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References

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Inorganic Chemistry

1-1 WHAT IS INORGANIC CHEMISTRY?

If organic chemistry is defined as the chemistry of hydrocarbon compounds and their derivatives, inorganic chemistry can be described broadly as the chemistry of "every-thing else." This includes all the remaining elements in the periodic table, as well as carbon, which plays a major role in many inorganic compounds. Organometallic chemistry, a very large and rapidly growing field, bridges both areas by considering compounds containing direct metal-carbon bonds, and includes catalysis of many organic reactions. Bioinorganic chemistry bridges biochemistry and inorganic chemistry, and environmental chemistry includes the study of both inorganic and organic compounds. As can be imagined, the inorganic realm is extremely broad, providing essentially limitless areas for investigation.

1-2 CONTRASTS WITH ORGANIC CHEMISTRY

Some comparisons between organic and inorganic compounds are in order. In both areas, single, double, and triple covalent bonds are found, as shown in Figure 1-1; for inorganic compounds, these include direct metal-metal bonds and metal-carbon bonds. However, although the maximum number of bonds between two carbon atoms is three, there are many compounds containing quadruple bonds between metal atoms. In addition to the sigma and pi bonds common in organic chemistry, quadruple bonded metal atoms contain a delta bond (Figure 1-2); a combination of one sigma bond, two pi bonds, and one delta bond makes up the quadruple bond. The delta bond is possible in these cases because metal atoms have d orbitals to use in bonding, whereas carbon has only s and p orbitals available. In organic compounds, hydrogen is nearly always bonded to a single carbon. In inorganic compounds, especially of the Group 13 (IIIA) elements, hydrogen is frequently encountered as a bridging atom between two or more other atoms. Bridging hydrogen atoms can also occur in metal cluster compounds. In these clusters, hydrogen atoms form bridges across edges or faces of polyhedral of metal atoms. Alkyl groups may also act as bridges in inorganic compounds, a function rarely encountered in organic chemistry (except in reaction intermediates). Examples of terminal and bridging hydrogen atoms and alkyl groups in inorganic compounds are shown in Figure 1-3.

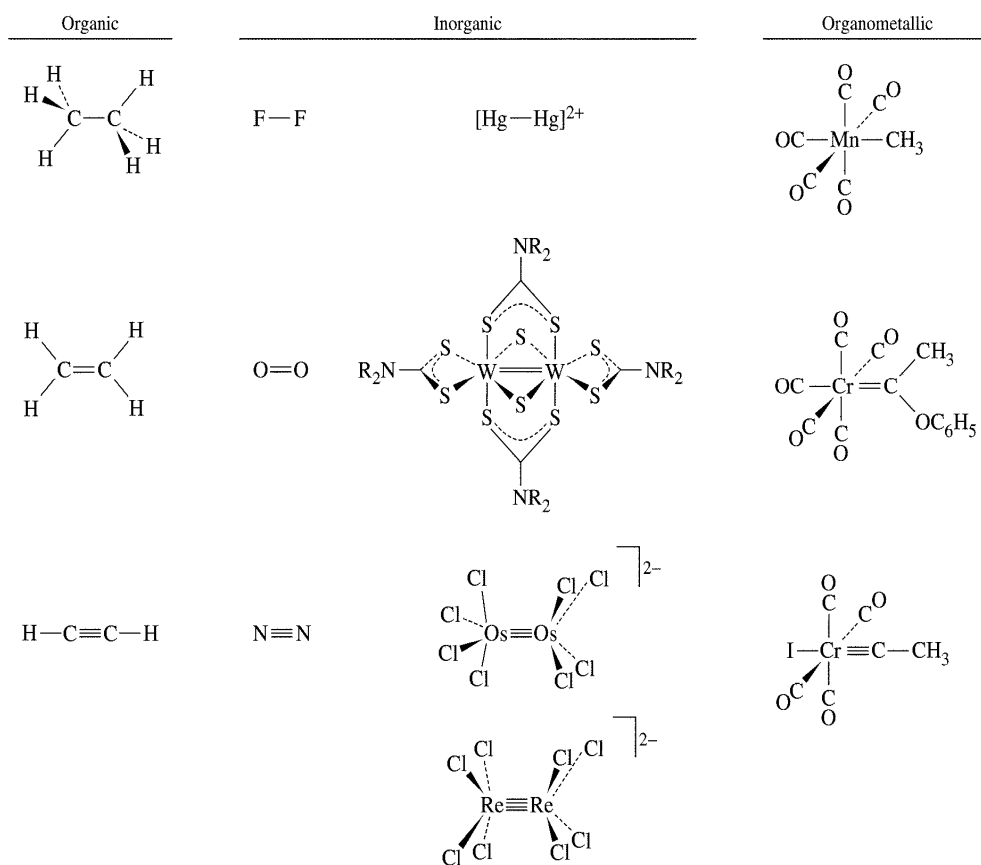


FIGURE 1-1 Single and Multiple Bonds in Organic and Inorganic Molecules.

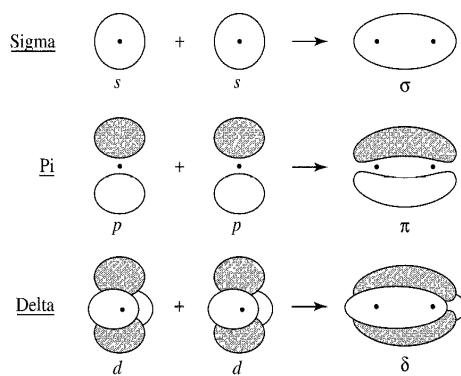


FIGURE 1-2 Examples of Bonding Interactions.

Some of the most striking differences between the chemistry of carbon and that of many other elements are in coordination number and geometry. Although carbon is usually limited to a maximum coordination number of four (a maximum of four atoms

bonded to carbon, as in CH₄), inorganic compounds having coordination numbers of five, six, seven, and more are very common; the most common coordination geometry is an octahedral arrangement around a central atom, as shown for [TiF₆]³⁻ in Figure 1-4.

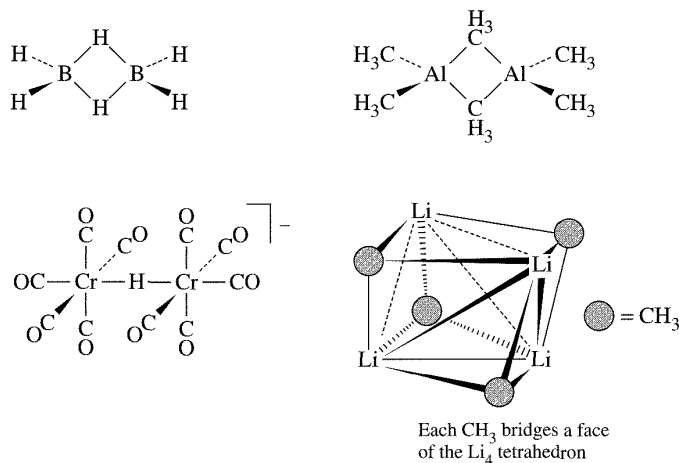


FIGURE 1-3 Examples of Inorganic Compounds Containing Terminal and Bridging Hydrogens and Alkyl Groups.

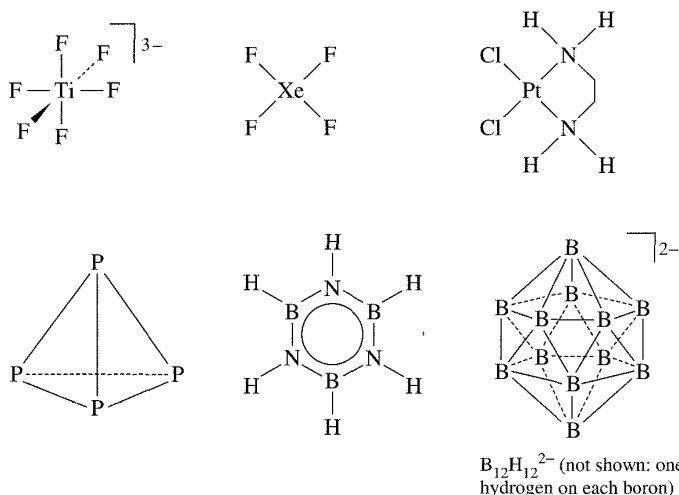


FIGURE 1-4 Examples of Geometries of Inorganic Compounds.

Furthermore, inorganic compounds present coordination geometries different from those found for carbon. For example, although 4-coordinate carbon is nearly always tetrahedral, both tetrahedral and square planar shapes occur for 4-coordinate compounds of both metals and nonmetals. When metals are the central atoms, with anions or neutral molecules bonded to them (frequently through N, O, or S), these are called coordination complexes; when carbon is the element directly bonded to metal atoms or ions, they are called organometallic compounds.

The tetrahedral geometry usually found in 4-coordinate compounds of carbon also occurs in a different form in some inorganic molecules. Methane contains four hydrogens in a regular tetrahedron around carbon. Elemental phosphorus is tetratomic (P₄) and also is tetrahedral, but with no central atom. Examples of some of the geometries found for

inorganic compounds are shown in Figure 1-4. Aromatic rings are common in organic chemistry, and aryl groups can also form sigma bonds to metals. However, aromatic rings can also bond to metals in a dramatically different fashion using their pi orbitals, as shown in Figure 1-5. The result is a metal atom bonded above the center of the ring, almost as if suspended in space. In many cases, metal atoms are sandwiched between two aromatic rings. Multiple-decker sandwiches of metals and aromatic rings are also known.

FIGURE 1-5 Inorganic Compounds Containing Pi-bonded Aromatic Rings.

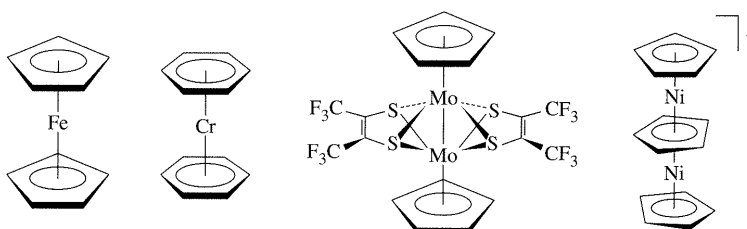


FIGURE 1-6 Carbon-centered Metal Clusters.

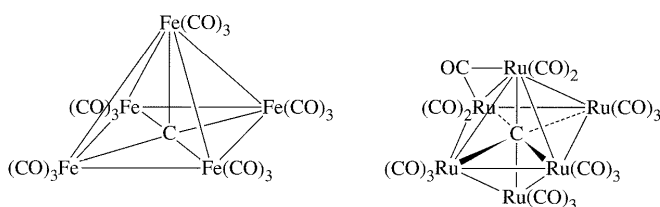
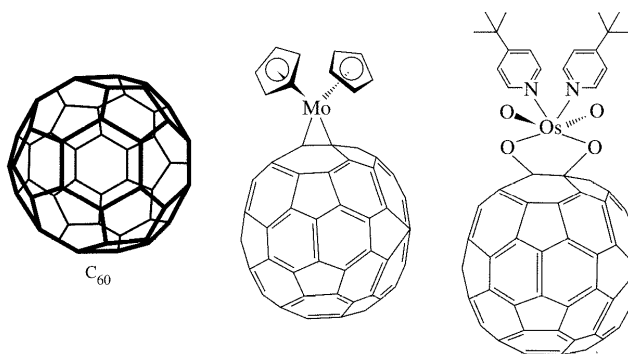


FIGURE 1-7 Fullerene Compounds.



Carbon plays an unusual role in a number of metal cluster compounds in which a carbon atom is at the center of a polyhedron of metal atoms. Examples of carbon-centered clusters of five, six, or more metals are known; two of these are shown in Figure 1-6. The contrast of the role that carbon plays in these clusters to its usual role in organic compounds is striking, and attempting to explain how carbon can form bonds to the surrounding metal atoms in clusters has provided an interesting challenge to theoretical inorganic chemists.

In addition, during the past decade, the realm of a new class of carbon clusters, the fullerenes, has flourished. The most common of these clusters, C_{60} , has been labeled "buckminsterfullerene" after the developer of the geodesic dome and has served as the core of a variety of derivatives (Figure 1-7).

There are no sharp dividing lines between subfields in chemistry, such as acid-base chemistry and organometallic reactions, are of vital interest to organic chemists. Others,

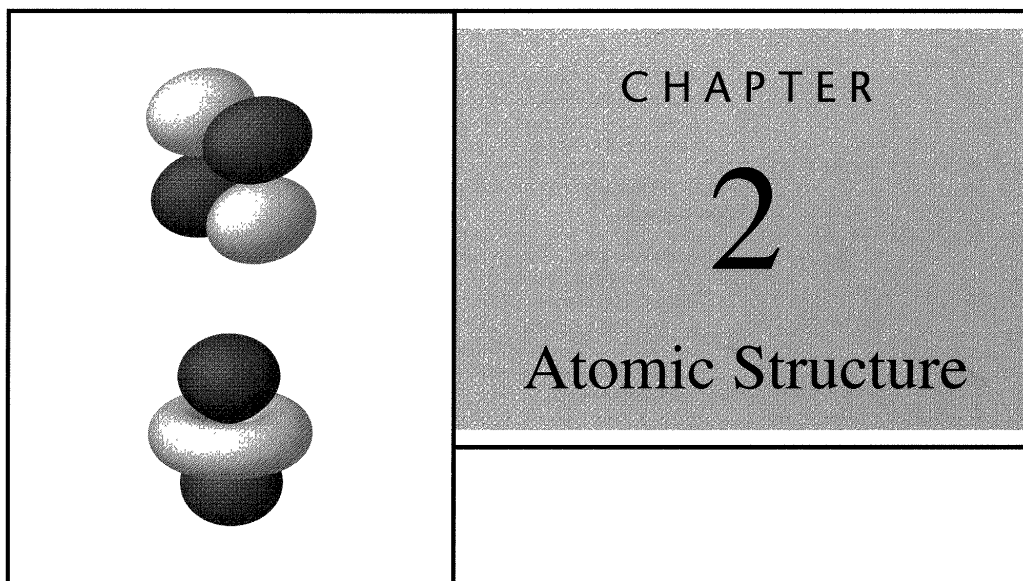
such as oxidation-reduction reactions, spectra, and solubility relations, also interest analytical chemists. Subjects related to structure determination, spectra, and theories of bonding appeal to physical chemists. Finally, the use of organometallic catalysts provides a connection to petroleum and polymer chemistry, and the presence of coordination compounds such as hemoglobin and metal-containing enzymes provides a similar tie to biochemistry. This list is not intended to describe a fragmented field of study, but rather to show some of the interconnections between inorganic chemistry and other fields of chemistry.

NUCLEAR REACTIONS AND RADIOACTIVITY

Some nuclei were formed that were stable, never undergoing further reactions. Others have lifetimes ranging from 10^{16} years to 10^{-16} second. The usual method of describing nuclear decay is in terms of the **half-life**, or the time needed for half the nuclei to react. Because decay follows first-order kinetics, the half-life is a well defined value, not dependent on the amount present. In addition to the overall curve of nuclear stability, which has its most stable region near atomic number $Z = 26$, combinations of protons and neutrons at each atomic number exhibit different stabilities. In some elements such as fluorine (^{19}F), there is only one stable **isotope** (a specific combination of protons and neutrons). In others, such as chlorine, there are two or more stable isotopes. ^{35}Cl has a natural abundance of 75.77%, and ^{37}Cl has a natural abundance of 24.23%. Both are stable, as are all the natural isotopes of the lighter elements. The radioactive isotopes of these elements have short half-lives and have had more than enough time to decay to more stable elements. ^3H , ^{14}C , and a few other radioactive nuclei are continually being formed by cosmic rays and have a low constant concentration.

