An Introduction to Structure and Bonding

To every thing there is a season, and a time to every purpose under the sun.
—Ecclesiastes 3

A. THE SOURCES OF CARBON COMPOUNDS

An ever-increasing amount of carbon dioxide (CO₂) is found in the atmosphere and the oceans, apparently as a result of continuing combustion of fossil fuels and normal life processes. Additionally, much of the biosphere contains carbon locked in plants (as carbohydrates [Chapter 11] and related materials about which you will learn). However, most of the compounds of carbon in use today in our technology are obtained either directly from coal or from petroleum—thought by many to have arisen by application of heat and pressure to the decaying products of earlier biosphere inhabitants or by laboratory modification of those materials.

Petroleum and coal consist mainly of compounds that contain only carbon and hydrogen. These materials are called hydrocarbons. While the reason for the name should appear clear, it is hoped you might ask how it is known that only hydrogen and carbon are present.

The complete combustion of a hydrocarbon in an oxygen atmosphere generates carbon dioxide (CO₂) and water (H₂O). If all of the carbon is converted to CO₂ and all of the hydrogen to H₂O, and if there are no other elements besides carbon and hydrogen present in the hydrocarbon, then, as matter is conserved, the amount of carbon in the CO₂ plus the amount of hydrogen in the water must equal the amount of carbon and hydrogen, respectively, in the hydrocarbon combusted.

Problem 1.1. A pure material is isolated from petroleum and 5.8 mg of the material is burned in a stream of oxygen to yield 17.6 mg of carbon dioxide (CO₂) and 9.0 mg of water (H₂O).

(a) Show how you know the material isolated from petroleum contains only carbon and hydrogen.

(b) Suggest an empirical formula for the material.
AN INTRODUCTION TO STRUCTURE AND BONDING

There is a significant amount of technology required to carry out the determination of the carbon dioxide and water produced in the process Problem 1.1 exemplifies. You will note that the material on which the combustion is being carried out is specified as “pure.” Second, a weight is given (5.8 mg). Third, a stream of oxygen (O$_2$) is needed. Fourth, the carbon dioxide (CO$_2$) must be weighed, as must the water (H$_2$O). Finally, having solved the problem, it should be clear to you that atomic weights for the elements involved were needed.

We will not deal here with the establishment of atomic weights, save to indicate that current usage assigns the atomic weight of $^{12}$C as 12 (exactly) and, for the calculations, it is sufficient to allow $^1$H to be 1.00 and $^{16}$O to be 16.00. Figure 1.1 is a pictorial representation of combustion analysis equipment.

You will note, as shown in Figure 1.1, that there are two removable sections (at the right-hand side of the combustion train). The first contains magnesium perchlorate [Mg(ClO$_4$)$_2$] and the second soda lime (a mixture of sodium hydroxide [NaOH] and calcium oxide [CaO]). Magnesium perchlorate [Mg(ClO$_4$)$_2$] readily absorbs water (H$_2$O), while soda lime (NaOH + CaO) absorbs carbon dioxide (CO$_2$). Thus, weighing the removable tubes before and after combustion will provide the weights of water (H$_2$O) and carbon dioxide (CO$_2$), respectively. Purified, dry oxygen (O$_2$) is currently obtained by distillation from liquefied air (another technology we will not discuss here). However, it should be clear to you that the development of the analytical balance, allowing accurate weights to be taken, is critical to the operation of the system. Finally, there is the problem of the analysis being carried out on pure material.

I. How Do We Know a Material Is Pure?

Classically, pure organic compounds were defined as those that had the correct elemental composition (within a few tenths of 1% of that calculated) and had sharp melting points (mp) or constant boiling points (bp).* However, your exposure to

*While these values are called “points,” you should keep in mind that they are really “temperatures,” and usually, for pure materials, the temperature range over which melting (or boiling) occurs is very small.
general principles of chemistry should be sufficient for you to recognize that, by today’s standards, these criteria may be insufficient. Nonetheless, significant basic principles were enunciated with work done on less-than-pure materials (errors often cancel, and frequently, within the limits of the errors, differences could not be detected).

Within the last few decades, powerful tools for purification of materials by separation have been developed. Distillation and crystallization are two with which you might already be familiar. A third is chromatography (from the Greek chroma, meaning color, and graph, meaning draw or record). The latter, as you might gather from its name, was originally developed as a tool to separate the colored components of a mixture by differences in the way they became distributed between a solid stationary adsorbing phase and a liquid mobile phase in which they were soluble.

Today, the original concept has been expanded to include materials without absorption in the visible region of the spectrum (color) and any two different phases, for example, gas–liquid and gas–solid, two immiscible liquids, etc.

As an example, consider the case of two gases, ammonia (NH₃) and nitrogen (N₂). Ammonia (NH₃) is soluble in water (H₂O) (at room temperature and 1 atm pressure) to the extent of about 90 g NH₃ per 100 g H₂O. Nitrogen (N₂), under the same conditions, is soluble to the extent of about 4 g N₂ per 100 g H₂O. If we have a mixture of N₂ and NH₃ gases in contact with water, ammonia will distribute (or partition) itself mostly into the aqueous phase, whereas nitrogen, being relatively insoluble, will remain in the gas phase. If we now replace the aqueous solution with fresh water, a second partitioning will occur, and repetition of this process again and again will lead to relatively pure nitrogen (perhaps contaminated with water vapor) and an aqueous solution of ammonia. This tedious procedure can be replaced so that the process can be carried out with greater simplicity, automatically, and nearly continuously by utilizing chromatographic columns that, as originally developed, permit a moving phase containing the materials to be separated to pass over and through particles of a stationary phase that selectively absorbs (or, if only on the surface, adsorbs) one or more of the materials in the moving phase. Thus, in the example given, if the gaseous mixture were to pass over and through a bed of glass beads, packed in a column and coated with water (H₂O), then, as the mixture of gases moved through the column, it would continuously encounter fresh water (H₂O). At each encounter, ammonia (NH₃) would be selectively absorbed into the water (H₂O) as a function of the amount of water (H₂O) and the various vapor pressures of the gases and water. The gases nitrogen (N₂) and ammonia (NH₃) could be pushed (continuously be adsorbed and desorbed as the vapor mixture changed) over this bed of beads by a carrier gas, which is relatively less soluble in water than either of them (e.g., helium [He], which has about half the solubility of nitrogen [N₂] in water). At a suitable detector (which might, e.g., measure changes in the thermal conductivity of the effluent gases), the pure helium (the carrier) would, as it left the column (or eluted), first find itself contaminated with nitrogen (N₂) since it is less soluble in water (H₂O) than ammonia (NH₃) and then with ammonia (NH₃), which was delayed by its greater absorption.

Such a process, in which material is partitioned between the gas and the liquid phases, is called gas–liquid partition chromatography (GLPC or, sometimes, GLC or GC). A schematic representation of such equipment is shown in Figure 1.2, and,
commonly, organic compounds can be readily separated from each other, eluted in pure form and analyzed by combustion. For materials that do not lend themselves to this technique because they are too high boiling or because appropriate solid/liquid phases cannot be found, other methods (which include column chromatography and high-pressure liquid chromatography) based on the same principle can be applied.

However, such techniques aside, large quantities of purified volatile materials were obtained, historically, by distillation through long columns packed with glass beads or other materials (to increase the surface area on which equilibrium between liquid and vapor could occur). Even today, such distillation columns are part of petroleum refining and most mixtures of fuels are prepared by remixing purified materials to obtain appropriate blends.

The technique of fractional distillation is a practical application of Raoult’s law.*

Consider an ideal solution containing two volatile components, \( x \) (bp 80°C) and \( y \) (bp 110°C), both at 1 atm. The total vapor pressure above a solution of the two materials (\( P_t \)) is equal to the sum of the partial vapor pressures of all components (Equation 1.1):

\[
P_t = P_x + P_y = P_x^N \times N_x + P_y^N \times N_y,
\]

where \( P_x, P_y \) = the partial vapor pressure of \( x \) and \( y \) components, respectively, in the solution at the given temperature; \( P_x^N, P_y^N \) = the vapor pressure of pure \( x \) and pure \( y \), respectively, at that temperature; and \( N_x, N_y \) = the mole fraction of \( x \) and \( y \), respectively, in the solution.

The composition of the vapor mixture in terms of the mole fraction in the vapor state is given by Equation 1.2 for the mole fraction of \( x \) (\( N'_x \)):

\[
N'_x = P_x/P_t = P_x^N \times N_x/(P_x^N \times N_x + P_y^N \times N_y).
\]

*François-Marie Raoult (1830–1901), French chemist who long held the chair of chemistry at Grenoble.
Similarly, for the mole fraction of \( y \) (\( N^*_y \)), Equation 1.3 applies:

\[
N^*_y = P_y / P = P_y \circ N_y / (P_x \circ N_x + P_y \circ N_y).
\] (1.3)

The temperature at which “boiling” occurs requires only that the vapor pressure of the mixture above the solution be equal to the external pressure. However, as dictated by Equation 1.1, the total vapor pressure is a function of the composition of the vapor and at lower temperatures, the vapor will be richer in the lower boiling component.

The relationship between boiling point and vapor composition for the mixture of \( x \) (bp 80°C) and \( y \) (bp 110°C), both at 1 atm, is shown in Figure 1.3, where the lower curve presents the boiling point of the liquid mixture at any temperature between 80 and 110°C, and the upper curve corresponds to the vapor composition as calculated from Equations 1.2 and 1.3.

As can be seen from Figure 1.3, the vapor, at any given temperature, is always richer in the more volatile component and, if the vapor is liquefied, the liquid corresponding to that vapor will also be richer in that component. For example, consider a liquid mixture composed of 20\% \( x \) and 80\% \( y \). As shown in Figure 1.3, at 102°C and 1 atm (point \( L_1 \)), the vapor above the liquid will consist of about 40\% \( x \) and 60\% \( y \) (point \( V_1 \)).

**Problem 1.2.** With reference to Figure 1.3,

(a) if the composition of the vapor at \( V_1 \) is, as stated, about 40\% \( x \) and 60\% \( y \), what will be the composition of the liquid obtained by direct condensation of that vapor?

(b) if the liquid so obtained (part a) is immediately reconverted to vapor, what will be the composition of that vapor?
Repeated condensation and redistillation allows, in this way, separation of the mixture of $x$ and $y$.

Although it was early found that freezing point lowering of a solvent could be used to determine the number of moles of solute dissolved in the solvent (and hence the molecular weight), Raoult's law applied to solutions of small concentrations of nonvolatile solutes also affords a method of approximately determining the molecular weights of the solutes. This is because the temperature at which the vapor pressure becomes equal to any specified external pressure is higher for the solution than for the pure solvent. Additionally, it should not come as a surprise to you that, other things being equal, it is generally true that materials with lower molecular weights boil at temperatures lower than those with higher molecular weights. So, given the results from Problems 1.1 and 1.2, it should be possible to determine the molecular weight of a pure, volatile sample by simply measuring the volume that a given mass of the vapor of the (pure, volatile) sample occupies at atmospheric pressure. The Victor Meyer method accomplishes that end (Problem 1.3).

