increases. As a result the effective radius of an atom or ion decreases sharply and the net attraction between the electrons and Z_{eff} increases sharply in a series $A, A^+, A^{2+}, A^{3+}, \dots$. The relative effective sizes of $\text{Li}, \text{Li}^+,$ and Li^{2+} are shown in Figure 2-2.

Table 2-1. Electronic configuration and ionization energies

Z	Atom	Orbital electronic configuration	IE_1 , electron volts	IE_2 , electron volts
1	H	$1s^1$	13.598	—
2	He	$1s^2$	24.587	54.416
3	Li	(He) $2s^1$	5.392	75.638
4	Be	(He) $2s^2$	9.322	18.211
5	B	(He) $2s^2 2p^1$	8.298	25.154
6	C	(He) $2s^2 2p^2$	11.260	24.383
7	N	(He) $2s^2 2p^3$	14.534	29.601
8	O	(He) $2s^2 2p^4$	13.618	35.116
9	F	(He) $2s^2 2p^5$	17.422	34.970
10	Ne	(He) $2s^2 2p^6$	21.564	40.962
11	Na	(Ne) $3s^1$	5.139	47.286
12	Mg	(Ne) $3s^2$	7.646	15.035
13	Al	(Ne) $3s^2 3p^1$	5.986	18.828
14	Si	(Ne) $3s^2 3p^2$	8.151	16.345
15	P	(Ne) $3s^2 3p^3$	10.486	19.725
16	S	(Ne) $3s^2 3p^4$	10.360	23.33
17	Cl	(Ne) $3s^2 3p^5$	12.967	23.81
18	Ar	(Ne) $3s^2 3p^6$	15.759	27.629
19	K	(Ar) $4s^1$	4.341	31.625
20	Ca	(Ar) $4s^2$	6.113	11.871
21	Sc	(Ar) $4s^2 3d^1$	6.54	12.80
22	Ti	(Ar) $4s^2 3d^2$	6.82	13.58
23	V	(Ar) $4s^2 3d^3$	6.74	14.65
24	Cr	(Ar) $4s^1 3d^5$	6.766	16.50
25	Mn	(Ar) $4s^2 3d^5$	7.435	15.640
26	Fe	(Ar) $4s^2 3d^6$	7.870	16.18
27	Co	(Ar) $4s^2 3d^7$	7.86	17.06
28	Ni	(Ar) $4s^2 3d^8$	7.635	18.168
29	Cu	(Ar) $4s^1 3d^{10}$	7.726	20.292
30	Zn	(Ar) $4s^2 3d^{10}$	9.394	17.964
31	Ga	(Ar) $4s^2 3d^{10} 4p^1$	5.999	20.51
32	Ge	(Ar) $4s^2 3d^{10} 4p^2$	7.899	15.934
33	As	(Ar) $4s^2 3d^{10} 4p^3$	9.81	18.633
34	Se	(Ar) $4s^2 3d^{10} 4p^4$	9.752	21.19
35	Br	(Ar) $4s^2 3d^{10} 4p^5$	11.814	21.8
36	Kr	(Ar) $4s^2 3d^{10} 4p^6$	13.999	24.359
37	Rb	(Kr) $5s^1$	4.177	27.28
38	Sr	(Kr) $5s^2$	5.695	11.030
39	Y	(Kr) $5s^2 4d^1$	6.38	12.24
40	Zr	(Kr) $5s^2 4d^2$	6.84	13.13
41	Nb	(Kr) $5s^1 4d^4$	6.88	14.32
42	Mo	(Kr) $5s^1 4d^5$	7.099	16.15
43	Tc	(Kr) $5s^2 4d^5$	7.28	15.26
44	Ru	(Kr) $5s^1 4d^7$	7.37	16.76
45	Rh	(Kr) $5s^1 4d^8$	7.46	18.08
46	Pd	(Kr) $4d^{10}$	8.34	19.43
47	Ag	(Kr) $5s^1 4d^{10}$	7.576	21.49
48	Cd	(Kr) $5s^2 4d^{10}$	8.993	16.908
49	In	(Kr) $5s^2 4d^{10} 5p^1$	5.786	18.869
50	Sn	(Kr) $5s^2 4d^{10} 5p^2$	7.344	14.632
51	Sb	(Kr) $5s^2 4d^{10} 5p^3$	8.641	16.53
52	Te	(Kr) $5s^2 4d^{10} 5p^4$	9.009	18.6

Table 2-1 (Continued)

Z	Atom	Orbital electronic configuration	I_{E_1} , electron volts	I_{E_2} , electron volts
53	I	(Kr)5s ² 4d ¹ 05p ⁵	10.451	19.131
54	Xe	(Kr)5s ² 4d ¹ 05p ⁶	12.130	21.21
55	Cs	(Xe)6s ¹	3.894	25.1
56	Ba	(Xe)6s ²	5.212	10.004
57	La	(Xe)6s ² 5d ¹	5.577	11.06
58	Ce	(Xe)6s ² 4f ¹ 5d ¹	5.47	10.85
59	Pr	(Xe)6s ² 4f ³	5.42	10.55
60	Nd	(Xe)6s ² 4f ⁴	5.49	10.72
61	Pm	(Xe)6s ² 4f ⁵	5.55	10.90
62	Sm	(Xe)6s ² 4f ⁶	5.63	11.07
63	Eu	(Xe)6s ² 4f ⁷	5.67	11.25
64	Gd	(Xe)6s ² 4f ⁷ 5d ¹	6.14	12.1
65	Tb	(Xe)6s ² 4f ⁹	5.85	11.52
66	Dy	(Xe)6s ² 4f ¹⁰	5.93	11.67
67	Ho	(Xe)6s ² 4f ¹¹	6.02	11.80
68	Er	(Xe)6s ² 4f ¹²	6.10	11.93
69	Tm	(Xe)6s ² 4f ¹³	6.18	12.05
70	Yb	(Xe)6s ² 4f ¹⁴	6.254	12.17
71	Lu	(Xe)6s ² 4f ¹⁴ 5d ¹	5.426	13.9
72	Hf	(Xe)6s ² 4f ¹⁴ 5d ²	7.0	14.9
73	Ta	(Xe)6s ² 4f ¹⁴ 5d ³	7.89	—
74	W	(Xe)6s ² 4f ¹⁴ 5d ⁴	7.98	—
75	Re	(Xe)6s ² 4f ¹⁴ 5d ⁵	7.88	—
76	Os	(Xe)6s ² 4f ¹⁴ 5d ⁶	8.7	—
77	Ir	(Xe)6s ² 4f ¹⁴ 5d ⁷	9.1	—
78	Pt	(Xe)6s ¹ 4f ¹⁴ 5d ⁹	9.0	18.563
79	Au	(Xe)6s ¹ 4f ¹⁴ 5d ¹⁰	9.225	20.5
80	Hg	(Xe)6s ² 4f ¹⁴ 5d ¹⁰	10.437	18.756
81	Tl	(Xe)6s ² 4f ¹⁴ 5d ¹⁰ 6p ¹	6.108	20.428
82	Pb	(Xe)6s ² 4f ¹⁴ 5d ¹⁰ 6p ²	7.416	15.032
83	Bi	(Xe)6s ² 4f ¹⁴ 5d ¹⁰ 6p ³	7.289	16.69
84	Po	(Xe)6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁴	8.42	—
85	At	(Xe)6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁵	—	—
86	Rn	(Xe)6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁶	10.748	—
87	Fr	(Rn)7s ¹	—	—
88	Ra	(Rn)7s ²	5.279	10.147
89	Ac	(Rn)7s ² 6d ¹	6.9	12.1
90	Th	(Rn)7s ² 6d ²	—	11.5
91	Pa	(Rn)7s ² 5f ² 6d ¹	—	—
92	U	(Rn)7s ² 5f ³ 6d ¹	—	—
93	Np	(Rn)7s ² 5f ⁴ 6d ¹	—	—
94	Pu	(Rn)7s ² 5f ⁶	5.8	—
95	Am	(Rn)7s ² 5f ⁷	6.0	—
96	Cm	(Rn)7s ² 5f ⁷ 6d ¹	—	—
97	Bk	(Rn)7s ² 5f ⁹	—	—
98	Cf	(Rn)7s ² 5f ¹⁰	—	—
99	Es	(Rn)7s ² 5f ¹¹	—	—
100	Fm	(Rn)7s ² 5f ¹²	—	—
101	Md	(Rn)7s ² 5f ¹³	—	—
102	No	(Rn)7s ² 5f ¹⁴	—	—
103	Lr	(Rn)7s ² 5f ¹⁴ 6d ¹	—	—