Heavier elements ($Z = 40$ or higher) may also have radioactive isotopes with longer half-lives. As a result, some of these radioactive isotopes have not had time to decay completely, and the natural substances are radioactive. Further discussion of isotopic abundances and radioactivity can be found in larger or more specialized sources.

As atomic mass increases, the ratio of neutrons to protons in stable isotopes gradually increases from 1 : 1 to 1.6 : 1 for $^{238}_{92}\text{U}$. There is also a set of nuclear energy levels similar to the electron energy levels described in Chapter 2 that result in stable nuclei with 2, 8, 20, 28, 50, 82, and 126 protons or neutrons. In nature, the most stable nuclei are those with the numbers of both protons and neutrons matching one of these numbers; ^4_2He , $^{16}_8\text{O}$, $^{40}_{20}\text{Ca}$, and $^{208}_{82}\text{Pb}$ are examples.



The theories of atomic and molecular structure depend on quantum mechanics to describe atoms and molecules in mathematical terms. Although the details of quantum mechanics require considerable mathematical sophistication, it is possible to understand the principles involved with only a moderate amount of mathematics. This chapter presents the fundamentals needed to explain atomic and molecular structures in qualitative or semiquantitative terms.

2-1-1 THE PERIODIC TABLE

The idea of arranging the elements into a periodic table had been considered by many chemists, but either the data to support the idea were insufficient or the classification schemes were incomplete. Mendeleev and Meyer organized the elements in order of atomic weight and then identified families of elements with similar properties. By arranging these families in rows or columns, and by considering similarities in chemical behavior as well as atomic weight, Mendeleev found vacancies in the table and was able to predict the properties of several elements (gallium, scandium, germanium, polonium) that had not yet been discovered. When his predictions proved accurate, the concept of a periodic table was quickly established. The discovery of additional elements not known in Mendeleev's time and the synthesis of heavy elements have led to the more complete modern periodic table, shown inside the front cover of this text.

In the modern periodic table, a horizontal row of elements is called a **period**, and a vertical column is a **group** or **family**. The traditional designations of groups in the United States differ from those used in Europe. The International Union of Pure and Applied Chemistry (IUPAC) has recommended that the groups be numbered I through 18, a recommendation that has generated considerable controversy. In this text, we will use the IUPAC group numbers, with the traditional American numbers in parentheses. Some sections of the periodic table have traditional names, as shown in Figure 2-1.

Groups (American tradition)																	
IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	VIIIA
Groups (European tradition)																	
IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII	IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB	0	0
Groups (IUPAC)																	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18

1																2
3	Transition metals										5					10
Alkali Metals	Alkaline Earth Metals	21	22								30	31		Chalcogens	Halogens	Noble Gases
55	Alkaline Earth Metals	57	*	72							Coinage Metals	80	81			86
87		89	**	104								112				

*	58	Lanthanides													71
**	90	Actinides													103

FIGURE 2-1 Names for Parts of the Periodic Table.

2-1-2 DISCOVERY OF SUBATOMIC PARTICLES AND THE BOHR ATOM

During the 50 years after the periodic tables of Mendeleev and Meyer were proposed, experimental advances came rapidly. Some of these discoveries are shown in Table 2-1. Parallel discoveries in atomic spectra showed that each element emits light of specific energies when excited by an electric discharge or heat. In 1885, Balmer showed that the energies of visible light emitted by the hydrogen atom are given by the equation

$$E = R_H \left(\frac{1}{2^2} - \frac{1}{n_h^2} \right)$$

where

$n_h =$ integer, with $n_h > 2$

$R_H =$ Rydberg constant for hydrogen = $1.097 \times 10^7 \text{ m}^{-1} = 2.179 \times 10^{-18} \text{ J}$ and the energy is related to the wavelength, frequency, and wave number of the light, as given by the equation

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

where⁹

h = Planck's constant = 6.626×10^{-34} J s

ν = frequency of the light, in s^{-1}

c = speed of light = 2.998×10^8 m s^{-1}

λ = wavelength of the light, frequently in nm

$\bar{\nu}$ = wavenumber of the light, usually in cm^{-1}

The Balmer equation was later made more general, as spectral lines in the ultraviolet and infrared regions of the spectrum were discovered, by replacing 22 by nf , with the condition that $nl < nh$. These quantities, ni , are called **quantum numbers**. (These are the **principal quantum numbers**; other quantum numbers are discussed in Section 2-2-2.) The origin of this energy was unknown until Niels Bohr's quantum theory of the atom," first published in 1913 and refined over the following 10 years. This theory assumed that negative electrons in atoms move in stable circular orbits around the positive nucleus with no absorption or emission of energy. However, electrons may absorb light of certain specific energies and be excited to orbits of higher energy; they may also emit light of specific energies and fall to orbits of lower energy. The energy of the light emitted or absorbed can be found, according to the Bohr model of the hydrogen atom, from the equation

$$E = R_H \left(\frac{1}{n_l^2} - \frac{1}{n_h^2} \right)$$

where

$$R = \frac{2\pi^2\mu Z^2 e^4}{(4\pi\epsilon_0)^2 h^2}$$

μ = reduced mass of the electron-nucleus combination

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_{\text{nucleus}}}$$

m_e = mass of the electron

m_{nucleus} = mass of the nucleus

Z = charge of the nucleus

e = electronic charge

h = Planck's constant

n_h = quantum number describing the higher energy state

n_l = quantum number describing the lower energy state

$4\pi\epsilon_0$ = permittivity of a vacuum

This equation shows that the Rydberg constant depends on the mass of the nucleus as well as on the fundamental constants. Examples of the transitions observed for the hydrogen atom and the energy levels responsible are shown in Figure 2-2. As the electrons drop from level nh to nl (h for higher level, l for lower level), energy is released in the form of electromagnetic radiation. Conversely, if radiation of the correct energy is absorbed by an atom, electrons are raised from level nl to level nh . The inverse-square dependence of energy on nl results in energy levels that are far apart in energy at small nl and become much closer in energy at larger nl . In the upper limit, as nl approaches infinity, the energy approaches a limit of zero. Individual electrons can have more energy, but above this point they are no longer part of the atom; an infinite quantum number means that the nucleus and the electron are separate entities.

EXERCISE 2-1

Find the energy of the transition from $nh = 3$ to $nl = 2$ for the hydrogen atom in both joules and cm^{-1} (a common unit in spectroscopy). This transition results in a red line in the visible emission spectrum of hydrogen.

When applied to hydrogen, Bohr's theory worked well; when atoms with more electrons were considered, the theory failed. Complications such as elliptical rather than circular orbits were introduced in an attempt to fit the data to Bohr's theory.' The developing experimental science of atomic spectroscopy provided extensive data for testing of the Bohr theory and its modifications and forced the theorists to work hard to explain the spectroscopists' observations. In spite of their efforts, the Bohr theory eventually proved unsatisfactory; the energy levels shown in Figure 2-2 are valid only for the hydrogen atom. An important characteristic of the electron, its wave nature, still needed to be considered. According to the de Broglie equation,¹² proposed in the 1920s, all moving particles have wave properties described by the equation

$$\lambda = \frac{h}{mv}$$

where

λ = wavelength of the particle

h = Planck's constant

m = mass of the particle

v = velocity of the particle

Particles massive enough to be visible have very short wavelengths, too small to be measured. Electrons, on the other hand, have wave properties because of their very small mass. Electrons moving in circles around the nucleus, as in Bohr's theory, can be thought of as forming standing waves that can be described by the de Broglie equation. However,

we no longer believe that it is possible to describe the motion of an electron in an atom so precisely. This is a consequence of another fundamental principle of modern physics, **Heisenberg's uncertainty principle**, which states that there is a relationship

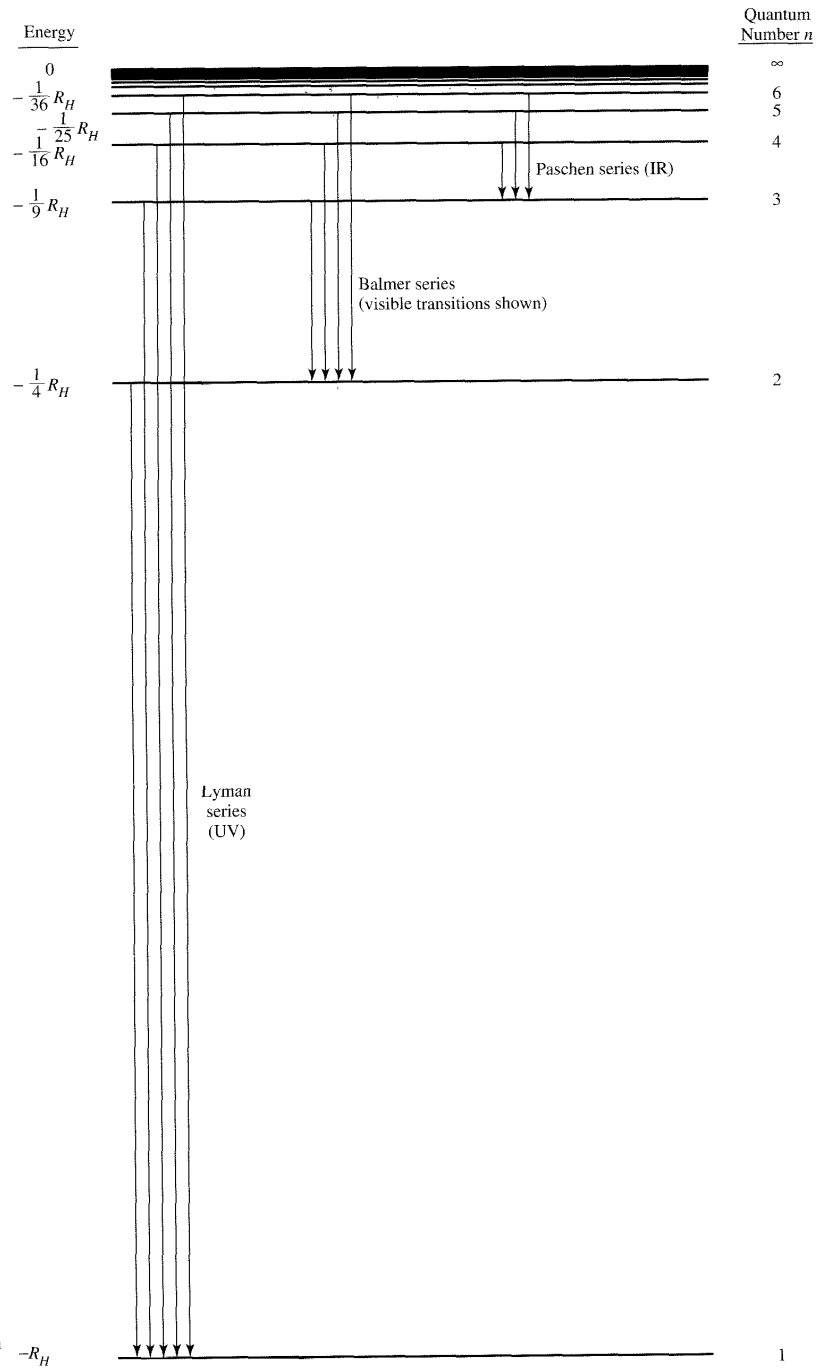


FIGURE 2-2 Hydrogen Atom Energy Levels.

2-2-2 QUANTUM NUMBERS AND ATOMIC WAVE FUNCTIONS

The particle in a box example shows how a wave function operates in one dimension. Mathematically, atomic orbitals are discrete solutions of the three-dimensional Schrodinger equations. The same methods used for the one-dimensional box can be expanded to three dimensions for atoms. These orbital equations include three quantum numbers, n , l , and m_l . A fourth quantum number, m_s , a result of relativistic corrections to the Schrodinger equation, completes the description by accounting for the magnetic moment of the electron. The quantum numbers are summarized in Tables 2-2, 2-3, and 2-4.

TABLE 2-2
Quantum Numbers and Their Properties

Symbol	Name	Values	Role
n	Principal	1, 2, 3, ...	Determines the major part of the energy
l	Angular momentum	0, 1, 2, ..., $n - 1$	Describes angular dependence and contributes to the energy
m_l	Magnetic	0, ± 1 , ± 2 , ..., $\pm l$	Describes orientation in space (angular momentum in the z direction)
m_s	Spin	$\pm \frac{1}{2}$	Describes orientation of the electron spin (magnetic moment) in space

Orbitals with different l values are known by the following labels, derived from early terms for different families of spectroscopic lines:

l	0	1	2	3	4	5, ...
Label	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	continuing alphabetically

TABLE 2-3
Hydrogen Atom Wave Functions: Angular Functions

Nodal surfaces

At large distances from the nucleus, the electron density, or probability of finding the electron, falls off rapidly. The $2s$ orbital also has a **nodal surface**, a surface with zero electron density, in this case a sphere with $r = 2a_0$ where the probability is zero. Nodes appear naturally as a result of the wave nature of the electron; they occur in the functions that result from solving the wave equation for ψ . A node is a surface where the wave function is zero as it changes sign (as at $r = 2a_0$, in the $2s$ orbital); this requires that $\psi = 0$, and the probability of finding the electron at that point is also zero. If the probability of finding an electron is zero ($\psi = 0$), ψ must also be equal to zero. Because

$$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

2-2-3 THE AUFBAU PRINCIPLE

Limitations on the values of the quantum numbers lead to the familiar **aufbau** (German, *Aufbau*, building up) **principle**, where the buildup of electrons in atoms results from continually increasing the quantum numbers. Any combination of the quantum numbers presented so far correctly describes electron behavior in a hydrogen atom, where there is only one electron. However, interactions between electrons in polyelectronic atoms require that the order of filling of orbitals be specified when more than one electron is in the same atom. In this process, we start with the lowest n , l , and m_l values (1, 0, and 0, respectively) and either of the m_s values (we will arbitrarily use $+\frac{1}{2}$ first). Three rules will then give us the proper order for the remaining electrons as we increase the quantum numbers in the order m_l , l , and n .

1. Electrons are placed in orbitals to give the lowest total energy to the atom. This means that the lowest values of n and l are filled first. Because the orbitals within each set (p , d , etc.) have the same energy, the orders for values of m_l and m_s are indeterminate.
2. The **Pauli exclusion principle** requires that each electron in an atom have a unique set of quantum numbers. At least one quantum number must be different from those of every other electron. This principle does not come from the Schrodinger equation, but from experimental determination of electronic structures.
3. **Hund's rule of maximum multiplicity** requires that electrons be placed in orbitals so as to give the maximum total spin possible (or the maximum number of parallel spins). Two electrons in the same orbital have a higher energy than two electrons in different orbitals, caused by electrostatic repulsion (electrons in the same orbital repel each other more than electrons in separate orbitals). Therefore, this rule is a consequence of the lowest possible energy rule (Rule 1). When there are one to six electrons in p orbitals, the required arrangements are those given in Table 2-6. The **multiplicity** is the number of unpaired electrons plus 1, or $n + 1$. This is the number of possible energy levels that depend on the orientation of the net magnetic moment in a magnetic field. Any other arrangement of electrons results in fewer unpaired electrons. This is only one of Hund's rules.

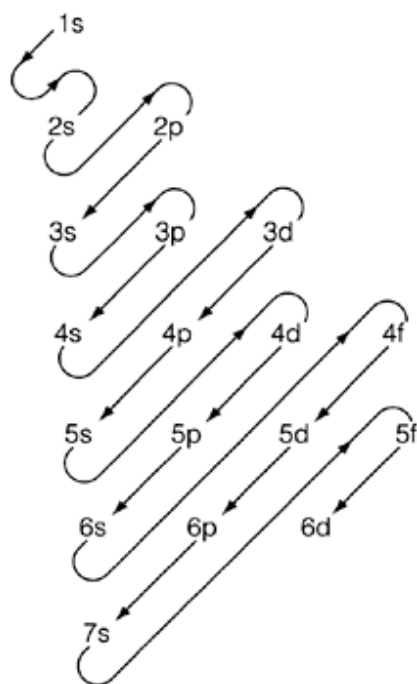


Fig. 1. Showing the order of filling of orbitals in the periodic table.