**Problem 1.3.** The Victor Meyer (1848–1897, professor of chemistry, University of Heidelberg) method for determination of molecular weights is quite general for low-boiling materials. A diagrammatic representation of the apparatus is shown in Figure 1.4.

Note that the cylindrical bulb with the long stem is filled with dry air and is heated, while still open to the atmosphere, to a constant temperature by a suitable boiling fluid within the hot bath. A small glass vial containing the volatile liquid substance is dropped into the heated bulb and, at the same time, the tube is stoppered at the top of the stem. The glass vial shatters and its liquid content rapidly vaporizes. The vapor drives out of the bulb that quantity of air that occupies the same volume at the temperature of the bulb and at the pressure of the atmosphere. This air is collected in the measuring tube.

![Figure 1.4. A schematic diagram of a Victor Meyer apparatus for the determination of the vapor density of a substance that is volatile at the temperature of the hot bath. The air displaced from the heated bulb by the volatilization of the sample in the bulb is measured in the inverted graduated tube.](image-url)
Assume that, to a first approximation, the vapor of the organic material analyzed in Problem 1.1 can be considered an ideal gas; that is, it obeys the ideal gas relationship \( PV = nRT \). If the pressure on the day the experiment was run was 728 torr and a volume of air corresponding to 15.2 cc was displaced from the hot tube at 373 K (but collected at 300 K) by introducing and vaporizing 34.3 mg of the material from Problem 1.1, what must be its molecular weight? (\( R = 0.083 \text{ L atm mol}^{-1} \text{ K}^{-1} \))

The process of fractional distillation is routinely applied to pretreated liquid mixtures of hydrocarbons from various sources of petroleum or from liquefaction of coal. The lower boiling fraction (up to about 40°C) is called gas and contains a mixture of hydrocarbons with (generally) fewer than five carbon atoms (and, of course, their associated hydrogens since they are hydrocarbons). The next higher boiling fraction, from about 40°C to about 170 or 180°C, is called gasoline* and generally contains hydrocarbons with up to 10 carbon atoms. Kerosene, which has a boiling temperature range of about 180–230°C, and which is used as a jet airplane fuel as well as a heating fuel, is composed of hydrocarbons with 11 and 12 carbon atoms. As the temperature of the crude oil distillation is raised even further, light gas oil, heavy gas oil, and then asphalt fractions are obtained. The amount of each of these materials, as well as the nature and amount of the various substances with which they are contaminated, varies with the source of the oil. Frequently, the impurities are not hydrocarbons. The nonhydrocarbon impurities contain, in addition to carbon and hydrogen, elements such as oxygen, nitrogen, and sulfur. Such impurities can sometimes be removed by chemical means because hydrocarbons are relatively unreactive materials compared to the others (Chapter 3). Indeed, the major reaction hydrocarbons undergo is oxidation, and when the oxidation is carried out under controlled conditions, the process is used to power our society—generating electricity as well as heat. Although electricity can, of course, be generated by other means (solar, hydroelectric, nuclear, etc.), the use of oil for this purpose as well as for refinement into gasoline amounted, in 1990 to the consumption of more than 18 million barrels of crude oil daily by the United States. Of this amount, the equivalent of about 20% was needed by the chemical industry to both power the industry and as crude feedstock for raw chemicals. Indeed, the equivalent (i.e., considering natural gas, liquids from coal gasification) of more than 1.2 million barrels of crude oil daily are needed as feedstock to produce the goods we use.

B. MORE ABOUT HYDROCARBONS

With the availability of relatively pure hydrocarbons from, for example, fractional distillation, taking ever-decreasing temperature ranges to get fractions as pure as possible (or, more recently, by gas chromatography), it becomes possible to attempt to determine how efficient our combustion engines for heat production really are; that is, ignoring for the moment (1) the important issues of economy of production and delivery; (2) social questions of purchase from, and dependency on, nations or

*The material purchased at the “gas pump,” also called gasoline, contains these and other hydrocarbons and many other materials, called additives, which presumably increase the efficiency of combustion.
individuals with whom we might not always agree; as well as (3) the planet-wide
danger of increased concentration of greenhouse gases from which all combustion
and most refining processes suffer, which fuel should we consume to heat our homes,
power our automobiles, and generate electricity?

In order to obtain this information, we want to first know how much heat is
potentially available per unit weight from the hydrocarbons we have; that is, what
is their heat content or, when completely combusted to give only carbon dioxide
\((\text{CO}_2)\) and water \((\text{H}_2\text{O})\), how much energy, in the form of heat, can we expect to
get?

I. Combustion—Heats of Reaction

At high temperature, all hydrocarbons are attacked by oxygen. If oxygen is present
in excess (see Problem 1.1), complete combustion occurs to give carbon dioxide
\((\text{CO}_2)\) and water \((\text{H}_2\text{O})\). Methane \((\text{CH}_4)\) is one of the main components of natural
gas. It is also formed by the action of anaerobic organisms during decomposition of
organic matter under water in marshes (from where it gets the name marsh gas),
during the treatment of sewage sludge, and in the normal digestive processes of
cows and other ruminants. The combustion of gaseous methane (indicated by the
subscript \((g)\)) (Equation 1.4) with the formation of gaseous carbon dioxide \((\text{CO}_2(g))\)
and liquid water \((\text{H}_2\text{O}(l))\) is accompanied by the evolution of heat. Careful measure-
ment of the amount of heat evolved with all species adjusted for their standard
states, \(\Delta H^\circ\) (in a calorimeter [Figure 1.5]) during this process has been made and
is found to be 890.4 kJ mol\(^{-1}\) (212.8 kcal mol\(^{-1}\)) at 25°C:

\[
\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)
\]

\[\Delta H^\circ = -890.4 \text{ kJ mol}^{-1} (-212.8 \text{ kcal mol}^{-1}).\]  

Now, since the same amount of heat is produced whenever a fixed amount of work
is done and since this amount is independent of the way the work is done (i.e., the
path, which may or may not involve intermediate reactions), it is possible to calcu-
late the heat of a specific reaction from measurements of heats of reactions of many different
reactions. The principle is now called Hess’s law, after Germain H. Hess (1802–1850),
who first published it (Hess, 1840) as the law of constant heat summation, and it is
quite useful in predicting the heats of reactions, which are otherwise most difficult
to carry out. In using Hess’s law, the following are accepted by convention:

1. Standard states will be used. A standard state for a substance is that state in
which it is stable at 25°C and 1 atm pressure.

\*Conversion of 1 mol of liquid water \((\text{H}_2\text{O}(l))\) to 1 mol of water vapor \((\text{H}_2\text{O}(g))\) (or the reverse) requires
correction for the heat of vaporization of water. For both at 25°C, 43.93 kJ mol\(^{-1}\) (10.5 kcal mol\(^{-1}\)) is
required.

\*The recommended units (Système international d’unités or SI units) for measurement of energy are
joules. The use of calories as a unit of measurement nonetheless remains widespread. Multiply the value
in kilocalories by 4.184 to convert it to kilojoules.

\*It is important to recognize that the heat measured here is the quantity liberated (hence the negative
sign), having begun with the reactants at 25°C and ending with the products at 25°C. The temperature
at which the reaction actually occurs does not matter.
2. Elements, in their standard states, have a heat content (enthalpy), $H$, of zero.

3. The standard enthalpy of any compound is thus the heat of the reaction by which it is formed from its elements—with the reactants and products in their standard states at 25°C and 1 atm.

4. The superscript ° indicates that the enthalpy is a standard heat of combustion (subscript $c$) (i.e., $\Delta H_c^\circ$) or formation (subscript $f$) (i.e., $\Delta H_f^\circ$).

5. If heat is evolved, $\Delta H^\circ$ is given a negative sign and the reaction is called exothermic, while if heat is absorbed, $\Delta H^\circ$ is given a positive sign and the reaction is called endothermic.

*In principle, there are two ways of carrying out such a combustion reaction. In the calorimeter described, the volume of the system is held constant, a pressure change is expected, but no mechanical work is done. It follows that the increase in energy is equal to the amount of heat absorbed by the water. Alternatively, as in the cylinder of an idealized automobile engine, a piston might be driven so that the volume of the system would change while the pressure remained constant. Strictly speaking, the change in heat content or enthalpy ($\Delta H$) equals the heat change at constant pressure—not at constant volume. While it is true that the heat of reaction at constant volume is greater than that at constant pressure (because work is done in the latter case), for reactions involving solids and liquids (most organic compounds are solids or liquids, unlike the example of methane [CH$_4$] chosen here), the difference is small. For reactions between gaseous species, the difference may be appreciable.
Thus, in the case at hand (Equation 1.4), the value of $\Delta H_c^\circ$ is the amount of heat liberated on complete combustion of 1 mol of the hydrocarbon methane (CH$_4$) when the reactants and products are in their standard states.

In an exactly analogous fashion, the hydrocarbon ethane (C$_2$H$_6$—or, better, CH$_3$CH$_3$ [mp –182.8°C, bp –88.6°C]), also a constituent of natural gas (which is about 85% methane [CH$_4$] and 10% ethane [CH$_3$CH$_3$]), undergoes combustion to carbon dioxide (CO$_2$) and water (H$_2$O) (Equation 1.5), while carbon* itself (Equation 1.6) and hydrogen (Equation 1.7) similarly burn:

$$\text{CH}_3\text{CH}_3(g) + 7/2\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l) \quad \Delta H_c^\circ = -1558.9 \text{ kJ mol}^{-1}$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_c^\circ = -395.4 \text{ kJ mol}^{-1}$$

$$\text{H}_2(g) + 1/2\text{O}_2(g) \rightarrow \text{H}_2\text{O}(g) \quad \Delta H_c^\circ = -285.8 \text{ kJ mol}^{-1}$$

Application of Hess’s law to the thermochemical data provided in Equations 1.5–1.7 then allows calculation of the heat of formation of ethane from carbon and hydrogen (Equation 1.8):

$$2C(s) + 3\text{H}_2(g) \rightarrow \text{CH}_3\text{CH}_3(g) \quad \Delta H_f^\circ = -89.1 \text{ kJ mol}^{-1}$$

Problem 1.4. Using the data provided in Equations 1.5–1.7, show how the expression of Equation 1.8 is obtained. The most recent widely quoted value, given in reference to Table 1.1 for $\Delta H_f^\circ$ for ethane, is $-83.7 \text{ kJ mol}^{-1} (-20.0 \text{ kcal mol}^{-1})$.

We interpret this kind of information to mean that there is more energy stored in the bonds holding together the nuclei of the atoms in the starting materials than there is in the bonds holding together the nuclei of the atoms in the products; that is, we have measured the amount of energy held in the methane (CH$_4$) and oxygen (O$_2$) molecules as compared to the energy in the carbon dioxide (CO$_2$) and water (H$_2$O) molecules, and we have found that there is more in the former than in the latter. We attribute this difference not to the nuclei but rather to the way the nuclei are held together, that is, the bonds. Thus, the word “bond” is taken to mean “the force holding nuclei to each other.” So it follows that although combustion is critical to energy production, and although heats of combustion, reaction, and formation provide analytical footing to the first law of thermodynamics, it is bond energies that have proven to be more generally useful in organic chemistry.