Table 2-2. Periodic behavior of ionization energies (IE)

General increase of IE , electron volts \longrightarrow								
Decrease of IE , electron volts \downarrow	H·							He:
	13.60							24.59
	Li·	Be·	·B·	·C·	·N·	·O·	·F·	·Ne:
	5.39	9.32	8.30	11.26	14.53	13.62	17.42	21.56
	Na·							
	5.14							

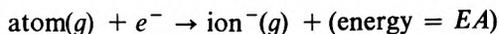
Ionization energies of atoms exhibit periodic behavior, as illustrated for IE_1 in Figure 2-3. We see that in any given row in the periodic table the ionization energies generally increase with increasing atomic number, being smallest for the lithium family and largest for the helium family. However, there are irregularities; atoms with filled or half-filled subshells have larger ionization energies than might be expected. For example, beryllium ($2s^2$) and nitrogen ($2s^2 2p^3$) have larger ionization energies than boron and oxygen atoms, respectively (Table 2-2).

The increase (although slightly irregular) in IE 's from lithium to neon is due to the steady increase in Z_{eff} with increasing atomic number. From lithium ($Z = 3$) to neon ($Z = 10$) all valence electrons are accommodated in $2s$ and $2p$ orbitals and are not able to shield each other completely from the increasing nuclear charge. Notice that the completely filled orbital structures in the helium family are especially stable. Electrons in helium and neon, which have the compact $1s^2$ and $2s^2 2p^6$ structures, respectively, are attracted relatively closely to the nucleus, thus the energies needed to remove an electron from these noble-gas atoms are correspondingly large.

Figure 2-3 also shows that in any given family of elements the ionization energies decrease with increasing atomic number. For example, the IE_1 of sodium is less than the IE_1 of lithium. Recall that the $3s$ valence orbital in sodium has a larger effective radius than the $2s$ valence orbital in lithium. According to Coulomb's law the net attraction between the $3s$ electron in a sodium atom and its effective nuclear charge is less than the net attraction between the $2s$ electron in a lithium atom and its effective nuclear charge. Thus it takes less energy to remove the $3s$ electron from the sodium atom than it does to remove the $2s$ electron from the lithium atom.

2-4 ELECTRON AFFINITY

The *electron affinity*, EA , of an atom is the energy change accompanying the addition of one electron to a neutral gaseous atom to produce a negative ion. Electron affinity is defined by the equation

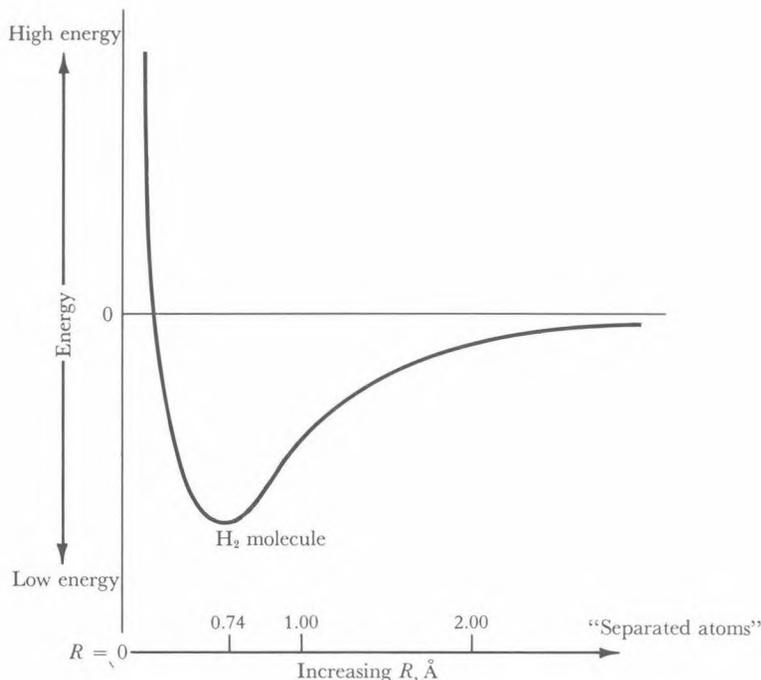


Thus if energy is released when an atom acquires one electron the atomic *EA* is positive. If energy is required for the reaction *EA* is negative. There are serious experimental problems in determining accurate *EA* values. As a result only a few *EA* values are known precisely. The better known electron affinities are listed in Table 2-3.

Table 2-3. Atomic electron affinities (*EA*)