TABLE 2-6
Hund's Rule and Multiplicity

<i>Number of Electrons</i>	<i>Arrangement</i>	<i>Unpaired e^-</i>	<i>Multiplicity</i>
1	\uparrow — — —	1	2
2	\uparrow \uparrow — —	2	3
3	\uparrow \uparrow \uparrow —	3	4
4	$\uparrow\downarrow$ \uparrow \uparrow —	2	3
5	$\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow —	1	2
6	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	0	1

This rule is a consequence of the energy required for pairing electrons in the same orbital. When two electrons occupy the same part of the space around an atom, they repel each other because of their mutual negative charges with a **Coulombic energy of repulsion, $\Pi\Pi$** , per pair of electrons. As a result, this repulsive force favors electrons in different orbitals (different regions of space) over electrons in the same orbitals. In addition, there is exchange **energy, $\Pi\Pi$** , which arises from purely quantum mechanical considerations. This energy depends on the number of possible exchanges between two electrons with

the same energy and the same spin. For example, the electron configuration of a carbon atom is $1S^2 2S^2 2P^2$. Three **arrangements** of the **2p** electrons can be considered:

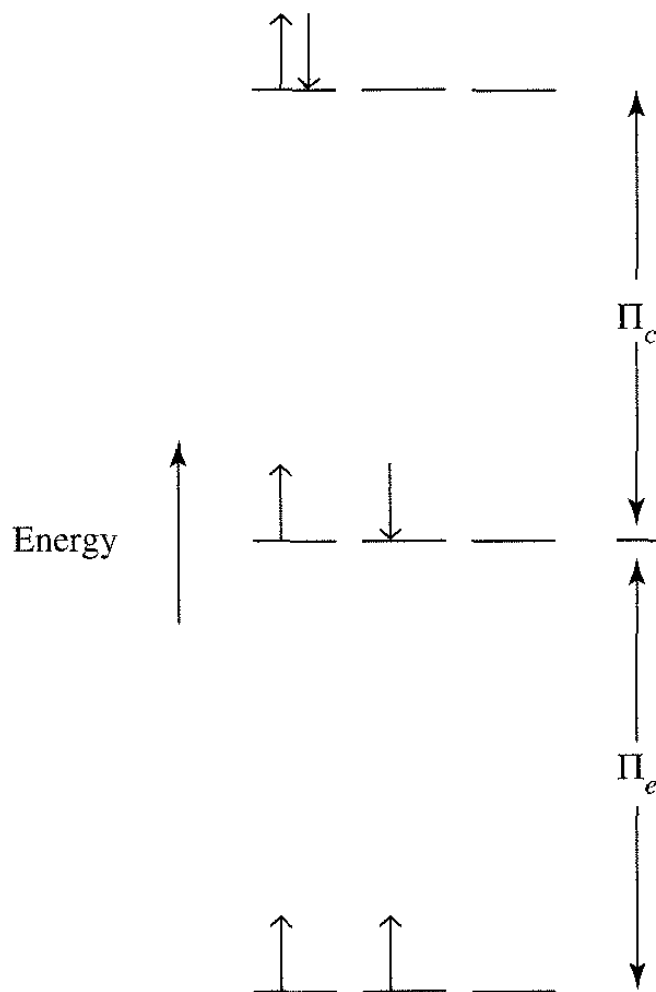


The first arrangement involves Coulombic energy, Π_c , because it is the only one that pairs electrons in the same orbital. The energy of this arrangement is higher than that of the other two by Π_c , as a result of electron-electron repulsion.

In the first two cases there is only one possible way to arrange the electrons to give the same diagram, because there is only a single electron in each having + or - spin. However, in the third case there are two possible ways in which the electrons can be arranged:



The exchange energy is n , per possible exchange of parallel electrons and is negative. The higher the number of possible exchanges, the lower the energy. Consequently, the third configuration is lower in energy than the second by Π_e . The results may be summarized in an energy diagram:



These two pairing terms add to produce the total pairing energy, Π :

$$\Pi = \Pi_c + \Pi_e$$

The Coulombic energy, Π_c , is positive and is nearly constant for each pair of electrons. The exchange energy, Π_e , is negative and is also nearly constant for each possible exchange of electrons with the same spin. When the orbitals are **degenerate** (have the same energy), both Coulombic and pairing energies favor the unpaired configuration over the paired configuration. If there is a difference in energy between the levels involved, this difference, in combination with the total pairing energy, determines the final configuration. For atoms, this usually means that one set of orbitals is filled before another has any electrons. However, this breaks down in some of the transition elements, because the $4s$ and $3d$ (or the higher corresponding levels) are so close in energy that the pairing energy is nearly the same as the difference between levels.

EXAMPLE

Oxygen With four p electrons, oxygen could have two unpaired electrons ($\uparrow\downarrow \quad \uparrow \quad \uparrow$), or it could have no unpaired electrons ($\uparrow\downarrow \quad \uparrow\downarrow \quad \quad$). Find the number of electrons that could be exchanged in each case and the Coulombic and exchange energies for the atom.

$\uparrow\downarrow \quad \uparrow \quad \uparrow$ has one pair, energy contribution Π_c .

$\uparrow\downarrow \quad \uparrow \quad \uparrow$ has one electron with \downarrow spin and no possibility of exchange.

$\uparrow \quad \uparrow \quad \uparrow$ has four possible arrangements, three exchange possibilities (1-2, 1-3, 2-3), energy contribution $3 \Pi_e$:

$\uparrow 1 \quad \uparrow 2 \quad \uparrow 3 \quad \uparrow 2 \quad \uparrow 1 \quad \uparrow 3 \quad \uparrow 3 \quad \uparrow 2 \quad \uparrow 1 \quad \uparrow 1 \quad \uparrow 3 \quad \uparrow 2$

Overall, $3 \Pi_e + \Pi_c$.

$\uparrow\downarrow \quad \uparrow\downarrow \quad \quad$ has one exchange possibility for each spin pair and two pairs.

Overall, $2 \Pi_e + 2 \Pi_c$.

Because Π_c is positive and Π_e is negative, the energy of the first arrangement is lower than the second; $\uparrow\downarrow \quad \uparrow \quad \uparrow$ has the lower energy.

EXERCISE 2-4

A nitrogen atom with three p electrons could have three unpaired electrons ($\uparrow \quad \uparrow \quad \uparrow$), or it could have one unpaired electron ($\uparrow\downarrow \quad \uparrow \quad \quad$). Find the number of electrons that could be exchanged in each case and the Coulombic and exchange energies for the atom. Which arrangement would be lower in energy?

Many schemes have been used to predict the order of filling of atomic orbitals. One, known as Klechkowsky's rule, states that the order of filling the orbitals proceeds from the lowest available value for the sum $n + l$. When two combinations have the same value, the one with the smaller value of n is filled first. Combined with the other rules, this gives the order of filling of most of the orbitals. One of the simplest methods that fits most atoms uses the periodic table blocked out as in Figure 2-9. The electron configurations of hydrogen and helium are clearly $1s^1$ and $1s^2$. After that, the elements in the first two columns on the left (Groups 1 and 2 or IA and IIA) are filling s orbitals, with $l = 0$; those in the six columns on the right (Groups 13 to 18 or IIIA to VIIIA) are filling p orbitals, with $l = 1$; and the ten in the middle (the transition elements, Groups 3 to 12 or IIIB to IIB) are filling d orbitals, with $l = 2$. The lanthanide and actinide series (numbers 58 to 71 and 90 to 103) are filling f orbitals, with $l = 3$. Either of these two methods is too simple, as shown in the following paragraphs, but they do fit most atoms and provide starting points for the others.

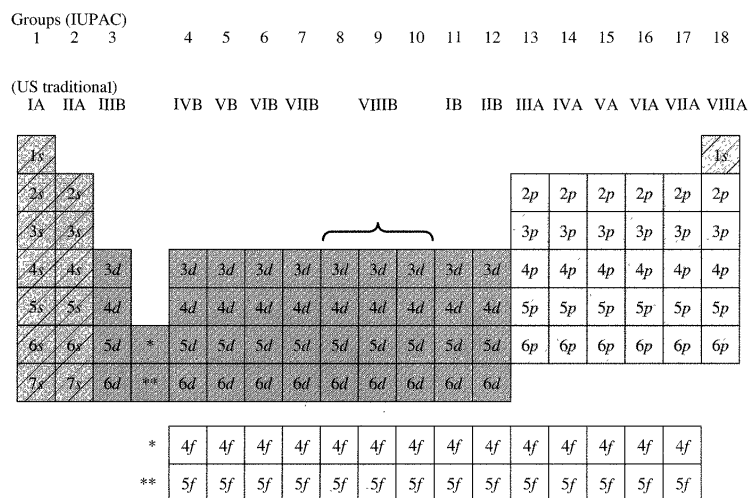
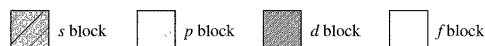


FIGURE 2-9 Atomic Orbital Filling in the Periodic Table.



2-2-4 SHIELDING

In atoms with more than one electron, energies of specific levels are difficult to predict quantitatively, but one of the more common approaches is to use the idea of shielding. Each electron acts as a shield for electrons farther out from the nucleus, reducing the attraction between the nucleus and the distant electrons.

Although the quantum number n is most important in determining the energy, l must also be included in the calculation of the energy in atoms with more than one electron. As the atomic number increases, the electrons are drawn toward the nucleus and the orbital energies become more negative. Although the energies decrease with increasing Z , the changes are irregular because of shielding of outer electrons by inner electrons. The resulting order of orbital filling for the electrons is shown in Table 2-7.

As a result of shielding and other more subtle interactions between the electrons, the simple order of orbitals (in order of energy increasing with increasing n) holds only at very low atomic number Z and for the innermost electrons of any atom. For the outer orbitals, the increasing energy difference between levels with the same n but different l values forces the overlap of energy levels with $n = 3$ and $n = 4$, and $4s$ fills before $3d$. In a similar fashion, $5s$ fills before $4d$, $6s$ before $5d$, $4f$ before $5d$, and $5f$ before $6d$ (Figure 2-10).

Slater formulated a set of simple rules that serve as a rough guide to this effect. He defined the effective nuclear charge Z^* as a measure of the nuclear attraction for an electron. Z^* can be calculated from $Z^* = Z - S$, where Z is the nuclear charge and S is the shielding constant. The rules for determining S for a specific electron are as follows:

1. The electronic structure of the atom is written in groupings as follows:
 $(1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p)$ etc .
2. Electrons in higher groups (to the right in the list above) do not shield those in lower groups.
3. For ns or np valence electrons:
 - a. Electrons in the same ns , np group contribute 0.35 , except the $1s$, where 0.30 works better.
 - b. Electrons in the $n - 1$ group contribute 0.85 .
 - c. Electrons in the $n - 2$ or lower groups contribute 1.00 .
4. For nd and nf valence electrons:
 - a. Electrons in the same nd or nf group contribute 0.35 .
 - b. Electrons in groups to the left contribute 1.00 .

The shielding constant S obtained from the sum of the contributions above is subtracted from the nuclear charge Z to obtain the effective nuclear charge Z^* affecting the selected electron. Some examples follow.

TABLE 2-7
Electron Configurations of the Elements

<i>Element</i>	<i>Z</i>	<i>Configuration</i>	<i>Element</i>	<i>Z</i>	<i>Configuration</i>
H	1	1s ¹	Ce	58	*[Xe]6s ² 4f ¹ 5d ¹
He	2	1s ²	Pr	59	[Xe]6s ² 4f ³
Li	3	[He]2s ¹	Nd	60	[Xe]6s ² 4f ⁴
Be	4	[He]2s ²	Pm	61	[Xe]6s ² 4f ⁵
B	5	[He]2s ² 2p ¹	Sm	62	[Xe]6s ² 4f ⁶
C	6	[He]2s ² 2p ²	Eu	63	[Xe]6s ² 4f ⁷
N	7	[He]2s ² 2p ³	Gd	64	*[Xe]6s ² 4f ⁷ 5d ¹
O	8	[He]2s ² 2p ⁴	Tb	65	[Xe]6s ² 4f ⁹
F	9	[He]2s ² 2p ⁵	Dy	66	[Xe]6s ² 4f ¹⁰
Ne	10	[He]2s ² 2p ⁶	Ho	67	[Xe]6s ² 4f ¹¹
Na	11	[Ne]3s ¹	Er	68	[Xe]6s ² 4f ¹²
Mg	12	[Ne]3s ²	Tm	69	[Xe]6s ² 4f ¹³
Al	13	[Ne]3s ² 3p ¹	Yb	70	[Xe]6s ² 4f ¹⁴
Si	14	[Ne]3s ² 3p ²	Lu	71	[Xe]6s ² 4f ¹⁴ 5d ¹
P	15	[Ne]3s ² 3p ³	Hf	72	[Xe]6s ² 4f ¹⁴ 5d ²
S	16	[Ne]3s ² 3p ⁴	Ta	73	[Xe]6s ² 4f ¹⁴ 5d ³
Cl	17	[Ne]3s ² 3p ⁵	W	74	[Xe]6s ² 4f ¹⁴ 5d ⁴
Ar	18	[Ne]3s ² 3p ⁶	Re	75	[Xe]6s ² 4f ¹⁴ 5d ⁵
K	19	[Ar]4s ¹	Os	76	[Xe]6s ² 4f ¹⁴ 5d ⁶
Ca	20	[Ar]4s ²	Ir	77	[Xe]6s ² 4f ¹⁴ 5d ⁷
Sc	21	[Ar]4s ² 3d ¹	Pt	78	*[Xe]6s ¹ 4f ¹⁴ 5d ⁹
Ti	22	[Ar]4s ² 3d ²	Au	79	*[Xe]6s ¹ 4f ¹⁴ 5d ¹⁰
V	23	[Ar]4s ² 3d ³	Hg	80	[Xe]6s ² 4f ¹⁴ 5d ¹⁰
Cr	24	*[Ar]4s ¹ 3d ⁵	Tl	81	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ¹
Mn	25	[Ar]4s ² 3d ⁵	Pb	82	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ²
Fe	26	[Ar]4s ² 3d ⁶	Bi	83	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ³
Co	27	[Ar]4s ² 3d ⁷	Po	84	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁴
Ni	28	[Ar]4s ² 3d ⁸	At	85	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁵
Cu	29	*[Ar]4s ¹ 3d ¹⁰	Rn	86	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁶
Zn	30	[Ar]4s ² 3d ¹⁰	Fr	87	[Rn]7s ¹
Ga	31	[Ar]4s ² 3d ¹⁰ 4p ¹	Ra	88	[Rn]7s ²
Ge	32	[Ar]4s ² 3d ¹⁰ 4p ²	Ac	89	*[Rn]7s ² 6d ¹
As	33	[Ar]4s ² 3d ¹⁰ 4p ³	Th	90	*[Rn]7s ² 6d ²
Se	34	[Ar]4s ² 3d ¹⁰ 4p ⁴	Pa	91	*[Rn]7s ² 5f ² 6d ¹
Br	35	[Ar]4s ² 3d ¹⁰ 4p ⁵	U	92	*[Rn]7s ² 5f ³ 6d ¹
Kr	36	[Ar]4s ² 3d ¹⁰ 4p ⁶	Np	93	*[Rn]7s ² 5f ⁴ 6d ¹
Rb	37	[Kr]5s ¹	Pu	94	[Rn]7s ² 5f ⁶
Sr	38	[Kr]5s ²	Am	95	[Rn]7s ² 5f ⁷
Y	39	[Kr]5s ² 4d ¹	Cm	96	*[Rn]7s ² 5f ⁷ 6d ¹
Zr	40	[Kr]5s ² 4d ²	Bk	97	[Rn]7s ² 5f ⁹
Nb	41	*[Kr]5s ¹ 4d ⁴	Cf	98	*[Rn]7s ² 5f ⁹ 6d ¹
Mo	42	*[Kr]5s ¹ 4d ⁵	Es	99	[Rn]7s ² 5f ¹¹
Tc	43	[Kr]5s ² 4d ⁵	Fm	100	[Rn]7s ² 5f ¹²
Ru	44	*[Kr]5s ¹ 4d ⁷	Md	101	[Rn]7s ² 5f ¹³
Rh	45	*[Kr]5s ¹ 4d ⁸	No	102	[Rn]7s ² 5f ¹⁴
Pd	46	*[Kr]4d ¹⁰	Lr	103	[Rn]7s ² 5f ¹⁴ 6d ¹
Ag	47	*[Kr]5s ¹ 4d ¹⁰	Rf	104	[Rn]7s ² 5f ¹⁴ 7p ¹
Cd	48	[Kr]5s ² 4d ¹⁰	Db	105	[Rn]7s ² 5f ¹⁴ 6d ²
In	49	[Kr]5s ² 4d ¹⁰ 5p ¹	Sg	106	[Rn]7s ² 5f ¹⁴ 6d ³
Sn	50	[Kr]5s ² 4d ¹⁰ 5p ²	Bh	107	[Rn]7s ² 5f ¹⁴ 6d ⁴
Sb	51	[Kr]5s ² 4d ¹⁰ 5p ³	Hs	108	[Rn]7s ² 5f ¹⁴ 6d ⁵
Te	52	[Kr]5s ² 4d ¹⁰ 5p ⁴	Mt	109	[Rn]7s ² 5f ¹⁴ 6d ⁶
I	53	[Kr]5s ² 4d ¹⁰ 5p ⁵	Uun	110	*[Rn]7s ¹ 5f ¹⁴ 6d ⁹
Xe	54	[Kr]5s ² 4d ¹⁰ 5p ⁶	Uuu	111	[Rn]7s ¹ 5f ¹⁴ 6d ¹⁰
Cs	55	[Xe]6s ¹	Uub	112	[Rn]7s ² 5f ¹⁴ 6d ¹⁰
Ba	56	[Xe]6s ²			
La	57	*[Xe]6s ² 5d ¹			