Considering, for the moment, that a bond between nuclei represents only a manifestation of some force holding the nuclei together, it is reasonable to inquire both

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*Different allotropic forms, for example, graphite, diamond, and the fullerenes (vide infra), have slightly different heats of combustion. The value given here is for diamond.
if the bond can be broken and how much force might be exerted, or energy expended, to accomplish that end. Hopefully, it is clear that, at least in principle, if expenditure of that energy allows a bond to be broken, the same amount of energy can be recouped if the bond is remade (i.e., the process is microscopically reversible). Further, as with Hess’s law, if bonds in the starting materials can be suitably broken and then new bonds are made in the products and the gain (or loss) in energy for the overall process is measured, some indication of whether a net overall gain or loss in enthalpy occurs can be realized. The anticipated value of this exercise, for the moment, will then lie in being able to predict whether a reaction might be exothermic or endothermic overall. Eventually, other values to understanding this process will become apparent.

Consider the hydrogen molecule (H₂). Figure 1.6 presents a schematic diagram of the potential energy curve for H₂. As thermal (or other) energy is supplied to H₂, the motions of the molecules and the motions of the atoms in the molecules increase. Much of the energy is expended in translation (i.e., the molecules move about faster relative to each other), but some increase in energy is manifested as increased vibration of the atomic nuclei in H₂, some quantized values of which are represented by the horizontal lines. At least in principle, when enough energy is supplied, the two atomic nuclei in H₂ can be separated into individual hydrogen atoms. This quantity is called the bond dissociation energy (or BDE) and is given the symbol $D$.*

For the dissociation of H₂ into two hydrogen atoms, $\Delta H_d^\circ$ or $D_H$ at 25°C is usually taken as 435.9 kJ mol⁻¹ (104.2 kcal mol⁻¹) (Equation 1.9). In an exactly analogous fashion, for the dissociation of O₂ into two oxygen atoms, $\Delta H_d^\circ$ or $D_O$ at 25°C is taken as 498.3 kJ mol⁻¹ (119.1 kcal mol⁻¹) (Equation 1.10). Combining these two with the calorimetric expression of Equation 1.6 (and adjusting for everything in the vapor phase) then allows the summation shown in Equation 1.11 and the conclusion that, since this $\Delta H_d^\circ$ or $D_H$ at 25°C is for two bonds between hydrogen and

*The value for $D$ is normally obtained in ways other than that described above. When using dissociation energies with enthalpic calculations, that is, $\Delta H_d^\circ$ or $D_H^\circ$, a small correction term is applied, which includes consideration of the dissociation as if it had occurred at 25°C.
AN INTRODUCTION TO STRUCTURE AND BONDING

In these and related ways, the bond energies of Table 1.1 have been accumulated:

\[
\begin{align*}
\text{H}_2(g) & \rightarrow 2\text{H}^\bullet(g) & \Delta H_d^\circ \text{ or } D H^\circ &= 435.9 \text{ kJ mol}^{-1} \\
& & (104.2 \text{ kcal mol}^{-1}) \\
\text{O}_2(g) & \rightarrow 2\text{O}^\bullet(g) & \Delta H_d^\circ \text{ or } D H^\circ &= 498.3 \text{ kJ mol}^{-1} \\
& & (119.1 \text{ kcal mol}^{-1}) \\
\text{H}_2(g) + 1/2\text{O}_2(g) & \rightarrow \text{H}_2\text{O}(g) & \Delta H_c^\circ &= -285.8 \text{ kJ mol}^{-1} \\
& & (-68.3 \text{ kcal mol}^{-1}) \\
2\text{H}^\bullet(g) + \text{O}^\bullet(g) & \rightarrow \text{H}_2\text{O}(l) & \Delta H_c^\circ &= -971.1 \text{ kJ mol}^{-1} \\
& & (-232.1 \text{ kcal mol}^{-1})
\end{align*}
\]

As shown in Table 1.1, the currently accepted value for the average bond strength for the O–H bond in water is 498 ± 4 kJ mol⁻¹ (119 ± 1 kcal mol⁻¹).
It is generally acknowledged, and must be emphasized, that the concept of bond energies (particularly as determined for polyatomic species), while useful, should not be substituted for calorimetric data where the latter is available. However, where there are no other data, it is possible to obtain crude estimates for the heats of formation ($\Delta H_f^\circ$) and combustion ($\Delta H_c^\circ$).

**Problem 1.5.** Assume that the heat of formation ($\Delta H_f^\circ$) at 25°C for hydrogen bromide (HBr) is not known to be $-36.4 \text{ kJ mol}^{-1} (-8.7 \text{ kcal mol}^{-1})$. Using the information given in Table 1.1, provide your own estimate for the value of $\Delta H_f^\circ$ at 25°C for HBr. Do you consider the answer “reasonable?”

C. ON THE NATURE OF THE CHEMICAL BOND

I. Ionic and Nonpolar Covalent Bonds

In the most general sense, when we ask about a chemical bond, we are inquiring into the nature of the force holding atoms together to form compounds. For example, in methane, CH$_4$, discussed above, we want to know how it is that the atoms (hydrogen and carbon in this case) are held to (or connected with) each other such that we must put in some energy to cause them to come apart. As we have already seen (e.g., in Table 1.1), different bonds have different energies (as measured by the cost to dissociate them into their component atomic nuclei and associated electrons) and even bonds connecting those same atoms to each other apparently have different energies, depending upon the compounds in which they are found.

Different approaches to describing bonds have been made over the years and, based largely on reactivity and physical properties, two limiting, idealized categories have been popular, viz., ionic and covalent. Ideally, the latter involves two identical nuclei sharing electrons equally (hence covalent), while the former involves the complete transfer of electrons to form ions.

Based largely upon spectroscopic measurements (i.e., the observation of quantized absorption and emission of energy—as in atomic spectroscopy, about which you may have already heard, and other forms of spectroscopy to be discussed in Chapter 2) and the utility of the concept in making successful predictions, we define as an orbital that particular volume in space, near a nucleus, in which there is a high probability of finding an electron associated with that nucleus. By the Pauli exclusion principle,* no more than two electrons can occupy a given orbital and if there are two electrons in the orbital, they must differ with regard to a property called spin. This property has only two possible values, frequently symbolized by the notations $\uparrow$ and $\downarrow$ (or sometimes by $+\frac{1}{2}$ and $-\frac{1}{2}$, respectively), and if two electrons have the same values (i.e., $\uparrow\uparrow$ or $\downarrow\downarrow$) for this property, they are said to be unpaired and they cannot occupy the same orbital. Only paired ($\uparrow\downarrow$) electrons can occupy the same orbital.

Orbitals are described by specifying their approximate size (even though there may be a finite probability of finding the electron very far from the nucleus), shape, and spatial orientation. Orbitals that are **spherically symmetrical** about the nucleus are called *s orbitals* and by using a numerical prefix, that is, 1, 2, ..., *(the principal quantum number)*, their relative energies and the volume of space (of highest probability) they enclose is defined. As measured spectroscopically, an electron in a *1s* orbital is closer to the nucleus and is lower in energy than an electron in a *2s* orbital. Additionally, when the principal quantum number is 2, a maximum of six more electrons can be accommodated and the spatial location assigned to them, in pairs, lies along the three normal coordinate axes (*x*, *y*, and *z*). These three *2p* orbitals (i.e., *2p_\text{x}* , *2p_\text{y}* , and *2p_\text{z}* ), each of which can contain no more than two electrons, are found to be of equal energy (and thus **mutually degenerate**). The geometry of the *p* orbitals differs from that of the *s* orbitals. In contrast to the spherical symmetry of the latter, the mathematical solution to the wave equation (ψ) for an electron in any of the *p* orbitals dictates that the region of highest electron probability (ψ^2) is best represented as a pair of slightly distorted spheres, symmetrically disposed about the intersection of the *x*-, *y*-, and *z*-axes.

The set of three *p* orbitals is thus mutually orthogonal and is drawn to show that there is essentially a zero probability of finding electron density at the nucleus. Figure 1.7 depicts the 90% probability radii of idealized representations of the one *2s* and the three *2p* orbitals; the sum of the volumes of the *2p* orbitals corresponds to a sphere.

The letter *s* here does not stand for either spherical or symmetrical but rather for **sharp**, a reference to a descriptor assigned on the basis of a spectroscopic transition observed from a particular atomic state of hydrogen. Similarly, the descriptors *p*, *d*, and *f* refer to principal, diffuse, and fundamental spectroscopic lines.

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**Figure 1.7.** Idealized representations of one *2s* and three *2p* orbitals with their respective 90% probability radii.
If we make the assumption that occupied (whether with one or two electrons) and unoccupied orbitals, regardless of the nucleus about which they are found, all look pretty much the same, then we can see how, at least in principle, an additional electron (in an appropriate orbital, which still cannot contain more than two) might be associated with one nucleus giving it a net negative charge (measured as its electron affinity). Similarly, another atom, having lost an electron (from an appropriate orbital), would then reasonably acquire a net positive charge (measured as its ionization potential). The two species, one negative and the other positive, resulting from an idealized complete electron transfer, are now capable of attracting each other and are held together by some electrostatic force, which is proportional to the charge, the mass, and the distance apart from each other the ions find themselves. The physical characteristics that have led to the conclusion that this picture of ionic bonding is useful include not only the general high crystallinity of these materials but also the ability of solutions of such substances to carry an electric current. Sodium chloride (NaCl) is often considered a typical example of such material. However, it is clear that the picture of bonding as a result of full transfer of an electron, rather than any sharing, does not accurately describe any diatomic species.

In the idealized picture of covalent bonding, on the other hand, commonly thought of as present in most liquids and in many solids and gases, and where electric current is usually not carried by solutions of the substances, there are two popular complementary approaches. For purposes of simplicity, we will first consider both of them using the hydrogen molecule. In more complicated cases, qualitative explanations, sometimes using one, sometimes the other, and, occasionally, both, are common. The first of these is called the valence bond (VB) method and is attributed to Heitler and London. According to the VB treatment, a system is imagined in which, at the beginning, each $1s$ orbital on a hydrogen atom has an electron (i.e., $[1s^1]$) and, at the end, each electron in the bonded species, $H_2$, is associated with both atoms; that is, at the end, one electron may be in the $1s$ on one hydrogen atom, and one electron may be in the $1s$ orbital on the other hydrogen atom. Alternatively, both electrons may be on one hydrogen atom and none on the other. Thus, in this method, electron configurations are combined and, in a case like hydrogen ($H_2$), almost all of the bonding lies between the nuclei but (by the Born–Oppenheimer approximation)

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*Walter H. Heitler (1904–1981) moved to the University of Bristol as a consequence of the rise of anti-Semitism in Germany, although he did his major work with Fritz London in Zurich on the VB method.

Fritz W. London (1900–1954), who made his major contributions to the weak forces of intermolecular bonding (London dispersion forces), was also forced to leave Germany (University of Berlin) for England, although he eventually enjoyed a professorship at Duke University, Durham, North Carolina.

†Max Born (1882–1970), Nobel Prize in Physics, 1954, worked at Göttingen until forced to leave by the Nazis because of his outspoken views. He subsequently held visiting posts at the University of Cambridge and the University of Edinburgh and became a British citizen.