Atom	Orbital electronic configuration	<i>EA</i> , electron volts	Orbital electronic configuration of anion
H	1s ¹	0.756	(He)
F	(He)2s ² 2p ⁵	3.45	(Ne)
Cl	(Ne)3s ² 3p ⁵	3.61	(Ar)
Br	(Ar)4s ² 3d ¹⁰ 4p ⁵	3.36	(Kr)
I	(Kr)5s ² 4d ¹⁰ 5p ⁵	3.06	(Xe)
O	(He)2s ² 2p ⁴	1.47	(He)2s ² 2p ⁵
S	(Ne)3s ² 3p ⁴	2.07	(Ne)3s ² 3p ⁵
Se	(Ar)4s ² 3d ¹⁰ 4p ⁴	(1.7)	(Ar)4s ² 3d ¹⁰ 4p ⁵
Te	(Kr)5s ² 4d ¹⁰ 5p ⁴	(2.2)	(Kr)5s ² 4d ¹⁰ 5p ⁵
N	(He)2s ² 2p ³	(-0.1)	(He)2s ² 2p ⁴
P	(Ne)3s ² 3p ³	(0.78)	(Ne)3s ² 3p ⁴
As	(Ar)4s ² 3d ¹⁰ 4p ³	(0.6)	(Ar)4s ² 3d ¹⁰ 4p ⁴
C	(He)2s ² 2p ²	1.25	(He)2s ² 2p ³
Si	(Ne)3s ² 3p ²	(1.39)	(Ne)3s ² 3p ³
Ge	(Ar)4s ² 3d ¹⁰ 4p ²	(1.2)	(Ar)4s ² 3d ¹⁰ 4p ³
B	(He)2s ² 2p ¹	(0.3)	(He)2s ² 2p ²
Al	(Ne)3s ² 3p ¹	(0.5)	(Ne)3s ² 3p ²
Ga	(Ar)4s ² 3d ¹⁰ 4p ¹	(0.18)	(Ar)4s ² 3d ¹⁰ 4p ²
In	(Kr)5s ² 4d ¹⁰ 5p ¹	(0.2)	(Kr)5s ² 4d ¹⁰ 5p ²
Be	(He)2s ²	(-0.6)	(He)2s ² 2p ¹
Mg	(Ne)3s ²	(-0.3)	(Ne)3s ² 3p ¹
Li	(He)2s ¹	0.6	(He)2s ²
Na	(Ne)3s ¹	(0.54)	(Ne)3s ²
Zn	(Ar)4s ² 3d ¹⁰	(-0.9)	(Ar)4s ² 3d ¹⁰ 4p ¹
Cd	(Kr)5s ² 4d ¹⁰	(-0.6)	(Kr)5s ² 4d ¹⁰ 5p ¹

Atoms in the fluorine family have relatively large electron affinities because an electron can be added to a valence *p* orbital relatively easily, thereby completing a closed-shell *s*²*p*⁶ configuration. Atoms that already have closed shells or subshells often have negative *EA* values. Examples are beryllium, magnesium, and zinc. Also, the nitrogen-family atoms, which have half-filled valence *p* subshells, have negative or very small positive *EA* values. Thus from the trends in both ionization energies and electron affinities it is apparent that a half-filled subshell is a particularly stable electronic arrangement.



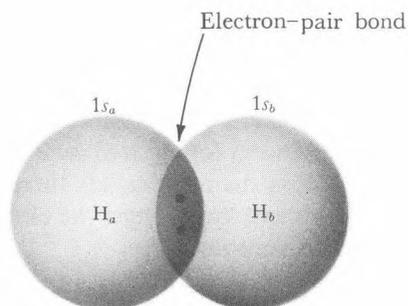
2-4

Potential energy curve for the H₂ molecule. As the distance between nuclei decreases the potential energy decreases because of electron–nucleus attraction, and then increases again because of nucleus–nucleus repulsion. The point of minimum energy corresponds to the equilibrium internuclear separation, or bond distance of H₂, which is 0.74 Å.

2-5 COVALENT BONDING

A covalent bond forms when atoms that have electrons of similar, or equal, valence-orbital energies combine. For example, two atoms of hydrogen are joined by a covalent bond in the H₂ molecule. To obtain some understanding of covalent bond formation we shall consider in detail the energy changes that occur if we allow two hydrogen atoms to come together from a large distance.

Each hydrogen atom consists of one electron and one proton. We will assume that the energy in the system is zero when the hydrogen atoms are isolated, because we want to focus our attention on the change in the energy of the system as we bring the two hydrogen atoms together. In each isolated atom there is a single important force of attraction, which is the force between the electron and the proton. However, if we bring two hydrogen atoms together there are additional attractive and repulsive forces that we must consider. Two such forces are the attractions of the first electron for the second nucleus and the second electron for the first nucleus. There also are repulsive forces: The



2-5

The two hydrogen $1s$ orbitals overlap to form an electron-pair covalent bond in H_2 .

two electrons repel each other and the two protons repel each other. Thus there are four new electrostatic forces, two of them are attractive and two are repulsive.

The most important force as the two hydrogen atoms come together is the force of attraction between the two electrons and the two protons. As the hydrogen atoms are brought together the energy of the system decreases, and it continues to decrease until the two hydrogen atoms are so close together that the nuclear repulsion—the repulsion between the protons—becomes significant, thereby causing the energy to increase. Figure 2-4 shows the energy curve for this process. Notice that there is a point—an equilibrium internuclear separation—at which the two hydrogen atoms are bound together in a stable configuration and the energy of the system is a minimum. The separation of hydrogen nuclei at the position of minimum energy is the *equilibrium internuclear separation*, or the *bond distance* of H_2 , which is 0.74 \AA .

To separate two atoms in a diatomic molecule (e.g., H_2) requires approximately the energy difference between the minimum potential energy of the system and the zero energy of the isolated atoms. This is called the *bond energy* of a diatomic molecule. The bond energy usually is expressed in kilocalories per mole, that is, the number of kilocalories required to break one mole of bonds. The bond energy of H_2 is $103 \text{ kcal mole}^{-1}$.

The two electrons in H_2 are shared equally by the two hydrogen $1s$ orbitals. This, in effect, gives each hydrogen atom a stable, closed-shell (He-type) configuration. A simple orbital representation of the electron-pair bond in H_2 is shown in Figure 2-5.

Hydrogen molecule-ion

Removal of one electron from H_2 during electron bombardment of hydrogen at very low pressures forms the transient species H_2^+ , which is the simplest of all molecules. This species, which is a combination of a proton and a hydrogen atom, is called the *hydrogen molecule-ion*. If a proton and a hydrogen atom come together, there is less net attractive force than when two hydrogen atoms approach each other. As a result the system's potential energy does not decrease as much, and the minimum energy occurs at a longer internuclear distance

than for H_2 . If we define one covalent bond as having two net bonding electrons, then H_2^+ , with one electron, has one half a bond. We find that H_2 , with two electrons, has a bond length of 0.74 Å and that H_2^+ , with one electron, has a bond length of 1.06 Å. The bond energy for H_2 is 103 kcal mole⁻¹ and the bond energy for H_2^+ is 61 kcal mole⁻¹. These comparisons illustrate the general fact that the more bonds there are between two atoms, the shorter the bond length and the stronger the bond. The number of bonds between two atoms is called the *bond order*.

2-6 PROPERTIES OF H_2 AND H_2^+ IN A MAGNETIC FIELD

Most substances can be classified as either paramagnetic or diamagnetic, depending on their behavior in a magnetic field. A *paramagnetic substance* is attracted to a magnetic field. A *diamagnetic substance* is repelled by a magnetic field. Generally, atoms and molecules with unpaired electrons are paramagnetic because there is a permanent magnetic moment associated with net electron spin. In many cases there is a further contribution to the permanent magnetic moment as a result of the movement of an electron in its orbital around the nucleus (or nuclei, in the case of molecules). In addition to the paramagnetic moment, magnetic moments are induced in atoms and molecules by applying an external magnetic field. Such induced moments are opposite to the direction of the external magnetic field, thus repulsion occurs. The magnitude of this repulsion is a measure of the diamagnetism of an atom or molecule.

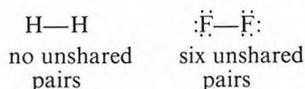
The paramagnetism of atoms and small molecules that results from unpaired electrons is larger than induced diamagnetism, thus such substances are attracted to a magnetic field. Atoms and molecules with no unpaired electrons, therefore having no paramagnetism due to electron spin, are diamagnetic and are repelled by a magnetic field. The H_2^+ ion, with one unpaired electron, is paramagnetic. The H_2 molecule, with two paired electrons, is diamagnetic.