* Elements with configurations that do not follow the simple order of orbital filling.

NOTE: Actinide configurations are from J. J. Katz, G. T. Seaborg, and L. R. Morss, *The Chemistry of the Actinide Elements*, 2nd ed., Chapman and Hall, New York and London, 1986. Configurations for elements 100 to 112 are predicted, not experimental.

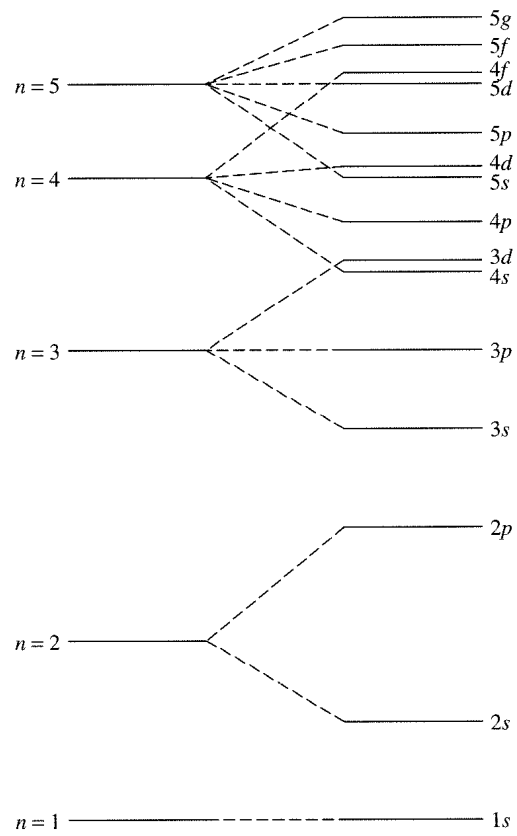


FIGURE 2-10 Energy Level Splitting and Overlap. The differences between the upper levels are exaggerated for easier visualization.

EXAMPLES

Oxygen The electron configuration is $(1s^2)(2s^2 2p^4)$.

For the outermost electron,

$$\begin{aligned}Z^* &= Z - S \\ &= 8 - [2 \times (0.85)] - [5 \times (0.35)] = 4.55 \\ &\qquad\qquad (1s) \qquad\qquad (2s, 2p)\end{aligned}$$

The two $1s$ electrons each contribute 0.85, and the five $2s$ and $2p$ electrons (the last electron is not counted, as we are finding Z^* for it) each contribute 0.35, for a total shielding constant $S = 3.45$. The net effective nuclear charge is then $Z^* = 4.55$. Therefore, the last electron is held with about 57% of the force expected for a +8 nucleus and a -1 electron.

Nickel The electron configuration is $(1s^2)(2s^2 2p^6)(3s^2 3p^6)(3d^8)(4s^2)$.

For a $3d$ electron,

$$\begin{aligned}Z^* &= Z - S \\ &= 28 - [18 \times (1.00)] - [7 \times (0.35)] = 7.55 \\ &\qquad\qquad (1s, 2s, 2p, 3s, 3p) \qquad (3d)\end{aligned}$$

The 18 electrons in the $1s$, $2s$, $2p$, $3s$, and $3p$ levels contribute 1.00 each, the other 7 in $3d$ contribute 0.35, and the $4s$ contribute nothing. The total shielding constant is $S = 20.45$ and $Z^* = 7.55$ for the last $3d$ electron.

For the $4s$ electron,

$$\begin{aligned}Z^* &= Z - S \\ &= 28 - [10 \times (1.00)] - [16 \times (0.85)] - [1 \times (0.35)] = 4.05 \\ &\qquad\qquad (1s, 2s, 2p) \qquad (3s, 3p, 3d) \qquad (4s)\end{aligned}$$

The ten $1s$, $2s$, and $2p$ electrons each contribute 1.00, the sixteen $3s$, $3p$, and $3d$ electrons each contribute 0.85, and the other $4s$ electron contributes 0.35, for a total $S = 23.95$ and $Z^* = 4.05$, considerably smaller than the value for the $3d$ electron above. The $4s$ electron is held less tightly than the $3d$ and should therefore be the first removed in ionization. This is consistent with experimental observations on nickel compounds. Ni^{2+} , the most common oxidation state of nickel, has an electron configuration of $[\text{Ar}]3d^8$ (rather than $[\text{Ar}]3d^6 4s^2$), corresponding to loss of the $4s$ electrons from nickel atoms. All the transition metals follow this same pattern of losing ns electrons more readily than $(n - 1)d$ electrons.

EXERCISE 2-5

Calculate the effective nuclear charge on a $5s$, a $5p$, and a $4d$ electron in a tin atom.

EXERCISE 2-6

Calculate the effective nuclear charge on a $7s$, a $5f$, and a $6d$ electron in a uranium atom.

Justification for Slater's rules (aside from the fact that they work) comes from the electron probability curves for the orbitals. The s and p orbitals have higher probabilities near the nucleus than do d orbitals of the same n , as shown earlier in Figure 2-7. Therefore, the shielding of 3d electrons by (3s, 3p) electrons is calculated as 100% effective (a contribution of 1.00). At the same time, shielding of 3s or 3p electrons by (2s, 2p) electrons is only 85% effective (a contribution of 0.85), because the 3s and 3p orbitals have regions of significant probability close to the nucleus. Therefore, electrons in these orbitals are not completely shielded by (2s, 2p) electrons.

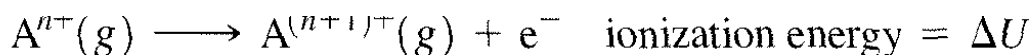
A complication arises at Cr ($Z = 24$) and Cu ($Z = 29$) in the first transition series and in an increasing number of atoms under them in the second and third transition series. This effect places an extra electron in the 3d level and removes one electron from the 4s level. Cr, for example, has a configuration of $[\text{Ar}] 4s^1 3d^5$ (rather than $[\text{Ar}] 4s^2 3d^4$). Traditionally, this phenomenon has often been explained as a consequence of the "special stability of half-filled subshells." Half-filled and filled d and f subshells are, in fact, fairly common, as shown in Figure 2-11. A more accurate explanation considers both the effects of increasing nuclear charge on the energies of the 4s and 3d levels and the interactions (repulsions) between the electrons sharing the same orbital. This approach requires totaling the energies of all the electrons with their interactions; results of the complete calculations match the experimental results.

هنا يوضع الشكل (١٠ - ٢)

PERIODIC PROPERTIES OF ATOMS

2-3-1 IONIZATION ENERGY

The ionization energy, also known as the ionization potential, is the energy required to remove an electron from a gaseous atom or ion:

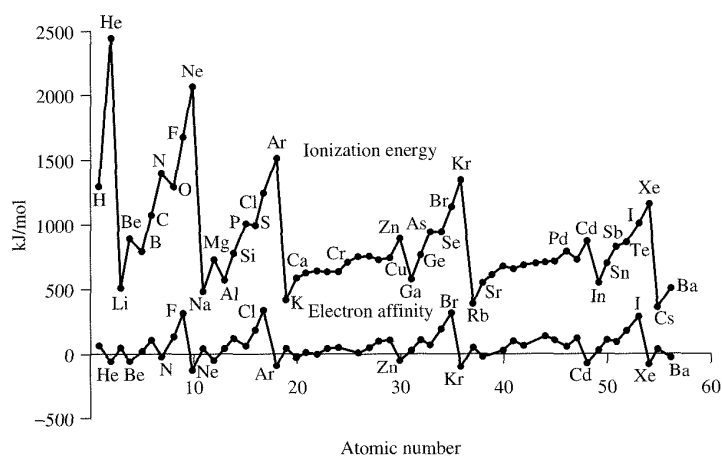


where $n = 0$ (first ionization energy), 1, 2, . . . (second, third, . . .)

As would be expected from the effects of shielding, the ionization energy varies with different nuclei and different numbers of electrons. Trends for the first ionization energies of the early elements in the periodic table are shown in Figure 2-13. The general trend across a period is an increase in ionization energy as the nuclear charge increases. A plot of Z''/r , the potential energy for attraction between an electron and the shielded nucleus, is nearly a straight line, with approximately the same slope as the shorter segments (boron through nitrogen, for example) shown in Figure 2-13 (a different representation is shown later, in Figure 8-3). However, the experimental values show a break in the trend at boron and again at oxygen. Because the new electron in B is in a

new p orbital that has most of its electron density farther away from the nucleus than the other electrons, its ionization energy is smaller than that of the 2s2 electrons of Be. At the fourth p electron, at oxygen, a similar drop in ionization energy occurs. Here, the new electron shares an orbital with one of the previous 2p electrons, and the fourth p electron has a higher energy than the trend would indicate because it must be paired with another in the same p orbital. The pairing energy, or repulsion between two electrons in the same region of space, reduces the ionization energy. Similar patterns appear in lower periods. The transition elements have smaller differences in ionization energies, usually with a lower value for heavier atoms in the same family because of increased shielding by inner electrons and increased distance between the nucleus and the outer electrons.

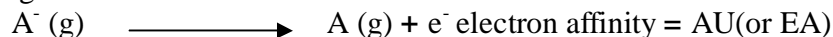
FIGURE 2-13 Ionization Energies and Electron Affinities. Ionization energy = ΔU for $M(g) \longrightarrow M^+(g) + e^-$ (Data from C.E. Moore, *Ionization Potentials and Ionization Limits*, National Standards Reference Data Series, U. S. National Bureau of Standards, Washington, DC, 1970, NSRDS-NBS 34) Electron affinity = ΔU for $M^-(g) \longrightarrow M(g) + e^-$ (Data from H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data*, 1985, 14, 731). Numerical values are in Appendices B-2 and B-3.



Much larger decreases in ionization energy occur at the start of each new period, because the change to the next major quantum number requires that the new *s* electron have a much higher energy. The maxima at the noble gases decrease with increasing *Z* because the outer electrons are farther from the nucleus in the heavier elements. Overall, the trends are toward higher ionization energy from left to right in the periodic table (the major change) and lower ionization energy from top to bottom (a minor change). The differences described in the previous paragraph are superimposed on these more general changes.

2-3-2 ELECTRON AFFINITY

Electron affinity can be defined as the energy required removing an electron from a negative ion:



(Historically, the definition is $-AU$ for the reverse reaction, adding an electron to the neutral atom. The definition we use avoids the sign change.) Because of the similarity of this reaction to the ionization for an atom, electron affinity is sometimes described as the zero ionization energy. This reaction is endothermic (positive *AU*), except for the noble gases and the alkaline earth elements. The pattern of electron affinities with changing *Z* shown in Figure 2-13 is similar to that of the ionization energies, but for one larger *Z* value (one more electron for each species) and with much smaller absolute numbers. For

either of the reactions, removal of the first electron past a noble gas configuration is easy, so the noble gases have the lowest electron affinities. The electron affinities are all much smaller than the corresponding ionization energies because electron removal from a negative ion is easier than removal from a neutral atom.

2-3-3 COVALENT AND IONIC RADII

The sizes of atoms and ions are also related to the ionization energies and electron affinities. As the nuclear charge increases, the electrons are pulled in toward the center of the atom, and the size of any particular orbital decreases. On the other hand, as the nuclear charge increases, more electrons are added to the atom and their mutual repulsion keeps the outer orbitals large. The interaction of these two effects (increasing nuclear charge and increasing number of electrons) results in a gradual decrease in atomic size across each period. Table 2-8 gives nonpolar covalent radii, calculated for ideal molecules with no polarity. There are other measures of atomic size, such as the van der Waals radius, in which collisions with other atoms are used to define the size. It is difficult to obtain consistent data for any such measure, because the polarity, chemical structure, and physical state of molecules change drastically from one compound to another. The numbers shown here are sufficient for a general comparison of one element with another. There are similar problems in determining the size of ions. Because the stable ions of the different elements have different charges and different numbers of electrons, as well as different crystal structures for their compounds, it is difficult to find a suitable set of numbers for comparison. Earlier data were based on Pauling's approach, in which the ratio of the radii of isoelectronic ions was assumed to be equal to the ratio of their effective nuclear charges. More recent calculations are based on a number of considerations, including electron density maps from X-ray data that show larger cations and smaller anions than those previously found. Those in Table 2-9 and Appendix B were called "crystal radii" by Shannon and are generally different from the older values of "ionic radii" by + 14 pm for cations and - 14 pm for anions, as well as being revised because of more recent measurements. The radii in Table 2-9 and Appendix B-1 can be used for rough estimation of the packing of ions in crystals and other calculations, as long as the "fuzzy" nature of atoms and ions is kept in mind. Factors that influence ionic size include the coordination number of the ion, the; covalent character of the bonding, distortions of regular crystal geometries, and delocalization of electrons (metallic or semiconducting character). The radius of the anion is also influenced by the size and charge of the cation (the anion exerts a smaller influence on the radius of the cation).