J. Robert Oppenheimer (1904–1967) who held positions at the University of California, Berkley, California Institute of Technology and the Institute for Advanced Studies, Princeton, New Jersey, is more widely known for his work on the development of the atomic bomb and his subsequent efforts toward peace. The approximation that, in essence, separates nuclear and electronic components of the wave function was developed with Max Born in the late 1920s.
since electrons move faster than nuclei, there might be some small contribution to \( \text{H}_2 \) from something that might look like \( \text{H}^+ \text{H}^- \). In this regard, all of the theories concur in the (warranted) assumption that as long as the two bonded nuclei are identical (as in \( \text{H}_2 \)), such ionlike contributions should be vanishingly small. However, when the two nuclei are not identical, the electrons need not be equally shared. Unequal sharing will be discussed briefly under the heading of Polar Covalent Bonds.

Again, for the case of \( \text{H}_2 \), as shown in Figure 1.8 (on the lower curve), when the two hydrogen atoms and their respective associated electrons (one electron on each) approach each other from a great distance, the energy of interaction will generally decrease, in the case of paired spins, reaching a minimum at the appropriate average equilibrium bond distance (74 pm or 0.74 Å [where 1 Å = 1 nm] for \( \text{H}_2 \)). Closer approach causes a rapid rise in energy because of internuclear repulsion. The upper curve in Figure 1.8 depicts what happens if the electrons associated with their respective hydrogen atoms have unpaired spins. Thus, in the \textbf{VB method}, if two atoms are to form a bond, the atomic orbitals (AOs) associated with those atoms each deliver one electron; two (paired) electrons are engaged in bond making; and the orbitals will tend to overlap with each other because overlap facilitates an exchange of electrons and the total energy of the system is lowered (since the volume in which it is most probable to find the electrons has increased). Regrettably, the VB method underemphasizes the extent to which the energy levels of the final system are modified by covalent bonding.

The alternative picture of covalent bonding, which is of equal merit, is called the \textbf{molecular orbital (MO) method} and is attributed to the insight of Pauling and

![Diagram](image-url)

\textbf{Figure 1.8.} An energy diagram for hydrogen (\( \text{H}_2 \)). Zero corresponds to two hydrogen nuclei at a very large distance. The lower curve corresponds to paired electrons and bonding, while the upper curve corresponds to unpaired electrons and antibonding.
ON THE NATURE OF THE CHEMICAL BOND

Slater,* who independently suggested the same concept in 1931. Just as AOs are associated with one nucleus, a similar probability description can be built up for molecules (MOs). Generally, the situation is more complicated for MOs because as the number of nuclei and their potential arrangements in space increase, so do the possible combinations of wave functions, and the precise solution requires that the electron density be spread out over the entire volume of the molecule (instead of being confined to a particular atom or bond) to minimize the total energy. Therefore, in complicated cases, a limited form of the MO approach (localized MOs) resulting from a linear combination of atomic orbitals (LCAO) is used.

For example, qualitatively, using the MO method for the relatively simple case of hydrogen (H₂), it is suggested that the 1s AOs from the two identical hydrogen atoms (H_A) and (H_B), respectively, be combined so that they might overlap in the volume of space between the two nuclei to create MOs. Because the result of that overlap is symmetric to rotation about the axis joining the nuclei, it is called sigma (σ). Further, since orbitals can be neither created nor destroyed, the combination of two orbitals must yield two orbitals and, indeed, the combination of the wave functions (ψ) of the AO 1s orbitals to make MO wave functions (Ψ) can occur in two different ways.

Any MO that concentrates electrons between nuclei is called bonding and results from an in-phase or constructive overlap of the two AOs, that is, from the adding together of the wave functions for the AOs or, for H_A and H_B, bonding Ψ_MO = (ψ₁s_A + ψ₁s_B). Similarly, the MO formed by combining the same 1s AOs of different signs, the result of an out-of-phase or destructive overlap, that is, for H_A and H_B, antibonding Ψ_MO = (ψ₁s_A − ψ₁s_B), is also symmetric about the internuclear axis, is called sigma star (σ*), and possesses a nodal plane halfway between the two nuclei. The presence of a nodal plane signifies zero electron density in the plane and requires that the electron density be concentrated near the ends of the molecule. The antibonding MO is less stable than the isolated hydrogen nuclei because the nuclei remain within bonding distance, but without bonding, and thus suffer internuclear repulsion. Figure 1.8 (vide supra) depicts the relative energies of the bonding (lower curve) and antibonding (upper curve) orbitals to internuclear separation, and Figure 1.9 is a representation showing the relative energies of the bonding and antibonding orbitals at their equilibrium internuclear separation.

Finally, although a number of assumptions have been made, both the VB and MO methods are currently justified by the fact that, over the years, they have led to predictions confirmed by experiment.

*Linus C. Pauling (1901–1994), professor, California Institute of Technology (Nobel Prize in Chemistry, 1954; Nobel Peace Prize, 1962) is the only person to win two unshared Nobel prizes. Independently from John Slater, he developed algorithms that describe atomic orbitals.

John C. Slater (1900–1976), Massachusetts Institute of Technology, developed the algorithms that describe atomic orbitals at the same time but independent from Linus Pauling. The use of “Slater-type orbitals” remains useful for depicting the regions in space near a nucleus where finding an electron is probable.
Figure 1.9. A schematic representation of the formation of bonding (σ) and antibonding (σ*) molecular orbitals of hydrogen (H₂) by the combination of two equivalent 1s hydrogen atomic orbitals. The signs (+) and (−) do not refer to charges but rather to the sign of the wave function ψ, whose square (ψ²) gives the probability of finding the electron(s) in the volume shown.

Problem 1.6. Using several schematic representations such as that shown in Figure 1.9 and the usual convention for electrons (i.e., up and down arrows, “↑” and “↓”), show the configuration for
(a) two uncombined hydrogen atoms,
(b) a hydrogen molecule with one electron (H₂⁺),
(c) an excited hydrogen molecule with two electrons,
(d) a hydrogen molecule with three electrons (H₂⁻), and
(e) a hydrogen molecule with four electrons (H₂²⁻).

Problem 1.7. There are three different electronic configurations for the excited hydrogen molecule (part c above), all of which conform to the Pauli exclusion principle. Describe them using the notation of Problem 1.6. Which configuration do you expect to be the most stable?

II. Polar Covalent Bonds
It has already been pointed out that the twin concepts of ionic bonding, on the one hand, and covalent bonding, on the other, are idealized; that is, electrons are neither completely transferred nor (except perhaps for identical nuclei) equivalently shared. In the most general case, as suggested by Lewis* early in this century,

*Gilbert N. Lewis (1875–1946), professor, University of California, Berkeley, was a physical chemist who worked on the reformulation of thermodynamics but is most widely known for his proposals about the distribution of electrons around nuclei as proposed in J. Am. Chem. Soc., 1916, 38, 762.
the noble gas configuration represents a particularly stable arrangement and, while such configurations might be arranged by the complete transfer of electrons, they can also be reached by electron sharing. Such sharing need not be equal. Indeed, hydrogen (H₂), which is composed of two identical atoms, and other such diatomic species composed of identical atoms (e.g., F₂, N₂) are atypical. What is done if the bonded elements are not the same? Consider then the case of hydrogen fluoride (HF). The electronic configuration of the highly electronegative* fluorine atom is represented as [(1s²)(2s²)(2p⁵)] and thus it might be expected to readily accept an electron to yield the anion (F⁻) [(1s²)(2s²)(2p⁶)] from, for example, a hydrogen atom [(1s¹)], and the resultant species H⁺F⁻ would then be expected to be ionic. However, the gas HF does not possess all of the properties typically associated with ionic materials, and thus, following the suggestion of Lewis, we might suppose that the electron is not completely transferred from hydrogen to fluorine, but rather it is shared by both hydrogen and fluorine. Considering the one electron from hydrogen and the seven electrons with the principal quantum number 2 on fluorine, representations such as that shown below can be written as

\[ \text{H:} \overset{\ddagger}{\text{F}}: \]

From the MO point of view, a first approximation would be to consider the interaction of the 1s orbital on hydrogen (in which there is already one electron) and one of the 2p orbitals on fluorine (with five 2p electrons, i.e., fluorine is [(1s²)(2s²)(2p⁵)], we assign four of the five as paired in two 2p orbitals and the fifth in the last) while keeping in mind that fluorine has a high nuclear charge and that the energy levels around fluorine will not be equivalent to those around hydrogen. If we then take the \( z \)-axis as the internuclear line and allow the 1s(H) and 2pₓ(F) to overlap, the \( \sigma \) bonding combination can be taken as [1s(H) + C₁2pₓ(F)], where the coefficient \( C_1 \) gives the relative weight of the 2pₓ(F) AO in the \( \sigma \) bonding MO. In contrast to a covalent bond between two identical nuclei, the combining valence AO orbitals have different weights in the MO because they have different energies. The more

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*The term electronegativity refers to the relative ability of an atom, in a bonding situation, to attract electrons to itself. A widely applied semiquantitative method is described by Pauling (vide supra), who suggested that a scale of electronegativities could be created by considering that if bonding electrons between two nonidentical nuclei, \( X \) and \( Y \), were equal, then it would be reasonable to expect the bond energy for \( XY \) to be the mean of \( X^2 + Y^2 \). Generally, it is found that \( X - Y \) is almost always greater than that mean, and thus the extra contribution to that energy must be due to a partial ionic character. Relative values for a scale can thus be arranged. Given the “electronegativity” of hydrogen as 2.2, an abbreviated electronegativity table can be created:

<table>
<thead>
<tr>
<th>Element</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2.2</td>
</tr>
<tr>
<td>Li</td>
<td>1.0</td>
</tr>
<tr>
<td>Na</td>
<td>0.9</td>
</tr>
<tr>
<td>K</td>
<td>0.8</td>
</tr>
<tr>
<td>Mg</td>
<td>1.2</td>
</tr>
<tr>
<td>Be</td>
<td>1.5</td>
</tr>
<tr>
<td>B</td>
<td>2.0</td>
</tr>
<tr>
<td>AI</td>
<td>1.5</td>
</tr>
<tr>
<td>C</td>
<td>2.5</td>
</tr>
<tr>
<td>Si</td>
<td>1.7</td>
</tr>
<tr>
<td>P</td>
<td>2.1</td>
</tr>
<tr>
<td>S</td>
<td>2.4</td>
</tr>
<tr>
<td>Cl</td>
<td>2.8</td>
</tr>
<tr>
<td>F</td>
<td>4.1</td>
</tr>
<tr>
<td>Ag</td>
<td>1.9</td>
</tr>
<tr>
<td>Cd</td>
<td>1.7</td>
</tr>
<tr>
<td>Zn</td>
<td>1.6</td>
</tr>
<tr>
<td>Ge</td>
<td>2.0</td>
</tr>
<tr>
<td>Sn</td>
<td>1.7</td>
</tr>
<tr>
<td>Pb</td>
<td>1.6</td>
</tr>
<tr>
<td>Bi</td>
<td>1.7</td>
</tr>
</tbody>
</table>

AN INTRODUCTION TO STRUCTURE AND BONDING

Electronegative fluorine will attract a greater electron “share” in the $\sigma_{\text{bonding}}$ orbital. In the same way, the antibonding sigma orbital ($\sigma^*$), taken as $[1\text{s}(H) - C_2 2p_z(F)]$, where $C_2$ gives the relative weight of the $2p_z(F)$ AO in the $\sigma^*$ orbital, will reduce electron density between the nuclei, but with most near the hydrogen. The filled $2p_x$ and $2p_y$ orbitals are also available for bonding, but since there is only an $s$ orbital on hydrogen, there is nothing with which they can overlap. The relative positions for some of the MOs of HF are shown in Figure 1.10.