2-7 LEWIS STRUCTURES FOR DIATOMIC MOLECULES

The Lewis structures for two H atoms can be combined to give $H:H$, or $H-H$, in which the electron-pair bond is abbreviated with a single line. Lewis suggested that the stability of H_2 is due to the tendency of each hydrogen atom to associate itself with two electrons, thereby achieving a closed-shell configuration (He:). The Lewis structure of a fluorine atom is $:\ddot{F}:$. Each fluorine atom lacks one electron to complete a closed-shell configuration. In the Lewis model two fluorine atoms achieve a closed-shell configuration by sharing two electrons, thereby forming an electron-pair bond ($:\ddot{F}-\ddot{F}:$).

The bond energy of F_2 is about 33 kcal mole⁻¹, compared to 103 kcal mole⁻¹ for H_2 . Thus it takes much less energy to separate two fluorine atoms in a fluorine molecule than it does to separate two hydrogen atoms in a

hydrogen molecule. The reason may be due to the repulsions of the unshared or lone-pair electrons that are not involved in the bond in a fluorine molecule. This type of interaction is not present in a hydrogen molecule because there are no unshared electron pairs:



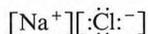
The H_2 and F_2 molecules are representative of many molecules in which electron-pair bonds are formed such that each atom achieves a closed-shell configuration. For hydrogen to achieve a closed-shell requires two electrons, which is the capacity of the $1s$ valence orbital. Each atom in the second row of the periodic table requires eight electrons (an octet) to achieve a closed shell because the $2s$ and $2p$ orbitals have a total capacity for eight electrons. This requirement commonly is known as the *octet rule*. In the example of the fluorine molecule, after bonding each fluorine atom has eight electrons associated with it. For third-row atoms eight electrons usually are associated with each atom because of their $3s$ and $3p$ valence orbitals. However, these atoms also have $3d$ orbitals (although their energy is substantially higher than that of the $3p$ orbitals), so more than eight electrons may be associated with atoms in the third and higher rows.

2-8 IONIC BONDING

In a pure covalent bond (e.g., in H_2) electrons are shared equally between two atoms. A pure ionic bond is the other extreme; that is, there is complete transfer of electrons from one atom to another and no sharing. There probably is no diatomic molecule that has a completely ionic bond. However, alkali-metal halide molecules have such unequal sharing of electrons that they may serve as models for ionic bonding.

Consider a sodium chloride diatomic molecule. If two atoms of different elements are involved in a two-electron bond, there must be unequal sharing of electrons. Unequal sharing is caused by differences in the ionization energies and electron affinities of the two atoms. In NaCl the sodium atom has a small ionization energy of about 5 eV and a small electron affinity of about 0.5 eV. Therefore it easily loses an electron to form Na^+ . The chlorine atom has a large ionization energy of more than 10 eV and a large electron affinity of almost 4 eV. Thus it does not easily lose an electron, rather it easily can gain an electron. The preceding data provide a quantitative measure of the tendency for Cl to add an electron and for Na to lose an electron to achieve closed-shell configurations. Thus a sodium atom and a chlorine atom can be assumed to form an ionic bond in which the one $3s$ valence electron in sodium is transferred to the one vacancy in the chlorine $3p$ orbitals.

We consider all ionic molecules as being composed of interacting ions. Thus sodium chloride contains the Na^+ ion, which has the inert neon configuration, and the Cl^- ion, which has the inert argon configuration. Therefore the correct Lewis structure for NaCl is



Ionic or “ion-pair” structures are reasonable models of bonds involving alkali and alkaline-earth metals with oxygen or one of the halogens. Ionic bonds are appropriate in these cases because the large differences in ionization energies and electron affinities lead to extremely unequal sharing of electrons.

A relatively simple calculation of the bond energy of sodium chloride will demonstrate that the ion-pair model is reasonable. We represent sodium chloride as a Na^+ ion and a Cl^- ion, separated by a bond distance R of 2.36 Å. Since from Coulomb’s law an energy of 332 kcal mole⁻¹ is required to dissociate completely oppositely charged bodies (each with unit charge) from a distance of 1 Å, the calculated energy for the process $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$ is 332/2.36 or 140 kcal mole⁻¹.

The *standard bond energy* (or bond dissociation energy) is the energy required to dissociate a molecule into its component atoms. For sodium chloride the process is $\text{NaCl} \rightarrow \text{Na} + \text{Cl}$. To find the energy required to dissociate NaCl into atoms we must add an electron to the Na^+ ion, which releases the atomic sodium ionization energy, and remove one electron from the Cl^- ion, which requires the atomic chlorine electron affinity energy. To complete the calculation we must convert the ionization energy and electron affinity from electron volts to kilocalories per mole through the relationship 1 eV = 23.069 kcal mole⁻¹. The molar ionization energy of sodium is 5.14 eV (119 kcal mole⁻¹) and the molar electron affinity of chlorine is 3.61 eV (83 kcal mole⁻¹). Thus in the transformation from ions to atoms 36 kcal mole⁻¹ is gained (119 - 83), so the total process $\text{Na}^+\text{Cl}^- \rightarrow \text{Na} + \text{Cl}$ requires 104 kcal mole⁻¹ (140 - 36). Therefore 104 kcal mole⁻¹ is the calculated bond dissociation energy. The experimental value is 98 kcal mole⁻¹, so the ion-pair approximation allows us to calculate the bond dissociation energy within 6% of the experimental value.

Using the “point-charge” model we ignored the repulsions between filled electron shells. A better calculation using the pure ionic model, but taking the repulsion of the closed shells into account, gives the bond energy of NaCl within 2% of the experimental value. This and similar calculations indicate that an ionic model is justified for molecules formed from lithium- or beryllium-family atoms and either oxygen or fluorine-family atoms. In addition, direct experimental evidence from electron-diffraction data shows that the electron distribution in a sodium chloride molecule is approximately that given by the ionic model.

2-9 ELECTRONEGATIVITY

Between the extremes of covalent and ionic bonds there are intermediate cases for which neither bond type is a sufficient description. A discussion of these intermediate cases is facilitated by introducing the concept of electronegativity.

Electronegativity (EN) is a term that describes the relative ability of an atom to attract electrons to itself in a chemical bond. For example, in a sodium chloride molecule the chlorine atom has a large electronegativity and the sodium atom has a small electronegativity. The result is a virtually complete transfer of one electron from sodium to chlorine in the molecule. The American scientist Robert S. Mulliken proposed that electronegativity be defined as proportional to the sum of the ionization energy and the electron affinity of an atom:

$$EN = c(IE + EA)$$

Ionization energy is a measure of the ability of an atom to hold one electron, and electron affinity is a measure of the ability of an atom to attract an electron. It follows that an atom such as chlorine, which has both a large ionization energy and a large electron affinity, will have a large electronegativity. A quantitative Mulliken scale of atomic electronegativities can be obtained by assigning one atom a specific *EN* value, thus fixing the constant of proportionality, *c*. Unfortunately, not many atomic electron affinities are known accurately, thus only a few *EN* values can be calculated in this way.