TABLE 2-8
Nonpolar Covalent Radii (pm)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 32																	He 31
Li 123	Be 89											B 82	C 77	N 75	O 73	F 71	Ne 69
Na 154	Mg 136											Al 118	Si 111	P 106	S 102	Cl 99	Ar 98
K 203	Ca 174	Sc 144	Ti 132	V 122	Cr 118	Mn 117	Fe 117	Co 116	Ni 115	Cu 117	Zn 125	Ga 126	Ge 122	As 120	Se 117	Br 114	Kr 111
Rb 216	Sr 191	Y 162	Zr 145	Nb 134	Mo 130	Tc 127	Ru 125	Rh 125	Pd 128	Ag 134	Cd 148	In 144	Sn 140	Sb 140	Te 136	I 133	Xe 126
Cs 235	Ba 198	La 169	Hf 144	Ta 134	W 130	Re 128	Os 126	Ir 127	Pt 130	Au 134	Hg 149	Tl 148	Pb 147	Bi 146	Po (146)	At (145)	Ra

Source: R. T. Sanderson, *Inorganic Chemistry*, Reinhold, New York, 1967, p. 74; and E. C. M. Chen, J. G. Dojahn, and W. E. Wentworth, *J. Phys. Chem. A*, 1997, 101, 3088.

The values in Table 2-10 show that anions are generally larger than cations with similar numbers of electrons (F^- and Na^+ differ only in nuclear charge, but the radius of fluoride is 37% larger). The radius decreases as nuclear charge increases for ions with the same electronic structure, such as O^{2-} , F^- , Na^+ and Mg^{2+} , with a much larger change with nuclear charge for the cations. Within a family, the ionic radius increases as Z increases because of the larger number of electrons in the ions and, for the same element, the radius decreases with increasing charge on the cation. Examples of these trends are shown in Tables 2- 10, 2- 11, and 2- 12.

TABLE 2-10
Crystal Radius and Nuclear Charge

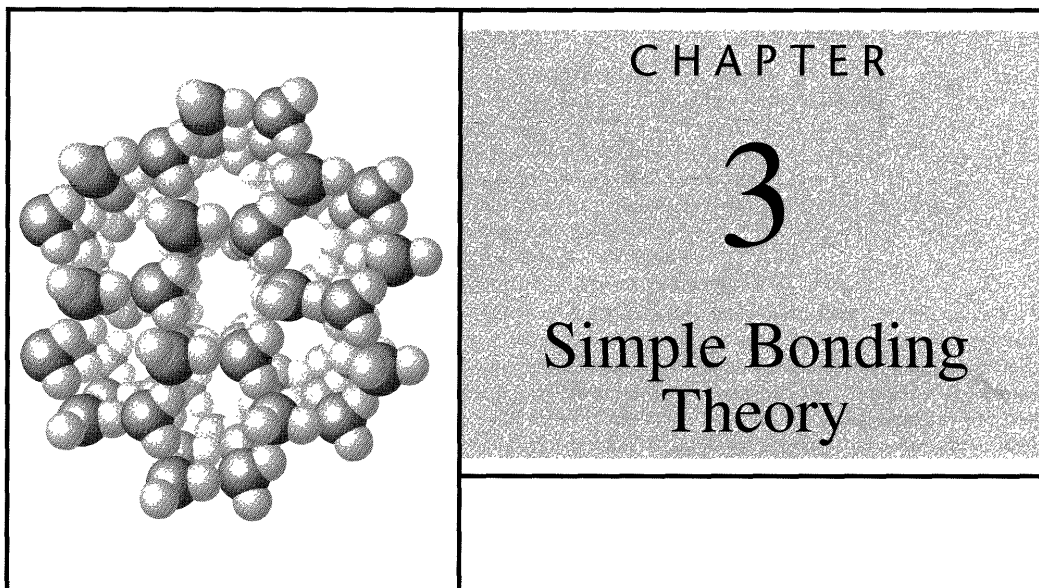
<i>Ion</i>	<i>Protons</i>	<i>Electrons</i>	<i>Radius (pm)</i>
O ²⁻	8	10	126
F ⁻	9	10	119
Na ⁺	11	10	116
Mg ²⁺	12	10	86

TABLE 2-11
Crystal Radius and Total Number of Electrons

<i>Ion</i>	<i>Protons</i>	<i>Electrons</i>	<i>Radius (pm)</i>
O ²⁻	8	10	126
S ²⁻	16	18	170
Se ²⁻	34	36	184
Te ²⁻	52	54	207

TABLE 2-12
Crystal Radius and Ionic Charge

<i>Ion</i>	<i>Protons</i>	<i>Electrons</i>	<i>Radius (pm)</i>
Ti ²⁺	22	20	100
Ti ³⁺	22	19	81
Ti ⁴⁺	22	18	75

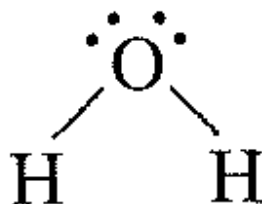


We now turn from the use of quantum mechanics and its description of the atom to an elementary description of molecules. Although most of the discussion of bonding in this book uses the molecular orbital approach to chemical bonding, simpler methods that provide approximate pictures of the overall shapes and polarities of molecules are also very useful. This chapter provides an overview of Lewis dot structures, valence shell electron pair repulsion (VSEPR), and related topics. General chemistry texts include discussions of most of these topics; this chapter provides a review for those who have not used them recently. Ultimately, any description of bonding must be consistent with experimental data on bond lengths, bond angles, and bond strengths. Angles and distances are most frequently determined by diffraction (X-ray crystallography, electron diffraction, neutron diffraction) or spectroscopic (microwave, infrared) methods. For many molecules, there is general agreement on the bonding, although there are alternative ways to describe it.

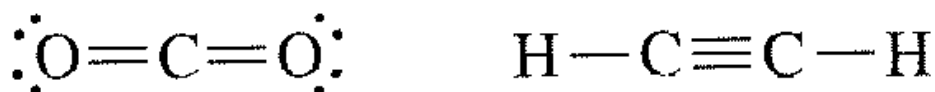
LEWIS ELECTRON DOT DIAGRAMS

Lewis electron-dot diagrams, although very much oversimplified, provide a good starting point for analyzing the bonding in molecules. Credit for their initial use goes to G. N. Lewis, an American chemist who contributed much to thermodynamics and chemical bonding in the early years of the 20th century. In Lewis diagrams, bonds between two atoms exist when they share one or more pairs of electrons. In addition, some molecules have nonbonding pairs (also called lone pairs) of electrons on atoms.

These electrons contribute to the shape and reactivity of the molecule, but do not directly bond the atoms together. Most Lewis structures are based on the concept that eight **valence electrons** (corresponding to *s* and *p* electrons outside the noble gas core) form a particularly stable arrangement, as in the noble gases with *s2p6* configurations. An exception is hydrogen, which is stable with two valence electrons. Also, some molecules require more than eight electrons around a given central atom. Simple molecules such as water follow the **octet rule**, in which eight electrons surround the oxygen atom. The hydrogen atoms share two electrons each with the oxygen, forming the familiar picture with two bonds and two lone pairs:



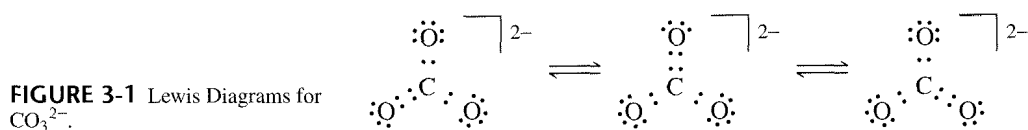
Shared electrons are considered to contribute to the electron requirements of both atoms involved; thus, the electron pairs shared by H and O in the water molecule are counted toward both the 8-electron requirement of oxygen and the 2-electron requirement of hydrogen. Some bonds are double bonds, containing four electrons, or triple bonds, containing six electrons:



3-1 -1 RESONANCE

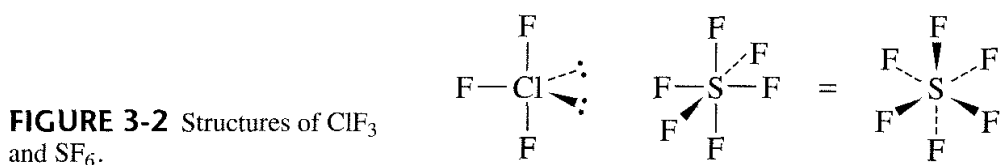
In many molecules, the choice of which atoms are connected by multiple bonds is arbitrary. When several choices exist, all of them should be drawn. For example, as shown in Figure 3-1, three drawings (resonance structures) of CO_3^{2-} are needed to show the double bond in each of the three possible C-O positions. In fact, experimental evidence shows that all the C-O bonds are identical, with bond lengths (129 pm) between double-bond and single-bond distances (116 pm and 143 pm respectively); none of the drawings alone is adequate to describe the molecular structure, which is a combination of all three, not an equilibrium between them. This is called **resonance** to signify that there is more than one possible way in which the valence electrons can be placed in a Lewis structure. Note that in resonance structures, such as those shown for CO_3^{2-} in Figure 3-1, the electrons are drawn in different places but the atomic nuclei remain in fixed positions.

The species CO_3^{2-} , NO_3^- , and SO_3 , are **isoelectronic** (have the same electronic structure). Their Lewis diagrams are identical, except for the identity of the central atom. When a molecule has several resonance structures, its overall electronic energy is lowered, making it more stable. Just as the energy levels of a particle in a box are lowered by making the box larger, the electronic energy levels of the bonding electrons are lowered when the electrons can occupy a larger space.



3-1-2 EXPANDED SHELLS

When it is impossible to draw a structure consistent with the octet rule, it is necessary to increase the number of electrons around the central atom. An option limited to elements of the third and higher periods is to use d orbitals for this expansion, although more recent theoretical work suggests that expansion beyond the s and p orbitals is unnecessary for most main group molecules. In most cases, two or four added electrons will complete the bonding, but more can be added if necessary. Ten electrons are required around chlorine in ClF_3 and 12 around sulfur in SF_6 (Figure 3-2). The increased number of electrons is described as an expanded shell or an expanded electron count.



There are examples with even more electrons around the central atom, such as IF_7 (14 electrons), $[\text{TaF}_8]^{-8}$ (16 electrons), and $[\text{XeF}_8]^{-2}$ (18 electrons). There are rarely more than 18 electrons (2 for S, 6 for P, and 10 for d orbitals) around a single atom in the top half of the periodic table, and crowding of the outer atoms usually keeps the number below this, even for the much heavier atoms with f orbitals energetically available.

3-1-3 FORMAL CHARGE

Formal charges can be used to help in the assessment of resonance structures. The use of formal charges is presented here as a simplified method of describing structures, just as the Bohr atom is a simple method of describing electronic configurations in atoms. Both of these methods are incomplete and newer approaches are more accurate, but they can be useful as long as their limitations are kept in mind. Formal charges can help in assigning bonding when there are several possibilities. This can eliminate the least likely forms when we are considering resonance structures and, in some cases, suggests multiple bonds beyond those required by the octet rule. It is essential, however, to remember that formal charge is only a tool for assessing Lewis structures, not a measure of any actual charge on the atoms. Formal charge is the apparent electronic charge of each atom in a molecule, based on the electron-dot structure. The number of valence electrons available in a free atom of an element minus the total for that atom in the molecule (determined by counting lone pairs as two electrons and bonding pairs as one assigned to each atom) is the formal charge on the atom:

$$\text{Formal charge} = \left(\begin{array}{c} \text{number of valence} \\ \text{electrons in a free} \\ \text{atom of the element} \end{array} \right) - \left(\begin{array}{c} \text{number of unshared} \\ \text{electrons on the atom} \end{array} \right) - \left(\begin{array}{c} \text{number of bonds} \\ \text{to the atom} \end{array} \right)$$

In addition,

Charge on the molecule or ion = sum of all the formal charges Structures minimizing formal charges, placing negative formal charges on more electronegative (in the upper right-hand part of the periodic table) elements, and with smaller separation of charges tend to be favored. Examples of formal charge calculations are given in Appendix D for those who need more review. Three examples, SCN^- , OCN^- , and CNO^- , will illustrate the use of formal charges in describing electronic structures.

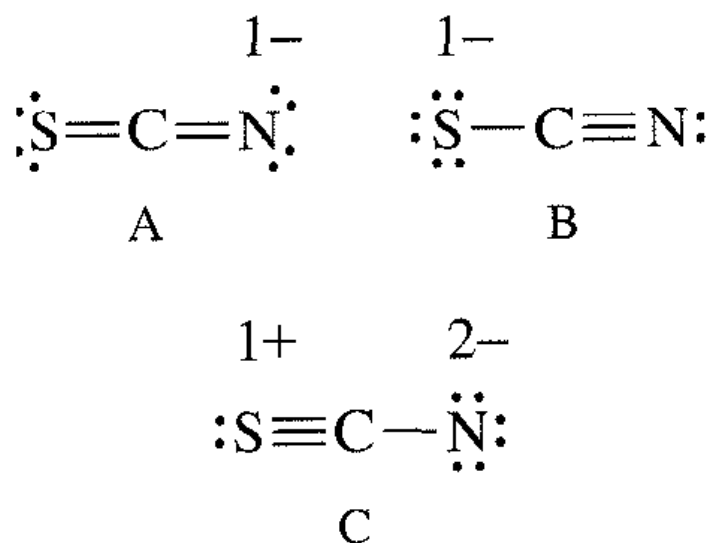


FIGURE 3-3 Resonance Structures of Thiocyanate, SCN^- .

3-1-4 MULTIPLE BONDS IN Be AND B COMPOUNDS

A few molecules, such as BeF_2 , BeCl_2 , and BF_3 , seem to require multiple bonds to satisfy the octet rule for Be and B, even though we do not usually expect multiple bonds for fluorine and chlorine. Structures minimizing formal charges for these molecules have only four electrons in the valence shell of Be and six electrons in the valence shell of B, in both cases less than the usual octet. The alternative, requiring eight electrons on the central atom, predicts multiple bonds, with BeF_2 analogous to CO_2 and BF_3 analogous to SO_3 (Figure 3-7). These structures, however, result in formal charges (2- on Be and 1+ on F in BeF_2 , and 1- on B and 1+ on the double-bonded F in BF_3), which are unlikely by the usual rules.

It has not been experimentally determined whether the bond lengths in BeF_2 and BeCl_2 are those of double bonds, because molecules with clear-cut double bonds are not available for comparison. In the solid, a complex network is formed with coordination number 4 for the Be atom (see Figure 3-7). BeCl_2 tends to dimerize to a 3-coordinate structure in the vapor phase, but the linear monomer is also known at high temperatures. The monomeric structure is unstable; in the dimer and polymer, the halogen atoms share lone pairs with the Be atom and bring it closer to the octet structure. The monomer is still frequently drawn as a singly bonded structure with only four electrons around the beryllium and the ability to accept more from lone pairs of other molecules (Lewis acid behavior).