A somewhat more sophisticated MO picture of a system as complicated as HF can also be created. In this picture, the LCAO is recognized as involving all of the electrons in the system. However, since an exact solution to the total energy of the resulting 10-electron system with two nuclei cannot currently be calculated, this self-consistent field (SCF) method assumes that the total energy can be approximated as some function that includes the potential energy of the repulsion of each nucleus toward the other, the attraction of each nucleus to each electron, the kinetic energy of each electron, and the potential energy of repulsion of each electron with every other electron. Using the Born–Oppenheimer approximation (vide supra), the kinetic energies associated with the nuclei can be ignored and the nuclei considered stationary. Since all of the electrons are moving relative to one another, the electron–electron repulsion energy is approximated in the SCF method by considering each electron to move in the average field of all of the other electrons. The MOs created in this way extend over the entire molecule and the resulting picture, even though restricted to $s$ and $p$ orbitals, is very different from that which contains more traditional-looking localized orbitals.

For HF, then, using the LCAO-MO-SCF method, there are a total of 10 electrons in the system that must be considered (nine from fluorine, originally $[(1s^2)(2s^2)(2p^5)]$. 

Figure 1.10. A schematic representation of a few of the molecular orbital energies in hydrogen fluoride (HF). The sigma ($\sigma$) and pi ($\pi$) bonding relative positions are shown, but only the sigma ($\sigma^*$) antibonding orbital position is provided.
and one from hydrogen, originally \((1s^1)\), and they can be accommodated in five MOs (i.e., two electrons per orbital). The lowest-lying occupied orbital in HF appears to be the \(1s\) orbital on fluorine and, (perhaps) in part because of the high nuclear charge, little mixing occurs. The next highest MO in HF has about the right energy for the \(2s\) orbital in fluorine, but perturbation by the hydrogen \(1s\) orbital is present; that is, the contribution of hydrogen to this orbital is small. In traditional terms, this suggests that the orbital is simply \(2s^2\) (as shown in the simpler representation of Figure 1.10). The third MO contains a large bonding contribution from a fluorine \(2p\) orbital and the hydrogen \(1s\) orbital, as well as some input from the fluorine \(2s\) orbital (!). This suggests that the bonding from fluorine to hydrogen has mixed \(s\) and \(p\) characters, about which we shall say more later. The fourth and fifth bonding MOs (now accounting for all 10 electrons) have the same energies (are thus degenerate) and look like the traditional \(2p\) orbitals (see http://www.webmo.net, about which more shall be said later).

Now, the ionic picture for HF, which supposes complete electron transfer, fails to account for the properties of the material but has merit on the basis of electronegativity arguments. The idealized Lewis dot structure more closely accounts for the lack of ionic character by suggesting a sharing of the electrons but formally neglects to account for the inequality of that sharing. The simplified MO picture is somewhat more detailed and it not only suggests that the bonding electrons are not equally distributed within the bond, but it also shows that the bond between hydrogen and fluorine can be considered as arising from an overlap of a \(2p\) orbital from fluorine with a \(1s\) orbital from hydrogen. Finally, the more comprehensive SCF-MO picture suggests that the bond between hydrogen and fluorine may actually involve a mixture of fluorine orbitals.

All of these pictures are usually thought of as complimentary approximations. The advantage to be gained by using one concept rather than another at any given time lies in developing an understanding of experimentally determined (i.e., observed) physical properties and reactivity (i.e., reality) so that predictions about other systems can be made. It is important to keep in mind that all of the methods dealing with orbitals are approximations, as are the orbitals themselves.

Rapid and convenient representations of such molecular systems, in which there is an unequal electron distribution in bonds (called polar bonds), are frequently represented simply with structures with an arrow drawn over the bond or by using the symbols (delta) \(\delta^+\) and \(\delta^-\) to indicate partial positive and negative character, respectively:

\[
+ \rightarrow - \quad \delta^+\delta^-
\]

H-F  H-F.

When such unlike charges (i.e., as \(q\) and \(-q\)) are separated, they constitute an electric dipole. The dipole moment, \(\mu\), is given by \(qR\), where \(R\) is the distance between the charges. The dipole moment is a vector quantity. Polar molecules possess permanent dipoles. When the charge \(q\) is that on the electron (assumed to be a point charge) whose value is taken as \(1.60 \times 10^{-19}\) Coulombs (C) and the distance \(R\) is about 1 Å (1 Å = \(10^{-10}\) m = 100 pm), then \(\mu = 1.6 \times 10^{-29}\) C m. The units of
μ are generally given in debye (D)* where \( 1 \text{D} = 3.34 \times 10^{-30} \text{Cm} \), and thus μ = 4.8D for point charges 1 Å (100 pm) apart.

Molecules with permanent electric dipoles have moments that can be measured by applying an electric field to remove the degeneracy seen in their rotational spectra (Chapter 2). This is called the Stark effect†

Alternatively, an average dipole moment on a bulk sample can be obtained through measurement of the potential difference between charged plates with and without the dielectric present. The latter is, of course, a macroscopic property of the sample, which assumes that the microscopic structure, from which the dipole moment comes, does not actually exist; that is, the entire medium is “continuous” and isotropic. However, despite the assumption of continuity, this macroscopic property, ε, the dielectric constant of the medium, can be related to the dipole moment, μ, through the density of the medium, the number of molecules between the charged plates, and thus the induced dipole per unit volume (but taking into account an initial contribution of preferential orientation).

The direct measurement of the dielectric constant is straightforward. Indeed, the electrical equipment only requires a variable capacitor (of known capacitance) in parallel with the capacitor whose capacitance is to be determined (i.e., between whose plates is placed a known quantity of material whose dielectric constant is to be found).

III. Orbital Hybridization

In drawing structures for hydrogen (H₂) and hydrogen fluoride (HF), it has been possible to account for the location of all (both) of the nuclei in a linear fashion with bonds that are symmetrical about the internuclear axis (i.e., σ bonds). However, with methane, CH₄, which cannot be linear, a geometry problem arises.

When enough experimental information had been gathered,‡ it became clear that all four hydrogen nuclei of methane (CH₄) are chemically identical; that is, they are all bonded to carbon and are incapable of being distinguished one from another by any chemical process. Thus, it was also clear that the most obvious way to minimize the total energy of the system would be to arrange the hydrogen nuclei around carbon on the surface of an imaginary sphere so that they were as far apart from each other as possible—to reduce any internuclear repulsions (as shown in Figure 1.11a). The radius of the sphere so created is the average carbon–hydrogen bond length (about 1.09 Å, 109 pm). This same arrangement would assure that the paired electrons in the bonds holding the hydrogen nuclei to the carbon would also be as far apart as possible (since once the electrons are paired in filled orbitals, they, too, repel other paired electrons, only two paired electrons being allowed in the bond).

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*Named such in honor of Peter J. W. Debye (1884–1966), who was awarded the Nobel Prize in 1936 for “contributions to our knowledge of molecular structure through his investigations on dipole moments …”

†Johannes Stark (1874–1957), Nobel Prize in Physics for his work on structural and spectral changes of atoms. His work is well described in Ann. Phys., 1914, 43, 965.

‡The insights and massive contributions of Louis Pasteur, Friedrich August Kekulé, Archibald Scott Couper, et al. (all in the middle of the nineteenth century) to structural organic chemistry require fuller acknowledgment and will be elaborated upon subsequently.
Alternative representations (all with the same internal H–C–H angle of about 109.5°) are shown (inscribed in a cube as shown in Figure 1.11b, inscribed in a tetrahedron as shown in Figure 1.11c, and, finally, as a stick figure as shown in Figure 1.11d).*

The difficulty of imagining how carbon, whose atomic configuration of [(1s²)(2s²)(2p³)] could form four equivalent bonds, was overcome by the independent introduction of the concept of orbital hybridization (L. Pauling and J. C. Slater, *vide supra*) and was already introduced above (for HF as orbital mixing). Orbital hybridization involves determining which (if any) combinations of s and p orbitals on a given atom can be utilized to form hybrid AOs on that atom. Subsequently, the hybrid orbitals can be used to make bonds between the atoms. The idea is to allow for both better orbital overlap and formation of equivalent bonds. Better orbital overlap (making stronger bonds) results because orbitals, once hybridized, occupy a greater volume of space. Equivalent bonds are required because, experimentally, the hydrogens are incapable of being distinguished. Implementation of orbital

*Bonds are not static like the sticks that are often used to model them. Connecting nuclei with rods is an oversimplification. In each of these representations, the line joining the carbon atom to each of the hydrogen atoms designates a carbon–hydrogen bond, which, being symmetrical to rotation about the internuclear axis, is a σ (sigma) bond. The H–C–H angle so subtended, in each case, is one of the internal angles of a regular tetrahedron, that is, 109°28´.
hybridization for carbon allows it to utilize the one \(2s\) orbital and the three \(2p\) orbitals to make fixed sets of hybridized orbitals consisting of any of (a) \textbf{four} orbitals, each composed of 25\% \(s\) and 75\% \(p\) (i.e., \(1/4 s + 3/4 p\), or \(s^{1/4}p^{3/4}\), or \(sp^3\)); (b) \textbf{four} orbitals, three of which are hybridized orbitals, and each hybridized orbital is composed of 33.3\% \(s\) and 66.6\% \(p\) (i.e., \(1/3 s + 2/3 p\), or \(s^{1/3}p^{2/3}\), or \(sp^2\)) \textit{and} one unhybridized \(p\) orbital left over; and (c) \textbf{four} orbitals, two of which are hybridized orbitals, and each hybridized orbital is composed of 50\% \(s\) and 50\% \(p\) (i.e., \(1/2 s + 1/2 p\), or \(s^{1/2}p^{1/2}\), or \(sp\)) \textit{and} two unhybridized \(p\) orbitals left over. Pictorial representations of the three \(sp^2\) orbitals and the two \(sp\) orbitals and the relative volumes of space they occupy are presented in Figure 1.12a,b.