A more widely applied quantitative treatment of electronegativity was introduced by the American chemist Linus Pauling in the early 1930's. The Pauling electronegativity value for a specific atom is obtained by comparing the bond energies of certain molecules containing that atom. If the bonding electrons were shared equally in a molecule *AB*, it would be reasonable to assume that the bond energy of *AB* would be the geometric mean of the bond energies of the molecules *A*₂ and *B*₂. However, the bond energy of an *AB* molecule almost always is greater than the geometric mean of the bond energies of *A*₂ and *B*₂. An example that illustrates this is the HF molecule. The bond energy of HF is 135 kcal mole⁻¹, whereas the bond energies of H₂ and F₂ are 103 kcal mole⁻¹ and 33 kcal mole⁻¹, respectively. The geometric mean of the latter two values is $(33 \times 103)^{1/2} = 58$ kcal mole⁻¹, which is much less than the observed bond energy of HF. This "extra" bond energy (designated Δ) in an *AB* molecule is assumed to be a consequence of the partial ionic character of the bond due to electronegativity differences between atoms *A* and *B*. In this model the electronegativity difference between two atoms *A* and *B* is defined as

$$EN_A - EN_B = 0.208\Delta^{1/2} \quad (2-1)$$

in which *EN*_{*A*} and *EN*_{*B*} are the electronegativities of atoms *A* and *B*, and Δ is

the extra bond energy in kilocalories per mole. The extra bond energy is calculated from the equation

$$\Delta = DE_{AB} - [(DE_{A_2})(DE_{B_2})]^{1/2}$$

in which DE is the particular bond dissociation energy.

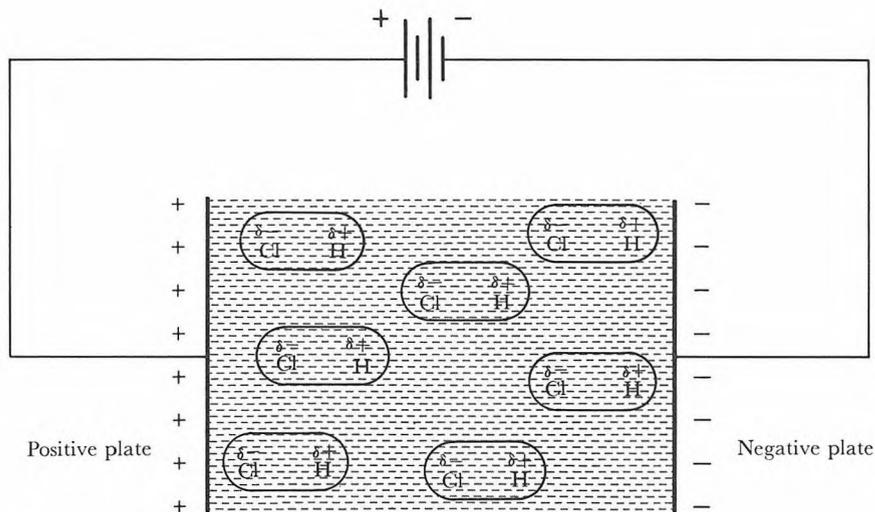
In Equation 2-1 the factor 0.208 converts kilocalories per mole to electron volts. The square root of Δ is used because it gives a more consistent set of atomic electronegativity values. Since only differences are obtained from Equation 2-1, one atomic electronegativity must be assigned a specific value, then the other values can be calculated easily. In a widely adopted version of the Pauling scale the most electronegative atom, fluorine, is assigned an electronegativity of 3.98. A compilation of EN values based on this scale is given in Table 2-4.

Table 2-4. Atomic electronegativities^a

I	II	III	II	II	II	II	II	II	II	I	II	III	IV	III	II	I
H																
2.20																
Li	Be											B	C	N	O	F
0.98	1.57											2.04	2.55	3.04	3.44	3.98
Na	Mg											Al	Si	P	S	Cl
0.93	1.31											1.61	1.90	2.19	2.58	3.16
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
0.82	1.00	1.36	1.54	1.63	1.66	1.55	1.83	1.88	1.91	1.90	1.65	1.81	2.01	2.18	2.55	2.96
Rb	Sr	Y	Zr		Mo			Rh	Pd	Ag	Cd	In	Sn	Sb		I
0.82	0.95	1.22	1.33		2.16			2.28	2.20	1.93	1.69	1.78	1.96	2.05		2.66
Cs	Ba	La			W			Ir	Pt	Au	Hg	Tl	Pb	Bi		
0.79	0.89	1.10			2.36			2.20	2.28	2.54	2.00	2.04	2.33	2.02		
		Ce	Pr	Nd		Sm		Gd		Dy	Ho	Er	Tm		Lu	
		1.12	1.13	1.14		1.17		1.20		1.22	1.23	1.24	1.25		1.27	
		(III)	(III)	(III)		(III)		(III)		(III)	(III)	(III)	(III)		(III)	
					U	Np	Pu									
					1.38	1.36	1.28									
					(III)	(III)	(III)									

^a Roman numerals refer to the oxidation numbers of the atoms in the molecules used in the calculation of atomic electronegativity values.

Electronegativity is a useful concept for qualitatively describing the sharing of electrons in a bond between two atoms of different elements. In the case of sodium and chlorine the difference in the electronegativities of the two atoms is so large that there effectively is complete transfer of the electron pair. However, there are many molecules in which the bond between dissimilar atoms is described better as covalent with some ionic character.

**2-6**

Effect of an electric field on the alignment of polar molecules. A polar molecule tends to align in an electric field, thereby maximizing the electrostatic attraction between the plates. In this illustration the preferred alignment of the polar molecule HCl is shown.

2-10 A COVALENT BOND WITH IONIC CHARACTER; THE HCl MOLECULE

The bond in a molecule composed of a hydrogen atom and a chlorine atom, HCl, is neither purely covalent nor purely ionic. In the Lewis structure for HCl an electron-pair bond between H· and ·Cl: is formed, thereby associating two electrons with hydrogen and eight electrons with chlorine (H—Cl:). The covalent structure is a more accurate representation of the bonding in HCl than an ion pair, such as we formulated for sodium chloride, because the electronegativity of the hydrogen atom is much larger (and closer to that of chlorine) than the electronegativity of the sodium atom. Although complete transfer of the pair of electrons to the chlorine atom in H—Cl: does not occur, the electron density in the bond is more concentrated in the region of the chlorine atom than in the region of the hydrogen atom. This unequal charge distribution is illustrated by



There is a small, net positive charge associated with the hydrogen atom because the electron pair is “pulled” toward the chlorine atom, which acquires a small net negative charge. Thus the HCl bond is said to have ionic character.

A molecule such as HCl is polar. The measure of the tendency of a polar molecule to become aligned in an electric field (Figure 2-6) gives a quantity

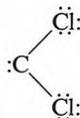
that is known as the electric *dipole moment*, which is related to the net charge separation in the most stable electronic state of the molecule. An HCl molecule has an electric dipole moment due to unequal sharing of the two electrons in the bond. An H₂ molecule (covalent bond) has a zero dipole moment, whereas an NaCl molecule (ionic bond) has a very large dipole moment. We will present a more detailed discussion of dipole moments and the properties of polar molecules in subsequent chapters.