Bond lengths in all the boron trihalides are shorter than expected for single bonds, so the partial double bond character predicted seems reasonable in spite of the formal charges. Molecular orbital calculations for these molecules support significant double bond character. On the other hand, they combine readily with other molecules that can contribute a lone pair of electrons (Lewis bases), forming a roughly tetrahedral structure with four bonds:

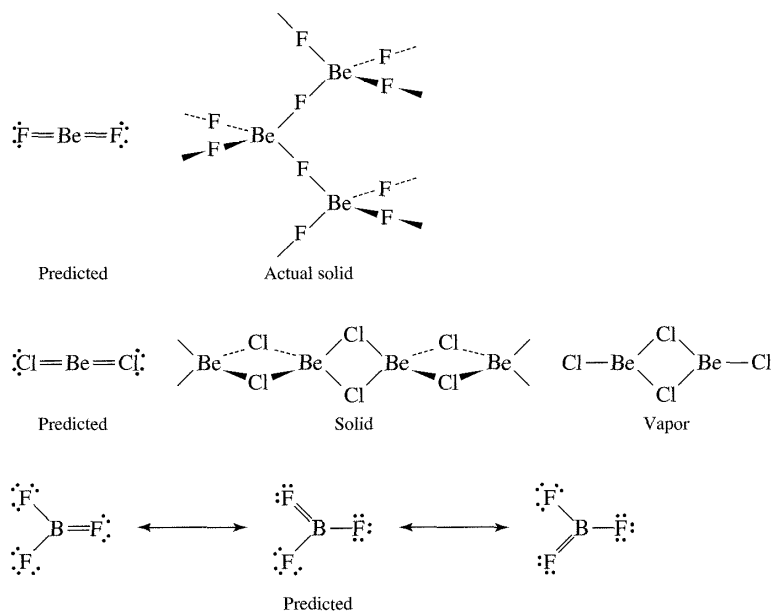
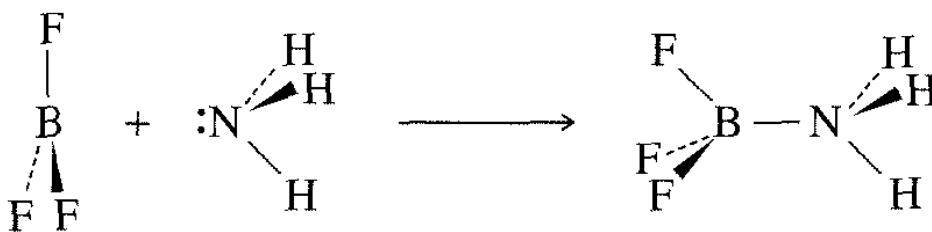


FIGURE 3-7 Structures of BeF_2 , BeCl_2 , and BF_3 . (Reference: A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, Oxford, England, 1984, pp. 412, 1047.)

The B—F bond length is 131 pm;
the calculated single-bond length is 152 pm.

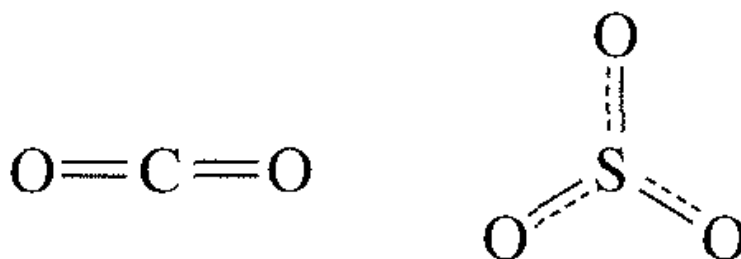


Because of this tendency, they are frequently drawn with only six electrons around the boron. Other boron compounds that do not fit simple electron-dot structures include the hydrides, such as B_2H_6 , and a large array of more complex molecules.

VALENCE SHELL ELECTROSTATIC REPULSION THEORY

Valence shell electron pair repulsion theory (VSEPR) provides a method for predicting the shape of molecules, based on the electron pair electrostatic repulsion. It was described by Sidgwick and Powell in 1940 and further developed by Gillespie and Nyholm in 1957. In spite of this method's very simple approach, based on Lewis electron-dot structures, the VSEPR method predicts shapes that compare favorably with those determined experimentally. However, this approach at best provides approximate shapes for molecules, not a complete picture of bonding. The most common method of determining the actual structures is X-ray diffraction, although electron diffraction, neutron diffraction, and many types of spectroscopy are also used.

Electrons repel each other because they are negatively charged. The quantum mechanical rules force some of them to be fairly close to each other in bonding pairs or lone pairs, but each pair repels all other pairs. According to the VSEPR model, therefore, molecules adopt geometries in which their valence electron pairs position themselves as far from each other as possible. A molecule can be described by the generic formula AX_mE_n where A is the central atom, X stands for any atom or group of atoms surrounding the central atom, and E represents a lone pair of electrons. The **steric number** ($SN = m + n$) is the number of positions occupied by atoms or lone pairs around a central atom; lone pairs and bonds are nearly equal in their influence on molecular shape.



Carbon dioxide is an example with two bonding positions ($SN = 2$) on the central atom and double bonds in each direction. The electrons in each double bond must be between C and O, and the repulsion between the electrons in the double bonds forces a linear structure on the molecule. Sulfur trioxide has three bonding positions ($SN = 3$), with partial double bond character in each. The best positions for the oxygen's in this molecule are at the corners of an equilateral triangle, with O - S - O bond angles of 120° . The multiple bonding does not affect the geometry because it is shared equally among the three bonds.

The same pattern of finding the Lewis structure and then matching it to a geometry that minimizes the repulsive energy of bonding electrons is followed through steric numbers four, five, six, seven, and eight, as shown in Figure 3-8. The structures for two, three, four, and six electron pairs are completely regular, with all bond angles and distances the same. Neither 5- nor 7-coordinate structures can have uniform angles and distances, because there are no regular polyhedra with these numbers of vertices. The 5-coordinate molecules have a trigonal bipyramidal structure, with a central triangular

plane of three positions plus two other positions above and below the center of the plane. The 7-coordinate molecules have a pentagonal bipyramidal structure, with a pentagonal plane of five positions and positions above and below with the top and bottom faces twisted 45° into the antiprism arrangement, as shown in Figure 3-9. It has three different bond angles for adjacent fluorines. $[\text{TaF}_8]^{3-}$ square antiprism symmetry, but is distorted from this ideal in the solid. (A simple cube has only the 109.5 and 70.5° bond angles measured between two corners and the center of the cube, because all edges are equal and any square face can be taken as the bottom or top.)


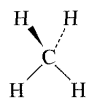
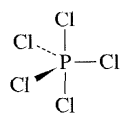
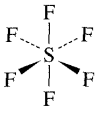
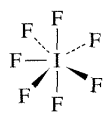
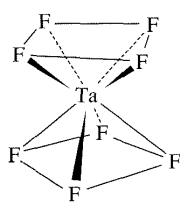
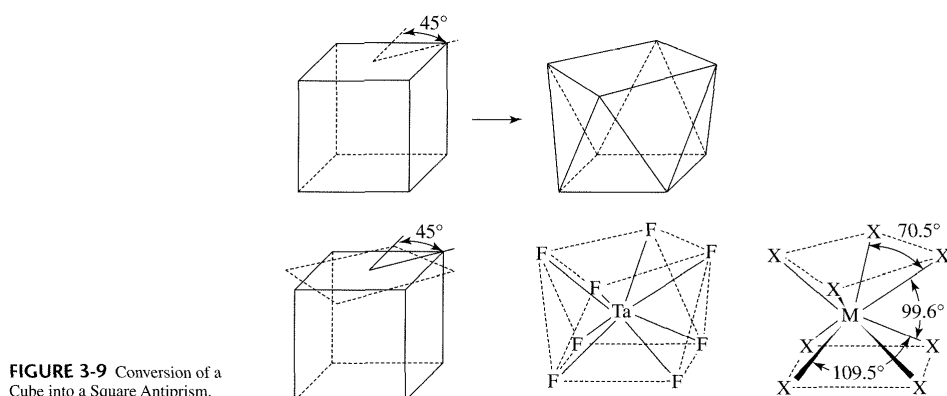
<i>Steric Number</i>	<i>Geometry</i>	<i>Examples</i>	<i>Calculated Bond Angles</i>	
2	Linear	CO_2	180°	$\text{O}=\text{C}=\text{O}$
3	Planar triangular (trigonal)	SO_3	120°	
4	Tetrahedral	CH_4	109.5°	
5	Trigonal bipyramidal	PCl_5	$120^\circ, 90^\circ$	
6	Octahedral	SF_6	90°	
7	Pentagonal bipyramidal	IF_7	$72^\circ, 90^\circ$	
8	Square antiprismatic	TaF_8^{3-}	$70.5^\circ, 99.6^\circ, 109.5^\circ$	

FIGURE 3-8 VSEPR Predictions.



3-2-1 LONE PAIR REPULSION

We must keep in mind that we are always attempting to match our explanations to experimental data. The explanation that fits the data best should be the current favorite, but new theories are continually being suggested and tested. Because we are working with such a wide variety of atoms and molecular structures, it is unlikely that a single, simple approach will work for all of them. Although the fundamental ideas of atomic and molecular structures are relatively simple, their application to complex molecules is not. It is also helpful to keep in mind that for many purposes, prediction of exact bond angles is not usually required. To a first approximation, lone pairs, single bonds, double bonds, and triple bonds can all be treated similarly when predicting molecular shapes.

However, better predictions of overall shapes can be made by considering some important differences between lone pairs and bonding pairs. These methods are sufficient to show the trends and explain the bonding, as in explaining why the H - N - H angle in ammonia is smaller than the tetrahedral angle in methane and larger than the H - O - H angle in water.

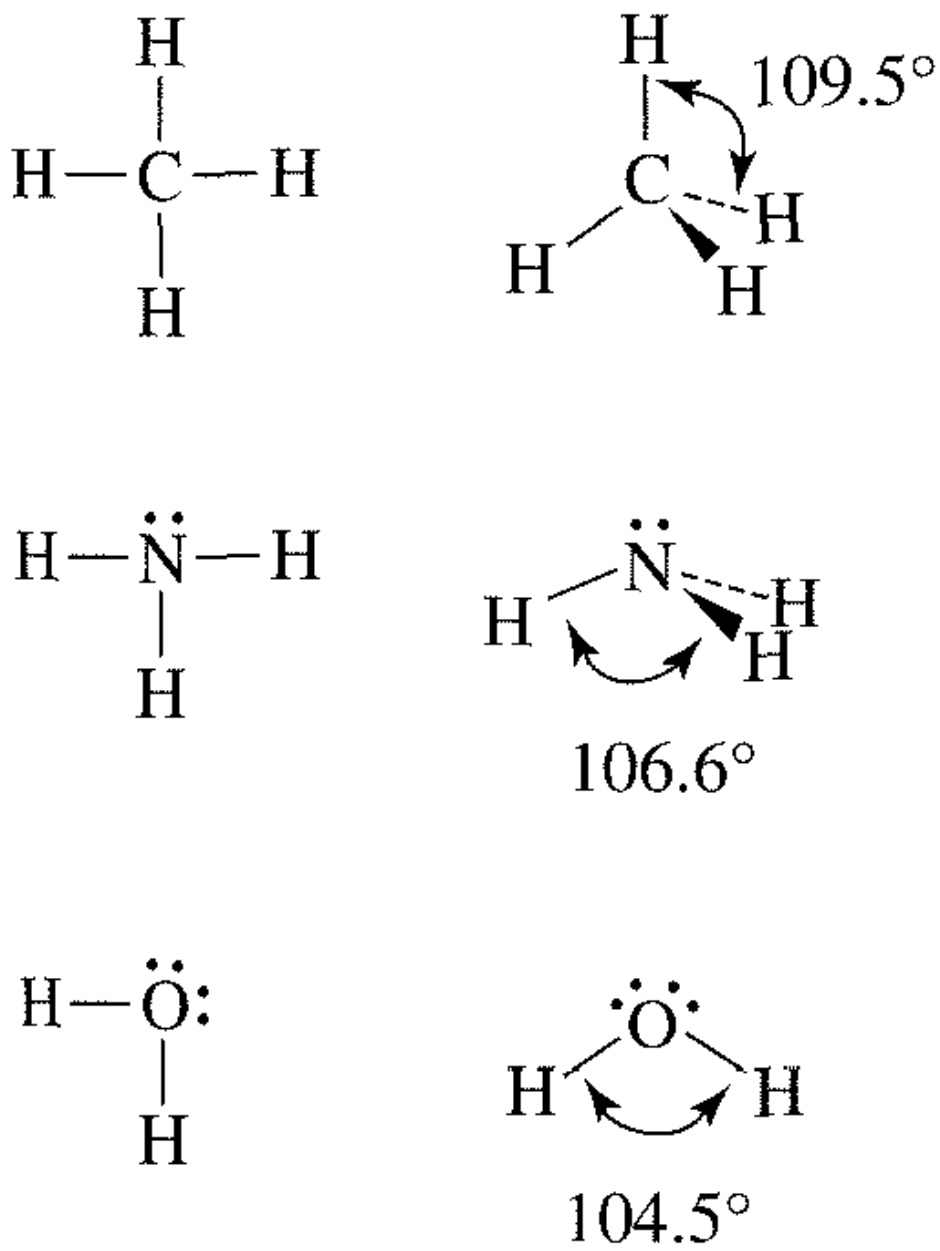


FIGURE 3-10 Shapes of Methane, Ammonia, and Water.

Steric number = 4

The isoelectronic molecules CH_4 , NH_3 , and H_2O (Figure 3-10) illustrate the effect of lone pairs on molecular shape. Methane has four identical bonds between carbon and each of the hydrogens. When the four pairs of electrons are arranged as far from each other as possible, the result is the familiar tetrahedral shape. The tetrahedron, with all H-C-H angles measuring 109.5° , has four identical bonds.

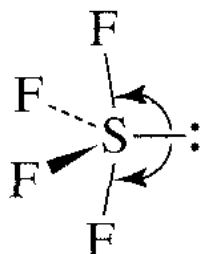
Ammonia also has four pairs of electrons around the central atom, but three are bonding pairs between **N** and **H** and the fourth is a lone pair on the nitrogen. The nuclei form a trigonal pyramid with the three bonding pairs; with the lone pair, they make a nearly tetrahedral shape. Because each of the three bonding pairs is attracted by two positively charged nuclei (**H** and **N**), these pairs are largely confined to the regions between the **H** and **N** atoms. The lone pair, on the other hand, is concentrated near the nitrogen; it has no second nucleus to confine it to a small region of space. Consequently, the lone pair tends to spread out and to occupy more space around the nitrogen than the bonding pairs. As a result, the **H-N-H** angles are 106.6° , nearly 3° smaller than the angles in methane. The same principles apply to the water molecule, in which two lone pairs and two bonding pairs repel each other. Again, the electron pairs have a nearly tetrahedral arrangement, with the atoms arranged in a V shape. The angle of largest repulsion, between the two lone pairs, is not directly measurable. However, the lone pair-bonding pair (**lp-bpr**) repulsion is greater than the bonding pair-bonding pair (**bp-bp**) repulsion, and as a result the **H-O-H** bond angle is only 104.5° , another 2.1° decrease from the ammonia angles. The net result is that we can predict approximate molecular shapes by assigning more space to lone electron pairs; being attracted to one nucleus rather than two, the lone pairs are able to spread out and occupy more space.

Steric number = 5

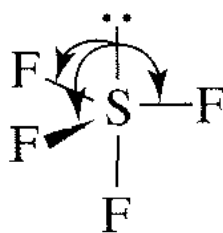
For trigonal bipyramidal geometry, there are two possible locations of lone pairs, axial and equatorial. If there is a single lone pair, for example in SF_4 , the lone pair occupies an equatorial position. This position provides the lone pair with the most space and minimizes the interactions between the lone pair and bonding pairs. If the lone pair were axial, it would have three 90° interactions with bonding pairs; in an equatorial position it has only two such interactions, as shown in Figure 3-11. The actual structure is distorted by the lone pair as it spreads out in space and effectively squeezes the rest of the molecule together.

ClF_3 provides a second example of the influence of lone pairs in molecules having a steric number of 5. There are three possible structures for ClF_3 , as shown in Figure 3-12. Lone pairs in the figure are designated **lp** and bonding pairs are **bp**. In determining the structure of molecules, the lone pair-lone pair interactions are most important, with the lone pair-bonding pair interactions next in importance. In addition, interactions at angles of 90° or less are most important; larger angles generally have less influence. In ClF_3 , structure B can be eliminated quickly because of the 90° **lp-lp** angle. The **lp-lp** angles are large for A and C, so the choice must come from the **lp-bp** and **bp-bp**

angles. Because the $Lp-bp$ angles are more important, C, which has only four 90° $lp-bp$ interactions, is favored over A, which has six such interactions.