The four \(sp^3\) orbitals (as shown in Figure 1.13a) would then also be directed to the corners of a regular tetrahedron and would be available for overlap with the \(1s\) orbitals from each of the four hydrogens forming the \(\sigma\) bonds necessary to make methane, \(\text{CH}_4\) (Figure 1.13b).*

The power of the concept of localized orbital hybridization, combined with the simple ideas that (a) internuclear repulsion of nonbonded nuclei should be minimized and (b) electron pairs filling orbitals also repel other filled orbitals (sometimes called valence shell electron pair repulsion [\textbf{VSEPR}]) is enormous. It allows us (1) to make predictions about the geometry of molecules or, (2) knowing the geometry, to make predictions about areas in space where electrons might be, and (3) to justify, to ourselves, why and how reactions might occur. The following examples are illustrative of these concepts:

(I) The (highly reactive) species \(\text{BeH}_2\) should be linear, with an H–Be–H angle of 180°. The hydrogens are equivalent and so the bonds are equivalent. The ground-state configuration of beryllium [(\(1s^2\))(\(2s^2\))] cannot accommodate any bonds at all if we are restricted to using unpaired electrons to

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*It should be clear that the idea of fixed, localized hybrid orbitals is simply another approximation used to attempt to rationalize experimental observation. The simplistic qualitative picture presented assumes, for example, that the combination of AOs cannot include fractional contributions to the molecular wave function. As a consequence, as will become clear, angular adjustments must be accounted for qualitatively. It should also be clear that, for the moment, all but the most gross symmetry arguments are ignored.
make bonds and reach a noble gas configuration. If BeH₂ is to exist, the only way to make bonds (other than using hybridized orbitals) would be to “promote” one 2s electron to the 2p level (making an excited [(1s²)(2s¹) (2p¹)] state beryllium) and then to combine this state with the two hydrogens using their respective 1s electrons. This would produce an undefined H–Be–H angle and nonequivalent hydrogen-to-beryllium bonds. The more appealing picture using the hybridization idea of Slater and Pauling suggests that equivalent and stronger bonds would consist of hybridization of the one 2s orbital with one of the 2p orbitals to produce two sp orbitals (leaving the two other 2p orbitals unhybridized). Since the angle formed by two localized sp hybridized orbitals is 180°, if each one of the orbitals was then allocated one of the original 2s electrons from beryllium for bonding, it would now be possible to form two equivalent σ bonds using the 1s electron from each of the hydrogens. Indeed, this process predicts that all compounds of beryllium in which there are two ligands attached should have the same bond angle (Figure 1.14d). The arrangement can be described as digonal.

Problem 1.8. Using appropriate drawings, show why you would predict that BeCl₂ might also have a Cl–Be–Cl angle of 180°. Predict the carbon–beryllium–carbon angle in dimethylberyllium, (CH₃)₂Be.

Problem 1.9. If, regardless of the nature of the nucleus, appropriate s and p orbitals can be combined (i.e., the principle quantum number can be 2, 3, …), predict the F–Hg–F angle in HgF₂. What is the principle quantum number of the Hg orbitals used in hybridization?

The LCAO-SCF-MO approach, which must also yield a digonal system, suggests a different approximation for BeH₂. Using a total of five orbitals (the two 1s orbitals on hydrogen and the 1s, 2s, and one 2p orbital on beryllium) and the six electrons available, three occupied (containing two
AN INTRODUCTION TO STRUCTURE AND BONDING

Electrons each) and two unoccupied (or virtual) MOs are created. The lowest-lying (occupied) MO is the 1s beryllium core, and this orbital is almost unaffected by the hydrogens. The next highest occupied (bonding) MO derives from the overlap of the beryllium 2s orbital and a positive contribution from both 1s orbitals on hydrogen (Figure 1.14a). The third, final, and highest occupied bonding MO arises from an overlap of the beryllium 2p orbital with the negative contribution of the two hydrogen 1s orbitals (Figure 1.14b).

These pictures clearly do not individually correspond to two sp hybridized orbitals on beryllium bonding as a result of an overlap with two 1s orbitals on hydrogen. However, if they are equally weighted, their positive and negative contributions give the same final result, which may be viewed as the sum of Figure 1.14c or, more traditionally, as Figure 1.14d.

(II) Considering internuclear repulsion or the repulsion between localized, paired electrons (VSEPR), molecular species, in which there are three ligands bonded to a fourth and in which there are no other electrons, are presumed to be planar, for example, boron trifluoride (BF₃) and (monomeric) borane (BH₃). This is confirmed experimentally. Boron, of course, has a \((1s^2)(2s^2)(2p^1)\) ground state. How then can it form three equivalent ligands? Since boron has only three electrons with the principal quantum number 2, in order to form three equivalent bonds, rehybridization to three localized sp² orbitals, arranged at angles of 120° to each other, can be effected. The result defines a plane to which the remaining unhybridized
2p orbital is orthogonal. Utilizing one electron in each of the sp\(^2\) orbitals makes all three equivalent and hence the bonds formed, using these electrons to pair with those brought in by the ligand, equivalent (Figure 1.15d). Such an arrangement is described as **trigonal**, and the bonds, each symmetrical about the internuclear axis, are sigma (\(\sigma\)). It might further be argued that the availability of a “vacant” 2p orbital, into which, in principle, two electrons might somehow be added, would encourage interactions of such trigonal species with electron-rich reactants. We will see that this is the case.

The LCAO-SCF-MO description for (monomeric) borane (BH\(_3\)) must also provide a trigonal species. As there are eight electrons (one each from the three hydrogens and five from boron), there will be four occupied MOs. The lowest-lying MO is primarily the 1s orbital on boron, only slightly perturbed by the three hydrogens. The second bonding MO is then derived primarily from the 2s orbital on boron and enjoys a positive contribution from all three hydrogens (Figure 1.15a). Bonding MOs three and four are of the same energy (degenerate); each has one node, and each is derived from overlap of one of the 2p orbitals on boron with a suitable linear combination of hydrogens; the first (Figure 1.15b) is shown with a node going through one of the hydrogens (which is thus not seen), and the second (Figure 1.15c) is at right angles (orthogonal) to the first. The
AN INTRODUCTION TO STRUCTURE AND BONDING

conversion of these MOs to localized MOs results in the three \( sp^2 \) orbitals given above using the ideas of localized rehybridization (Figure 1.15d). The schematic energy level diagram relating these two different approaches is shown as Figure 1.16.

**Problem 1.10.** Based on the conclusions drawn concerning monomeric compounds of boron, predict the hybridization in
(a) the methyl cation, \( \text{CH}_3^+ \);
(b) the methyl radical, \( \cdot\text{CH}_3 \); and
(c) aluminum trichloride, \( \text{AlCl}_3 \).

(III) As already noted, the ground-state configuration of carbon \([1s^2)(2s^2)(2p^2)]\) requires rehybridization (using the localized two-center MO approach) if four localized, equivalent bonds are to be formed. Thus, four equivalent localized \( sp^3 \) orbitals, directed toward the corners of a regular tetrahedron, are expected. One electron can be placed in each of the \( sp^3 \) orbitals and sigma (\( \sigma \)) bonding to four equivalent ligands is effected (e.g., using four \( 1s \) orbitals, one from each of four hydrogen atoms, each with one electron). The geometry is described as **tetrahedral** (Figures 1.11 and 1.13).

The LCAO-SCF-MO delocalized picture for methane \((\text{CH}_4)\) begins, as is usual with the basis set of five orbitals on carbon (one \( 1s \), one \( 2s \), and three \( 2p \)) and the four hydrogen \( 1s \) orbitals, which yield nine linear combinations. There are 10 electrons (six from carbon and one each from each of the four hydrogens) that must fit into the nine combinations and, using them pairwise, we can fill the lowest five orbitals. The first and lowest-lying orbital is the carbon core MO consisting primarily of the carbon \( 1s \) orbital. The second and next highest MO is made up of the carbon \( 2s \) orbital and a positive combination of the four hydrogen \( 1s \) orbitals; this is shown in Figure 1.17a. The next three MOs are mutually degenerate. They are found
Figure 1.17. (a–d) Schematic representations of four (bonding) SCF-MOs of methane (CH$_4$). The representations were created using the MOViewer in WebMO version 6.0.002p. (e) Utilization of “unrehybridized” AOs on carbon and hydrogen to create four MOs in methane, CH$_4$. (See Hamrin, K.; Johansson, G.; Gelius, U.; Fahlman, A.; Nordling, C.; Siegbahn, K. Chem. Phys. Lett., 1968, 1, 613.)
in three mutually orthogonal planes, each with a single node and formed by a combination of each of the carbon 2p orbitals, with an appropriate combination of hydrogens. One possible schematic representation for these three is shown in Figure 1.17b–d. These MOs can be transformed into localized MOs that are approximately the same as those four resulting from an interaction of localized sp$^3$ orbitals from carbon interacting with the four 1s orbitals obtained, one each from each hydrogen. As shown in Figure 1.18, the heights of the energy levels using delocalized MOs does not correspond exactly to that from localized MOs, but the overall geometric result is the same.

An alternative way of viewing the same picture is to utilize unrehybridized carbon and four hydrogen (i.e., H$_4$) MOs made up of a combination of the four hydrogen AOs. If the four hydrogen (H) 1s AOs are arranged in a linear fashion, four MOs, increasing in energy (with increasing numbers of nodes) can be written as shown on the left-hand side of Figure 1.17e. An alternative arrangement (in a plane) is shown in the center of Figure 1.17e, and, finally, the same orbitals, now arranged as a tetrahedron (and depicted in relationship to the 2s and three 2p orbitals of carbon) are shown on the right of Figure 1.17e.

Thus, instead of viewing the system as the rehybridization of one 2s and three 2p AOs at carbon (ignoring the 1s core) to yield four new equivalent sp$^3$ orbitals at carbon and then permitting a combination of each of these with one, each, of the 1s orbitals of the four hydrogens, the view is one of “unrehybridized” carbon creating suitable MOs with a set of four “rehybridized” hydrogens.

(IV) Nitrogen (N) ground state [(1s$^2$)(2s$^2$)(2p$^3$)] provides three electrons (one each in each of the 2p orbitals) and the remaining two electrons with principal quantum number 2 paired in the 2s orbital. Thus, nitrogen with three ligands, for example, as in ammonia (NH$_3$), might be expected to have a geometry in which the H–N–H angle is 90° (Figure 1.19a). However, in ammonia, NH$_3$, spectroscopic measurements (Chapter 2) show that the equilibrium H–N–H bond angle is about 107°!
There are three possible explanations we can consider using localized orbitals. First, we might imagine that since filled, localized bonding orbitals repel each other and since nonbonded nuclei within bonding distance repel each other, these forces make the expected 90° angle (dictated by simply using the unhybridized $2p$ orbitals) wider. Alternatively, for a second choice, we might imagine that rehybridization has been effected to produce three localized $sp^2$ orbitals, making angles of 120°, with one localized $2p$ orbital, orthogonal to the plane of the three $sp^2$ orbitals and containing the remaining two electrons. Here we would then argue that repulsion between the pair in the localized $2p$ orbital and the pairs in the bonds holding the hydrogens to nitrogen cause a diminution in the H–N–H bond angle from the expected 120° to the observed 107°. Finally, granting rehybridization, we might imagine that four localized $sp^3$ orbitals are formed and that three of these, with one electron in each, are used to make σ bonds with the localized $1s$ orbitals of each of the three hydrogens, and that the fourth $sp^3$ orbital contains the remaining (paired) two electrons (in a nonbonding orbital). Here we might anticipate that (in concert with tetrahedral geometry) the H–N–H angle should be about 109.5° but that the angle is diminished by repulsion between the electron pair in the one localized $sp^3$ orbital with the pairs in the localized orbitals to which the hydrogens are bonded. In each case, with only an $s$ orbital available on hydrogen, the resulting bond would enjoy the same symmetry along the internuclear axis and would be described as σ.