2-11 LEWIS STRUCTURES FOR POLYATOMIC MOLECULES

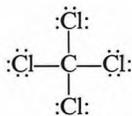
Communication among chemists commonly involves a language filled with Lewis structures for the molecules under discussion. It is important to develop considerable facility in formulating these “line and dot” structures for all types of molecules. In the following sections we will discuss several representative polyatomic molecules.

Carbon tetrachloride molecule

In CCl₄ the four chlorine atoms are bonded to the carbon atom. We could begin writing the Lewis structure for CCl₄ by making electron-pair bonds with the unpaired electrons in the ground-state carbon atom:

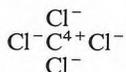


But in :CCl₂ the bonding capacity of carbon is not saturated. That is, the carbon atom can accommodate eight valence electrons, but in :CCl₂ it has only six electrons. If energy is added to the carbon atom to unpair its two 2s electrons, four bonds can be made between the carbon atom and the chlorine atoms. Thus the correct Lewis structure for carbon tetrachloride is



The carbon atom now is saturated; that is, it has achieved a closed-shell configuration. The energy required to unpair the 2s electrons is small compared to the energy released in forming the two additional single bonds. Therefore carbon tetrachloride is much more stable than the system CCl₂ + 2Cl. Notice that there are eight valence electrons associated with each atom. The valence electrons in CCl₄ not involved in bonding are the unshared-pair (or lone-pair) electrons associated with the chlorine atoms.

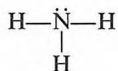
Carbon tetrachloride is a covalent molecule. Although carbon and chlorine both are nonmetals with relatively large electronegativities, atomic chlorine has a larger electronegativity than atomic carbon, but not large enough to effect a complete transfer of the pair of electrons in each bond to give the ionic structure



However, in each bond there is partial ionic character of the type $\text{C}^{\delta+}\text{Cl}^{\delta-}$ because each pair of electrons is associated more with the chlorine atom than with the carbon atom. The symbol $\text{Cl}^{\delta-}$ is used to indicate a “partial negative charge,” which is less than that if there were complete electron transfer to the chlorine atom. Similarly, $\text{C}^{\delta+}$ implies a corresponding partial positive charge associated with the carbon atom. However, because carbon tetrachloride is symmetrical the molecule has no *net* dipole moment. The individual bond dipoles, $\text{C}^{\delta+}\text{Cl}^{\delta-}$, are oriented in different directions and the shape of the molecule is such that they cancel each other. Thus a zero dipole moment does not always mean that there is equal sharing of electron pairs in bonds. A zero dipole moment may arise from the cancellation of several bond dipoles due to the shape of the molecule. We will discuss this topic in more detail in Chapter 4.

Ammonia molecule

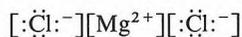
The correct Lewis structure for ammonia, NH_3 , is



with three N–H bonds and one unshared pair of electrons. There are eight valence electrons around the nitrogen atom and two electrons associated with each hydrogen atom, thereby providing a closed-shell configuration for each atom.

Magnesium chloride, an ionic molecule

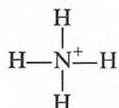
A magnesium atom has a small electronegativity and atomic chlorine has a large electronegativity, thus magnesium chloride requires a structure showing an ionic bond. One electron is transferred from the magnesium atom to each of the chlorine atoms in MgCl_2 . The correct structure indicates the charges:



There are two large bond dipoles ($\overset{\leftarrow +}{\text{Cl}} \overset{+ +}{\text{Mg}} \overset{+ \rightarrow}{\text{Cl}}$) in opposite directions and of equal magnitude (since the chloride ions are equivalent). These two bond dipoles cancel because the geometrical structure of the molecule is linear, as indicated in the preceding structure. This is another case of a zero dipole moment resulting from a symmetrical molecular shape.

Ammonium chloride molecule

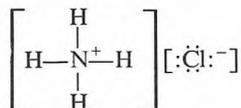
The ammonium chloride molecule, NH_4Cl , contains NH_4^+ and Cl^- ions. First we will describe the bonding in the ammonium ion, NH_4^+ . The Lewis structure for the nitrogen atom is $:\ddot{\text{N}}\cdot$ and for each hydrogen atom it is $\text{H}\cdot$. However, the NH_4^+ ion has one positive charge, which means that one of the nine electrons has been lost. Since all the hydrogen atoms in the ion are equivalent we give the nitrogen atom the positive charge, $\cdot\ddot{\text{N}}^+$, and write



Thus the correct Lewis structure of the NH_4^+ ion has four single bonds and no unshared electrons.

The charge on the nitrogen atom is called a *formal charge*. Formal charges are assigned in the following way. In a bond involving two atoms joined by an electron pair, we consider that each atom “owns” one of the electrons. Thus each hydrogen atom in the ammonium ion owns one electron. But each neutral hydrogen atom has one electron to begin with, so it has no formal charge in the molecule. However, the nitrogen atom has only four electrons in the NH_4^+ ion. Since this is one less than the five electrons in atomic nitrogen, we assign a formal charge of +1 to the nitrogen atom in NH_4^+ .

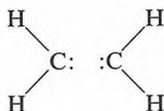
Finally, we assign the electron that was removed from NH_4 (to give NH_4^+) to the chlorine atom to give the “ion-pair” structure for ammonium chloride molecule:



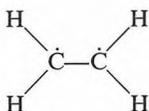
In summary, the N-H bonds in NH_4^+ are viewed as covalent with some ionic character, whereas the NH_4^+ ion is attached to Cl^- by an ionic bond.

2-12 MOLECULES WITH DOUBLE AND TRIPLE BONDS

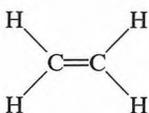
Now we consider molecules in which more than one electron pair are involved in a bond between two atoms. An example is the ethylene molecule, C_2H_4 , in which the four hydrogen atoms are attached to the two carbon atoms and the two carbon atoms are attached to each other. First we can make the bonds to the hydrogen atoms:



Then by forming a single bond between the carbon atoms and substituting a line for the bonding electron pair we have

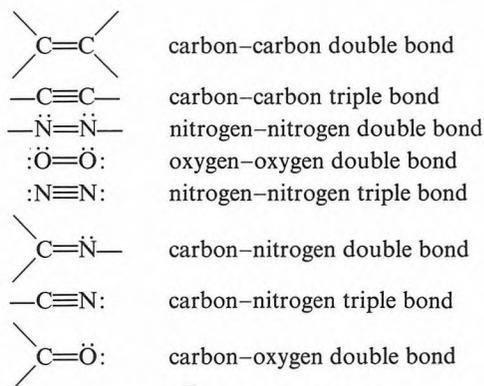


One unshared valence electron remains on each carbon atom. Counting the electrons we find that there are seven valence electrons associated with each carbon atom and two electrons with each hydrogen atom. If we make an additional electron-pair bond between the two carbon atoms, then each carbon atom has the required eight electrons:



The bond between the two carbon atoms involves two electron pairs and is called a *double bond*. Therefore the carbon-carbon bond order in ethylene is two.