Equatorial lone pair



Axial lone pair

FIGURE 3-11 Structure of SF_4 .

	<i>Calculated</i>			<i>Experimental</i>
	A	B	C	
$lp-lp$	180°	90°	120°	cannot be determined
$lp-bp$	6 at 90°	3 at 90°	4 at 90°	cannot be determined
$bp-bp$	3 at 120°	2 at 120°	2 at 120°	2 at 87.5°
		2 at 90°	2 at 90°	Axial Cl—F 169.8 pm
		1 at 120°		Equatorial Cl—F 159.8 pm

FIGURE 3-12 Possible Structures of ClF_3 .

Experiments have confirmed that the structure is based on C, with slight distortions due to the lone pairs. The lone pair-bonding pair repulsion causes the **lp-bp** angles to be larger than 90° and the **bp-bp** angles less than 90 (actually, 87.5). The C1 -F bond distances show the repulsive effects as well, with the axial fluorines (approximately 90° **lp-bp** angles) at 169.8 pm and the equatorial fluorine (in the plane with two lone pairs) at 159.8 pm. Angles involving lone pairs cannot be determined experimentally. The angles in Figure 3-12 are calculated assuming maximum symmetry consistent with the experimental shape.

Additional examples of structures with lone pairs are illustrated in Figure 3-13. Notice that the structures based on a trigonal bipyramidal arrangement of electron pairs around a central atom always place any lone pairs in the equatorial plane, as in SF₄, BrF₃, and XeF₂. These are the shapes that minimize both lone pair-lone pair and lone pair-bonding pair repulsions. The shapes are called teeter-totter or seesaw (SF₄), distorted T (BrF₃), and linear (XeF₂)

Steric Number	Number of Lone Pairs on Central Atom			
	None	1	2	3
2	:Cl=Be=Cl:			
3				
4				
5				
6				

FIGURE 3-13 Structures Containing Lone Pairs.

3-2-2 MULTIPLE BONDS

The VSEPR model considers double and triple bonds to have slightly greater repulsive effects than single bonds because of the repulsive effect of a electrons. For example, the $\text{H}_3\text{C}-\text{C}-\text{CH}_3$ angle in $(\text{CH}_3)_2\text{C}=\text{CH}_2$ is smaller and the $\text{H}_3\text{C}-\text{C}=\text{CH}_2$ angle is larger than the trigonal 120 (Figure 3-14).~ Additional examples of the effect of multiple bonds on molecular geometry are shown in Figure 3-15. Comparing Figures 3-14 and 3-15 indicates that multiple bonds tend to occupy the same positions as lone pairs. For example, the double bonds to oxygen in SOF_4 , ClO_2F_3 , and XeO_3F_2 are all equatorial, as are the lone pairs in the matching compounds of steric number 5, SF_4 , BrF_3 , and XeF_2 . Also, multiple bonds, like lone pairs, tend to occupy more space than single bonds and to cause distortions that in effect squeeze the rest of the molecule together. In molecules that have both lone pairs and multiple bonds, these features may compete for space; examples are shown in Figure 3-16.

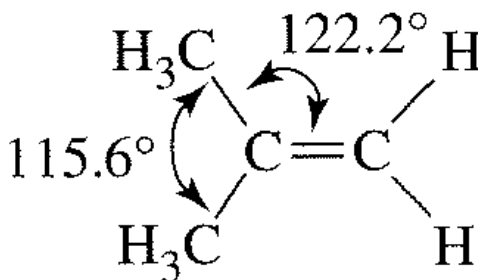


FIGURE 3-14 Bond Angles in $(\text{CH}_3)_2\text{C}=\text{CH}_2$.

POLAR MOLECULES

Whenever atoms with different electronegativities combine, the resulting molecule has polar bonds, with the electrons of the bond concentrated (perhaps very slightly) on the more electronegative atom; the greater the difference in electronegativity, the more polar the bond. As a result, the bonds are dipolar, with positive and negative ends. This polarity causes specific interactions between molecules, depending on the overall structure of the molecule. Experimentally, the polarity of molecules is measured indirectly by measuring the dielectric constant, which is the ratio of the capacitance of a cell filled with the substance to be measured to the capacitance of the same cell with a vacuum between the electrodes. Orientation of polar molecules in the electric field

partially cancels the effect of the field and results in a larger dielectric constant. Measurements at different temperatures allow calculation of the **dipole moment** for the molecule, defined as

$$\mu = Qr$$

Where Q is the charge on each of two atoms separated by a distance, r. Dipole moments of diatomic molecules can be calculated directly. In more complex molecules, vector addition of the individual bond dipole moments gives the net molecular dipole moment. However, it is usually not possible to calculate molecular dipoles directly from bond dipoles. Table 3-7 shows experimental and calculated dipole moments of chloromethanes. The values calculated from vectors use C-H and C-Cl bond dipoles of 1.3 and 4.9×10^{-30} C m, respectively, and tetrahedral bond angles. Clearly, calculating dipole moments is more complex than simply adding the vectors for individual bond moments, but we will not consider that here. For most purposes, a qualitative approach is sufficient.

TABLE 3-7
Dipole Moments of Chloromethanes

<i>Molecule</i>	<i>Experimental (D)</i>	<i>Calculated (D)</i>	
		<i>Calculated from Vectors</i>	<i>Calculated by PC Spartan</i>
CH ₃ Cl	1.87	1.77	1.51
CH ₂ Cl ₂	1.60	2.08	1.50
CHCl ₃	1.01	1.82	1.16

The dipole moments of NH₃, H₂O, and NF₃ (Figure 3-17) reveal the effect of lone pairs, which can be dramatic. In ammonia, the averaged N - H bond polarities and the lone pair all point in the same direction, resulting in a large dipole moment. Water has an even larger dipole moment because the polarities of the O -H bonds and the two lone pairs results in polarities all reinforcing each other. On the other hand, NF₃ has a very small dipole moment, the result of the polarity of the three N-F bonds opposing polarity of the lone pair. The sum of the three N-F bond moments is larger than the lone pair effect, and the lone pair is the positive end of the molecule. In cases such as those of NF₃ and SO₂, the direction of the dipole is not easily predicted because of the opposing polarities. SO₂ has a large dipole moment (1.63 D), with the polarity of the lone pair prevailing over that of the S - O bonds. Molecules with dipole moments interact electrostatically with each other and with other polar molecules. When the dipoles are large enough, the molecules orient themselves with the positive end of one molecule toward the negative end of another because of these attractive forces, and higher melting and boiling points result.

On the other hand, if the molecule has a very symmetric structure or if the polarities of different bonds cancel each other, the molecule as a whole may be nonpolar, even though the individual bonds are quite polar. Tetrahedral molecules such as CH₄ and CCl₄ and trigonal molecules and ions such as SO₃, NO₃⁻, and CO₃⁻ are -all nonpolar. The

C - H bond has very little polarity, but the bonds in the other molecules and ions are quite polar. In all these cases, the sum of all the polar bonds is zero because of the symmetry of the molecules, as shown in Figure 3-18. Nonpolar molecules, whether they have polar bonds or not, still have intermolecular attractive forces acting on them. Small fluctuations in the electron density in such

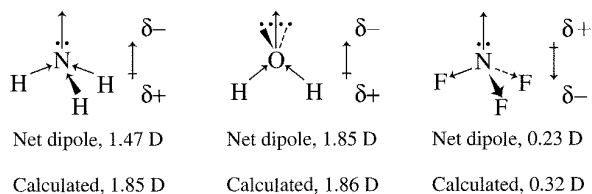


FIGURE 3-17 Bond Dipoles and Molecular Dipoles.

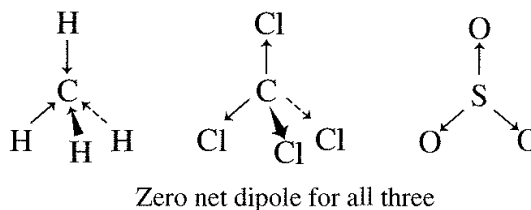


FIGURE 3-18 Cancellation of Bond Dipoles due to Molecular Symmetry.

molecules create small temporary dipoles, with extremely short lifetimes. These dipoles in turn attract or repel electrons in adjacent molecules, setting up dipoles in them as well. The result is an overall attraction among molecules. These attractive forces are called **London** or **dispersion forces**, and make liquefaction of the noble gases and nonpolar molecules such as hydrogen, nitrogen, and carbon dioxide possible. As a general rule, London forces are more important when there are more electrons in a molecule, because the attraction of the nuclei is shielded by inner electrons and the electron cloud is more polarizable.

HYDROGEN BONDING

Ammonia, water, and hydrogen fluoride all have much higher boiling points than other similar molecules, as shown in Figure 3-19. In water and hydrogen fluoride, these high boiling points are caused by hydrogen bonds, in which hydrogen atoms bonded to O or F also form weaker bonds to a lone pair of electrons on another O or F. Bonds between hydrogen and these strongly electronegative atoms are very polar, with a partial positive charge on the hydrogen. This partially positive H is strongly attracted to the partially negative O or F of neighboring molecules. In the past, the attraction among these molecules was considered primarily electrostatic in nature, but an alternative molecular orbital approach, gives a more complete description of this phenomenon. Regardless of the detailed explanation of the forces involved in hydrogen bonding, the strongly positive H and the strongly negative lone pairs tend to line up and hold the molecules together.

Other atoms with high electronegativity, such as Cl, can also form hydrogen bonds in strongly polar molecules such as chloroform, CHCl_3 .

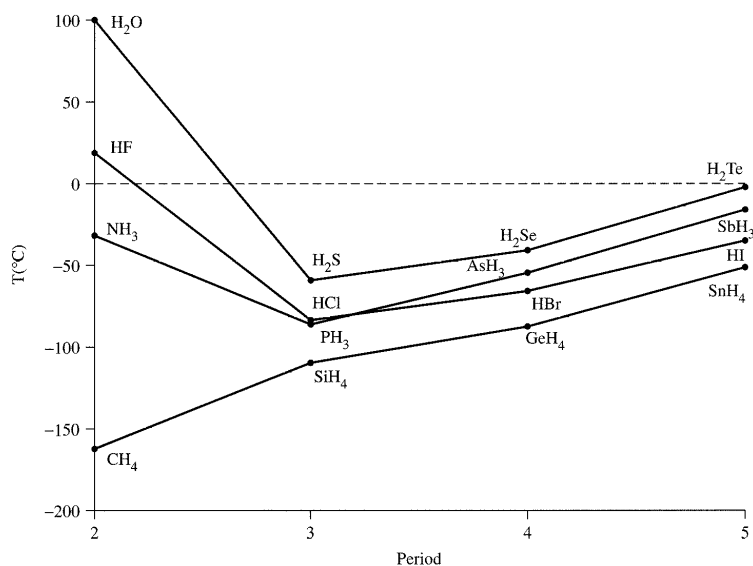


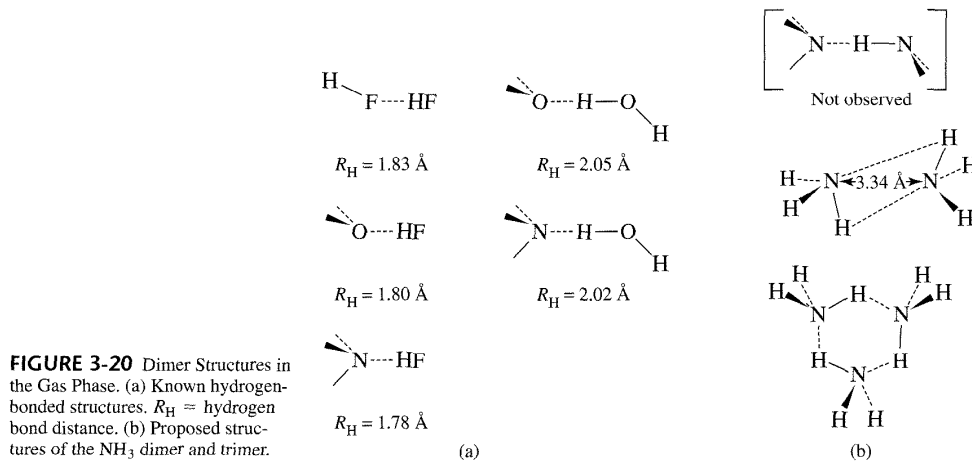
FIGURE 3-19 Boiling Points of Hydrogen Compounds.

In general, boiling points rise with increasing molecular weight, both because the additional mass requires higher temperature for rapid movement of the molecules and because the larger number of electrons in the heavier molecules provides larger London forces. The difference in temperature between the actual boiling point of water and the extrapolation of the line connecting the boiling points of the heavier analogous compounds is almost 200 C. Ammonia and hydrogen fluoride have similar but smaller differences from the extrapolated values for their families. Water has a much larger effect, because each molecule can have as many as four hydrogen bonds (two through the lone pairs and two through the hydrogen atoms). Hydrogen fluoride can average no more than two, because HF has only one H available.

Hydrogen bonding in ammonia is less certain. Several experimental studies⁴ in the gas phase fit a model of the dimer with a "cyclic" structure, although probably asymmetric, as shown in Figure 3-20(b). Theoretical studies depend on the method of calculation, the size of the basis set used (how many functions are used in the fitting), and the assumptions used by the investigators, and conclude that the structure is either linear or cyclic, but that in any case it is very far from rigid. The umbrella vibrational mode (inverting the NH_3 tripod like an umbrella in a high wind) and the interchange mode (in which the angles between the molecules switch) appear to have transitions that allow easy conversions between the two extremes of a dimer with a near-linear N - H - N hydrogen bond and a centrosymmetric dimer with C_{2h} symmetry. Linear N-H-N bonds seem more likely in larger clusters, as confirmed by both experiment and calculation.

There is no doubt that the ammonia molecule can accept a hydrogen and form a hydrogen bond through the lone pair on the nitrogen atom with H_2O , HF, and other polar molecules, but it does not readily donate a hydrogen atom to another molecule. On the

other hand, hydrogen donation from nitrogen to carbonyl oxygen is common in proteins and hydrogen bonding in both directions to nitrogen is found in the DNA double helix.



Water has other unusual properties because of hydrogen bonding. For example, the freezing point of water is much higher than that of similar molecules. An even more striking feature is the decrease in density as water freezes. The tetrahedral structure around each oxygen atom with two regular bonds to hydrogen and two hydrogen bonds to other molecules requires a very open structure with large spaces between ice molecules (Figure 3-21). This makes the solid less dense than the more random liquid water surrounding it, so ice floats. Life on earth would be very different if this were not so. Lakes, rivers, and oceans would freeze from the bottom up, ice cubes would sink, and ice fishing would be impossible. The results are difficult to imagine, but would certainly require a much different biology and geology. The same forces cause coiling of protein and polynucleic acid molecules (Figure 3-22); a combination of hydrogen bonding with other dipolar forces imposes considerable secondary structure on these large molecules.

In Figure 3-22(a), hydrogen bonds between carbonyl oxygen atoms and hydrogens attached to nitrogen atoms hold the molecule in a helical structure. In Figure 3-22(b), similar hydrogen bonds hold the parallel peptide chains together; the bond angles of the chains result in the pleated appearance of the sheet formed by the peptides. These are two of the many different structures that can be formed from peptides, depending on the side-chain groups R and the surrounding environment.