Generally, the explanation invoking $sp^3$ hybridization is preferred. The preference arises because (1) in geometric terms, 107° is closer to 109.5° than it is to 90° or 120°, so that there will be minimum additional distortion required, and (2) the overlapping ability of $sp^3$ orbitals is significantly better than that of $p$ orbitals, and somewhat better than $sp^2$ orbitals, so that stronger bonds will be formed if rehybridization to localized $sp^3$ orbitals is effected.
Because of the distortion from a tetrahedron, the geometry is described as \textbf{trigonal pyramidal} (Figure 1.19 b).

The presence of a pair of electrons in an \textit{sp}\textsuperscript{3} orbital directed toward an apex of the trigonal pyramid suggests that the reactivity of ammonia might be governed largely by interactions with electron-poor species, which would thus form a bond with the “nonbonding” pair [e.g., as in the ammonium ion (NH\textsubscript{4}\textsuperscript{+})].

In the LCAO-SCF-MO approach, ammonia is considered composed of three equivalent hydrogens and a lone pair. Thus, there are the usual five orbitals on nitrogen (one 1s, one 2s, and three 2p orbitals) and three orbitals, each 1s, from each of three hydrogens. There are, as there were for methane (CH\textsubscript{4}) above, 10 electrons. Again, there are only four orbitals and eight electrons once one pair of electrons has been assigned to the 1s core at nitrogen. Interestingly, the next two MOs result from linear combinations of three equivalent hydrogen 1s orbitals with the nitrogen 2s orbital \textit{and} that 2p orbital lying along the threefold rotational axis passing through the vacant axis of the trigonal pyramid! As a consequence, these two MOs contribute both to bonding between nitrogen and hydrogen as well as to the characteristic reactivity of ammonia with electron-poor species. The last two MOs (compare the three highest MOs in methane) are mutually degenerate and are composed of the appropriate combinations using the remaining two 2p orbitals from nitrogen and the 1s orbitals from the hydrogens. As before, appropriate combinations of these delocalized MOs generate the localized, hybridized MOs typical of \textit{sp}\textsuperscript{3} orbitals.

(V) With oxygen \{[(1s\textsuperscript{2})(2s\textsuperscript{2})(2p\textsuperscript{4})]\}, the situation is very similar to that of nitrogen. The H–O–H bond angle in water is found to be 105°, and a variety of possibilities using hybridized and unhybridized orbitals exist. However, from the previous discussion, it could be concluded that of all the possibilities, the most likely results from hybridization to four localized \textit{sp}\textsuperscript{3} orbitals. Here, the hydrogens would be expected to be identical, forming an H–O–H angle of about 109.5°, and the remaining two pairs of electrons, each pair in one of the remaining two nonbonding, localized \textit{sp}\textsuperscript{3} orbitals, also forming an angle of about 109.5°. It is suggested that this is so because the best overlap, generating the σ bonds of the lowest energy, is obtained when the hydrogens are bonded using localized \textit{sp}\textsuperscript{3} orbitals from oxygen and the s orbitals from hydrogen. That the observed H–O–H angle of 105° is less than the tetrahedral 109.48° is then ascribed to repulsion between the pairs of electrons in the remaining localized, nonbonding \textit{sp}\textsuperscript{3} orbitals (Figure 1.20). Interestingly, the LCAO-SCF-MO approach suggests only a smooth increase in electron density in the plane of the lone pairs and, specifically, the presence of two discrete orbitals (not equivalent in energy) and both of which are occupied. Representations of these orbitals are provided in Figure 1.20a.

**Problem 1.11.** Based on the foregoing discussion,

(a) Draw an orbital picture of ethane (C\textsubscript{2}H\textsubscript{6}) or, better, H\textsubscript{3}CCH\textsubscript{3}.

(b) Label the σ bonds with their respective localized orbital notation, for example, a bond between hydrogen and carbon should be labeled with both an s and an \textit{sp}\textsuperscript{3}. 
(c) In another drawing, replace the orbital lobes with straight lines and draw a representation of ethane emphasizing the tetrahedral nature of each of the carbon atoms.

(VI) The compound ethene (also called ethylene), \( \text{C}_2\text{H}_4 \), is known to consist of a planar array with the geometry shown in Figure 1.21a,b.

As discussed (e.g., with boron trihydride [monomeric borane BH\(_3\)] above), localized trigonal hybridization with bond angles approximating...
120° suggests $sp^2$ hybridization. Unlike the case of boron (ground-state configuration $[(1s^2)(2s^2)(2p^1)]$), the ground-state configuration of carbon has one more electron (i.e., $[(1s^2)(2s^2)(2p^2)]$) so that if rehybridization is effected as suggested, the localized $2p$ orbital, which was vacant for the compounds of boron, must now contain one electron for this compound of carbon. The bonds formed from carbon to hydrogen, the latter having only the localized $1s$ orbital with which to bond, can be called sigma ($\sigma$) in accord with what has gone before.

Furthermore, as the H–C–C angle at both carbon atoms is close to 120°, it seems clear that we must argue that the bond formed from one carbon to the next is made by a constructive overlap of an $sp^2$ orbital from each. Such overlap would result in a bond, which was symmetrical about the internuclear axis and would therefore also be designated as sigma ($\sigma$). The $2p$ orbitals, with one electron in each, might now be expected to overlap. However, they cannot overlap end to end to yield a bond that is symmetrical about the internuclear axis; they can only overlap edge to edge (Figure 1.21b). Bonds formed from orbitals that overlap in this way, and which lack the symmetry of the sigma ($\sigma$) bonds, are called pi ($\pi$) bonds.

This orbital picture of ethene (ethylene, $C_2H_4$), in which there is to be a pi ($\pi$) bond arising from edge on overlap of localized, adjacent unhybridized $p$ orbitals on adjacent $sp^2$-hybridized carbons, linked by a sigma ($\sigma$) framework, is an unusually valuable, but oversimplified, representation. Thus, having formed bonds, the approach argues that the electrons associated with each carbon are localized to their respective orbitals so that there is no mixing or exchange. Even with a “localized picture,” it might reasonably be argued that the four electrons lying between the two carbons could be expected to hybridize to some new kind of bonding so as to make them equivalent. However, as we will see, first in Chapter 2 and again later, the approximation that there are two kinds of bonds such that either (1) there is no exchange between sigma ($\sigma$) and pi ($\pi$) electrons or (2) that if there is an exchange, it does not affect the overall energy of the system, works very well. In that vein, if we consider only the sigma ($\sigma$) and pi ($\pi$) bonds lying between the two carbon atoms as a separate subset of bonds in the molecule, then in terms of the traditional MO viewpoint, a picture showing both bonding and antibonding orbitals (Figure 1.22) can be constructed.

(VII) Ethyne (also called acetylene) corresponds to $C_2H_2$. Its structure is represented as tubelike with H–C–C angles of 180°. Spectroscopic evidence (Chapter 2) allows for the representation shown in Figure 1.23.

As was the case for beryllium, a digonal carbon atom suggests that the localized hybridization is $sp$. Unlike beryllium $[(1s^2)(2s^2)]$ discussed in (I) above, carbon $[(1s^2)(2s^2)(2p^2)]$ will have two electrons, one each in each localized $2p$ orbital even after hybridization has been effected. Using the two localized $sp$ hybrid orbitals on each carbon (which will form stronger bonds than those that might be made by an overlap of other localized available orbitals), three $\sigma$ bonds can form: one carbon–carbon bond and two carbon–hydrogen bonds. There are two localized $2p$ orbitals on each carbon available to form two, mutually orthogonal $\pi$ bonds by sidewise overlap.
Again, as was the case with ethene (ethylene), the most widely used (because it seems to work best) approximation avoids rehybridization of the electrons between the carbons into some new kind of bonding in favor of the formation of $\sigma$ and $\pi$ bonds, with their corresponding $\sigma^*$ and $\pi^*$ antibonding orbitals (unoccupied in the ground-state configuration).

IV. Allotropes of Carbon

As was noted earlier in this chapter, the heat of combustion used for carbon in Hess’s law (Equation 1.6) computations is a function of the allotrope of carbon used. The difference in allotropic forms is a function of the bonding present. Thus, as shown in Figure 1.24, the idealized lattice network of flawless diamond is that of a continuous and endless array of $sp^3$-hybridized carbons about 154 pm apart ($\Delta H_c^\circ$ of $C_{(s, \text{diamond})}$ is $-94.5 \text{ kcal mol}^{-1}$ [$-395.4 \text{ kJ mol}^{-1}, -32.95 \text{ kJ gm}^{-1}$]). In the same Figure 1.24 there is also shown the idealized concept of graphite, an endless array of sheets of planar carbon networks, the planes about 341 pm apart, but the carbon–carbon distance is now 142 pm. Here, in contrast to the idealized $sp^3$ hybridization found in diamond, it is argued that the hybridization at carbon is $sp^2$-like and that a continuous $\pi$ network cloaks each planar sheet ($\Delta H_c^\circ$ of $C_{(s, \text{graphite})}$ is $-94.1 \text{ kcal mol}^{-1}$ [$-393.5 \text{ kJ mol}^{-1}, -32.79 \text{ kJ gm}^{-1}$]). Recently, a new family of carbon compounds, initially observed in interstellar gas clouds by infrared spectroscopy (Chapter 2, Part 3), and which are composed only of closed localized networks, have been isolated by

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**Figure 1.22.** A schematic representation of the mixing of $2p$ and $sp^2$ orbitals in ethene (ethylene, $\text{H}_2\text{C-CH}_2$) to form $\sigma$ and $\pi$ bonding and antibonding ($\sigma^*$ and $\pi^*$) orbitals and cartoon representations of those orbitals. The representations were created using the MOViewer in WebMO version 6.0.002p.

**Figure 1.23.** A pictorial representation of ethyne (acetylene, $\text{C}_2\text{H}_2$).
heating graphite rods in an inert atmosphere. The bonding in these compounds, called fullerenes (after Buckminster Fuller [1895–1983], designer of geodesic domed structures, c.f. Pawley, M. Buckminster Fuller. New York: Taplinger (1991)), is presumed to be very much graphite-like. Figure 1.24 also depicts the structure of the truncated icosahedron \( C_{60} \) buckminsterfullerene, the value for the enthalpy of combustion being recently determined \( (\Delta H^\circ_c \text{ of } C_{\text{\textit{c}}} \text{ for } C_{60} \text{ buckminsterfullerene itself is } -5639.2 \text{ kcal mol}^{-1} \text{ [}-23,594.4 \text{ kJ mol}^{-1}, -32.77 \text{ kJ gm}^{-1}\text{]}).^* \)

V. Combination of Ionic and Covalent Bonding

Although there are a number of compounds whose aqueous solutions are characterized by the formation of ions, this discussion will be limited to consideration of sodium carbonate (\( \text{Na}_2\text{CO}_3 \)).