There are many compounds that require Lewis structures with double or triple bonds.



The preceding structures include that for the nitrogen molecule, N_2 , which has a bond order of three. Nitrogen contributes about 80% of the earth's atmosphere, and it generally is regarded as being almost entirely unreactive. The inert character of nitrogen results because atoms of the element are very strongly bound together in diatomic molecules.

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 there is an odd number of valence electrons. Nitric oxide has eleven valence electrons, five valence electrons

originally associated with the nitrogen atom and six electrons with the oxygen atom. Thus either N or O will own only seven electrons in the NO molecule. We choose N because it is less electronegative than O. Therefore the best structure for NO is



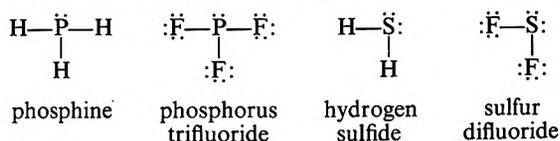
Lewis structures for molecules such as NO, which have an odd number of electrons, necessarily cannot have closed shells associated with each atom. At least one atom, nitrogen in the NO example, is left with an "open shell."

The odd electron in NO is unpaired. Consequently we would predict nitric oxide to be paramagnetic, a prediction that is in agreement with experimental data. 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 $:\ddot{\text{O}}\equiv\ddot{\text{O}}:$ or $:\ddot{\text{O}}-\ddot{\text{O}}:$ 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 $:\ddot{\text{O}}=\ddot{\text{O}}:$. We will see in the next chapter that the molecular orbital theory provides a satisfactory explanation of both the paramagnetism and the bond properties of the oxygen molecule.

2-13 BONDING TO HEAVIER ATOMS

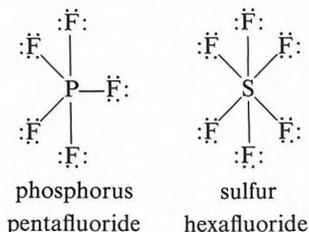
The octet rule has been extremely valuable as a guide in writing electronic formulas. For second-row nonmetallic elements (B, C, N, O, F) exceptions to the rule are very rare. It is easy to rationalize why this is so. Atoms of the second-row elements have stable $2s$ and $2p$ orbitals, and the "magic number" of eight corresponds to the closed valence-orbital configuration $2s^2 2p^6$. Adding a ninth, tenth, or larger number of electrons to such a configuration is impossible because the next atomic orbital available to a second-row element is the highly energetic $3s$ 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 :



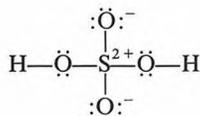
Atoms of the heavier elements do more than obey the octet rule. Some of them show a surprising ability to bind more atoms (or associate with more

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:

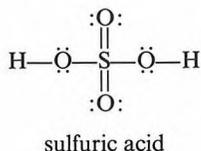


That phosphorus shares ten electrons and sulfur shares twelve electrons obviously violates the octet rule. The theory of atomic structure helps us see why the violation has occurred. The noble gas in the third row with phosphorus and sulfur is argon. The argon electronic structure fills the $3s$ and $3p$ 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.

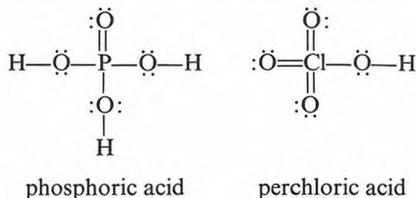
Perhaps the most important consequence of the use of d orbitals is the existence of an important series of oxyacids. The most well-known examples are phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4), and perchloric acid (HClO_4). It is possible to write a Lewis structure for sulfuric acid that obeys 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 S–O double bonds, thereby allowing the sulfur atom to share 12 electrons:

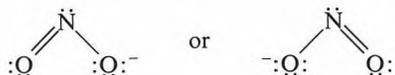


Similar Lewis formulas can be written for other oxyacids:



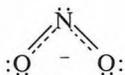
2-14 RESONANCE

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



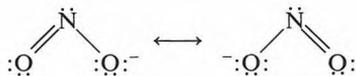
In either case the octet rule is satisfied. If either of these structures were the “correct” one, the ion would have two distinguishable nitrogen–oxygen bonds, one single and one double. Double bonds are shorter than single bonds, but structural studies of NO_2^- show that the two N–O bonds are indistinguishable.

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 is 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 formulas shown previously and superimposed the pictures, we would obtain a new formula having the same symmetry as the molecule. The photographic double-exposure method is the same as writing a formula such as



This formula would imply, “ NO_2^- is a symmetrical ion, having partial double-bond character in each of the N–O bonds.” For some purposes the formula is adequately informative. However, keeping track of the electrons in such a formula requires the addition of some rather special notation. What we actually do most of the time in such situations is to write two or more Lewis formulas and connect them with a symbol that means: “Superimpose these formulas to

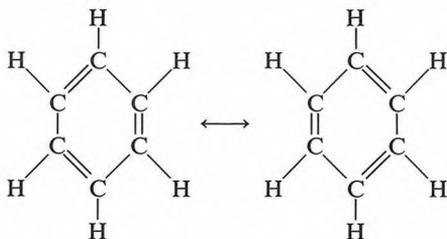
get a reasonable representation of the molecule.” Applied to NO_2^- the formulas are



The double-headed arrow is the symbol reserved for this purpose. It should not be confused with the symbol consisting of two arrows pointing in opposite directions, \rightleftharpoons , which indicates that a reversible chemical reaction occurs. The double-headed arrow conveys no implication of dynamic action.

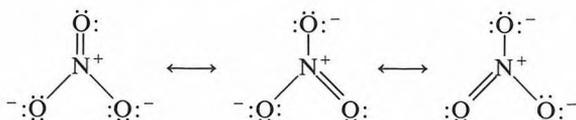
The method of combining two or more structural formulas to represent a single chemical species is called the *resonance method*. The method is used not only for the construction of electronic formulas, but also as the basis of one method for doing approximate quantum-mechanical analyses of molecular structures.

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



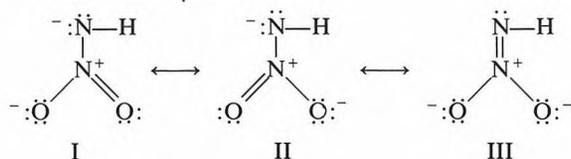
Both resonance structures show the ring to be composed of alternate single and double bonds. However, structural studies reveal that all of the carbon-carbon bond distances are equal. The full symmetry of the molecule is indicated by a double-headed arrow between the two structures.