Another example is a theory of anesthesia by non-hydrogen bonding molecules such as cyclopropane, chloroform, and nitrous oxide, proposed by Pauling. These molecules are of a size and shape that can fit neatly into a hydrogen-bonded water structure with even larger open spaces than ordinary ice. Such structures, with molecules trapped in holes in a

solid, are called **clathrates**. Pauling proposed that similar hydrogen-bonded microcrystals form even more readily in nerve tissue because of the presence of other solutes in the tissue. These microcrystals could then interfere with the transmission of nerve impulses. Similar structures of methane and water are believed to hold large quantities of methane in the polar ice caps. The amount of methane in such crystals can be so great that they burn if ignited .

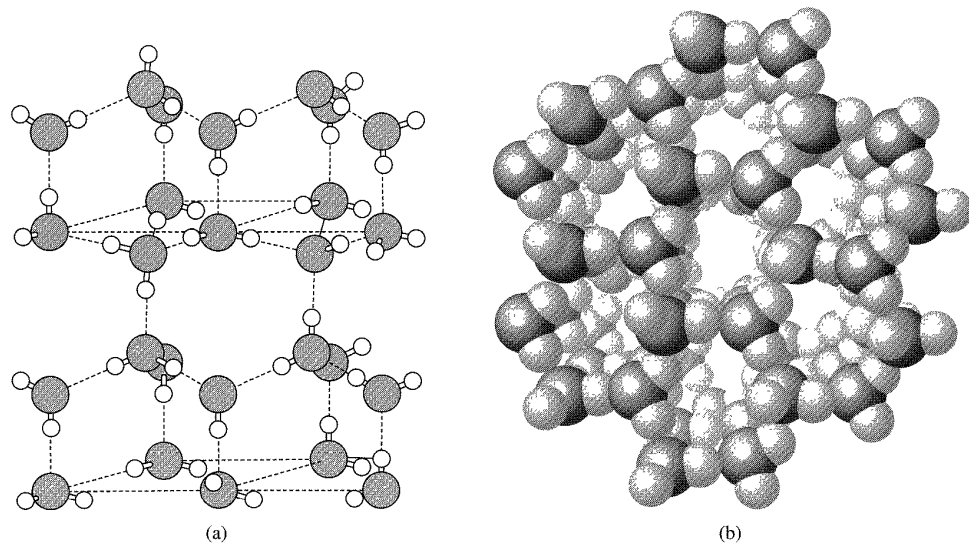
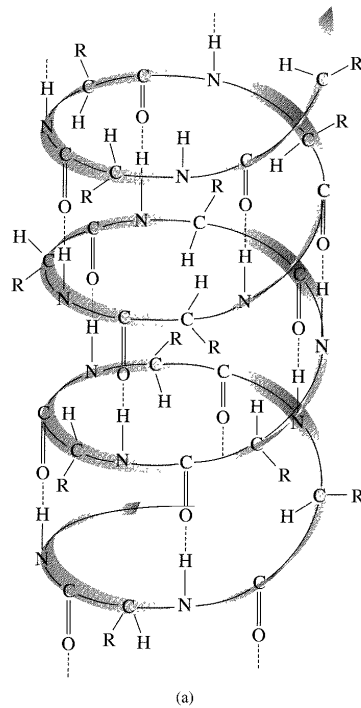
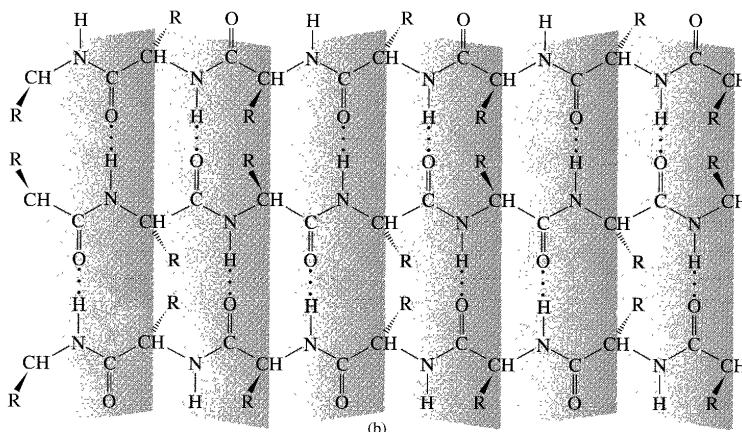


FIGURE 3-21 Two Drawings of Ice. (a) From T. L. Brown and H. E. LeMay, Jr., *Chemistry, The Central Science*, Prentice Hall, Englewood Cliffs, NJ, 1988, p. 628. Reproduced with permission. The rectangular lines are included to aid visualization; all bonding is between hydrogen and oxygen atoms. (b) Copyright © 1976 by W. G. Davies and J. W. Moore, used by permission; reprinted from *Chemistry*, J. W. Moore, W. G. Davies, and R. W. Collins, McGraw-Hill, New York, 1978. All rights reserved.



(a)



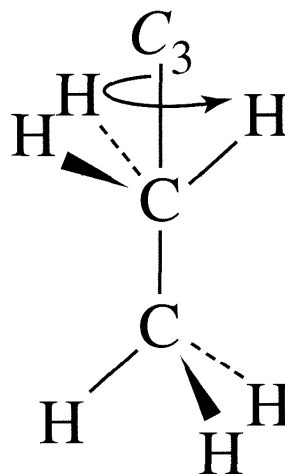
(b)

FIGURE 3-22 Hydrogen-Bonded Protein Structures. (a) A protein α helix. Peptide carbonyls and N—H hydrogens on adjacent turns of the helix are hydrogen-bonded. (From T. L. Brown and H. E. LeMay, Jr., *Chemistry, the Central Science*, Prentice Hall, Englewood Cliffs, NJ, 1988, p. 946. Reproduced with permission.) (b) The pleated sheet arrangement. Each peptide carbonyl group is hydrogen-bonded to a N—H hydrogen on an adjacent peptide chain. (Reproduced with permission from L. G. Wade, Jr., *Organic Chemistry*, Prentice Hall, Englewood Cliffs, NJ, 1988, pp. 1255–1256.)

CHAPTER

4

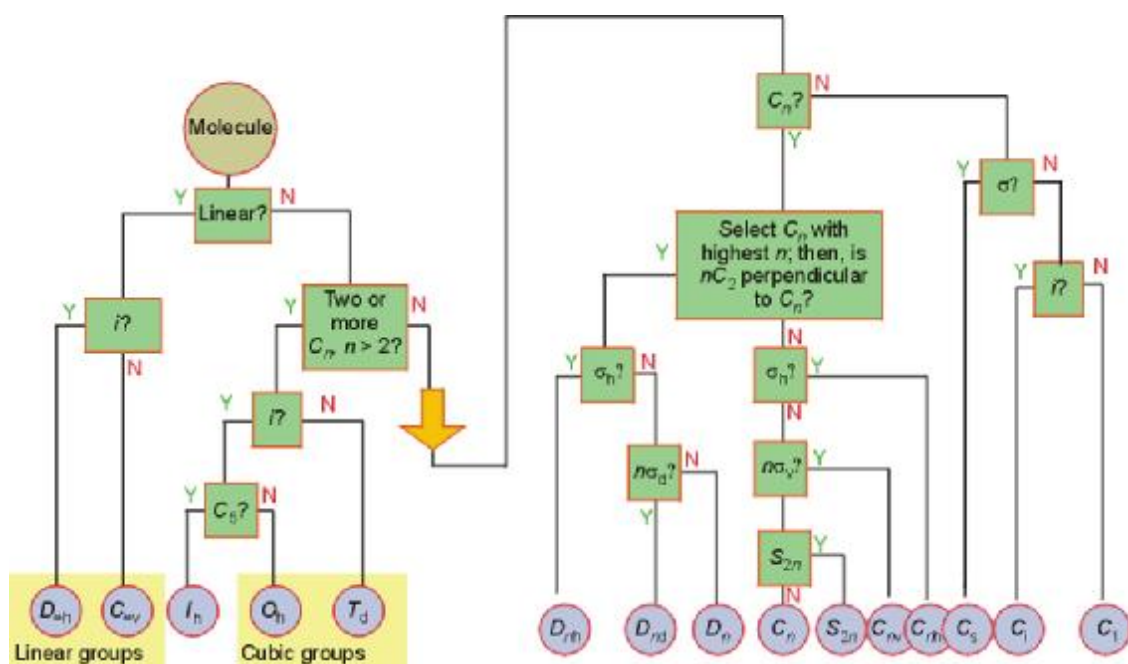
Symmetry and
Group Theory



Symmetry is a phenomenon of the natural world, as well as the world of human invention (Figure 4-1). In nature, many types of flowers and plants, snowflakes, insects, certain fruits and vegetables, and a wide variety of microscopic plants and animals exhibit characteristic symmetry. Many engineering achievements have a degree of symmetry that contributes to their esthetic appeal. Examples include cloverleaf intersections, the pyramids of ancient Egypt, and the Eiffel Tower.

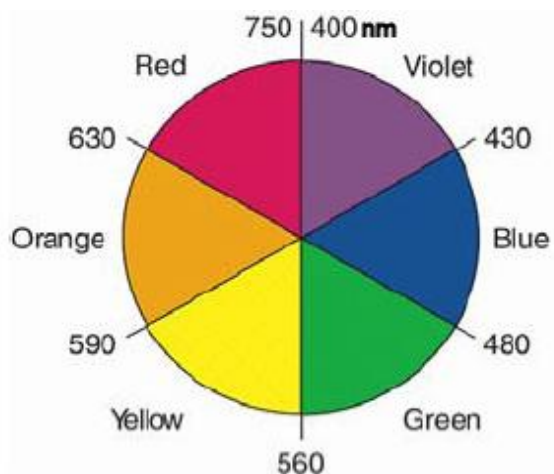
Symmetry concepts can be extremely useful in chemistry. By analyzing the symmetry of molecules, we can predict infrared spectra, describe the types of orbitals used in bonding, predict optical activity, interpret electronic spectra, and study a number of additional molecular properties. In this chapter, we first define symmetry very specifically in terms of five fundamental symmetry operations. We then describe how molecules can be classified on the basis of the types of symmetry they possess. We conclude with examples of how symmetry can be used to predict optical activity of molecules and to determine the number and types of infrared-active stretching vibrations.

Symmetry will be a valuable tool in the construction of molecular orbitals and in the interpretation of electronic spectra of coordination compounds and vibrational spectra of organometallic compounds. A molecular model kit is a very useful study aid for this chapter, even for those who can visualize three-dimensional objects easily. We strongly encourage the use of such a kit.



In explaining the colors of coordination compounds, we are dealing with the phenomenon of *complementary* colors: if a compound absorbs light of one color, we see the complement of that color. For example, when white light (containing a broad spectrum of all visible wavelengths) passes through a substance that absorbs red light, the color observed is green. Green is the complement of red, so green predominates visually when red light is subtracted from white. Complementary colors can conveniently be remembered as the color pairs on opposite sides of the color wheel shown in the margin.

An example from coordination chemistry is the deep blue color of aqueous solution of copper (II) compounds, containing the ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. The blue color is a consequence of the absorption of light between approximately 600 and 1000 nm (maximum near 800 nm; Figure 11- I), in the yellow to infrared region of the spectrum. The color observed, blue, is the average complementary color of the light absorbed. It is not always possible to make a simple prediction of color directly from the absorption spectrum, in large part because many coordination compounds contain two or more absorption bands of different energies and intensities. The net color observed is the color predominating after the various absorptions are removed from white light. For reference, the approximate wavelengths and complementary colors to the principal colors of the visible spectrum are given in Table 1 1 -1.



11 -1 -1 BEER-LAMBERT ABSORPTION LAW

If light of intensity I_0 at a given wavelength passes through a solution containing a species that absorbs light, the light emerges with intensity I , which may be measured by a suitable detector (Figure 11-2).

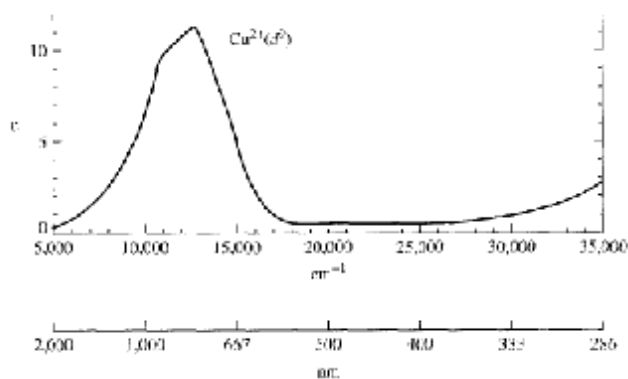


FIGURE 11-1 Absorption Spectrum of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ (Reproduced with permission from B. N. Figgis, *Introduction to Ligand Fields*, Wiley-Interscience, New York, 1966, p. 221.)

TABLE 11-1 Visible Light and Complementary Colors

Wavelength Range (nm)	Wave Numbers (cm^{-1})	Color	Complementary Color
<400	>25,000	Ultraviolet	
400–450	22,000–25,000	Violet	Yellow
450–490	20,000–22,000	Blue	Orange
490–530	18,000–20,000	Green	Red
530–580	17,000–18,000	Yellow	Violet
580–590	15,000–17,000	Orange	Blue
600–700	14,000–15,000	Red	Green
>700	<14,000	Infrared	

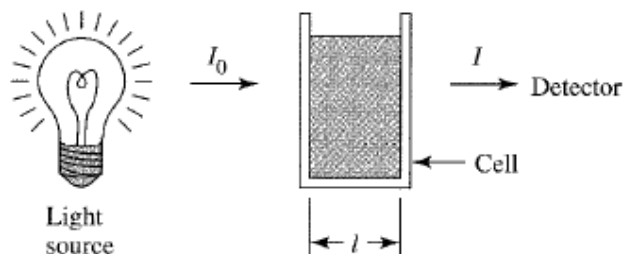


FIGURE 11-2 Absorption of Light by Solution.

The Beer-Lambert law may be used to describe the absorption of light (ignoring scattering and reflection of light from cell surfaces) at a given wavelength by an absorbing species in solution:

$$I_0 \log \frac{I_0}{I} = A = dc$$

I

where A = absorbance

ϵ = molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$) (also known as molar extinction coefficient)

l = path length through solution (cm)

c = concentration of absorbing species (mol L^{-1})

Absorbance is a dimensionless quantity. An absorbance of 1.0 corresponds to 90% absorption at a given wavelength, an absorbance of 2.0 corresponds to 99% absorption, and so on. The most common units of the other quantities in the Beer-Lambert law are shown in parentheses above.

Spectrophotometers commonly obtain spectra as plots of absorbance versus wavelength. The molar absorptivity is a characteristic of the species that is absorbing the light and is highly dependent on wavelength. A plot of molar absorptivity versus wavelength gives a spectrum characteristic of the molecule or ion in question, as in Figure 11-1. As we will see, this spectrum is a consequence of transitions between states of different energies and can provide valuable information about those states and, in turn, about the structure and bonding of the molecule or ion. Although the quantity most commonly used to describe absorbed light is the wavelength, energy and frequency are also used. In addition, the wavenumber (the number of waves per centimeter), a quantity proportional to the energy, is frequently used, especially in reference to infrared light. For reference, the relations between these quantities are given by the equations

$$E = h\nu = \frac{hc}{\lambda} = hc\left(\frac{1}{\lambda}\right) = hc\bar{\nu}$$

where

E = energy

h = Planck's constant = $6.626 \times 10^{-34} \text{ J s}$

c = speed of light = $2.998 \times 10^8 \text{ m s}^{-1}$

ν = frequency (s^{-1})

λ = wavelength (often reported in nm)

$\frac{1}{\lambda} = \bar{\nu} = \text{wavenumber (cm}^{-1}\text{)}$