Dissolution of sodium carbonate generates sodium cations and the carbonate anion (Equation 1.12):

\[
\text{Na}_2\text{CO}_3\text{(aq)} \rightarrow 2\text{Na}^+\text{(aq)} + \text{CO}_3^{2-}\text{(aq)}. \quad (1.12)
\]

We will assume that the state of hydration of the anion can be ignored and that, for the moment, the anion itself can be considered as an isolated system. In that

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* I am grateful to Dr. Y. H. Wing for early communication of this value. A later value is given as 25,899.1 ± 14.2 kJ mol⁻¹ (Rojas-Aguilar, A. J. Chem. Thermodyn., 2002, 34, 1729).
anion, studies with isotopically labeled oxygen (e.g., $^{16}$O, $^{17}$O, and $^{18}$O), as we shall see, demonstrate that all three of the oxygens are equivalent, and the structure of the anion is best represented by allowing the plane defined by the three oxygens to also contain the carbon (Figure 1.25).

Based upon the foregoing discussion of MOs, it is argued that the carbon atom might best be described with localized $sp^2$ hybridization (i.e., trigonal) and with one electron in the $2p$ orbital orthogonal to the plane of those three $sp^2$ orbitals. The bonds to each oxygen are symmetrical about the internuclear axis and are described as $\sigma$. However, what is to be done with the bonds from oxygen to carbon? Without considering hybridization, all three of the oxygens $[(1s^2)(2s^2)(2p^4)]$, presumably using $2p$ orbitals, could participate in forming the $\sigma$ bonds to carbon (i.e., the $\sigma$ bond would be $sp^2$ from carbon and $p$ from oxygen), but only one oxygen could use a second one-electron-containing $2p$ orbital with which to form a $\pi$ bond by sidewise overlap with the occupied localized $2p$ orbital on carbon (as with ethene [ethylene, CH$_2$=CH$_2$] and ethyne [acetylene, HC≡CH]). This is because even the $\pi$ bond cannot contain more than two electrons. Thus, we are left with the two remaining oxygens, each containing one electron available for bonding, but without the ability to form a bond because there are no other orbitals available on carbon. However, this picture, in which two of the oxygens are different from the third, is contrary to the experimental observation that all three oxygens are equivalent.

While the problem can be approximately treated by examining the total MO description for the system in detail (e.g., see Figure 1.25b), that treatment is cumbersome. Further, it is clear that the problem results from the idea that bonding is localized and can only be described in terms of electron pairs. However, bonding electrons can be associated with more than two nuclei, and in such circumstances, stability is enhanced because when electrons can distribute themselves over a greater volume of space, the extent of orbital overlap, and thus bonding, increases. Compare, for example, the volume of space made available using $sp^3$-hybridized orbitals to the volume using only $2p$ orbitals (e.g., see Figure 1.12). However, it should be very clear that symmetry plays an important role, and the extent to which
such bonding occurs will be dramatically dependent upon the geometry or spatial orientation of the participating nuclei and orbitals.

The distribution of electrons over more than two bonds is called electron delocalization and the process is described as resonance. The qualitative picture of resonance generally uses VB structures such as those shown in Figure 1.26 for the carbonate anion ($\text{CO}_3^-$) and, in general, results from an inability to draw a single structure, with lines representing bonds, to depict the object; that is, none of the real pictures in Figure 1.26 can describe the carbonate anion ($\text{CO}_3^-$). Rather, the carbonate anion ($\text{CO}_3^-$), which nonetheless is real, is a hybrid of all of them. Alternatively, we are describing a real object in terms of unreal representations, all of which are necessary, but none of which is sufficient.

The rules for writing valence bond descriptions of a species like the carbonate anion allow for understanding what constitutes a reasonable set of structures and, with discussion, follow:

1. The individual resonance structures constituting the set are connected by a double-headed arrow (Figures 1.26 and 1.27a) or double-headed arrows. Double-headed arrows are not used for any other purpose and are not the same as, nor should they be confused with, two single-headed arrows (Figure 1.27b) that might be used to signify something else, for example, equilibrium.
2. The members of the set of structures have no individual reality. They are hypothetical representations of different electron-pairing schemes.
3. A curved arrow (or curved arrows, Figures 1.27c and 1.28) may be drawn on one representation to show “movement” of electrons from one location on (or between) atoms to another location on (or between) atoms, thus creating a new representation. By convention, electrons “move” in the direction of the arrowhead. If a curved arrow (or set of curved arrows) is used, (a) the nucleus at the terminus of the arrow (or set) becomes poorer in electrons and that at the head of the arrow (or set) becomes richer in electrons, and (b) an identical
Figure 1.28. Some resonance forms for the carbonate anion (CO$_3^{2-}$) (compare with Figure 1.26) connected by resonance arrows and with curved arrows indicating “movement” of pairs of electrons showing a path from one resonance form to another.

An arrow or set of arrows may be drawn on the resultant structure, which returns to the initial representation.

4. All representations of the structures reached by the curved-arrow approach and connected with double-headed arrows must have all atoms in the same positions in space. Only electron “motion” is considered.

5. All representations in a set of resonance structures must have the same number of paired and/or unpaired electrons.

6. The amount that any specific resonance structure representation actually contributes to the overall hybrid will depend on the presumed energy of that contributor. Generally, the larger the number of identical representations of the lowest-energy contributor, the more stable the structure.

7. Separation of unlike charges on adjacent atoms should be avoided in writing resonance structures since, even though they are acceptable, they are not likely to be major contributors to the minimum energy representation.

8. Finally, it must be understood that the curved arrows are no more than an accounting technique. They must not be mistaken for reality and lent more credence than they are worth lest they be taken seriously as the movement of electrons.

**NOTICE TO THE STUDENT**

The curved-arrow approach, showing the “movement” of a pair (or pairs) of electrons, will be used subsequently, repeatedly, and relentlessly in other connections. It is worth your time and effort to practice (Problem 1.12).

**Problem 1.12.** Using the resonance method described, draw structures for NO$_3^-$, SO$_4^{2-}$, CH$_3$CO$_2^-$, N$_2$O, NO$_2^-$, and N$_3^-$.

**ADDITIONAL PROBLEMS**

In the following problems, use $^{12}$C = 12.00 exactly, $^1$H = 1.00, and $^{16}$O = 16.00.

**Problem 1.13.** Benzoic acid (C$_6$H$_5$CO$_2$H) is often used as a primary standard for the calibration of thermometers (its melting point is 122°C), for calibration of adiabatic calorimeters (the energy of combustion of benzoic acid is −26.41 kJ g$^{-1}$), such
Problem 1.14. In Problem 1.13 and in Table 1.1 (as well as elsewhere in the chapter), numerical values are given with an expressed degree of uncertainty. Why cannot we be more specific? What is the difference (if there is one) between “accuracy” and “precision”?

Problem 1.15. The standard heat of formation ($\Delta H^\circ_{298}$) of methane ($\text{CH}_4$) is frequently given as $-17.87 \pm 0.74 \text{ kcal mol}^{-1}$ (74.70 ± 3.10 kJ mol$^{-1}$). When graphite is sublimed to carbon atoms (i.e., C$(s)$ to C$(g)$), the heat evolved can be considered as the “heat of vaporization” of carbon, and it has been estimated at 170 kcal mol$^{-1}$ (711 kJ mol$^{-1}$).

Using the information in Table 1.1 for the strength of the H-H bond, calculate $\Delta H^\circ$ for the reaction C$(g) + 4\text{H}(g) = \text{CH}_4(g)$. Why do you suppose it is frequently argued that one-fourth of this number is significant?

Problem 1.16. In 1951, C. A. Coulson (1910–1974, professor of chemistry, Oxford University) pointed out that “It is the behavior and distribution of the electrons around the nucleus that give the fundamental character of an atom: it must be the same for molecules.” Utilizing WebMO (http://www.WebMo.net) and a small basis set (e.g., STO-3G), create the MOs of hydrogen ($\text{H}_2$) and show that they can be approximated as in Figure 1.9. (Note that 1 hartree = 627.51 kcal mol$^{-1}$ = 27.25 eV.)

Problem 1.17. In 1951, C. A. Coulson (1910–1974, professor of chemistry, Oxford University) pointed out that “It is the behavior and distribution of the electrons around the nucleus that give the fundamental character of an atom: it must be the same for molecules.” Utilizing WebMO (http://www.WebMo.net) and a small basis set (e.g., STO-3G), create the MOs of hydrogen fluoride ($\text{HF}$) and show that they can be approximated as in Figure 1.10. (Note that 1 hartree = 627.51 kcal mol$^{-1}$ = 27.25 eV.)

Problem 1.18. In 1951, C. A. Coulson (1910–1974, professor of chemistry, Oxford University) pointed out that “It is the behavior and distribution of the electrons around the nucleus that give the fundamental character of an atom: it must be the same for molecules.” Utilizing WebMO (http://www.WebMo.net) and a small basis set (e.g., STO-3G), create the MOs of monomeric boron hydride ($\text{BH}_3$) and create a diagram of the orbitals such as in Figure 1.10. Note the symmetry in the sets of orbitals and their shapes. (Note that 1 hartree = 627.51 kcal mol$^{-1}$ = 27.25 eV.)
**Problem 1.19.** Interestingly, suppose you determined that boron hydride was largely dimeric (how might you do this?) with a structure as shown in the figure

![Boron Hydride Structure](image)

In place of the eight MOs (four bonding occupied orbitals and four unoccupied antibonding orbitals) seen in Problem 1.18, you will now find 16 orbitals. Optimize the structure of diborane at the restricted Hartree–Fock (RHF) 3-21G level (set the charge = 0) and then resubmit the structure at the STO-3G level for the MO picture. What does the structure of MO3 suggest?

**Problem 1.20.** The sulfate anion (SO$_4^{2-}$) is, apparently, tetrahedral rather than planar. Using the concepts of the “resonance arrow” and “curved arrow” notations, convince a reader that all four oxygens are identical.

**Problem 1.21.** The phosphate anion (PO$_4^{3-}$) is, apparently, tetrahedral rather than planar. Using the concepts of the “resonance arrow” and “curved arrow” notations, convince the reader that all four oxygens are identical.

Utilizing WebMO (http://www.WebMo.net), first draw the phosphate (PO$_4^{3-}$) anion and optimize the geometry (at the RHF/3-21G level, singlet, charge = −3). Then, with a small basis set (e.g., STO-3G), create the MOs of the phosphate anion (PO$_4^{3-}$). Note the symmetry in the sets of orbitals and their shapes. In particular, of the 29 MOs, 25 of which are doubly occupied, note the large energy gap between MO 9 and MO 10 and the shape of MO 10. (Note that 1 hartree = 627.51 kcal mol$^{-1}$ = 27.25 eV.)

**Problem 1.22.** There is a completely different way to look at bonding. Consider the well-known story of *The Wizard of Oz* by L. F. Baum. There are four witches (before, so the story goes, Dorothy’s house landed in Oz) on the sphere “Oz” who need to be as far away from each other and from the Wiz (whose throne is at the center of the sphere). L. F. Baum put them at the poles and the equator (east, west, north and south) where the angle subtended between any pair is 90°. At what angle would the separation be greater? After the “wicked witch” was dead, and knowing that three points define a plane, what angle is best? Could one argue that geometry dictates hybridization rather than vice versa? Why or why not?

**REFERENCE**