Resonance notation is required in many cases other than those in which it is demanded by symmetry. For example, compare two well-known anions, nitrate (NO_3^-) and nitroamide ($^- \text{O}_2\text{NNH}$). Nitrate has threefold symmetry, so we can write a set of three equivalent resonance structures:



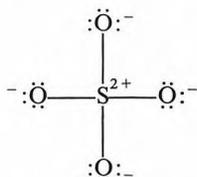
For the nitroamide ion we can write two equivalent structures, plus a third

that is not equivalent to the other two:



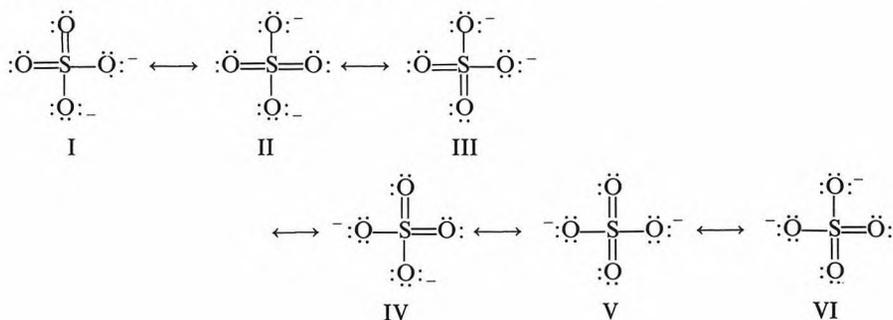
Common sense tells us that all three structures should contribute to our description of the ion. Since the structures are not equivalent, the resonance symbol no longer means: "Mix these structures equally in your thinking." It merely means: "Mix them." Therefore no quantitative implications are intended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

Finally, we will discuss 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:



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 $\text{S}=\text{O}$ bonds and two $\text{S}-\text{O}$ 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 S–O bond order of $1\frac{1}{2}$. In accord with this model of partial double-bond character is the fact that the observed S–O bond length in SO_4^{2-} (1.49 Å) is 0.21 Å shorter than the standard S–O 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 2–1).

SUGGESTIONS FOR FURTHER READING

- A. Companion, *Chemical Bonding*, McGraw-Hill, New York, 1964.
 H. B. Gray, *Electrons and Chemical Bonding*, Benjamin, Menlo Park, Calif., 1965.
 J. L. Hall and D. A. Keyworth, *Brief Chemistry of the Elements*, Benjamin, Menlo Park, Calif., 1971.
 L. Pauling, *The Chemical Bond*, Cornell Univ. Press, Ithaca, N.Y., 1967.
 R. L. Rich, *Periodic Correlations*, Benjamin, Menlo Park, Calif., 1965.
 G. E. Ryschkewitsch, *Chemical Bonding and the Geometry of Molecules*, Reinhold, New York, 1962.
 R. T. Sanderson, *Chemical Periodicity*, Reinhold, New York, 1960.

QUESTIONS AND PROBLEMS

- Write orbital electronic configurations and then draw Lewis structures for atomic sodium, silicon, phosphorus, and sulfur. How many unpaired electrons are there in each atom?
- The ionization energies of francium (Fr) and astatine (At) are not given in Table 2–1 because these elements are not available in large quantities and no accurate *IE* measurements have been made. Using the information available in Table 2–1 estimate the values of *IE* for francium and astatine atoms.
- Explain why the electron affinities of both silicon and sulfur are larger than that of phosphorus.
- Make a plot of IE_2 values versus atomic number for the elements helium through calcium. Explain the differences between this plot and that given for the IE_1 values (Figure 2–3). Why are the maximum IE_2 values not those of the noble gases?
- The ionization energy of atomic hydrogen is 13.6 eV and the electron affinity is 0.756 eV. Convert these quantities to cm^{-1} and to kcal mole^{-1} .
- Predict the relative effective radii of the species H^- , He, and Li^+ . Explain your choice.
- 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. Based on 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. Show that e^2 has a value of $332 \text{ kcal mole}^{-1} \text{ \AA}$.
9. The bond distance in diatomic LiF is 1.52 \AA . Assuming ionic bonding calculate the energy required to dissociate LiF into Li^+ and F^- .
10. Calculate the electronegativity of hydrogen (EN_{H}) assuming the value 3.98 for EN_{F} from Table 2-4. Do this calculation for both the Pauling and the Mulliken scales. The value you obtain on the Pauling scale will not agree exactly with that given in Table 2-4 because many EN differences (Equation 2-1) were averaged to give the best values reported in the table.
11. 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 . Discuss possible explanations for the fact that PF_5 is stable, whereas NF_5 is not. From your treatment, which of the following molecules would you expect not to exist: OF_2 , OF_4 , OF_6 , SF_2 , SF_4 , and SF_6 ? Write Lewis structures and appropriate comments to support your case.
12. Write Lewis structures for CO_2 and SO_2 . Are the C-O bonds primarily ionic or covalent? The SO_2 molecule has a dipole moment, whereas CO_2 does not. What shape do you expect for each molecule?
13. 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 . Is C_2H_2 polar or nonpolar?
14. Iodine forms several oxyions 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 oxyions.
15. Write a Lewis structure for S_2 . Do you expect the molecule to be paramagnetic or diamagnetic?
16. Write Lewis structures for BF_3 and NO_3^- . Do these molecular species have anything in common? The dipole moment of BF_3 is zero. What geometrical structure do you expect for BF_3 ? What geometrical structure might NO_3^- have?
17. Write Lewis structures for CN^- and CO . Is the C-O bond length in CO shorter than in CO_2 ? Explain.
18. Assuming an ionic model calculate standard bond dissociation energies for the following molecules: CsF , KBr , and LiF . Bond lengths and experimental bond-energy data (for comparison) are given in Table 3-5.
19. Write Lewis structures for H_2O and HF . The water molecule is nonlinear. Do H_2O and HF have dipole moments?
20. Write Lewis structures for the following molecules and ions. Show resonance structures if appropriate. Also indicate in each case if 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

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|---------------------------|--------------------------|-------------------|------------------|
| 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 | |

21. Calculate the standard bond energies of RbF, CsBr, NaI, and KCl. Assume an ionic model. Bond-length data and experimental bond energies are given in Table 3–5.
22. Calculate the dissociation energies of BeO and CaO to M^{2+} and O^{2-} ions using an ionic bonding model. Bond distances are given in Table 3–5.
23. Write the electronic configuration ($1s^2 2s^2 \dots$) for the following: F^- , Na^+ , Ne, O^{2-} , and N^{3-} . What would you predict about the relative sizes of these species?
24. Which atom in each of the following pairs would you expect to have the larger electron affinity (EA)? (a) Cu or Zn; (b) K or Ca; (c) S or Cl; (d) H or Li; (e) As or Ge.
25. 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 C–N and C–S bond orders for each structure.
26. For each of the following cases 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
27. The atoms of the yet-to-be-discovered “hypotransition” elements, starting at $Z = 121$, will have electrons in the $5g$ orbitals.
 - a) How many elements will there be in the hypotransition metal series?
 - b) How many of the atoms will be diamagnetic?
 - c) Which electronic configurations in the series will have seven unpaired electrons?
 - d) What is the maximum number of unpaired electrons an atom can have in the series? Will this be a new record for atoms in the periodic table?
 - e) What is the IE of an electron in a $5g$ orbital of atomic hydrogen? Is this likely to be larger, or smaller, than the IE of a $5g$ electron in one of the hypotransition elements? Briefly explain your choice.
 - f) In atomic hydrogen the $5s$, $5p$, $5d$, $5f$, and $5g$ orbitals all have the same energy. Will this be true for the hypotransition elements? If not, what will the energy order be? Explain briefly.